

My multiple scattering theory primer

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Paul Durham

Scientific Computing Department, STFC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

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Abstract

This document contains the notes on multiple scattering theory on which my real space package of codes is based. These notes are intended to be a full and detailed set of formulae which I need never derive again! They are based as closely as possible on the review article of Lloyd and Smith [1], Pendry's book [4] and Brink and Satchler [9] on angular momentum, all of which seem reliable references. Gonis and Butler [11] must be a good book too, but I haven't yet been through it properly. Errors in other published works on multiple scattering theory are noted whenever I find them. All the key results have been tested in full numerical calculations. At present only non-relativistic scattering by spherical potentials is treated.

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1 Preamble

These notes derive a formula for the 1-electron Green's function of an arbitrary set of "scatterers", essentially atomic potentials, based on the scattering solutions for a single scatterer. The full system may be a periodic crystal but doesn't have to be. Multiple scattering theory, through its central quantity, the scattering path operator, builds up the full wave function or Green's function as a sum to all orders over all the scattered waves from the individual atoms, including correctly all the interferences. For a periodic crystal these interferences produce energy bands, gaps etc. For molecules or clusters they produce molecular orbitals.

As always with scattering theory, there is much to be learned from studying the analytical properties of the various wave functions, Green's functions and scattering matrices as a function of a complex energy variable. Indeed, working at complex energies is frequently useful in numerical calculations (see section 12). I don't pay much attention to this aspect in these notes. The references (especially the works of Faulkner) treat it with the importance it deserves.

The essential language of this version of multiple scattering theory is that of the partial wave (angular momentum) analysis of potential scattering, generalised from a single "atomic" potential to a non-overlapping assembly of such scatterers. We nearly always have it in mind that each of these atomic potentials will be of so-called muffin-tin form – spherical within some cut-off radius (the muffin-tin radius) and zero beyond it¹. In this language, atoms are characterised by a set of phase shifts. When these phase shifts are small the scattering is weak and something perturbative like a pseudopotential method is a viable alternative. When the phase shifts are large, perhaps passing through $\pi/2$ as a function of energy (resonant scattering), the (multiple) scattering is strong and a possible alternative approach would be some form of tight binding. Multiple scattering theory elegantly encompasses the whole range of possible potentials and binding strengths within the same, exact, formalism.

These notes are concerned only with this formalism. None of the many possible illuminating examples of it in action are described. Somebody should do this!

¹ There is no shortage of theory on non-spherical atomic potentials that may fill space with no interstitial regions – see Gonis and Butler [11]. Most of this results in single-scatterer t matrices that are not diagonal in angular momentum, which is easily accommodated within the formalism. However, there are probably pathological circumstances (oddly shaped potentials etc) for which the convergence of the multiple scattering series don't necessarily converge. We don't consider such things in these notes.

2 Summary of Key Results

This section summarises the key results of the theory. Details are given on the following sections and appendices.

2.1 Notation

Angular Momentum

When possible we denote the angular momentum quantum numbers by the following double indices:

$$\begin{aligned} L &\equiv (l, m) \\ \bar{L} &\equiv (l, -m) \end{aligned} \tag{2.1}$$

Bessel functions

The forms defined in Schiff are used, but the argument is just written as r , rather than the strictly correct $r\sqrt{\varepsilon}$, just to simplify equations.

Free space solutions

For simplicity we define upper case Bessel functions as follows:

$$J_L(\mathbf{r}) = j_l(r) Y_L(\hat{\mathbf{r}}) \tag{2.2}$$

and likewise for Neumann and Hankel functions. Even though the radial functions may be real, the vector function is complex because of the spherical harmonic. We use the following notation to denote this:

$$\begin{aligned} \bar{J}_L(\mathbf{r}) &= j_l(r) Y_L^*(\hat{\mathbf{r}}) \\ \bar{H}_L^+(\mathbf{r}) &= h_l^+(r) Y_L^*(\hat{\mathbf{r}}) \end{aligned} \tag{2.3}$$

Single scatterer solutions

In a similar way, the following types of single-scatterer solution are used

$$\begin{aligned} Z_L^i(r) &= z_l^i(r) Y_L(\hat{\mathbf{r}}) \\ \bar{Z}_L^i(r) &= z_l^i(r) Y_L^*(\hat{\mathbf{r}}) \end{aligned}$$

2.2 The single scatterer

We want to find the scattering solutions of the Schrödinger equation

$$(\varepsilon^+ - \mathcal{H}_0) \psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) = v(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) \tag{2.4}$$

where \mathcal{H}_0 is the kinetic energy and $v(\mathbf{r})$ the scattering potential, assumed to be spherically symmetrical. The wave functions can obviously be decomposed into radial and angular parts, the latter being spherical harmonics. The solutions can be written in terms of the standard regular radial solution R_l as follows:

$$\psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) = 4\pi \sum_L i^l e^{im_l(k)} R_l(r, k) Y_L(\hat{\mathbf{r}}) Y_L^*(\hat{\mathbf{k}}) \quad (2.5)$$

where the radial solution is regular at $r=0$ and satisfies the boundary condition that outside the muffin-tin radius

$$R_l(r, k) = j_l(kr) \cos \eta_l(k) - n_l(kr) \sin \eta_l(k) \quad (2.6)$$

defining the phase shift η_l . The t matrix of the single scatterer is then given by

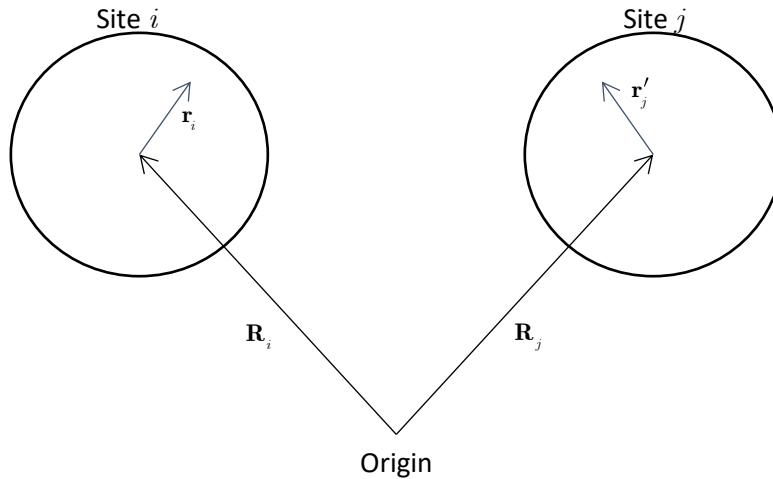
$$t_l(k) = -\frac{1}{k} \sin \eta_l(k) e^{im_l(k)} \quad (2.7)$$

It's useful to introduced two ancillary radial solutions $z_l(r, k)$ and $x_l(r, k)$, the first regular and the second irregular, defined in section 3.1. These are normalised in an especially convenient way for this version of multiple scattering theory.

Any real calculation starts with these quantities – one determines the phase shifts, wave functions and t matrices of each single “atomic” potential by the standard methods of partial wave scattering (matching logarithmic derivatives etc). These, together with the location of each potential, are the essential inputs to any multiple scattering calculation.

2.3 The free space Green's function

Consider two sites or scatterers with the geometric definitions indicated in the following diagram:



The free space Green's function, referred to the above geometry, is

$$G_0(\mathbf{r} + \mathbf{R}_i, \mathbf{r}' + \mathbf{R}_j) = \sum_{L, L'} \bar{J}_L(\mathbf{r}) g_{L, L'}^j J_{L'}(\mathbf{r}') \quad (2.8)$$

where the “real space structure constant” is

$$g_{LL'}^{ij} = -4\pi ik(-1)^m i^{l'-l} \sum_{L_1} i^{-L_1} C(\bar{L}, L', L_1) H_{L_1}^+(\mathbf{R}_{ij}) \quad (2.9)$$

$C(\bar{L}, L', L_1)$ being a Gaunt number (see Appendix A: Notation and Mathematical Preliminaries) and $\kappa = \sqrt{2\varepsilon}$.

2.4 The scattering path operator

The T matrix of a system made up of an arbitrary number of scatterers at sites labelled i, j is given by

$$T = \sum_{i,j} \tau^{ij} \quad (2.10)$$

with

$$\tau^{ij} = \mathbf{t}^i \delta_{ij} + \mathbf{t}^i \mathbf{G}_0 \sum_{k \neq i} \tau^{kj} = \mathbf{t}^i \delta_{ij} + \sum_{k \neq j} \tau^{ik} \mathbf{G}_0 \mathbf{t}^j \quad (2.11)$$

τ^{ij} was called by Gyorffy the scattering path operator - it sums up the contributions to the total T-matrix of scattering paths starting from site j and ending at site i .

On shell elements of τ^{ij} are given by

$$\tau_{LL'}^{ij} = \mathbf{t}_{LL'}^i \delta_{ij} + \sum_{\substack{n \neq i \\ L_1, L_2}} \mathbf{t}_{LL_1}^i g_{L_1 L_2}^{in} \tau_{L_2 L'}^{nj} \quad (2.12)$$

(2.12) is the key equation of multiple scattering theory. Defining matrices (bold-face notation) in site and angular momentum, we can write (2.12) as

$$\boldsymbol{\tau} = \mathbf{t} + \mathbf{t} \mathbf{g} \boldsymbol{\tau} = \left[\mathbf{t}^{-1} - \mathbf{g} \right]^{-1}$$

So here is how to calculate the τ -matrix; set up a matrix $\mathbf{M} \equiv \mathbf{t}^{-1} - \mathbf{g}$ and invert it.

2.5 The multiple scattering Green's function

The tau matrix provides a convenient expression for the real space Green's function

$$G(\mathbf{r}, \mathbf{r}') = \sum_{L, L'} \left(\bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) \tau_{LL'}^{nm} Z_{L'}^m(\mathbf{r}' - \mathbf{R}_m) - \bar{Z}_L^n(\mathbf{r}_<) X_L^n(\mathbf{r}_>) \delta_{LL'} \delta_{nm} \right) \quad (2.13)$$

where $r_>$ ($r_<$) is the greater (smaller) of $|\mathbf{r} - \mathbf{R}_n|$ and $|\mathbf{r}' - \mathbf{R}_n|$ and in which the energy dependence is left implicit.

From this formula for the full Green's function of the system, any one-electron observable can be calculated. The most important examples are the density of states and the Bloch spectral function.

2.6 The Density of states

Define the local density of states by spatially integrating the r -resolved density of states over a specified site i ,

$$\bar{n}^i(\varepsilon) = \int_{\text{site-}i} d\mathbf{r} \bar{\rho}(\mathbf{r}, \varepsilon) = -\frac{1}{\pi} \int_{\text{site-}i} d\mathbf{r} \text{Im} G(\mathbf{r}, \mathbf{r}; \varepsilon) \quad (2.14)$$

Then (2.13) gives, assuming a spherical scatterer/site:

$$\bar{n}^i(\varepsilon) = -\frac{1}{\pi} \text{Im} \sum_L [Q_L^i(E) \tau_{LL}^i(E) - \tilde{Q}_L^i(E)] \quad (2.15)$$

with

$$Q_L^i(E) = \int_{\text{site-}i} drr^2 (Z_L^i(r, E))^2, \quad \tilde{Q}_L^i(E) = \int_{\text{site-}i} drr^2 Z_L^i(r, E) X_L^i(r, E) \quad (2.16)$$

This suggests that an angular momentum-resolved local density of states be defined:

$$\bar{n}^i(\varepsilon) = \sum_L \bar{n}_L^i(\varepsilon) \quad (2.17)$$

where

$$\bar{n}_L^i(\varepsilon) = -\frac{1}{\pi} \text{Im} [Q_L^i(E) \tau_{LL}^i(E) - \tilde{Q}_L^i(E)] \quad (2.18)$$

All this holds for complex energies $E = \varepsilon + i\gamma$. Standard results for the densities of states are recovered for $\gamma = 0$. For $\gamma > 0$ the densities of states are “smoothed”.

2.7 The Bloch spectral function

Multiple scattering theory gives a convenient way of finding the band structure of a periodic crystal – the eigenvalue spectrum as a function of the crystal momentum \mathbf{k} - by finding the zeros of the KKR determinant. It also provides a quantity that conveniently represents the band structure but is somewhat more general in that it can be calculated for complex energies and used for disordered systems. This is the Bloch spectral function, defined by

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \text{Im} \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \int_{\text{cell } 0} d\mathbf{r}_0 G(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{R}_n; \varepsilon) \quad (2.19)$$

The multiple scattering formula for this quantity is found, using (2.13), to be

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \sum_{LL'} a_{LL'}(\varepsilon) \text{Im} \tau_{LL'}(\mathbf{k}, \varepsilon) \quad (2.20)$$

where

$$a_{LL'}(\varepsilon) = \int_{\text{cell } 0} d\mathbf{r}_0 \bar{Z}_L(\mathbf{r}_0, \varepsilon) Z_{L'}(\mathbf{r}_0, \varepsilon) \quad (2.21)$$

3 The Single Scatterer

In this section the problem of a single muffin-tin-type potential is considered. Various solutions, regular and irregular, of the Schrödinger equation are defined, and then the Green's function is obtained. This result is required in deriving the multiple scattering Green's function.

3.1 Radial Solutions for the Single Scatterer

The scattering solutions of the Schrödinger equation

$$(\varepsilon^+ - H_0)\psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) = v(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) \quad (3.1)$$

where H_0 is the kinetic energy, $\varepsilon^+ = \varepsilon + i0^+$ and $v(\mathbf{r})$ the scattering potential, are given formally by the Lipmann-Schwinger equation

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) &= \phi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) + \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}'; \varepsilon^+) v(\mathbf{r}') \psi_{\mathbf{k}}(\mathbf{r}', \varepsilon^+) \\ &= \phi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) + \int d\mathbf{r}' \psi_{\mathbf{k}}(\mathbf{r}', \varepsilon^+) v(\mathbf{r}') G_0(\mathbf{r}, \mathbf{r}'; \varepsilon^+) \end{aligned} \quad (3.2)$$

in which $\phi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) = e^{i\mathbf{k}\cdot\mathbf{r}}$, $|\mathbf{k}| = \sqrt{\varepsilon}$.

We can also write a formal solution in terms of the t-matrix:

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) &= \phi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) + \int d\mathbf{r}' \int d\mathbf{r}'' G_0(\mathbf{r}, \mathbf{r}'; \varepsilon^+) t(\mathbf{r}', \mathbf{r}'') \phi_{\mathbf{k}}(\mathbf{r}'', \varepsilon^+) \\ &= \phi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) + \int d\mathbf{r}' \int d\mathbf{r}'' \phi_{\mathbf{k}}(\mathbf{r}', \varepsilon^+) t(\mathbf{r}', \mathbf{r}'') G_0(\mathbf{r}, \mathbf{r}'') \end{aligned} \quad (3.3)$$

Given a spherically symmetrical potential, ie $v(\mathbf{r}) = v(r)$, the wave functions can obviously be decomposed into radial and angular parts, the latter being spherical harmonics. The solution (3.2) can be written in terms of the standard regular radial solution R_l as follows:

$$\psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) = 4\pi \sum_L i^l e^{im(k)} R_l(r, k) Y_L(\hat{\mathbf{r}}) Y_L^*(\hat{\mathbf{k}}) \quad (3.4)$$

where the radial solution has the property of regularity at $r=0$ and the boundary condition that outside the muffin-tin radius

$$R_l(r, k) = j_l(kr) \cos \eta_l(k) - n_l(kr) \sin \eta_l(k) \quad (3.5)$$

defining the phase shift η_l . Using

$$G_0(\mathbf{R}, \mathbf{R}') = -ik \sum_L \bar{J}_L(\mathbf{R}_<) H_L^+(\mathbf{R}_>) \quad (3.6)$$

the Lipmann-Schwinger equation can be written in radial form as follows:

$$\begin{aligned} R_l(r, k) &= j_l(kr) e^{-i\eta_l(k)} - ik h_l^+(kr) \int_0^r dx x^2 j_l(kx) v(x) R_l(x, k) \\ &\quad - ik j_l(kr) \int_r^\infty dx x^2 h_l^+(kx) v(x) R_l(x, k), \quad \forall r \end{aligned} \quad (3.7)$$

or, in terms of the t-matrix,

$$e^{i\eta_l(k)} R_l(r, k) Y_l(\hat{\mathbf{r}}) = J_l(\mathbf{r}) + \int d\mathbf{r}_1 \int d\mathbf{r}_2 J_l(\mathbf{r}_1) t(\mathbf{r}_1, \mathbf{r}_2) G_0(\mathbf{r}_2, \mathbf{r}) \quad (3.8)$$

Using (3.6) and defining the on-shell matrix element of the t-matrix (diagonal for a spherical scatterer) by

$$t_l = \int d\mathbf{r} \int d\mathbf{r}' J_l(\mathbf{r}) t(\mathbf{r}, \mathbf{r}') \bar{J}_l(\mathbf{r}')$$

it can be seen that when \mathbf{r} lies outside the scatterer (ie $r >$ the muffin-tin radius)

$$e^{i\eta_l} R_l(r, k) = j_l(kr) - ikt_l h_l^+(kr)$$

which implies, in view of (3.5), that

$$t_l(k) = -\frac{1}{k} \sin \eta_l(k) e^{i\eta_l(k)} \quad (3.9)$$

In addition to the regular solution R_l , two more irregular solutions need to be defined:

$$R_l^\pm(r, k) = h_l^\pm(kr) \pm ik \int_0^\infty dr_1 r_1^2 j_l(kr_1) h_l^\pm(kr_1) v(r_1) R_l^\pm(r_1, k)$$

where $r_>$ ($r_<$) is the greater (smaller) of r and r_1 , together with the condition

$$\int_0^\infty dr r^2 h_l^\pm(kr) v(r) R_l^\pm(r, k) = 0$$

$R_l^\pm(r, k)$ matches on to $h_l^\pm(kr)$ at the muffin-tin radius.

There is a useful relation between the regular and irregular solutions:

$$R_l(r, k) = \frac{1}{2} \left(e^{i\eta_l(k)} R_l^+(r, k) + e^{-i\eta_l(k)} R_l^-(r, k) \right) \quad (3.10)$$

Finally, Faulkner and Stocks introduced the alternative radial solutions $z_l(kr)$ and $x_l(kr)$ defined as indicated in the following table:

Function	Type ²	Behaviour at $r=0$	Boundary Condition at r =muffin-tin radius
$R_l(r, k)$	real	regular	$= j_l(kr) \cos \eta_l(k) - n_l(kr) \sin \eta_l(k)$ $= e^{-i\eta_l(k)} (j_l(kr) - ikt_l(k) h_l^+(kr))$
$R_l^+(r, k)$	complex	irregular	$= h_l^+(kr)$
$z_l(kr)$	real	regular	$= j_l(kr) t_l^{-1} - ik h_l^+(kr)$ $= -\frac{k}{\sin \eta_l(k)} R_l(r, k)$
$x_l(kr)$	real	irregular	$= j_l(kr)$

² These properties hold for real energies - for complex energies all the radial solutions are complex.

Note that z_l is proportional to R_l . In fact

$$e^{i\eta(k)}R_l(r,k)=t_l(k)z_l(r,k) \quad (3.11)$$

from which integral equations for z_l can be obtained using (3.7) or (3.8). These new functions give neater forms for the multiple scattering Green's function.

3.2 The Green's Function

The standard derivation of the single scatterer Green's function uses the eigenfunction expansion

$$G(\mathbf{r},\mathbf{r}';\varepsilon^+)=\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{\psi_{\mathbf{k}}^*(\mathbf{r},\varepsilon)\psi_{\mathbf{k}}(\mathbf{r}',\varepsilon)}{\varepsilon-k^2+i\eta} \quad (3.12)$$

into which the expression (3.4) can be inserted to give

$$G(\mathbf{r},\mathbf{r}';\varepsilon^+)=\frac{1}{\pi}\sum_l Y_l^*(\hat{\mathbf{r}})Y_l(\hat{\mathbf{r}}')\int_{-\infty}^{\infty}dkk^2\frac{R_l(r,k)R_l(r',k)}{\varepsilon-k^2+i\eta} \quad (3.13)$$

Here η is a small positive number whose limit $\eta\rightarrow 0^+$ will be taken, and the range of the k integral has been extended from $0\leq k\leq\infty$ to $-\infty\leq k\leq\infty$ because the integrand is an even function of k . (3.13) can be worked out as a contour integral, but some careful manipulation is necessary. First, define

$$\alpha_+=\sqrt{\varepsilon}+\frac{i\eta}{2\sqrt{\varepsilon}}, \quad \kappa=\sqrt{\varepsilon}$$

such that, to first order in η ,

$$(\alpha_+)^2=\varepsilon+i\eta$$

The integrand in (3.13) thus contains the factor

$$\begin{aligned} \frac{k^2}{\alpha_+^2-k^2} &= -\frac{1}{2}\left[\frac{k}{k+\alpha_+}+\frac{k}{k-\alpha_+}\right] \\ &= -\frac{1}{2}\left[\frac{2k}{k-\alpha_+}+\left(\frac{k}{k+\alpha_+}-\frac{k}{k-\alpha_+}\right)\right] \end{aligned}$$

The term in round brackets is odd in k and therefore does not contribute to the integral. Thus

$$G(\mathbf{r},\mathbf{r}';\varepsilon^+)=\frac{1}{\pi}\sum_l Y_l^*(\hat{\mathbf{r}})Y_l(\hat{\mathbf{r}}')\int_{-\infty}^{\infty}dk\frac{k}{k-\alpha_+}R_l(r,k)R_l(r',k)$$

Thus, the integrand has a pole at $k=\alpha_+$ in the upper half-plane. Now suppose that $r'>r$, and use (3.10) to replace $R_l(r',k)$ by the corresponding irregular solutions, giving two terms involving R_l^+ and R_l^- respectively. Because R_l^+ behaves like h_l^+ , we close the contour for the first term in the upper half-plane - $R_l^+(r',k)$ must kill any contribution from $R_l(r,k)$ since $r'>r$. For similar reasons we close the

contour for the second term in the lower half-plane. Thus, the second term does not contribute and working out the residue at $k = \alpha_+$ for the first term gives

$$G(\mathbf{r}, \mathbf{r}'; \varepsilon^+) = -ik \sum_L Y_L^*(\hat{\mathbf{r}}) Y_L(\hat{\mathbf{r}}') R_L(r_<, k) R_L^+(r_>, k) e^{im_L(k)} \quad (3.14)$$

where now $r_> (r_<)$ is the greater (smaller) of r and r' and $k = \sqrt{\varepsilon}$.

Equation (3.14) is the key result. For future use, it is helpful to write it in terms of the Faulkner solutions defined above:

$$G(\mathbf{r}, \mathbf{r}'; \varepsilon^+) = \sum_L [\bar{Z}_L(\mathbf{r}, k) t_L(k) Z_L(\mathbf{r}', k) - \bar{Z}_L(\mathbf{r}_<, k) X_L(\mathbf{r}_>, k)] \quad (3.15)$$

Remember, the bar symbols on the Z – functions in (3.15) indicate that the implied spherical harmonic is complex-conjugated. Note that the reality of the radial solutions implies that the irregular (ie second) term does not contribute to the imaginary part of the Green's function (for real energies).

Finally, note that (3.15) (and previous equations) assumes that the origin of coordinates is at the centre of the spherical scatterer. If \mathbf{r} and \mathbf{r}' are measured from an arbitrary origin with respect to which the centre of the scatterer is located at \mathbf{R} then (3.15) reads

$$G(\mathbf{r}, \mathbf{r}'; \varepsilon^+) = \sum_L [\bar{Z}_L(\mathbf{r} - \mathbf{R}, k) t_L(k) Z_L(\mathbf{r}' - \mathbf{R}, k) - \bar{Z}_L(\mathbf{r}_<, k) X_L(\mathbf{r}_>, k)] \quad (3.16)$$

where now $\mathbf{r}_> (\mathbf{r}_<)$ is the greater (smaller) of $\mathbf{r} - \mathbf{R}$ and $\mathbf{r}' - \mathbf{R}$.

4 The Free Space Green's Function

The objective here is to derive the following expression for the free space Green's function

$$G_0(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) = \sum_{L,L'} \bar{J}_L(\mathbf{r}) g_{L,L'}^{jj} J_{L'}(\mathbf{r}')$$

in terms of the structure constant matrix $g_{L,L'}^{jj}$. The relevant geometry is as follows:

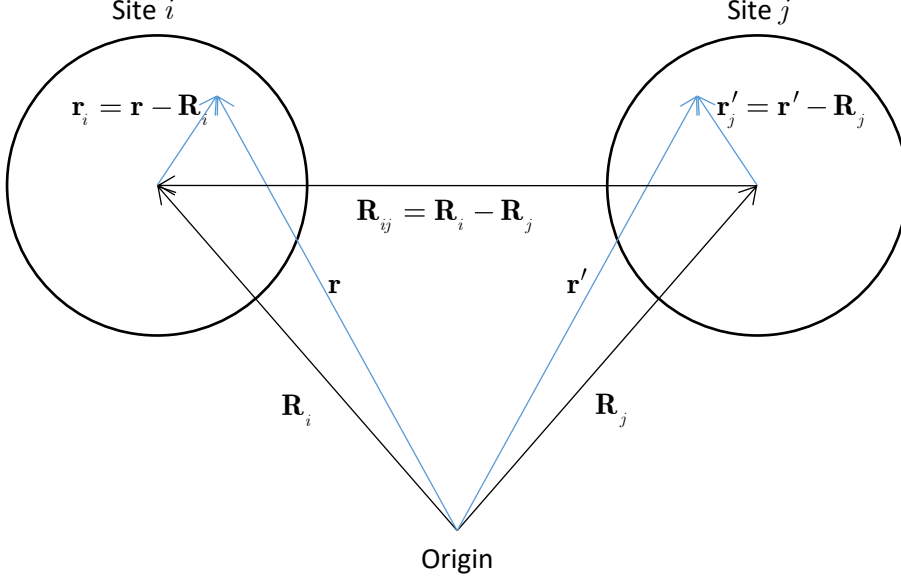


Figure 1: The definitions of position vectors multiple scattering calculations

First note the translational invariance properties of the free space Green's function G_0 :

$$G_0(\mathbf{R}, \mathbf{R}') = -\frac{1}{4\pi} \frac{e^{ik|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}, \quad k = \sqrt{\varepsilon} \quad (4.1)$$

Hence

$$G_0(\mathbf{r}+\mathbf{R}, \mathbf{r}') = -\frac{1}{4\pi} \frac{e^{ik|\mathbf{r}+\mathbf{R}-\mathbf{r}'|}}{|\mathbf{r}+\mathbf{R}-\mathbf{r}'|} = G_0(\mathbf{r}, \mathbf{r}'-\mathbf{R}) \quad (4.2)$$

Now use the angular momentum resolution of G_0 :

$$G_0(\mathbf{R}, \mathbf{R}') = -ik \sum_L \bar{J}_L(\mathbf{R}_{<}) H_L^+(\mathbf{R}_{>}) = -ik \sum_L J_L(\mathbf{R}_{<}) \bar{H}_L^+(\mathbf{R}_{>}) \quad (4.3)$$

with $\mathbf{R}_{<(>)}$ being the smaller (greater) of \mathbf{R} and \mathbf{R}' . The second equality follows from the fact that (4.3) contains

$$\sum_m Y_L^*(\hat{\mathbf{r}}) Y_L(\hat{\mathbf{r}}') = \frac{2l+1}{4\pi} P_l(\cos \alpha) = \sum_m Y_L(\hat{\mathbf{r}}) Y_L^*(\hat{\mathbf{r}}')$$

using the spherical harmonic addition theorem. Thus (4.3) implies that

$$G_0(\mathbf{R}, \mathbf{R}') = G_0(\mathbf{R}', \mathbf{R})$$

which is guaranteed by (4.1).

Because of (4.2) we can write

$$\begin{aligned} G_0(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) &= G_0(\mathbf{r}, \mathbf{r}'-\mathbf{R}_{ij}) \\ \mathbf{R}_{ij} &\equiv \mathbf{R}_i - \mathbf{R}_j \end{aligned}$$

Since, by hypothesis, \mathbf{r} lies within site i , \mathbf{r}' lies within site j and sites i and j do not overlap, we must have

$$|\mathbf{r}| < |\mathbf{r}' - \mathbf{R}_{ij}|$$

Hence

$$G_0(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) = -ik \sum_L \bar{J}_L(\mathbf{r}) H_L^+(\mathbf{r}' - \mathbf{R}_{ij}) \quad (4.4)$$

Now use the *Multiple Scatterer's Friend*, (see Lloyd and Smith [1])

$$-ik H_L^+(\mathbf{r}' - \mathbf{R}_{ij}) = \sum_{L'} g_{LL'}(\mathbf{R}_{ij}) J_{L'}(\mathbf{r}') \quad \text{for } R_{ij} > r' \quad (4.5)$$

where (see (A25) in Appendix A: Notation and Mathematical Preliminaries)

$$g_{LL'}(\mathbf{R}_{ij}) = -4\pi i k (-1)^m i^{(l'-l)} \sum_{L_1} i^{-L_1} C(\bar{L}, L', L_1) H_{L_1}^+(\mathbf{R}_{ij}) \quad (4.6)$$

in which the Gaunt number

$$C(L_1, L_2, L_3) \equiv \int d\hat{r} Y_{L_1}(\hat{r}) Y_{L_2}(\hat{r}) Y_{L_3}(\hat{r}) \quad (4.7)$$

has been used. Hence from (4.4) and (4.5) we get

$$G_0(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) = \sum_{L, L'} \bar{J}_L(\mathbf{r}) g_{LL'}(\mathbf{R}_{ij}) J_{L'}(\mathbf{r}') \quad (4.8)$$

which is the desired result. Equation (4.6) defines the *real space structure constants* which appear everywhere in multiple scattering theory.

5 The Real Space Structure Constants

In the previous section, the following formula for the real space structure constants occurred:

$$g_{LL'}^{jj} = -4\pi ik(-1)^m i^{l(l-l)} \sum_{L_1} i^{-L_1} C(\bar{L}, L', L_1) H_{L_1}^+(\mathbf{R}_{ij}) \quad (5.1)$$

Here we have decided, for convenience later, to write the structure constant as a matrix with site indices rather than a function of the vector between the sites:

$$g_{LL'}^{jj} \equiv g_{LL'}(\mathbf{R}_{ij}) = g_{LL'}(\mathbf{R}_i - \mathbf{R}_j) \quad (5.2)$$

5.1 Symmetries

This matrix has various symmetries. Consider first interchanging angular momentum indices:

$$g_{L'L}^{jj} = -4\pi ik(-1)^{m'} i^{l'(l'-l')} \sum_{L_1} i^{-L_1} C(\bar{L}', L, L_1) H_{L_1}^+(\mathbf{R}_{ij}) \quad (5.3)$$

Now recall a property of the Gaunt numbers (see Appendix A: Notation and Mathematical Preliminaries):

$$C(L_1, L_2, L_3) = C(L_2, L_1, L_3)$$

Hence we can write (5.3) as

$$g_{L'L}^{jj} = -4\pi ik(-1)^{m'} i^{l'(l'-l')} \sum_{L_1} i^{-L_1} C(L, \bar{L}', L_1) H_{L_1}^+(\mathbf{R}_{ij}) \quad (5.4)$$

Thus, comparing with (5.1), we have

$$g_{L'L}^{jj} = (-1)^{l-l'+m+m'} g_{LL'}^{jj} \quad (5.5)$$

Now consider interchanging site indices:

$$g_{LL'}^{jj} = -4\pi ik(-1)^m i^{l(l-l)} \sum_{L_1} i^{-L_1} C(\bar{L}, L', L_1) H_{L_1}^+(-\mathbf{R}_{ij})$$

The inversion property of the spherical harmonics (see (A6)) gives

$$g_{LL'}^{jj} = -4\pi ik(-1)^m i^{l(l-l)} \sum_{L_1} i^{-L_1} (-1)^{L_1} C(\bar{L}, L', L_1) H_{L_1}^+(\mathbf{R}_{ij})$$

which, using the parity property of the Gaunt numbers (see (A19)), becomes

$$g_{LL'}^{jj} = -4\pi ik(-1)^m i^{l(l-l)} (-1)^{l+l'} \sum_{L_1} i^{-L_1} C(\bar{L}, L', L_1) H_{L_1}^+(\mathbf{R}_{ij})$$

Hence, comparing with (5.1),

$$g_{LL'}^{jj} = (-1)^{l+l'} g_{LL'}^{jj} \quad (5.6)$$

Finally, combining (5.5) and (5.6) gives

$$g_{LL'}^{jj} = (-1)^{(m+m')} g_{L'L}^{jj} \quad (5.7)$$

These symmetries also hold for the other structure constant defined in Appendix A: see (A26)

$$\begin{aligned}
 d_{L'L}(\mathbf{R}) &= (-1)^{(l-l'+m+m')} d_{\bar{L}\bar{L}}(\mathbf{R}) \\
 d_{LL'}(-\mathbf{R}) &= (-1)^{l+l'} d_{LL'}(\mathbf{R}) \\
 d_{LL'}(\mathbf{R}) &= (-1)^{(m+m')} d_{\bar{L}\bar{L}}(-\mathbf{R})
 \end{aligned} \tag{5.8}$$

For these quantities complex conjugation is straightforward (because the spherical Bessel functions are real) and we can easily obtain

$$d_{LL'}(\mathbf{R}) = (-1)^{l+l'} [d_{L'L}(\mathbf{R})]^* = [d_{L'L}(-\mathbf{R})]^* \tag{5.9}$$

5.2 Other people's structure constants

These notes work with formulae given by Lloyd and Smith (L&S) [1]. In fact, L&S use a form of the multiple scatterer's friend containing a structure constant $\gamma_{L'L}(\mathbf{R}_{ji})$, which is related to the structure constant used here by

$$g_{LL'}^{jj} = i^{l'-l} \gamma_{L'L}(\mathbf{R}_{ji})$$

Pendry [4] (p272) quotes a version of the multiple scatterer's friend involving a structure constant $E_{LL'}(\mathbf{R}_{ji})$ which is related to mine by

$$g_{LL'}^{jj} = -ik E_{LL'}(\mathbf{R}_{ji})$$

Pendry's formula is

$$E_{LL'}(\mathbf{R}_{ji}) = 4\pi \sum_{L_1} i^{l-l'-L_1} (-1)^{m'+m_1} C(L, \bar{L}', L_1) H_{L_1}^+(\mathbf{R}_{ji})$$

By repeated using the properties of spherical harmonics and Gaunt numbers it is easy to show that this agrees with my formula (5.1).

It is difficult to establish consistency with Faulkner et al [5], [10] because they tend to use real spherical harmonics. I think the formula given in Weinberger's book [6] is wrong, presumably a typo.

5.3 The norm of the structure constants

Define a norm matrix P by

$$P_{ll'}^{jj} = \sqrt{\sum_{mm'} |g_{LL'}^{jj}|^2} \tag{5.10}$$

Using (5.1) we get

$$(P_{ll'}^{jj})^2 = (4\pi k)^2 \sum_{L_1 L_2} i^{-L_1+L_2} H_{L_1}^+(\mathbf{R}_{ji}) \bar{H}_{L_2}^+(\mathbf{R}_{ji}) \sum_{mm'} C(\bar{L}, L', L_1) C(\bar{L}, L', L_2)$$

But expressing the Gaunt numbers in terms of 3J symbols and using the orthogonality of the 3Js, we get

$$\sum_{mm'} C(\bar{L}, L', L_1) C(\bar{L}, L', L_2) = \frac{(2l+1)(2l'+1)}{4\pi} \begin{pmatrix} l l' l_1 \\ 0 0 0 \end{pmatrix}^2 \delta_{l_1 l_2} \delta_{m_1 m_2} \quad (5.11)$$

Thus

$$(P_{ij}^{jj})^2 = 4\pi k^2 (2l+1)(2l'+1) \sum_{l_1} |H_{l_1}^+(\mathbf{R}_{ij})|^2 \begin{pmatrix} l l' l_1 \\ 0 0 0 \end{pmatrix}^2$$

Now note that in the summation m_1 appears only in the (implicit) spherical harmonics, and therefore we can use the sum rule

$$\sum_{m_1} |Y_{l_1}(\hat{\mathbf{R}})|^2 = \frac{2l_1+1}{4\pi}$$

to obtain

$$(P_{ij}^{jj})^2 = k^2 (2l+1)(2l'+1) \sum_{l_1} |h_{l_1}^+(R_{ij})|^2 (2l_1+1) \begin{pmatrix} l l' l_1 \\ 0 0 0 \end{pmatrix}^2 \quad (5.12)$$

This is the basic expression for the norm of the structure constants. Note that it depends only on the magnitude of \mathbf{R}_{ij} , not its direction.

5.4 Asymptotic behaviour

Here we give some formulae relating to the behaviour of the structure constants for large distances and energies (see [8]). This can be done by noting the asymptotic form for the Hankel functions:

$$\lim_{kr \rightarrow \infty} h_l^+(kr) = i^{-(l+1)} \frac{e^{ikr}}{kr} \quad (5.13)$$

Using this in (5.1) gives

$$\lim_{kR_{ij} \rightarrow \infty} g_{LL'}^{jj} = \frac{e^{ikR_{ij}}}{R_{ij}} D_{LL'}(\hat{\mathbf{R}}_{ij}) \quad (5.14)$$

where

$$D_{LL'}(\hat{\mathbf{R}}_{ij}) = -4\pi (-1)^m i^{-(l+l')} \sum_{l_1} C(\bar{L}, L', L_1) Y_{l_1}(\hat{\mathbf{R}}_{ij}) \quad (5.15)$$

in deriving which the parity rule for the Gaunt number has been used. This shows that asymptotically the dependence of the structure constants on energy and distance is entirely contained in the wave-like first factor in (5.14), with the coefficient $D_{LL'}$ being a complex number of order 1 which depends only on the *direction* of \mathbf{R}_{ij} .

We can also give a nice asymptotic expression for the norm of the structure constants. Use (5.13) in (5.12) to obtain

$$\lim_{kR_{ij} \rightarrow \infty} (P_{ll'}^{ij})^2 = \frac{1}{R_{ij}^2} (2l+1)(2l'+1) \sum_{l_1} (2l_1+1) \begin{pmatrix} l' l' l_1 \\ 000 \end{pmatrix}^2$$

But, by the orthogonality property (A14) of the 3J symbols,

$$\sum_{l_1} (2l_1+1) \begin{pmatrix} l' l' l_1 \\ 000 \end{pmatrix}^2 = 1 \quad (5.16)$$

And therefore

$$\lim_{kR_{ij} \rightarrow \infty} P_{ll'}^{ij} = \frac{1}{R_{ij}} \sqrt{(2l+1)(2l'+1)} \quad (5.17)$$

6 The Scattering Path Operator

The objective here is to define and give the important operator identity for the scattering path operator τ . We start by writing the total potential as a sum of contributions from each scatterer at site i , position \mathbf{R}_i :

$$V(\mathbf{r}) = \sum_i v^i(\mathbf{r} - \mathbf{R}_i) \quad (6.1)$$

Later, in considering the on-shell matrix elements of τ , it will turn out that the site potentials v^i must be non-overlapping. From now on, in this section we will drop the explicit dependence on spatial variables - it's irrelevant here.

The Green's function corresponding to the potential V is given by the Dyson equation

$$G = G_0 + G_0 V G = G_0 + G V G_0 \quad (6.2)$$

where G_0 is the free space propagator. This equation has the formal solution

$$G = G_0 + G_0 T G_0 \quad (6.3)$$

in which T is the total scattering operator or T matrix³, given by

$$T = V + V G_0 T = V + T G_0 V \quad (6.4)$$

We can define the single-site t matrix t^i in the same way:

$$\begin{aligned} t^i &= v^i + v^i G_0 t^i = (1 - v^i G_0)^{-1} v^i \\ &= v^i + t^i G_0 v^i = v^i (1 - G_0 v^i)^{-1} \end{aligned} \quad (6.5)$$

Clearly the total T matrix can be written

$$T = \sum_i v^i + \sum_i v^i G_0 T$$

Now introduce operator Q^i describing the total scattering from site i :

$$T = \sum_i Q^i \quad (6.6)$$

Thus

$$\sum_i Q^i = \sum_i v^i + \sum_{i,n} v^i G_0 Q^n$$

and

$$\begin{aligned} Q^i &= v^i + \sum_n v^i G_0 Q^n \\ &= v^i + v^i G_0 Q^i + \sum_{n \neq i} v^i G_0 Q^n \\ &= t^i + \sum_{n \neq i} t^i G_0 Q^n \end{aligned} \quad (6.7)$$

³ We should say T operator here, but everyone says T matrix (and S matrix, R matrix etc) in scattering theory.

This eliminates the potentials v^i in favour of the single-site scattering matrix t^i . Now write

$$Q^i = \sum_j \tau^{ij} \quad (6.8)$$

whence

$$T = \sum_{i,j} \tau^{ij} \quad (6.9)$$

and

$$\begin{aligned} \tau^{ij} &= t^i \delta_{ij} + \sum_{k \neq i} t^i G_0 \tau^{kj} \\ &= t^i \delta_{ij} + \sum_{k \neq j} t^{ik} G_0 t^j \end{aligned} \quad (6.10)$$

Note that in a term such as $t^i G_0 t^k$ the propagator links sites i and k , and can thus be thought of as a matrix G_0^{ik} (actually a matrix-operator like τ^{ij}) – see section 7. If we make this explicit in (6.10) we get

$$\begin{aligned} \tau^{ij} &= t^i \delta_{ij} + \sum_{k \neq i} t^i G_0^{ik} \tau^{kj} \\ &= t^i \delta_{ij} + \sum_k t^i G_0^{ik} \tau^{kj} (1 - \delta_{ik}) \end{aligned}$$

Introducing a modified propagator matrix with the diagonal elements set to zero,

$$\tilde{G}_0^{ik} \equiv G_0^{ik} (1 - \delta_{ik}) \quad (6.11)$$

we obtain

$$\tau^{ij} = t^i \delta_{ij} + \sum_k t^i \tilde{G}_0^{ik} \tau^{kj} \quad (6.12)$$

The point is that in any term of (6.10) or, equivalently, (6.12), adjacent scatterings on the same site are excluded.

τ^{ij} was called by Gyorffy the scattering path operator - it sums up the contributions to the total T matrix of scattering paths starting from site j and ending at site i , as can be seen by iterating (6.12):

$$\tau^{ij} = t^i \delta_{ij} + t^i \tilde{G}_0^{ij} t^j + \sum_n t^i \tilde{G}_0^{in} t^n \tilde{G}_0^{nj} t^j + \dots \quad (6.13)$$

7 On-Shell Elements of the Tau Matrix

Define the on-shell matrix elements of τ^{ij} and t^i as follows:

$$\begin{aligned}\tau_{LL'}^{ij} &= \int d\mathbf{r} \int d\mathbf{r}' J_L(\mathbf{r}-\mathbf{R}_i) \tau^{ij}(\mathbf{r}, \mathbf{r}') \bar{J}_{L'}(\mathbf{r}'-\mathbf{R}_j) \\ t_{LL'}^i &= \int d\mathbf{r} \int d\mathbf{r}' J_L(\mathbf{r}-\mathbf{R}_i) t^i(\mathbf{r}, \mathbf{r}') \bar{J}_{L'}(\mathbf{r}'-\mathbf{R}_i)\end{aligned}\quad (7.1)$$

involving Bessel functions centred at sites i and j . For spherical single scatterer potentials, $t_{LL'}^i$ is diagonal in angular momentum. The explicit formula for the on-shell elements of t^i in terms of the phase shifts of the potential at site i was given in section 3.1, equation (3.9). For non-spherical single scatterer potentials, the t matrix will not be diagonal but can nevertheless be calculated by more complicated methods into which we won't go here. The on-shell elements of t^i can therefore be regarded as known input quantities here.

The integrals in (7.1) are confined to run over sites i and j by the spatial property of the τ matrix, namely

$$\tau^{ij}(\mathbf{r}, \mathbf{r}') = 0, \text{ unless } \mathbf{r} \text{ lies in site } i \text{ and } \mathbf{r}' \text{ lies in site } j. \text{ Likewise}$$

$$t^i(\mathbf{r}, \mathbf{r}') = 0, \text{ unless } \mathbf{r} \text{ lies in site } i.$$

Changing the integration variables, we get

$$\tau_{LL'}^{ij} = \int d\mathbf{r} \int d\mathbf{r}' J_L(\mathbf{r}) \tau^{ij}(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) \tilde{J}_{L'}(\mathbf{r}') \quad (7.2)$$

Putting the defining operator equation into real space gives

$$\tau^{ij}(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) = t^i(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) \delta_{ij} + \sum_{n \neq i} \int d\mathbf{r}_1 \int d\mathbf{r}_2 t^i(\mathbf{r}+\mathbf{R}_i, \mathbf{r}_1) G_0(\mathbf{r}_1, \mathbf{r}_2) \tau^{nj}(\mathbf{r}_2, \mathbf{r}'+\mathbf{R}_j)$$

where the \mathbf{r}_1 integral runs over site i and the \mathbf{r}_2 integral runs over site n . Changing the origin of these integration variables gives

$$\begin{aligned}\tau^{ij}(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) &= t^i(\mathbf{r}+\mathbf{R}_i, \mathbf{r}'+\mathbf{R}_j) \delta_{ij} \\ &+ \sum_{n \neq i} \int d\mathbf{r}_1 \int d\mathbf{r}_2 t^i(\mathbf{r}+\mathbf{R}_i, \mathbf{r}_1+\mathbf{R}_i) G_0(\mathbf{r}_1+\mathbf{R}_i, \mathbf{r}_2+\mathbf{R}_n) \tau^{nj}(\mathbf{r}_2+\mathbf{R}_n, \mathbf{r}'+\mathbf{R}_j)\end{aligned}$$

Since n cannot be the same site as i and $\mathbf{r}_1, \mathbf{r}_2$ are confined to be within a site, we are entitled to use

$$G_0(\mathbf{r}_1+\mathbf{R}_i, \mathbf{r}_2+\mathbf{R}_n) = \sum_{L, L'} \bar{J}_L(\mathbf{r}_1) g_{L, L'}^{in} J_{L'}(\mathbf{r}_2)$$

Using the last two equations in (7.2) clearly gives

$$\tau_{LL'}^{ij} = t_{LL'}^i \delta_{ij} + \sum_{\substack{n \neq i \\ L_1, L_2}} t_{LL_1}^i g_{L_1 L_2}^{in} \tau_{L_2 L'}^{nj} \quad (7.3)$$

Equation (7.3) is the key equation of multiple scattering theory. Defining underlined matrices in site and angular momentum:

$$\begin{aligned}
[\boldsymbol{\tau}]_{LL'}^{jj} &= \tau_{LL'}^j, \\
[\mathbf{t}]_{LL'}^{jj} &= t_{LL'}^j \delta_{ij} \\
[\tilde{\mathbf{g}}]_{LL'}^{jj} &= (1 - \delta_{ij}) g_{LL'}^j.
\end{aligned}
\tag{7.4}$$

we can write (6.12) as

$$\begin{aligned}
\boldsymbol{\tau} &= \mathbf{t} + \mathbf{t} \tilde{\mathbf{g}} \boldsymbol{\tau} \\
&= [\mathbf{t}^{-1} - \tilde{\mathbf{g}}]^{-1}
\end{aligned}$$

Here, then, is how to calculate the scattering path matrix, ie the matrix of the on-shell elements of the scattering path operator: set up a matrix \underline{M}

$$\mathbf{M} \equiv \mathbf{t}^{-1} - \tilde{\mathbf{g}}
\tag{7.5}$$

and invert it. This is the heart of all multiple scattering calculations. Once one has the scattering path matrix, one can calculate the full 1-electron Green's function of the system (see section 11) and hence any 1-electron observable.

8 The Scattering Amplitude of a Cluster

Most applications of multiple scattering theory to condensed matter have to do with the eigenvalue spectrum or spectral density, leading through into spectroscopic and transport properties. Some of these are developed in the following sections. In this section, however, we calculate a quantity central to the scattering process itself, namely the scattering amplitude of a cluster of atoms or scatterers. This is relevant for LEED and related experiments.

Consider a plane wave incident on a cluster, by which we mean anything from a single atom to a crystal. The scattering amplitude of any such object is defined by the asymptotic form of the wave function at distances large compared with the size of the cluster and therefore far away from any scattering potential. In general this asymptotic form is

$$\lim_{r \rightarrow \infty} \psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) = e^{i\mathbf{k} \cdot \mathbf{r}} + \psi_{\mathbf{k}}^{scat}(\mathbf{r}, \varepsilon^+) = e^{i\mathbf{k} \cdot \mathbf{r}} + f(\mathbf{k}) \frac{e^{ikr}}{r} \quad (8.1)$$

Here $\varepsilon^+ = \varepsilon + i0^+ = k^2 + i0^+$

To determine the scattering amplitude $f(\mathbf{k})$ we will use the geometry depicted in Figure 1 and write the total wave function = incident wave plus scattered wave by means of the Lipmann-Schwinger equation (cf equation (3.3)):

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r}, \varepsilon^+) &= e^{i\mathbf{k} \cdot \mathbf{r}} + \int d\mathbf{r}' \int d\mathbf{r}'' G_0(\mathbf{r}, \mathbf{r}'; \varepsilon^+) T(\mathbf{r}', \mathbf{r}'') e^{i\mathbf{k} \cdot \mathbf{r}'} \\ &= e^{i\mathbf{k} \cdot \mathbf{r}} + \sum_{ij} \int d\mathbf{r}' \int d\mathbf{r}'' G_0(\mathbf{r}, \mathbf{r}'; \varepsilon^+) \tau^{ij}(\mathbf{r}', \mathbf{r}'') e^{i\mathbf{k} \cdot \mathbf{r}'} \end{aligned} \quad (8.2)$$

in which the second line uses (6.9). In this equation the integrals over \mathbf{r}' and \mathbf{r}'' are confined to sites i and j respectively – see the argument in section 7. This means we can change variables according to the geometry of Figure 1 and write

$$\psi_{\mathbf{k}}^{scat}(\mathbf{r}, \varepsilon^+) = \sum_{ij} \int_{site i} d\mathbf{r}' \int_{site j} d\mathbf{r}'' G_0(\mathbf{r}, \mathbf{r}' + \mathbf{R}_i; \varepsilon^+) \tau^{ij}(\mathbf{r}' + \mathbf{R}_i, \mathbf{r}'' + \mathbf{R}_j) e^{i\mathbf{k} \cdot (\mathbf{r}' + \mathbf{R}_i)} \quad (8.3)$$

Now, we are after the asymptotic case in which $|\mathbf{r}| > |\mathbf{r}' + \mathbf{R}_i|$, and so we can use (4.3) to write

$$G_0(\mathbf{r}, \mathbf{r}' + \mathbf{R}_i; \varepsilon^+) = -ik \sum_L H_L^+(\mathbf{r}) \bar{J}_L(\mathbf{r}' + \mathbf{R}_i) = -ik \sum_L \bar{H}_L^+(\mathbf{r}) J_L(\mathbf{r}' + \mathbf{R}_i) \quad (8.4)$$

If we now also use the asymptotic form of the Hankel functions (see Appendix B):

$$\lim_{x \rightarrow \infty} h_l^+(x) = \frac{e^{i(x-(l+1)\pi/2)}}{x} = i^{-(l+1)} \frac{e^{ix}}{x} \quad (8.5)$$

we can easily see that the scattered wave has the asymptotic form required by (8.1) with the scattering amplitude given by

$$f(\mathbf{k}) = - \sum_{ij} \sum_L i^{-l} Y_L^*(\hat{\mathbf{r}}) \int_{site i} d\mathbf{r}' \int_{site j} d\mathbf{r}'' J_L(\mathbf{r}' + \mathbf{R}_i) \tau^{ij}(\mathbf{r}' + \mathbf{R}_i, \mathbf{r}'' + \mathbf{R}_j) e^{i\mathbf{k} \cdot (\mathbf{r}' + \mathbf{R}_i)} \quad (8.6)$$

Now if we use the angular momentum resolution of the plane wave:

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_L i^l j_l(kr) Y_L(\hat{\mathbf{r}}) Y_L^*(\hat{\mathbf{k}}) = 4\pi \sum_L i^l j_l(kr) Y_L^*(\hat{\mathbf{r}}) Y_L(\hat{\mathbf{k}}) \quad (8.7)$$

we can write

$$f(\mathbf{k}) = -4\pi \sum_{ij} \sum_{LL'} i^{(l'-l)} Y_L^*(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{k}}) \times \int_{site\ i} d\mathbf{r}' \int_{site\ j} d\mathbf{r}'' J_L(\mathbf{r}' + \mathbf{R}_i) \tau^{ij}(\mathbf{r}' + \mathbf{R}_i, \mathbf{r}'' + \mathbf{R}_j) \bar{J}_{L'}(\mathbf{r}'' + \mathbf{R}_j) \quad (8.8)$$

Now we use one of the multiple scatterer's friends (Appendix A:) to expand the Bessel functions in terms of Bessel functions centred on a different origin:

$$J_L(\mathbf{r} - \mathbf{R}) = \sum_{L'} d_{LL'}(\mathbf{R}) J_{L'}(\mathbf{r})$$

$$\bar{J}_L(\mathbf{r} - \mathbf{R}) = \sum_{L'} (d_{LL'}(\mathbf{R}))^* \bar{J}_{L'}(\mathbf{r}) \quad (8.9)$$

where the structure constants are given by (A26). This change of origin allows us to recognise the on-shell matrix element of τ^{ij} defined in (7.2) and write

$$f(\mathbf{k}) = -4\pi \sum_{ij} \sum_{LL'} i^{(l'-l)} Y_L^*(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{k}}) \sum_{L_1 L_2} d_{LL_1}(-\mathbf{R}_i) \tau_{L_1 L_2}^{ij}(d_{L' L_2}(-\mathbf{R}_j))^*$$

$$= -4\pi \sum_{ij} \sum_{LL'} i^{(l'-l)} Y_L^*(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{k}}) \sum_{L_1 L_2} d_{LL_1}(-\mathbf{R}_i) \tau_{L_1 L_2}^{ij} d_{L_2 L'}(\mathbf{R}_j) \quad (8.10)$$

where we have used (5.9).

The single scatterer result $f^{SS}(\mathbf{k})$ is obtained by letting $\tau_{L_1 L_2}^{ij} = t_{L_1} \delta_{L_1 L_2} \delta_{ij}$, $\mathbf{R}_i = 0$ and noting that $\lim_{R \rightarrow 0} d_{LL'}(\mathbf{R}) = \delta_{LL'}$ - this is easily obtained from (A26). Thus, we easily find the familiar result (see, for example, Schiff [2])

$$f^{SS}(\mathbf{k}) = -\sum_l (2l+1) t_l(k) P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{k}})$$

$$= \frac{1}{k} \sum_l (2l+1) \sin \eta_l(k) e^{i\eta_l(k)} P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{k}}) \quad (8.11)$$

9 Energy eigenstates

In a typical electronic structure calculation, the goal is to find the energy eigenvalues: the energies of molecular or cluster orbitals, the energy bands in a periodic crystal, etc. Multiple scattering gives access to these quantities by noting that the resolvent, the Green's function and therefore the T matrix has poles at the required energies. Thus, we can determine the eigenvalues of the Hamiltonian by locating the poles of the T matrix.

9.1 Lattice Fourier transforms for periodic crystals

Consider a periodic crystal with one atom per unit cell – the generalisation to more complicated crystal lattices is trivial. For such a system the single site t matrix is the same for all sites ($t^i = t \quad \forall i$) and the position vectors \mathbf{R}_i fall on a regular lattice. This allows us to define the lattice Fourier transforms of the real space matrices (7.4) defined in section 7.

$$\begin{aligned} [\tilde{\mathbf{g}}(\varepsilon)]_{ll'}^{jj} &= \sum_{\mathbf{k}} \tilde{g}_{ll'}(\mathbf{k}, \varepsilon) e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_l)} \\ [\boldsymbol{\tau}(\varepsilon)]_{ll'}^{jj} &= \sum_{\mathbf{k}} \tau_{ll'}(\mathbf{k}, \varepsilon) e^{i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_l)} \end{aligned} \quad (9.1)$$

where the sum runs over all the allowed crystal momentum vectors \mathbf{k} in the Brillouin zone (BZ). It's then straightforward to show that the lattice Fourier transform of the key multiple scattering equation (7.3) is

$$\tau_{ll'}(\mathbf{k}, \varepsilon) = t_{ll'} + \sum_{l_1 l_2} t_{ll_1} \tilde{g}_{l_1 l_2}(\mathbf{k}, \varepsilon) \tau_{l_2 l'}(\mathbf{k}, \varepsilon) \quad (9.2)$$

Lattice periodicity means that this equation is “diagonal” in \mathbf{k} . Defining \mathbf{k} -dependent matrices in angular momentum by

$$\begin{aligned} [\tilde{\mathbf{g}}(\mathbf{k}, \varepsilon)]_{ll'} &= \tilde{g}_{ll'}(\mathbf{k}, \varepsilon) \\ [\boldsymbol{\tau}(\mathbf{k}, \varepsilon)]_{ll'} &= \tau_{ll'}(\mathbf{k}, \varepsilon) \end{aligned} \quad (9.3)$$

we can write (9.2) as follows:

$$\boldsymbol{\tau}(\mathbf{k}, \varepsilon) = \left[\mathbf{t}(\varepsilon)^{-1} - \tilde{\mathbf{g}}(\mathbf{k}, \varepsilon) \right]^{-1} \quad (9.4)$$

9.2 The KKR method

In view of the introductory remarks in this section, it's now easy to see how to find the energy bands of a periodic crystal by multiple scattering theory. For each “quantum number” \mathbf{k} one evaluates the **KKR matrix** as a function of energy:

$$\mathbf{M}(\mathbf{k}, \varepsilon) = \mathbf{t}(\varepsilon)^{-1} - \tilde{\mathbf{g}}(\mathbf{k}, \varepsilon) \quad (9.5)$$

The poles of the T matrix of the crystal are then located by finding the energies $\varepsilon_v(\mathbf{k})$ at which the **KKR determinant** is zero:

$$\det \mathbf{M}(\mathbf{k}, \varepsilon_\nu(\mathbf{k})) = 0 \quad (9.6)$$

In general there's more than one zero for each \mathbf{k} - hence the need for the band index ν .

That, in a nutshell, is the Korringa-Kohn-Rostoker (KKR) method of band theory. In real calculations, the big computational task is evaluating the Lattice Fourier transform $\tilde{\mathbf{g}}(\mathbf{k}, \varepsilon)$ of the structure constants. This is the inverse of (9.1) and thus involves a sum over real space lattice vectors \mathbf{R}_l . There is a whole technology – Ewald methods, fitting procedures etc – to make this convergent and efficient; we don't go into that here. Also there are other tricks of the trade. What's described above is called a constant \mathbf{k} search. One could also fix the energy and look for zeroes as a function of \mathbf{k} - this is called a constant ε search and is good for mapping the Fermi surface.

10 The Lloyd formula

The Lloyd formula was of central importance to the development of the multiple scattering description of electrons in condensed matter and is still used in actual calculations. It relates the density of electron states $n(\varepsilon)$ of a system consisting of set of scatterers (atoms) – ie a molecule, a cluster, an infinite ordered or disordered crystal, etc – to the density of states $n_0(\varepsilon)$ of a free electron system – ie the same system with all the scattering potentials removed. The formula reads

$$n(\varepsilon) - n_0(\varepsilon) = -\frac{1}{\pi} \frac{d}{d\varepsilon} \text{Im} \log(\det \mathbf{M}(\varepsilon)) \quad (10.1)$$

where $\mathbf{M}(\varepsilon) = \mathbf{t}^{-1} - \tilde{\mathbf{g}}$ is the matrix introduced in (7.5). The quantity $\det \mathbf{M}(\varepsilon)$ is often called the **Lloyd determinant**. Clearly one could also write this in terms of the integrated density of states

$N(\varepsilon) = \int^{\varepsilon} d\varepsilon' n(\varepsilon')$, ie the number of electron states below energy ε :

$$N(\varepsilon) - N_0(\varepsilon) = -\frac{1}{\pi} \text{Im} \log(\det \mathbf{M}(\varepsilon)) \quad (10.2)$$

This is the form in which the Lloyd formula is often used. It gives a convenient way to find the Fermi energy ε_F , the energy for which $N(\varepsilon_F) = N$ where N is the total number of electrons in the system per unit volume. The way this works is that every time the energy passes through an eigenvalue of the Hamiltonian the Lloyd determinant passes through zero (and the T matrix has a pole) and the phase of the determinant jumps by π , whereupon the right hand side of (10.2) jumps by one. Thus, the eigenvalues are counted one by one as the energy parameter increases and passes through them.

The Lloyd formula is the multiple scattering generalisation of Friedel's formula for a single (spherical) scatterer:

$$n(\varepsilon) - n_0(\varepsilon) = \frac{1}{\pi} \sum_l (2l+1) \frac{d\eta_l(\varepsilon)}{d\varepsilon} \quad (10.3)$$

where η_l is the l wave phase shift for the single scattering potential (see section 3.1).

10.1 Krein's theorem

The theorem (see [5], [7]) is

$$\text{Tr} [G(z) - G_0(z)] = \int_{-\infty}^{\infty} dE \frac{\xi(E)}{(E-z)^2} \quad (10.4)$$

where the resolvents are the following functions of the complex variable z :

$$G_0(z) = (z - K)^{-1}, \quad G(z) = (z - H)^{-1} \quad (10.5)$$

in which K is the kinetic energy operator and H is the full Hamiltonian of the system. $\xi(E)$ is called the **spectral displacement function**. Equation (10.4) is a special case of a more general theorem stating that for any sufficiently smooth function Φ

$$\text{Tr}[\Phi(H) - \Phi(K)] = \int_{-\infty}^{\infty} dE \xi(E) \frac{d\Phi(E)}{dE}$$

It can be shown that for the scattering potentials we encounter the spectral displacement operator is given in terms of the S matrix (recall that $S = 1 - 2i\sqrt{\varepsilon}T$):

$$\begin{aligned} \xi(E) &= \frac{i}{2\pi} \text{tr}[\log S(E)] = \frac{i}{2\pi} \sum_l [\log S(E)]_{ll} \\ &= \frac{i}{2\pi} \log[\det S(E)] \end{aligned} \quad (10.6)$$

Now, considered as a function of a complex variable, $\xi(z)$ is analytical everywhere except the negative real axis, where it has poles corresponding to bound states of H , and the positive real axis, where there is a branch cut corresponding to the continuum states. It also approaches zero for $|z| \rightarrow \infty$, and has the reflection property $\xi(x+i\eta) = (\xi(x-i\eta))^*$ as $\eta \rightarrow 0$. From the theory of functions of a complex variable, then, $\xi(z)$ satisfies

$$\frac{d\xi}{dz} = \lim_{\eta \rightarrow 0^+} \frac{1}{\pi} \int_{-\infty}^{\infty} dx \frac{\text{Im} \xi(x+i\eta)}{(x-z)^2}$$

Using this with (10.4) gives

$$\text{Im Tr}[G(\varepsilon^+) - G_0(\varepsilon^+)] = \pi \frac{d\xi(\varepsilon)}{d\varepsilon} \quad (10.7)$$

where we use the notation $G(\varepsilon^+) = \lim_{\eta \rightarrow 0^+} (\varepsilon - H + i\eta)^{-1}$.

Now for a single spherical scatterer the S matrix elements are given in terms of the phase shifts by $S_{ll'}(\varepsilon) = e^{2i\eta_l(\varepsilon)} \delta_{ll'}$ (cf equation (3.9)) and the density of states is related to the resolvent by

$$n(\varepsilon) = \sum_i \delta(\varepsilon - \varepsilon_i) = - \lim_{\eta \rightarrow 0^+} \frac{1}{\pi} \text{Im Tr}(\varepsilon - H + i\eta)^{-1} = - \frac{1}{\pi} \text{Im Tr} G(\varepsilon^+) \quad (10.8)$$

A very brief calculation then yields Friedel's formula (10.3).

For a cluster of scatterers, it's convenient to write the spectral displacement operator in terms of the on-shell elements of T matrix of the cluster as follows⁴:

$$\xi(\varepsilon) = - \frac{1}{\pi} \text{Im log}[\det T(\varepsilon)] \quad (10.9)$$

But the required matrix elements are given by (7.4) if we recall that the matrices defined in section 7 have a composite index running over sites and angular momenta. In this way, the Lloyd formula itself (10.1) is quickly obtained.

⁴ It takes a certain amount of manipulation to obtain this from the S matrix formula (10.6). It helps to proceed via the Wigner reaction matrix, which is Hermitian. See [7].

11 The Green's Function

This section derives the important formula for the multiple scattering Green's function in terms of the real space τ matrix. I follow the derivation given by Faulkner and Stocks⁹. This is a long and complicated derivation, but it is fully convincing. A briefer treatment is sketched in Peter Jewsbury's PhD thesis, but I suspect that if this were written out in full it would be rather long too. Still, it's odd that such an elegant and simple result needs such a lengthy derivation...

We start from the operator equations relating G to τ :

$$G = G_0 + G_0 T G_0 \quad (11.1)$$

$$T = \sum_{i,j} \tau^{ij} \quad (11.2)$$

$$\tau^{ij} = t^i \delta_{ij} + \sum_{k \neq i} t^i G_0 \tau^{kj} \quad (11.3)$$

The Faulkner/Stocks treatment considers two cases.

11.1 Case 1: r and r' lie near site n

We begin by obtaining an operator relation between G and the single scatterer Green's function G^n . From (11.1), (11.2) and (11.3)

$$\begin{aligned} G &= G_0 + G_0 \sum_{i,j} \tau^{ij} G_0 \\ &= G_0 + G_0 \sum_j \tau^{nj} G_0 + G_0 \sum_{i \neq n, j} \tau^{ij} G_0 \\ &= G_0 + G_0 \sum_j \left(t^n \delta_{nj} + t^n G_0 \sum_{i \neq n} \tau^{ij} \right) G_0 + G_0 \sum_{i \neq n, j} \tau^{ij} G_0 \\ &= G_0 + G_0 t^n G_0 + G_0 t^n G_0 \sum_{i \neq n, j} \tau^{ij} G_0 + G_0 \sum_{i \neq n, j} \tau^{ij} G_0 \end{aligned}$$

Thus, noting that the single-scatterer Green's function is

$$G^n = G_0 + G_0 t^n G_0 \quad (11.4)$$

we get

$$\begin{aligned} G &= G^n + G^n \sum_{i \neq n, j} \tau^{ij} G_0 \\ &= G^n + G^n \sum_{i \neq n, j \neq n} \tau^{ij} G_0 + G^n \sum_{i \neq n} \tau^{in} G_0 \end{aligned}$$

Now introduce T^{nm} :

$$T^{nm} = \sum_{i \neq n, j \neq n} \tau^{ij} \quad (11.5)$$

so that

$$\begin{aligned}
G &= G^n + G^n T^{nn} G_0 + G^n \sum_{i \neq n} \left(t^n \delta_{in} + \sum_{j \neq n} \tau^{ij} G_0 t^n \right) G_0 \\
&= G^n + G^n T^{nn} G_0 + G^n T^{nn} G_0 t^n G_0 \\
&= G^n + G^n T^{nn} (G_0 + G_0 t^n G_0)
\end{aligned}$$

Hence

$$G = G^n + G^n T^{nn} G^n \quad (11.6)$$

The next step is to put this equation into real space:

$$G(\mathbf{r}, \mathbf{r}') = G^n(\mathbf{r}, \mathbf{r}') + \sum_{i \neq n, j \neq n} \int d\mathbf{r}_1 \int d\mathbf{r}_2 G^n(\mathbf{r}, \mathbf{r}_1) \tau^{ij}(\mathbf{r}_1, \mathbf{r}_2) G^n(\mathbf{r}_2, \mathbf{r}') \quad (11.7)$$

For the single scatterer Green's function we can use the formula derived in section 3.2, namely

$$G^n(\mathbf{r}, \mathbf{r}') = \sum_L \left[\bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_L^n Z_L^n(\mathbf{r}' - \mathbf{R}_n) - \bar{Z}_L^n(\mathbf{r}_<) X_L^n(\mathbf{r}_>) \right] \quad (11.8)$$

where $r_>(r_<)$ is the greater (smaller) of $\mathbf{r} - \mathbf{R}_n$ and $\mathbf{r}' - \mathbf{R}_n$, and in which the energy dependence is left implicit. Inside the integrals, \mathbf{r}_1 runs only over site i and \mathbf{r}_2 runs only over site j , because the τ -matrix is zero otherwise. Thus \mathbf{r}_1 and \mathbf{r}_2 lie outside site n , and we can use the following expression for the single scatterer Green's function, which follows from (11.8) by using the forms to which the radial functions Z and J match at the muffin-tin radius:

$$G^n(\mathbf{r}, \mathbf{r}_1) = -ik \sum_L \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_L^n H_L^+(\mathbf{r}_1 - \mathbf{R}_n) \quad (11.9)$$

Now expand the Hankel function about site i using the Multiple Scatterer's Friend (see Appendix A: Notation and Mathematical Preliminaries)

$$-ik H_L^+(\mathbf{r}_1 - \mathbf{R}_n) = \sum_{L_1} g_{LL_1}^{ni} J_{L_1}(\mathbf{r}_1 - \mathbf{R}_i)$$

to obtain

$$G^n(\mathbf{r}, \mathbf{r}_1) = -ik \sum_L \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_L^n H_L^+(\mathbf{r}_1 - \mathbf{R}_n) \quad (11.10)$$

The same reasoning leads to

$$G^n(\mathbf{r}_2, \mathbf{r}') = \sum_{L', L_2} \bar{J}_{L_2}(\mathbf{r}_2 - \mathbf{R}_j) g_{L'L_2}^{jn} t_{L'}^n Z_{L'}^n(\mathbf{r}' - \mathbf{R}_n) \quad (11.11)$$

So, if we recall that the definition of the on-shell matrix elements of the τ -matrix (section 7) is

$$\tau_{L'L'}^{ij} = \int d\mathbf{r} \int d\mathbf{r}' J_{L'}(\mathbf{r} - \mathbf{R}_i) \tau^{ij}(\mathbf{r}, \mathbf{r}') \bar{J}_{L'}(\mathbf{r}' - \mathbf{R}_j)$$

we see that (11.7), (11.10) and (11.11) give

$$G(\mathbf{r}, \mathbf{r}') = G^n(\mathbf{r}, \mathbf{r}') + \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) \left[\sum_{i \neq n, j \neq n} \sum_{L_1, L_2} t_L^n g_{LL_1}^{ni} \tau_{L_1 L_2}^{ij} g_{L_2 L'}^{jn} t_{L'}^n \right] Z_{L'}^n(\mathbf{r}' - \mathbf{R}_n) \quad (11.12)$$

The final step is to do some manipulations on the τ -matrix equation (here we are really using the equation for the on-shell matrix elements, but we'll suppress the angular momentum indices for simplicity):

$$\tau^{nn} = t^n + \sum_{i \neq n} t^n g^{ni} \tau^{in}$$

with

$$\tau^{in} = \sum_{j \neq n} \tau^{ij} g^{jn} t^n \quad \text{if } i \neq n$$

Thus

$$\tau^{nn} = t^n + \sum_{i \neq n, j \neq n} t^n g^{ni} \tau^{ij} g^{jn} t^n \quad (11.13)$$

and

$$G(\mathbf{r}, \mathbf{r}') = G^n(\mathbf{r}, \mathbf{r}') + \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) (\tau_{LL'}^{nn} - t^n \delta_{LL'}) Z_{L'}^n(\mathbf{r}' - \mathbf{R}_n)$$

and comparison with (11.8) immediately gives

$$G(\mathbf{r}, \mathbf{r}') = \sum_{L, L'} (\bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) \tau_{LL'}^{nn} Z_{L'}^n(\mathbf{r}' - \mathbf{R}_n) - \bar{Z}_L^n(\mathbf{r}_<) X_L^n(\mathbf{r}_>) \delta_{LL'}) \quad (11.14)$$

11.2 Case 2: \mathbf{r} lies near site n and \mathbf{r}' lies near site m

As with case 1, we begin by deriving an operator relationship between G and single scatterer Green's functions G^n and G^m . Proceeding as before, we get

$$\begin{aligned} G &= G^n + G^n \sum_{i \neq n, j} \tau^{ij} G_0 \\ &= G^n + G^n \sum_{i \neq n} \tau^{im} G_0 + G^n \sum_{i \neq n, j \neq m} \tau^{ij} G_0 \end{aligned}$$

Now define

$$T^{nm} = \sum_{i \neq n, j \neq m} \tau^{ij} \quad (11.15)$$

and write

$$\begin{aligned} G &= G^n + G^n \sum_{i \neq n} \left(t^m \delta_{im} + \sum_{j \neq m} \tau^{ij} G_0 t^m \right) G_0 + G^n T^{nm} G_0 \\ &= G^n + G^n \sum_{i \neq n} t^m \delta_{im} G_0 + G^n T^{nm} (G_0 t^m G_0 + G_0) \\ &= G^n + G^n \sum_{i \neq n} t^m \delta_{im} G_0 + G^n T^{nm} G^m \end{aligned}$$

If $m = n$, the second term is zero and we recover (11.6). If $m \neq n$, then the second term counts and

$$\begin{aligned}
G &= G^n + G^n t^m G_0 + G^n T^{nm} G^m \\
&= (G_0 + G_0 t^n G_0) (1 + t^m G_0) + G^n T^{nm} G^m
\end{aligned}$$

Thus, defining

$$G^{nm} = (1 + G_0 t^n) G_0 (1 + t^m G_0) \quad (11.16)$$

we get

$$G = G^{nm} + G^n T^{nm} G^m \quad \text{iff } m \neq n \quad (11.17)$$

We now put this into real space and express the result in terms of the on-shell matrix elements of the τ matrix. This time we take the origin for \mathbf{r} to be site n and that for \mathbf{r}' to be site m . Then, working through just as in case 1, we get

$$G(\mathbf{r}, \mathbf{r}') = G^{nm}(\mathbf{r}, \mathbf{r}') + \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) (\tau_{LL'}^{nm} - t_l^n g_{LL'}^{nm} t_{l'}^m) Z_{L'}^m(\mathbf{r}' - \mathbf{R}_m) \quad (11.18)$$

Now consider G^{nm} in real space:

$$G^{nm}(\mathbf{r}, \mathbf{r}') = G^n(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}_1 \int d\mathbf{r}_2 G^n(\mathbf{r}, \mathbf{r}_1) t^m(\mathbf{r}_1, \mathbf{r}_2) G_0(\mathbf{r}_2, \mathbf{r}')$$

By hypothesis, \mathbf{r} lies in site n and \mathbf{r}' lies in site m . Moreover, the t matrix confines \mathbf{r}_1 and \mathbf{r}_2 to site m . Thus, as above, we can use

$$\begin{aligned}
G^n(\mathbf{r}, \mathbf{r}') &= -ik \sum_L \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_l^n H_L^+(\mathbf{r}' - \mathbf{R}_n) \\
&= \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_l^n g_{LL'}^{nm} J_{L'}(\mathbf{r}' - \mathbf{R}_m)
\end{aligned}$$

and

$$G^n(\mathbf{r}, \mathbf{r}_1) = \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_l^n g_{LL'}^{nm} J_L(\mathbf{r}_1 - \mathbf{R}_m)$$

Thus

$$G^{nm}(\mathbf{r}, \mathbf{r}') = \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_l^n g_{LL'}^{nm} \left\{ J_{L'}(\mathbf{r}' - \mathbf{R}_m) + \int d\mathbf{r}_1 \int d\mathbf{r}_2 J_{L'}(\mathbf{r}_1 - \mathbf{R}_m) t^m(\mathbf{r}_1, \mathbf{r}_2) G_0(\mathbf{r}_2, \mathbf{r}') \right\}$$

and the quantity in brackets can be recognised as the Lipmann-Schwinger equation for $t_{l'}^m Z_{L'}^m(\mathbf{r}' - \mathbf{R}_m)$. Hence

$$G^{nm}(\mathbf{r}, \mathbf{r}') = \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) t_l^n g_{LL'}^{nm} t_{l'}^m Z_{L'}^m(\mathbf{r}' - \mathbf{R}_m) \quad (11.19)$$

Comparing (11.19) with (11.18) we immediately find

$$G(\mathbf{r}, \mathbf{r}') = \sum_{L, L'} \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) \tau_{LL'}^{nm} Z_{L'}^m(\mathbf{r}' - \mathbf{R}_m) \quad (11.20)$$

11.3 Summary

From (11.14) and (11.20) we see that, taking both cases together,

$$G(\mathbf{r}, \mathbf{r}') = \sum_{L, L'} \left\{ \bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n) \tau_{LL'}^{nm} Z_{L'}^m(\mathbf{r}' - \mathbf{R}_m) - \bar{Z}_L^n(\mathbf{r}_<) X_L^n(\mathbf{r}_>) \delta_{LL'} \delta_{nm} \right\} \quad (11.21)$$

which is the desired result (cf (2.13)).

(11.21) is clearly valid when \mathbf{r} and \mathbf{r}' lie in sites n and m respectively. Faulkner and Stocks [10] claim that this derivation shows it to be valid *when \mathbf{r} and \mathbf{r}' lie in no site other than n and m respectively.*

12 The Local Density of States

Start with the fully \mathbf{r} -resolved density of states (the diagonal part of the density matrix)

$$\rho(\mathbf{r}, \varepsilon) = \sum_n |\psi_n(\mathbf{r})|^2 \delta(\varepsilon - \varepsilon_n) \quad (12.1)$$

But

$$G(\mathbf{r}, \mathbf{r}', \varepsilon^+) = \lim_{\eta \rightarrow 0^+} \sum_n \frac{\psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}')}{(\varepsilon - \varepsilon_n + i\eta)} \quad (12.2)$$

so that

$$\rho(\mathbf{r}, \varepsilon) = -\frac{1}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}, \varepsilon^+) \quad (12.3)$$

We can use the multiple scattering formula for the Green's function to evaluate this expression, but first we develop the idea that it may be useful to do this for complex energies. The clear analytical properties of all scattering quantities are among the many formal attractions of this theory, and have practical benefits too. For example, suppose we want to "smooth out" the energy-dependence of the density matrix by folding it with a Lorentzian of width γ :

$$\begin{aligned} \bar{\rho}(\mathbf{r}, \varepsilon) &= \int d\varepsilon' \rho(\mathbf{r}, \varepsilon') \frac{\gamma / \pi}{(\varepsilon' - \varepsilon)^2 + \gamma^2} \\ &= \int d\varepsilon' \sum_n |\psi_n(\mathbf{r})|^2 \delta(\varepsilon' - \varepsilon_n) \frac{\gamma / \pi}{(\varepsilon' - \varepsilon)^2 + \gamma^2} \\ &= \sum_n |\psi_n(\mathbf{r})|^2 \frac{\gamma / \pi}{(\varepsilon - \varepsilon_n)^2 + \gamma^2} \end{aligned} \quad (12.4)$$

But from (12.2) we can write

$$G(\mathbf{r}, \mathbf{r}', \varepsilon + i\gamma) = \sum_n \frac{\psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}')}{(\varepsilon - \varepsilon_n + i\gamma)}$$

and

$$\text{Im} G(\mathbf{r}, \mathbf{r}, \varepsilon + i\gamma) = -\sum_n \frac{|\psi_n(\mathbf{r})|^2 \gamma}{(\varepsilon - \varepsilon_n)^2 + \gamma^2}$$

Hence

$$\bar{\rho}(\mathbf{r}, \varepsilon) = -\frac{1}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}, \varepsilon + i\gamma) \quad (12.5)$$

Now make use of the multiple scattering Green's function, with the shorthand $E = \varepsilon + i\gamma$:

$$G(\mathbf{r}, \mathbf{r}', E) = \sum_{L, L'} \left(\bar{Z}_L^i(\mathbf{r} - \mathbf{R}_i, E) \tau_{LL'}^{ij}(E) Z_{L'}^j(\mathbf{r}' - \mathbf{R}_j, E) - \bar{Z}_L^i(\mathbf{r}_<, E) X_L^i(\mathbf{r}_>, E) \delta_{LL'} \delta_{ij} \right) \quad (12.6)$$

Defining the local density of states by spatially integrating the density matrix over a specified site i ,

$$\bar{n}^i(\varepsilon) = \int_{\text{site-}i} d\mathbf{r} \bar{\rho}(\mathbf{r}, \varepsilon) \quad (12.7)$$

we can use (12.5) to obtain

$$\bar{n}^i(\varepsilon) = -\frac{1}{\pi} \text{Im} \int_{\text{site-}i} d\mathbf{r} \left[\sum_{L,L'} (\bar{Z}_L^i(\mathbf{r}, E) \tau_{LL'}^{ii}(E) Z_{L'}^i(\mathbf{r}, E) - \bar{Z}_L^i(\mathbf{r}, E) X_L^i(\mathbf{r}, E) \delta_{LL'}) \right]$$

Assuming a spherical scatterer/site, the angular integral involving the implied spherical harmonics gives $\delta_{LL'}$, so that

$$\begin{aligned} \bar{n}^i(\varepsilon) &= -\frac{1}{\pi} \text{Im} \int_{\text{site-}i} drr^2 \left[\sum_L \left((z_L^i(r, E))^2 \tau_{LL}^{ii}(E) - z_L^i(r, E) x_L^i(r, E) \right) \right] \\ &= -\frac{1}{\pi} \text{Im} \sum_L \left[Q_L^i(E) \tau_{LL}^{ii}(E) - \tilde{Q}_L^i(E) \right] \end{aligned}$$

This suggests that an L -resolved local density of states be defined:

$$\bar{n}^i(\varepsilon) = \sum_L \bar{n}_L^i(\varepsilon) \quad (12.8)$$

where

$$\bar{n}_L^i(\varepsilon) = -\frac{1}{\pi} \text{Im} \left[Q_L^i(E) \tau_{LL}^{ii}(E) - \tilde{Q}_L^i(E) \right] \quad (12.9)$$

with

$$Q_L^i(E) = \int_{\text{site-}i} drr^2 (z_L^i(r, E))^2 \quad (12.10)$$

and

$$\tilde{Q}_L^i(E) = \int_{\text{site-}i} drr^2 z_L^i(r, E) x_L^i(r, E) \quad (12.11)$$

For completeness, note that (12.9) is the L -resolved local density of states. The l -resolved LDOS is given by

$$\begin{aligned} \bar{n}_l^i(\varepsilon) &= \sum_m \bar{n}_m^i(\varepsilon) \\ &= -\frac{1}{\pi} \text{Im} \left[Q_l^i(E) \sum_m \tau_{ll}^{ii}(E) - (2l+1) \tilde{Q}_l^i(E) \right] \end{aligned} \quad (12.12)$$

All this is for complex energies $E = \varepsilon + i\gamma$, and all densities of states are “smoothed” in the sense defined above. The radial functions z and x are thus complex and all terms in (12.12) contribute. In numerical calculations (12.12) gives positive values for the LDOS, as the definition (12.4) demands. The standard formulae for the unsmoothed LDOS are immediately obtained by setting $\gamma=0$, when E becomes real as do the radial functions z and x , and the imaginary part of the irregular term given by (12.11) vanishes.

13 The Bloch Spectral Function

Consider a periodic crystal lattice. For such a system, the energy eigenvalues, as a function of crystal momentum \mathbf{k} , are the energy bands of conventional electronic structure theory. The Bloch spectral function provides another very convenient multiple scattering description of the \mathbf{k} -resolved electronic structure, one which can be generalised to some non-crystalline systems such as substitutionally disordered lattices (see [10]).

According to Faulkner and Stocks [10], the Bloch spectral function is defined by

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \text{Im} \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \int_{\text{cell } 0} d\mathbf{r}_0 G(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{R}_n; \varepsilon) \quad (13.1)$$

in which \mathbf{R}_n is a lattice vector and the Green's function is assumed to satisfy a periodicity condition

$$G(\mathbf{r} + \mathbf{R}_n, \mathbf{r}' + \mathbf{R}_n; \varepsilon) = G(\mathbf{r}, \mathbf{r}'; \varepsilon) \quad (13.2)$$

This is always true for an ordered crystal, and also for the configurationally averaged Green's function of a substitutionally disordered crystal.

If we use the eigenfunction expansion of the Green's function using Bloch states $\psi_{\mathbf{k}, \nu}$ for an ordered crystal

$$G(\mathbf{r}, \mathbf{r}'; \varepsilon) = \sum_{\mathbf{k}, \nu} \frac{\psi_{\mathbf{k}, \nu}(\mathbf{r}) \psi_{\mathbf{k}, \nu}^*(\mathbf{r}')}{\varepsilon - \varepsilon_{\mathbf{k}, \nu} + i\eta}$$

in which

$$\psi_{\mathbf{k}, \nu}(\mathbf{r}) = u_{\mathbf{k}, \nu}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad u_{\mathbf{k}, \nu}(\mathbf{r}) \text{ being periodic: } u_{\mathbf{k}, \nu}(\mathbf{r} + \mathbf{R}_n) = u_{\mathbf{k}, \nu}(\mathbf{r}),$$

we find

$$\begin{aligned} G(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{R}_n; \varepsilon) &= \sum_{\mathbf{k}', \nu} \frac{u_{\mathbf{k}', \nu}(\mathbf{r}_0) u_{\mathbf{k}', \nu}^*(\mathbf{r}_0)}{\varepsilon - \varepsilon_{\mathbf{k}', \nu} + i\eta} e^{i\mathbf{k}' \cdot (\mathbf{r}_0 - \mathbf{r}_0 - \mathbf{R}_n)} \\ &= \sum_{\mathbf{k}', \nu} \frac{|u_{\mathbf{k}', \nu}(\mathbf{r}_0)|^2}{\varepsilon - \varepsilon_{\mathbf{k}', \nu} + i\eta} e^{-i\mathbf{k}' \cdot \mathbf{R}_n} \end{aligned}$$

Hence, from (13.1)

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \text{Im} \sum_{\mathbf{k}', \nu} \int_{\text{cell } 0} d\mathbf{r}_0 |u_{\mathbf{k}', \nu}(\mathbf{r}_0)|^2 \sum_n \frac{e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_n}}{\varepsilon - \varepsilon_{\mathbf{k}', \nu} + i\eta}$$

But

$$\sum_n e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_n} = N \sum_{\mathbf{g}} \delta_{\mathbf{k}', \mathbf{k} + \mathbf{g}}$$

\mathbf{g} being a reciprocal lattice vector. Now if the Bloch functions are normalised over the crystal:

$$1 = \int d\mathbf{r} |\psi_{\mathbf{k}, \nu}(\mathbf{r})|^2 = \sum_i \int_{\text{cell } i} d\mathbf{r}_i |u_{\mathbf{k}, \nu}(\mathbf{r}_i)|^2 = N \int_{\text{cell } 0} d\mathbf{r}_0 |u_{\mathbf{k}, \nu}(\mathbf{r}_0)|^2$$

we get

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \text{Im} \sum_{\mathbf{g}, \nu} \frac{1}{N} \frac{N}{\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{g}, \nu} + i\eta} = \sum_{\mathbf{g}, \nu} \delta(\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{g}, \nu}) \quad (13.3)$$

Thus, for an ordered crystal the spectral function takes the form of a set of delta functions mapping out the band structure. If the energy bands are given in the reduced zone scheme this reads simply

$$A_B(\mathbf{k}, \varepsilon) = \sum_{\nu} \delta(\varepsilon - \varepsilon_{\mathbf{k}, \nu}) \quad (13.4)$$

The band energies $\varepsilon_{\mathbf{k}, \nu}$ are, of course, just the eigenvalues that are found in KKR theory (see section 9.2).

We now return to equation (13.1) and obtain a multiple scattering formula for the spectral function using

$$G(\mathbf{r}, \mathbf{r}'; \varepsilon) = \sum_{L, L'} (\bar{Z}_L^n(\mathbf{r} - \mathbf{R}_n, \varepsilon) \tau_{LL'}^{nm}(\varepsilon) Z_{L'}^m(\mathbf{r}' - \mathbf{R}_m, \varepsilon) - \bar{Z}_L^n(\mathbf{r}_<, \varepsilon) X_L^n(\mathbf{r}_>, \varepsilon) \delta_{LL'} \delta_{nm}) \quad (13.5)$$

Suppose the crystal is monatomic; then we can drop the site labels on the single scatterer functions Z and X . Note also that since these functions are, by definition, real (for real energies), we can ignore the last term in (13.5). Defining

$$a_{LL'}(\varepsilon) = \int_{\text{cell } 0} d\mathbf{r}_0 \bar{Z}_L(\mathbf{r}_0, \varepsilon) Z_{L'}(\mathbf{r}_0, \varepsilon) \quad (13.6)$$

we obtain

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \text{Im} \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \sum_{LL'} a_{LL'}(\varepsilon) \tau_{LL'}^{0n}(\varepsilon)$$

But this contains the lattice Fourier transform of the τ matrix:

$$\tau_{LL'}(\mathbf{k}, \varepsilon) = \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} \tau_{LL'}^{0n}(\varepsilon) \quad (13.7)$$

So, the multiple scattering formula for the Bloch spectral function of a monatomic ordered crystal is

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \sum_{LL'} a_{LL'}(\varepsilon) \text{Im} \tau_{LL'}(\mathbf{k}, \varepsilon) \quad (13.8)$$

KKR theory (section 9.2) ensures that $\text{Im} \tau(\mathbf{k}, \varepsilon)$ has exactly the pole structure defining the energy bands needed to agree with equation (13.4).

The generalisation to an ordered multi-atomic crystal is clear. Let the distinct atoms within the unit cell be labelled α, β , etc. The lattice Fourier transform eliminates the spatial coordinates relating to the origin of each unit cell, and both the $\tau_{LL'}$ and $a_{LL'}$ matrices in (13.8) now become matrices in α, β , etc also. Thus

$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \sum_{\alpha\beta} \sum_{LL'} a_{LL'}^{\alpha\beta}(\varepsilon) \text{Im} \tau_{LL'}^{\alpha\beta}(\mathbf{k}, \varepsilon) \quad (13.9)$$

and the spectral function breaks up into components relating to both site and angular momentum.

14 Reference Systems

Consider the on-shell τ matrix equation, defined in section 7,

$$\boldsymbol{\tau} = (\mathbf{t}^{-1} - \tilde{\mathbf{g}})^{-1} \quad (14.1)$$

Now add and subtract the inverse of a single-site t -matrix t_R describing a reference system:

$$\boldsymbol{\tau} = (\mathbf{t}^{-1} - \mathbf{t}_R^{-1} + \mathbf{t}_R^{-1} - \tilde{\mathbf{g}})^{-1} \quad (14.2)$$

This may be associated with a single-site *potential*, but it doesn't have to be. The reference system is defined for our purposes as that system which has the τ matrix τ_R , given by

$$\boldsymbol{\tau}_R = (\mathbf{t}_R^{-1} - \tilde{\mathbf{g}})^{-1} \quad (14.3)$$

Clearly, using (14.3) in (14.2), we can write

$$\begin{aligned} \boldsymbol{\tau} &= (\boldsymbol{\tau}_R^{-1} - \Delta)^{-1} \\ &= \boldsymbol{\tau}_R + \boldsymbol{\tau}_R \Delta \boldsymbol{\tau} \end{aligned} \quad (14.4)$$

where

$$\Delta = \mathbf{t}_R^{-1} - \mathbf{t}^{-1} \quad (14.5)$$

(14.4) looks like a Dyson equation and has the formal solution

$$\boldsymbol{\tau} = \boldsymbol{\tau}_R + \boldsymbol{\tau}_R \mathbf{K} \boldsymbol{\tau}_R \quad (14.6)$$

where

$$\mathbf{K} = \Delta + \Delta \boldsymbol{\tau}_R \mathbf{K} \quad (14.7)$$

Clearly the K matrix is given by

$$\mathbf{K} = (\Delta^{-1} - \boldsymbol{\tau}_R)^{-1} \quad (14.8)$$

Equations (14.3), (14.6) and (14.8) show how to express the τ matrix in terms of that of a reference system. This turns out to be useful when the reference system can be chosen to have especially convenient properties and to be close to the real system. Examples are the KKRCPA [12] and Swiss cheese.

Zeller et al [8] derive a similar set of equations using what they term the "structural Green's function matrix" \mathbf{G} , which is extremely close to the τ matrix and is given in the implied site and angular momentum representation by

$$\mathbf{G} = \tilde{\mathbf{g}} + \tilde{\mathbf{g}} \mathbf{t} \mathbf{G}$$

which is to be compared with

$$\boldsymbol{\tau} = \mathbf{t} + \mathbf{t} \tilde{\mathbf{g}} \boldsymbol{\tau}$$

It is easy to see by iterating these equations that the relationship between the two quantities is just

$$\begin{aligned} \mathbf{G} &= \tilde{\mathbf{g}} + \tilde{\mathbf{g}} \boldsymbol{\tau} \tilde{\mathbf{g}} \\ \boldsymbol{\tau} &= \mathbf{t} + \mathbf{t} \mathbf{G} \mathbf{t} \end{aligned}$$

For completeness, the following table gives parallel “skeleton” derivations of the present equations and those of Zeller et al:

This treatment	Zeller et al
$\boldsymbol{\tau} = (\mathbf{t}^{-1} - \tilde{\mathbf{g}})^{-1}$	$\mathbf{G} = \tilde{\mathbf{g}}(\mathbf{1} - \mathbf{t}\tilde{\mathbf{g}})^{-1}$
$\boldsymbol{\tau}_R = (\mathbf{t}_R^{-1} - \tilde{\mathbf{g}})^{-1}$	$\mathbf{G}_R = \tilde{\mathbf{g}}(\mathbf{1} - \mathbf{t}_R\tilde{\mathbf{g}})^{-1}$
Hence	Hence
$\boldsymbol{\tau}^{-1} = \mathbf{t}^{-1} - \tilde{\mathbf{g}}$	$\mathbf{G}^{-1} = \tilde{\mathbf{g}}^{-1} - \mathbf{t}$
$\boldsymbol{\tau}_R^{-1} = \mathbf{t}_R^{-1} - \tilde{\mathbf{g}}$	$\mathbf{G}_R^{-1} = \tilde{\mathbf{g}}^{-1} - \mathbf{t}_R$
and	and
$\boldsymbol{\tau}^{-1} = \boldsymbol{\tau}_R^{-1} - \Delta$	$\mathbf{G}^{-1} = \mathbf{G}_R^{-1} - \delta\mathbf{t}$
where	where
$\Delta = \mathbf{t}_R^{-1} - \mathbf{t}^{-1}$	$\delta\mathbf{t} = \mathbf{t} - \mathbf{t}_R$
Thus	Thus
$\boldsymbol{\tau} = \boldsymbol{\tau}_R + \boldsymbol{\tau}_R \Delta \boldsymbol{\tau}$	$\mathbf{G} = \mathbf{G}_R + \mathbf{G}_R \delta\mathbf{t} \mathbf{G}$
Formally	Formally
$\boldsymbol{\tau} = \boldsymbol{\tau}_R + \boldsymbol{\tau}_R \mathbf{K} \boldsymbol{\tau}_R$	$\mathbf{G} = \mathbf{G}_R + \mathbf{G}_R \boldsymbol{\tau}_\delta \mathbf{G}_R$
where	where
$\mathbf{K} = \Delta + \Delta \boldsymbol{\tau}_R \mathbf{K}$ $= (\Delta^{-1} - \boldsymbol{\tau}_R)^{-1}$	$\boldsymbol{\tau}_\delta = \delta\mathbf{t} + \delta\mathbf{t} \mathbf{G}_R \boldsymbol{\tau}_\delta$ $= (\delta\mathbf{t}^{-1} - \mathbf{G}_R)^{-1}$

For some applications, especially in deriving the KKRPCA and its fluctuation formulae [12], it is helpful to do a little more development. Writing out the site indices in (14.7) and defining

$$\Delta^i \equiv (\mathbf{t}_R^i)^{-1} - (\mathbf{t}^i)^{-1} \quad (14.9)$$

gives

$$K^{ij} = \Delta^i \delta_{ij} + \sum_n \Delta^i \tau_r^{in} K^{nj}$$

Following the standard manipulations (see section 6) it is obvious that

$$K^{ij} = k^i \delta_{ij} + \sum_{n \neq i} k^i \tau_r^{in} K^{nj} \quad (14.10)$$

where

$$k^i \equiv \left[\mathbf{1} - \Delta^i \tau_r^{ij} \right]^{-1} \Delta^i \quad (14.11)$$

or, reverting to matrix notation,

$$\mathbf{K} = \left[\mathbf{k}^{-1} - \tilde{\boldsymbol{\tau}}_R \right]^{-1} \quad (14.12)$$

where

$$\begin{aligned} [\mathbf{k}]_{ij} &= k^i \delta_{ij} \\ [\tilde{\boldsymbol{\tau}}_R]_{ij} &= \tau_r^{ij} (1 - \delta_{ij}) \end{aligned} \quad (14.13)$$

1.1 The single impurity problem

Consider a lattice of pure A atoms, each described by a t-matrix t_A . Its τ matrix can be found by the KKR methods outlined in section 9.2:

$$\tau_A^{ij} = \int d\mathbf{q} e^{i\mathbf{q} \cdot \mathbf{R}_{ij}} \tau_A(\mathbf{q}) \quad \tau_A(\mathbf{q}) = \left[\mathbf{t}_A^{-1} - \tilde{\mathbf{g}}(\mathbf{q}) \right] \quad (14.14)$$

Now imagine that the atom on site 0 is replaced by a B atom with t-matrix t_B . In the language of this section, we take the reference system to be the pure A lattice, and express the τ matrix of the impurity system in terms of τ_A by means of (14.4) and (14.5). From (14.4) we have

$$\tau^{ij} = \tau_A^{ij} + \sum_{m,n} \tau_A^{im} \Delta^{mn} \tau^{nj} = \tau_A^{ij} + \sum_{m,n} \tau^{im} \Delta^{mn} \tau_A^{nj}$$

where

$$\Delta^{mn} = \Delta \delta_{mn} \delta_{m0} \quad \Delta = (t_A^{-1} - t_B^{-1})$$

Thus, for our impurity system, the τ matrix is given by

$$\tau^{ij} = \tau_A^{ij} + \tau_A^{i0} \Delta \tau^{0j} = \tau_A^{ij} + \tau^{i0} \Delta \tau_A^{0j} \quad (14.15)$$

It is now very easy to give the full solution of (14.15) by working out the following four cases:

$$\begin{aligned} \tau^{00} &= \left[\mathbf{1} - \tau_A^{00} (t_A^{-1} - t_B^{-1}) \right]^{-1} \tau_A^{00} \\ \tau^{i0} &= \tau_A^{i0} \left[\mathbf{1} - (t_A^{-1} - t_B^{-1}) \tau_A^{00} \right]^{-1} & i \neq 0 \\ \tau^{0j} &= \left[\mathbf{1} - \tau_A^{00} (t_A^{-1} - t_B^{-1}) \right]^{-1} \tau_A^{0j} & j \neq 0 \\ \tau^{ij} &= \tau_A^{ij} + \tau_A^{i0} (t_A^{-1} - t_B^{-1}) \left[\mathbf{1} - \tau_A^{00} (t_A^{-1} - t_B^{-1}) \right]^{-1} \tau_A^{0j} & i, j \neq 0 \end{aligned} \quad (14.16)$$

It's satisfying that this reference system formalism gives such a rapid solution for the full τ matrix of the impurity system [12]. Most treatments (see [13], for examples) content themselves with solving for the site-diagonal element τ^{00} .

1.2 The coherent potential approximation in multiple scattering theory – the KKRCPA

A random substitutional alloy has a regular lattice the sites of which are occupied randomly by A atoms and B atoms with probabilities c and $1-c$ respectively; c is the *concentration* of A in the alloy. Examples are Cu-Ni, Ag-Pd and so on. How to calculate the electronic structure of such a disordered system? The coherent potential approximation is one (good) approach. The goal of the CPA is to define an effective ordered system that describes the electronic structure averaged over all possible alloy configurations. Now in MST, an ordered system has translational symmetry; in the simplest cases each of the lattice sites is occupied by the same kind of effective scatterer, described by a t-matrix t_c . To mimic a disordered system, the effects of disorder must somehow be smuggled into t_c . The CPA does this by a kind of mean field argument:

1. Take the effective, ie coherent, lattice on which every site has scatterer t_c and the system as a whole has τ matrix τ_c , and replace the atom on site 0 by a real A atom. Calculate the τ matrix of this impurity system in terms of t_c , τ_c and t_A . Call the result $\tau^A(t_c, t_A)$; it's clearly a function of t_c and t_A .
2. Repeat with a B impurity at site 0 to obtain $\tau^B(t_c, t_B)$.
3. Determine t_c by requiring that the single-site average of the two impurity τ matrices is equal to τ_c

$$c\tau^{A,00} + (1-c)\tau^{B,00} = \tau_c^{00} \quad (14.17)$$

This requires a self-consistency cycle: guess an initial t_c as input to a calculation of the τ matrices of the coherent lattice and the impurity systems using (9.4) and (14.16), then use (14.17) to generate an output t_c , and keep going until output equals input.

Clearly, the impurity results (14.16) are the key to making this scheme possible. What you find, interestingly, is that the resulting coherent t-matrix t_c corresponds to a *complex* potential. Thus, amongst other things, repeated scatterings lead to something like a mean free path for the electrons and the energy bands are smeared out as a function of wave-vector⁵. A final comment is that while the KKRCPA condition (14.17) pertains only to the diagonal element at the impurity site 0, it can be shown [12] from (14.16) that the t_c thus obtained guarantees that all the elements of the τ matrices satisfy the KKRCPA condition, which can thus be written in matrix form:

$$c\tau^A + (1-c)\tau^B = \tau_c \quad (14.18)$$

⁵ This means that one can't define bands – energy versus momentum relations – at all. But the Bloch spectral function (section 13) now comes into its own as the right way to describe the average electronic structure, Fermi surfaces etc.

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Appendix A: Notation and Mathematical Preliminaries

Notation

Here are some details of the notation used in these notes. Most of these are standard. The dependence of most quantities on energy is usually suppressed, unless explicitly required.

Angular momentum

$$\begin{aligned} L &\equiv (l, m) \\ \bar{L} &\equiv (l, -m) \end{aligned} \tag{A1}$$

Bessel functions

The forms defined in Schiff [2] are used, but the argument is just written as r , rather than the strictly correct $r\sqrt{\varepsilon}$, just to simplify equations.

Free space solutions

For notational simplicity, we define upper case Bessel functions (with vector arguments) as follows:

$$J_L(\mathbf{r}) = j_l(r) Y_L(\hat{\mathbf{r}}) \tag{A2}$$

and likewise for Neumann and Hankel functions. Even though the radial functions may be real, the vector function is complex because of the spherical harmonic. We use the following notation to denote this:

$$\bar{J}_L(\mathbf{r}) = j_l(r) Y_L^*(\hat{\mathbf{r}}) \tag{A3}$$

Single-scatterer solutions

In a similar way, the following types of single-scatterer solution are used

$$\begin{aligned} Z_L(\mathbf{r}) &= z_l^i(r) Y_L(\hat{\mathbf{r}}) \\ \bar{Z}_L(\mathbf{r}) &= z_l^i(r) Y_L^*(\hat{\mathbf{r}}) \end{aligned} \tag{A4}$$

Spherical harmonics

The forms defined by Pendry ([4], p268) are used. These are complex functions with the well-known non-analyticity

$$Y_L^*(\hat{\mathbf{r}}) = (-1)^m Y_L(\hat{\mathbf{r}}) \tag{A5}$$

Further useful relations include:

Inversion:

$$Y_l(-\hat{\mathbf{r}}) = Y_l(\pi - \vartheta, \phi + \pi) = (-1)^l Y_l(\hat{\mathbf{r}}) \quad (\text{A6})$$

Orthonormality:

$$\int d\hat{\mathbf{r}} Y_l^*(\hat{\mathbf{r}}) Y_{l'}(\hat{\mathbf{r}}) = \delta_{ll'} \quad (\text{A7})$$

Addition theorem:

$$\sum_m Y_l^*(\hat{\mathbf{r}}) Y_l(\hat{\mathbf{r}}') = \frac{2l+1}{4\pi} P_l(\cos \alpha) \quad (\text{A8})$$

α being the angle between \mathbf{r} and \mathbf{r}' . Here P_l is a Legendre polynomial. A special case of this is the

Sum rule:

$$\sum_m |Y_l(\hat{\mathbf{r}})|^2 = \frac{2l+1}{4\pi} \quad (\text{A9})$$

Wigner 3J symbols

The general 3J symbol obeys the triangle rules:

$$\begin{pmatrix} l & l' & l'' \\ m & m' & m'' \end{pmatrix} = 0 \quad \text{unless } |l-l'| \leq l'' \leq l+l' \text{ and } m+m'+m''=0 \quad (\text{A10})$$

A parity rule also applies to the special symbol

$$\begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} = 0 \quad \text{unless } l+l'+l'' = \text{even} \quad (\text{A11})$$

When these conditions hold, the explicit formulae for the 3J symbols (taken from Brink and Satchler [9], p.34) are as follows:

$$\begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} = (-1)^g \frac{g!}{(g-l)!(g-l')!(g-l'')} \Delta(l, l', l'') \quad (\text{A12})$$

and

$$\begin{pmatrix} l & l' & l'' \\ m & m' & m'' \end{pmatrix} = \frac{(-1)^{l'-m''}}{(2l''+1)^{1/2}} \Delta(l, l', l'') F(L, L', L'') S(L, L', l'') \quad (\text{A13})$$

where $2g = l+l'+l''$ (note that the parity rule (A11) means that g is an integer in (A12)), and

$$\Delta(l, l', l'') = \left[\frac{(l+l'-l'')!(l+l''-l')!(l'+l''-l)!}{(l+l'+l''+1)!} \right]^{1/2}$$

$$F(L, L', L'') = [(2l''+1)(l+m)!(l-m)!(l'+m')!(l'-m')!(l''+m'')!(l''-m'')]^{1/2}$$

$$S(L, L', L'') = \sum_n (-1)^n [(l-m-n)!(l''-l'+m+n)!(l'+m'-n)!(l''-l-m'+n)!n!(l+l'-l''-n)!]^{-1}$$

in which n runs over all integers which do not lead to negative factorials. Further useful properties include

Orthogonality:

$$\sum_{l_1 l_2} (2l_3 + 1) \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \delta_{l_3 l'_3} \delta_{m_3 m'_3} \quad (\text{A14})$$

$$\sum_{l_3 m_3} (2l_3 + 1) \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m'_1 & m'_2 & m_3 \end{pmatrix} = \delta_{m_1 m'_1} \delta_{m_2 m'_2} \quad (\text{A15})$$

Symmetry:

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{l_1+l_2+l_3} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (\text{A16})$$

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} l_2 & l_3 & l_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = (-1)^{l_1+l_2+l_3} \begin{pmatrix} l_2 & l_1 & l_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \quad (\text{A17})$$

Gaunt numbers

The Gaunt number defined by

$$C(L, L', L'') = \int d\hat{r} Y_L(\hat{r}) Y_{L'}(\hat{r}) Y_{L''}(\hat{r}) \quad (\text{A18})$$

is clearly invariant under any interchange between the L s. Reversing the direction of the variable of integration and using (A6) gives

$$C(L, L', L'') = (-1)^{l+l'+l''} C(L, L', L'') \quad (\text{A19})$$

Hence the sum of the l s must be even, as guaranteed by the parity rule (A11) for the 3J symbols occurring in the explicit formula

$$C(L, L', L'') = \left[\frac{(2l+1)(2l'+1)(2l''+1)}{4\pi} \right] \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l' & l'' \\ m & m' & m'' \end{pmatrix} \quad (\text{A20})$$

Clearly, then, the Gaunt Number also conforms to the triangle rules (A10). Because the 3J symbols (and therefore the Gaunt numbers) are real (*Why? see Brink and Satchler [9], p.34*) this gives another useful relation:

$$\begin{aligned} C(L, L', L'') &= \int d\hat{r} Y_L^*(\hat{r}) Y_{L'}^*(\hat{r}) Y_{L''}^*(\hat{r}) \\ &= (-1)^{m+m'+m''} C(\bar{L}, \bar{L}', \bar{L}'') \end{aligned}$$

Hence

$$C(L, L', L'') = C(\bar{L}, \bar{L}', \bar{L}'') \quad (\text{A21})$$

which is also evident from (A16).

The Multiple Scatterer's Friend(s)

The standard Multiple Scatterer's Friend⁶ expands a Hankel function centred on one site in terms of Bessel functions centred on another site. In fact, as quoted by Lloyd and Smith [1] (p. 89), there is a family of similar relations:

$$J_L(\mathbf{r} - \mathbf{R}) = \sum_{L'} d_{LL'}(\mathbf{R}) J_{L'}(\mathbf{r}) \quad (\text{A22})$$

$$H_L^+(\mathbf{r} - \mathbf{R}) = \sum_{L'} d_{LL'}(\mathbf{R}) H_{L'}^+(\mathbf{r}) \text{ for } |\mathbf{r}| > |\mathbf{R}| \quad (\text{A23})$$

$$-ikH_L^+(\mathbf{r} - \mathbf{R}) = \sum_{L'} g_{LL'}(\mathbf{R}) H_{L'}(\mathbf{r}) \text{ for } |\mathbf{r}| < |\mathbf{R}| \quad (\text{A24})$$

(A24) is the form most often used in multiple scattering theory. Here

$$g_{LL'}(\mathbf{R}) = -4\pi ik(-1)^m i^{(l'-l)} \sum_{L_1} i^{-L_1} C(\bar{L}, L', L_1) H_{L_1}^+(\mathbf{R}) \quad (\text{A25})$$

and

$$d_{LL'}(\mathbf{R}) = 4\pi(-1)^m i^{(l'-l)} \sum_{L_1} i^{-L_1} C(\bar{L}, L', L_1) J_{L_1}(\mathbf{R}) \quad (\text{A26})$$

⁶ I recall that John Pendry once told me that this term was coined by Paul Marcus. It stuck with me.

Appendix B: Notes on Spherical Bessel Functions

Properties

Taken from the book “Nonrelativistic Quantum Mechanics” by A Z Capri. Checked against Schiff’s “Quantum Mechanics” and J R Taylor’s “Scattering Theory” (which uses Riccati-Bessel functions). In this appendix, the function z_l stands for *any* of the four functions $j_l, n_l, h_l^{(1)}, h_l^{(2)}$ related by

$$h_l^{(1)} = j_l + in_l$$

$$h_l^{(2)} = j_l - in_l$$

Differential equation $\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + k^2 \right] z_l(kr) = 0$

Wronskian $W(x) = j_l(x) \frac{dn_l(x)}{dx} - n_l(x) \frac{dj_l(x)}{dx} = \frac{1}{x^2}$

Integral representation $z_l(x) = \frac{x^l}{2^{(l+1)} l!} \int_{-1}^1 (1-t^2)^l \cos(xt) dt$

Recursion formulae

$$\left. \begin{aligned} z_{l-1} + z_{l+1} &= \left(\frac{2l+1}{x} \right) z_l \\ \frac{dz_l}{dx} &= z_{l-1} - \left(\frac{l+1}{x} \right) z_l \\ j_l(x)n_{l-1}(x) - n_l(x)j_{l-1}(x) &= \frac{1}{x^2} \\ \frac{d}{dx} [x^{l+1}z_l] &= x^{l+1}z_{l-1} \end{aligned} \right\} l > 0$$

$$\frac{d}{dx} [x^{-l}z_l] = -x^{-l}z_{l+1}$$

$$z_l = \left(\frac{l-1}{x} - \frac{d}{dx} \right) z_{l-1}$$

$$z_l = -x^{(l-1)} \frac{d}{dx} \left(\frac{z_{l-1}}{x^{(l-1)}} \right)$$

Generator

$$z_l = x^l \left(-\frac{1}{x} \frac{d}{dx} \right)^l z_0$$

Asymptotic behaviour

As $x \rightarrow \infty$:

$$j_l(x) \rightarrow \frac{1}{x} \sin \left(x - \frac{l\pi}{2} \right) = \frac{1}{x} \cos \left(x - \frac{(l+1)\pi}{2} \right)$$

$$n_l(x) \rightarrow -\frac{1}{x} \cos \left(x - \frac{l\pi}{2} \right) = \frac{1}{x} \sin \left(x - \frac{(l+1)\pi}{2} \right)$$

Numerical tests show that convergence to these asymptotic limits is slow; apart from the trivial case of $l=0$, only about 3-figure accuracy is obtained at $x=10^4$.

As $x \rightarrow 0$:

$$j_l(x) \rightarrow \frac{x^l}{(2l+1)!!}$$

$$n_l(x) \rightarrow -\frac{(2l-1)!!}{x^{l+1}}$$

Numerical tests show that these asymptotic formulae give 7-figure accuracy for $x \leq 5 \times 10^{-4}$.

Relationship to standard cylinder functions

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

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

Some integrals

$$\int j_0(x)^2 x^2 dx = \frac{1}{2} x^3 \left[j_0(x)^2 + n_0(x) j_1(x) \right]$$

$$\int n_0(x)^2 x^2 dx = \frac{1}{2} x^3 \left[n_0(x)^2 - j_0(x) n_1(x) \right]$$

$$\int j_l(x)^2 x^2 dx = \frac{1}{2} x^3 \left[j_l(x)^2 - j_{l-1}(x) j_{l+1}(x) \right] \quad l > 0$$

$$\int j_0(x)x^2 dx = x^2 j_1(x)$$

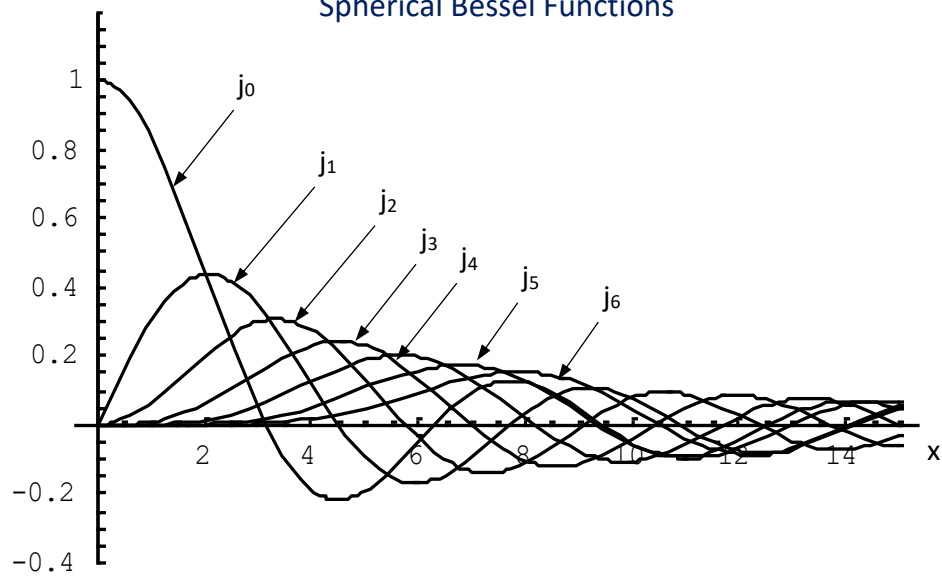
$$\int j_1(x) dx = -j_0(x)$$

Explicit Formulae

$l=0$	$j_0 = \frac{1}{x} \sin(x)$ $n_0 = -\frac{1}{x} \cos(x)$
$l=1$	$j_1 = \frac{1}{x^2} \sin(x) - \frac{1}{x} \cos(x)$ $n_1 = -\frac{1}{x} \sin(x) - \frac{1}{x^2} \cos(x)$
$l=2$	$j_2 = \left(\frac{3}{x^3} - \frac{1}{x} \right) \sin(x) - \frac{3}{x^2} \cos(x)$ $n_2 = -\frac{3}{x^2} \sin(x) - \left(\frac{3}{x^3} - \frac{1}{x} \right) \cos(x)$
$l=3$	$j_3 = \left(\frac{15}{x^4} - \frac{6}{x^2} \right) \sin(x) - \left(\frac{15}{x^3} - \frac{1}{x} \right) \cos(x)$ $n_3 = \left(-\frac{15}{x^3} + \frac{1}{x} \right) \sin(x) + \left(-\frac{15}{x^4} + \frac{6}{x^2} \right) \cos(x)$
$l=4$	$j_4 = \left(\frac{105}{x^5} - \frac{45}{x^3} + \frac{1}{x} \right) \sin(x) + \left(-\frac{105}{x^4} + \frac{10}{x^2} \right) \cos(x)$ $n_4 = \left(-\frac{105}{x^4} + \frac{10}{x^2} \right) \sin(x) + \left(-\frac{105}{x^5} + \frac{45}{x^3} - \frac{1}{x} \right) \cos(x)$
$l=5$	$j_5 = \left(\frac{945}{x^6} - \frac{420}{x^4} + \frac{15}{x^2} \right) \sin(x) + \left(-\frac{945}{x^5} + \frac{105}{x^3} - \frac{1}{x} \right) \cos(x)$ $n_5 = \left(-\frac{945}{x^5} + \frac{105}{x^3} - \frac{1}{x} \right) \sin(x) + \left(-\frac{945}{x^6} + \frac{420}{x^4} - \frac{15}{x^2} \right) \cos(x)$
$l=6$	$j_6 = \left(\frac{10395}{x^7} - \frac{4725}{x^5} + \frac{210}{x^3} - \frac{1}{x} \right) \sin(x) + \left(-\frac{10395}{x^6} + \frac{1260}{x^4} - \frac{21}{x^2} \right) \cos(x)$ $n_6 = \left(-\frac{10395}{x^6} + \frac{1260}{x^4} - \frac{21}{x^2} \right) \sin(x) + \left(-\frac{10395}{x^7} + \frac{4725}{x^5} - \frac{210}{x^3} + \frac{1}{x} \right) \cos(x)$

These functions are depicted in the following figures.

Spherical Bessel Functions



Spherical Neumann Functions

