

Chapter 3

The (L)APW+lo Method

3.1 Choosing A Basis Set

The Kohn-Sham equations (Eq. (2.17)) provide a formulation of how to practically find a solution to the Hohenberg-Kohn functional (Eq. (2.15)). Nevertheless also the Kohn-Sham orbitals φ_i have to be expanded in some way. In principle it would be possible to find a purely numerical solution, but in practice most applications of Kohn-Sham density-functional theory use to date an expansion of the Kohn-Sham orbitals φ_i into basis functions ϕ_μ

$$\varphi_i = \sum_{\mu=1}^L c_{\mu i} \phi_\mu \quad . \quad (3.1)$$

For $L \rightarrow \infty$ Eq. (3.1) would give an exact expression for φ_i . In reality the expansion has to be truncated and the actually needed number of basis functions ϕ_μ to obtain a good representation of φ_i strongly depends on the choice of the basis set. Whether or not a basis set is a good choice again depends on the given problem. To begin with one has to distinguish between calculations with or without periodic boundary conditions. In this work density-functional theory is mainly applied to the calculation of solids. Since solids are infinite in all three dimensions and therefore contain an infinite number of atoms, periodic boundary conditions are used in most cases. The following discussion is thus concentrated on basis sets that are favorable to periodic boundary conditions.

In a crystalline solid the electrons are moving in a periodic, effective potential V_{eff} , that is created by the periodically arranged nuclei and consequently reflects the symmetry of the crystal

$$V_{\text{eff}}(\mathbf{r} + \mathbf{R}_n) = V_{\text{eff}}(\mathbf{r}) \quad \text{with} \quad \mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad . \quad (3.2)$$

\mathbf{R}_n is the translational lattice vector and \mathbf{a}_i are the unit cell vectors of the crystal. According to Bloch's theorem the eigenfunctions, i.e. the electronic wave functions,

resulting from a Schrödinger equation including a periodic potential in the Hamiltonian are described by a product of a plane wave and a function, which exhibits the periodicity of the crystal

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = u_{\mathbf{k}}(\mathbf{r}) \quad . \quad (3.3)$$

Here, \mathbf{k} is the wave vector within the first Brillouin zone. An obvious choice of basis functions to expand the Kohn-Sham wave functions satisfying Eq. (3.3) are plane waves. Plane waves are periodic and mathematically fairly simple. A disadvantage of an expansion in plane waves is the rather large number of basis functions needed for a proper description of the valence wave functions. In contrast to the core electrons, which are quite strongly bound and essentially confined to the core region, the valence electrons have a much larger spatial distribution and are considered as mainly determining the bonding between atoms. Outside of the atomic core region the valence wave functions are rather smooth, whereas in the vicinity of the atomic core they are strongly oscillating. These strong oscillations are induced by the orthogonalization of the valence wave functions to the wave functions of the inner core electrons.

One approach to overcome this problem, which is widely used in the solid state community, is the pseudopotential method [52]. Here, the inner core electrons are not treated explicitly, but they are merged with the nuclei to form the so-called pseudopotential. The wave functions of the valence electrons moving in such a pseudopotential are then much smoother and can thus be described by a much smaller number of plane waves.

Another approach, which in contrast to the pseudopotential method can include all electrons, is the separation of real space into regions close to the nuclei and in between them. The Kohn-Sham orbitals are then expanded differently in each region. The augmented plane wave method (APW) [53], which is used in this work, is such an approach and will be described in more detail in the next sections.

3.2 The APW Method

The augmented plane wave (APW) method was formulated by Slater in 1937 [54]. Starting from the so-called muffin-tin approximation he constructed a basis set, which consists of a combination of plane waves in regions of a slowly varying potential and atomic orbital like functions in regions of faster varying wave functions. In the muffin-tin approximation the crystal is divided into the muffin-tin (MT) region and the interstitial (I). The muffin-tin region consists of non-overlapping spheres centered around each atom. The potential can then be defined as

$$V_{\text{MT}}(\mathbf{r}) \equiv \begin{cases} \text{constant} & \mathbf{r} \in \text{I} \\ V(r_\alpha) & \mathbf{r} \in \text{MT}_\alpha \end{cases} \quad (3.4)$$

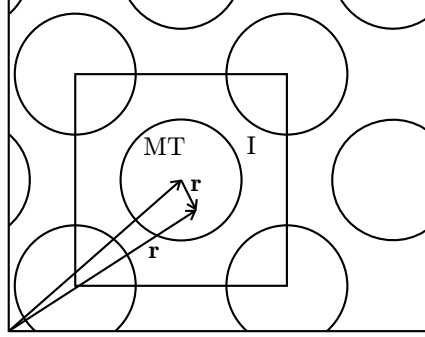


Figure 3.1: Schematic illustration of the muffin-tin potential approximation. Space is divided into muffin-tin spheres (MT_α) centered at each nuclei and the interstitial region (I). (After Ref. [55])

Here α is the index for counting the spheres and r_α is the length of the local position vector $\mathbf{r}_\alpha = \mathbf{r} - \boldsymbol{\tau}_\alpha$ (cf. Fig. (3.1)). The potential $V_{\text{MT}}(\mathbf{r})$ is constant in the interstitial and spherical in the muffin-tin region. The APW basis functions can be written as

$$\phi_{\mathbf{k}+\mathbf{G}}^{\text{APW}}(\mathbf{r}, \epsilon) = \begin{cases} \Omega^{-1/2} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & \mathbf{r} \in \text{I} \\ \sum_{lm} A_{lm}^{\alpha, \mathbf{k}+\mathbf{G}} u_l(r_\alpha, \epsilon) Y_{lm}(\hat{\mathbf{r}}_\alpha) & \mathbf{r} \in \text{MT}_\alpha \end{cases} \quad (3.5)$$

where Ω is the unit cell volume, Y_{lm} is the spherical harmonic function and $\hat{\mathbf{r}}_\alpha$ is the angular part of the local vector \mathbf{r}_α . A_{lm} is an expansion coefficient to match the function ϕ at the boundary between the muffin-tin and the interstitial and u_l is the regular solution of the radial Schrödinger equation

$$-\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{du_l}{dr} \right) + \left[\frac{l(l+1)}{r^2} + V(r) - \epsilon \right] r u_l = 0 \quad , \quad (3.6)$$

with the spherical potential $V(r)$ from Eq. (3.4). Each basis function is connected to a special \mathbf{k} -point \mathbf{k} and a reciprocal lattice vector \mathbf{G} .

In the APW method the augmenting function $u_l(r, \epsilon)$ corresponds to the exact muffin-tin potential eigenstate of eigenenergy ϵ . Because of this energy dependence of the function $u_l(r, \epsilon)$ the eigenvalue problem will be non-linear in energy and has to be solved iteratively. This is, however, computationally very costly. On the other hand, any eigenstate of a different eigenenergy will be poorly described without adapting ϵ . To overcome this problem linearized versions of the APW method have been developed, where the energy ϵ is set to a fixed value ϵ_1 and the basis functions are modified to gain extra flexibility to cover a larger energy region around their linearization energy. The linearized APW method (LAPW) and the APW+ local orbitals (APW+lo) method will be discussed in more detail in the next two sections.

3.3 The LAPW Method

The traditional way of linearizing the APW method is the LAPW method, which was developed in the beginning of the 1970s [53, 56]. In this approach the basis functions are expanded in the same way as in Eq. (3.5) in the interstitial, but inside the muffin-tin the basis functions do not only depend on $u_l(r, \epsilon_1)$, but also on its derivative $\dot{u}_l(r, \epsilon_1) \equiv \partial u_l / \partial \epsilon$,

$$\phi_{\mathbf{k}+\mathbf{G}}^{\text{LAPW}}(\mathbf{r}, \epsilon_1) = \begin{cases} \Omega^{-1/2} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} & \mathbf{r} \in \text{I} \\ \sum_{lm} [A_{lm}^{\mathbf{k}+\mathbf{G}} u_l(r, \epsilon_1) + B_{lm}^{\mathbf{k}+\mathbf{G}} \dot{u}_l(r, \epsilon_1)] Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in \text{MT} \end{cases} \quad (3.7)$$

Here and also in the further equations, the sphere index α has been omitted for clarity. The LAPW's are thus more flexible than the APW's, since for any linearization energy ϵ_1 , that differs only slightly from the real eigenenergy ϵ , the radial function $u_l(r, \epsilon)$ can be obtained by a Taylor expansion

$$u_l(r, \epsilon) = u_l(r, \epsilon_1) + (\epsilon - \epsilon_1) \dot{u}_l(r, \epsilon_1) + O((\epsilon - \epsilon_1)^2) \quad (3.8)$$

The additional term $O((\epsilon - \epsilon_1)^2)$ leads to a second order error in the wave function and a fourth order error in the eigenenergy. However, the two coefficients $A_{lm}^{\mathbf{k}+\mathbf{G}}$ and $B_{lm}^{\mathbf{k}+\mathbf{G}}$ are not fixed through the Taylor expansion, but by matching both the value and the slope of the augmenting function to a planewave at \mathbf{R}_{MT} . Due to the matching constraints the shape of the function resulting from the linear combination of $u_l(r, \epsilon_1)$ and $\dot{u}_l(r, \epsilon_1)$ will in general not resemble the physical solution u_l . By linearizing the APWs the problem of having energy dependent basis functions is resolved, but the optimal shape of the basis functions inside the muffin-tin sphere is sacrificed (cf. Fig. (3.2)).

3.3.1 Semi-Core States

In the LAPW method there is only one linearization energy ϵ_1 for every l quantum number. This leads to a problem in systems with states having the same l quantum number, but different n quantum number and therefore also clearly different energies. The problem occurs mainly for systems with so-called semi-core states, which do not lie in the valence region, but also not as low in energy as the core states. Semi-core states are treated by introducing local orbitals in the LAPW method. Local orbitals do not depend on \mathbf{k} and \mathbf{G} , but only belong to one atom and have a specific l character. They are called *local*, since they are confined to the muffin-tin spheres and thus zero in the interstitial

$$\phi^{\text{LO}} = \begin{cases} 0 & \mathbf{r} \in \text{I} \\ [A_{lm} u_l(r, \epsilon_1) + B_{lm} \dot{u}_l(r, \epsilon_1) + C_{lm} u_l(r, \epsilon_2)] Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in \text{MT} \end{cases} \quad (3.9)$$

Inside the muffin-tin spheres local orbitals involve an additional radial function evaluated at a new linearization energy ϵ_2 . Two of the coefficients are determined by

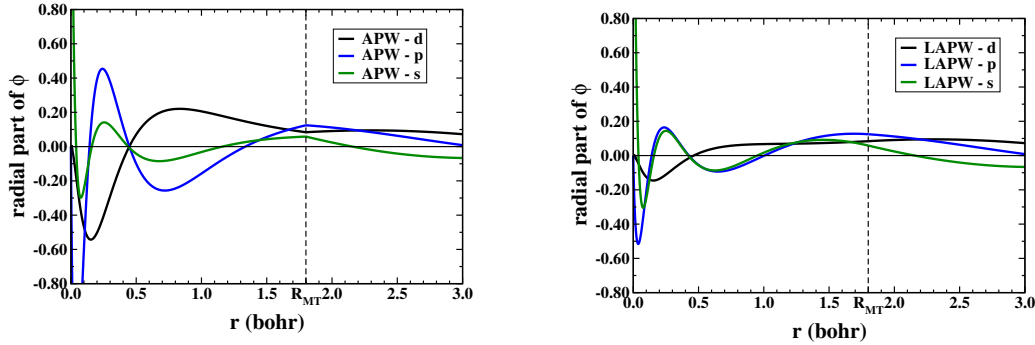


Figure 3.2: Radial part u_l of the l -composition of an APW basis function (left) and the linear combination of u_l and \dot{u}_l of the l -composition of an LAPW basis function (right) for a specific \mathbf{k} -point. The planewaves are expanded into Bessel functions.

the conditions that the value and first derivative of the local orbitals go to zero at the sphere boundary. The third one can be set to some fixed number, e.g. unity (a modification is used for lattices with inversion symmetry, cf. Section 5.9 in Ref. [53]). The resulting LAPW+LO basis set can be used to describe both the valence region and the already quite localized semi-core states appropriately.

3.4 The APW+lo Method

An alternative method to linearize the APW method is the APW+local orbitals method [55, 57, 58]. Also in this method the eigenvalue problem is linearized by choosing a fixed linearization energy ϵ_1 . However, the necessary gain in flexibility is not obtained by adding an additional term to the original APW basis functions, but by a complementary set of local orbitals

$$\phi^{\text{lo}_1} = \begin{cases} 0 & \mathbf{r} \in \text{I} \\ [A_{lm} u_l(r, \epsilon_1) + B_{lm} \dot{u}_l(r, \epsilon_1)] Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in \text{MT} \end{cases} \quad (3.10)$$

Each local orbital is matched to zero value at the sphere boundary having no restriction on the derivatives at the muffin-tin boundaries. Thus, a surface term for the kinetic energy has to be taken into account [53]. The complete APW+lo basis set consists therefore of two different types of basis functions, the APWs (Eq. (3.5)) at a fixed linearization energy ϵ_1 and the lo's (Eq. (3.10)), so that the basis set is defined as

$$\phi_i = \begin{cases} \phi_i^{\text{APW}} & i \leq N_{\text{APW}} \\ \phi_i^{\text{lo}_1} & i > N_{\text{APW}} \end{cases} \quad (3.11)$$

Here, N_{APW} is some integer number, which depends on the total basis set size and the number of included local orbitals. The advantage of this alternative linearization

compared to the LAPW method is, that the optimal shape of the basis functions inside the muffin-tin is maintained (cf. Fig. 3.2), which leads to a better description of the eigenstate and therefore to a smaller basis set size to reach the same accuracy.

3.4.1 Semi-Core States

Just as in the LAPW method there is only one linearization energy ϵ_1 per l quantum number, which leads to a problem in the description of semi-core states. In the APW+lo method these semi-core states are treated by a *second* set of local orbitals

$$\phi^{\text{lo}_2} = \begin{cases} 0 & \mathbf{r} \in \text{I} \\ [A_{lm} u_l(r, \epsilon_1) + C_{lm} u_l(r, \epsilon_2)] Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in \text{MT} \end{cases} \quad (3.12)$$

Here again the local orbital is introduced with a second linearization energy ϵ_2 , which can be chosen to lie in the semi-core region, so that eigenstates with the same l quantum number but different principle quantum number n can be treated properly. Also these local orbitals are matched to zero value at the sphere boundary without any restriction on the first derivative.

3.5 Mixed Augmentation

It has been shown by Madsen *et al.* [58] that the APW+lo method usually converges much faster than the LAPW method. This means that the same accuracy in e.g. the total energy is reached in the APW+lo method already with a smaller basis set compared to the LAPW method. Normally additional lo's are only needed for the expansion up to the *physical* l quantum numbers (i.e. l quantum numbers contained in the electronic configuration of the corresponding element), whereas the higher l quantum numbers are sufficiently treated by pure APW's. However, for some cases also higher l quantum numbers require additional lo's in the complementary basis set, which lessens the gain in basis set size. On the other hand, radial functions of physically not significant l -character do not have a particular advantage of the exact shape of u_l . Therefore a mixed augmentation has been proposed [58], where the physically important l quantum numbers are treated by APW+lo and the higher l quantum numbers are augmented using LAPW, the so-called (L)APW+lo method. All results presented in this work were obtained using the mixed (L)APW+lo scheme.

3.6 The Full Potential (L)APW+lo Method

The accuracy of the (L)APW+lo method can be further improved by using the full potential (FP), i.e. the muffin-tin potential in Eq. (3.4) is replaced by a non-constant

potential in the interstitial and a non-spherical part inside the muffin-tin

$$V(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} & \mathbf{r} \in \text{I} \\ \sum_{lm} V_{lm}(r) Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in \text{MT} \end{cases} \quad (3.13)$$

These corrections are also called non-muffin-tin corrections. The choice of basis functions in the interstitial is not effected by the non-muffin-tin corrections, but the radial functions u_l as defined in Eq. (3.6) are no longer the exact solutions inside the muffin-tin sphere. In principle the function u_l would have to be evaluated using the true crystal potential of the muffin-tin region, which is, however, not expected to greatly improve the results, since the non-muffin-tin correction represent only a modest change of the muffin-tin potential. In addition the basis functions in the linearized APW methods should be flexible enough to describe the eigenstates altered by the non-muffin-tin corrections as well as the ones in the muffin-tin potential [59].

3.7 Application To Solids And Surfaces

As already mentioned in Section 3.1 crystalline solids can be best described by exploiting their inherent symmetry and therefore using periodic boundary conditions. Besides an appropriate choice of basis functions the integration over the Brillouin zone is an important factor regarding both the accuracy and the computational cost. A second point, that will be discussed in this Section is the treatment of semi-infinite surfaces in periodic boundary conditions by applying the so-called supercell approach. In the last part of this Section the calculation of surface core-level shifts within the FP-(L)APW+lo method is described.

3.7.1 Integration Over The Brillouin Zone

To evaluate many of the physical quantities of a solid (e.g. electron density, total energy, forces etc.) a summation over all occupied states has to be accomplished. For a crystalline solid this leads to an integration over the Brillouin zone, resp. if the symmetry of the system is considered, to an integration over the *irreducible* part of the Brillouin zone. Numerically this is solved by replacing the integral by a sum over a finite number of \mathbf{k} -points

$$\int_{\text{BZ}} \frac{1}{\Omega_{\text{BZ}}} d\mathbf{k} \rightarrow \sum_{\mathbf{k}} \omega_{\mathbf{k}} \quad (3.14)$$

Several methods have been suggested to obtain a most efficient summation over the \mathbf{k} -points, the two most prominent examples are the tetrahedron method [60] and the special \mathbf{k} -point method according to Monkhorst and Pack [61]. The results presented in this work were obtained using the Monkhorst-Pack (MP) method. In this method a weighted summation over a grid consisting of representative \mathbf{k} -points is performed.

These special \mathbf{k} -points are identified by the following steps: (1) generating a homogeneous grid over the full Brillouin zone, (2) combining symmetry related \mathbf{k} -points into groups, (3) choosing one representative \mathbf{k} -point out of every group of equivalent \mathbf{k} -points and assigning the proper weight $\omega(\mathbf{k})$. $\omega(\mathbf{k})$ is given by the number of \mathbf{k} -points in a specific group divided by the total number of \mathbf{k} -points.

In the case of metals one has to cope with an additional problem. Since in metals the bands are crossing the Fermi level ϵ_F the occupation and therefore also the integration over the Fermi surface is discontinuous. This can lead to difficulties in the convergence of the self-consistent field cycle. One solution to overcome this problem is the implementation of a Fermi distribution at a finite temperature to artificially broaden the Fermi surface. After the integration the free energy will be extrapolated again to $T = 0\text{K}$.

3.7.2 The Supercell Approach

The supercell approach is one possibility to model surfaces using periodic boundary conditions. In principle it would be possible to use only two-dimensional periodicity, but in the (L)APW+lo approach this would require an additional matching constraint to determine the layer for the decay of the planewaves. For systems including e.g. the adsorption of oxygen, as described within this work, such a two-dimensional approach is not necessarily advantageous. In the here applied method the surfaces are modeled with periodic boundary conditions in all three dimensions. The semi-infinite surface is described by slabs, that are infinite in the xy -direction, but only consist of several layers in z -direction. The periodicity in z -direction is artificially maintained by a supercell containing the slab and a vacuum region as shown in Fig. 3.3. To obtain reliable results using a supercell two main parameters have to be considered, the number of layers in the slab and the vacuum thickness. Having two surfaces at the top and the bottom of the slab the number of layers has to be big enough to avoid interactions between these two surface. Atoms in the center of the slab should already exhibit the physical properties of atoms in the bulk. To avoid interactions between the surfaces of consecutive slabs the vacuum region has to be large enough. In planewave based methods, like the (L)APW+lo method, calculations of surfaces can become computational very costly, since also the vacuum region is described by the planewaves, which increases the basis set considerably.

A alternative approach, which is not based on periodic boundary conditions, is the cluster method. Here, the surface is modeled by a large cluster. The decisive parameter in this approach is the cluster size, which strongly influences both the accuracy and the computational cost.

3.7.3 Surface Core-Level Shifts

Evaluating the results of a DFT calculation there are, besides the total energy, also several other quantities available regarding the electronic structure of the investigated

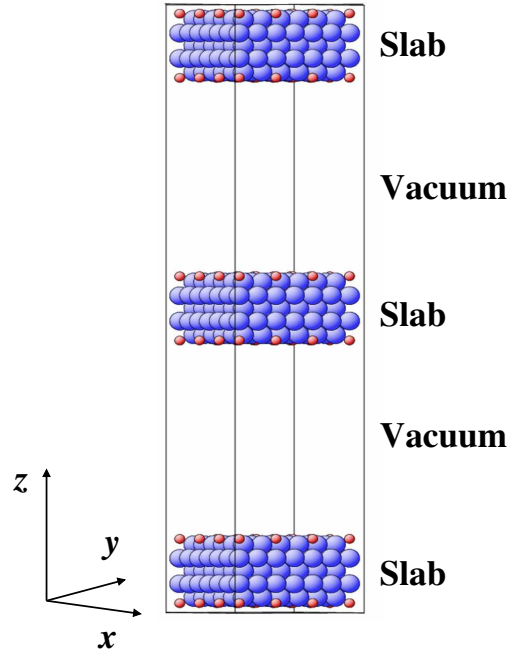


Figure 3.3: Schematic representation of the supercell approach for the calculation of a (100) surface including adsorbate atoms. In the z -direction the supercell consists of a slab (containing several atomic layers) and vacuum. Repeating the supercell periodically in all three dimensions results in the shown figure.

system, which can then be compared to experimental findings. One of these quantities is the surface core-level shift (SCLS), which results from the change in the core-level position of a surface atom compared to the core-level of the corresponding atom in the bulk. The respective SCLS is then given by the difference in energy, that is needed, to remove an electron from the core-level of either a bulk or a surface atom [62, 63]

$$\Delta_{\text{SCLS}} = [E^{\text{surf}}(n_c - 1) - E^{\text{surf}}(n_c)] - [E^{\text{bulk}}(n_c - 1) - E^{\text{bulk}}(n_c)] \quad . \quad (3.15)$$

$E^{\text{surf}}(n_c)$ is the total energy of the surface (slab) depending on the number of electrons n_c in the core-level c , $E^{\text{bulk}}(n_c)$ the respective total energy of the bulk system. In the theoretical description it is possible to separate the total SCLS into an initial and a final state contribution. The initial state contribution includes the change in the electronic distribution before the excitation of the core electron and can be approximated by a Taylor expansion of Eq. (3.15)

$$\Delta_{\text{SCLS}}^{\text{initial}} \approx - [\epsilon_c^{\text{surf}}(n_c) - \epsilon_c^{\text{bulk}}(n_c)] \quad . \quad (3.16)$$

Here, ϵ_c is the Kohn-Sham eigenvalue of the core state c . Since the FP-(L)APW+lo method used in this work is an all electron method it is particularly straightforward to obtain the initial state contribution to the SCLS.

In addition to this initial state contribution the experimentally measured SCLS also contains a final state contribution, which arises from the different screening capabilities of the valence electrons in the core-ionized system at the surface and in the bulk. One possibility to determine the corresponding ionization energy is the calculation of the total energy of an impurity with a core hole in the respective core state. The difference in the total energies of the system with the impurity located at the surface and of the one with the impurity in the bulk gives then the SCLS [64]. This difference can also be approximated within the Slater-Janak transition state approach [65]. Here, total energy differences are evaluated as

$$E(n_c - 1) - E(n_c) = \int_{n_c}^{n_c-1} \frac{\partial E(n')}{\partial n'} dn' = \int_{n_c}^{n_c-1} \epsilon_c(n') dn' \quad , \quad (3.17)$$

and using the mean value theorem of integration

$$\int_{n_c}^{n_c-1} \epsilon_c(n') dn' \approx -\epsilon_c(n_c - 1/2) \quad , \quad (3.18)$$

the total SCLS, including both initial and final state contributions, is then given by combining Eq. (3.15) and Eq. (3.18)

$$\Delta_{\text{SCLS}}^{\text{total}} \approx - [\epsilon_c^{\text{surf}}(n_c - 1/2) - \epsilon_c^{\text{bulk}}(n_c - 1/2)] \quad . \quad (3.19)$$

In the two described approaches the total SCLS is approximated by the energy difference of two *ground states*, which is only valid, if the screening is perfect, i.e. if the excited electron contains the whole screening energy. For the actual calculation of the total SCLS half an electron is removed from the core level of the respective atom, and for metallic systems having a Fermi reservoir of electrons this half electron is then again added at the Fermi level to simulate the effect of a perfect screening. Within the supercell approach a further complication has to be considered. Here, the ionized atoms can interact with their periodic images, so that the supercell has to be large enough to avoid such an artificial interaction.

Considering these uncertainties, the total SCLS might not always fully agree with the experimental results, but is still more suitable for a direct comparison than the initial SCLS. Additional information can be obtained from the difference between the initial and total SCLS, the screening, which might be related to the electronic hardness and surface chemical activity of the system [66].

3.8 The WIEN2k Code

All DFT calculations presented in this work have been performed using the WIEN2k software package [67]. The WIEN2k code is based on the full potential (L)APW+lo method and was mainly developed for the use in solid state physics. Since calculations are only possible using periodic boundary conditions, all surface calculations are performed within the supercell approach.

The WIEN2k code consists of two parts, the initialization and the main selfconsistent-field cycle. Each part again is composed of several independent programs, that are linked via shell-scripts. In addition many analytical tools are implemented to calculate e.g. band structure, density of states, charge densities etc.

Since the FP-(L)APW+lo method is considered one of the most accurate methods in DFT, results obtained with this method are often taken as benchmark. However, the prize for the high accuracy is the comparable high computational cost. For bulk systems the WIEN2k code performs actually rather well, but for surface calculations using a supercell the calculations become quite time consuming [68]. For this work it was therefore also quite important, that a good parallelization is implemented in the WIEN2k code. There are two kinds of parallelization available, the first one parallelizes over the \mathbf{k} -points, so that every \mathbf{k} -point can be calculated separately on a single CPU. This method needs only very little communication between the CPUs and scales quasi linear with the number of CPUs, so that there is almost no loss of resources due to the parallelization. On the other hand, in big systems the number of \mathbf{k} -points becomes small and therefore also the number of CPUs, that can be used for the parallelization. For big systems with few \mathbf{k} -points the second parallelization method becomes very attractive. The so-called fine grained parallelization uses different strategies in different parts of the program. The most important part is the parallelization of the setup and diagonalization of the Hamilton and overlap matrices. This parallelization is much more involved and requires a fast communication between the CPUs. The efficiency of the parallelization depends strongly on the number of CPUs and the matrix size [69]. The number of CPUs, N_{CPU} , has to be $N_{\text{CPU}} = 2^n$, where n is an integer number, and a minimum number of four CPUs, $N_{\text{CPU}} \geq 4$, should be used. The matrix size, N_{MAT} , should be $N_{\text{MAT}} \geq 3000$. The scaling ($t_{\text{single}}/(N_{\text{CPU}} \cdot t_{\text{parallel}})$) can then be as good as ≈ 0.7 , which means, that e.g. for a parallelization over 8 CPUs the speed up is ≈ 5.6 compared to a single CPU. For a matrix size of $N_{\text{MAT}} \approx 3000$ the scaling becomes slightly less efficient for $N_{\text{CPU}} \geq 32$ due to the increasing amount of communication compared to gain in computing time. For larger matrices, though, also a larger number of CPUs can be used, for $N_{\text{MAT}} \geq 10000$ the scaling is efficient up to $N_{\text{CPU}} \leq 128$ and for $N_{\text{MAT}} \geq 22000$ even up to $N_{\text{CPU}} \leq 256$.

In the WIEN2k code these two parallelization method can also be combined, so that also quite big supercells can be calculated in a reasonable time provided that the necessary computer resources are available.

