

# Kapitel 16

## The Green's function method (KKR method)

J. Korringa, *On the calculation of the energy of a Bloch wave in a metal*, Physica **13**, 392 (1947).

W. Kohn and N. Rostoker, *Solution of the Schrödinger equation in periodic lattices with an application to metallic lithium*, Phys. Rev. **94**, 1111 (1954).

### 16.1 Introduction

This band structure method has been developed by Korringa, Kohn and Rostoker (1947; 1954). Especially for muffin-tin potentials, KKR is a proper alternative to APW, both fast convergent and numerically (*not: analytically!*) simple.

Let's start again with the one-particle Schrödinger equation

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + E(\mathbf{k}) \right] \psi_{\mathbf{k}}(\mathbf{r}) = V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}).$$

The corresponding *potential-free* differential equation (DE) reads

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + E_{n,\mathbf{k}}^0 \right] \psi_{n,\mathbf{k}}^0(\mathbf{r}) = 0 \quad (16.1)$$

with the eigenfunctions and eigenenergies

$$\psi_{n,\mathbf{k}}^0(\mathbf{r}) = \frac{1}{\sqrt{\Omega_0}} \exp[i\mathbf{k}_n \cdot \mathbf{r}] \quad \text{and} \quad E_{n,\mathbf{k}}^0 = \frac{\hbar^2}{2m} |\mathbf{k}_n|^2 \quad (16.2)$$

with  $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$ .

The starting point of KKR is given by the *inhomogenous* DE

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + E(\mathbf{k}) \right] G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (16.3)$$

Because of the fact that the plane waves fulfill the completeness relation

$$\sum_n \psi_{n,\mathbf{k}}^{0*}(\mathbf{r}') \psi_{n,\mathbf{k}}^0(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}'),$$

the *Green's function* in Eq. (16.3) can be written as

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}') = \frac{1}{\Omega_0} \sum_n \frac{\exp[i(\mathbf{k}_n) \cdot (\mathbf{r} - \mathbf{r}')] }{E(\mathbf{k}) - \frac{\hbar^2}{2m} |\mathbf{k}_n|^2}. \quad (16.4)$$

This Green's function has, obviously, the properties

$$G_{\mathbf{k}}(\mathbf{r}, \mathbf{r}') = G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') = G_{\mathbf{k}}^*(\mathbf{r}' - \mathbf{r}), \quad (16.5)$$

and it fulfills Bloch's condition

$$G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}' + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \quad (16.6)$$

erfüllt.

For a crystal, we have the Schrödinger equation including the potential  $V(\mathbf{r})$

$$\left[ \frac{\hbar^2}{2m} \nabla^2 + E(\mathbf{k}) \right] \psi_{\mathbf{k}}(\mathbf{r}) = V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}). \quad (16.7)$$

Following the theory of partial homogenous DE's, one can make the *ansatz*

$$\psi_{\mathbf{k}}(\mathbf{r}) = \int_{\Omega_0} d^3 r' G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}'), \quad (16.8)$$

in order to transform the DE (16.7) into the integral equation (16.8).

Note that - due to Eq. (16.6) - the above wavefunction is a Blochfunction.

A further advantage of the *ansatz* (16.8) is the fact that the whole dependence on  $\mathbf{k}$  and on the crystal structure is completely included *alone* in the Green's function.

## 16.2 The variational principle of KKR

We set up a proper *variational ansatz* by defining the function

$$\bar{\Lambda} = \int_{\Omega_0} d^3 r \psi_{\mathbf{k}}^*(\mathbf{r}) \left( \hat{H} - E \right) \psi_{\mathbf{k}}(\mathbf{r}).$$

Using  $\hat{H} = -(\hbar^2/2m)\nabla^2 + V$ , one gets

$$\bar{\Lambda} = \int_{\Omega_0} d^3 r \psi_{\mathbf{k}}^*(\mathbf{r}) V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) - \int_{\Omega_0} d^3 r \psi_{\mathbf{k}}^*(\mathbf{r}) \left[ \frac{\hbar^2}{2m} \nabla^2 + E \right] \psi_{\mathbf{k}}(\mathbf{r})$$

with  $\Omega_0$  as the volume of the unit cell of the crystal.

Inserting Eqs. (16.8) and (16.7) into the second term of  $\psi_{\mathbf{k}}^*(\mathbf{r})$ , one obtains

$$\begin{aligned} \bar{\Lambda} = & \int_{\Omega_0} d^3r \psi_{\mathbf{k}}^*(\mathbf{r}) V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) - \\ & \int_{\Omega_0} \int_{\Omega'_0} d^3r d^3r' \underbrace{G_{\mathbf{k}}^*(\mathbf{r} - \mathbf{r}')}_{=G_{\mathbf{k}}(\mathbf{r}' - \mathbf{r})} V(\mathbf{r}') \psi_{\mathbf{k}}^*(\mathbf{r}') V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) \end{aligned}$$

and - by interchanging  $\mathbf{r}$  with  $\mathbf{r}'$

$$\begin{aligned} \bar{\Lambda} = & \int_{\Omega_0} d^3r \psi_{\mathbf{k}}^*(\mathbf{r}) V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) - \\ & \int_{\Omega_0} \int_{\Omega'_0} d^3r d^3r' \psi_{\mathbf{k}}^*(\mathbf{r}) V(\mathbf{r}) G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}'). \end{aligned} \quad (16.9)$$

The solution of the variational principle

$$\delta \bar{\Lambda} = 0 \quad (16.10)$$

immediately leads to the solution of the integral equation (16.8).

### 16.3 The secular equation for the *muffin-tin* potential

A significant simplification of the KKR theory comes from the approximation of the *real* crystal potential by a *muffin-tin* potential

$$V(\mathbf{r}) = \begin{cases} V(|\mathbf{r}|) & r \leq r_{\text{MT}} \\ 0 & r > r_{\text{MT}}. \end{cases} \quad (16.11)$$

In that case, all integrals over the unit cell  $\Omega_0$  can be reset by integrals over the *muffin-tin sphere* MTK with the radius  $r_{\text{MT}}$ .

$$\begin{aligned} \bar{\Lambda} = & \int_{\text{MTK}} d^3r \psi_{\mathbf{k}}^*(\mathbf{r}) V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) - \\ & \int_{\text{MTK}} \int_{\text{MTK}'} d^3r d^3r' \psi_{\mathbf{k}}^*(\mathbf{r}) V(\mathbf{r}) G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}'). \end{aligned} \quad (16.12)$$

As a consequence, the *trial function* for the desired wavefunction has only be defined inside and above the MTK. In that region, the potential is *per definitionem* spherically symmetric [see Eq. (16.11)], and one may write

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm}(\mathbf{k}) \phi_{lm}(\mathbf{r}; E) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} c_{lm}(\mathbf{k}) R_l(r; E) Y_{lm}(\vartheta, \varphi). \quad (16.13)$$

Compare this equation with the *ansatz* (14.4) in the chapter on *cell methods*: in this chapter, the expansion of  $\psi_{\mathbf{k}}(\mathbf{r})$  could not be used because of the complicated boundary conditions of the wavefunction on the surface of the unit cell (WSC).

In the present context, this problem does not appear, because the *trial function* for the variational principle (16.10) is only needed inside the MTK.

- This leads to a very simple *trial function* - a great advantage of the KKR method!

By insertion of the function (16.13) into Eq. (16.12), one gets

$$\begin{aligned} \bar{\Lambda} = & \sum_{lm} \sum_{l'm'} c_{lm}^*(\mathbf{k}) c_{l'm'}(\mathbf{k}) \\ & \times \left\{ \int_{MTK} d^3r \phi_{lm}^*(\mathbf{r}; E) V(r) \phi_{l'm'}(\mathbf{r}; E) - \right. \\ & \left. \int_{MTK} \int_{MTK'} d^3r d^3r' \phi_{lm}^*(\mathbf{r}; E) V(r) G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') V(r') \phi_{l'm'}(\mathbf{r}'; E) \right\}. \end{aligned}$$

where the expression in the brackets  $\{\dots\}$  defines the component of the KKR secular matrix  $\Lambda$  for the row  $(l, m)$  and the column  $(l', m')$ :

$$\bar{\Lambda} = \sum_{lm} \sum_{l'm'} c_{lm}^*(\mathbf{k}) c_{l'm'}(\mathbf{k}) \Lambda_{lm;l'm'}(\mathbf{k}).$$

A derivation of  $\bar{\Lambda}$  with respect to the parameters  $c_{lm}^*(\mathbf{k})$  leads to

$$\frac{\delta \bar{\Lambda}}{\delta c_{lm}^*(\mathbf{k})} = \sum_{l'm'} \Lambda_{lm;l'm'}(\mathbf{k}) c_{l'm'}(\mathbf{k}) = 0,$$

and, consequently, to the *system of homogeneous linear equations*

$$\sum_{l'm'} \Lambda_{lm;l'm'}(\mathbf{k}) c_{l'm'}(\mathbf{k}) = 0 \quad (16.14)$$

with  $l = 1, 2, \dots, \infty$  and  $m = -l, -l + 1, \dots, l - 1, l$ . The components of the corresponding *secular matrix* are

$$\begin{aligned} \Lambda_{lm;l'm'}(\mathbf{k}) = & \int_{MTK} d^3r \phi_{lm}^*(\mathbf{r}; E) V(r) \phi_{l'm'}(\mathbf{r}; E) - \\ & \int_{MTK} \int_{MTK'} d^3r d^3r' \phi_{lm}^*(\mathbf{r}; E) V(r) G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') V(r') \phi_{l'm'}(\mathbf{r}'; E). \end{aligned} \quad (16.15)$$

Of course, for numerical evaluations, one has to take into account that the secular matrix  $\Lambda$  has to be reset by a matrix of finite order: limiting the angular momentum by  $l \leq l_{max}$ , one gets a KKR matrix (16.14) of order

$$(l_{max} + 1)^2. \quad (16.16)$$

For many simple structures (bcc, fcc, hcp, ...), a good convergence of KKR bandstructure results can be achieved by relatively small values of  $l_{max}$ . As it is demonstrated in Table 16.1,  $l_{max} = 3 - 4$  is sufficient in many cases, leading to an order of 16-25 for the KKR matrix.

Now back to the matrix elements  $\Lambda_{lm,l'm'}$ : these contain the basis functions  $\phi_{lm}(\mathbf{r}; E)$ , and -therefore - the radial functions  $R_l(r; E)$  that are solutions of the DE (14.3):

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) - E \right] R_l(r; E) = 0$$

That means that these radial functions include implicitly the information about the crystal potential  $V(r)$ .

- From the theoretical point of view, it would be desirable that  $\Lambda$  could be transformed such that the potential would **explicitly** disappear in Eq. (16.15).

Such a transformation is really possible, as it is demonstrated at the end of this chapter (see appendix 16.5). The result is as follows:

$$\begin{aligned} \Lambda_{lm,l'm'}(\mathbf{k}) = & \lim_{\epsilon \rightarrow 0} \left( \frac{\hbar^2}{2m} \right)^2 \int_{S_{MTK-\epsilon}} \int_{S_{MTK-2\epsilon}} dS dS' \left[ \frac{\partial}{\partial r} \phi_{lm}^*(\mathbf{r}; E) - \phi_{lm}^*(\mathbf{r}; E) \frac{\partial}{\partial r} \right] \\ & \times \left[ \phi_{l'm'}(\mathbf{r}'; E) \frac{\partial}{\partial r'} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') - G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \frac{\partial}{\partial r'} \phi_{l'm'}(\mathbf{r}'; E) \right], \end{aligned} \quad (16.17)$$

where  $S_{MTK-\epsilon}$  and  $S_{MTK-2\epsilon}$  mean that the integrations go over two muffin-tin spheres with radii  $r_{MT} - \epsilon$  and  $r_{MT} - 2\epsilon$  ( $\epsilon > 0$  infinitely small). By this trick, singularities of the Green's function for  $|\mathbf{r} - \mathbf{r}'|$  are avoided.

Inserting the relation

$$\phi_{lm}(\mathbf{r}; E) = R_l(r; E) Y_{lm}(\vartheta, \varphi)$$

into Eq. (16.17), the KKR matrix elements read

$$\begin{aligned} \Lambda_{lm,l'm'}(\mathbf{k}) = & \lim_{\epsilon \rightarrow 0} \left( \frac{\hbar^2}{2m} \right)^2 r_{MT}^4 \int \int d\Omega_{\mathbf{r}} d\Omega_{\mathbf{r}'} Y_{lm}^*(\vartheta, \varphi) Y_{l'm'}(\vartheta', \varphi') \\ & \times \left[ R_l'(r_{MT}; E) - R_l(r_{MT}; E) \frac{\partial}{\partial r} \right] \\ & \times \left[ R_{l'}(r_{MT}; E) \frac{\partial}{\partial r'} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') - G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') R_{l'}'(r_{MT}; E) \right] \end{aligned} \quad (16.18)$$

with

$$|\mathbf{r}| = r_{MT} - 2\epsilon, \quad |\mathbf{r}'| = r_{MT} - \epsilon$$

and

$$R'_l(r_{\text{MT}}; E) = \left[ \frac{d}{dr} R_l(r; E) \right]_{r=r_{\text{MT}}}.$$

Additionally, we use the abbreviations  $d\Omega_{\mathbf{r}} = d\vartheta \sin \vartheta d\varphi$  and  $d\Omega_{\mathbf{r}'} = d\vartheta' \sin \vartheta' d\varphi'$ .

In order to facilitate the integrations over  $d\Omega_{\mathbf{r}}$  and  $d\Omega_{\mathbf{r}'}$  in Eq. (16.18), it is useful to expand the Green's function (16.4) with respect of spherical Bessel functions and spherical harmonics:

$$\begin{aligned} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') &= \frac{(4\pi)^2}{\Omega_0} \sum_{\substack{l,m \\ l',m'}} \sum_n i^{l-l'} \frac{j_l(|\mathbf{k}_n| |\mathbf{r}|) j_{l'}(|\mathbf{k}_n| |\mathbf{r}'|)}{E(\mathbf{k}) - \frac{\hbar^2}{2m} |\mathbf{k}_n|^2} \\ &\quad \times Y_{lm}(\vartheta, \varphi) Y_{l'm'}^*(\vartheta', \varphi') Y_{lm}^*(\vartheta_{\mathbf{k}}, \varphi_{\mathbf{k}}) Y_{l'm'}(\vartheta_{\mathbf{k}}, \varphi_{\mathbf{k}}), \end{aligned} \quad (16.19)$$

where  $\vartheta_{\mathbf{k}}$  and  $\varphi_{\mathbf{k}}$  mean the angle that belongs to the vector  $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$ .

**Note:** that next step is done *for technical reasons*: for the following, the Green's function shall be written as

$$\begin{aligned} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') &= \sum_{\substack{l,m \\ l',m'}} [A_{lm;l'm'}(\mathbf{k}; E) j_l(\kappa r) j_{l'}(\kappa r')] \\ &\quad + \kappa \delta_{l,l'} \delta_{m,m'} j_l(\kappa r) n_l(\kappa r')] Y_{lm}(\vartheta, \varphi) Y_{l'm'}^*(\vartheta', \varphi') \end{aligned} \quad (16.20)$$

where  $\kappa^2 = E$ , and the functions  $j_l(x)$  and  $n_l(x)$  mean the spherical Bessel and Neumann functions

$$j_l(x) = \left( \frac{\pi}{2x} \right)^{1/2} J_{l+1/2}(x) \quad ; \quad n_l(x) = \left( \frac{\pi}{2x} \right)^{1/2} J_{-l-1/2}(x).$$

The equivalence of the expressions (16.19) and (16.20) is obtained by a determination of the coefficients  $A_{lm;l'm'}$  in Eq. (16.20) by a *comparison of coefficients* with respect of the terms  $Y_{lm}(\vartheta, \varphi) Y_{l'm'}^*(\vartheta', \varphi')$ :

$$\begin{aligned} A_{lm;l'm'}(\mathbf{k}; E) &= \\ &= \frac{(4\pi)^2}{\Omega_0} \frac{i^{l-l'}}{j_l(\kappa r) j_{l'}(\kappa r')} \sum_n \frac{j_l(|\mathbf{k}_n| r) j_{l'}(|\mathbf{k}_n| r')}{E(\mathbf{k}) - \frac{\hbar^2}{2m} |\mathbf{k}_n|^2} \\ &\quad \times Y_{lm}^*(\vartheta_{\mathbf{k}}, \varphi_{\mathbf{k}}) Y_{l'm'}(\vartheta_{\mathbf{k}}, \varphi_{\mathbf{k}}) - \frac{\kappa n_l(\kappa r')}{j_l(\kappa r')} \delta_{l,l'} \delta_{m,m'}. \end{aligned} \quad (16.21)$$

These (new) parameters are exclusively determined by the structure of the lattice and are completely independent from the crystal potential.

Including the expression (16.20) into Eq. (16.18) and taking account the well-known orthogonality relations between the spherical harmonics, one obtains after some elementary but tedious calculations

$$\begin{aligned} \Lambda_{lm;l'm'}(\mathbf{k}) &= \left( \frac{\hbar^2}{2m} \right)^2 r_{\text{MT}}^4 R_l(r_{\text{MT}}; E) R_{l'}(r_{\text{MT}}; E) [L_l j_l(\kappa r_{\text{MT}}) - j'_l(\kappa r_{\text{MT}})] \times \\ &\quad \{ [A_{lm;l'm'} j'_{l'}(\kappa r_{\text{MT}}) + \kappa \delta_{m,m'} \delta_{l,l'} n'_{l'}(\kappa r_{\text{MT}})] - \\ &\quad [A_{lm;l'm'} j_{l'}(\kappa r_{\text{MT}}) + \kappa \delta_{m,m'} \delta_{l,l'} n_{l'}(\kappa r_{\text{MT}})] L_l \}, \end{aligned} \quad (16.22)$$

with the definitions

$$L_l = \frac{1}{R_l(r_{\text{MT}}; E)} \cdot \left. \frac{d R_l(r; E)}{d r} \right|_{r=r_{\text{MT}}}, \quad (16.23)$$

$$j'_l(\kappa r_{\text{MT}}) = \left. \frac{d j_l(\kappa r)}{d r} \right|_{r=r_{\text{MT}}}, \quad (16.24)$$

$$n'_l(\kappa r_{\text{MT}}) = \left. \frac{d n_l(\kappa r)}{d r} \right|_{r=r_{\text{MT}}}. \quad (16.25)$$

For the calculation of the eigenvalues of the secular matrix (16.22), only the positions of the zero values of the corresponding determinant are of interest, not the values of the determinant themselves! Now, looking at Eq. (16.22), it can be shown that *all prefactors that influence all coefficients of a distinct row or column of the matrix, do not influence the zeros of its determinant.*

That means that the *eigenvalue equation* for Eq. (16.22) reads

$$\begin{aligned} & \text{Det} \{ \Lambda_{lm, l'm'} \} = \\ & \text{const} \cdot \text{Det} \{ [A_{lm, l'm'} j'_{l'}(\kappa r_{\text{MT}}) + \kappa \delta_{m, m'} \delta_{l, l'} n'_{l'}(\kappa r_{\text{MT}})] - \\ & [A_{lm, l'm'} j_{l'}(\kappa r_{\text{MT}}) + \kappa \delta_{m, m'} \delta_{l, l'} n_{l'}(\kappa r_{\text{MT}})] L_l \}, \end{aligned}$$

and further, after some elementary transformations,

$$\text{Det} \{ \Lambda_{lm, l'm'} \} = \text{const} \cdot \text{Det} \left\{ A_{lm, l'm'} + \kappa \frac{n_l(\kappa r_{\text{MT}}) L_l - n'_{l'}(\kappa r_{\text{MT}})}{j_{l'}(\kappa r_{\text{MT}}) L_l - j'_{l'}(\kappa r_{\text{MT}})} \delta_{ll'} \delta_{mm'} \right\}.$$

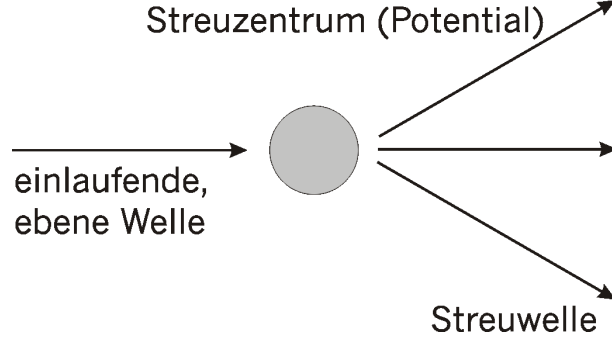
As a final result, the secular equation for the KKR method is given by

$$\text{Det} \left\{ A_{lm, l'm'} + \kappa \frac{n_l(\kappa r_{\text{MT}}) L_l - n'_{l'}(\kappa r_{\text{MT}})}{j_{l'}(\kappa r_{\text{MT}}) L_l - j'_{l'}(\kappa r_{\text{MT}})} \delta_{ll'} \delta_{mm'} \right\} = 0. \quad (16.26)$$

- This equation demonstrates again a quite advantageous aspect of KKR: the coefficients of the secular matrix consist of two terms, where the first one is only determined by the geometry of the lattice, and the second one is determined by the crystal potential.
- However, the KKR method shares with APW a great disadvantage: it also leads to a *non-linear* eigenvalue problem, because the energy values  $E$  do not only appear linearly in the secular equation, but also - in a non-trivial manner - in the coefficients  $A_{lm, l'm'}$  and  $L_l$ , and within the functions  $j_l(\kappa r_{\text{MT}})$  and  $n_l(\kappa r_{\text{MT}})$ .  
The mathematical and computational consequences for that have been already discussed in Ch. 15 over the APW method.
- Therefore, it is no surprise that - during the last decades - *linearized KKR programs* have been developed, as, e.g., based on such successful methods like the *linear muffin-tin-orbital method* LMTO (Andersen 1975) and the *augmented spherical wave method* ASW (Williams, Kübler, Gelatt 1979).

### 16.3.1 The KKR secular equation and scattering theory

Korringa derived in 1947 an equation equivalent to Eq. (16.26) by using the *general scattering theory*:



*Far away* from the center of the scattering potential, the scattered wave can be asymptotically described by a sum of the incoming plane wave and a spherical wave caused by the scattering potential

$$\Psi \propto e^{i\mathbf{k}\cdot\mathbf{r}} + f(\vartheta) \frac{e^{ikr}}{r}$$

with the *scattering amplitude*  $f$  and the *scattering angle*  $\vartheta \equiv \angle(\mathbf{k}, \mathbf{r})$ .

If the scattering potential is zero,  $\Psi$  remains a plane wave that can be described in partial waves as

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_l \sum_m i^l j_l(kr) Y_{lm}(\vartheta, \varphi) Y_{lm}^*(\vartheta_{\mathbf{k}}, \varphi_{\mathbf{k}}),$$

i.e. that the  $\ell^{\text{th}}$  partial wave is characterized by the spherical Bessel function  $j_\ell(kr)$  with the *asymptotic limit*

$$j_\ell(kr) \rightarrow \frac{1}{kr} \sin\left(kr - \frac{l\pi}{2}\right).$$

In case of a non-zero scattering potential, an equivalent expansion contains instead of Bessel functions radial functions  $R_\ell(kr)$  with the asymptotic representation

$$R_\ell(kr) \rightarrow \frac{c_\ell}{kr} \sin\left(kr - \frac{l\pi}{2} + \eta_\ell\right).$$

$c_\ell$  means the intensity of the  $\ell^{\text{th}}$  partial wave, and  $\eta_\ell$  is the corresponding *phase shift*.

Because of

$$\sin\left(kr - \frac{l\pi}{2} + \eta_\ell\right) = \cos \eta_\ell \left[ \sin\left(kr - \frac{l\pi}{2}\right) + \tan \eta_\ell \cos\left(kr - \frac{l\pi}{2}\right) \right]$$



one further gets

$$R_l(kr) \rightarrow c_l \left[ j_l(kr) + \tan \eta_l \frac{1}{kr} \cos \left( kr - \frac{l\pi}{2} \right) \right].$$

The cosine in the above expression can be considered the asymptotic limit of the *Neumann function*  $n_\ell(kr)$ , namely

$$n_l(kr) \rightarrow -\frac{1}{kr} \cos \left( kr - \frac{l\pi}{2} \right),$$

Using these equations, one can write

$$\begin{aligned} R_l(kr) &\propto c_l [j_l(kr) - \tan \eta_l n_l(kr)], \\ R'_l(kr) &\propto c_l [j'_l(kr) - \tan \eta_l n'_l(kr)], \end{aligned}$$

and together with the definition (16.23), one gets

$$L_l = \frac{R'_l(r_{\text{MT}}; E)}{R_l(r_{\text{MT}}; E)} = \frac{j'_l(\kappa r_{\text{MT}}) - \tan \eta_l n'_l(\kappa r_{\text{MT}})}{j_l(\kappa r_{\text{MT}}) - \tan \eta_l n_l(\kappa r_{\text{MT}})}.$$

Resolving this equation with respect to  $\tan \eta_\ell$ , one obtains

$$\tan \eta_l = \frac{j_l(\kappa r_{\text{MT}}) L_l - j'_l(\kappa r_{\text{MT}})}{n_l(\kappa r_{\text{MT}}) L_l - n'_l(\kappa r_{\text{MT}})}.$$

As an interesting result, the KKR secular equation (16.26) can also be written in the form

$$\text{Det} \{ A_{lm, l'm'} + \kappa \cot \eta_l \delta_{ll'} \delta_{mm'} \} = 0. \quad (16.27)$$

## 16.4 The KKR method in practice

### 16.4.1 Convergence

Experiences with KKR calculations for aluminum, copper and some alkali methods teach us that even for small values of  $\ell_{\text{max}}=3$  the errors of the resulted energy values only amount to some mRy (see Table 16.1).

Aus den praktisch gemachten Erfahrungen für leichte Metalle kann geschlossen werden, daß die Streuphasen für Partialwellen vierter und höherer Ordnung vernachlässigbar werden. Dies entspricht vollständig dem aus der Atomphysik bekannten Verhalten. Dies läßt für schwere Metalle den Analogieschluß zu, daß es auch hier genügt, bis zur Partialwelle einschließlich vierter Ordnung zu gehen, um befriedigende Ergebnisse zu erhalten; dies wird durch die Praxis voll bestätigt.

Vergleicht man dies mit den Ergebnissen aus analogen APW – Rechnungen, bei denen für ähnlich gute Energiewerte Entwicklungen bis zu  $\ell_{\text{max}} = 6$  und mehr erforderlich sind, so wird die Überlegenheit der KKR-Methode in diesem Punkt deutlich.

Tabelle 16.1: Some examples of the convergence of selected energy eigenvalues of electrons in various metals.

$l_{max}$	energy eigenvalues				
	Li	Na	K	Al	Cu
1	+0.2715	+0.2920	+0.3130	-0.1723	-0.3192
2	+0.2635	+0.2810	+0.2875	-0.1799	-0.2328
3	+0.2635	+0.2805	+0.2870	-0.1801	-0.2350
5	+0.2640	+0.2805	+0.2870	-0.1801	-0.2350

Wie bereits oben diskutiert wurde, bestimmt bei einer APW-Rechnung nicht  $l_{max}$  die Dimension der Säkulargleichung, sondern die Zahl der APW's, welche für eine bestimmte Genauigkeit erforderlich erscheint. Man kann also sagen, daß *typische Ordnungen* von KKR-Säkularmatrizen für nicht zu komplizierte Bandstrukturprobleme im Bereich von 16 bis 25 liegen, für die APW-Rechnung hingegen bei 80-150. Ein gewisser Nachteil von KKR gegenüber APW stellt jedoch die numerisch recht aufwändige Berechnung. Allerdings brauchen diese Koeffizienten für jede Kristallstruktur nur einmal berechnet zu werden und können dann für viele Problemstellungen verwendet werden, weil sie ja unabhängig vom konkreten Kristallpotential sind.

As further discussed, the dimension of an APW secular matrix is not determined by  $l_{max}$  but by a certain number of APWs that is necessary to reach the desired accuracy.

From this aspect one can say that the order of KKR secular matrices for not too complicated bandstructure problems is about 16-25; in contrast to that, typical APW matrices have orders of 80 to 150 what shows a marked superiority of the KKR method compared to APW.

On the other hand, a disadvantage of KKR compared to APW is the relatively complicated calculation of the structure coefficients  $A_{lm,l'm'}$  [see (16.21)].

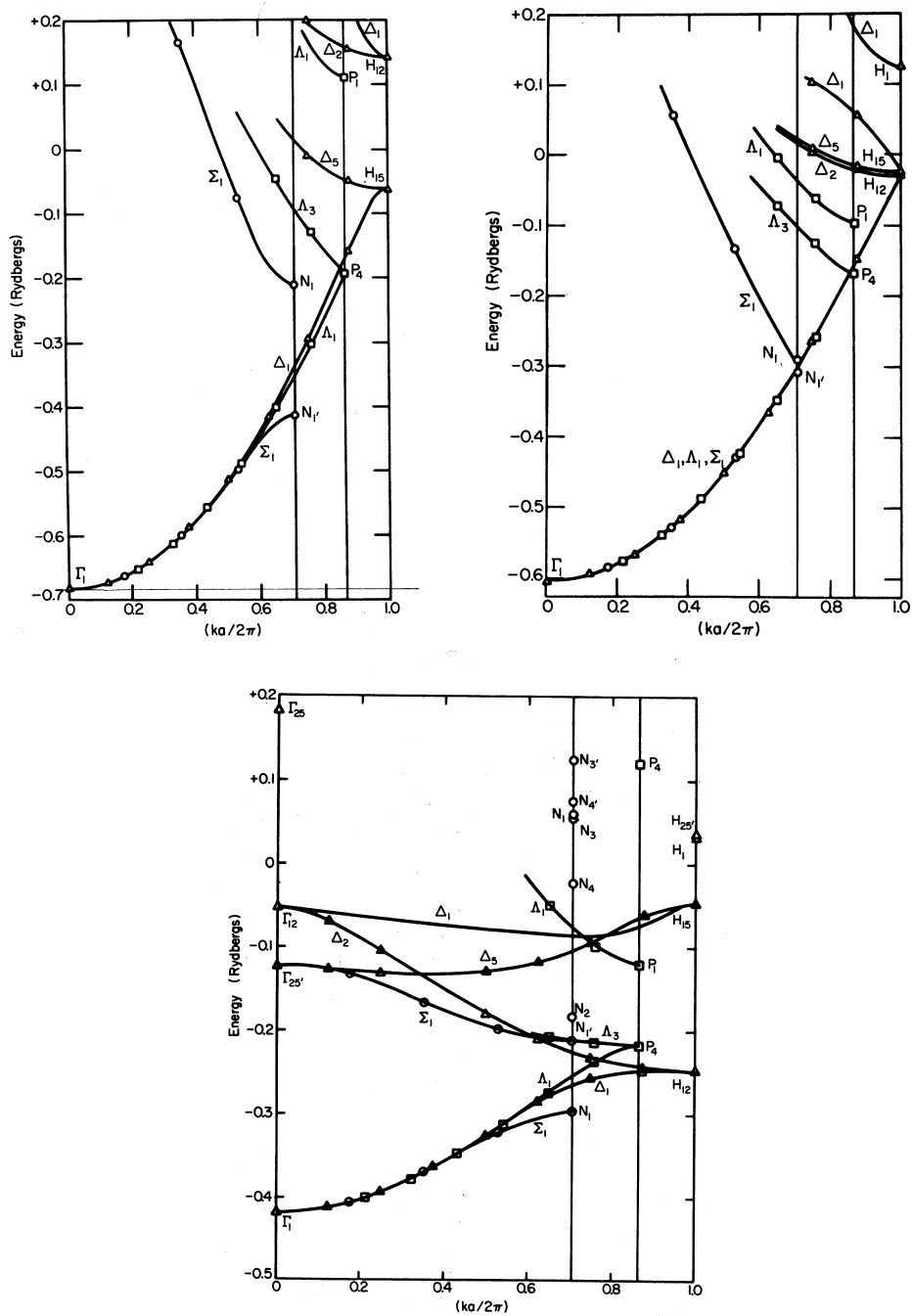


Abbildung 16.1: KKR bandstructure results of the alkali metals Li (top left), Na (top right), and Cs (bottom) (F.S. Ham, Phys. Rev. **128**, 82 (1962)).

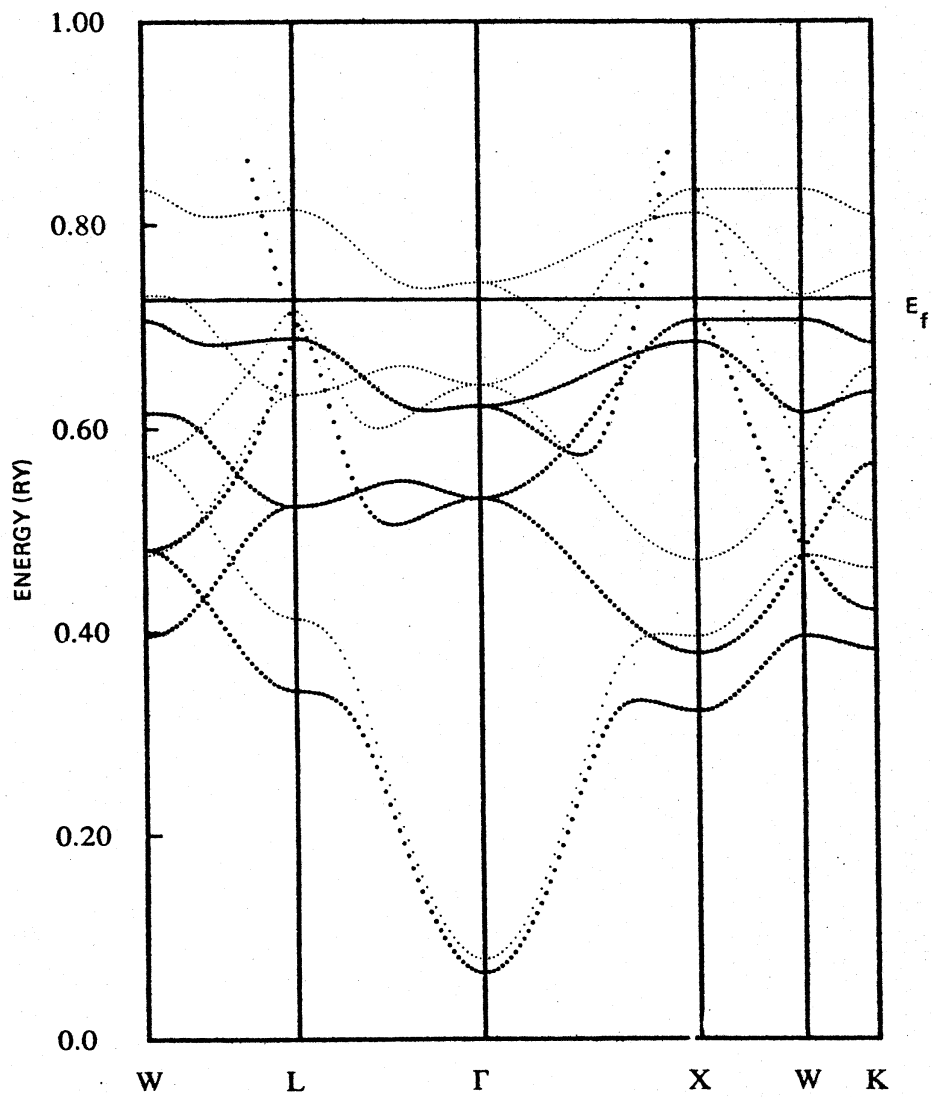


Abbildung 16.2: KKR bandstructure of electrons in ferromagnetic cobalt, obtained from the book of V.L. Moruzzi, J.F. Janak, and A.R. Williams, *Calculated Electronic Properties of Metals*, Pergamon Press 1978.

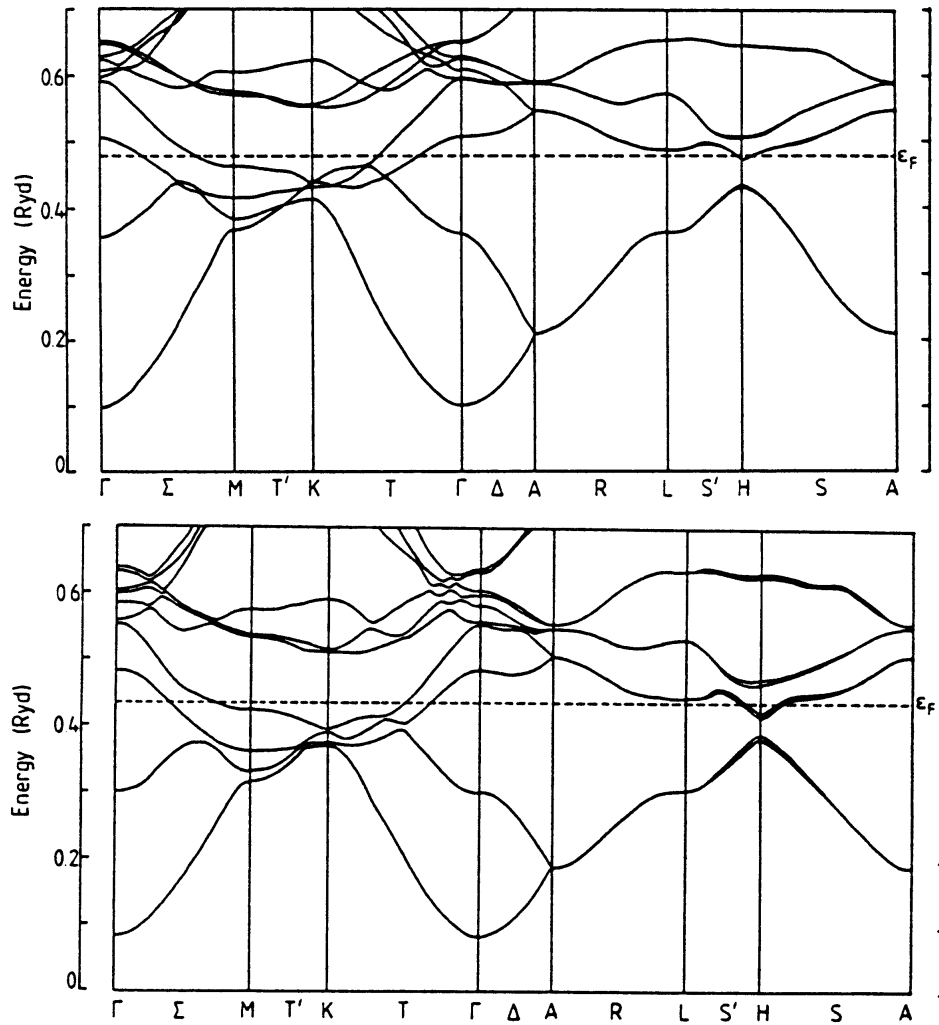


Abbildung 16.3: KKR bandstructures of hcp scandium (a) und hcp yttrium (b) (M. Matsumoto, *et al.*, J. Phys.: Condens. Matter **3**, 1453 (1991)).

## 16.5 'Potential-free form' of the KKR-Matrix-elemente

The starting-point of the following calculation is the KKR secular matrix with their components (16.15):

$$\Lambda_{lm,l'm'}(\mathbf{k}) = \lim_{\epsilon \rightarrow 0} \int_{MTK-2\epsilon} d^3r \phi_{lm}^*(\mathbf{r}; E) V(r) \times \left\{ \phi_{l'm'}(\mathbf{r}; E) - \int_{MTK-\epsilon} d^3r' G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \phi_{l'm'}(\mathbf{r}'; E) \right\}. \quad (16.28)$$

This equation differs from Eq. (16.15) only *formally* insofar the radii of the spheres to be integrated are infinitesimally smaller (by  $\epsilon$  and  $2\epsilon$ ) than the muffin-tin radius  $r_{MT}$ . By this trick, a singularity of the Green's function in case  $\mathbf{r} = \mathbf{r}'$  can be avoided. *After the evaluation of the integrals*, the limit  $\epsilon \rightarrow 0$  is calculated.

The transformation starts with the second term ( $I_1$ ) within the above brackets  $\{\dots\}$ . One gets with  $V(\mathbf{r}') = -\hat{T} + \hat{H}$  and under consideration of  $\hat{H}\phi = E\phi$ :

$$\begin{aligned} I_1 &= \int_{MTK-\epsilon} d^3r' G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \left[ \frac{\hbar^2}{2m} \nabla_{\mathbf{r}'}^2 + E \right] \phi_{l'm'}(\mathbf{r}'; E) \\ &\quad - \int_{MTK-\epsilon} d^3r' \phi_{l'm'}(\mathbf{r}'; E) \left[ \frac{\hbar^2}{2m} \nabla_{\mathbf{r}'}^2 + E \right] G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \\ &\quad + \int_{MTK-\epsilon} d^3r' \phi_{l'm'}(\mathbf{r}'; E) \left[ \frac{\hbar^2}{2m} \nabla_{\mathbf{r}'}^2 + E \right] G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}'). \end{aligned}$$

The terms including  $E$  in the first and second line of the above expression cancel each other, and taking into account Eq. (16.3)

$$\left[ \frac{\hbar^2}{2m} \nabla_{\mathbf{r}'}^2 + E \right] G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'),$$

one gets

$$\begin{aligned} I_1 &= \phi_{l'm'}(\mathbf{r}; E) + \frac{\hbar^2}{2m} \int_{MTK-\epsilon} d^3r' [G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}'}^2 \phi_{l'm'}(\mathbf{r}'; E) \\ &\quad - \phi_{l'm'}(\mathbf{r}'; E) \nabla_{\mathbf{r}'}^2 G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}')] \end{aligned}$$

and

$$\begin{aligned} I_1 &= \phi_{l'm'}(\mathbf{r}; E) + \frac{\hbar^2}{2m} \int_{MTK-\epsilon} d^3r' \vec{\nabla}_{\mathbf{r}'} \left[ G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \vec{\nabla}_{\mathbf{r}'} \phi_{l'm'}(\mathbf{r}'; E) \right. \\ &\quad \left. - \phi_{l'm'}(\mathbf{r}'; E) \vec{\nabla}_{\mathbf{r}'} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \right]. \end{aligned}$$

By application of the *Gaussian integration rule*

$$\int_{(V)} dV (\vec{\nabla}, \mathbf{y}) = \int_{(S)} (d\mathbf{n}, \mathbf{y}),$$

and taking into account that  $S$  is the surface of a sphere, one further gets

$$(d\mathbf{n}, \vec{\nabla}_{\mathbf{r}'}) \equiv dS' \frac{\partial}{\partial r'}$$

and for  $I_1$  the expression

$$\begin{aligned} I_1 = & \phi_{l'm'}(\mathbf{r}; E) + \frac{\hbar^2}{2m} \int_{S_{MTK-\epsilon}} dS' \left[ G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \frac{\partial}{\partial r'} \phi_{l'm'}(\mathbf{r}'; E) \right. \\ & \left. - \phi_{l'm'}(\mathbf{r}'; E) \frac{\partial}{\partial r'} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \right]. \end{aligned} \quad (16.29)$$

If one inserts this formula into Eq. (16.28), a short calculation leads to

$$\begin{aligned} \Lambda_{lm,l'm'}(\mathbf{k}) = & \lim_{\epsilon \rightarrow 0} \left( -\frac{\hbar^2}{2m} \right) \int_{S_{MTK-\epsilon}} dS' \left[ \frac{\partial}{\partial r'} \phi_{l'm'}(\mathbf{r}'; E) - \phi_{l'm'}(\mathbf{r}'; E) \frac{\partial}{\partial r'} \right] \\ & \times \int_{MTK-2\epsilon} d^3r G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \phi_{lm}^*(\mathbf{r}; E) V(r). \end{aligned} \quad (16.30)$$

The remaining integral as  $I_2^*$  with

$$I_2 \equiv \int_{MTK-2\epsilon} d^3r G_{\mathbf{k}}(\mathbf{r}' - \mathbf{r}) \phi_{lm}(\mathbf{r}; E) V(r), \quad (16.31)$$

corresponds to the already discussed integral  $I_1$  (if  $\mathbf{r}$  and  $\mathbf{r}'$  are interchanged), but with the following important difference:

- The integral  $I_2$  goes over a sphere with the radius  $r_{MT} - 2\epsilon$ . Therefore, the situation  $\mathbf{r} = \mathbf{r}'$  will never appear, and - consequently- the first term in Eq. (16.29) is no more necessary.

Apart this detail, in accordance to Eq. (16.29), one gets for  $I_2$

$$I_2 = \frac{\hbar^2}{2m} \int_{S_{MTK-2\epsilon}} dS \left[ G_{\mathbf{k}}(\mathbf{r}' - \mathbf{r}) \frac{\partial}{\partial r} \phi_{lm}(\mathbf{r}; E) - \phi_{lm}(\mathbf{r}; E) \frac{\partial}{\partial r} G_{\mathbf{k}}(\mathbf{r}' - \mathbf{r}) \right].$$

Inserting this expression in Eq. (16.30), one yields for the KKR matrix elements

$$\begin{aligned} \Lambda_{lm,l'm'}(\mathbf{k}) = & \lim_{\epsilon \rightarrow 0} \left( \frac{\hbar^2}{2m} \right)^2 (-1) \int_{S_{MTK-\epsilon}} dS' \left[ \frac{\partial}{\partial \mathbf{r}'} \phi_{l'm'}(\mathbf{r}'; E) - \phi_{l'm'}(\mathbf{r}'; E) \frac{\partial}{\partial \mathbf{r}'} \right] \\ & \times \int_{S_{MTK-2\epsilon}} dS \left[ G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \frac{\partial}{\partial r} \phi_{lm}^*(\mathbf{r}; E) - \phi_{lm}^*(\mathbf{r}; E) \frac{\partial}{\partial r} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \right]. \end{aligned}$$

After a simple transformation of this formula, one gets the desired result (16.17):

$$\begin{aligned} \Lambda_{lm,l'm'}(\mathbf{k}) = & \\ & \lim_{\epsilon \rightarrow 0} \left( \frac{\hbar^2}{2m} \right)^2 \int_{S_{MTK-\epsilon}} \int_{S_{MTK-2\epsilon}} dS dS' \left[ \frac{\partial}{\partial r} \phi_{lm}^*(\mathbf{r}; E) - \phi_{lm}^*(\mathbf{r}; E) \frac{\partial}{\partial r} \right] \\ & \times \left[ \phi_{l'm'}(\mathbf{r}'; E) \frac{\partial}{\partial r'} G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') - G_{\mathbf{k}}(\mathbf{r} - \mathbf{r}') \frac{\partial}{\partial r'} \phi_{l'm'}(\mathbf{r}'; E) \right] . \end{aligned}$$

So, the aim of this calculation is reached: a representation of  $\Lambda_{lm,l'm'}$  without any *explicit* appearance of the lattice potential  $V(r)$ .