Elimination of the linearization error and improved basis-set convergence within the FLAPW method

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Abstract
We analyze in detail the error that arises from the linearization in linearized augmented-plane-wave (LAPW) basis functions around predetermined energies $E_f$ and show that it can lead to undesirable dependences of the calculated results on method-inherent parameters such as energy parameters $E_f$ and muffin-tin sphere radii. To overcome these dependences, we evaluate approaches that eliminate the linearization error systematically by adding local orbitals (LOs) to the basis set. We consider two kinds of LOs: (i) constructed from solutions $u_l(r,E_f)$ to the scalar-relativistic approximation of the radial Dirac equation with $E > E_f$ and (ii) constructed from second energy derivatives $\partial^2 u_l(r,E_f)/\partial E^2$ at $E = E_f$. We find that the latter eliminates the error most efficiently and yields the density functional answer to many electronic and materials properties with very high precision. Finally, we demonstrate that the so constructed LAPW+LO basis shows a more favorable convergence behavior than the conventional LAPW basis due to a better decoupling of muffin-tin and interstitial regions, similarly to the related APW+lo approach, which requires an extra set of LOs to reach the same total energy, though.

Keywords: density functional theory, linearized augmented plane wave method, linearization error

1. Introduction

In the past decades, material simulations have become an invaluable approach in condensed matter physics and materials science. Ever increasing computer power as well as theoretical and methodological progress in the description of materials are the main incentives for more and more accurate calculations on more and more complex materials. Within the wide range of theoretical approaches, density functional theory (DFT) [1] is the method of choice for the calculation of electronic ground-state properties of materials.

Practical realizations of DFT almost invariably rely on the Kohn-Sham (KS) formalism [2], which employs an auxiliary system of noninteracting electrons whose number density coincides with that of the real interacting system. Most codes make use of a set of basis functions to represent the quantum mechanical wave functions of these noninteracting electrons, which enables a formulation of the underlying differential KS equation as a generalized eigenvalue problem. In recent years we witnessed a trend toward the investigation of solids of increasing electronic, chemical, and structural complexity, solids that exhibit narrow electronic bands, large band gaps, electrons that contribute to physisorption and chemisorption, which are in turn described by more sophisticated exchange and correlation functionals, e.g., hybrid functionals, the exact-exchange functional in the optimized-effective-potential method, van der Waals functionals, or correlation functionals based on the random phase approximation (RPA), just to name a few. The description of the electronic structure and the application of the new functionals raise new challenges to the efficiency and ability of the basis set to precisely represent the density-functional answer. The aim of this paper is to evaluate and improve the LAPW basis for this purpose.

The simplest basis set for systems with periodic boundary conditions is certainly the plane-wave basis. The accuracy of which is controlled by a single convergence parameter, the momentum cutoff radius $\mathbf{G}_{\text{max}}$. However, the rapid variations of the wave functions close to the atomic nuclei cannot be resolved in practice with this basis, and one has to resort to pseudopotentials and pseudized wave functions within a certain distance from the atomic nuclei [3]. The core electrons are then incorporated into the pseudopotentials, and only the valence electrons are treated explicitly.

The pseudopotential approximation effectively restricts the range of materials that can be examined. Compounds containing 4f and 5f elements, and transition-metals as well as oxides, nitrides, and carbides cannot be treated efficiently within this approach. Among the all-electron approaches that describe core and valence electrons on an equal footing (Gaussian functions [4], the projector augmented-wave [5] and the linearized muffin-tin orbitals method [6, 7, 8] to name a few), the full-potential linearized augmented-plane-wave (FLAPW) method [9, 10] provides one of the most precise basis sets for all-electron calculations. It allows for studying the electronic structure of a large variety of materials, including open systems with low symmetry and compounds of any chemical composition.

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Preprint submitted to Computer Physics Communications

June 25, 2013
The FLAPW method is based on a partitioning of space into non-overlapping spheres centered at the atomic nuclei, the so-called muffin-tin (MT) spheres, and the interstitial region (IR). The core states are completely confined within the spheres, which allows to treat them as localized states in a spherically symmetric atomic potential. For the valence electrons, on the other hand, the APW basis functions are defined piecewise: plane waves of all reciprocal lattice vectors up to the maximal momentum \( G_{\text{max}} \) in the IR, which are augmented by radial functions in the MT spheres that are solutions of the scalar-relativistic approximation to the Dirac equation for the spherically averaged effective potential. Employing the linearized APW (LAPW) basis set, the energy-dependent radial functions are approximated by energy-independent functions evaluated at predetermined energy parameters \( E_l \). The functions are linearly combined so as to match to the plane waves in value and slope at the MT sphere boundaries. In the conventional LAPW basis there are two radial functions per angular momentum quantum number \( l \), the solution \( u_l(r, E_l) \) and its energy derivative \( \dot{u}_l(r, E) = \frac{\partial u_l(r, E)}{\partial E_l} \bigg|_{E=E_l} \). In this way, radial functions \( u_l(r, E) \) with \( E \) close to \( E_l \) can be described up to linear order in \( E - E_l \).

This conventional LAPW basis set is a very accurate one for a wide range of materials. In comparison to the pure plane-wave basis, the LAPW basis requires far less basis functions, while still being able to provide an all-electron description. However, no matter how large the momentum cutoff radius is chosen, the flexibility of the basis in the MT spheres is restricted to the two radial functions \( u_l(r, E_l) \) and \( \dot{u}_l(r, E_l) \) per \( l \) quantum number and the energy-dependent radial function is approximated by these energy-independent functions. This gives rise to a linearization error that can notably affect the accuracy, for example, for materials with large bandwidths, large bandgaps, or if states are considered that are energetically far away from the energy parameters \([1, 2]\). It is obvious that the linearization error depends on two sets of method-inherent parameters, (i) the energy parameters \( E_l \) and (ii) the MT radii, \( R_{\text{MT}} \), as they define the region of space in which the wave function is represented by \( u_l(r, E) \) and \( \dot{u}_l(r, E) \). None of the parameters can be chosen on the basis of a variational principle. Optimally, the final results should not depend on \( E_l \) and \( R_{\text{MT}} \) as long as they are chosen within a reasonable range of values.

Over time, several approaches have been proposed to reduce the linearization error. The first approach that we mention here is the quadratic APW (QAPW) method \([13, 14]\). In this method the MT augmentation is extended by including the second-order energy derivative \( \ddot{u}_l(r, E) \) and employing an algebraic relation for the matching coefficients of \( \ddot{u}_l(r, E_l) \) and \( \dot{u}_l(r, E_l) \).

Next, Singh \([15, 16]\) investigated how to deal with semicore states. These are high-lying core states that are not completely confined within the MT spheres and therefore cannot be treated separately from the valence states. He introduced the radial functions \( u_l(r, E_{\text{SC}}) \) that solve the scalar-relativistic Dirac equation with energy parameters \( E_{\text{SC}} \ll E_l \) that correspond to the energy of the respective semicore state. He introduced and compared the inclusion of these functions by either enforcing continuity of the basis-function curvature as additional matching condition at the MT boundaries or constructing additional local orbitals (LOs) with \( u_l(r, E_l) \), \( \dot{u}_l(r, E_l) \), and \( u_l(r, E_{\text{SC}}) \) that are nonzero only in the MT spheres. He found that the first approach is effective in describing the semicore states, on the expense of creating stiffer basis functions across the MT boundary imposed by the additional matching conditions. As a result, the basis set becomes less flexible and larger basis sets are required to achieve the same accuracy. On the other hand, the extension of the basis with LOs avoids this problem.

The extended LAPW (ELAPW) basis developed by Krasovskii et al. \([17, 18, 19]\) is another approach amending the conventional LAPW basis set by LOs to improve the description of the electronic structure over a wide energy window. Here, pairs of LOs are constructed from \( u_l(r, E_l^{\text{LO}}) \) and \( \dot{u}_l(r, E_l^{\text{LO}}) \), respectively, at energy parameters \( E_l^{\text{LO}} \) that are typically placed at energies above the Fermi energy. However, the authors did not give a prescription of how to choose them in an optimal way. Friedrich et al. \([20]\) considered LOs that are constructed from second-order energy derivatives \( \ddot{u}_l(r, E_l) \) taken at the valence energy parameters \( E_l \) to improve the description of high-lying states for GW calculations. Betzinger et al. \([21]\) employed LOs defined at higher energies to refine the susceptibility matrix in optimized-effective-potential calculations.

Sjöstedt et al. \([22]\) used LOs to achieve a linearization of the basis set, known as the APW+lo method, in which the condition of continuous slope across the MT sphere boundary is dropped for the basis functions. The functions \( u_l(r, E_l) \) are not used anymore as augmentation functions but instead are included in LOs. This makes the basis set more flexible when compared with the FLAPW method. Thus, the same accuracy can be achieved with less basis functions and this saves computation time. We will show later that the inclusion of LOs, in particular second-derivative LOs, into the LAPW basis can yield a similar gain in flexibility.

In this article we evaluate the conventional LAPW basis set for a set of systems exhibiting large muffin-tin radii and large band gaps. We have chosen fcc Ce, KCl in the rock-salt structure, fcc Ar and bcc V as test systems. We examine the linearization error and find that physical quantities such as the total energies, lattice constants, or band structures are susceptible to slight variations of method-inherent parameters such as MT radii and energy parameters. We apply two types of local orbitals to extend the LAPW basis set, (i) one based on functions of higher energy derivative (LAPW+HDLO) and (ii) one based on energy parameters at higher energy (LAPW+HELO). We show that these LOs are very effective in reducing or, within the relevant degree of accuracy, even in eliminating the linearization error. Here, the second-derivative HDLOs are particularly efficient.

The article continues with a brief introduction to the LAPW basis and the definition of the LO extensions in Sec. 2. In Sec. 3 we introduce the test set of materials for which our evaluations are carried out. We continue in Sec. 4 with a discussion of the linearization error for the conventional and the LO extended LAPW basis sets. In detail, in Sec. 4.1 we evaluate the quality of the various basis sets in their ability to represent Kohn-Sham states inside the MT sphere, discuss dependences of computed...
physical properties on method-inherent parameters in Sec. 4.2 and investigate the effect of the linearization error on unoccupied states, in particular, the KS band gap in Sec. 4.3. Finally, we discuss in Sec. 5 the effect of the LOs on the convergence behavior of the total energy with respect to the basis set size for the different basis sets and also in comparison with the APW+lo approach, before we conclude in Sec. 6.

2. LAPW basis and LO extensions

In the KS formalism of DFT \cite{2} one considers a fictitious system of noninteracting electrons moving under the influence of an effective potential \( V^{\text{eff}}(r) \). For lattice periodic potentials the electronic quantum mechanical wave functions \( \varphi_{\mu}(r) \) with the Bloch vector \( \mathbf{k} \) and the band index \( \alpha \) are thus solutions of

\[
\left\{ \frac{1}{2} \mathbf{\nabla}^2 + V^{\text{eff}}(r) \right\} \varphi_{\mu}(r) = \epsilon_{\mu} \varphi_{\mu}(r), \tag{1}
\]

where the spin index has been suppressed. The effective potential is defined such that the KS system exhibits the same number density as that of the real interacting system. It comprises the electrostatic potential created by the charged particles — electrons and nuclei — as well as an exchange-correlation potential, for which we use here the Perdew-Zunger parametrization of the local-density approximation \cite{22}. For simplicity, we present in Eq. (1) and in the following the non-relativistic equations, while in practice the scalar- or fully relativistic Dirac equation is employed.

Close to the atomic nuclei the effective potential is predominantly spherical, which allows the core states to be determined efficiently from the fully relativistic radial Dirac equation. The core states fall off quickly toward the MT sphere boundary, where they are practically zero. It can be shown \cite{12, 16} that this property guarantees that the core states are orthogonal to the radial functions used for the construction of the LAPW basis for the valence electrons, which we introduce in the following. The valence states are represented by the set of basis functions

\[
\varphi_{kG}(r) = \begin{cases} \sum_{\alpha} R_{L_{\alpha}}^{K_{\alpha}}(r, E_{\alpha}) Y_l(\hat{r}) & \text{for } r \in \mathbb{R} \\ \sum_{\alpha} R_{L_{\alpha}}^{K_{\alpha}}(r, E_{\alpha}) Y_l(\hat{r}) & \text{for } r \in \text{MT}_\alpha \end{cases}, \tag{2}
\]

where the \( \mathbf{G} \) are reciprocal lattice vectors, \( \Omega \) is the unit-cell volume, \( L = (l, m) \) comprises the angular momentum and the magnetic quantum number, \( r_\alpha \) is the position vector relative to the MT sphere center \( \mathbf{R}_\alpha \) of atom \( \alpha \), and \( Y_l(\hat{r}) \) are the spherical harmonics. In practice, one employs the cutoff parameter \( G_{\text{max}} \) that controls the number of basis functions through \( |\mathbf{k}+\mathbf{G}| \leq G_{\text{max}} \) and implies the cutoff parameter \( R_{\text{max}} \) with \( l \leq R_{\text{max}} \) through the rule of thumb \( R_{\text{max}} = G_{\text{max}} R_{\text{MT}2} \) \cite{16}.

For each angular momentum quantum number \( l \), the radial functions

\[
R_{L_{\alpha}}^{K_{\alpha}}(r, E_{\alpha}) = a_{L_{\alpha}}^{K_{\alpha}} u_{L_{\alpha}}(r, E_{\alpha}) + b_{L_{\alpha}}^{K_{\alpha}} u_{L_{\alpha}}(r, E_{\alpha}) \tag{3}
\]

are linear combinations of the normalized solution to

\[
\begin{cases} \left\{ \frac{1}{2} \mathbf{\nabla}^2 + \frac{l(l+1)}{2r^2} + V^{\text{eff}}(r) \right\} r u_{L_{\alpha}}(r, E) = E r u_{L_{\alpha}}(r, E) \end{cases} \tag{4}
\]

for \( r \in \text{MT}_\alpha \) and its energy derivative \( u'_{L_{\alpha}}(r, E_{\alpha}) \), where \( E = E_{\alpha} \) and \( V^{\text{eff}}(r) \) is the spherical part of \( \text{V}^{\text{eff}}(r) \) inside of \( \text{MT}_\alpha \) and expressed in Hartree units (1 Hartee = 2 Ryd = 27.2 eV). The matching coefficients \( a_{L_{\alpha}}^{K_{\alpha}} \) and \( b_{L_{\alpha}}^{K_{\alpha}} \) are determined such that the \( \varphi_{kG}(r) \) are continuous in value and slope at the MT sphere boundaries.

The energy \( E_{\alpha} \) is a parameter that is fixed for each iteration of a self-consistent-field run. If it happens to be identical to the KS eigenvalue \( \epsilon_{\alpha} \), the function \( u_{L_{\alpha}}(r, E_{\alpha}) \) already solves Eq. (1) pointwise in the MT sphere by construction (provided that we restrict ourselves to the spherical part of the effective potential, which is indeed much larger than the nonspherical terms). In this sense, the inclusion of the energy derivative \( u'_{L_{\alpha}}(r, E_{\alpha}) \) makes it possible that states with energies different from but close to \( E_{\alpha} \) can also be described accurately, in accordance with the Taylor expansion to linear order

\[
u_{L_{\alpha}}(r, E) \approx u_{L_{\alpha}}(r, E_{\alpha}) + (E - E_{\alpha}) u'_{L_{\alpha}}(r, E_{\alpha}). \tag{5}
\]

The energy parameters \( E_{\alpha} \) should be chosen as close as possible to the corresponding band energies. While the bands of a crystal exhibit a strong dependence on the Bloch vector \( \mathbf{k} \) and the band index \( n \), the energy parameters only depend on the atom and the angular momentum \( l \). Thus, differences between the band energies and the energy parameters are unavoidable.

In practice, several methods are in use to choose the energy parameters automatically in each iteration of the self-consistent-field cycle. One example for such a method solves for each sphere an atomic Hamiltonian employing the spherical part of the effective KS potential in the MT sphere with a confining potential outside. The energy parameters of the valence states are then set to the corresponding atomic eigenenergies. The so-chosen energy parameter, that we denote as atomic energy parameter, is motivated by the fact that the bands in a solid form out of the atomic states. However, this approach may yield energy parameters above the Fermi energy since it does not take the occupation of states into account. Energy parameters below the Fermi energy are obtained by another method that sets them at the energy center of mass of the \( l \)-resolved partial density of the occupied valence states. The disadvantage of the latter method is that systems with narrow bands at the Fermi energy, where changes in the occupation of bands can occur easily between two subsequent self-consistent-field iterations, exhibit a stronger variation of the energy parameters, which at the end may reduce the speed to self-consistency or even make the self-consistency process less stable than the former choice of \( E_{\alpha} \), which is less sensitive to these band reorderings. Both methods also depend on the chosen MT radii.\cite{1}

Of course, the more the KS eigenvalues differ from the energy parameter, the less adequate the basis becomes for the corresponding KS eigenfunctions, which we refer to as the linearization error. From Eq. (5) a solution seems obvious: one simply adds the second-order derivative \( u''_{L_{\alpha}}(r, E_{\alpha}) \) to Eq. (1). However, this would require an additional expansion coefficient

\footnote{For completeness we note that we employ the atomic energy parameters for \( E_{\alpha} \) if not stated otherwise. The qualitative results do not depend on the particular choice of the parameters.}
and, as a consequence, an additional matching condition at the MT boundaries. It was shown [15] that this leads to a less flexible (slower convergent) basis set. The LO construction [15] avoids this problem.

LOs are additional basis functions

\[ \phi_{1,\ell}^{LO}(r) = R_{\ell}^{LO}(r_a) Y_{\ell}(\hat{r}_a) \]  

(6)

that are completely confined to a MT sphere. There are 2\ell + 1 LOs per \ell quantum number. Their radial part is a linear combination

\[ R_{\ell}^{LO}(r_a) = a_{\ell}^{LO} u_{\ell}(r, E_{\ell}) + b_{\ell}^{LO} u_{\ell}(r, E_{\ell}) + c_{\ell}^{LO} u_{\ell}(r_a), \]  

(7)

where the coefficients are determined by enforcing normalization \( \int r^2 R_{\ell}^{LO}(r)^2 dr_a = 1 \) as well as zero value and slope at the MT boundary, implying that the LOs are zero in the IR. The third radial function \( u_{\ell}(r_a) \) can be chosen rather arbitrarily. For a semicore state it should be the solution of Eq. (4) with the eigenenergy of the semicore state as the energy parameter for the given angular momentum \( j \) [15]. The conduction-band spectrum may be improved by adding LOs with energy parameters chosen in the corresponding energy range [20, 23]. The third radial function can also be taken to be the second-order energy derivative \( u_{\ell}(r, E_{\ell}) \) which would correspond to the next higher term in Eq. (5) [12].

We consider here two kinds of LOs: (i) Higher-derivative LOs (HDLOs), where the third radial function \( u_{\ell}(r) \) is set equal to \( u_{\ell}(r, E_{\ell}) \) (here we only consider the second derivative) and (ii) Higher-energy LOs (HELOs), where \( u_{\ell}(r) = u_{\ell}(r, E_{LO}^\alpha) \) with \( E_{LO}^\alpha > E_{\ell} \). The functions \( u_{\ell}(r, E_{\ell}) \) for the HDLOs are obtained by solving the second energy derivative of Eq. (4). For the HELOs we determine \( E_{LO}^\alpha \) by the condition that the logarithmic derivative

\[ D_{\ell}^\alpha(E) = \frac{u_{\ell}^{LO}(r, E)}{u_{\ell}^{LO}(r_a, E)} \]  

(8)

is equal to the constant \(-(l + 1)\), corresponding to the evanescent solution of Eq. (4) with \( V_{eff} = E = 0 \) [20]. Because of the form of \( D_{\ell}^\alpha(E) \) there are infinitely many solutions that are all orthogonal to each other and each being related to a particular principal quantum number. This allows a systematic extension of the basis. Figure 1(a) displays the logarithmic derivatives for the channel of fcc cerium as an example, where the intersection with \( D_3 = -3 \) gives the set of energy parameters \( E_{LO}^{l=2} \) for Ce. For reference, we plot in Fig. 1(b) the radial function \( u_{\ell=2}(r, E) \) for different energies \( E \) covering a range of 1.8 Hartree. The pole of \( D_3 \) at around \( E = 0.4 \) Hartree in Fig. 1(a) marks the transition from 5d to 6d orbitals and is related to the zero value of the corresponding radial function at the sphere boundary, the node at around \( E = 1.3 \) Hartree in Fig. 1(a) corresponds to a vanishing slope in (b).

Fig. 1(b) displays the energy dependence of the Ce 5d wave function, \( u_{\ell}(r, E) \), inside the MT sphere. In the vicinity of the atomic nucleus up to a radius of about 1.5 \( a_0 \), \( u_{\ell}(r, E) \) is not very sensitive to the particular choice of energy \( E \), but it is determined by the singularity of the effective potential and the angular momentum barrier. This changes towards the MT boundary, where chemical bonding determines the details of the potential, and a strong energy dependence of the basis function is displayed. As a consequence, one can expect that the choice of the MT radius may have a significant influence on the linearization error. With increasing MT radius we expect an increase of the error. On the other hand a larger MT radius is advantageous since it implies a smaller number of required basis functions or error. With increasing MT radius we expect an increase of the error. On the other hand a larger MT radius is advantageous since it implies a smaller number of required basis functions or error. With increasing MT radius we expect an increase of the error.

In this work, we investigate and compare HDLO and HELO extensions to the LAPW basis. We work with two different sets of HELOs that include one and two sets of LOs of successive principle numbers, denoted by HELO1 and HELO2, respectively. The LAPW+HDLO×1 and LAPW+HELO×1 basis sets comprise 16 additional LOs per atom with \( l = 0, 1, 2, 3 \), while the LAPW+HELO×2 basis contains 32 additional LOs.

![Figure 1](image-url)

Figure 1: (a) Logarithmic derivative \( D_3(E) \) for the d channel of fcc Ce as a function of the energy relative to the 5d energy parameter \( E_{5d} \). The energy parameters for the two additional sets of LOs in the LAPW+HELO×1 and LAPW+HELO×2 basis sets are marked. (b) Solutions of Eq. (4) obtained for different energies \( E \). The functions are normalized but scaled to coincide at the first maximum. The energy dependence increases towards the MT sphere boundary at 3.14 \( a_0 \).
per atom.

3. Investigated materials and calculational parameters

The quality of the different basis sets is analyzed by studying the linearization error and its consequences for calculated physical quantities for a test set of representative materials, i.e., materials for which a significant linearization error can be expected. This includes materials with large MT radii (around 3 $a_0$), large band gaps (between 5–10 eV), or cases where the choice of energy parameters deviates significantly from the electronic state to be described. In total we have selected fcc Ce, KCl in the rock-salt structure, fcc Ar, and bcc V. Typical cut-off parameters such as the number of $k$ points in the irreducible wedge of the Brillouin zone (IBZ) or the number of basis functions per atom controlled by the product $G_{\text{max}}R_{\text{MT}}$ are chosen such that the quantities discussed in the paper are converged with respect to these parameters. The calculational parameters for the different materials are shown in Table 1.

The first material to be taken under scrutiny is fcc cerium. The second material, KCl in the rock-salt structure, features a large band gap and enables the usage of a large MT radius which is typically chosen to be larger than 3 $a_0$ ($a_0$ is the Bohr radius). As we will see in Sec. 5, the chosen valence states, which cover an energy interval of 3 eV below the Fermi level.

The second material, KCl in the rock-salt structure, features a large KS band gap of about 5 eV. To describe this gap accurately, electronic states over a broad energy range have to be represented accurately. Figure 3 shows the density of states together with the energy parameters. The band structure is investigated in detail in Sec. 4.3 and is shown in Fig. 13. We remark that the Cl 3$p$ states give rise to small $d$ and $f$ contributions to the DOS in K, which are energetically far away from the $E_{3d,K}$ and $E_{4f,K}$ energy parameter, respectively (cf. Table 1).

Fcc Argon is the third material that we investigate. It also features a large band gap and enables the usage of a large MT radius. Density of states and energy parameters for this material are shown in Fig. 4. Similarly to KCl, we discuss the band structure of Ar in detail in Sec. 4.3 and show it in Fig. 14.
4. Linearization error

In this section we quantify the linearization error for the different basis sets. First, we define a basis representation error that quantifies the linearization error and examine its dependence on the energy parameters and MT sphere radii. Up to that point, we only consider non-selfconsistent calculations, where the ability of the basis to represent the exact single-particle wavefunctions in the spheres to a given effective potential is assessed. Then, we turn to self-consistent calculations. In particular, we examine how total energies, lattice constants, and KS band gaps depend on the energy parameters and the MT sphere radii. We will see that the LO extension reduces these undesirable dependences to a great extent.

4.1. MT basis representation

In order to assess the quality of the basis representation in the MT spheres, we define the representation error

$$\Delta_l(E) = \|u_l - \tilde{u}_l\| = \left( \int r^2 |u_l(r, E) - \tilde{u}_l(r, E)|^2 \, dr \right)^{\frac{1}{2}},$$

where $u_l(r, E)$ is a normalized solution of Eq. 4 for a given energy $E$ and $\tilde{u}_l(r, E)$ is the best representation of $u_l(r, E)$ in terms of the radial functions of the given basis in the MT sphere, i.e., $\tilde{u}_l(r, E) - u_l(r, E)$ is orthogonal to the basis. The error $\Delta_l(E)$ becomes zero if $u_l(r, E)$ can be represented pointwise by the basis. This is the case if $E$ is identical to an energy parameter. On the other hand, $\Delta_l = 1$ if $u_l(r, E)$ is orthogonal to the function space spanned by the available radial functions. Note that the representation error defined above only covers that part of the wave functions that is inside the MT sphere. It does not include the additional boundary conditions imposed by the matching of the radial functions to the plane waves at the MT boundary. This matching reduces the flexibility of the basis such that the representation error of $u_l$ represents a lower bound for the error with respect to the entire LAPW basis.

In the following, we investigate the energy dependence of the representation error $\Delta_l(E)$ for the conventional LAPW basis and its HDLO and HELO extensions. Based on the effective potential from a self-consistent DFT calculation, Figure 5 shows the error for $l = 2$ in the vicinity of the energy parameter for the $5d$ states of bulk fcc Ce.

For an accurate representation of the electron density, which is the central quantity of DFT, the valence states must be described accurately. Therefore, the energy parameters are chosen in the valence band. The inset of Fig. 5 shows an energy interval of about ±0.3 Htr ≈ ±8 eV around the Ce 5d energy parameter. In this energy range the linearization error of the conventional LAPW basis for the $d$ channel of Ce amounts to maximally $1.5 \times 10^{-2}$. This error can be further reduced by adding LOs. While the HELOx1 and HELOx2 basis sets reduce the maximal error to $3.3 \times 10^{-3}$ and $1.1 \times 10^{-3}$, respectively, the LAPW+HDLOx1 exhibits a maximal error of only $3.8 \times 10^{-4}$, a factor of 40 smaller than in the case of the conventional LAPW basis. We note that in the immediate vicinity of the energy parameter, $\Delta_l(E)$ scales as $|E - E_l|^2$ for the conventional LAPW basis and as $|E - E_l|^3$ for the HDLOx1 basis.

For energetically high-lying states the conventional LAPW basis quickly becomes inadequate, while LOs, especially the HELOs (cp. Fig. 5), can improve the basis substantially in a systematic and controllable manner. Methods that rely on the empty states such as the GW approximation [24] or RPA correlation functionals [25, 26] thus require an LAPW basis that is thoroughly converged with respect to LOs.

For all basis sets we observe a sharp peak at $-3.87$ Htr ($= -105$ eV) where $\Delta_l(E)$ becomes 1, which signals a state that is orthogonal to the basis functions and therefore cannot be described by the basis. In practice, this is no problem as this is the $4d$ core state of Ce which is treated separately from the valence states. As it is completely confined to the MT sphere, it lies...
outside the space spanned by the basis sets. On the other hand, the wave function of a semi-core state extends significantly over the MT sphere. In particular, it does not vanish at the boundary and will therefore have a finite overlap with the valence basis. Figure 6 shows such a case in the p channel of bcc vanadium. The representation error features a shallow peak (or merely a shoulder) at $-1.7$ Hr ($\approx -46$ eV), which corresponds to the 3p state. This impedes a treatment of the 3p state separate from the valence states, and we must employ LOs of $l = 1$ at the appropriate energy, especially if the LAPW+HDLOx1 basis is applied. We note that although the semi-core state could also be described by systematically including LOs with higher and higher orders of derivatives, the more traditional way \cite{[13]} of employing a single LO, constructed from the solution to Eq. (4) with $E$ being the semi-core energy, is much more efficient since the semi-core states form very flat bands with hardly any dispersion and should therefore be readily representable by a single LO. It is evident that the rest of the diagram looks rather similar to the one in Fig. 5(a), which demonstrates that the qualitative behavior of the representation error is essentially independent of the material and the angular momentum $l$.

While the energy parameters can be adapted to the material in each iteration of the self-consistent-field run, the MT radius must be chosen before starting the calculation and then stays at this fixed value. One condition for the choice of the radius is that the MT spheres must not overlap. On the other hand, they should be chosen as large as possible in order to keep the reciprocal cutoff radius $G_{\text{max}}$ small. (The larger the spheres, the smaller the IR, and the less plane waves are necessary to represent the wave functions there.) Finally, if one considers more than one chemical element, the sizes of the MT spheres relative to each other can be chosen according to tabulated atomic radii. This shows that there is no optimal choice of the radii. Ideally, the calculated results should be independent of the choice of the MT radii.

In Fig. 7 we show the representation error for 5d states in Ce as a function of the MT radius for the different basis sets and at a fixed energy $E$ of 0.1 Hr below the 5d energy parameter. In the calculations we increased the cutoff $G_{\text{max}}$ while reducing the MT radius to keep the product $G_{\text{max}}R_{\text{MT}}$ fixed to 13. The effective potential was determined from self-consistent calculations for each MT radius. All other numerical parameters, as well as the method to choose the energy parameters, are identical to the previous Ce calculation.

We observe that, independently of the basis chosen, the representation error becomes smaller as the MT radius is reduced. This is related to the growing independence of $u(r, E)$ on the energy parameter $E$ with decreasing radius observed in Fig. 1(b) and is most pronounced for the conventional LAPW basis, which has no additional LOs apart from those for the semi-core states. From 3.15 $a_0$ to 2.4 $a_0$ the error decreases from $1.3 \cdot 10^{-3}$ to $2.5 \cdot 10^{-4}$. In the case of the LAPW+HELO and LAPW+HDLO basis sets, the dependence on the MT radius is strongly reduced. In particular, the LAPW+HDLOx1 basis exhibits a very small representation error for this wide range of MT radii, nearly a factor 100 smaller than in the conventional LAPW basis. Such a stability with respect to non-convergence parameters like MT radii is clearly desired.

### 4.2 Total energies and lattice constants

Now we move to self-consistent calculations and address the questions whether the observations of the previous section translate to physical properties, such as the total energy $E_{\text{total}}$ or the equilibrium lattice constant $a$ after self-consistency in the electron density is achieved. Thus, we write the total energy $E_{\text{total}}(\Omega | \{ E_l \}, \{ R_{\text{MT}} \})$ in a form where besides its dependence on the lattice constant $\tilde{a}$, the number of Bloch vectors, and the size of the basis set, which both have been chosen sufficiently large that the total energy can be considered converged with respect to these parameters, its dependence on the set of energy parameters and MT radii becomes explicit. It is clear that the equilibrium lattice constant $a$ is obtained by minimization of the total
lies about 1
the total energy becomes lower (due to the increase of the vari-
ational freedom enabled by the larger basis sets), but, moreim-
portant, its dependence on

Figure 8: Total energy of fcc Ce for the different basis sets from self-consistent-field calculations as a function of the energy parameter \( E_{l=2} \) relative to the Fermi energy. The total energy is plotted relative to the minimal energy obtained with the basis set including HDLOs. The inset shows a detailed view, revealing that the LAPW+HDLO\( \times 1 \) basis exhibits the smallest error by far. We also mark the energetic positions of the energy parameter as determined from two common approaches, which are described in the text. In these calculations HDLOs and HELOs are only added in the \( d \) channel.

energy with respect to variations of the lattice constant. The to-
tal energy \( E_{\text{total}} \) itself is dependent on the method-inherent pa-
rameters. As in the previous section, we focus on the stability of the results with respect to variations of the energy parameters and the muffin-tin radii.

In several respects, self-consistent calculations are more de-
manding on the performance of basis sets than what we have con-
sidered so far. Firstly, we now account for the full non-
spherical potential in the MT spheres, while we have restricted ourselves to the spherical potential before. Second, the IR is now taken into account as well, and the wave functions must be described accurately over the complete space. Third, the wave functions must also be described accurately over a sufficiently wide energy range to yield a precise valence electron density in each self-consistent-field iteration.

In Fig. 8 we show the dependence of the calculated total en-
ergy of fcc Ce on the energy parameter \( E_{l=2} \) for different basis sets, where, as an exception, the LAPW basis for the valence electrons is only extended by LOs of \( d \) character. While keeping all other energy parameters fixed (to values taken from a previous self-consistent-field calculation), we vary \( E_{l=2} \) in the range from \(-0.29\) to \( 0.08 \) Hr (\( \approx -7.9\) to \( 2.2 \) eV) relative to the Fermi level. As seen in the figure, the total energy calculated with the conventional LAPW basis set depends significantly on the choice of the energy parameter. The marked energy parameters determined from the two automatic approaches yield total energies that deviate substantially from each other and from the minimal total energy obtained with \( E_{l=2} \) = \( -0.16 \) Hr which lies about \( 1.3 \) eV below the lower valence band edge.

When extending the LAPW basis with LOs, we observe that the total energy becomes lower (due to the increase of the vari-
ational freedom enabled by the larger basis sets), but, more im-
portant, its dependence on \( E_{l=2} \) is strongly suppressed, most

Figure 9: Ground-state total energy of fcc Ce from self-consistent-field calculations as a function of the MT radius for different basis sets. HDLOs and HELOs are added for \( l = 0, 1, 2, 3 \). The inset shows again that the LAPW+HDLO\( \times 1 \) basis exhibits the smallest error.

strongly again for the LAPW+HDLO\( \times 1 \) set, which exhibits a variation that is two orders of magnitude smaller than for the conventional LAPW basis and, thus, negligible for all practi-
cal purposes. Although the HELO\( \times 2 \) extension contains one
set of LOs more than HDLO\( \times 1 \), the corresponding total energy exhibits a larger variation albeit still a very small one when compared to the conventional set. Of course, the calculations with the HELOs still depend on \( E_{l=2}^{\text{LO}} \), i.e. the energy parameter of the HELOs. As already explained above, we employ for the HELOs energy parameters determined from Eq. 8. The HDLO accuracy could be realized with normal LOs if their en-
ergy parameter \( E_{l=2}^{\text{LO}} \) was chosen close to \( E_{l=2} \). In fact, in the
limit \( E_{l=2}^{\text{LO}} \rightarrow E_{l=2} \) the two approaches are theoretically identi-

cal. However, if the distance between the two energy param-
eters gets too small, the near linear dependence of the basis might easily cause numerical problems, which is avoided by using HDLOs.

Besides its dependence on the energy parameters, in Fig. 7
we already showed that the linearization error also strongly depends on the MT radii. The error decreases for smaller radii, but then the IR becomes larger, which entails a larger reciprocal cutoff radius giving rise to an increase of the basis set size and thus higher computational demands. As we have seen, a more effective means to reduce or even eliminate the linearization error is the introduction of LOs, in particular the HDLOs.

We observe the same behavior for the total energy and the equilibrium lattice constant, for which the total energy assumes a minimum. The latter is calculated from a series of total-energy calculations for different lattice constants together with a Murnaghan fit \[27\]. We show results for Ce and KCl. To avoid overcompleteness of the basis at small MT radii, we neither include HDLOs nor HELOs in the \( s \) and \( p \) channels of K, where we already have LOs to describe the semicore states.

In Figs. 9 and 10 the total energy is shown as a function of the MT radius. In fact, the diagrams look qualitatively very similar to the MT representation error shown in Figs. 5 and 7 respectively. The variation in the total energy is between one and two orders of magnitude smaller with the HDLO extension than without for both compounds.

Even without the LOs, the total energy is accurate up to few mH\( r \). However, the equilibrium lattice constant determined from the minimum of the total energy depends on small energy differences. It is thus particularly susceptible to inaccuracies in the total energies. As shown in Fig. 11 and 12, the variation of the lattice constant \( a \) is on the order of 1 percent for Ce (\( a_{\text{exp}} = 9.05 \) \( a_0 \), \( a_{\text{LAPW}} = 8.55 \) to 8.69 \( a_0 \)) and KCl (\( a_{\text{exp}} = 11.89 \) \( a_0 \), \( a_{\text{LAPW}} = 11.49 \) to 11.54 \( a_0 \)) and thus in the same ballpark as the supposed accuracy of the LDA functional. After addition of one set of HDLOs the variation of \( a \) is strongly suppressed to less than 0.1% (Ce: \( a_{\text{LAPW+HDLO}} = 8.539 \) to 8.544 \( a_0 \), KCl: \( a_{\text{LAPW+HDLO}} = 11.487 \) to 11.488 \( a_0 \)).

We note that each additional set of LOs (for \( l = 0, \ldots, 3 \)) increases the basis-set size by only 16 functions per atom. Thus, adding LOs is computationally much more efficient than reducing the MT radius, which would make many more augmented plane waves necessary to enable an adequate description of the wave functions in the interstitial region.

4.3. KS band gap

The band gap is a fundamental quantity of semiconductors and insulators and is given by the energy difference of the lowest unoccupied and the highest occupied state. Its calculated value also depends on the ability of the basis set to describe both, the valence and the conduction bands with sufficient accuracy. Since the energy parameters are located typically in the energy range of the valence bands (see Sec. 4.2), one might expect deviations of the conduction states from the true KS eigenstates having an adverse effect on the accuracy of the band-gap value. We demonstrate for KCl and Ar that the inaccuracies of the KS gap due to the linearization error can indeed be sizable unless LOs are used to ensure a proper description in the MT spheres. With the LAPW basis set, the KS band gap is calculated to be larger than with the extended basis sets, leading to an underestimation of the KS band gap error when compared to experimental values.

In Figs. 13 and 14 the KS band structures of rock-salt KCl and crystalline Ar, respectively, are shown. Both exhibit a direct band gap at \( \Gamma \). We show band structures calculated with the conventional LAPW and the LAPW+HDLO\(_1\) basis (results obtained by the HELO extensions lie on top of the LAPW+HDLO\(_1\) ones on the scale of the diagrams). As expected, the occupied states, being close to the energy parameters, are already well described in the conventional LAPW basis and the occupied bands are indistinguishable on the energy scale of the diagrams. However, there are clear deviations in the unoccupied states. In particular, the lowest unoccupied band, which is of 4\( s \) character, shifts down by 0.19 eV for KCl and even by 1.87 eV for Ar upon introducing the LOs; the band dispersion is also affected noticeably. The downward shift of the lowest unoccupied band entails, of course, a reduction of the KS band gaps, which amounts to 4% for KCl and 19% for Ar.
As a result, the linearization error has an even more pronounced effect on the band gap than it has on the total energy and equilibrium lattice constant. Higher-lying unoccupied states will be affected even more strongly so that a thorough convergence of the basis set is mandatory in the calculation of quantities that involve the unoccupied states in a perturbative way such as response quantities used, e.g., in the optimized-effective-potential method and the GW approximation [20, 23].

5. Basis-set size

In this section, we compare for the example of fcc Ce the speed of convergence of the total energy with respect to the cutoff radius of reciprocal lattice vectors achieved with the different basis sets. In Fig. [15] the convergence of the total energy is shown as a function of $G_{\text{max}}R_{\text{MT}}$ with $R_{\text{MT}} = 3.14 a_0$. In addition to the conventional LAPW basis and those extended by HDLOs and HELOs, we also consider the convergence for the APW+lo basis and its HELO$\times 1$ extension. In contrast to the LAPW basis, the APW+lo approach [21] augments the interstitial plane waves solely by the functions $u_l(r, E_l)Y_{lm}(\hat{r})$, while the energy derivatives $\dot{u}_l(r, E_l)$ up to a given angular momentum (here, $l = 3$) are treated as LOs (for which we have adopted the common lower case notation “lo”). For higher $l$ we depart from the original APW+lo approach and follow the idea of Madsen et al. [22] to use both radial functions for augmentation as in LAPW. As a consequence of the altered linearization, the APW+lo basis is only continuous in value but shows a discontinuity in the slope at the MT sphere boundary, i.e., the basis functions exhibit a kink there. The less stringent matching at the MT sphere boundary leads to a more flexible basis set, which manifests in a faster convergence of the total energy with respect to $G_{\text{max}}R_{\text{MT}}$ in comparison to the conventional LAPW basis. This effect is clearly visible in Fig. [15] While the conventional LAPW basis does not yield a converged total energy even with $G_{\text{max}}R_{\text{MT}} = 13$, the APW+lo curve reaches its converged value already for $G_{\text{max}}R_{\text{MT}} \approx 10$. We note that the LAPW basis finally converges to the same total energy as the APW+lo approach, but at a considerably larger basis, even when taking account of the extra set of LOs in APW+lo. (The same holds for the APW+lo+HELO$\times 1$ and LAPW+HELO$\times 1$ curves.) This is in agreement with earlier investigations on fcc Ce performed by Sjöstedt et al. [21].

However, if we extend the LAPW basis by one set of LOs (rather than increasing $G_{\text{max}}$), thus making the basis set as large as in the APW+lo method, we reach a lower and more accurate total energy than in the APW+lo method due to a larger variational freedom in the MT spheres. Among the evaluated basis sets the LAPW+HDLO$\times 1$ basis reaches the variationally lowest total energy. We note that adding further HDLOs (i.e., the third and higher derivatives) hardly changes the converged value.

We can also observe that the corresponding calculations converge more rapidly than those employing the conventional LAPW basis. The reason for that is the increased flexibility brought about by the additional LOs. This increased flexibility plays a similar role as allowing for a kink in the APW+lo basis functions. So, it acts toward a decoupling of the two regions of space, allowing to some extent a separate variational search for the eigenstates in the two regions. The decoupling is somewhat less effective in the LAPW basis sets, where the radial derivatives of the wave functions are forced to be continuous at the MT sphere boundaries. However, it should be pointed out that every kinkless wave function that is given as a linear combination of plane waves in the IR and the $u_l(r, E_l)$ and $\dot{u}_l(r, E_l)$ in the MT spheres is representable by the LAPW basis functions, which are constructed to fulfill exactly these matching conditions. Hence, whenever an APW+lo calculation yields a smaller total energy than the corresponding LAPW calculation, then the wave functions necessarily exhibit a kink at the MT
spans leading to many additional basis functions. A much more improve the description of unoccupied states, but can also be
fined with higher energy parameters. HELOs are often used to
this extends the IR and thus entails a larger reciprocal cuto
though choosing small MT radii reduces the linearization error,
the results to depend appreciably on numerical parameters that
are inherent to the FLAPW method and are not convergence
parameters, i.e., the energy parameters and the MT radii. Al-
results insensitive to variations of the energy parametersand
failure that arises in the LAPW basis due to the restriction to only
spheres, which from a physical point of view might be unsatisfactory. Loosely speaking, the variational search for
the wave functions reached a lower total energy by accepting a
kink with a singular kinetic energy density at the sphere bound-
sphere boundaries, which from a physical point of view might be unsatisfactory. Loosely speaking, the variational search for
the wave functions reached a lower total energy by accepting a
kink with a singular kinetic energy density at the sphere bound-

6. Conclusion

In foresight of new challenges treating solids with greater electronic and chemical complexity with more sophisticated functionals, we have explored in this work the capability of the
LAPW basis set to deal with these challenges and evaluated extensions of the basis set by two types of local orbitals that basically offer the potential to provide the density functional answer to the problem at hand with very high precision.

In detail we have analyzed the effects of the linearization error that arises in the LAPW basis due to the restriction to only two radial functions, \( u(r, E) \) and \( \tilde{u}(r, E) \), per \( l \) quantum number in the MT spheres. While the LAPW basis is established to be very accurate for a wide range of materials and material properties, there are cases where the linearization error causes the results to depend appreciably on numerical parameters that are inherent to the FLAPW method and are not convergence parameters, i.e., the energy parameters and the MT radii. Although choosing small MT radii reduces the linearization error, this extends the IR and thus entails a larger reciprocal cutoff radius leading to many additional basis functions. A much more effective way is to add LOs, for example HELOs, which are defined with higher energy parameters. HELOs are often used to improve the description of unoccupied states, but can also be employed to greatly reduce the linearization error for the oc-
cupied states. An even more efficient way to eliminate the linearization error for the occupied states, and thereby to make the results insensitive to variations of the energy parameters and MT radii, is to extend the basis with HDLOs, which are constructed from the second energy derivatives \( \tilde{u}\tilde{u}(r, E) \).

The addition of LOs allows to employ large MT spheres, which keeps the reciprocal cutoff radius small and thus keeps the basis-set size to a minimum. Using large spheres also ensures that the orthogonality of the basis functions for the valence states to the core states is maximized, which avoids ghost bands to appear in the valence and conduction band structure. The inclusion of extra sets of LOs might not always be necessary, but in the light of the present results we recommend it to be a routine part in the convergence of FLAPW calculations with respect to the basis set, in particular in systems with large valence band widths and if large MT radii are employed. We have found that a single set of HDLOs (16 additional functions per atom) already improves the accuracy of the results by one or even two orders of magnitude, yielding sufficient accuracy for all practical purposes. On the other hand, HELOs are very effective in improving the description of high-lying conduction states. This is of importance when Kohn-Sham wave functions are used as input for more sophisticated methods, such as the GW approximation or the total energy in the random-phase approximation.

Beyond the efficient elimination of the linearization error, the flexibility of the basis at the MT sphere boundaries is a major aspect controlling the required basis-set size. Extend-
ing the conventional LAPW basis set by LOs helps to decouple the two regions of space (MT spheres and interstitial region) in a similar way as in the related APW+lo approach resulting in a faster basis-set convergence. However, the decoupling is somewhat less effective than in APW+lo, where the matching condition of the radial derivative is dropped completely admitting single-particle wave functions that exhibit a kink at the MT sphere boundary. However, the LAPW+lo basis—here, HDLOs are most efficient—contains one radial function more than the APW+lo method so that a higher precision is achieved at equal basis-set sizes, in cases where the linearization error is large.

7. Acknowledgment

We thank Eugene Krasowskii for a careful reading of the manuscript.

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