Chapter 2

Theoretical Background

2.1   Many-Body Problem

A significant part of condensed matter physics would be solved if the electronic structure of atoms, molecules and solids could be determined exactly. The starting point to investigate properties of materials is to solve the many-body Schrödinger equation. The problematic issue concerns the number of particles that are involved and the coupling and interactions of the particles (10^{23} particles per cm^3). This problem can be overcome using approximate methods.

The N-electron quantum system is described by a function of the spatial ($\mathbf{r}$) and spin (σ) coordinates of each electron, as well as the spatial coordinates $\mathbf{R}$ of the nuclei, $\Psi(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_n, \sigma_n, \mathbf{R}_1, ..., \mathbf{R}_N)$. The properties of any (non-relativistic) time-independent quantum system are determined by the Schrödinger equation:

$$H\Psi(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_n, \sigma_n, \mathbf{R}_1, ..., \mathbf{R}_N) = E\Psi(\mathbf{r}_1\sigma_1, ..., \mathbf{r}_n, \sigma_n, \mathbf{R}_1, ..., \mathbf{R}_N) \,, \qquad (2.1)$$

H, Ψ and E are the Hamiltonian, many-body wave-function and total energy of the system.

The Hamiltonian for a solid system is given by

$$H = -\sum_{I=1}^{N} \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 - \sum_{k=1}^{n} \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_k}^2 + \frac{1}{4\pi\epsilon_0} \sum_{I}^{N} \sum_{I>J}^{N} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

$$- \frac{1}{4\pi\epsilon_0} \sum_{k=1}^{n} \sum_{I=1}^{N} \frac{Z_I \, e}{|\mathbf{r}_k - \mathbf{R}_I|} + \frac{1}{4\pi\epsilon_0} \sum_{k=1}^{n} \sum_{k'>k}^{n} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}'_k|} \,, \qquad (2.2)$$

where N, M_I, Z_I and $\mathbf{R}_I$ represent the number, mass, charge and position of the nuclei and n, m, e and $\mathbf{r}_k$ are the number, mass, charge and position of an electron.

The first two terms are the kinetic energy contributions from the nuclei, T_i and the electrons, T_e. The remaining terms are Coulombic potential energy terms arising from the ion-ion repulsion, V_{ii}, ion-electron attraction, V_{ie} and the electron-electron repulsion, V_{ee}.

Although in principle everything is known exactly, the Schrödinger equation with this Hamiltonian is too difficult to be solved directly. Hence, the quantum many-body problem is centred upon finding intelligent approximations for the Hamiltonian and the many body wave-function that keep the correct physics and are computationally tractable.

This problem can be solved using three different levels of approximations:

2.2   Approximation for the Hamiltonian

The adiabatic (Born-Oppenheimer)/static approximations

The first simplification of the many-body problem is to eliminate the dependency of the electron's and nuclear dynamics by breaking it down into two sub-systems, one for the electrons and one for the nuclei.

The electrons move so fast that they follow the ionic (lattice) geometries almost without delay. In fact, from the electron point of view, the ions are fixed. The concept behind this approximation comes from the fact that the mass of a nucleus is much larger than the mass of an electron ($M \sim 10^3 \times m_e$). If we assume that $\frac{m}{M_I} \to 0$, the many-body equation 2.1 for each ionic configuration, $\mathbf{R}_I$, turns to the electron equation:

$$H^e(\{\mathbf{R}_I\})\Phi_v(\{\mathbf{R}_I\}, \{\mathbf{r}_k, \sigma\}) = (T^e + V^{e-ion} + V^{e-e})\Phi_v = E^e\Phi_v . \qquad (2.3)$$

Please note that the $\{\mathbf{R}_I\}$ in the wave function are not variables but parameters. Now we expand the solution of the many-body Hamiltonian, Ψ, into a sum of eigenfunctions of the electron Hamiltonian, Φ_v :

$$\Psi = \sum_v \Lambda_v(\{\mathbf{R}_I\})\Phi_v(\{\mathbf{R}_I\}, \{\mathbf{r}_k, \sigma\}). \qquad (2.4)$$

Therefore, one can consider H^e and Φ_v for a certain ionic geometry, and the dependence of the many-body Hamiltonian, H and and wavefunction Ψ on $\{\mathbf{R}_I\}$ enters only through the coefficients $\Lambda_v(\{\mathbf{R}_I\})$.

Using the above definition of the many-body wave function in equation (2.1) and

multiplying from the left hand side by Φ_μ^*, one can get the ground state energy for a certain lattice geometry and electron wave function, Φ_μ, and the integration over all electronic coordinates gives the ground state energy of the many-body system. Equation 2.1 turns to:

$$(T^I + V^{I-I} + E_\mu^e)\Lambda_\mu = E\Lambda_\mu + \text{electron \& phonon interaction terms.} \qquad (2.5)$$

Up to now everything is exact. In order to decouple the electron and ion dynamics, we assume that (i) the electron-phonon interaction is negligible, (ii) the electronic wave function belonging to different eigenstates of the nuclear system are independent from each other (*i.e.* $\langle \Phi_v | \Phi_\mu \rangle = 0$ for $v \neq \mu$). In other words, the electrons are always in the ground state. This is the *adiabatic principle* or *Born-Oppenheimer approximation* (BO).

With multiplying the Eq. 2.5 from the left with Λ_0, the ground state energy will be obtained:

$$E_0 = E^e + V^{I-I} + \text{kinetic energy of the lattice vibrations} \qquad (2.6)$$

The kinetic energy of the lattice vibrations is given by $\langle \Lambda_0 | T^I | \Lambda_0 \rangle$. The many-body wave function of the ground state is

$$\Psi_0 = \Lambda_0(\{\mathbf{R}_I\})\Phi_0(\{\mathbf{R}_I\}, \{\mathbf{r}_k, \sigma\}). \qquad (2.7)$$

In the BO approximation, the solution of Eq. 2.3 is the ground state energy of the electronic system for a specific configuration and motion of the ions that follows from Eq. 2.5.

In the *static approximation* we assume that the nuclei are fixed at their equilibrium positions (their average positions), $\{\mathbf{R}_I^0\}$. In the other words, the nuclei are considered to be at rest with respect to the electrons $\Psi_0(\{\mathbf{r}, \sigma\}, \{\mathbf{R}_I^0\}) = \Phi_0(\{\mathbf{r}, \sigma\}, \{\mathbf{R}_I^0\})\, \Lambda_0(\{\mathbf{R}_I^0\})$.

The static and the adiabatic (BO) approximations come from different assumptions about the position of the nuclei. In the adiabatic (BO) approximation the wavefunction of the electrons is defined by the momentary configurations, $\{\mathbf{R}_I\}$, of the nuclei while in the static approximation the nuclei are in their equilibrium positions, $\{\mathbf{R}_I^0\}$. Therefore, in the adiabatic (BO) approximation these instantaneous nuclear configurations appear as parameters. These parameters are no longer fixed, but they are variables that the energy and wave function depend on.

Solving the Schrödinger equation with the above Hamiltonian is however still too

complex for most cases, since the many-electron wave-function contains $3N$ variables.

One approach to solve the many-electron problem is using the electron density as the central unknown variable, rather than the many-electron wave-function. This approach was proposed initially by Thomas and Fermi in the 1920s [23, 24]. This model simplifies the problem considerably since the density contains only three degrees of freedom.

A significant leap in electronic structure theory was made in the remarkable theorems of '*density functional theory*' (DFT), proved by Hohenberg and Kohn [25]. DFT allows the ground-state properties of a many-electron system to be determined exactly through the electron density.

2.3   Density-Functional Theory (DFT)

2.3.1   Basic Principles

As mentioned previously, Thomas and Fermi were the first who suggested the model for the electron many-body problem based on the electron density. Due to the some shortcomings of this method, it could not describes the properties of molecules or solids quantitatively. However, almost forty years later, Hohenberg and Kohn proposed a powerful and exact theory which is based on the original idea by Thomas and Fermi. In the following section this theory will be discussed briefly. For a more comprehensive discussion one of the many review articles and books (e.g. review by Jones & Gunnarsson [26] and books by Parr & Yang [27] and Dreizler & Gross [28]) can be consulted.

In two remarkably powerful theorems Kohn and co-workers formally established the electron density as the central quantity describing electron interactions, and so devised the method which determines the ground state density exactly, known as density functional theory (DFT). The ground state density determines many body Hamiltonian and therefore all properties of the system.

● **The Hohenberg-Kohn Theorems**

The Hohenberg-Kohn theorems relate to any system consisting of electrons (fermions) moving under the influence of an external potential . These theorems are as follows:

THEOREM 1. *There is a one-to-one mapping between a specific external potential, $V_{\text{ext}}(\boldsymbol{r})$,*

and certain electron density, $n(\mathbf{r})$.

In the other words: The density determines the complete Hamiltonian and ground state energy, since the lowest eigenvalue of this Hamiltonian gives the ground state energy. Therefore, the ground state energy is obtained as a functional of the density.

$$E_v = \langle \Phi | \, H^e \, [n(\mathbf{r})] \, | \Phi \rangle = \langle \Phi | \, \underbrace{T[n(\mathbf{r})] + V_{int}[n(\mathbf{r})]}_{F_{HK}[n(\mathbf{r})]} + V_{\text{ext}}[n(\mathbf{r})] \, | \Phi \rangle \, . \qquad (2.8)$$

The sum of $T[n(\mathbf{r})]$ and $V_{int}[n(\mathbf{r})]$ is a *universal functional* of the electron density. The expression for this unknown functional is the same for every system and is independent from the external potential. Therefore, a specific kind of system is determined only by $V_{\text{ext}}[n(\mathbf{r})]$.

The density, $n(\mathbf{r})$ which is a summation of the density of spin up $n_\uparrow(\mathbf{r})$, and spin down $n_\downarrow(\mathbf{r})$, is defined as:

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) = \langle \Phi | \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \, | \Phi \rangle \, . \qquad (2.9)$$

The total energy can be written as a functional of the density in terms of the external potential and the universal functional in the following way,

$$E_v[n(\mathbf{r})] \equiv \langle \Phi | \, H^e \, [n(\mathbf{r})] \, | \Phi \rangle$$

$$\equiv \int V_{\text{ext}}(\mathbf{r}) \, n(\mathbf{r}) \, d^3\mathbf{r} + \mathcal{F}[n(\mathbf{r})] \, , \qquad (2.10)$$

where $\mathcal{F}[n(\mathbf{r})] = \langle \Phi | \, F_{HK}[n(\mathbf{r})] \, | \Phi \rangle$.

THEOREM 2. *The ground state energy can be obtained variationally, the density that minimises the total energy is the exact ground state density.*

This means, that $E_v[n_0]$ is the ground-state energy if and only if the true ground-state density $n_0(r)$ is inserted. For any other density $n(r)$ (which is solution of Eq. 2.8 and satisfies the constraint of the constant number of electrons, $\int n(\mathbf{r}) \, d\mathbf{r} = N$), the obtained energy is larger than $E_v[n_0]$

$$E_v[n_0] = \min_{n(\mathbf{r})} \, (E_v \, [n(\mathbf{r})]) \, \leq \, E_v[n] \, . \qquad (2.11)$$

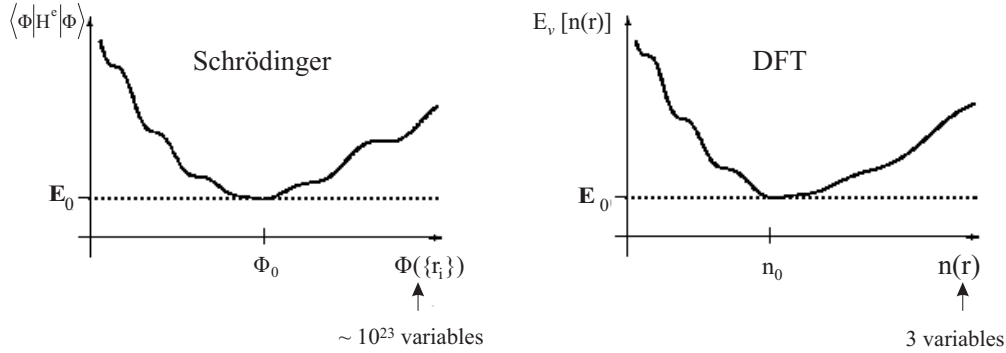The ground state energy can be obtained from the variation principle, under the

Fig. 2.1: Schematic figure of variation principle for $\langle\Phi_0|\ H\ |\Phi_0\rangle$ and $E_v[n(\mathbf{r})]$. Figure is adapted from [1]

constraint of conserving the number of electrons of the system. In other words:

$$\delta\langle\Phi|\ H^e\ [n(\mathbf{r})]\ |\Phi\rangle\ = \delta\ \{E_v[n(\mathbf{r})] - \mu\ (\int n(\mathbf{r})\ d^3\mathbf{r} - N)\} = 0\ . \tag{2.12}$$

Hence the constraint of a constant total number of electrons being equal to N is taken into account by the method of Lagrange multipliers. The important physical conditions which have to be satisfied is that $n(\mathbf{r}) \geq 0$ and the assumption of continuous $n(\mathbf{r})$.

$$\int n(\mathbf{r})\ d^3\mathbf{r} = N, \tag{2.13}$$

Solving the equation above leads to the following Euler-Lagrange equation

$$\mu = \frac{\delta E_v[n]}{\delta n(\mathbf{r})} = V_{\text{ext}} + \frac{\delta F_{HK}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\ , \tag{2.14}$$

where the Lagrange multiplier, μ, is known as a chemical potential of the electrons.

The second Hohenberg-Kohn theorem states that there is a one to one correspondence between the ground-state wave function and the v-representable electron densities [1].

Now the many-electron problem with 10^{23} variable in three-dimensions turn into a problem with just one variable in three-dimensions.

Figure 2.1 is a schematical comparison of the solution of the Schrödinger equation using the wave function of electrons (10^{23} wave functions) and the DFT approach using the electron density[2]. The significant advantage is achieved in DFT. In the

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[1]A density is v-representable, if it is associated with the electronic ground-state wave function of a Hamiltonian in form of $H = F_{KH} + V_{\text{ext}}$.

[2]Figure is taken from the presentation of Prof. M. Scheffler in density-functional theory workshop at Los Angeles, IPAM, (2005).

treatments which are based on the wave function, one has to insert 10^{23} variables to the functional while in the DFT approach the functional depends only on one variable with three coordinates. One must use a separate wave function of each electron which sums up to 10^{23} variables.

• The Kohn-Sham Equations

The Kohn-Sham equations published in 1965, turn DFT into a practical tool for obtaining the ground state energy [29]. The Kohn-Sham formulation centres on mapping the full interacting system, onto a virtual non-interacting system. The Kohn-Sham method gives an exact solution since the virtual system yields the same ground state density as the real system. The kinetic energy functional of the non-interacting system, $T_s[n]$ (which is known), is not the same as the unknown kinetic energy of the real system. Therefore the difference between them contributes to the *correlation energy*, E_c . The potential energy of the real system contains two terms: the classic part or Coulomb interaction, V_H, (which is known) and the unknown quantum part. The difference between these two parts is named *exchange energy*, E_x . Therefore the functional $E_v[n(\mathbf{r})]$ can be written as a function of known quantities, kinetic energy (T_s) and Coulomb (Hartree) energy (E^H) of a non-interacting classical system and the unknown E_c and E_x functional,

$$E_v[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r}) \, n(\mathbf{r}) \, d^3\mathbf{r} + E^H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] \,, \qquad (2.15)$$

here, $E_{xc} = E_c + E_x$.

With the assumption above the Hamiltonian of the real system turns into the following formalism which is called *Kohn-Sham Hamiltonian*:

$$H_{KS}[n(\mathbf{r})] = T_s[n(\mathbf{r})] + V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})]. \qquad (2.16)$$

Here, V_{xc} is called exchange-correlation potential. It is a variational derivative of the exchange-correlation energy, E_{xc},

$$V_{xc} = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \,. \qquad (2.17)$$

The Kohn-Sham Hamiltonian transforms the many-electron Schrödinger equation into a set of one-particle Kohn-Sham equations which are much easier to solve than the Schrödinger equation.

$$H_{KS}\Phi^{oi}(\mathbf{r}) = \epsilon_{oi}\Phi_{oi}(\mathbf{r}) \,, \qquad (2.18)$$

here, Φ_{oi} 's and ϵ_{oi} 's are Kohn-Sham orbitals and eigenvalues. The Kohn-Sham equations are a set of equations which describe the behavior of non-interacting classical particles inside an external potential, V_{ext}. Please note that the eigenvalue of the single Kohn-Sham equations are not the energy of electrons but just mathematical objects and have no physical meaning.

The construction of Kohn-Sham equations guarantees that the ground state density of this virtual system is exactly the electron ground state density of the real system, $n(\mathbf{r}) = \sum_i \Phi_{oi}^*(\mathbf{r})\Phi_{oi}(\mathbf{r})$.

Since the Kohn-Sham Hamiltonian depends on the density, $n(\mathbf{r})$, which is driven from Φ_i, a *' self consistency problem '* has to be considered to obtain a solution.

$$\underbrace{(-\frac{\hbar^2}{2m}\nabla_i^2}_{T_s[n]} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\int\frac{n(\mathbf{r})\,d^3\mathbf{r}}{|\mathbf{r}-\mathbf{r}'|}}_{V_H} + V_{xc} + V_{\text{ext}})\Phi_i(\mathbf{r}) = \epsilon_i\Phi_i(\mathbf{r}) \,. \tag{2.19}$$
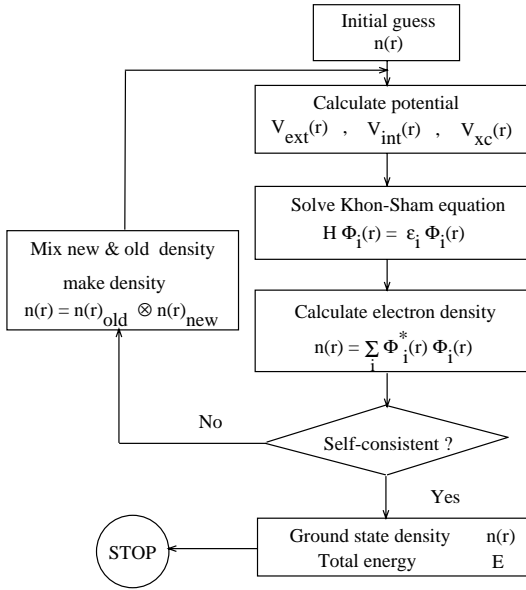

Fig. 2.2: The Self-consistent field approach for solving Kohn-Sham equations.

In the self-consistent field (SCF) approach (cf. Fig. 2.2), the solutions, Φ_i, determine the Hamiltonian, and the equations cannot be solved before its solutions to be known. This paradox can be solved by an iterative procedure: a initial density, $n_i(\mathbf{r})$ is guessed and the Hamiltonian is constructed. The equations are solved and the resulting Φ_i lead to a new density, $n_1(\mathbf{r})$, which most probably is different from the initial density. Again, new Hamiltonian with new density is constructed which yields $n_2(\mathbf{r})$ and so on.

This procedure is set up in such a way that it converges this series to a final density, $n_f(\mathbf{r})$, which generates a Hamiltonian with the solution of previous density, $n_f(\mathbf{r})$, again. This final density is consistent with the Hamiltonian.

Kohn and Sham devised an ingeniously practical single-particle scheme for performing DFT calculations, which is still exact, in principle. An additional approximations must be made for the unknown component, $E_{xc}[n(\mathbf{r})]$, which accounts for

electron many-body effects. The exchange and correlation energy is an important contribution since the binding energy of the systems is defined in an accurate description of $E_{xc}[n(\mathbf{r})]$ which is crucial for the prediction of binding properties.

Description of some present approximations for the exchange-correlation energy (potential) in DFT is the object of following part.

2.4   Approximation to The Exchange Correlation Potential

Hohenberg and Kohn in their original paper, considered the exchange-correlation potential for an inhomogeneous electron gas of almost constant density [25].

$$n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r}) , \qquad (2.20)$$

with $\tilde{n}(\mathbf{r})/n_0 \ll 1$ and $\int \tilde{n}(\mathbf{r})\, d\mathbf{r} = 0$. Then the exchange-correlation energy functional is expanded in terms of the assumed density:

$$E_{xc}[n] = \int \epsilon_{xc}^{homo}[n(\mathbf{r})]n(\mathbf{r})d\mathbf{r} , \qquad (2.21)$$

where $\epsilon_{xc}^{homo}[n]$ is the exchange-correlation energy per electron of a uniform (homogeneous) electron gas of density n. The ϵ_{xc} is a functional of the local density, so that this approximation is known as *Local-Density Approximation* (LDA). The analogous formalism, in which it describes a spin-polarized system, is known as *Local -Spin -Density Approximation* (LSDA). The E_{xc} is a functional of both spin up and spin down density. LDA predicts a too high cohesive energy and underestimates the equilibrium volume, due to overbinding.

There are several approximations for the ϵ_{xc}. The most widely used approximations were proposed by:

Wigner [30]: $\epsilon_x = \frac{-0.09164}{r_s}$ and $\epsilon_c = \frac{-0.88}{7.8+r_s}$. $r_s = (4\pi n/3)^{-1/3}$ is the Wigner-Seitz radius.

Hedin and Lundqvist [31] : $\epsilon_x = \frac{-0.9164}{r_s}$ and $\epsilon_c = -0.045[(1 + (\frac{r_s}{21})^3)h(1 + \frac{21}{r_s} + \frac{r_s}{42} - (\frac{r_s}{21})^2 - \frac{1}{3})]$

Perdew and Wang [32]: which used the Ceperley and Alder [33] parameterization

for $r_s \geq 1 : \epsilon_x = \frac{-0.4582}{r_s}$

$$\epsilon_c = \begin{cases} \frac{-0.1423}{1+11.0529 \sqrt{r_s}+0.333\ r_s} & r_s \geq 1 \\ -0.0480 + 0.0311\ \ln r_s - 0.0166\ r_s + 0.002\ r_s\ \ln r_s & 0 \leq r_s \leq 1 \end{cases}$$

For a system with smooth electron density LDA provides an accurate enough description, but for strongly inhomogeneous systems, in which the density variations are significant, the performance of an LDA-E_{xc} functional is not satisfactory.

An Alternative to LDA can be obtained by letting E_{xc} depend on the gradient of density as well, which allows for more flexibility in dealing with density fluctuations.

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r})\ \epsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))d^3\mathbf{r} \ . \tag{2.22}$$

This approach leads to the *Generalized Gradient Approximation*(GGA).

The idea of using the gradient of density beside density, was found for the first time in Kohn and Sham original paper from 1965 [29]. They used a gradient expansion of the density as a correction:

$$E_{xc}[n] = \int \epsilon_{xc}[n(\mathbf{r})]n(\mathbf{r})d\mathbf{r} + \int \epsilon_{xc}^2[n(\mathbf{r})]|\nabla n|^2 d\mathbf{r}\ +\ ... \tag{2.23}$$

There is not a unique generalized gradient approximation for the exchange- correlation functional. Indeed, there are several modifications and some of the most popular functionals, implemented also in the WIEN2k code are: the PW91 formalism, proposed by Perdew and Wang [32] and the modified version, PBE-96 by Perdew-Burke-Ernzerhof [34]. The latter one is used throughout the present work.

In the PBE-96 functional, a correction term, $h(n, r_s, t)$ is added to the correlation part, ϵ_c. The correlation energy is a functional of the relative spin polarization density, $\bar{n} = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$,

$$E_c^{GGA}[n_\uparrow, n_\downarrow] = \int n(\mathbf{r})(\epsilon_c^{homo}(\bar{n}, r_s) + H(\bar{n}, r_s, t))d^3\mathbf{r} \ , \tag{2.24}$$

where $t \propto |\nabla n|/n$.

The functional h has a logarithmic shape and obeys the following conditions [34]:
i) For a slowly varying density gradient, h is given by its (the densities) second-order gradient expansion.
ii) For a rapidly varying density gradient, $h \longrightarrow -\epsilon_c^{homo}$.

iii) Under uniform scaling h is a constant.

The exchange energy is constructed as:

$$E_x^{GGA} = \int n(\mathbf{r})\epsilon_x^{homo}(n)F_x(s)d^3\mathbf{r} \ , \qquad (2.25)$$

where $s = |\nabla n|/(2k_f n)$ and $k_f = (9\pi/4r_s^3)^{-1/3}$. F_x is given as:

$$F_x(s) = 1.804 - \frac{0.804}{1 + 0.235s^2/0.804} \ . \qquad (2.26)$$

Note that the energy in the PBE formalism is given in Hartree unit.

The last level of approximation is applied to solve the Kohn-Sham equation.

2.5   Approximation for Solving The Kohn-Sham Equations

A most important step for solving Kohn-Sham equations is to find a suitable basis set for the expansion of wave function. Using the suitable basis set that describes the behavior of the electrons leads to a solution of Kohn-Sham equations, not be computationally very demanding but still accurate. For example, the behavior of an electron in a constant potential can be described quite well by a set of plane waves.

The DFT orbital wave functions, Φ_is, are then expanded in terms of a basis set, φ^i,

$$\Phi_{oi} = \sum_{\mathbf{K}}^{M} c_{\mathbf{K}}^i \ \varphi_{\mathbf{K}}^i \quad , \qquad \mathbf{K} = \mathbf{k} + \mathbf{G} \ , \qquad (2.27)$$

where k is the crystal momentum vector in the irreducible Brillouin zone and G is a reciprocal lattice vector.

In order to find the density, one must set up the basis set and determine the c_K^i co-efficients. In principle, the expansion of the wave functions should be infinite, but in practice they are truncated at some point. The choice of the truncation value, M, turns the infinite number of the basis functions into a finite set of those. This represent the third level in a hierarchy of approximations necessary to solve a many-body system Hamiltonian, discussed in the beginning of this chapter.

There are several different methods to define the orbital wave function and solve the DFT equations. One of the common used methods is the pseudo-potential plane waves (PP-PWs) method. They are quite suitable for describing periodic solids when using pseudo-potentials, but are an inefficient basis for describing the rapid

variations of wave-functions close to the nucleus.

One solution for this difficulty is using the pseudopotential concept, in which the oscillations of the electron wave-function near a nucleus are considered in a pseudised fashion. Another possibility, used in the calculations presented in this work, is to augment the plane waves basis set in the vicinity of a nucleus.

In the following sections, the augmented plane waves (APW), the linearized augmented plane waves (LAPW) method and the effect of local orbitals on the efficiency of the basis set will be discussed.

2.5.1   Basis Functions: APW, LAPW, APW + lo

• The Augmented Plane Wave Method (APW)

Slater was the first to introduce Augmented Plane Waves (APW) as possible basis functions to solve one-electron equations [35]. In this method the unit cell is divided into two regions: i) the rigion around the nuclei, which is a sphere with radius R, the so called '*Muffin-Tin*' sphere (MT). ii) the remaining part of the unit cell which is called '*interstitial*' region (IR), see Fig. 2.3. Loucks describes this methods in detail [36].

Fig. 2.3: Division of the unit cell into two parts: the Muffin-Tin spheres, with radius R, around the nucleus and an interstitial region.

The idea behind APW is that the potential in the interstitial region is almost constant. This means, that the behavior of electrons can be efficiently described by a plane waves basis set[3]. Close to the nuclei it is assumed that electrons behave like in a free-atom. The atomic like functions are efficient to describe the behavior of the electrons in this region. Therefore, the wave function of electron over the whole unit cell can be obtained as below:
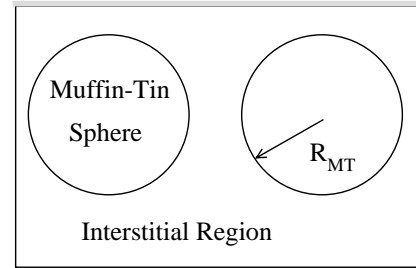
$$\varphi_{\mathbf{K}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i\mathbf{K}.\mathbf{r}} & \mathbf{r} \in IR \\ \\ \sum_{l,m} A_{lm}^{\mathbf{K}} \, u_l(r, E) \, Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in MT \end{cases} \qquad (2.28)$$

Here, V is the unit cell volume, Y_{lm} are spherical harmonics and u_l is the numerical solution to the radial Schrödinger equation at the energy ϵ:

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[3]The solution of a Hamiltonian with constant potential is plane waves.

$$\left\{ -\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \left[\frac{l(l+1)}{r^2} + V_{\text{eff}}(r) - \epsilon\right]\right\} u_l(r,\epsilon) = 0 \ . \qquad (2.29)$$

The coefficients $A_{lm}^{\mathbf{K}}$ are chosen in such way that satisfy the boundary conditions. The only boundary condition in the APW method is that the basis functions must be continuous at the MT-sphere boundaries [4]. Therefore, with expanding the plane wave into Bessel functions and matching the basis functions inside and outside the sphere, the coefficients are

$$A_{lm}^{\mathbf{K}} = 4\pi i^l Y_L^*(\hat{\mathbf{K}}_{\mathbf{G}})\frac{j_l(\mathbf{K}_{\mathbf{G}}R)}{u_l(R,E)} \ , \qquad (2.30)$$

where $j_l(\mathbf{K}_{\mathbf{G}}r)$ are Bessel functions and R is radius of MT sphere.

The Kohn-Sham eigenstates are expressed as linear combination of APW functions, $\varphi_{\mathbf{K}}(\mathbf{r})$:

$$\Phi_{oi}(\mathbf{r}) = \sum_{\mathbf{K}} C_{\mathbf{K}}^i \, \varphi_{\mathbf{K}}(\mathbf{r}) \ . \qquad (2.31)$$

The expansion coefficients $C_{\mathbf{K}}^i$, can be determined variationally [36]. This requires a variational expression for energy with respect into the linear combination of APW basis set:

$$\frac{\delta\langle\Phi_o\,|H|\,\Phi_o\rangle}{\delta C_{\mathbf{K}}} = 0 \ . \qquad (2.32)$$

Although the APW basis set can describe the behavior of the electron near the nuclei, there are two shortcomings for this method:

i) First, the coefficients $A_{lm}^{\mathbf{K}}$ are not defined for the energies that yield a radial solution equal to zero at MT-sphere boundaries, $u_l(E,R) = 0$. In this case, the basis sets are decoupled, since the boundary conditions would not be satisfied [37].

ii) Second, the Kohn-Sham wave functions, $\Phi_i(r)$ can be described by the APW basis set only if the radial solutions are evaluated at Kohn-Sham eigenvalues,$(E = \epsilon_i)$. Therefore a different energy-dependent set of APW basis functions must be found for each Kohn-Sham eigenenergy. One should start with a guessed energy value, solve the radial Schrödinger equation to construct the APW basis and set up the matrix elements . Then the determinant $|H - ES|$ must be computed, where S is the overlap matrix [5]. So in order to find the root of the determinant, several trial energies have to be tested. A similar procedure is repeated to determine all matrix

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[4]The kinetic energy is not well-defined for discontinuous basis functions.
[5]Since the APW basis sets are not orthogonal, overlap matrix would not vanish from the secular equation.
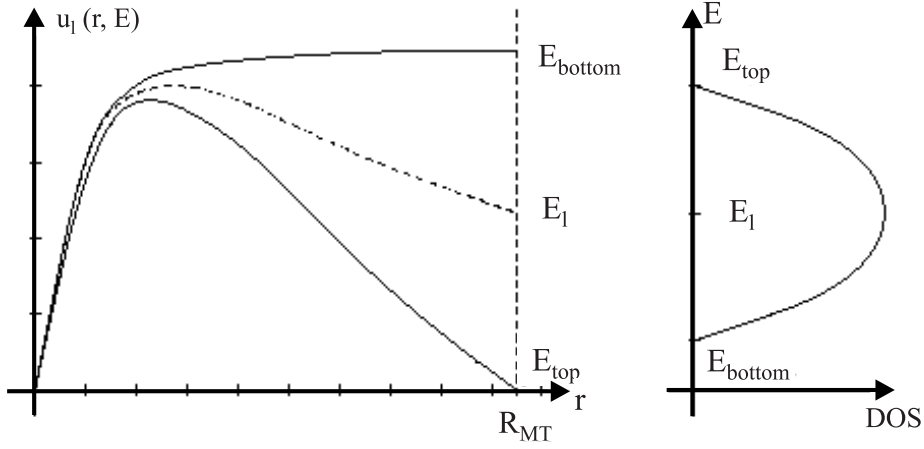
Fig. 2.4: Schematic dependence of $u_l(r, \epsilon_l)$ **(a) and DOS (b) on the energy** ϵ.

elements. This is computationally very expensive [38].

• The Linearized Augmented Plane Wave Method (LAPW)

In 1975 Andersen [39] and Koelling and Arbman [40] in two different works, improved the APW methodology and solved the problem of energy-dependence of the basis set. In this modified method which is called ' *Linearized Augmented Plane Wave* **' (LAPW), an energy independent radial solution is expanded in a Taylor-like series around a fixed energy. Such a Taylor expansion of** u_l **around fixed energy value[6]** E_l **is given by:**

$$u_l(r, \epsilon) = u_l(r, \epsilon_l) + (\epsilon_l - \epsilon) \underbrace{\left.\frac{\partial u_l(r, \epsilon)}{\partial \epsilon}\right|_{\epsilon = \epsilon_l}}_{\dot{u}_l(r, \epsilon_l)} + O(\epsilon_l - \epsilon)^2 \ . \qquad \textbf{(2.33)}$$

The basis functions in the interstitial region are considered to be PW while the basis set inside the MT-spheres are taken as a linear combination of a radial solution, u_l, **at fixed linearization energy,** E_l, **and its energy derivative ,** $\dot{u}_l$, **at the same energy. Note that both** u_l **and** $\dot{u}_l$ **are regular at the origin.** E_l **should be chosen in such a way that its value is close to the center of the energy band with the appropriate** l-**character.**

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[6]It is not essential that E_l is equal to the Kohn-Sham eigenvalues.

$$\varphi_{\mathbf{K}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i\mathbf{K}.\mathbf{r}} & \mathbf{r} \in IR \\ \\ \sum_{l,m} (A_{lm}^{\mathbf{K}} \ u_l(r, E_l) \ + \ B_{lm}^{\mathbf{K}} \ \dot{u}_l(r, E_l)) \ Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in MT \end{cases} \tag{2.34}$$

The coefficients $A_{lm}^{\mathbf{K}}$ and $B_{lm}^{\mathbf{K}}$ will be determined by requiring that the basis function as well as its derivative are continuous at the boundary of the MT-sphere.

Since the shape of the radial solution $u_l(r, \epsilon)$ depends on the ϵ_l, choosing the suitable linearization energy ϵ_l is quite important. The most simple way for doing this is the Wigner-Seitz method. In this method the linearized energy is chosen to be the average of two energies ϵ_{top} and ϵ_{bottom}, i.e. $\epsilon_l = (\epsilon_{top} + \epsilon_{bottom})/2$, see Fig. 2.4 [7]. ϵ_{top} is the highest antibonding energy state, i.e. the top of the band. It is also an energy, for which the radial solution becomes zero at the MT-sphere boundaries, $u_l(R, E_{top}) = 0$. The other energy is chosen in a similar fashion: E_{bottom} is the lowest bonding energy state, i.e. the bottom of the band and for it the derivative of the radial solution becomes zero at the MT-sphere boundaries, $\dot{u}_l(R, E_{top}) = [\partial u_l(r, E_{bottom})/\partial r]_R = 0$, see Fig. 2.4-a.

Solutions to the radial Schrödinger equation, u_l, for *s*, *p*, *d* and *f* orbitals are shown for an APW basis set in Fig. 2.5-a and an LAPW basis function in Fig. 2.5-b. The Figure is taken from work by Sjöstedt *et al.* [37]. As mentioned before and can be seen from the figure, due to the discontinuous behavior of the slopes of the functions in the APW approach, it possesses a kink at the MT-sphere boundary. In contrast, the LAPW functions have smooth behavior at the MT-sphere boundary.

The LAPW basis set can provide sufficient basis functions for Kohn-Sham eigenstates in the energy range around the linearization energy. Therefore, all the Kohn-Sham eigenvalues can be found with just a single diagonalization of the secular matrix. However, the number of basis functions in LAPW is larger than in the APW method, thus the secular matrix of LAPW is enlarged in comparison to APW.

• The Augmented Plane Wave plus local orbital Method (APW+lo)

In an alternative approach to LAPW one can combine advantages of both the APW and the LAPW method to optimized basis functions. It can be done by removing the energy dependence of the original APW basis functions (which is the characteristic of LAPW functions) but retaining the lower cutoff, i.e. smaller matrix associated with the original APW functions. In the so called APW+lo method (de-

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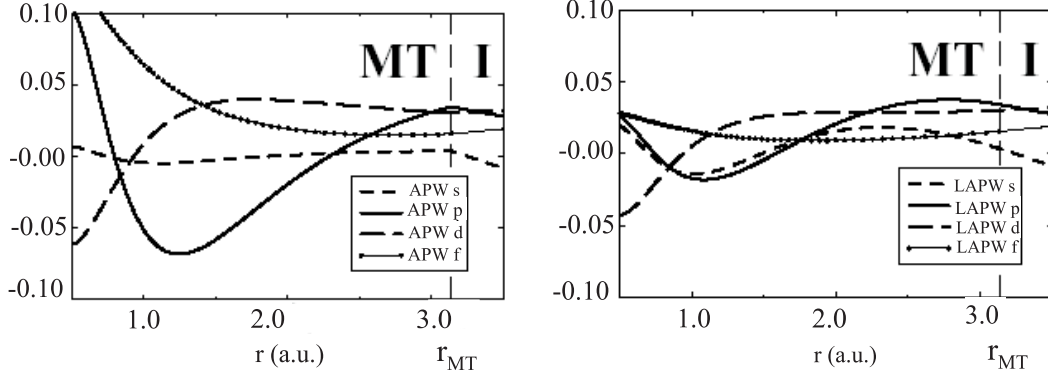[7]Figure is adapted from WIEN2k userguide (http://www.wien2k.at).

Fig. 2.5: Radial solution, u_l, of the l-composition and its behavior at MT-sphere boundaries in an APW (a) and LAPW (b) basis function are compared.

veloped by Sjöstedt *et al.*) Sjöstedt *et al.* proposed an energy-independent basis set of APW which combines with a new basis set in the MT-sphere which belongs to the local orbitals. This new basis set is called local orbital basis set (lo). It is applied in order to increase the flexibility of the basis set and to recover the effect of the missing derivative of the radial wave functions. They (the local orbitals), neither impose extera boundary condition of the APW basis set nor affect the number of basis functions in the interstitial region. This local orbitals are restricted only inside the MT-sphere, therefore the interstitial region will remain unaffected.

$$\varphi_{lm}^{lo}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in IR \\ \\ \sum_{l,m} \left(A_{lm}^{lo}\, u_l(r, E_l)\, +\, B_{lm}^{lo}\, \dot{u}_l(r, E_l) \right) Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in MT \end{cases} \quad (2.35)$$

For simplification, one can use the same linearization energy for the local orbital basis functions. The coefficient A_{lm}^{lo} and B_{lm}^{lo} are determined by normalization and using $\varphi_{lm}^{lo} = 0$ at the MT-sphere boundary. The APW and local orbital are continuous at the MT-sphere while their first derivatives are discontinuous (the slope of the local orbital has a non-zero value at the MT-sphere).

The new APW+lo basis set includes the radial solutions of the Schrödinger equation in their original APW form, which efficiently describes the eigenfunctions at energies close to E_l, but also a (less restricted) linear combination of $u_l(r, E_l)$ and $\dot{u}_l(r, E_l)$, which improves the description of states away from E_l.
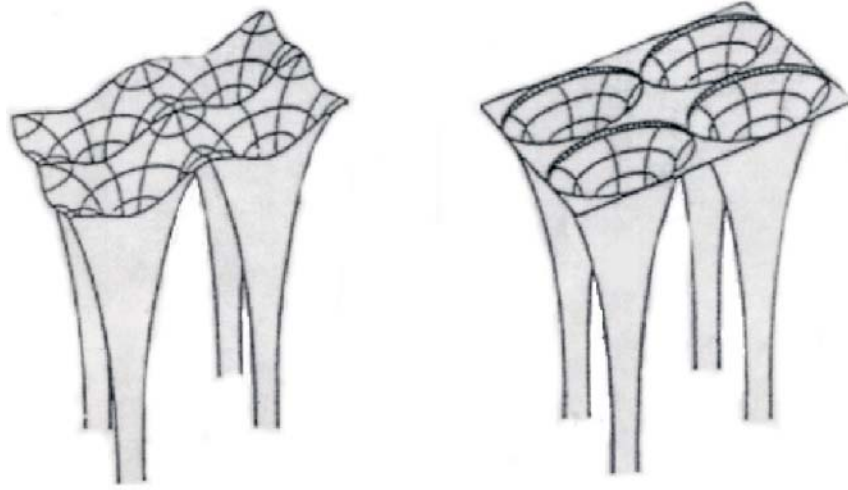
Fig. 2.6: Schematic shape of the full potential (a) and the Muffin-Tin potential (b).

2.5.2   Representation of The Potential

The (L)APW method allows an accurate description of the rapidly changing (oscillating) wave-functions, potential and electron density close to the nuclei as well as the smoother part of these quantities in between the atoms (interstitial region). Therefore the representation of the potential will be similar to the wave-functions, the potential is a hybrid of two adjacent regions of space.

M. Weinert [41] and E. Wimmer *et al.* [42] proposed a method to describe the all electron potential in the solid using the multipole potentials concept. As there is no shape approximation for the potential, such an approach is called a full-potential treatment. In this method the Poisson equation is solved for the general periodic potential, including the non-spherical contributions of the potential inside the MT-sphere to the Hamiltonian matrix elements.

The Hamiltonian , and hence the potential, contains three contributions:

$$V_{eff} \; = \; V_S + V_{NS} + V_{IR} \, , \tag{2.36}$$

where the V_S, V_{NS} and V_{IR} terms are due to the spherical and non-spherical part of the potential in the MT-sphere and the potential in interstitial regions [43].

The potential in the interstitial region is described by the Fourier representation (of the smooth interstitial charge density), which means that the full potential has then

the following form:

$$V(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} V_{\mathbf{G}} \, e^{i\mathbf{G}.\mathbf{r}} & \mathbf{r} \in IR \\ \\ \sum_{L,M} V_{LM}(\hat{\mathbf{r}}) \, Y_{LM}(\hat{\mathbf{r}}) & \mathbf{r} \in MT \end{cases} \tag{2.37}$$

Here, G is a reciprocal vector and its maximum value is required to be larger than the one of a reciprocal vector in the PW expansion in the interstitial region, K. This is due to the fact that the Fourier expansion represents the potential while the quadratic form of the wave functions determine the density.

Y_{LM}s are lattice harmonics represent the point group symmetry which is applied to the spherical harmonics. The quality of the full-potential is controlled by the cutoff parameter G which truncates the sum over lattice vectors in the interstitial region and L, M which restricts the number of the non-spherical terms inside the MT-sphere which contributes to the potential.

Neglecting non-spherical terms, ($l \neq 0$), in the expansion of the potential inside a MT-sphere and considering just a constant potential in the interstitial region ($G = 0$) leads to an approximate crystal potential called Muffin-Tin (MT) potential. The MT-potentials are a reasonable approximation to describe the potential for bulk materials but for reduced symmetry solid (such as films or interface) it is not a very useful treatment. The schematic shape of the full potential and the MT-potential is shown in Fig. 2.6.

2.6   k-point Sampling

According to Bloch's theorem [44], any real-space integral over a periodic system with infinite extent can be replaced by an integral in reciprocal-space over the (finite) first Brillouin zone. Thus in order to study the properties of crystals, one needs to calculate the integration of the periodic functions over the first Brillouin-zone (1BZ) in the reciprocal space in [45]; For a example quantity I can be defined as:

$$I = \int_{BZ} F(\mathbf{K}) \, d^3\mathbf{k} \,, \tag{2.38}$$

where the periodic function, $F(\mathbf{k}) = \sum_R f(\mathbf{R}) \, e^{i\mathbf{k}.\mathbf{R}}$ is the Fourier transform of a periodic function in real space. In practice for the numerical evaluation, this integral turns into the sum over a large number of discrete points. To make calculations feasible only a finite set of such points in the BZ is used to compute these functions.

Such a set of special points is called $'\mathbf{k} - point'$ set. [46]:

$$\Omega^{-1} \int_{BZ} F(\mathbf{k})\, d^3k = \sum_n w_n F(\mathbf{k}_n) \,. \tag{2.39}$$

Here Ω is the unit cell volume in the real space and w_n is a weight factor [8] and the sum over all weights is equal to one.

$$\sum_n w_n = 1 \tag{2.40}$$

The error introduced by using a discrete k-point set can be reduced by increasing the density of the k-point mesh.

The symmetries of a crystal allow further reduction of the number of k-points used for an actual calculation. There are several methods to find such set of points [47–49]. The most applicable and famous approach is that of Monkhorst and Pack, [49] which is employed for the calculations in this work. This scheme contains equispaced grid points which are distributed homogeneously throughout the BZ with rows and columns parallel to the reciprocal vectors. These equispaced grid of k-points are constructed as follows:

$$\mathbf{k} = x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3 \,, \tag{2.41}$$

where $\mathbf{b}_i$s are the reciprocal lattice vectors, and the coefficients are obtained:

$$x_i = \frac{(2i - q - 1)}{2q} \qquad , \qquad i = 1, 2, ...q \tag{2.42}$$

q is an integer number that determines the number of special points in the set.

Typically, the point-group symmetry of the crystal is used to produce a smaller subset of the full k-point set, containing points located within the irreducible part of the Brillouin zone. The values of the weighting factors will be adjusted according to this new k-point set. This k-point in the irreducible BZ results in a significant reduction in the computational expense since a smaller number of k-points is used in the summations.

Choosing a sufficiently dense mesh of integration points is crucial for the convergence of the results. Therefore, it is one of the major parameters for which one should perform convergence tests before setting up the calculations.

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[8]A weight factor, w_n, is defined as a fraction of k-points equivalent under symmetry consideration.
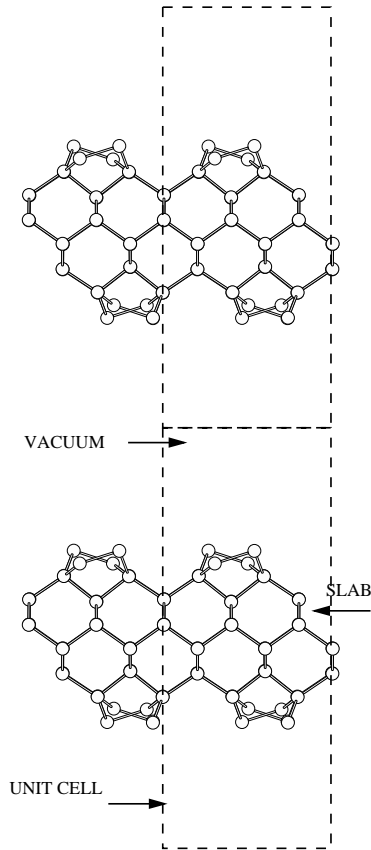
2.7   The Slab Model and The Supercell Approach

Fig. 2.7: Side view of a slab model containing 8 layers Si(001)(2×2) with alterating dimer reconstruction and vacuum.

The goal of this work is to predict and simulate the behavior of magnetic adatoms (such as adatom adsorption, diffusion pathways and thin film growth) on semiconductor surfaces. To perform such calculations, one needs a proper model that describes the system reasonably well and is computationally not (too) expensive.

Normally, in the bulk material with three dimensional periodicity, the periodic boundary conditions of solids can be satisfied in the surfaces. However, due to the lack of the translation symmetry in the direction normal to the surface, the periodicity will be reduced to two dimensions. The slab approach is suitable for such a purpose and is utilized in this work to simulate the studied system. In the slab model the unit cell is described by a finite number of layers and a vacuum region is introduced into the unit cell. This leads to a reduction of the symmetry (compared to the bulk material) in z-direction, but also introduces a surface into the calculation. Periodic boundary conditions ensure that the slab is infinte in x and y direction, but also that there are periodically repeated slabs in z-direction, which are separated by the vacuum region. The slabs used in this work are constructed in such a way, that inversion symmetry is retained. The thickness of the slab and the vacuum region are chosen with the requirement that both surfaces would not have interaction with each other through the vacuum or the slab. The adequate value for slab and vacuum thickness must be determined in convergence tests.

There are two different interpretations and descriptions of the slab model within the (L)APW method and the shape of the full-potential:

i) Film geometry approach, in this model which was proposed by Krakauer *et al.* [42, 43, 50], the vacuum region is described by an alternative basis set and potential term. The basis function is considered to be a product of a two-dimensional plane-wave and a z-dependent function and its energy derivative. The z-dependent func-

tion is defined by the solution of the one-dimensional Schrödinger equation with z-dependent potential. The applied boundary condition requires that the basis function and its energy derivative are continuous across the slabs boundaries.

ii) Supercell approach: this model is used in the present work. It is based on the three dimensional periodicity of the unit cell. It means the periodic boundary conditions are applied for the slabs in z-direction as well as in x and y directions. The conditions of an adequate thickness of the vacuum and the slab, requires that the the electronic wave function of the slabs vanishes around the middle of the vacuum region. The middle layers of the slabs should have a bulk-like representation.

A side view ball-stick model of a supercell with an eight layer Si(001)(2×2) slab and a vacuum region, which is approximately 1.5 times as thick as the slab, is shown in Fig. 2.7.

2.8   The WIEN2k Code

The calculations in this work are performed using the WIEN2k computer package [51, 52]. This program contains several sub-programs, which are described briefly in the following parts. There are two major parts in the program, the initialization and the self-consistent field [(SCF)] cycle. The flow chart of the code is given in Fig. 2.8.

• Initialization:
setting up the unit cell and generating the initial density

In this sub-program, atomic densities are generated and superimposed to obtain a initial crystal density for the SCF calculation. Additionally, the atomic potentials and, optionally, atomic valence densities are created. Information about l, m values of the lattice harmonics representation and number of Fourier coefficients of the interstitial charge density are inserted as input file in this part.

• LAPW0:
Construction of the effective potential:

The Poisson equation is solved and the total potential is computed as the sum of the Coulomb and the exchange-correlation potential in the LAPW0 program. The electron (spin) density is used as input and the spherical (l=0) and the non-spherical parts of the potential are generated. The Coulomb potential is calculated by a multipolar Fourier expansion introduced by Weinert [41]. The exchange-correlation
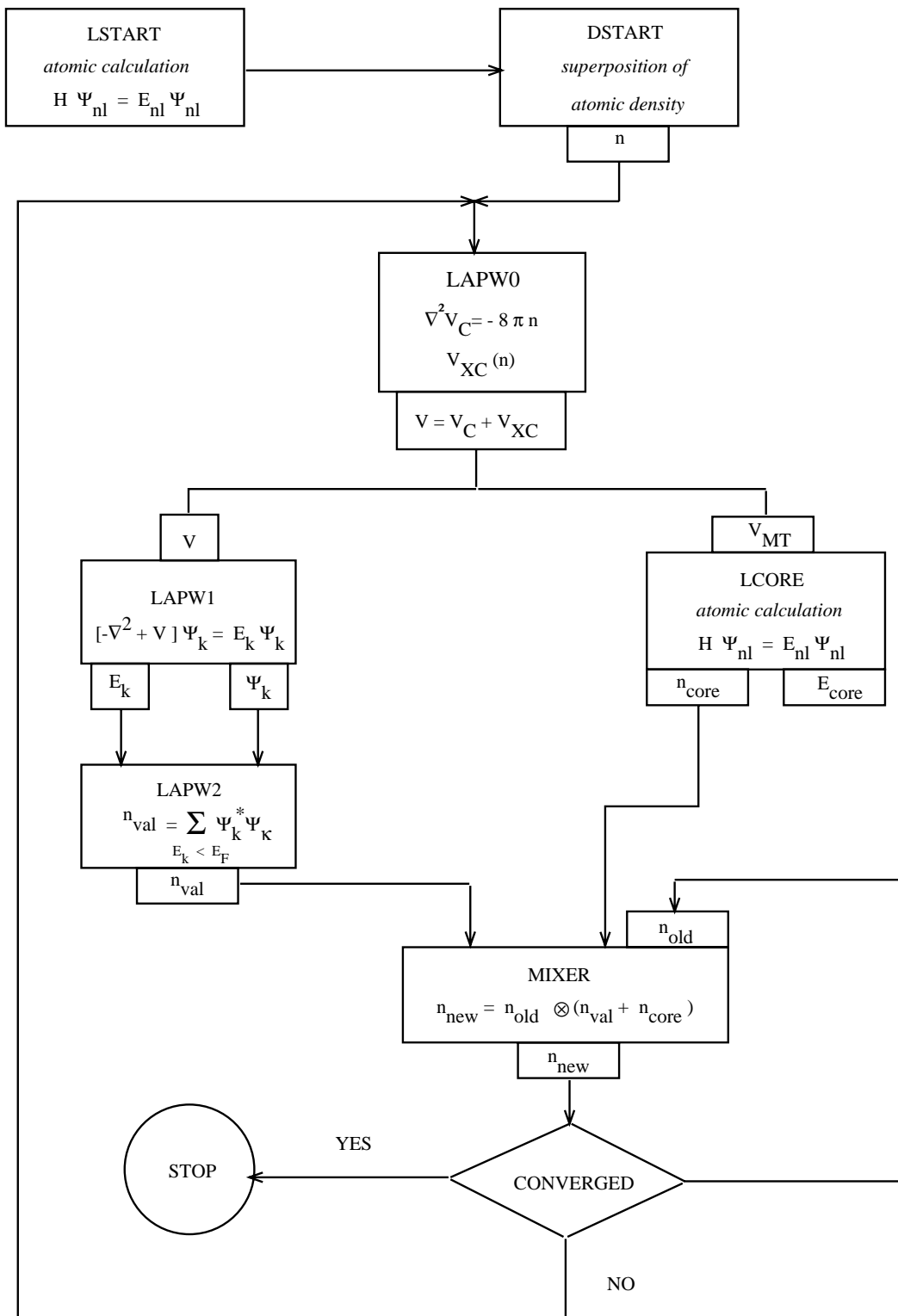
LSTART
atomic calculation
$H \, \Psi_{nl} = E_{nl} \, \Psi_{nl}$

DSTART
superposition of
atomic density

n

LAPW0
$\nabla^2 V_C = -8 \pi n$
$V_{XC} \, (n)$

$V = V_C + V_{XC}$

V

LAPW1
$[-\nabla^2 + V] \, \Psi_k = E_k \, \Psi_k$

E_k Ψ_k

V_{MT}

LCORE
atomic calculation
$H \, \Psi_{nl} = E_{nl} \, \Psi_{nl}$

n_{core} E_{core}

LAPW2
$n_{val} = \sum_{E_k < E_F} \Psi_k^* \Psi_\kappa$

n_{val}

n_{old}

MIXER
$n_{new} = n_{old} \otimes (n_{val} + n_{core})$

n_{new}

STOP

YES

CONVERGED

NO

Fig. 2.8: Flow chart of SCF cycle in WIEN2k compter code.

potential is computed numerically on a grid. Additionally, the Hellmann-Feynman force contribution to the force is also determined [53].

• LAPW1:

Solving the Kohn-Sham equations of valence electrons:

The Hamiltonian and the overlap matrix [40] are set up in LAPW1. Their diagonalization provides the eigenvalues and eigenvectors. Both the LAPW and the APW+lo methods are supported. For maximum efficiency a mix of both is recommended, i.e. the APW+lo basis functions are used for physically meaningful l values, while LAPW basis functions are employed to describe higher l-values functions.

• LAPW2:

Construction of the new electron density

The Fermi-energy is computed. The electronic charge densities are expanded according to the representation of Eq. 2.28 for each occupied state and each k-vector. Afterwards the corresponding (partial) charges inside the atomic spheres are obtained by integration. In addition, Pulay-corrections to the forces are calculated.

• LCORE :

The treatment of the core electrons

The potential and the charge density of the core electrons are computed.

• LMIXER:

Generating the input density for the next iteration

The electron densities of core, semi-core, and valence states are combined to yield the total new density. Taking only the new densities would, however, lead to instabilities in the iterative SCF process. To have a stable SCF cycle new and old densities need to be mixed, to obtain a new density.
$n_{new}^{m+1} = (1 - \alpha)n_{new}^m + \alpha\, n_{old}^m$, here α is a mixing parameter. In the WIEN2k code this is done (mainly) using the Broyden scheme.
The total energy and the atomic forces are computed in mixer, as well.