

# Chapter 6

## The APW method

The *pseudopotential method* is not very suitable if one is interested in the piece of information contained in the region near the nucleus (for instance, hyperfine fields or core level excitations, etc.). The *LMTO method* allows to describe this region but is only good for closely packed structures because of the simplified treatment of energy-independent MTO's in the interstitial, where they are taken to be solutions of the Laplace equation and therefore have zero kinetic energy.

Let us introduce now the *augmented plane wave (APW) method*. As in the LMTO method, the space is partitioned into two regions: near the nuclei and away from them (Fig. 6.1). In the region far away from the nuclei, electrons are almost free and, as we know, can

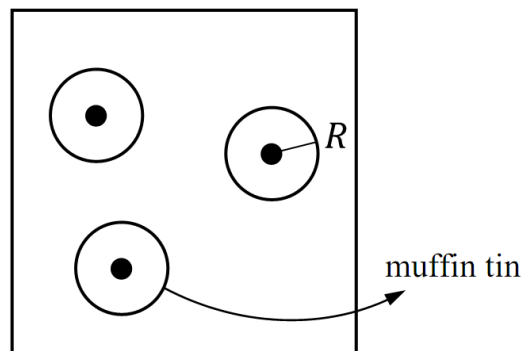


Figure 6.1: Partitioning of space into muffin-tin spheres and interstitial region.

be quite well described by plane waves. Close to the nuclei, electrons behave almost as if they were in a free atom and therefore can be described by atomic-like wavefunctions.

For the two regions, the electron potential  $V(\vec{r})$  is expanded as

$$V(\vec{r}) = \begin{cases} \sum_{LM} V_{LM}(r) Y_{LM}(\hat{r}), & r < R, \\ \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}, & r > R. \end{cases} \quad (6.1)$$

The APW is a "full-potential" method since there is no shape approximation for  $V(\vec{r})$  in eq. (6.1). In terms of expansions (6.1), the "muffin-tin" approximation, introduced in the previous section, corresponds to retaining only the  $L = 0$  component in the first expression and the  $\vec{G} = 0$  component in the second expression.

In the same spirit, the crystal wavefunction  $\Psi_{\vec{k}}^n$  is expanded in the APW method into augmented waves  $\phi_{\vec{G}}^{\vec{k}}$ :

$$\Psi_{\vec{k}}^n(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}}^{\vec{k}} \phi_{\vec{G}}^{\vec{k}}(\vec{r}, E);$$

$$\phi_{\vec{G}}^{\vec{k}}(\vec{r}, E) = \begin{cases} \sum_{lm} A_{lm}^{\alpha, \vec{k} + \vec{G}} u_l^\alpha(r, E) Y_m^l(\hat{r}), & r < R, \\ \frac{1}{\sqrt{V}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}, & r > R. \end{cases} \quad (6.2)$$

Here,  $u_l^\alpha(r, E)$  is the solution of the radial equation of a free atom:

$$h_l u_l^\alpha(r, E) - E u_l^\alpha(r, E) = 0;$$

$$h_l = -\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{l(l+1)}{r^2} + V(r).$$

In eq. (6.2), expansion coefficients  $A_{lm}^{\alpha, \vec{k} + \vec{G}}$  as well as energy  $E$  are undetermined parameters.

For a true free atom, the boundary condition for  $u$  is that it should vanish at  $r \rightarrow \infty$ . This condition limits the number of energies  $E$ , for which there exists a solution  $u(E)$ . In our case, however, this boundary condition cannot be applied. Instead, we require that, for each muffin-tin sphere, the plane wave outside the sphere matches the function inside the sphere over the complete surface of the sphere. In order to realize this requirement, we use the expansion of plane waves into spherical harmonics  $Y_l^m$  and Bessel functions  $j_l$  (i.e., partial waves),

$$\frac{1}{\sqrt{V}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} = \frac{4\pi}{\sqrt{V}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}_\alpha} \sum_{lm} i^l j_l(|\vec{k} + \vec{G}| |\vec{r}'|) Y_m^{l*}(\widehat{\vec{k} + \vec{G}}) Y_m^l(\hat{r}'). \quad (6.3)$$

The real space vectors appearing in eq. (6.3) are shown in Fig. 6.2. By equating expression (6.3) to the  $lm$ -part of the function inside the sphere at  $\vec{r}' = \vec{R}_\alpha$ , we get

$$A_{lm}^{\alpha, \vec{k} + \vec{G}} = \frac{4\pi i^l e^{i(\vec{k} + \vec{G}) \cdot \vec{r}_\alpha}}{\sqrt{V} u_l^\alpha(R_\alpha, E)} j_l(|\vec{k} + \vec{G}| R_\alpha) Y_m^{l*}(\widehat{\vec{k} + \vec{G}}),$$

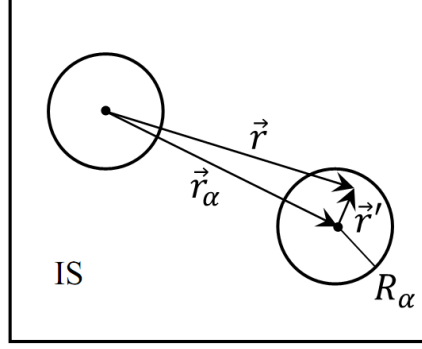


Figure 6.2: The real space vectors notation in eq. (6.3).

which uniquely defines  $A_{lm}^{\alpha, \vec{k} + \vec{G}}$ . Thus, we are now left with the only undetermined parameter being the energy  $E$ .

Since in eq. (6.3) there are an infinite number of terms, we are forced to use an infinite number of  $A_{lm}^{\alpha, \vec{k} + \vec{G}}$  coefficients in order to have the matching. In practice, one truncates the sum in eq. (6.3) at some value  $l_{\max}$ . In order to know where to truncate, let us consider the following. For a given  $l_{\max}$ , the spherical harmonics  $Y_m^{l_{\max}}(\theta, \varphi)$  can have at

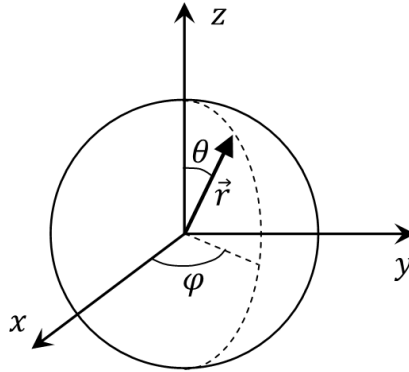


Figure 6.3: Angles  $\varphi$  and  $\theta$  in the spherical coordinate system.

most  $2l_{\max}$  nodes along a great circle of sphere  $\alpha$ . For instance,

$$Y_{m=2}^{l=2} = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{2i\phi}$$

has two nodes:  $\theta = 0$  and  $\theta = \pi$ . Or,

$$Y_{m=1}^{l=2} = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\varphi}$$

has four nodes.  $2l_{\max}$  nodes per sphere results in  $2l_{\max}/(2\pi R_\alpha) = l_{\max}/(\pi R_\alpha)$  nodes per unit length. For a plane wave expansion outside the sphere to match such a function inside the sphere, there should be available plane waves with at least a similar number of nodes per unit length. This means that the plane wave with the shortest period  $\lambda$ ,

$$\lambda = \frac{2\pi}{G_{\max}},$$

should have

$$\frac{2}{2\pi/G_{\max}} = G_{\max}/\pi$$

nodes per unit length. The cut-off for the plane waves,  $G_{\max}$ , and for the angular functions,  $l_{\max}$ , are of comparable quality if the number of nodes per unit length is identical in the two cases. This leads to the condition that

$$\frac{G_{\max}}{\pi} = \frac{l_{\max}}{\pi R_\alpha} \Rightarrow$$

$$\boxed{R_\alpha G_{\max} = l_{\max}}.$$

This condition allows to determine a good  $l_{\max}$  for a given  $G_{\max}$  and defines

$$\left. \begin{array}{l} \text{the parameters to be fixed at} \\ \text{the beginning of a calculation:} \end{array} \right\} \begin{array}{l} R_\alpha \rightarrow \text{muffin-tin radii,} \\ G_{\max}, \\ l_{\max}. \end{array}$$

Note that, in order to fulfill the condition  $R_\alpha G_{\max} = l_{\max}$  approximately, one should not choose too different muffin-tin radii  $R_\alpha$  for various ions  $\alpha$  in the unit cell since  $G_{\max}$  and  $l_{\max}$  are the same for all ions.

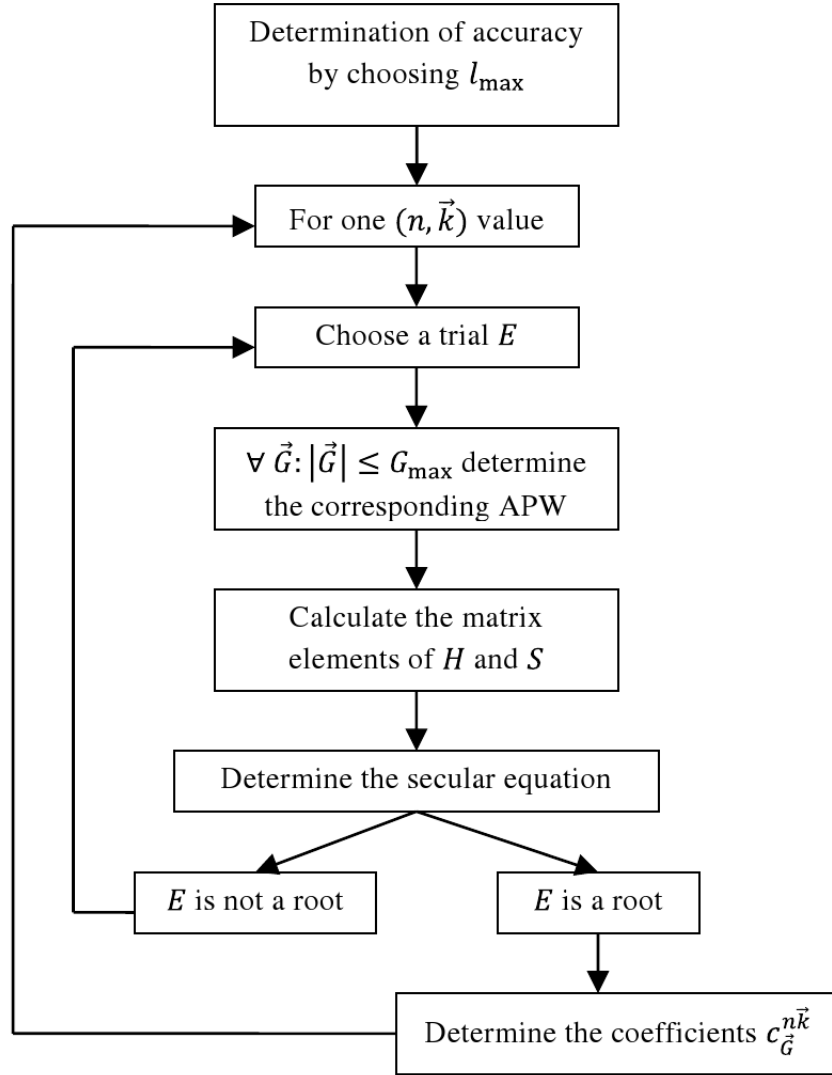
So far, we have obtained the APW basis functions and determined the boundary conditions. Now, in order to accurately describe an eigenstate  $\Psi_{\vec{k}}^n(\vec{r})$  with APW's, one has to set the energy  $E$  in  $u_l^\alpha(E)$  of each APW equal to the eigenvalue (or band energy)  $\epsilon_{\vec{k}}^n$  of the eigenstate  $\Psi_{\vec{k}}^n(\vec{r})$ . But  $\epsilon_{\vec{k}}^n$  is exactly the quantity we want to determine.

This situation is handled by starting a calculation with a guessed value for  $\epsilon_{\vec{k}}^n$ . We take the guessed  $\epsilon_{\vec{k}}^n$  as  $E$  for determining APW's and then construct the Hamiltonian matrix and overlap matrix (APW's are not orthogonal). This gives us the secular equation,

$$(\hat{H} - E\hat{S}) \cdot \vec{a} = 0,$$

whose root should be our guessed  $\epsilon_{\vec{k}}^n$ . Usually, this is not the case, and one tries another guess for  $E$ . Once again, one determines APW's with the new  $E$  and then proceeds as before. With the help of root determination algorithms, this guessing continues until a root is found. This search is repeated for each root  $n$ .

### The APW scheme



## 6.1 The LAPW method

The APW method is very slow since the radial functions  $u_l^\alpha(r', E)$  have to be constructed at unknown energies  $E = \epsilon_{\vec{k}}^n$  of the searched eigenstate. In order to avoid this procedure, one employs the same linearization scheme as in the LMTO method. Namely, one

performs a Taylor expansion of  $u_l^\alpha(r', E)$  in the neighbourhood of a certain energy  $E_0$ :

$$u_l^\alpha(r', E) = u_l^\alpha(r', E_0) + (E_0 - E) \underbrace{\left. \frac{\partial u_l^\alpha(r', E)}{\partial E} \right|_{E=E_0}}_{\dot{u}_l^\alpha(r', E_0)} + \mathcal{O}(E_0 - E)^2.$$

Then, the linearized augmented plane waves (LAPW) will be

$$\phi_{\vec{G}}^{\vec{k}}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}, & r > R, \\ \sum_{lm} \left( A_{lm}^{\alpha, \vec{k}+\vec{G}} u_l^\alpha(r', E_0) + B_{lm}^{\alpha, \vec{k}+\vec{G}} \dot{u}_l^\alpha(r', E_0) \right) Y_l^m(\hat{r}'), & r < R. \end{cases}$$

Since now we have two parameters,  $A$  and  $B$ , to be determined through boundary conditions, there must be two such conditions. One therefore requires that the function inside the sphere matches the plane waves both in *value* and in *slope* at the sphere boundary. By using the Rayleigh expansion of plane waves, as was done in the APW method, we obtain the coefficients  $A_{lm}^{\alpha, \vec{k}+\vec{G}}$  and  $B_{lm}^{\alpha, \vec{k}+\vec{G}}$ :

$$\begin{aligned} A_{lm}^{\vec{k}_n} &= 4\pi R^2 \Omega^{-1/2} i^l Y_l^{m*}(\hat{k}_n) a_l, \\ a_l &= [j'_l(n) \dot{u}_l - j_l(n) \dot{u}'_l]; \\ B_{lm}^{\vec{k}_n} &= 4\pi R^2 \Omega^{-1/2} i^l Y_l^{m*}(\hat{k}_n) b_l, \\ b_l &= [j_l(n) u'_l - j'_l(n) u_l]. \end{aligned}$$

Now, it remains to be seen how to choose  $E_0$ .

Let us consider the situation when we want to describe by LAPW's an eigenstate  $\Psi_{\vec{k}}^n$  with a predominantly  $p$ -character ( $l = 1$ ). In this case, in the expansion of  $\Psi_{\vec{k}}^n$  in LAPW's, the coefficients  $A_{l=1,m}^{\alpha, \vec{k}+\vec{G}}$  are *large*. It is therefore advantageous to choose  $E_0$  near the center of the  $p$ -band since then the  $\mathcal{O}(E_0 - E)^2$  term should be small, and cutting in the linear expansion after the linear term is not a bad approximation. This argument can be applied to every physically important  $l$  ( $s$ -,  $p$ -,  $d$ -,  $f$ -states) and to every atom, so that one can choose a set of  $E_l^\alpha$  up to  $l = 3$ . With these considerations, the LAPW's take over the following form:

$$\phi_{\vec{G}}^{\vec{k}}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}, & \vec{r} \in \text{IS}, \\ \sum_{lm} \left( A_{lm}^{\alpha, \vec{k}+\vec{G}} u_l^\alpha(r', E_l^\alpha) + B_{lm}^{\alpha, \vec{k}+\vec{G}} \dot{u}_l^\alpha(r', E_l^\alpha) \right) Y_l^m(\hat{r}'), & \vec{r} \in S_\alpha. \end{cases}$$

With the LAPW's thus defined, one constructs and solves the secular equation.  $u_l^\alpha$  and  $\dot{u}_l^\alpha$  are obtained by numerical integration of the radial Schrödinger equation on a radial mesh. In the alternative notation,

$$\vec{k} + \vec{G} = \vec{k}_n, \quad \phi_{\vec{G}}^{\vec{k}} = \phi_{\vec{k}_n},$$

$n$  defines the band index. Then,

$$\Psi_{\vec{k}} = \sum_n^p c_n \phi_{\vec{k}_n};$$

$$Hc = ESC; \tag{6.4}$$

$$H_{nm} = \langle \phi(\vec{k}_n) | H | \phi(\vec{k}_m) \rangle,$$

$$S_{nm} = \langle \phi(\vec{k}_n) | \phi(\vec{k}_m) \rangle.$$

Diagonalization of the matrix resulting from (6.4) yields  $p$  different band energies for a given  $\vec{k}$ . As in the pseudopotential method, one needs to solve the secular equation (i.e., to perform a diagonalization) for a  $\vec{k}$ -sampling in the first Brillouin zone.

### Accuracy

The accuracy in the plane wave method is determined by  $G_{\max}$ . In the APW and LAPW methods, a better accuracy controlling parameter is the product  $R_{\alpha}^{\min} K_{\max}$  of the smallest muffin-tin radius  $R_{\alpha}^{\min}$  and  $K_{\max}$  ( $G_{\max}$ ).

- ✓ A small  $R_{\alpha}$  requires plane waves with small wavelengths, i.e., large  $G_{\max}$ , since otherwise it would not be possible to describe an atom near the nucleus.
- ✓ A too big  $R_{\alpha}$  is also not good because atomic functions are not suitable for describing the wavefunction in the region far away from the nucleus.
- ✓ Working with a large  $G_{\max}$  is expensive because of the quickly increasing number of plane waves in the basis.

Because of this interplay between  $G_{\max}$  and  $R_{\alpha}$ , the product  $R_{\alpha}^{\min} K_{\max}$  regulates the accuracy quite well. For instance, the value of  $R_{\alpha}^{\min} K_{\max}$  being  $\sim 7.5 \div 9$  implies ( $R_{\alpha} \sim 2 \text{ ua}^{-1}$ )

$$G_{\max} \sim \frac{7.5 \div 9}{R_{\alpha}^{\min}} \approx 4 \text{ ua}^{-1},$$

which yields  $p \approx 195$  basis functions.

### LAPW with local orbitals (LAPW+LO)

While partitioning space into the interstitial region and MT spheres, the criterion used is to separate *core states* and *valence states*.

Let us consider, as an illustration, the  $1s$  orbital of Fe in bcc Fe. The  $1s$  electron is tightly bound to the nucleus ( $-514 \text{ Ry}$ ) and behaves almost exactly as if it were in a free Fe atom. Such an electron state is a *core state*.

**Core states** do not participate directly in chemical bonding with other atoms and must be confined within the muffin-tin sphere.

The states that leak out of the muffin-tin sphere are *valence states*.

**Valence states** participate in chemical bonding and are considered during the construction of the LAPW basis.

Core states are treated as those of free atoms, which are yet also subject to the potential due to valence states.

Sometimes, it can happen that two states with the *same*  $l$  but *different*  $n$ 's (principal quantum numbers) are both valence states. For instance, bcc Fe has a  $4p$  valence state at 0.2 Ry below the Fermi level  $E_F$  and a  $3p$  valence state at 4.3 Ry below  $E_F$ , which is not confined to the core. Such low-lying states are called *semi-core states*. Now, the question is how to choose in this situation the energy  $E_{(l=1)}^{\text{Fe}}$ . The problem is solved by introducing "local orbitals" (LO)  $\phi_{\alpha',\text{LO}}^{lm}(\vec{r})$ , defined as

$$\phi_{\alpha',\text{LO}}^{lm}(\vec{r}) = \begin{cases} 0, & \vec{r} \notin S_{\alpha'}, \\ \left[ A_{lm}^{\alpha',\text{LO}} u_l^{\alpha'}(r', E_{1,l}^{\alpha'}) + B_{lm}^{\alpha',\text{LO}} \dot{u}_l^{\alpha'}(r', E_{1,l}^{\alpha'}) \right. \\ \left. + C_{lm}^{\alpha',\text{LO}} u_l^{\alpha'}(r', E_{2,l}^{\alpha'}) \right] Y_m^l(\hat{r}'), & \vec{r} \in S_{\alpha'}, \end{cases}$$

$E_{1,l}^{\alpha'}$ : an energy value suitable for the highest in energy state out of the two valence states (the  $4p$  state in our example);

$E_{2,l}^{\alpha'}$ : an energy value at which the the lower valence state is peaked.

Since LO's are not connected to plane waves in the interstitial, they have no  $\vec{k}$  or  $\vec{G}$  dependence. Coefficients  $A$ ,  $B$  and  $C$  are determined by requiring that the LO's are

- normalized,
- zero at the sphere boundary  $R$
- and have zero slope at  $R$ .

If one adds local orbitals for  $p$  and  $d$  states of each atom, the basis set increases by  $3+5 = 8$  functions per atom, which is not much.



## 6.2 The APW+lo method

The problem that we had with the APW method was the *energy dependence* of the APW basis set. This energy dependence was removed in the LAPW+LO method by enlarging the basis set size (through linearization and introduction of local orbitals).

In the APW+lo method, the basis set

- is energy-independent and
- has the same size as in the APW method.

The APW+lo basis set contains two types of functions.

1. The first type is APW's, with a set of fixed energies  $E_l^\alpha$ ,

$$\phi_{\vec{G}}^{\vec{k}}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{(\vec{k}+\vec{G})\cdot\vec{r}}, & \vec{r} \in \text{IS}, \\ \sum_{lm} A_{lm}^{\alpha, \vec{k}+\vec{G}} u_l^\alpha(r', E_l^\alpha) Y_m^l(\hat{r}'), & \vec{r} \in S_\alpha. \end{cases}$$

APW's alone are not sufficient to form a good basis set since the choice of fixed energies does not, in principle, provide a good description of crystal eigenfunctions.

2. The APW basis set is augmented with a second type of functions, which are called "local orbitals" (these local orbitals have nothing to do with the local orbitals "LO" introduced in the previous chapter in order to solve the problem of valence states with equal  $l$  and different  $n$ ). Here, we shall label these local orbitals as "lo":

$$\phi_{\alpha', \text{lo}}^{lm}(\vec{r}) = \begin{cases} 0, & \vec{r} \in \text{IS}, \\ \left( A_{lm}^{\alpha', \text{lo}} u_l^{\alpha'}(r', E_l^{\alpha'}) + B_{lm}^{\alpha', \text{lo}} \dot{u}_l^{\alpha'}(r', E_l^{\alpha'}) \right) Y_m^l(\hat{r}'), & \vec{r} \in S_\alpha. \end{cases}$$

Index  $\alpha'$  indicates *all* atoms (and not only non-equivalent atoms). One considers the same set of energies  $E_l^{\alpha'}$  for lo's as for the corresponding APW's. The two coefficients  $A_{lm}^{\alpha', \text{lo}}$  and  $B_{lm}^{\alpha', \text{lo}}$  are determined by *normalization* and by requiring that lo's have *zero value* at the muffin-tin sphere boundary. Both the APW's and lo's are *continuous* at the sphere boundary, but their *first derivatives* are *discontinuous*.

In order to obtain accurate results with the APW+lo method, one requires a basis set with a size comparable to that of the APW method. For instance, in the APW+lo method,  $G_{\text{max}} \approx 3.5 \text{ au}^{-1}$  gives  $p \approx 130$  plane waves, which is less than in the LAPW+LO method, where  $G_{\text{max}} \approx 4 \text{ au}^{-1}$  gives  $p \approx 200$  plane waves.

### 6.2.1 Mixed LAPW/APL+lo basis sets

There are two reasons why the LAPW basis needs a larger  $G_{\max}$  than the APW+lo basis. Those are

- the presence of valence  $d$ - and  $f$ -states and
- the presence of atoms in the unit cell whose MT spheres are much smaller than the other MT spheres.

In either case, one uses APW+lo's for problematic states and LAPW's for all the other states. This approach proves efficient because of the following. Using an APW+lo for a state means that we add  $2l + 1$  lo's per atom. This makes an APW+lo basis set for the same  $R_{\alpha}^{\min} G_{\max}$  considerably larger than an LAPW basis set. This is, however, compensated by the fact that one needs a lower  $R_{\alpha}^{\min} K_{\max}$  for accurate results. A mixed LAPW/APW+lo basis set turns out to be the best approach.