

CHAPTER II

KORRINGA-KOHN-ROSTOKER EQUATIONS AND THEIR PLANE WAVE REPRESENTATION

The Green's function method or Korringa-Kohn-Rostoker (KKR) method has been invented independently by Korringa¹⁶ and by Kohn and Rostoker¹⁵. This method is known as a powerful technique for practical calculation of energy band of solids.

In this chapter, we present only the nonvariational derivation of the method. The variational derivation can be found in the original paper¹⁵. Korringa's approach can be examined in his original paper¹⁶. We also give in this chapter the derivation of the KKR secular equation in a plane wave representation as it will be referred to in the subsequent chapters.

1. Nonvariational derivation of the KKR secular equation

To calculate the electronic band structure of a solid we have to solve a one electron Schrödinger equation

$$\left[-\nabla^2 + v(\underline{r}) - E(\underline{k}) \right] \psi_{\underline{k}}(\underline{r}) = 0 \quad \dots 1)$$

¹⁶ J. Korringa, "On the Calculation of the Energy of a Bloch Wave in a Metal," Physica, XIII, 392-400 (1947).

where the crystal potential $V(\underline{r})$ is periodic, \underline{k} is the propagation vector of the electron and $E(\underline{k})$ is the value of one electron energy corresponding to \underline{k} . The energy and length are expressed in terms of atomic units. The unit of energy (Rydberg) is the ionization energy of the hydrogen atom of infinite nuclear mass, $me^4/2\hbar^2$, and the unit of length is the radius of the smallest Bohr orbit of the hydrogen atom, \hbar^2/me^2 . This set of units is widely used to carry out band calculations. For convenience, we shall drop the suffix \underline{k} from the wave function and the energy but shall always understand that these energies pertain to a specific value of \underline{k} . Thus eq. 1) becomes

$$[-\nabla^2 + V(\underline{r}) - E] \Psi(\underline{r}) = 0. \quad \dots 2)$$

For any translation vector \underline{r}_S of the crystal lattice, the periodicity of the crystal potential yields the condition

$$V(\underline{r} + \underline{r}_S) = V(\underline{r}) \quad \dots 3)$$

and the Bloch condition must be imposed on the wave function:

$$\Psi(\underline{r} + \underline{r}_S) = \exp(i\underline{k} \cdot \underline{r}_S) \Psi(\underline{r}). \quad \dots 4)$$

As discussed in chapter I, in practice it is necessary to make calculation only for arbitrary \underline{k} lying within the first Brillouin zone. Our solutions must satisfy the following boundary conditions in the central polyhedron surrounding the origin;

$$\begin{aligned} \Psi(\underline{r}^c) &= \exp(i\underline{k} \cdot \underline{r}_r) \Psi(\underline{r}), \\ \partial \Psi(\underline{r}^c) / \partial n^c &= - \exp(i\underline{k} \cdot \underline{r}_r) \partial \Psi(\underline{r}) / \partial n. \end{aligned} \quad \dots 5)$$

The \underline{r}^c and \underline{r} are conjugate points on the surface of the polyhedron and $\underline{\tau}_r$ is a fundamental translation vector joining them as illustrated schematically in Fig. 3. The notations $\partial/\partial n$ and $\partial/\partial n^c$ denote differentiation along the outward normal vectors at \underline{r} and \underline{r}^c respectively. Now it is sufficient only to look for solutions of eq. 1) which satisfy boundary conditions 5) in the atomic polyhedron.

The standard method of solving a differential equation with boundary conditions is to convert the differential equation into an integral equation involving the Green's function appropriate for the boundary conditions. Here we introduce the Green's function defined in terms of the arbitrary vectors \underline{r} and \underline{r}' in the atomic polyhedron by

$$(\nabla^2 + E)G(\underline{r}, \underline{r}') = \delta(\underline{r} - \underline{r}') \quad \dots 6)$$

and, for conjugate boundary points \underline{r} and \underline{r}^c ,

$$G(\underline{r}^c, \underline{r}') = \exp(i\mathbf{k} \cdot \underline{\tau}_r) G(\underline{r}, \underline{r}') \quad \dots 7)$$

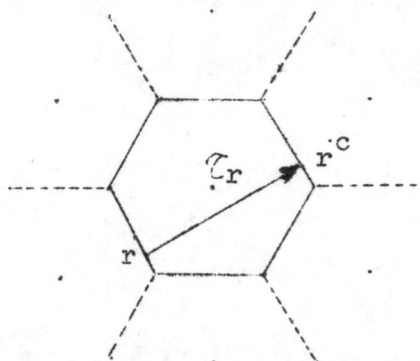
$$\text{and } \partial G(\underline{r}^c, \underline{r}') / \partial n^c = - \exp(i\mathbf{k} \cdot \underline{\tau}_r) \partial G(\underline{r}, \underline{r}') / \partial n.$$

Let \underline{k}_n represent the vectors of the reciprocal lattice defined by

$$\underline{k}_n \cdot \underline{\tau}_i = 2\pi \times (\text{integer}); \quad i = 1, 2, 3 \quad \dots 8)$$

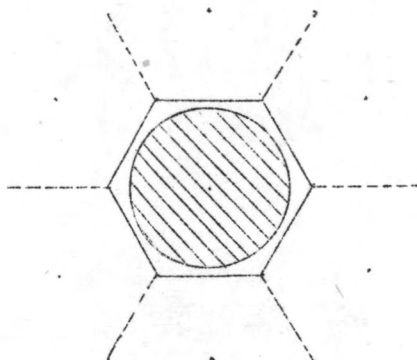
where $\underline{\tau}_i$ are the fundamental translation vectors of the crystal lattice. The Green's function may be constructed by introducing the Fourier transform through

Fig. 3

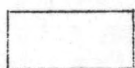


Showing the conjugate boundary points: r and r^c ;
and the fundamental translation vector \underline{C}_r joining
them.

Fig. 4



Showing the cross section of the inscribed sphere
in the atomic polyhedron;



the region of constant potential,



the region of spherically symmetric
potential.

$$G(\underline{r}, \underline{r}') = \frac{1}{\mathcal{V}} \sum_{\underline{n}} g_{\underline{k}}(\underline{K}_{\underline{n}} + \underline{k}) \exp[i(\underline{K}_{\underline{n}} + \underline{k}) \cdot (\underline{r} - \underline{r}')] \quad \dots 9)$$

Here \mathcal{V} denotes the volume of the atomic polyhedron, $g_{\underline{k}}$ are the coefficients of the Fourier expansion and $\sum_{\underline{n}}$ is over all the vectors $\underline{K}_{\underline{n}}$ of the reciprocal space. Substituting eq. 9) into eq. 6) and recalling that

$$\delta(\underline{r} - \underline{r}') = \frac{1}{\mathcal{V}} \sum_{\underline{n}} \exp[i(\underline{K}_{\underline{n}} + \underline{k}) \cdot (\underline{r} - \underline{r}')] \quad \dots 10)$$

we have

$$\left[-(\underline{K}_{\underline{n}} + \underline{k})^2 + E \right] g_{\underline{k}}(\underline{K}_{\underline{n}} + \underline{k}) = 1,$$

$$g_{\underline{k}}(\underline{K}_{\underline{n}} + \underline{k}) = - \frac{1}{(\underline{K}_{\underline{n}} + \underline{k})^2 - E} \cdot$$



The substitution of $g_{\underline{k}}$ into eq. 9) yields the Green's function in the reciprocal space representation as

$$G(\underline{r}, \underline{r}') = - \frac{1}{\mathcal{V}} \sum_{\underline{n}} \frac{\exp[i(\underline{K}_{\underline{n}} + \underline{k}) \cdot (\underline{r} - \underline{r}')] }{(\underline{K}_{\underline{n}} + \underline{k})^2 - E} \quad \dots 11)$$

Eq. 11) is the standard expansion of the Green's function in terms of the eigenfunctions of the homogeneous boundary value problem. We note from eq. 11) that G is Hermitian since

$$G^*(\underline{r}, \underline{r}') = G(\underline{r}', \underline{r}). \quad \dots 12)$$

Another alternative representation of eq. 11) is given in appendix A and it will be referred to in the next section.

In order to incorporate conditions 5) into eq. 2) by an integral equation, we multiply eq. 2) by $G^*(\underline{r}, \underline{r}')$

$$G^*(\underline{r}, \underline{r}') [-\nabla^2 + V(\underline{r}) - E] \Psi(\underline{r}) = 0$$

and multiply the complex conjugate of eq. 6) by $\Psi(\underline{r})$

$$\Psi(\underline{r}) [\nabla^2 + E] G^*(\underline{r}, \underline{r}') = \Psi(\underline{r}) \delta^*(\underline{r} - \underline{r}')$$

then the integration of the sum of these two equations over \underline{r} within the atomic polyhedron of volume \mathcal{T} gives

$$\begin{aligned} \int_{\mathcal{T}} [\Psi(\underline{r}) \nabla^2 G^*(\underline{r}, \underline{r}') - G^*(\underline{r}, \underline{r}') \nabla^2 \Psi(\underline{r})] d\tau + \int_{\mathcal{T}} G^*(\underline{r}, \underline{r}') V(\underline{r}) \Psi(\underline{r}) d\tau \\ = \int_{\mathcal{T}} \Psi(\underline{r}) \delta^*(\underline{r}' - \underline{r}) d\tau, \\ = \Psi(\underline{r}'), \end{aligned}$$

or

$$\begin{aligned} \Psi(\underline{r}') - \int_{\mathcal{T}} G^*(\underline{r}, \underline{r}') V(\underline{r}) \Psi(\underline{r}) d\tau &= \int_{\mathcal{T}} [\Psi(\underline{r}) \nabla^2 G^*(\underline{r}, \underline{r}') - G^*(\underline{r}, \underline{r}') \nabla^2 \Psi(\underline{r})] \\ &\quad \cdot d\tau, \\ &= \int_S \left[\Psi(\underline{r}) \frac{\partial G^*(\underline{r}, \underline{r}')}{\partial n} - G^*(\underline{r}, \underline{r}') \frac{\partial \Psi(\underline{r})}{\partial n} \right] ds \end{aligned}$$

... 13)

when we have used the Green's theorem. S denotes the surface of the polyhedron. We note that for any pair of conjugate points \underline{r} and \underline{r}^c the integral on the right of eq. 13) contributes zero because

of the boundary conditions 5). Thus the integral over S vanishes and gives

$$\Psi(\underline{r}') - \int_{\tau} G^*(\underline{r}, \underline{r}') V(\underline{r}) \Psi(\underline{r}) d\tau = 0$$

or

$$\Psi(\underline{r}) = \int_{\tau'} G(\underline{r}, \underline{r}') V(\underline{r}') \Psi(\underline{r}') d\tau'. \quad \dots 13)$$

To avoid the complication of the problem of the region of integration Kohn and Rostoker introduced a potential with the muffin-tin form which satisfies the following properties

$$V(\underline{r}) = V(r); \text{ spherically symmetrical for } r < r_i - \epsilon,$$

and

$$V(\underline{r}) = V_0, \text{ for } r \geq r_i - \epsilon,$$

where r_i is the radius of the inscribed sphere in the atomic polyhedron (as shown in Fig. 4). One can choose the zero of the energy scale such that $V(\underline{r})$ can be taken as zero for $r \geq r_i$.

The choice of a potential of this kind makes it possible to convert the volume integral in eq. 13) into a form which does not depend explicitly on the potential but involves surface integrals over the sphere inscribed.

In order to avoid the singularities of the Green's function we must use a limiting procedure in eq. 13). By defining the domains $r < r_i - 2\epsilon$ and $r' < r_i - \epsilon$ where ϵ is positive, eq. 13) becomes

$$\Psi(\underline{r}) - \int_{r' < r_i - \epsilon} G(\underline{r}, \underline{r}') V(r') \Psi(\underline{r}') d\tau' = 0. \quad \dots 14)$$

Replacing $V(r') \Psi(\underline{r}')$ by $(\nabla'^2 + E) \Psi(\underline{r}')$ we get

$$\Psi(\underline{r}) - \int_{r' < r_i - \epsilon} G(\underline{r}, \underline{r}') (\nabla'^2 + E) \Psi(\underline{r}') d\tau' = 0. \quad \dots 15)$$

$$\begin{aligned} \text{Since } & \int_{r' < r_i - \epsilon} [G(\underline{r}, \underline{r}') (\nabla'^2 + E) \Psi(\underline{r}') - \Psi(\underline{r}') (\nabla'^2 + E) G(\underline{r}, \underline{r}')] d\tau' \\ & = \int_{r' < r_i - \epsilon} [G(\underline{r}, \underline{r}') \nabla'^2 \Psi(\underline{r}') - \Psi(\underline{r}') \nabla'^2 G(\underline{r}, \underline{r}')] d\tau', \\ & = \int_{S'(r=r_i - \epsilon)} [G(\underline{r}, \underline{r}') \frac{\partial}{\partial n'} \Psi(\underline{r}') - \Psi(\underline{r}') \frac{\partial}{\partial n'} G(\underline{r}, \underline{r}')] dS' \quad \dots 16) \end{aligned}$$

where $\frac{\partial}{\partial n'}$ denotes the normal derivative over the surface S' of the sphere of radius $r_i - \epsilon$. In eq. 16) we can put

$$(\nabla'^2 + E)G(\underline{r}, \underline{r}') = (\nabla'^2 + E)G^*(\underline{r}', \underline{r}) = \delta(\underline{r}' - \underline{r}).$$

Thus

$$\begin{aligned} & \int_{r' < r_i - \epsilon} G(\underline{r}, \underline{r}') (\nabla'^2 + E) \Psi(\underline{r}') d\tau' - \int_{r' < r_i - \epsilon} \Psi(\underline{r}') \delta(\underline{r}' - \underline{r}) d\tau' \\ & = \int_{S'(r=r_i - \epsilon)} [G(\underline{r}, \underline{r}') \frac{\partial}{\partial n'} \Psi(\underline{r}') - \Psi(\underline{r}') \frac{\partial}{\partial n'} G(\underline{r}, \underline{r}')] dS' \end{aligned}$$

which gives the condition at $r=r_i - 2\epsilon$:

$$\int_{r' < r_i - \epsilon} G(\underline{r}, \underline{r}') (\nabla'^2 + E) \Psi(\underline{r}') d\tau' - \Psi(\underline{r})$$

$$= \int_{S'(r'=r_i - \epsilon)} \left[G(\underline{r}, \underline{r}') \frac{\partial}{\partial n'} \Psi(\underline{r}') - \Psi(\underline{r}') \frac{\partial}{\partial n'} G(\underline{r}, \underline{r}') \right] dS'$$

or

$$\int_{S'(r'=r_i - \epsilon)} \left[G(\underline{r}, \underline{r}') \frac{\partial}{\partial n'} \Psi(\underline{r}') - \Psi(\underline{r}') \frac{\partial}{\partial n'} G(\underline{r}, \underline{r}') \right] dS' = 0, \dots 17)$$

where we have put eq. 14) into the above equation. This condition must hold for all $r \leq r_i - 2\epsilon$.

For the next step, we recall that for such a muffin-tin potential with spherical symmetry in the inscribed sphere our unknown wave function $\Psi(\underline{r})$ in the sphere has an expansion in terms of spherical harmonics Y_{lm} and radial wave functions R_l as the following;

$$\Psi(\underline{r}) = \sum_{l,m} C_{lm} Y_{lm}(\hat{r}) R_l(E,r) \quad \dots 18)$$

with coefficients C_{lm} to be determined. $R_l(E,r)$ is defined by

$$\left[-\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + V(r) - E \right] R_l(E,r) = 0, \dots 19)$$

$$R_l(0) = \text{finite}, \quad R_l(r_i) = 1.$$

The spherical harmonics $Y_{lm}(\hat{r})$ or $Y_{lm}(\theta, \phi)$ can be expanded in the form

$$Y_{lm}(\hat{r}) = \left[\frac{(2l+1)}{4\pi} \cdot \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) \exp(im\phi) \quad \dots 20)$$

and satisfy orthonormality relation

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta Y_{lm}(\theta, \varphi) Y_{l'm'}^*(\theta, \varphi) = \delta_{ll'} \delta_{mm'} \quad \dots 21)$$

where θ, φ are the directional angles of \underline{r} .

To make use of the spherical symmetry we also need an expansion of G in spherical harmonics. This rather complicated analytical problem has been resolved by Kohn and Rostoker as follows.

The expansion of $G(\underline{r}, \underline{r}')$ for $r < r' < r_i$ needs the following standard expressions:

Addition theorem

$$P(\cos \Theta) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta', \varphi') \quad \dots 22)$$

where Θ is the angle between the directions (θ, φ) and (θ', φ') , Y_{lm} are defined in eq. 20).

Expansion of plane wave

$$\exp(i\underline{k} \cdot \underline{R}) = 4\pi \sum_{l,m} i^l j_l(kR) Y_{lm}(\hat{R}) Y_{lm}^*(\hat{K}) \quad \dots 23)$$

\hat{R} and \hat{K} denote the directions of \underline{R} and \underline{K} respectively. j_l are the spherical Bessel functions defined in terms of the Bessel functions J :

$$j_l(x) = \left[\frac{\pi}{2x} \right]^{1/2} J_{l+1/2}(x).$$

Expansion of free space Green's function

$$\begin{aligned}
 G_0(\underline{r}, \underline{r}') &= - \frac{1}{4\pi} \frac{\exp(i\kappa|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|} \\
 &= \kappa \sum_{l,m} j_l(\kappa r) [n_l(\kappa r') - i j_l(\kappa r')] Y_{lm}(\hat{r}) Y_{lm}^*(\hat{r}') \dots 24)
 \end{aligned}$$

for $r < r'$ and a symmetrical expression when $r' < r$. n_l are the spherical Neumann functions related to the Bessel functions J by

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

We now use eq. 11) as a starting point. Let us introduce a function $D(\underline{r}, \underline{r}')$ given by

$$D(\underline{r}, \underline{r}') = G(\underline{r}, \underline{r}') - G_0(\underline{r}, \underline{r}') \dots 25)$$

where $G_0(\underline{r}, \underline{r}')$ is the real part of the free space Green's function and is given by

$$\begin{aligned}
 G_0(\underline{r}, \underline{r}') &= - \frac{1}{4\pi} \frac{\cos(\kappa|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|} \\
 &= \begin{cases} \kappa \sum_{l,m} j_l(\kappa r) n_l(\kappa r') Y_{lm}(\hat{r}) Y_{lm}^*(\hat{r}'); & r < r'. \\ \kappa \sum_{l,m} n_l(\kappa r) j_l(\kappa r') Y_{lm}^*(\hat{r}) Y_{lm}(\hat{r}'); & r > r'. \end{cases} \dots 26)
 \end{aligned}$$

Since this is the singular part of the Green's function, the function

$D(\underline{r}, \underline{r}')$ will satisfy the homogeneous equation

$$(\nabla^2 + E) D(\underline{r}, \underline{r}') = 0 \quad \dots 27)$$

such that we can write its solution as

$$D(\underline{r}, \underline{r}') = \sum_{l,m} \sum_{l',m'} A_{lm;l'm'} j_l(\kappa r) j_{l'}(\kappa r') Y_{lm}(\hat{r}) Y_{l'm'}^*(\hat{r}') \dots 28)$$

for $r < r' < r_i$. $A_{lm;l'm'}$ are coefficients of expansion which can be shown to be dependent only on the associated crystal structure.

Using eqs. 25), 26) and 28), we can express G for $r < r' < r_i$ as follows.

$$G(\underline{r}, \underline{r}') = \sum_{l,m} \sum_{l',m'} \left[A_{lm;l'm'} j_l(\kappa r) j_{l'}(\kappa r') + \kappa \delta_{ll'} \delta_{mm'} j_l(\kappa r) n_l(\kappa r') \right] \cdot Y_{lm}(\hat{r}) Y_{l'm'}^*(\hat{r}') \dots 29)$$

where we have expressed G_0 as a double sum. The Hermiticity of $G(\underline{r}, \underline{r}')$ implies that

$$A_{lm;l'm'} = A_{l'm';lm}^* \quad \dots 30)$$

We now substitute eqs. 18) and 29) into eq. 17) and carrying out the angular integration using eq. 21) we have

$$\begin{aligned}
& \int_{S'(r=r_i-\epsilon)} \sum_{l,m} \sum_{l',m'} \left\{ A_{lm;l'm'} j_l(\kappa r) j_{l'}(\kappa r') + \kappa \delta_{ll'} \delta_{mm'} j_l(\kappa r) n_{l'}(\kappa r') \right\} \\
& \cdot \frac{\partial}{\partial n'} \sum_{l',m'} C_{l'm'} Y_{l'm'}(\hat{r}') R_{l'}(E, r') - \sum_{l',m'} C_{l'm'} Y_{l'm'}(\hat{r}') R_{l'}(E, r') \\
& \cdot \frac{\partial}{\partial n'} \left\{ A_{lm;l'm'} j_l(\kappa r) j_{l'}(\kappa r') + \kappa \delta_{ll'} \delta_{mm'} j_l(\kappa r) n_{l'}(\kappa r') \right\} Y_{lm}(\hat{r}) Y_{l'm'}^*(\hat{r}') ds' \\
& = 0,
\end{aligned}$$

$$\begin{aligned}
& \sum_{l,m} \sum_{l',m'} A_{lm;l'm'} \left[j_l(\kappa r) j_{l'}(\kappa r') \frac{\partial}{\partial n'} R_{l'} + \kappa \delta_{ll'} \delta_{mm'} j_l(\kappa r) n_{l'}(\kappa r') \frac{\partial}{\partial n'} R_{l'} \right. \\
& \left. - R_{l'} j_l(\kappa r) \frac{\partial}{\partial n'} j_{l'}(\kappa r') - \kappa \delta_{ll'} \delta_{mm'} R_{l'} j_l(\kappa r) \frac{\partial}{\partial n'} n_{l'}(\kappa r') \right] C_{l'm'} Y_{lm}(\hat{r}) = 0
\end{aligned}$$

which gives, for a given l, m ,

$$\begin{aligned}
& \sum_{l',m'} \left[A_{lm;l'm'} \left\{ j_{l'}(\kappa r') \frac{\partial}{\partial n'} R_{l'}(r') - R_{l'}(r') \frac{\partial}{\partial n'} j_{l'}(\kappa r') \right\} \right. \\
& \left. + \kappa \delta_{ll'} \delta_{mm'} \left\{ n_{l'}(\kappa r') \frac{\partial}{\partial n'} R_{l'}(r') - R_{l'}(r') \frac{\partial}{\partial n'} n_{l'}(\kappa r') \right\} \right] C_{l'm'} = 0,
\end{aligned}$$

$$\begin{aligned}
& \sum_{l',m'} \left\{ A_{lm;l'm'} \left[j_{l'}(\kappa r'), R_{l'}(r') \right]_{r=r_i-\epsilon} \right. \\
& \left. + \kappa \delta_{ll'} \delta_{mm'} \left[n_{l'}(\kappa r'), R_{l'}(r') \right]_{r=r_i-\epsilon} \right\} C_{l'm'} = 0
\end{aligned}$$

... 31)

where we define

$$\begin{aligned} \left[F(r), G(r) \right]_{r=r_i} &= F(r) \frac{dG(r)}{dr} - G(r) \frac{dF(r)}{dr}, \\ &= F(r)G'(r) - G(r)F'(r); \text{ evaluated at } r=r_i. \end{aligned}$$

We now take the limit $\epsilon \rightarrow 0$ to obtain the end result:

$$\sum_{l,m'} \left\{ A_{lm;l'm'} \left[j_l(\kappa r'), R_l(r') \right]_{r'=r_i} + \kappa \delta_{ll'} \delta_{mm'} \left[n_l(\kappa r'), R_l(r') \right]_{r'=r_i} \right\} C_{lm'} = 0 \quad \dots 32)$$

whose nontrivial solution provides the nontrivial solution to eq. 13). Next, we must equate the determinant of the coefficients $C_{lm'}$ and recall that the nontrivial solution can be obtained by the zero of it.

Before seeking the zero of the determinant we divide each linear equation of 32) by $\left[j_l(\kappa r'), R_l(r') \right]_{r'=r_i}$, yielding

$$\sum_{l,m'} \left\{ A_{lm;l'm'} + \kappa \delta_{ll'} \delta_{mm'} \frac{\left[n_l(\kappa r'), R_l(r') \right]_{r'=r_i}}{\left[j_l(\kappa r'), R_l(r') \right]_{r'=r_i}} \right\} C_{lm'} = 0.$$

... 33)

The term

$$\begin{aligned} \frac{\left[n_l(\kappa r'), R_l(r') \right]_{r'=r_i}}{\left[j_l(\kappa r'), R_l(r') \right]_{r'=r_i}} &= \frac{n_l(\kappa r') R_l'(r') - R_l(r') n_l'(\kappa r')}{j_l(\kappa r') R_l'(r') - R_l(r') j_l'(\kappa r')} \Bigg|_{r'=r_i}, \\ &= \frac{n_l' L_l' - n_l'}{j_l' L_l' - j_l'} \Bigg|_{r=r_i} \end{aligned}$$

where we have divided both of the denominator and the numerator by $R_l(r_i)$. L_l' is defined by

$$L_{l'} = [R_{l'}(r')]^{-1} \cdot \frac{dR_{l'}(r')}{dr'}$$

Hence eq. 33) yields

$$\sum_{l', m'} \left\{ A_{lm; l'm'} + \kappa \delta_{ll'} \delta_{mm'} \frac{n_{l'}' - n_{l'} L_{l'}}{j_{l'}' - j_{l'} L_{l'}} \right\}_{r'=r_i} C_{l'm'} = 0 \quad \dots 34)$$

which have nontrivial solutions only if

$$\det \left| A_{lm; l'm'} + \kappa \delta_{ll'} \delta_{mm'} \frac{n_{l'}' - n_{l'} L_{l'}}{j_{l'}' - j_{l'} L_{l'}} \right|_{r'=r_i} = 0. \quad \dots 35)$$

This is the so-called "KKR secular equation" which is the main purpose of our derivation. We note that the determinant to be solved, eq. 35), depends only on the logarithmic derivative of the radial function at r_i , i.e. $L_{l'}$, and the coefficients $A_{lm; l'm'}$. The terms $L_{l'}$ are obtained by numerical integration of the radial equation 19) or directly from atomic spectra. Hence, if $A_{lm; l'm'}$ were calculated for a sequence of values of E for a certain k or vice versa, one could interpolate the roots of the determinant.

Another form of the secular equation 35) may be given in terms of the scattering phase shifts of the muffin-tin potential. We shall obtain this form by introducing two parameters namely A_1 and the phase shifts η_1 such that

$$R_1(r_i) = A_1 \left[j_1(\kappa r_i) - \tan \eta_1 n_1(\kappa r_i) \right], \quad \dots 36)$$

$$R_1'(r_i) = \frac{dR_1(r)}{dr} \Big|_{r=r_i} = A_1 \left[j_1'(\kappa r_i) - \tan \eta_1 n_1'(\kappa r_i) \right] \quad \dots 37)$$

where $j_1'(\kappa r) = \frac{d}{dr} j_1(\kappa r)$ and $n_1'(\kappa r) = \frac{d}{dr} n_1(\kappa r)$. Using the Wronskian relation of the spherical Bessel and Neumann functions together with eqs. 36) and 37), we get

$$\begin{aligned}
 [R_1(r), j_1(\kappa r)]_{r=r_i} &= \{R_1 j_1' - j_1 R_1'\}_{r=r_i} \\
 &= \left\{ A_1 [j_1 - \tan \eta_1 n_1] j_1' - j_1 A_1 [j_1' - \tan \eta_1 n_1'] \right\}_{r=r_i}, \\
 &= [A_1 \tan \eta_1] [j_1 n_1' - n_1 j_1']_{r=r_i}, \\
 &= A_1 \tan \eta_1 \frac{1}{\kappa r_i^2} \dots 38)
 \end{aligned}$$

and, similarly,

$$[R_1(r), n_1(\kappa r)]_{r=r_i} = A_1 / \kappa r_i^2. \dots 39)$$

Deviding eq. 39) by eq. 38), we obtain

$$\frac{[R_1(r), n_1(\kappa r)]_{r=r_i}}{[R_1(r), j_1(\kappa r)]_{r=r_i}} = \cot \eta_1,$$

$$\text{or } \left. \frac{n_1' - n_1 L_1}{j_1' - j_1 L_1} \right|_{r=r_i} = \cot \eta_1. \dots 40)$$

The substitution of eq. 40) into eq. 35) gives

$$\det \left| A_{1m; 1m'} + \kappa \delta_{11'} \delta_{mm'} \cot \eta_1 \right| = 0. \dots 41)$$

This formula is equivalent to eq. 35) and is often used as the starting point of various approximate schemes for the calculations of transition metal band structures. The advantage of this formula is that all the properties of the ions are expressed through the phase shifts η_1 .

In addition to obtaining the explicit expression of $A_{lm;l'm'}$ we need the expansion of the exponential factors occurring in $G(\underline{r}, \underline{r}')$ in terms of spherical harmonics. With the aid of eq. 23), eq. 11) becomes

$$G(\underline{r}, \underline{r}') = -\frac{1}{\tau} \sum_n \left[4\pi \sum_{l,m} i^l j_l(|\underline{K}_n + \underline{k}|r) Y_{lm}(\hat{r}) Y_{lm}^*(\widehat{K_n + k}) \right] \cdot \frac{1}{(\underline{K}_n + \underline{k})^2 - E}$$

$$\cdot \left[4\pi \sum_{l',m'} (-i)^{l'} j_{l'}(|\underline{K}_n + \underline{k}|r') Y_{l'm'}^*(\hat{r}') Y_{l'm'}(\widehat{K_n + k}) \right],$$

$$G(\underline{r}, \underline{r}') = -\frac{(4\pi)^2}{\tau} \sum_n \sum_{l,m} \sum_{l',m'} i^{l-l'} \frac{j_l(|\underline{K}_n + \underline{k}|r) j_{l'}(|\underline{K}_n + \underline{k}|r')}{(\underline{K}_n + \underline{k})^2 - E}$$

$$\cdot Y_{lm}^*(\widehat{K_n + k}) Y_{l'm'}(\widehat{K_n + k}) Y_{lm}(\hat{r}) Y_{l'm'}^*(\hat{r}'). \quad \dots 42)$$

Comparing eq. 42) to eq. 29), we obtain

$$A_{lm;l'm'} = -\frac{(4\pi)^2}{\tau} i^{l-l'} \sum_n \left[j_l(\kappa r) j_{l'}(\kappa r') \right]^{-1} \frac{j_l(|\underline{K}_n + \underline{k}|r) j_{l'}(|\underline{K}_n + \underline{k}|r')}{(\underline{K}_n + \underline{k})^2 - E}$$

$$\cdot Y_{lm}^*(\widehat{K_n + k}) Y_{l'm'}(\widehat{K_n + k}) - \kappa \delta_{ll'} \delta_{mm'} \frac{n_l(\kappa r')}{j_{l'}(\kappa r')} ; \quad r < r' < r_i .$$

$$\dots 43)$$

It is obvious that $A_{lm;l'm'}$ are independent of the particular choice of r and r' , and in view of the asymptotic behaviour, the sum in eq. 43) is absolutely convergent. Apart from the Hermitian relationship, i.e. eq. 30), $A_{lm;l'm'}$ are not all independent but are derivable from a smaller number of independent constants. We note that $A_{lm;l'm'}$ are characteristic for the lattice under consideration and they are also functions of \underline{k} and E . Because they are dependent on the lattice structure but not on the lattice constant, they are called the "structure constants."

These original formulae have been modified and extended by Ham and Segall¹⁷ to make them suitable for practical use. $A_{lm;l'm'}$ may be found in terms of another set of constants which has been worked out and tabulated for body-centered-cubic and face-centered-cubic lattices at various \underline{k} along the three principal symmetry axes $[100]$, $[110]$, and $[111]$ in the Brillouin zone. These constants at more general points in k -space can be worked out with the ready-made formulae^{17a}. With these constants at hand one can easily locate the zero of the determinant in eq. 35) or eq. 41). Thus the band structure is solved.

¹⁷ F.S. Ham and B. Segall, "Energy Bands in Periodic Lattices - Green's Function Method," Physical Review B, 124, 1786-1796(1961).

^{17a} B. Segall and S. Ham, "Tables of Structure Constants for Energy Band Calculations with the Green's Function Method." Unpublished tables for the bcc and fcc lattices.

To summarize, to solve the one electron approximation Schrödinger equation 2) an appropriate Green's function is introduced to convert the differential equation 2) into the integral equation 13). The lattice potential is assumed to be of the "muffin-tin" form. It is constructed by superposing suitably chosen atomic potentials centered at each lattice site; the potential at a point \underline{r} being the sum of the various overlapping contributions originating from different sites. A sphere is inscribed in the unit cell. The potential is taken to have the value computed inside the sphere but is replaced by an average constant value, which is taken to be zero for simplicity, in the region between the sphere and the boundary of the unit cell. By expanding the wave function and the Green's function in real space representation, i.e. in terms of spherical harmonics, and using either the variational or the nonvariational procedure given by Kohn and Rostoker, this method yields a set of linear homogeneous equations, given in eq. 34). Eq. 34) yields nontrivial solutions only if condition 35) holds. To carry out the band structure for each \underline{k} one has to solve the KKR secular equation, eq. 35), instead of eq. 2). The method leads one to determine the band structure of the lattice through the geometrical structure constants, $A_{lm}; I'_{lm}$, and the logarithmic derivatives of the s, p, d, ... functions corresponding to the muffin-tin potential at the inscribed radius r_i . This method may appear to be unfamiliar as only a set of algebraic equations has emerged in place of the usual differential equation.

2. KKR-equations in a plane wave representation

The KKR formulae presented in the previous section are based upon a Schrödinger representation by using an integral equation with a Green's function as a kernel. It has been shown by the work of Beeby and Edwards¹⁸ and of Beeby¹⁹ that the KKR method is not just a manipulative trick but that it is a representation of a deeper mathematical property of the lattice. Beeby¹⁹ has derived the KKR equations from a study of a Green's function concerning with the properties of disordered systems. After this work, the KKR method for the calculation of electronic band structures has been investigated by Ziman²⁰. The general T-matrix theory of Beeby and Edwards is used in order to transform the KKR formulae into a "plane wave or reciprocal lattice representation" which is equivalent to a "nearly free electron" formalism. The argument of the theory is as follows.

The starting point is the well-known expansion for the Green's function

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- ¹⁸ J.L. Beeby and S.F. Edwards, "The Electronic Structure of Liquid Insulators," Proceeding of the Physical Society of London, A274, 395-412(1963).
- ¹⁹ J.L. Beeby, "The Electronic Structure of Disordered Systems," Proceeding of the Physical Society of London, A279, 82-97(1964).
- ²⁰ J.M. Ziman, "The T Matrix, the K Matrix, d Bands and l-dependent Pseudo-potentials in the Theory of Metals," Proceeding of the Physical Society of London, 86, 337-353(1965).



$$\begin{aligned}
 G &= \mathcal{G}_0 + \mathcal{G}_0 V \mathcal{G}_0 + \mathcal{G}_0 V \mathcal{G}_0 V \mathcal{G}_0 + \dots, \\
 &= \mathcal{G}_0 + \mathcal{G}_0 \sum_{\underline{l}} U(\underline{r}-\underline{l}) \mathcal{G}_0 + \mathcal{G}_0 \sum_{\underline{l}} U(\underline{r}-\underline{l}) \mathcal{G}_0 \sum_{\substack{\underline{l}' \\ \underline{l} \neq \underline{l}'}} U(\underline{r}-\underline{l}') \mathcal{G}_0 + \dots, \\
 &= \mathcal{G}_0 + \mathcal{G}_0 \sum_{\underline{l}} t_{\underline{l}} \mathcal{G}_0 + \mathcal{G}_0 \sum_{\underline{l}} t_{\underline{l}} \mathcal{G}_0 \sum_{\substack{\underline{l}' \\ \underline{l} \neq \underline{l}'}} t_{\underline{l}'} \mathcal{G}_0 + \dots, \\
 &= \mathcal{G}_0 + \mathcal{G}_0 \sum_{\underline{l}} t_{\underline{l}} \mathcal{G}_0 + \mathcal{G}_0 \sum_{\substack{\underline{l}, \underline{l}' \\ \underline{l} \neq \underline{l}'}} (t_{\underline{l}} \mathcal{G}_0 t_{\underline{l}'}) \mathcal{G}_0 + \dots \quad \dots \quad 44)
 \end{aligned}$$

\mathcal{G}_0 is the free-space propagator defined by eq. 24). V is the crystal potential of the muffin-tin form:

$$V(\underline{r}) = \sum_{\underline{l}} U(\underline{r}-\underline{l}) = \sum_{\underline{l}} U_{\underline{l}} \quad \dots \quad 45)$$

where \underline{l} is the position vector of the center of the l th ion and U is an atomic potential which is zero outside the inscribed radius r_i . The $t_{\underline{l}}$ -matrix, or $t_{\underline{l}}$ -scattering function, in eq. 44) is a transition matrix associated with the scattering from an atomic potential at the l th site, $U_{\underline{l}}$, and is defined by

$$\begin{aligned}
 t_{\underline{l}} &= U_{\underline{l}} + U_{\underline{l}} \mathcal{G}_0 t_{\underline{l}}, \\
 &= U_{\underline{l}} + U_{\underline{l}} \mathcal{G}_0 (U_{\underline{l}} + U_{\underline{l}} \mathcal{G}_0 t_{\underline{l}}), \\
 &= U_{\underline{l}} + U_{\underline{l}} \mathcal{G}_0 U_{\underline{l}} + U_{\underline{l}} \mathcal{G}_0 U_{\underline{l}} \mathcal{G}_0 U_{\underline{l}} + \dots \quad \dots \quad 46)
 \end{aligned}$$

The potential $U_{\underline{1}}$ defines a corresponding matrix $t_{\underline{1}}$ through the integral equation

$$t_{\underline{1}}(\underline{r}-\underline{r}') = U_{\underline{1}} \delta(\underline{r}-\underline{r}') + \int U_{\underline{1}}(\underline{r}) \mathcal{G}_0(\underline{r}-\underline{r}'') t_{\underline{1}}(\underline{r}''-\underline{r}') dr'' \dots 47)$$

Let us denote the t-function corresponding to G by

$$T = \sum_{\underline{1}} t_{\underline{1}} + \sum_{\substack{\underline{1}, \underline{1}' \\ \underline{1} \neq \underline{1}'}} t_{\underline{1}} \mathcal{G}_0 t_{\underline{1}'} + \sum_{\substack{\underline{1}, \underline{1}', \underline{1}'' \\ \underline{1} \neq \underline{1}' \\ \underline{1}' \neq \underline{1}''}} t_{\underline{1}} \mathcal{G}_0 t_{\underline{1}'} \mathcal{G}_0 t_{\underline{1}''} + \dots \dots 48)$$

Then we have, instead of eq. 44)

$$G = \mathcal{G}_0 T \mathcal{G}_0 \dots 49)$$

which is the shorthand for the integral equation

$$G(\underline{r}, \underline{r}') = \iint \mathcal{G}_0(\underline{r}-\underline{r}'') T(\underline{r}'', \underline{r}''') \mathcal{G}_0(\underline{r}''-\underline{r}') dr'' dr''' \dots 50)$$

In the work of Beoby and Edwards, the T-matrix of the whole system is used to derive density of states through the formula

$$\rho(\underline{k}, E) = - \frac{1}{E - k^2} \frac{1}{\pi} \text{Im } T(\underline{k}), \dots 51)$$

where we have introduced the Fourier transform $T(\underline{k})$ given by

$$T(\underline{k}) = \iiint \exp[-i\underline{k} \cdot (\underline{r}-\underline{r}')] T(\underline{r}, \underline{r}') dr dr' \dots 52)$$

Eq. 52) represents a diagonal element of the T-matrix in a momentum representation and $T(\underline{k})$ may be properly called $T(\underline{k}, \underline{k})$. The formula 51) is obtained from the study of disordered systems. However, we do not need all of eq. 51) in the case of an ordered system for we know that $\rho(\underline{k}, E)$ considered as a function of E is of the form

$$\rho(\underline{k}, E) = \delta\{E - E(\underline{k})\} \quad \dots 53)$$

where $E(\underline{k})$ is the dispersion law for energy as a function of \underline{k} . From the well-known rules concerning the interpretation of complex variable operators, it follows that the $E(\underline{k})$ may be found by locating the singularities of $T(\underline{k})$ as a function of energy. Thus the function $E(\underline{k})$ for which we are looking is just the locus of these singularities as we vary \underline{k} .

This is consistent with the properties of the t-matrix for a single center. For positive energies, this matrix is related to the scattering produced by the potential $U_{\underline{1}}$ and it may be defined in another way equivalent to eq. 47) by

$$t = \frac{1}{2i\kappa} (1 - s) \quad \dots 54)$$

where s is the scattering matrix of the center $U_{\underline{1}}$ and the t-matrix is diagonal in an angular momentum representation with diagonal elements

$$t_{\underline{1}} = -\kappa^{-1} \sin \eta_{\underline{1}} \exp(i \eta_{\underline{1}}). \quad \dots 55)$$

Eq. 55) is achieved by substituting for the s-scattering matrix in

eq. 54) with

$$s = \exp(2i \eta_1) . \quad \dots 56)$$

When the energy is negative the s -matrix may still be defined and has singularities at the bound states of the center. These singularities will also be observed in the t -matrix. The only difference when dealing with the states of the crystal as a whole is that we are seeking a whole band of bound states, so we must choose the wave vector \underline{k} before looking for the singularities of $T(\underline{k})$.

The difference between the expansion for G and T in eqs. 44) and 48) is that in the latter we can exclude terms containing immediate repetition of the index of a particular lattice site since the t -matrix has already allowed for all such repetitions. The algebraic relations of the t -matrix provide valuable formal connections among the elementary partial-wave scattering theory, Green's function theory and the general theory of the s -matrix. In practice it is equivalent to solving the scattering problem for a single center only.

We now try to write down $T(\underline{k})$ from eq. 48) by assuming that each of the centers has the same t -matrix. This yields

$$T(\underline{r}, \underline{r}') = \sum_{\underline{l}} t_{\underline{l}}(\underline{r}-\underline{l}, \underline{r}'-\underline{l}) + \sum_{\substack{\underline{l}, \underline{l}' \\ \underline{l} \neq \underline{l}'}} \iint t_{\underline{l}}(\underline{r}-\underline{l}, \underline{r}''-\underline{l}) \mathcal{G}_0(\underline{r}'', \underline{r}''') \cdot t_{\underline{l}'}(\underline{r}''-\underline{l}', \underline{r}'-\underline{l}') d\underline{r}'' d\underline{r}''' + \dots, \quad \dots 57)$$

and using eq. 52) we have, instead of eq. 57)

$$\begin{aligned}
T(\underline{k}) = & \sum_{\underline{l}} \iint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}')] t_{\underline{l}}(\underline{r} - \underline{l}, \underline{r}' - \underline{l}) d\underline{r} d\underline{r}' \\
& + \sum_{\substack{\underline{l}, \underline{l}' \\ \underline{l} \neq \underline{l}'}} \iiint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}'')] t_{\underline{l}}(\underline{r} - \underline{l}, \underline{r}'' - \underline{l}) \mathcal{G}_0(\underline{r}'', \underline{r}''') \\
& \cdot \exp[-i\underline{k} \cdot (\underline{r}'' - \underline{r}''')] \exp[-i\underline{k} \cdot (\underline{r}'' - \underline{r}''')] t_{\underline{l}'}(\underline{r}'' - \underline{l}', \underline{r}' - \underline{l}') d\underline{r} d\underline{r}' d\underline{r}'' d\underline{r}''' + \dots
\end{aligned} \quad \dots 58)$$

Taking into account the translational symmetry of the lattice and defining

$$G'_{\underline{k}}(\underline{r} - \underline{r}') = \sum_{\substack{\underline{l}, \underline{l}' \\ \underline{l} \neq \underline{l}'}} \mathcal{G}_0(\underline{r} + \underline{l} - \underline{r}' - \underline{l}') \exp[-i\underline{k} \cdot (\underline{l} - \underline{l}')], \quad \dots 59)$$

eq. 58) becomes

$$\begin{aligned}
T(\underline{k}) = & \sum_{\underline{l}} \iint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}')] t(\underline{r}, \underline{r}') d\underline{r} d\underline{r}' + \iiint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}'')] t(\underline{r}, \underline{r}'') \sum_{\substack{\underline{l}, \underline{l}' \\ \underline{l} \neq \underline{l}'}} \\
& \cdot \mathcal{G}_0(\underline{r} + \underline{l}, \underline{r}'' + \underline{l}') \exp[-i\underline{k} \cdot (\underline{l} - \underline{l}')] t(\underline{r}'', \underline{r}') \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}')] \\
& \cdot d\underline{r} d\underline{r}' d\underline{r}'' d\underline{r}''' + \dots, \\
= & N \iint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}')] t(\underline{r}, \underline{r}') d\underline{r} d\underline{r}' + N \iiint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}'')] t(\underline{r}, \underline{r}'') \\
& \cdot G'_{\underline{k}}(\underline{r}'', \underline{r}') t(\underline{r}'', \underline{r}') \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}')] d\underline{r} d\underline{r}' d\underline{r}'' d\underline{r}''' + \dots
\end{aligned} \quad \dots 60)$$

where N is the number of the scatterers or equivalently the number of the ion cores.

The series in eq. 60) is now of the form that may be summed:

$$\begin{aligned}
T(\underline{k}) &= N \iint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}')] \left\{ t + tG'_{\underline{k}}t + tG'_{\underline{k}}tG'_{\underline{k}}t + \dots \right\} d\underline{r} d\underline{r}', \\
&= N \iint \exp[-i\underline{k} \cdot (\underline{r} - \underline{r}')] \left\{ t^{-1} - G'_{\underline{k}} \right\}^{-1} d\underline{r} d\underline{r}', \quad \dots 61)
\end{aligned}$$

provided that the matrices t and $G'_{\underline{k}}$ are well-behaved. Hence we can look for singularities of the matrix $\left\{ t^{-1} - G'_{\underline{k}} \right\}^{-1}$. We should certainly expect such singularities at the zeroes of the determinant of this matrix, and that turns out to be just the KKR condition, eq. 41).

To show this we must study the properties of the t -matrix and of the $G'_{\underline{k}}$ matrix. According to Beeby¹⁹, t -matrix has the following momentum representation,

$$t(\underline{k}, \underline{k}') = \sum_L t_1(\underline{k}, \underline{k}') Y_L(\hat{k}) Y_L^*(\hat{k}'), \quad \dots 62)$$

where l is angular momentum and L stands for l, m . The coefficients t_1 defined by eq. 55) are just the values of $t_1(\kappa, \kappa')$, since they measure the transition amplitudes between two states having different directions of propagation but the same energy κ^2 .

To study the matrix $G'_{\underline{k}}$, we recall the free space propagator representation given by eq. 24), i.e.

$$G_0(\underline{r} - \underline{r}') = - \frac{1}{4\pi} \frac{\exp(i\kappa|\underline{r} - \underline{r}'|)}{|\underline{r} - \underline{r}'|} \quad \dots 63)$$

and make use of the Green's function in the following representation (cf. appendix A for detailed derivation)

$$G(\underline{r}-\underline{r}') \text{ or } G(\underline{R}) = -\frac{1}{4\pi} \sum_{\underline{l}} \frac{\exp(i\kappa|\underline{R}-\underline{l}|)}{|\underline{R}-\underline{l}|} \exp(i\kappa \cdot \underline{l}) \quad \dots \quad 64)$$

which was called the "Greenian of the system" by Phariseau and Ziman²¹. Because G is a function of \underline{k} and κ we can not use eqs. 52) and 61) to identify T with $\{t^{-1} - G'_{\underline{k}}\}^{-1}$. Without defining a special matrix $G'_{\underline{k}}$ for each value of \underline{k} we could not have decomposed the integrals in eq. 57) and summed the geometric series in eq. 61). We note also that $G'_{\underline{k}}$ excludes the term $\underline{l}=\underline{l}'$ in eq. 59) which would be the contribution from the origin in eq. 64).

The matrix $G'_{\underline{k}}$ also has a simple representation in reciprocal space. It is a function only of $\underline{r}-\underline{r}'$ or \underline{R} and is therefore diagonal in wave vector indices. As can be seen from eqs. 59) and 63) it only contains the wave number κ . As shown by Beeby¹⁹ it can be represented in spherical harmonics

$$G'_{\underline{k}}(\underline{k}', \underline{k}'') = \delta_{\underline{k}'\underline{\kappa}} \delta_{\underline{k}''\underline{\kappa}} \sum_{L, L'} G'_{LL'} Y_L(\hat{\kappa}) Y_{L'}^*(\hat{\kappa}) \quad \dots \quad 65)$$

where L and L' stand for l, m , and l', m' respectively, $\underline{\kappa}$ is a vector of modulus κ and the argument $\hat{\kappa}$ denotes the directional angles of $\underline{\kappa}$. To find the coefficients $G'_{LL'}$ of this expansion we recall the definition of eq. 25) and noting that

²¹ P. Phariseau and J.M. Ziman, "The Theory of the Electronic Structure of Liquid Metals," Philosophical Magazine, 8, 1487-1501(1963).

$$\begin{aligned}
 \underline{G}'_{\underline{k}}(\underline{R}) &= \left\{ G(\underline{R}) - G_0(\underline{R}) \right\} \\
 &= G(\underline{R}) - \frac{1}{4\pi} \frac{\exp(i\kappa R)}{R} \quad \dots 66)
 \end{aligned}$$

we have

$$\begin{aligned}
 \underline{G}'_{\underline{k}}(\underline{R}) - D(\underline{R}) &= \left\{ G(\underline{R}) - \frac{1}{4\pi} \frac{\exp(i\kappa R)}{R} \right\} - \left\{ G(\underline{R}) - G_0(\underline{R}) \right\}, \\
 &= -\frac{1}{4\pi} \frac{\exp(i\kappa R)}{R} + \frac{1}{4\pi} \frac{\cos(\kappa R)}{R},
 \end{aligned}$$

$$\underline{G}'_{\underline{k}}(\underline{R}) = D(\underline{R}) + \frac{i}{4\pi} \frac{\sin(\kappa R)}{R} \quad \dots 67)$$

Using eq. 24), the expansion of the second term on the right of eq. 67) for $r < r'$ in spherical harmonics is

$$i\kappa \sum_L j_1(\kappa r) j_1(\kappa r') Y_L(\hat{r}) Y_L^*(\hat{r}') \quad \dots 68)$$

According to this expansion, eq. 67) and eq. 28), $\underline{G}'_{\underline{k}}(\underline{R})$ must have an expansion in terms of spherical harmonics

$$\underline{G}'_{\underline{k}}(\underline{R}) = \sum_{L, L'} G'_{LL'} j_1(\kappa r) j_1(\kappa r') Y_L(\hat{r}) Y_L^*(\hat{r}') \quad \dots 69)$$

Hence eq. 67) yields

$$G'_{LL'} = A_{LL'} + i\kappa \delta_{LL'} \quad \dots 70)$$

We now use eqs. 62) and 65) to transform the matrices of eq. 60) into an angular momentum representation,

$$\begin{aligned}
T(\underline{k}) &= N \iint \exp\{-i\underline{k}\cdot(\underline{r}-\underline{r}')\} t(\underline{r},\underline{r}') d\underline{r} d\underline{r}' \\
&+ N \iiint \iiint t(\underline{r},\underline{r}'') G'_{\underline{k}}(\underline{r},\underline{r}'') t(\underline{r}'',\underline{r}') \exp\{-i\underline{k}\cdot(\underline{r}-\underline{r}')\} d\underline{r} d\underline{r}' d\underline{r}'' d\underline{r}''' + \dots, \\
&= N t(\underline{k},\underline{k}) + N \iint t(\underline{k},\underline{k}') G'_{\underline{k}}(\underline{k},\underline{k}') t(\underline{k}',\underline{k}) d\underline{k}' d\underline{k}'' + \dots, \\
&= N \sum_{\underline{L}} t_1(\underline{k},\underline{k}) Y_{\underline{L}}(\underline{k}) Y_{\underline{L}}^*(\underline{k}) + N \sum_{\underline{L}} \sum_{\underline{L}'} t_1(\underline{k},\underline{k}') G'_{\underline{L}\underline{L}'}(\underline{k},\underline{k}') Y_{\underline{L}}(\underline{k}) Y_{\underline{L}'}^*(\underline{k}) \\
&\quad \cdot t_1'(\underline{k}',\underline{k}) + \dots, \\
&= N \sum_{\underline{L},\underline{L}'} Y_{\underline{L}}(\underline{k}) Y_{\underline{L}'}^*(\underline{k}) \left[t_1(\underline{k},\underline{k}) \delta_{\underline{L}\underline{L}'} + t_1(\underline{k},\underline{k}') G'_{\underline{L}\underline{L}'}(\underline{k},\underline{k}') t_1'(\underline{k}',\underline{k}) \right. \\
&\quad \left. + t_1(\underline{k},\underline{k}') \left\{ \sum_{\underline{L}''} G'_{\underline{L}\underline{L}''}(\underline{k},\underline{k}') t_1''(\underline{k}',\underline{k}') G'_{\underline{L}''\underline{L}'}(\underline{k}',\underline{k}') \right\} t_1'(\underline{k}',\underline{k}) + \dots \right], \\
&= N \sum_{\underline{L},\underline{L}'} Y_{\underline{L}}(\underline{k}) Y_{\underline{L}'}^*(\underline{k}) \left[t_1(\underline{k},\underline{k}) \delta_{\underline{L}\underline{L}'} + t_1(\underline{k},\underline{k}') \left\{ G' + G' t G' + \dots \right\} t_1'(\underline{k}',\underline{k}) \right], \\
&= N \sum_{\underline{L},\underline{L}'} Y_{\underline{L}}(\underline{k}) Y_{\underline{L}'}^*(\underline{k}) \left[t_1(\underline{k},\underline{k}) \delta_{\underline{L}\underline{L}'} + t_1(\underline{k},\underline{k}') \left\{ G'(1-tG')^{-1} \right\}_{\underline{L}\underline{L}'} t_1'(\underline{k}',\underline{k}) \right] \\
&\quad \dots 71)
\end{aligned}$$

where we have summed over all intermediate terms in the geometric series, just as in eq. 61).

Every term along the diagonal of the matrix $\left[G' \{ 1 - tG' \}^{-1} \right]_{\underline{L}\underline{L}'}$ will have the determinant of the matrix $\left[1 - tG' \right]_{\underline{L}\underline{L}'}$ in its denominator. Thus, zeroes of this determinant should give us the singularities of $T(\underline{k})$. To make comparison with eq. 41) we divide through the

determinant by the matrix t_1 which is diagonal and whose determinant will not vanish unless we include spherical harmonics with zero phase-shift in our expansion. The criterion for bound state will read

$$\det \left| G'_{LL'} - t_1^{-1} \delta_{LL'} \right| = 0. \quad \dots 72)$$

This is equivalent to the theory originally derived by Korringa ¹⁶. To make this agree with the Kohn-Rostoker formula, i.e. eq. 41), we note from eq. 55) that

$$t_1^{-1} = -\kappa \cot \eta_1 + i\kappa. \quad \dots 73)$$

The imaginary part $i\kappa$ cancels with the imaginary part occurring in eq. 70) leaving the matrix $A_{LL'}$. In this way we have obtained the KKR theory from a summation of the perturbation series for the T matrix of the whole system.

The angular momentum representation of eq. 71) is not the only possible explicit formula for the location of the singularities of the matrix $(t^{-1} - G')^{-1}$ which we found in eq. 61). Here we are seeking a representation in terms of plane waves $\exp\{i(\underline{K}_n + \underline{k}) \cdot \underline{r}\}$ as in the pseudopotential formalism, i.e.

$$\det \left| \{(\underline{K}_n + \underline{k})^2 - E\} \delta_{nn'} + \Gamma_{nn'} \right| = 0. \quad \dots 74)$$

We note from eq. 11) that the complete Greenian $G(\underline{R})$ is diagonal in the plane wave representation with matrix elements

$$G_{nn'} = -\frac{1}{\tau} \frac{1}{(\underline{K}_n + \underline{k})^2 - E} \delta_{nn'} \quad \dots 75)$$

where \mathcal{V} denotes the volume of the atomic polyhedron. The diagonal matrix elements of eq. 74) may be generated by inverting the matrix G :

$$(\underline{K}_n + \underline{k})^2 - E = -\mathcal{V}^{-1} [G^{-1}]_{nn}. \quad \dots 76)$$

To put this into an expression for $T(\underline{k})$, we note from eq. 59) that the complete Greenian $G(\underline{R})$ differs from the incomplete Greenian $G'(\underline{R})$ by an amount

$$\begin{aligned} G - G' &= \mathcal{G}_0(\underline{R}), \\ &= -\frac{1}{4\pi} \frac{\exp(i\kappa R)}{R} \quad \dots 77) \end{aligned}$$

which, in fact, is the free space propagator. Hence we have

$$\begin{aligned} t^{-1} - G' &= t^{-1} - G + \mathcal{G}_0, \\ &= (t^{-1} + \mathcal{G}_0) - G, \\ &= [1 - G \{t^{-1} + \mathcal{G}_0\}^{-1}] (t^{-1} + \mathcal{G}_0), \\ &= \mathcal{V}G \{ \mathcal{V}^{-1}G^{-1} - \mathcal{V}^{-1}(t^{-1} + \mathcal{G}_0)^{-1} \} (t^{-1} + \mathcal{G}_0). \quad \dots 78) \end{aligned}$$

Now singularities of $T(\underline{k})$ should arise from zero of the determinant of the matrix

$$\{ \mathcal{V}^{-1}G^{-1} - \mathcal{V}^{-1}(t^{-1} + \mathcal{G}_0)^{-1} \} = \mathcal{V}^{-1}G^{-1} - \Gamma \quad \dots 79)$$

where we define

$$\Gamma \equiv \mathcal{V}^{-1}(t^{-1} + \mathcal{G}_0)^{-1}. \quad \dots 80)$$

That is, the effective potential in eq. 74) should be defined in terms of the t matrix as the plane wave representation of the matrix Γ .

To make the formula of Γ more explicit we need the plane wave representation of t^{-1} and \mathcal{G}_0 . Using eq. 24) we note that \mathcal{G}_0 is diagonal in the angular momentum representation, and for $r < r'$ we have

$$[\mathcal{G}_0]_{LL'} = \kappa \left[\frac{n_1(\kappa r')}{j_1(\kappa r)} - i \right] \delta_{LL'}. \quad \dots 81)$$

We also note that t^{-1} is diagonal in the same representation. If we define a modified phase shift η'_1 by the relation

$$\cot \eta'_1 = \cot \eta_1 - \frac{n_1(\kappa r')}{j_1(\kappa r)} \quad \dots 82)$$

then Γ is diagonal in the angular momentum representation with matrix elements

$$\Gamma_{LL} = \Gamma_1(\kappa, \kappa) = -\kappa^{-1} \mathcal{E}^{-1} \tan \eta'_1. \quad \dots 83)$$

This is easily found by the substitution of eqs. 73) and 81) into eq. 80).

However, the plane wave representation of Γ cannot be defined from this result alone. The formal transformations are as follows:

$$\Gamma_1(\kappa, \kappa) = \iint \Gamma_1(r, r') j_1(\kappa r) j_1(\kappa r') r^2 dr r'^2 dr', \quad \dots 84)$$

$$\Gamma_1(r, r') \delta_{LL'} = \iint \Gamma(\underline{r}, \underline{r}') Y_L(\hat{r}) Y_L^*(\hat{r}') d\Omega d\Omega', \quad \dots 85)$$

$$\Gamma(\underline{k}, \underline{k}') = \iint \Gamma(\underline{r}, \underline{r}') \exp(-i\underline{k} \cdot \underline{r}) \exp(i\underline{k}' \cdot \underline{r}') d\underline{r} d\underline{r}' \quad \dots 86)$$

where $d\Omega$ and $d\Omega'$ denote the solid angles of \underline{r} and \underline{r}' respectively. It is well-known that the t matrix is of physical significance only if it is well-defined on the "energy shell". Hence, we cannot invert eq. 82) unless we know the behaviour of Γ off the energy shell.

Since we are working at only one energy κ^2 , we can make an arbitrary assumption about the matrix $\Gamma_1(\underline{r}, \underline{r}')$ consistent with eq. 84). Suppose we write

$$\Gamma_1(\underline{r}, \underline{r}') = A \delta(\underline{r} - \underline{r}_i) \delta(\underline{r}' - \underline{r}_i) \quad \dots 87)$$

where A is a constant and r_i is the inscribed radius. Eq. 86) gives

$$\begin{aligned} \Gamma(\underline{k}, \underline{k}') &= (4\pi)^2 \iiint \Gamma(\underline{r}, \underline{r}') \sum_L (-i)^L j_L(\kappa r) Y_L^*(\hat{r}) Y_L(\hat{k}) \\ &\quad \cdot \sum_{L'} i^{L'} j_{L'}(\kappa r') Y_{L'}(\hat{r}') Y_{L'}^*(\hat{k}') r^2 dr r'^2 dr' d\Omega d\Omega', \\ &= (4\pi)^2 \left\{ \iint \sum_{L, L'} \Gamma(\underline{r}, \underline{r}') Y_L^*(\hat{r}) Y_{L'}(\hat{r}') d\Omega d\Omega' \right\} \\ &\quad \cdot i^{L'-L} j_L(\kappa r) j_{L'}(\kappa r') r^2 dr r'^2 dr' \cdot Y_L(\hat{k}) Y_{L'}^*(\hat{k}'). \end{aligned}$$

With the aid of eq. 85), this becomes

$$\begin{aligned} \Gamma(\underline{k}, \underline{k}') &= (4\pi)^2 \iint \sum_{L, L'} \Gamma_1(\underline{r}, \underline{r}') \delta_{LL'} i^{L'-L} j_L(\kappa r) j_{L'}(\kappa r') r^2 dr r'^2 dr' \\ &\quad \cdot Y_L(\hat{k}) Y_{L'}^*(\hat{k}') \quad \dots 88) \end{aligned}$$

and substitution of eq. 87) into eq. 84) gives

$$\Gamma_1(\underline{k}, \underline{k}') = \iint A \delta(\underline{r} - \underline{r}_i) \delta(\underline{r}' - \underline{r}_i) j_L(\kappa r) j_{L'}(\kappa r') r^2 dr r'^2 dr',$$

$$\begin{aligned} \bar{V}_1(\kappa, \kappa) &= A j_1(\kappa r_i) j_1(\kappa r_i) r_i^4, \\ A &= \frac{\bar{V}_1(\kappa, \kappa)}{r_i^4 j_1^2(\kappa r_i)}. \end{aligned} \quad \dots 89)$$

Substituting eq. 89) into eq. 87) and eq. 87) into eq. 88) one gets, with an application of the addition theorem,

$$\begin{aligned} \bar{V}(\underline{k}, \underline{k}') &= (4\pi)^2 \sum_L \left(\int \frac{\bar{V}_1(\kappa, \kappa)}{r_i^4 j_1^2(\kappa r_i)} \delta(r-r_i) \delta(r'-r_i) j_1(\kappa r) j_1(\kappa r') \right. \\ &\quad \left. \cdot r^2 dr r'^2 dr' Y_L(\hat{k}) Y_L^*(\hat{k}'), \right. \\ &= (4\pi)^2 \sum_L \bar{V}_1(\kappa, \kappa) Y_L(\hat{k}) Y_L^*(\hat{k}') \frac{j_1(\kappa r_i) j_1(\kappa r_i)}{j_1^2(\kappa r_i)}, \\ &= (4\pi)^2 \sum_L \frac{(2L+1)}{4\pi} \bar{V}_1(\kappa, \kappa) P_L(\cos \theta_{\underline{k}\underline{k}'}) \frac{j_1(\kappa r_i) j_1(\kappa r_i)}{j_1^2(\kappa r_i)} \dots 90) \end{aligned}$$

Here $\theta_{\underline{k}\underline{k}'}$ denotes the angle between \underline{k} and \underline{k}' and P_L is the Legendre function. Putting eq. 83) into eq. 90), we obtain

$$\begin{aligned} \bar{V}(\underline{K}_n + \underline{k}, \underline{K}_n + \underline{k}') &= - \frac{4\pi'}{\kappa \mathcal{C}} \sum_L (2L+1) \tan \gamma_L' \frac{j_1(|\underline{K}_n + \underline{k}| r_i) j_1(|\underline{K}_n + \underline{k}'| r_i)}{j_1^2(\kappa r_i)} \\ &\quad \cdot P_L(\cos \theta_{nn'}) \dots 91) \end{aligned}$$

where $\theta_{nn'}$ denotes the angle between $\underline{K}_n + \underline{k}$ and $\underline{K}_n + \underline{k}'$. Eq. 91)

represents the pseudopotential matrix elements in the plane wave representation. Now we have completed the transformation of the KKR equation 41) into the pseudopotential formalism, eq. 74).

Equation 74) with \bar{V} given by eq. 91) is known as Korringa-Kohn-Rostoker-Ziman (KKR-Z) equation or Ziman's plane wave representation

of the KKR equation.

In other words, the KKR-Z secular equation is really the reciprocal space representation of the KKR secular equation. The only difference is that instead of expanding the wave functions of electrons in terms of spherical harmonics, we expand the wave functions in terms of pseudowavefunctions in the plane wave representation for all wave vectors $\underline{k}_n + \underline{k}$. That is ,

$$\Psi = \frac{1}{C^{1/2}} \sum_n B_n \exp(i\underline{k}_n \cdot \underline{r}). \quad \dots 92)$$

Here $\underline{k}_n = \underline{K}_n + \underline{k}$; \underline{K}_n being vectors of the reciprocal lattice, and B_n are the coefficients of expansion which are to be determined. The KKR-Z formulae are similar in structure to those of the nearly-free-electron (NFE) method except that we have replaced the Fourier components of the muffin-tin atomic potential by a more complicated expression of $\bar{V}(\underline{k}_n, \underline{k}_n)$, i.e. eq.91). Equivalently, $\bar{V}(\underline{k}_n, \underline{k}_n)$ are the Fourier components of an effective atomic potential. However this method is still exact.