Multiple-scattering theory

Christian Brouder

19 décembre 2002

Résumé : This chapter introduces the reader to the formalism of the multiple-scattering theory in the real space. After a description of the Green function for a general potential, the calculation of the Green function for a set of scatterers is described.

1 Introduction

At first, the multiple-scattering theory was not really a physical model. It was a mathematical method to solve the Schrödinger equation for a general potential. Therefore, the range of validity of the multiple-scattering method is that of the one-electron model. Thus, it applies to delocalised electronic states, and is a basis for band-structure calculation of solids or molecular orbital calculation of molecules. It enables us to calculate wavefunctions and Green function for bound and scattering states, as well as all one-electron quantities, such as density of states or x-ray absorption spectra. After many years of experience, it is now clear the multiple-scattering method has a deep physical meaning. It describes the wavefunctions as the result of repeated scattering of the electron on the atomic sites.

Two approaches are possible to present the multiple-scattering theory. The first approach calculates the wave function, the second one the Green function. The first approach seems simpler at the beginning, but becomes much more involved when considered in detail, because state normalisation and density of states must be calculated. Moreover, the use of the Green function dispenses with various optical theorems which are required in the wave function approach. After this short introduction, a second section introduces the reader to the calculation of the Green function for a general potential. The third section uses the multiple-scattering method to calculate the Green function of a set of scatterers. The fourth section gives a somewhat detailed calculation of the reexpansion theorems. The last section is a list of rigorous results that can be found in the mathematical literature.

2 Green function

2.1 Introduction

The basic idea of Green functions is quite simple, and its usefulness is so universal that the efforts of learning this technique are largely repaid. Taking an elementary image, when a school girl has to solve the equation $ax = b$, where a is fixed and various b are given, she calculates $1/a$, and finds the solutions by a simple multiplication $x = (1/a) * b$. This method is particulary useful when no pocket calculator is available, or when the equation must be solved very many times (a division takes more time than a multiplication for a computer too). Let us consider now a differential equation, such as $y'' + 3y = f(x)$, where f is given and we look for the function $y(x)$. Let us rewrite the equation as $Ly = f$, where L is a symbol meaning that the function $y(x)$ is tranformed into $y'' + 3y$. The brilliant idea of Green was to look for an analogue of the school girl's method and to define something (we say now an operator), which can be denoted as L^{-1}, and such that $y = L^{-1}f$. Using Dirac's notation, we have $|y\rangle = L^{-1}|f\rangle$, multiplying on the left by $\langle x|$ and using the identity $1 = \int dx'|x'\rangle\langle x'|$ we obtain $\langle x|y\rangle = \int dx'\langle x|L^{-1}|x'\rangle\langle x'|f\rangle$. Defining now the Green function $G(x, x') = \langle x|L^{-1}|x'\rangle$ we obtain the solution of the differential equation as

$$y(x) = \int dx' G(x, x')f(x'). \tag{1}$$

"The fascinating concept of the Green's function is due to the insight and intuition of George Green (1793-1841), an English mathematician, whose original work was unappreciated for nearly all of his life - largely due to his unusual methodology. George Green was born in 1793 and was 44 years old when he received his degree of Bachelor of Arts in 1837 at Cambridge. His age and his inability to submit to the systematic training worked against him and few seemed to realize his remarkable ability at the time... He was entirely self-taught and faced great difficulty in publishing his work." [1]

In the very first paper of his scientific life (1928), Green invented Green's theorem and the Green functions, and he coined the word "potential" for the function representing the potential energy. [2]

Let us explore a few properties of the Green functions. If we multiply Eq.(1) by L, and note that L acts only on variable x, we obtain $Ly(x) = \int dx' LG(x, x')f(x')$. Since $Ly = f$ we find $LG(x, x') = \delta(x - x')$, which is another defining equation for G. The analogy with the school girl's solution is not complete because of boundary conditions. In other words, L does not completely define G because the solution of $Ly = f$ is completely defined only when appropriate boundary conditions are satisfied by y. The next section explores this aspect for the case of a Sturm-Liouville problem.

2.2 Sturm-Liouville problem

We want to solve the differential equation $Ly = f$ where

$$L = \frac{d^2}{dx^2} + q(x)$$

with the boundary conditions $y(0) = 0$, $y(\infty) = 0$. Therefore, we must find the Green function $G(x, x')$, such that $LG(x, x') = \delta(x - x')$ and $y(x) = \int dx' G(x, x')f(x')$ has the appropriate boundary conditions. It can be shown that $G(x, x')$ is continuous at $x = x'$

([3] p.47). Then we integrate $LG(x,x') = \delta(x-x')$ over x between $x'-\epsilon$ and $x'+\epsilon$ and take the limit when ϵ shrinks to zero. The second term (coming from $q(x)G(x,x')$) tends to zero because the Green function is continuous and we obtain:

$$\begin{aligned}
\int_{x'-0}^{x'+0} dx LG(x,x') &= \int_{x'-0}^{x'+0} dx \left[\frac{d^2}{dx^2} + q(x)\right] G(x,x') \\
&= \int_{x'-0}^{x'+0} dx \frac{d^2G(x,x')}{dx^2} = \frac{dG(x,x')}{dx}\Big|_{x'+0} - \frac{dG(x,x')}{dx}\Big|_{x'-0} \\
&= \int_{x'-0}^{x'+0} dx \delta(x-x') = 1. \qquad (2)
\end{aligned}$$

Since $G(x,x')$ must be a solution of $LG(x,x') = 0$ for $x \neq x'$, we can write $G(x,x') = A\phi_1(x)$ for $x < x'$ and $G(x,x') = B\phi_2(x)$ for $x > x'$, where ϕ_1 and ϕ_2 are solutions of the homogeneous equation $L\phi = 0$. Because of Eq.(1), y has the appropriate boundary conditions if $G(0,x') = 0$ and $G(\infty,x') = 0$, that is if $\phi_1(0) = 0$ and $\phi_2(\infty) = 0$. These conditions define ϕ_1 and ϕ_2 up to a multiplicative constant. The continuity equation at $x = x'$ gives us $A\phi_1(x') = B\phi_2(x')$, the jump equation (2) gives $B\phi_2'(x') - A\phi_1'(x') = 1$ and the solution is $A = \phi_2(x')/W(x')$, $B = \phi_1(x')/W(x')$ where $W(x') = \phi_1(x')\phi_2'(x') - \phi_1'(x')\phi_2(x')$ is called the Wronskian of ϕ_1 and ϕ_2. This yields the final solution for the Green function:

$$G(x,x') = \frac{\theta(x'-x)\phi_1(x)\phi_2(x') + \theta(x-x')\phi_2(x)\phi_1(x')}{W(x')}, \qquad (3)$$

where θ is the step function. Substituting Eq.(3) into Eq.(1) shows that y is indeed the solution of the Schrödinger equation with the required boundary conditions. When $W(x') \neq 0$ in Eq.(3), the expression for the Green function is well defined, when $W(x') = 0$, there is in general no solution y, except when f satisfies some constraint. This result is a simple example of a general theorem of linear operator theory, called the Fredholm alternative (see ref.[4] p.200). Figure 1 shows an example of Green function. The symmetry $G(x,x') = G(x',x)$ is clear on this figure.

For certain applications, the following expression for the real Green function can also be useful [5]:

$$G(x,x') = \sqrt{\rho(x)\rho(x')} \exp\left(-\frac{1}{2}\left|\int_x^{x'} \frac{dt}{\rho(t)}\right|\right),$$

where $\rho(x) = G(x,x)$.

2.3 Three dimensional examples

In three dimensions, a famous use of Green functions is provided by the charge problem. The electric potential ϕ due to a distribution of charges ρ is the solution of $\Delta\phi = -\rho/\epsilon_0$ with the boundary conditions that ϕ is zero at infinity. The solution of this problem is [6]

$$\phi(\mathbf{r}) = -\frac{1}{\epsilon_0}\int d\mathbf{r}' G(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')$$

where the Green function is

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}.$$

3

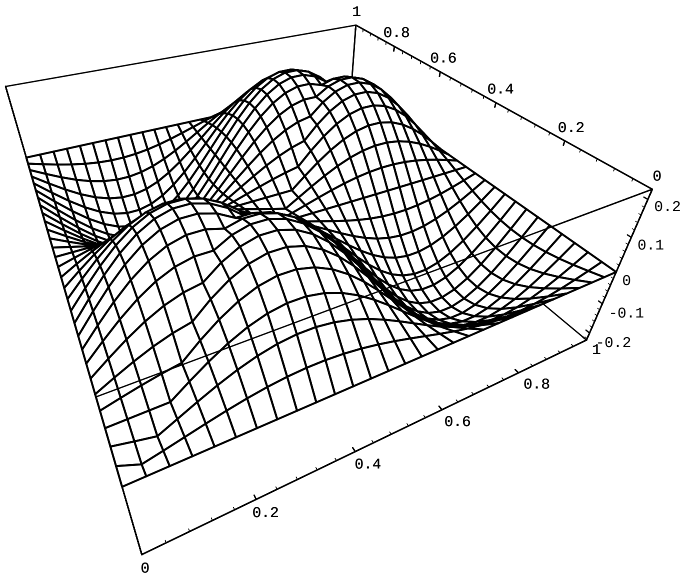

FIG. 1 – *Green function of the equation $y'' + 49y = 0$, with the boundary conditions $y(0) = 0$ and $y(1) = 0$.*

The last expression represents the electric potential at point $\mathbf{r}$ due to a point charge at point $\mathbf{r}'$. In this sense, the Green function propagates to $\mathbf{r}$ the effect of the charge at point $\mathbf{r}'$. In three dimensions, the Green function is *not* continuous at $\mathbf{r} = \mathbf{r}'$ (it is only continuous in one dimension).

The previous expression for the Green function was derived for an electrostatic (Poisson) equation. The problem of finding the potential corresponding to a time-varying density of charge can be solved in a similar way. We have now a wave equation :

$$\Delta\phi(\mathbf{r}, t) - (1/c^2)\frac{\partial^2\phi(\mathbf{r}, t)}{\partial t^2} = -\rho(\mathbf{r}, t).$$

To solve this, $\rho(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$ are expanded as a Fourier integral over the time variable. Then, for each component $\phi_\omega(\mathbf{r})\exp(-i\omega t)$ one finds

$$(\Delta + z)\phi_\omega(\mathbf{r}) = -\rho_\omega(\mathbf{r}),$$

with $z = \omega^2/c^2$.

For this last equation, the Green function G_0 which corresponds to outgoing waves boundary conditions was calculated in detail in [7] p.198, [3] p.336, [6] p.223 and [4] p.261.

$$G_0(\mathbf{r}, \mathbf{r}'; z) = -\frac{\exp(i\kappa|\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|}, \tag{4}$$

where $\mathrm{Im}z \geq 0$, $\kappa^2 = z$, $\mathrm{Im}\kappa \geq 0$. It is useful to define the Green function for any complex energy z. This can be used to avoid singularities or to convoluate the results. The Green function defined by Eq.(4) is called the free Green function because it corresponds to the Schrödinger equation without potential.

This Green function can be used to solve for the potential of a radiating source. It is our basic results, from which most of the rest follows, because this Green function forces the correct boundary condition. Much physical insight is required to choose the Green function corresponding to a radiating source. The outgoing wave boundary condition is also called Sommerfeld's radiation condition after the name of the first author of this analysis. Its physical meaning is that no energy may be radiated from infinity into the prescribed source of the field and its mathematical meaning is to make the solution of the Green function equation unique, since the usual requirement of a function that vanishes at infinity is not sufficient. The best discussion of the outgoing wave condition is still Ref.[7] p.188. For modern development of this subject, see Ref.[8].

Notice that the limit of Eq.(4) for $\kappa \to 0$ is the Green function of electrostatics. The result generalises to arbitrary dimension $n \geq 2$, the Green function with outgoing boundary conditions is [7]

$$G_0(x, x'; z) = -\frac{i}{4}\left(\frac{\kappa}{2\pi|x - x'|}\right)^{(n-2)/2} H^{(1)}_{(n-2)/2}(\kappa|x - x'|),$$

where $H^{(1)}_\nu$ is the Hankel function of the first kind of order ν.

The free Green function can be expanded over spherical harmonics. The calculation is standard ([9] p.430,[6] p.742) and gives us

$$\begin{aligned} G_0(\mathbf{r}, \mathbf{r}'; z) &= -i\kappa \sum_{\ell m} Y^m_\ell(\hat{\mathbf{r}}) j_\ell(\kappa r_<) h^+_\ell(\kappa r_>) Y^{m*}_\ell(\hat{\mathbf{r}'}) \\ &= -i\kappa \sum_{\ell m} Y^{m*}_\ell(\hat{\mathbf{r}}) j_\ell(\kappa r_<) h^+_\ell(\kappa r_>) Y^m_\ell(\hat{\mathbf{r}'}), \end{aligned}$$

where $r_< = r$ and $r_> = r'$ if $r \leq r'$, $r_< = r'$ and $r_> = r$ if $r' \leq r$. Moreover, $\mathbf{r}$ is a vector, r is its length, and $\hat{\mathbf{r}} = \mathbf{r}/r$ is the unit vector along $\mathbf{r}$. In spherical coordinates, $\hat{\mathbf{r}}$ is defined by the two angles θ and ϕ, and $Y^m_\ell(\hat{\mathbf{r}})$ means $Y^m_\ell(\theta, \phi)$.

In the following, we shall make use of the notation $L = (\ell, m)$, $Y_L = Y^m_\ell$ and $Y_{-L} = Y^{m*}_\ell = (-1)^m Y^{-m}_\ell$. Moreover, we define $j_L(\kappa\mathbf{r}) = j_\ell(\kappa r) Y^m_\ell(\hat{\mathbf{r}})$, $h_L(\kappa\mathbf{r}) = h^+_\ell(\kappa r) Y^m_\ell(\hat{\mathbf{r}})$, $j_{-L}(\kappa\mathbf{r}) = (-1)^m j_\ell(\kappa r) Y^{-m}_\ell(\hat{\mathbf{r}})$, $h_{-L}(\kappa\mathbf{r}) = (-1)^m h^+_\ell(\kappa r) Y^{-m}_\ell(\hat{\mathbf{r}})$. With this notation, the previous relation becomes

$$G_0(\mathbf{r}, \mathbf{r}'; z) = -i\kappa \sum_L j_L(\kappa\mathbf{r}_<) h_{-L}(\kappa\mathbf{r}_>) = -i\kappa \sum_L j_{-L}(\kappa\mathbf{r}_<) h_L(\kappa\mathbf{r}_>). \tag{5}$$

At this point, both $\mathbf{r}$ and $\mathbf{r}'$ are referred to a common origin O. In the multiple-scattering section, we shall obtain the corresponding expression for the Green function $G_0(\mathbf{r}, \mathbf{r}'; z)$ where $\mathbf{r}$ and $\mathbf{r}'$ will have different origins.

2.4 Green function with potential

In the previous section, we discussed the Green operator in general terms. We specify now to the case of the Schrödinger equation: $H = -\Delta + V$. The potential $V(\mathbf{r})$ is a real function, whose behaviour must be smooth enough to be a "small" perturbation of the Laplacian. The meaning of the word small will be explained below, and the purpose of this smallness is that some basic properties of the system are conserved. The physical aspects of these properties are: (i) the electrons can be considered to be free at a large distance from the sample, (ii) there is no bound state in the continuum. These mathematical precautions are not superfluous since condition (i) is not true for a Coulomb potential.

2.4.1 Molecular potential

The potential that we use is supposed to represent a collection of atoms in the one-electron approximation. Therefore $V(\mathbf{r}) = \sum_i V_i(\mathbf{r} - \mathbf{R}_i)$, where the sum is made over a finite number of atomic sites i centered at $\mathbf{R}_i$ and each potential $V_i(\mathbf{r})$ is such that $V_i(\mathbf{r}) = -2Z_i/r + \hat{V}_i(\mathbf{r})$ where $\hat{V}_i(\mathbf{r})$ is bounded and $V_i(\mathbf{r})$ is zero outside a finite domain Ω_i. Because of the singularity at the nucleus, some ambiguity exists in the choice of the boundary conditions. In particular, the wavefunction that behaves as a s-state at the origin can have a logarithmic singularity which is avoided by choosing a solution of the type $R(r) = \text{Cte}+O(r)$ at the origin. This is called the Friedrichs extension and is generally considered to be the physical solution [10, 11]. Although they are singular at the origin these potentials have many nice properties that enable us to use the standard quantum mechanical formalism. [1] In the muffin-tin approximation, the potential representing the influence of each atom is assumed to be spherical, i.e. radial around the corresponding nucleus: $V(r)$. In the present section, we shall find the Green function corresponding to the Schrödinger equation with the total molecular potential $V(\mathbf{r})$. It is possible to consider the whole molecule as just one potential for which the Schrödinger equation can be solved. This is, for instance, the finite-difference approach of Joly [13]. The advantage of this method is that no particular potential shape (e.g. muffin-tin) is assumed. However, when the muffin-tin approximation is reasonable, it is numerically faster and physically useful to cut this molecular potential into atomic spheres. This will be the multiple-scattering theory of section 3.

2.5 General properties of the Green function

It is sometimes convenient to distinguish Green operators, defined by $G(z) = (z - H)^{-1}$, and Green functions, which can be shown to be the space representation of the Green operator: $G(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r}|G(z)|\mathbf{r}'\rangle$. The Green functions depend also on z but, in the following, we do not write it explicitly to simplify notation. Product of operators must be understood as integrals over space variables. For example: $G(z)V \to \int d^3r' G(\mathbf{r}, \mathbf{r}')V(\mathbf{r}')$.

The basic equation for the Green function with potential is derived from the operator identity:

$$B^{-1} = A^{-1} - A^{-1}BB^{-1} + A^{-1}AB^{-1} = A^{-1} - A^{-1}(B - A)B^{-1}. \qquad (6)$$

If we introduce $H = H_0 + V$, $H_0 = -\Delta$, $A = z - H_0$, $B = z - H$, $G_0(z) = (z - H_0)^{-1}$ and $G(z) = (z - H)^{-1}$ in eq.(6) we obtain the "resolvent identity":

$$G(z) = G_0(z) + G_0(z)VG(z). \qquad (7)$$

Starting from $B^{-1} = A^{-1} - B^{-1}(B - A)A^{-1}$ gives the mirror image of eq.(7):

$$G(z) = G_0(z) + G(z)VG_0(z). \qquad (8)$$

2.5.1 Asymptotic behaviour

The resolvent equations can be used to prove two basic properties of the Green function. The first property we investigate is the behaviour of the Green function outside the potential range. Let the potential $V(\mathbf{r})$ be zero outside a finite volume Ω and let ρ be the diameter of a sphere centered at the origin and circumscribing Ω (see Fig.2). Introducing

1. For a review of the Schrödinger equation with singular potentials, see [12].

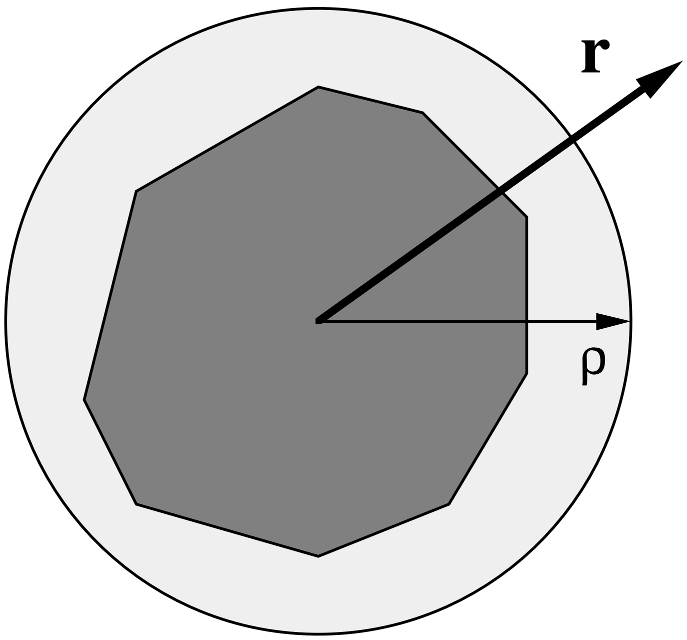

FIG. 2 – *The dark grey region is the volume where the potential is non zero* (Ω)*. The light grey region is the bounding sphere, with radius* ρ*. Radius vector* $\mathbf{r}$ *is outside the bounding sphere*

the expansion of the free Green function over spherical harmonics eq.(5) for $r' < r$ and $r \geq \rho$, in the resolvent equation eq.(7) we obtain:

$$G(\mathbf{r}, \mathbf{r}') = -i\kappa \sum_L h_{-L}(\kappa\mathbf{r}) j_L(\kappa\mathbf{r}') - i\kappa \sum_L h_{-L}(\kappa\mathbf{r}) \int_\Omega d\mathbf{s} j_L(\kappa\mathbf{s}) V(\mathbf{s}) G(\mathbf{s}, \mathbf{r}')$$

where $s \leq \rho \leq r$ since $\mathbf{s} \in \Omega$.

Therefore, for $r > \rho$ (beyond the sphere circumscribing the potential) and $r' < r$, the Green function can be written:

$$G(\mathbf{r}, \mathbf{r}') = -i\kappa \sum_L h_{-L}(\kappa\mathbf{r}) \psi_L(\mathbf{r}'), \tag{9}$$

where the wavefunction $\psi_L(\mathbf{r})$ is the solution of the integral equation

$$\psi_L(\mathbf{r}) = j_L(\kappa\mathbf{r}) + \int_\Omega d\mathbf{s} j_L(\kappa\mathbf{s}) V(\mathbf{s}) G(\mathbf{s}, \mathbf{r}). \tag{10}$$

The expansion (9) for the Green function is not valid when the decay of the potential is too slow (for instance Coulombic). However, finite range potential is not necessary (see section 5) for details). For future use, we can replace L by $-L$ to show that

$$G(\mathbf{r}, \mathbf{r}') = -i\kappa \sum_L h_L(\kappa\mathbf{r}) \psi_{-L}(\mathbf{r}'), \tag{11}$$

where

$$\psi_{-L}(\mathbf{r}) = j_{-L}(\kappa\mathbf{r}) + \int_\Omega d\mathbf{s} j_{-L}(\kappa\mathbf{s}) V(\mathbf{s}) G(\mathbf{s}, \mathbf{r}).$$

2.5.2 Symmetry of the Green function

This first result enables us to prove another basic property of our Green functions: they are symmetric. To show this, we write twice the equation for the Green function: $[z+\Delta-V(\mathbf{r})]G(\mathbf{r},\mathbf{r}_1)=\delta(\mathbf{r}-\mathbf{r}_1)$ and $[z+\Delta-V(\mathbf{r})]G(\mathbf{r},\mathbf{r}_2)=\delta(\mathbf{r}-\mathbf{r}_2)$. We multiply the first equation by $G(\mathbf{r},\mathbf{r}_2)$, the second by $G(\mathbf{r},\mathbf{r}_1)$, and we subtract the two equations to obtain:

$$G(\mathbf{r},\mathbf{r}_2)\Delta G(\mathbf{r},\mathbf{r}_1)-G(\mathbf{r},\mathbf{r}_1)\Delta G(\mathbf{r},\mathbf{r}_2)=G(\mathbf{r},\mathbf{r}_2)\delta(\mathbf{r}-\mathbf{r}_1)-G(\mathbf{r},\mathbf{r}_1)\delta(\mathbf{r}-\mathbf{r}_2).$$

Integrating over a sphere containing $\mathbf{r}_1$, $\mathbf{r}_2$ and Ω and using Green's theorem gives

$$\int_S [G(\mathbf{r},\mathbf{r}_2)\nabla G(\mathbf{r},\mathbf{r}_1)-G(\mathbf{r},\mathbf{r}_1)\nabla G(\mathbf{r},\mathbf{r}_2)].\hat{\mathbf{n}}dS=G(\mathbf{r}_1,\mathbf{r}_2)-G(\mathbf{r}_2,\mathbf{r}_1).$$

Since the radius R of the integration sphere is greater than r_1, r_2 and ρ, we can use expressions (9) and (11) to obtain

$$\begin{aligned} G(\mathbf{r}_1,\mathbf{r}_2)-G(\mathbf{r}_2,\mathbf{r}_1) &= -i\kappa\sum_{L,L'}\psi_L(\mathbf{r}_1)\psi_{-L'}(\mathbf{r}_2) \\ &\times \int_S [h_{L'}(\kappa\mathbf{r})\nabla h_{-L}(\kappa\mathbf{r})-h_{-L}(\kappa\mathbf{r})\nabla h_{L'}(\kappa\mathbf{r})].\hat{\mathbf{n}}dS. \end{aligned} \tag{12}$$

Using $\nabla f\cdot\hat{\mathbf{n}}=\partial f/\partial r$, the integral over the sphere transforms the first term of the integral into:

$$\begin{aligned} \int_S [h_{L'}(\kappa\mathbf{r})\nabla h_{-L}(\kappa\mathbf{r})].\hat{\mathbf{n}}dS &= R^2 h^+_{\ell'}(\kappa R)h'(\kappa R)\int d\Omega Y_{-L}(\hat{\mathbf{r}})Y_{L'}(\hat{\mathbf{r}}) \\ &= \delta_{\ell,\ell'}\delta_{m,m'}h^+_\ell(\kappa R)h'(\kappa R) \end{aligned}$$

where h' is the derivative of $h^+_\ell(\kappa r)$ with respect to r, and $d\Omega=\sin\theta d\theta d\phi$. Similarly, we obtain that

$$\int_S [h_{-L}(\kappa\mathbf{r})\nabla h_{L'}(\kappa\mathbf{r})].\hat{\mathbf{n}}dS = R^2\delta_{\ell,\ell'}\delta_{m,m'}h^+_\ell(\kappa R)h'(\kappa R),$$

so that the difference of the two surface integrals is zero and $G(\mathbf{r}_1,\mathbf{r}_2)=G(\mathbf{r}_2,\mathbf{r}_1)$.

The function ψ_L is a solution of the Schrödinger equation, because $\psi_L=(1+GV)j_L$ and $(z-H)(1+GV)=z-H_0$ so that $(z-H)\psi_L=(z-H_0)j_L=0$. Moreover, it can be shown that ψ_L is regular at the origin (because j_L and G are regular).

Since the Green function is continuous for $r\neq r'$ and symmetric, it seems reasonable to extend the expansion (9) into the potential sphere and write

$$G(\mathbf{r},\mathbf{r}')=-i\kappa\sum_L H_L(\mathbf{r}_>)\psi_{-L}(\mathbf{r}'_<)=-i\kappa\sum_L H_{-L}(\mathbf{r}_>)\psi_L(\mathbf{r}'_<),$$

where $H_L(\mathbf{r}_>)$ is the solution of the Schrödinger equation $(z-H)H_L=0$ that matches smoothly to $h_L(\kappa\mathbf{r})$ beyond the potential range. H_L is not regular at the origin.

2.5.3 The t-matrix

We start by deriving a few relations that are central to the multiple-scattering theory. These relations are formal manipulations of the Green function and t-matrix. As for the

Green function, the t-matrix can be considered to be an operator $T(z)$ (defined as $T(z) = V + VG(z)V$), a function defined as $T(\mathbf{r},\mathbf{r}') = \langle \mathbf{r}|T(z)|\mathbf{r}'\rangle$ or, finally, a matrix defined as $T_{L'L} = \int d\mathbf{s}d\mathbf{s}' j_{-L'}(\kappa\mathbf{s})T(\mathbf{s},\mathbf{s}')j_L(\kappa\mathbf{s}')$. Note that the matrix $T_{L'L}$ does not contain as much information as the function $T(\mathbf{r},\mathbf{r}')$ because the matrix elements are taken between too Bessel function that correspond to the same energy as the energy of the t-operator. In other words κ^2 is equal to z. The meaning of the Green function is the following. If the dynamics of a physical system is described by the Hamiltonian H, then the reaction of the system to an external perturbation $f(\mathbf{r})\exp(i\omega t)$ will be $G(z)f\exp(i\omega t)$ where $z = \omega^2/c^2$. The physical meaning of the t-operator is different. If a function $f(\mathbf{r})\exp(i\omega t)$ is a solution to the Schrödinger equation without potential (a free electron with energy z), then the corresponding solution for the equation with potential is $T(z)f\exp(i\omega t)$. In other words, if a free electron f comes from a region outside the potential and hits the potential, the scattered wave is $T(z)f$. In this section, t-matrix and t-operator will be used interchangeably.

After this introduction, we start again with the definition of the t-matrix as

$$T(z) = V + VG(z)V. \tag{13}$$

Right multiplying (13) by $G_0(z)$ and left multiplying the resolvent equation (7) by V leads to

$$T(z)G_0(z) = VG(z). \tag{14}$$

Using the mirror resolvent equation (8), we obtain similarly:

$$G_0(z)T(z) = G(z)V. \tag{15}$$

This expression gives us the form of the regular wavefunction beyond the potential range. Introducing Eq.(15) into the integral equation (10) for $\psi_L(\mathbf{r})$ we obtain $\psi_L = j_L + G_0 T j_L$. Beyond the range of the potential, we can use Eq.(5) which yields

$$\psi_L(\mathbf{r}) = j_L(\kappa\mathbf{r}) - i\kappa \sum_{L'} h_{L'}(\kappa\mathbf{r})T_{L'L} \tag{16}$$

where the t-matrix for potential V was defined as

$$T_{L'L} = \int d\mathbf{s}d\mathbf{s}' j_{-L'}(\kappa\mathbf{s})T(\mathbf{s},\mathbf{s}')j_L(\kappa\mathbf{s}'). \tag{17}$$

Combining eqs.(14) and (15) with the definition (13) gives a kind of resolvent equation for the t-matrix:

$$\begin{aligned} T(z) &= V + VG_0(z)T(z) && (18) \\ T(z) &= V + T(z)G_0(z)V. && (19) \end{aligned}$$

A physical picture of this equation will be given in the next section. From the last equation we obtain a formal expression for the t-matrix:

$$T(z) = (1 - VG_0)^{-1}V = V(1 - G_0V)^{-1}. \tag{20}$$

3 Multiple-scattering theory

There are mainly two approaches to the calculation of the Green function for a multi-center problem. The first one considers explicitely the scattering by the neighbours and sums the scattering events up to all orders. The second approach considers the Green function in each atomic center and matches the solutions so that the total Green function is continuous with continuous derivative across the potential boundaries. In the present section, we shall assume that the cluster is confined into non-overlapping spheres. Inside each sphere, the potential can be non spherical. The extension of these results to general potentials (not necessarily included in non-overlapping spheres) is not fully understood yet.

3.1 Multiple-scattering operator

The earliest presentation of the multiple-scattering algorithm was given in the Avatamsaka Sutra (The Flower Ornament Scripture) where Indra's Net is described: "Far away in the heavenly abode of the great god Indra, there is a wonderful net which has been hung by some cunning artificer in such a manner that it stretches out infinitely in all directions. In accordance with the extravagant tastes of the deities, the artificer has hung a single glittering jewel in each eye of the net, and since the net itself is infinite in dimension, the jewels are infinite in number. There hang the jewels, glittering like stars of the first magnitude, a wonderful sight to behold. If we now arbitrarily select one of the jewels for inspection and look closely at it, we will discover that in its polished surface there are reflected *all* the other jewels in the net, infinite in number. Not only that, but each of the jewels reflected in this one jewel is also reflecting all other jewels, so that there is an infinite reflecting process occurring."[14]

In the Indra net picture, the equation for the t-matrix $T(z) = V + VG_0(z)T(z)$ has the following meaning. T would represent the image seen from any point, V would be the reflection at a specific site and G_0 is the propagation from one site to another. The equation means that the image seen at any point is the reflection on the different sites plus the reflection of all the images on the different sites.

The core of the multiple-scattering method is to simplify the solution of the Schrödinger equation for a cluster of atoms by writing it as the composition of the solutions of the Schrödinger equations for each atom. The influence of the electrons in the cluster is represented by a potential $V(\mathbf{r})$ which is zero outside a domain Ω (the cluster volume). This volume is divided into cells Ω_i, such that the cells do not overlap. Each atomic centre has its own cell, but there can be cells that do not contain any atomic nucleus (the so-called empty cells). Then, the potential of the cluster can be written as: $V = \sum_i V^i$, where $V^i(\mathbf{r}) = V(\mathbf{r})$ for $\mathbf{r} \in \Omega_i$, $V^i(\mathbf{r}) = 0$ otherwise. The mathematical ground of the multiple-scattering method is that the solution for the complete cluster can be written as the sum of solutions for each atom. Therefore, the problem is decomposed into two simpler problems: solve the Schrödinger equation inside each site and make these solutions match between sites. The physical ground of the method is that one considers matter to be made of atoms. It would be possible to consider a molecule as a set of nucleons and electrons, but is illuminating to consider it as a set of atoms. The detailed definition of an atom in a molecule is a complex problem to which whole books were devoted [15], but it is a very efficient picture, and many spectral features can be explained as a consequence of the scattering by aligned scatterers or by the influence of atoms that are stronger scatterers at some energies, and so on. The multiple-scattering method is a way to take this picture into account.

From the decomposition of the cluster in potential centers, it is natural to define corresponding t-matrices by

$$T^{ij}(z) = V^i \delta_{i,j} + V^i G(z) V^j. \tag{21}$$

This definition is clearest in the real space representation:

$$T^{ij}(\mathbf{r},\mathbf{r}') = V^i(\mathbf{r})\delta_{i,j}\delta(\mathbf{r}-\mathbf{r}') + V^i(\mathbf{r})G(\mathbf{r},\mathbf{r}')V^j(\mathbf{r}'). \tag{22}$$

In the following, it will sometimes convenient to use position vectors with origins at atomic sites. The following notation will be used: $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_i$, where $\mathbf{R}_i$ is the position vector of the nucleus of atom i. Moreover, we define the interatomic vectors $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$.

Equation(22) implies the important property that $T^{ij}(\mathbf{r},\mathbf{r}') = T(\mathbf{r},\mathbf{r}')$ when $\mathbf{r} \in \Omega_i$ and $\mathbf{r}' \in \Omega_j$, and $T^{ij}(\mathbf{r},\mathbf{r}') = 0$ otherwise. From (21) we have also $\sum_{ij} T^{ij} = V + VGV = T$.

To derive an equation for T^{ij}, we start from eq.(18) in the real space representation:

$$\begin{aligned} T(\mathbf{r},\mathbf{r}') &= V(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + V(\mathbf{r})\int_\Omega d\mathbf{s} G_0(\mathbf{r},\mathbf{s})T(\mathbf{s},\mathbf{r}') \\ &= \sum_i V^i(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + \sum_{ijk} V^i(\mathbf{r})\int_{\Omega_k} d\mathbf{s} G_0(\mathbf{r},\mathbf{s})T^{kj}(\mathbf{s},\mathbf{r}') \end{aligned}$$

If we take $\mathbf{r} \in \Omega_i$ and $\mathbf{r}' \in \Omega_j$, this gives

$$T^{ij}(\mathbf{r},\mathbf{r}') = V^i(\mathbf{r})\delta_{i,j}\delta(\mathbf{r}-\mathbf{r}') + \sum_k V^i(\mathbf{r})\int_{\Omega_k} d\mathbf{s} G_0(\mathbf{r},\mathbf{s})T^{kj}(\mathbf{s},\mathbf{r}')$$

or more compactly $T^{ij} = V^i\delta_{i,j} + \sum_k V^i G_0 T^{kj}$. Since expression (37) for $G_0(\mathbf{r},\mathbf{r}')$ is valid when its arguments $\mathbf{r}$ and $\mathbf{r}'$ lie in different cells, (so that $r_i + r_j < R_{ij}$) we shall try to get rid of the term T^{ij} in the right-hand side. To do this, we transport the term T^{ij} from the right-hand side to the left-hand side to obtain

$$(1 - V^i G_0)T^{ij} = V^i \delta_{ij} + V^i \sum_{k\neq i} G_0 T^{kj}$$

multiplying both sides by $(1 - V^i G_0)^{-1}$ and using eq.(20) for the local t-matrix of the i-th site yields

$$T^{ij} = T^i \delta_{i,j} + \sum_{k\neq i} T^i G_0 T^{kj}. \tag{23}$$

Starting similarly from eq.(19) yields the mirror relation:

$$T^{ij} = T^i \delta_{i,j} + \sum_{k\neq j} T^{ik} G_0 T^j. \tag{24}$$

These equations are finally solved by taking matrix elements of eq.(23) between spherical Bessel functions $j_{-L}(\kappa\mathbf{r}_i)$ and $j_{L'}(\kappa\mathbf{r}_j)$ and using Eq.(37):

$$G_0(\mathbf{s},\mathbf{s}') = \kappa \sum_{\Lambda\Lambda'} j_\Lambda(\kappa\mathbf{s}_i) H^{ik}_{\Lambda\Lambda'} j_{-\Lambda'}(\kappa\mathbf{s}'_k). \tag{25}$$

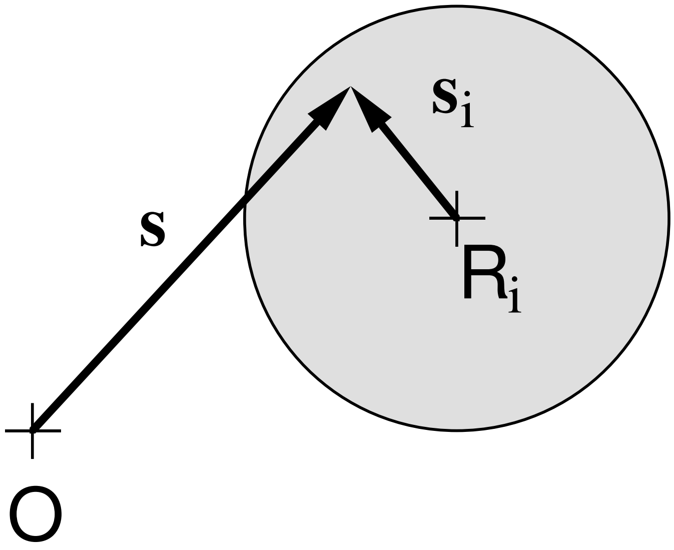

FIG. 3 – *The Bessel or Hankel function of vector* $\mathbf{s}$ *centere at* O *is expanded as a sum of Bessel functions of vector* $\mathbf{s}_i$ *centered at the atomic site* $\mathbf{R}_i$.

The meaning of Eq.(25) is the following. From Fig.3, the Green function of variables $\mathbf{s}$ and $\mathbf{s}'$ is written as a sum of product of Bessel functions of variables $\mathbf{s}_i = \mathbf{s} - \mathbf{R}_i$ and $\mathbf{s}_k = \mathbf{s}' - \mathbf{R}_k$. This is certainly possible because the Bessel functions form a complete set, but the discovery of an analytical form is rather difficult (see section 4) for details). This change of origin is necessary because the t-matrix for each site is calculated from Eq.(17) where the Bessel functions are centered at the atomic nucleus. Only with this origin can the t-matrix be diagonal when the potential is sherical.

Equation (23) is multiplied on the left by $j_{-L}(\kappa\mathbf{r}_i)$, on the right by $j_{L'}(\kappa\mathbf{r}_j)$, then G_0 is replace by the sum (25)[2]. Then the expression is integrated over $\mathbf{r}_i$, $\mathbf{r}_j$, $\mathbf{s}_i$ and $\mathbf{s}_k$. This gives us

$$\tau^{ij}_{LL'} = T^i_{LL'}\delta_{i,j} + \kappa\sum_{k\neq i}\sum_{\Lambda\Lambda'} T^i_{L\Lambda}H^{ik}_{\Lambda\Lambda'}\tau^{kj}_{\Lambda'L'},$$

where $\tau^{ij}_{LL'} = \int_{\Omega_i\Omega_j} d\mathbf{r}_i d\mathbf{r}_j j_{-L}(\kappa\mathbf{r}_i)T^{ij}(\mathbf{r}_i,\mathbf{r}_j)j_{L'}(\kappa\mathbf{r}_j)$, and $T^i_{LL'}$ is the t-matrix for site i. Considering τ^{ij}, H^{ij} and T^i as matrices, the previous equation can be written more compactly

$$\tau^{ij} = T^i\delta_{i,j} + \kappa\sum_k T^iH^{ik}\tau^{kj}. \tag{26}$$

Since the error is often made in the literature,[3] it is important to notice that we did not use a resolution of the identity because this would have involved an integral over real κ. Here, we have no integral over energy and the relation is true for complex κ. In other words, to separage the t-matrices from the free Green function in Eq.(23) we do not have to insert a complete set of $j_L(\mathbf{r})$, since this would involve integration over the whole space. This speeds up the derivation but is wrong in principle.

2. Equation(25) is valid (absolutely convergent) only when $s_i + s_j < R_{ij}$. This condition is fulfilled when the potentials are included in non-overlapping spheres. Here is the origin of the non-overlapping condition.

3. See, e.g., [16] p.148.

In the basic equation (26), the sum is over all k and not only over $k \neq i$ because we have defined $H^{ii}_{\Lambda\Lambda'} = 0$ for all Λ and Λ' (see section 4). Equation (26) is true for non-spherical potentials, but the condition of validity of eq.(25) requires that the cells Ω_i are embedded in non-overlapping spheres.

Similarly, we can derive the mirror equation

$$\tau^{ij} = T^i\delta_{i,j} + \kappa \sum_k \tau^{ik} H^{kj} T^j, \tag{27}$$

Equation(26) is the equation for the multiple-scattering operators τ^{ij}. The relation with Indra's net is clear when one uses a kind of Born expansion:

$$\tau^{ij} = T^i\delta_{i,j} + \kappa T^i H^{ij} T^j + \kappa^2 \sum_k T^i H^{ik} T^k H^{kj} T^j + \dots$$

which describes the full multiple-scattering as the scattering by site i, plus the scattering by site j followed by the transport from j to i plus the scattering by site i plus etc. Or, in Indra's words, there is the reflection in jewel i plus the reflection of jewel j in jewel i, plus the reflection of jewel j in jewel k which is reflected in jewel i, and so on. However, it is important to notice that the Born expansion does not always converge, in particular, at low energy, and eq.(26) cannot be solved by expansion. This non-convergence region of the Born expansion is called the full-multiple scattering regime.

3.2 The multiple-scattering Green function

The final purpose of our calculation is an expression for the Green function. The Green function can then be used to calculate very many properties, such as x-ray absorption spectra, density of states, etc.

Introducing eq.(14) into the resolvent equation (7) we obtain an expression for the Green function in terms of the t-matrix: $G = G_0 + G_0 T G_0$. Following the convergence condition of Eqs.(41) and (42), we shall avoid the situation where both arguments of the Green function G_0 belong to the same atomic cell. A fast way of doing this is to include potential V^i into the non perturbed potential $H_0 = -\Delta + V^i$, this gives us

$$G = G^i + \sum_{a\neq i, b\neq i} G^i T^{ab} G^i, \tag{28}$$

where $G^i(z) = (z + \Delta - V^i)^{-1}$ is the Green function corresponding to the Schrödinger equation with potential V^i.[4]

We know that, if $\mathbf{r} \in \Omega_i$ and $\mathbf{s} \notin \Omega_i$ then $G^i(\mathbf{r}_i, \mathbf{s}_i) = -i\kappa \sum_L \psi_L(\mathbf{r}_i) h_{-L}(\mathbf{s}_i)$. Since $a \neq i$, $h_{-L}(\mathbf{s}_i) = i \sum_\Lambda H^{ia}_{L\Lambda} j_{-L}(\kappa \mathbf{r}_a)$. Treating the second G^i similarly, the second term of eq.(28) can be written:

$$\sum_{a\neq i, b\neq i} G^i T^{ab} G^i = \kappa^2 \sum_{a\neq i, b\neq i} \sum_{LL'\Lambda\Lambda'} \psi_L(\mathbf{r}_i) H^{ia}_{L\Lambda} \tau^{ab}_{\Lambda\Lambda'} H^{bi}_{\Lambda' L'} \psi_{-L'}(\mathbf{r}'_i).$$

Using eq.(26) we can write the sum over a as $\kappa \sum_a H^{ia}\tau^{ab} = (T^i)^{-1}\tau^{ib}$, using now eq.(27) we find $\kappa^2 \sum_{ab} H^{ia}\tau^{ab}H^{bi} = (T^i)^{-1}\tau^{ii}(T^i)^{-1} - (T^i)^{-1}$. This gives us the basic result

4. The careful reader can check this equation directly by writing $G^i = G_0 + G_0 T^i G_0$ and using repeatedly eqs.(23) and (24) to find that the right-hand side of Eq.(28) is $G_0 + \sum_{ij} G_0 T^{ij} G_0 = G_0 + G_0 T G_0 = G$.

for the Green function of a set of scatterers:

$$G(\mathbf{r}_i, \mathbf{r}'_i) = G^i(\mathbf{r}_i, \mathbf{r}'_i) + \sum_{LL'} \psi_L(\mathbf{r}_i) \left[(T^i)^{-1}\tau^{ii}(T^i)^{-1} - (T^i)^{-1}\right]_{LL'} \psi_{-L'}(\mathbf{r}'_i). \tag{29}$$

This is the basic result of the whole chapter. The full Green function in the neighbourhood of a site is written as the Green function of the isolated site plus a term that describes the influence of the rest of the cluster. For completeness, we give the corresponding result when the first variable belongs to site i and the second to site j:

$$G(\mathbf{r}_i, \mathbf{r}_j) = \sum_{LL'} \psi_L(\mathbf{r}_i) \left[(T^i)^{-1}\tau^{ij}(T^j)^{-1}\right]_{LL'} \psi_{-L'}(\mathbf{r}'_j). \tag{30}$$

3.3 Continuity equations

The second method to calculate the Green function of a set of scatterers is presented, for instance, in an excellent early paper by Vedrinskiy and Novakovich [17]. In this approach, the problem is divided into two cases. In the first case, the two arguments of the Green function belong to different sites and, therefore, the Green function is not singular (it is only singular when both arguments are identical). Therefore, the Green function can be written as a sum of regular solutions:

$$G(\mathbf{r}_i, \mathbf{r}_j) = \sum_{LL'} \psi_L(\mathbf{r}_i) M^{ij}_{LL'} \psi_{-L}(\mathbf{r}_j).$$

When both arguments belong to the same site, they can be identical. Therefore, the singularity must be explicitely taken into account. This is done by using the single-site Green function and the Green function is written as:

$$G(\mathbf{r}_i, \mathbf{r}'_i) = G^i(\mathbf{r}_i, \mathbf{r}'_i) + \sum_{LL'} \psi_L(\mathbf{r}_i) M^{ii}_{LL'} \psi_{-L}(\mathbf{r}'_i).$$

Then, the compatibility between these various expressions for the Green function leads to the equations for $M^{ij}_{LL'}$ which gives us the solutions (29) and (30). These forms are not self-evident, and we preferred to start with the multiple-scattering operators which lead more naturally to these forms.

Instead of doing everyting all over again, we shall start from Eqs.(29) and (30) and show that they are compatible with the continuity equation.

In fact, the equation we start from is the resolvent identity for the total potential V:

$$G(\mathbf{r}, \mathbf{r}') = G_0(\mathbf{r}, \mathbf{r}') + \int_\Omega d\mathbf{s} G_0(\mathbf{r}, \mathbf{s}) V(\mathbf{s}) G(\mathbf{s}, \mathbf{r}').$$

Since $(z + \Delta - V)G = 1$ we have $V(\mathbf{s})G(\mathbf{s}, \mathbf{r}') = (z + \Delta)G(\mathbf{s}, \mathbf{r}') - \delta(\mathbf{s} - \mathbf{r}')$. Therefore

$$G(\mathbf{r}, \mathbf{r}') = G_0(\mathbf{r}, \mathbf{r}') + \int_\Omega d\mathbf{s} G_0(\mathbf{r}, \mathbf{s})(z + \Delta)G(\mathbf{s}, \mathbf{r}') - \int_\Omega d\mathbf{s} G_0(\mathbf{r}, \mathbf{s})\delta(\mathbf{s} - \mathbf{r}').$$

The last term is $G_0(\mathbf{r}, \mathbf{r}')$ if $\mathbf{r}' \in \Omega$ and zero otherwise. Let $\chi_\Omega(\mathbf{r})$ be 1 if $\mathbf{r} \in \Omega$ and 0 otherwise, then

$$G(\mathbf{r}, \mathbf{r}') = (1 - \chi_\Omega(\mathbf{r}'))G_0(\mathbf{r}, \mathbf{r}') + \int_\Omega d\mathbf{s} G_0(\mathbf{r}, \mathbf{s})(z + \Delta)G(\mathbf{s}, \mathbf{r}'). \tag{31}$$

Now we can use Green's theorem to rewrite

$$\begin{aligned}\int_\Omega d\mathbf{s} G_0(\mathbf{r},\mathbf{s})(z+\Delta)G(\mathbf{s},\mathbf{r}') &= \int_\Omega d\mathbf{s} G(\mathbf{s},\mathbf{r}')(z+\Delta)G_0(\mathbf{r},\mathbf{s}) \\ &+ \int_S \left[G_0(\mathbf{r},\mathbf{s})\nabla_s G(\mathbf{s},\mathbf{r}') - G(\mathbf{s},\mathbf{r}')\nabla_s G_0(\mathbf{r},\mathbf{s})\right].\hat{\mathbf{n}} dS.\end{aligned}$$

If we use $(z+\Delta)G_0(\mathbf{r},\mathbf{s}) = \delta(\mathbf{r}-\mathbf{s})$, eq.(31) gives us the main equation of the section

$$\begin{aligned}G(\mathbf{r},\mathbf{r}')(1-\chi_\Omega(\mathbf{r})) &= G_0(\mathbf{r},\mathbf{r}')(1-\chi_\Omega(\mathbf{r}')) \\ &+ \int_S \left[G_0(\mathbf{r},\mathbf{s})\nabla_s G(\mathbf{s},\mathbf{r}') - G(\mathbf{s},\mathbf{r}')\nabla_s G_0(\mathbf{r},\mathbf{s})\right].\hat{\mathbf{n}} dS.\end{aligned}$$

3.3.1 $\mathbf{r} \in \Omega_i$ and $\mathbf{r}' \in \Omega_i$

The basic equation (32) should be checked for all possible values of $\mathbf{r}$ and $\mathbf{r}'$. We shall treat only the case where $\mathbf{r} \in \Omega_i$ and $\mathbf{r}' \in \Omega_i$. In that case, $\chi_\Omega(\mathbf{r}) = 1$ and $\chi_\Omega(\mathbf{r}') = 1$, Ω is written as a sum over sites Ω_k and eq.(32) becomes

$$\sum_k D^k(\mathbf{r}_i, \mathbf{r}'_i) = 0$$

where

$$D^k(\mathbf{r},\mathbf{r}') = \int_{S_k} \left[G_0(\mathbf{r},\mathbf{s}_k)\nabla_s G(\mathbf{s}_k,\mathbf{r}') - G(\mathbf{s}_k,\mathbf{r}')\nabla_s G_0(\mathbf{r},\mathbf{s}_k)\right].\hat{\mathbf{n}} dS_k.$$

Two cases must be distinguished, according to $k=i$ and $k \neq i$:

(i) The first case is when $k=i$. According to eq.(29) The Green function is the sum of a local Green function G^i and an additional term. The contribution of the local Green function to $D^i(\mathbf{r}_i,\mathbf{r}'_i)$ is zero, as can be readily proved. $\mathbf{r}_i$ is in Ω_i and the integral is at the edge of Ω_i, therefore $G_0(\mathbf{r}_i,\mathbf{s}_i) = -i\kappa\sum_L j_L(\kappa\mathbf{r}_i)h_{-L}(\kappa\mathbf{s}_i)$ and the local Green function is $G^i(\mathbf{s}_i,\mathbf{r}'_i) = -i\kappa\sum_{L'}\psi_{-L'}(\mathbf{r}'_i)h_{L'}(\kappa\mathbf{s}_i)$. Therefore, the contribution of the local Green function to $D^i(\mathbf{r}_i,\mathbf{r}'_i)$ is

$$-\kappa^2 \sum_{LL'} j_L(\kappa\mathbf{r}_i)\psi_{-L'}(\mathbf{r}'_i)\int_{S_i}\left[h_{-L}(\kappa\mathbf{s}_i)\nabla h_{L'}(\kappa\mathbf{s}_i) - h_{L'}(\kappa\mathbf{s}_i)\nabla h_{-L}(\kappa\mathbf{s}_i)\right].\hat{\mathbf{n}} dS_i.$$

Since S_i is a sphere, we can use $\nabla.\hat{\mathbf{n}} = \partial/\partial s$ and the last surface integral reduces to $\delta_{LL'}R^2[h^+_\ell(\kappa R)h^{+'}_{\ell'}(\kappa R) - h^+_{\ell'}(\kappa R)h^{+'}_\ell(\kappa R)] = 0$.

The second term of the Green function (29) is treated analogously. We expand the free Green function over spherical harmonics and we obtain for the contribution of the second term to D^i:

$$\begin{aligned}D^i(\mathbf{r}_i,\mathbf{r}'_i) &= -i\kappa \sum_{L\Lambda\Lambda'} j_L(\kappa\mathbf{r}_i)\psi_{-\Lambda'}(\mathbf{r}'_i)\left[(T^i)^{-1}\tau^{ii}(T^i)^{-1} - (T^i)^{-1}\right]_{\Lambda\Lambda'} \\ &\int_{S_i}\left[h_{-L}(\kappa\mathbf{s}_i)\nabla\psi_\Lambda(\mathbf{s}_i) - \psi_\Lambda(\mathbf{s}_i)\nabla h_{-L}(\kappa\mathbf{s}_i)\right].\hat{\mathbf{n}} dS_i.\end{aligned}$$

Since ψ_L and its derivatives are continuous across the potential boundary, they can be represented at the boundary by the free form (16): $\psi_\Lambda(\mathbf{s}) = j_\Lambda(\mathbf{s}) - i\kappa\sum_{L'} h_{L'}(\mathbf{s})T_{L'\Lambda}$. Once again, the integral over angles gives $\delta_{L,\Lambda}$ and the terms in $h_{L'}$ drop. The only terms that remain come from $j_\Lambda(\mathbf{s})$ and the surface integral becomes $R_i^2\delta_{L,\Lambda}W[h^+_\ell, j_\ell]$.

The Wronskian is defined by $W[f,g] = f(R_i)g'(R_i) - f'(R_i)g(R_i)$. From eq.(10.1.6) of [18] we find $W[h_\ell^+, j_\ell] = iW[n_\ell, j_\ell] = -i/(\kappa R_i^2)$. Gathering all the results we find

$$D^i(\mathbf{r}_i, \mathbf{r}'_i) = -\sum_{LL'} j_L(\kappa \mathbf{r}_i)\psi_{-L'}(\mathbf{r}'_i)\left[(T^i)^{-1}\tau^{ii}(T^i)^{-1} - (T^i)^{-1}\right]_{LL'} \qquad (32)$$

(ii) The second case is when $k \neq i$. According to eq.(30) The Green function is made only with combinations of regular solutions ψ_L. Using eq.(30) for the full Green function and eq.(37) for the free Green function yields:

$$\begin{aligned} D^k(\mathbf{r}_i, \mathbf{r}'_i) &= \kappa \sum_{LL'\Lambda\Lambda'} j_L(\kappa \mathbf{r}_i) H^{ik}_{L\Lambda}\left[(T^k)^{-1}\tau^{ki}(T^i)^{-1}\right]_{L'\Lambda'}\psi_{-\Lambda'}(\mathbf{r}'_i) \\ &\quad \int_{S_k}\left[h_{-\Lambda}(\kappa \mathbf{s}_k)\nabla\psi_{L'}(\mathbf{s}_k) - \psi_{L'}(\mathbf{s}_k)\nabla j_{-\Lambda}(\kappa \mathbf{s}_k)\right].\hat{\mathbf{n}}dS_k. \end{aligned}$$

As for case (i), ψ_Λ can be written as a linear combination of Bessel function and the surface integral becomes $-i\kappa R_k^2 T^k_{\Lambda L'} W[j_\lambda, h^+_\lambda] = T^k_{\Lambda L'}$. Therefore

$$D^k(\mathbf{r}_i, \mathbf{r}'_i) = \kappa \sum_{LL'\Lambda\Lambda'} j_L(\kappa \mathbf{r}_i) H^{ik}_{L\Lambda}\tau^{ki}_{\Lambda L'}(T^i)^{-1}_{L'\Lambda'}\psi_{-\Lambda'}(\mathbf{r}'_i).$$

With this and eq.(26), we can sum over k and Λ:

$$\sum_{k\neq i} D^k(\mathbf{r}_i, \mathbf{r}'_i) = \sum_{LL'} j_L(\kappa \mathbf{r}_i)\psi_{-L'}(\mathbf{r}'_i)\left[(T^i)^{-1}\tau^{ii}(T^i)^{-1} - (T^i)^{-1}\right]_{LL'}.$$

This, together with the corresponding result for $k = i$, shows that $\sum_k D^k(\mathbf{r}_i, \mathbf{r}'_i) = 0$ and that eq.(32) is satisfied for $\mathbf{r}_i$ and $\mathbf{r}'_i$ in Ω_i. The other cases can be checked similarly.

4 Reexpansion theorems

Here again, we define the compound index $L = (\ell, m)$ and the spherical harmonics $Y_L = Y_\ell^m$. We define also $Y_{-L} = (-1)^m Y_\ell^{-m}$.

In this section, we derive the reexpansion theorem which is the basis of the multiple-scattering theory. We start with the definition of free generalized wavefunctions $|\mathbf{k}\rangle$ by $\langle \mathbf{r}|\mathbf{k}\rangle = \exp(i\mathbf{k}.\mathbf{r})$. For these states the resolution of identity writes

$$1 = \int \frac{d^3k}{(2\pi)^3}|\mathbf{k}\rangle\langle\mathbf{k}|.$$

Therefore, the free Green function can be written as a function of the eigenstates as

$$\begin{aligned} G_0(\mathbf{r}, \mathbf{r}'; z) = G_0(\mathbf{r} - \mathbf{r}'; z) &= \int \frac{d^3k}{(2\pi)^3}\frac{\langle \mathbf{r}|\mathbf{k}\rangle\langle\mathbf{k}|\mathbf{r}\rangle}{z - k^2} \\ &= \int \frac{d^3k}{(2\pi)^3}\frac{\exp[i\mathbf{k}\cdot(\mathbf{r} - \mathbf{r}')]}{z - k^2} \end{aligned} \qquad (33)$$

Using $\mathbf{r} - \mathbf{r}' = \mathbf{r} - \mathbf{R}_i - (\mathbf{r}' - \mathbf{R}_j) + \mathbf{R}_i - \mathbf{R}_j = \mathbf{r}_i - \mathbf{r}_j + \mathbf{R}_{ij}$, where we have defined $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_i$, $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$ and $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$, the exponential function in Eq.(33) can be written $\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')] = \exp(i\mathbf{k}\cdot\mathbf{r}_i)\exp(i\mathbf{k}\cdot\mathbf{R}_{ij})\exp(-i\mathbf{k}\cdot\mathbf{r}_j)$. Now, we make use of different forms of the Bauer identity (see Eq.(10.1.47) of Ref.[18]):

$$\begin{aligned}
\exp(i\mathbf{k}\cdot\mathbf{r}_i) &= 4\pi\sum_L i^\ell j_\ell(kr_i)Y_L(\hat{\mathbf{r}}_i)Y_{-L}(\hat{\mathbf{k}}) \\
\exp(i\mathbf{k}\cdot\mathbf{R}_{ij}) &= 4\pi\sum_\Lambda i^\lambda j_\lambda(kR_{ij})Y_\Lambda(\hat{\mathbf{R}}_{ij})Y_{-\Lambda}(\hat{\mathbf{k}}) \\
\exp(-i\mathbf{k}\cdot\mathbf{r}_j) &= 4\pi\sum_{L'} i^{-\ell'} j_{\ell'}(kr_j)Y_{-L'}(\hat{\mathbf{r}}_j)Y_{L'}(\hat{\mathbf{k}})
\end{aligned}$$

The sum is uniformly convergent [19], so that the sum and the integral can be interchanged. The integral over d^3k in Eq.(33) is written as $d^3k = k^2dkd\Omega$. The integral over angles is standard. The Gaunt coefficients $C_{LL'\Lambda}$ are defined by

$$C_{LL'\Lambda} = \int d\Omega Y_\ell^m(\hat{\mathbf{k}})Y_{\ell'}^{m'}(\hat{\mathbf{k}})Y_\lambda^\mu(\hat{\mathbf{k}}).$$

The Gaunt coefficients $C_{LL'\Lambda}$ can be calculated from the formula:

$$C_{LL'\Lambda} = \sqrt{\frac{(2\ell+1)(2\ell'+1)(2\lambda+1)}{4\pi}}\begin{pmatrix}\ell & \ell' & \lambda\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell & \ell' & \lambda\\ m & m' & \mu\end{pmatrix}.$$

An important property of the Gaunt coefficients states that $C_{LL'\Lambda}=0$ when $\ell+\ell'+\lambda$ is odd. [5] Therefore, we must only consider the Gaunt coefficients for which $\ell+\ell'+\lambda$ is even. Moreover, because of the triangle inequality, the Gaunt coefficients are zero for $\lambda > \ell+\ell'$ or $\lambda < |\ell-\ell'|$. Finally, the value of $C_{LL'\Lambda}$ does not depend on the order of L, L' and Λ (in other words $C_{LL'\Lambda} = C_{L'L\Lambda} = C_{\Lambda LL'} = \ldots$) From the properties of the spherical harmonics, it is clear that $C_{-L'L\Lambda} = C_{L'-L-\Lambda}$ where, naturally, $C_{-L'L\Lambda} = (-1)^{m'}C_{(\ell',-m')L\Lambda}$.

With all these definitions, integral (33) can be rewritten:

$$G_0(\mathbf{r}-\mathbf{r}';z) = 8\sum_{L,L',\Lambda} C_{-L'L\Lambda}i^{\ell+\lambda-\ell'}Y_L(\hat{\mathbf{r}}_i)Y_\Lambda(\hat{\mathbf{R}}_{ij})Y_{-L'}(\hat{\mathbf{r}}_j)I(z), \tag{34}$$

where the remaining integral is

$$I(z) = \int_0^{+\infty} k^2dk\frac{j_\ell(kr_i)j_\lambda(kR_{ij})j_{\ell'}(kr_j)}{z-k^2}. \tag{35}$$

To calculate the last integral, we use the identity $j_\lambda(kR_{ij}) = (h_\lambda^+(kR_{ij})+h_\lambda^-(kR_{ij}))/2$. Therefore, Eq.(35) becomes the sum of two integrals, the first one involves $h_\lambda^+(kR_{ij})$ and the second one $h_\lambda^-(kR_{ij})$. In the second integral, we change variable k to $-k$. Then, we make use of the identities (see Ref. [18], Eqs.(10.1.34) and (10.1.36)) $j_\ell(-kr_i) = (-1)^\ell j_\ell(kr_i)$, $j_{\ell'}(-kr_j) = (-1)^{\ell'}j_{\ell'}(kr_j)$ and $h_\lambda^-(-kR_{ij}) = (-1)^\lambda h_\lambda^+(kR_{ij})$. Since $\ell+\ell'+\lambda$ is even, the second integrand becomes identical with the first integrand, but the integral is from $-\infty$ to 0. Therefore,

$$I(z) = \frac{1}{2}\int_{-\infty}^{+\infty} k^2dk\frac{j_\ell(kr_i)h_\lambda^+(kR_{ij})j_{\ell'}(kr_j)}{z-k^2}.$$

This integral can be carried out by the residue theorem, using the contour of Fig.4.

5. This can be proven from Eq.(4) by using the parity of spherical harmonics: $Y_\ell^m(-\hat{\mathbf{k}}) = (-1)^\ell Y_\ell^m(\hat{\mathbf{k}})$.

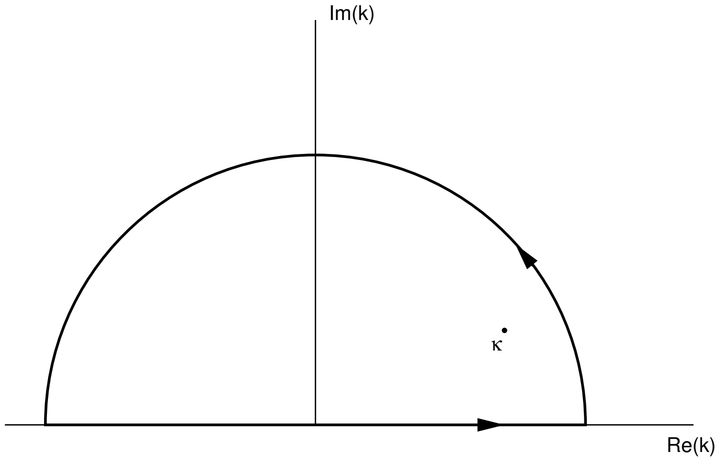

FIG. 4 – *Contour used to calculate $I(z)$.*

For the complex energy $z = E + i\Gamma$, we define $\kappa = \sqrt{z}$ by $\kappa = a + ib$ with

$$a = \sqrt{\frac{E + \sqrt{E^2 + \Gamma^2}}{2}} \quad b = \frac{\Gamma}{2a},$$

and, $a = 0$, $b = \sqrt{-E}$ if $\Gamma = 0$ and $E \leq 0$. Therefore, the imaginary part of κ is positive when the imaginary part of z is positive. To use the residue theorem, we must make sure that the contribution of the half-circle is zero. Using Eq.(10.1.16) of Ref.[18], we know that, for large k, $h^+_\ell(kR)$ behaves as $i^{-\ell-1}\exp(ikR)/(kR)$. In the upper half plane, k has a positive imaginary part and $h^+_\ell(kR)$ tends exponentially fast to zero on the half-circle. However, from Eqs.(10.1.1) and (10.1.17) of Ref.[18], $j_\ell(kr)$ behaves as $i^{\ell+1}\exp(-ikr)/(2kr)$, and the integrand of Eq.(35) behaves as $\exp[ik(R_{ij} - r_i - r_j)]$. Therefore, the contribution of the half-circle is zero if $R_{ij} > (r_i + r_j)$. This condition is the basis of the muffin-tin condition. Moreover, the origin $k = 0$ is a regular point for $z \neq 0$, as can be seen from the series expansions (10.1.2) and (10.1.3) of Ref.[18] and from the fact that λ is bounded by $\ell + \ell'$. Since $k^2/(z - k^2) = -(k/2)(1/(k-\kappa) + 1/(k+\kappa))$, the contour contains only one singular point: $k = \kappa$. The residue theorem (Ref.[9] p.358) gives us

$$I(z) = -i\frac{\pi}{2}\kappa j_\ell(\kappa r_i) h^+_\lambda(\kappa R_{ij}) j_{\ell'}(\kappa r_j). \tag{36}$$

From Eqs.(36) and (34) we arrive at the reexpansion theorem:

$$G_0(\mathbf{r}_i, \mathbf{r}_j; z) = \kappa \sum_{L,L'} Y_L(\hat{\mathbf{r}}_i) j_\ell(\kappa r_i) H^{ij}_{LL'} Y_{-L'}(\hat{\mathbf{r}}_j) j_{\ell'}(\kappa r_j) = \kappa \sum_{L,L'} j_L(\kappa \mathbf{r}_i) H^{ij}_{LL'} j_{-L'}(\kappa \mathbf{r}_j) \tag{37}$$

where

$$H^{ij}_{LL'} = -4\pi i \sum_\Lambda C_{-L'L\Lambda} i^{\ell+\lambda-\ell'} Y^\mu_\lambda(\hat{\mathbf{R}}_{ij}) h^+_\lambda(\kappa R_{ij}). \tag{38}$$

By manipulating the definition (38) of the H-matrix, one can show the following symmetry relation:

$$H^{ji}_{\ell'-m',\ell-m} = (-1)^{m'-m} H^{ij}_{\ell m,\ell' m'}. \tag{39}$$

This symmetry relation gives us an alternative form of the reexpansion theorem:

$$G_0(\mathbf{r}_i, \mathbf{r}_j; z) = \kappa \sum_{L,L'} j_{-L}(\kappa \mathbf{r}_i) H^{ji}_{L'L} j_{L'}(\kappa \mathbf{r}_j) \tag{40}$$

Note that the two expressions (37) and (40) are compatible because the Green function is symmetric.

From Eqs.(37) and (5) we obtain the reexpansion theorem for Hankel functions:

$$h_{-L}(\kappa\mathbf{r}_i) = i\sum_{L'} H^{ij}_{LL'} j_{-L'}(\kappa\mathbf{r}_j) \tag{41}$$

which is convergent when $r_j < R_{ij}$ or

$$h_{L'}(\kappa\mathbf{r}_j) = i\sum_{L} j_L(\kappa\mathbf{r}_i) H^{ij}_{LL'}, \tag{42}$$

which is convergent when $r_i < R_{ij}$. In these reexpansions, $\mathbf{r}_i = \mathbf{r}_j - \mathbf{R}_{ij}$.

5 Rigorous results

In the present section, we give without proofs a number of mathematical results which are the basis of a rigorous derivation of the results obtained in the chapter. The previous introduction to the Green function technique was inspired by the old-fashioned treatment of differential equations. The modern way to present Green functions is more formal. Let H be an essentially self-adjoint operator (a Hermitian operator in the physical language) in a Hilbert space $\mathcal{H}$. The Hilbert space is normally the set of square integrable function, denoted $\mathcal{L}^2(\mathbf{R}^3)$ to fulfill the physical condition that the wavefunction is normalisable. Let z be a complex number and define the Green operator of H in $\mathcal{H}$ as $G(z) = (z - H)^{-1}$.[6] Since H is Hermitian, its eigenvalues are real. Therefore, when z is not purely real, the equation $(z - H)G(z) = 1$ has a unique solution and $G(z) = (H - z)^{-1}$ is well-defined. More precisely, the Green operator is an analytic operator [4] p.204 outside the real axis. According to the limiting absorption theorem, the limits $G^+(E) = \lim_{\epsilon\to 0} G(E + i\epsilon)$ and $G^-(E) = \lim_{\epsilon\to 0} G(E - i\epsilon)$ exist. The Green function for electrodynamics correspond to $H = \Delta$, $\mathcal{H} = \mathcal{L}^2(\mathbf{R}^3)$, $G = G^+$ and $\kappa = \sqrt{z}$ (κ is the principal square root of z as defined in Ref.[18], p. 17).[7] Note that the boundary conditions, which were so delicate in the previous sections, do not seem to enter the new definition. As a matter of fact the boundary conditions are hidden in the definition of the Hilbert space and in the choice of G^+.

A generalized eigenfunction is a regular function $\phi_L(\mathbf{r}; E)$ such that $H\phi_L(\mathbf{r}; E) = E\phi_L(\mathbf{r}; E)$. For the moment, L is just an index to discriminate between different eigenfunctions of the same energy. For the Hamiltonians that we use, the negative eigenenergies are discrete and the corresponding $\phi_L(\mathbf{r}; E)$ are standard eigenfunctions (i.e. they belong to $\mathcal{H}$), whereas the positive eigenenergies form a continuum and the corresponding $\phi_L(\mathbf{r}; E)$ are not normalisable, the eigenvalue $E = 0$ can have both behaviours [4] p.280.

By suitably normalising the eigenfunctions, we can choose a complete set of eigenfunctions which make a kind of resolution of the identity (in the weak topology sense)

$$\sum_{E_n\le 0}\sum_{L} \phi_L(\mathbf{r}; E_n)\phi^*_L(\mathbf{r}'; E_n) + \int_0^\infty dE \sum_L \phi_L(\mathbf{r}; E)\phi^*_L(\mathbf{r}'; E) = \delta(\mathbf{r} - \mathbf{r}').$$

6. In the mathematical literature, $G(z)$ is often called the resolvent (denoted $R(z)$) and the definition $R(z) = (H - z)^{-1} = -G(z)$ is also used.

7. The new definition of the Green operator does not refer to any basis. The expression of the Green operator in the coordinate basis is called the kernel of the Green operator, or the Green function.

To simplify notation, the sum over the negative eigenenergies and the integral over the positive energy continuum will be simply denoted by $\sum_E$. Introducing the resolution of the identity into the definition of the Green operator yields the classical form:

$$G(\mathbf{r}, \mathbf{r}'; z) = \sum_E \sum_L \frac{\phi_L(\mathbf{r}; E)\phi_L^*(\mathbf{r}'; E)}{z - E}.$$

A mathematical problem is completely solved when the spaces to which the functions belong are known. An excellent treatment of the Schroödinger equation for the potentials that are used in practice is given in ref.[20]. We consider a molecule as represented by a potential $V(\mathbf{r})$. This potential is a sum of atomic potentials V_i which are zero outside a finite volume Ω_i and which can be written as $V_i(\mathbf{r}) = -2Z_i/|\mathbf{r}-\mathbf{R}_i|+\hat{V}_i(\mathbf{r})$, where $\hat{V}_i(\mathbf{r})$ has no singularity. It is possible to add an outersphere potential, but this is restricted to neutral cluster, because an essential condition of the following results is that $V(\mathbf{r}) = O(|\mathbf{r}|^{-1-\epsilon})$ for some positive ϵ as $|\mathbf{r}| \to 0$. Then no positive eigenvalue exist. Let $L^2(\mathbf{R}^3)$ be the set of complex functions for which the integral of the squared modulus over $\mathbf{R}^3$ is finite (physically, these are the normalisable wavefunctions). Let $\mathcal{H}_2(\mathbf{R}^3)$ be the set of functions $f \in L^2(\mathbf{R}^3)$ such that all first and second derivative belong to $L^2(\mathbf{R}^3)$ (this is called a Sobolev space). The $H = -\Delta + V$ acting on $L^2(\mathbf{R}^3)$ has domain $\mathcal{H}_2(\mathbf{R}^3)$. For the Green function we need additional function spaces: $L^{2,s} = \{u(\mathbf{r}) : (1 + r^2)^{s/2}u(\mathbf{r}) \in L^2(\mathbf{R}^3)$ and $\mathcal{H}_{2,s}$ which is the set of functions of $L^{2,s}$ such that all first and second derivatives are in $L^{2,s}$. Finally, let $B(L^{2,s}, \mathcal{H}_{2,s})$ the set of bounded linear operators from $L^{2,s}$ to $\mathcal{H}_{2,s}$. A theorem of Ref.[20] is that the Green function $(z - H)^{-1}$ is an analytic operator valued function on $\mathbf{C}\backslash\sigma(H)$ with values in $B(L^{2,s}, \mathcal{H}_{2,s})$ for any $s > 1/2$. Moreover, the limits on the real axis exist for $E > 0$ and, for any $f \in L^{2,s}$, the resolvent identity is true on the real axis:

$$G^{\pm}(E)f = G_0^{\pm}(E)f + G_0^{\pm}(E)VG^{\pm}(E)f.$$

Another useful result of Ref.[20] is that the operator $1-G_0(z)V$ is a compact operator on $\mathbf{C}^+$ (the set of z such that $\Im z > 0$ or z real greater than 0), and its inverse $(1 - G_0(z)V)^{-1}$ exists in $B(\mathcal{H}_{2,-s}\mathcal{H}_{2,-s})$. It is continuous in operator norm topology on $\mathbf{C}^+$ and $G(z) = (1 - G_0(z)V)^{-1}G_0(z)$ on $\mathbf{C}^+$.

Agmon proves also the completeness of the generalised eigenfunctions. Taking spherical harmonics for $g(\omega)$ in Eq.(5.17) of Ref.[20], we have that for any "incident" wavefunction $\phi_L(\mathbf{r}; \kappa) = j_\ell(\kappa)Y_\ell^m(\hat{(r)})$, there is a generalised eigenfunction $\psi_L(\mathbf{r}; \kappa)$ in $\mathcal{H}_{2,-s} \cap C^{0,-s}$ for any $s > 1/2$, such that $(H - \kappa^2)\psi_L = 0$ and $\psi_L = \phi_L + G^+(\kappa^2)V\phi_L$ (the Lippmann-Schwinger equation). $C^{0,-s}$ is the class of continuous functions $u(\mathbf{r})$ such that $|(1+r)^s u(\mathbf{r})|$ is bounded on $\mathbf{R}^3$. We shall also use the existence of completeness of the waveoperators for the above potential, from which one can deduce that ψ_L form a complete basis of functions when ϕ_L does and that the norm of ψ_L is the same as the norm of ϕ_L.

Agmon proved the above results for real energies. They can be obtained more easily for complex energies, when κ has a positive imaginary part, as discussed in Ref.[21].

We can add to this some bounds that were proved for the potentials we used. In Ref.[22], it is shown that, for $z \in Z_0$ large enough, one has

$$|G(\mathbf{r}, \mathbf{r}'; z)| \leq c\frac{\exp(-\alpha|\mathbf{r} - \mathbf{r}'||\kappa|)}{|\mathbf{r} - \mathbf{r}'|}$$

for c and α constants > 0, uniformly in $\mathbf{r}$, $\mathbf{r}'$ and κ. In this formula, $\kappa^2 = z$ and for some number ϵ (with $0 < \epsilon < \pi$) and $Z_0 = \{z \in \mathbf{C} : \epsilon \leq \arg z \leq \pi - \epsilon\}$.

In Ref.[23], Simon has derived the following results:

Let σ be the set of eigenvalues of H and $\Sigma = \inf \sigma$. Let $z < \Sigma$ or $z \notin \sigma$, then the Green function $G(\mathbf{r}, \mathbf{r}'; z)$ is continuous away from $\mathbf{r} = \mathbf{r}'$, there exists constants C_1 and C_2 such that

$$\frac{C_1}{|\mathbf{r} - \mathbf{r}'|} \leq |G(\mathbf{r}, \mathbf{r}'; z)| \leq \frac{C_2}{|\mathbf{r} - \mathbf{r}'|}.$$

The first inequality is true only when $|\mathbf{r} - \mathbf{r}'|$ is sufficiently small. Moreover, for $|\mathbf{r} - \mathbf{r}'| \geq 1$,

$$|G(\mathbf{r}, \mathbf{r}'; z)| \leq C_{\alpha,\delta,z} \exp(-\delta|\mathbf{r} - \mathbf{r}'|),$$

for some $\delta > 0$ and if $\Re z < \Sigma$, for all δ with $\frac{1}{2}\delta^2 < \Sigma - \Re z$.

6 Acknowledgements

I would like to thank Prof. E. Dartyge, Dr. F. Baudelet and the unknown referee for their thorough readings of the manuscript. Their remarks greatly improved the presentation.

Références

[1] R. Bellman and G. Adomian. *Partial Differential Equations, New Methods for their Treatment and Solution.* Mathematics and its Applications. D. Reidel Publishing Company, Dordrecht, Holland, first edition, 1985.

[2] J. Gray. Green and Green's functions. *Math. Intelligencer*, 16(1):45–7, 1994.

[3] G. Barton. *Elements of Green's Function and Propagation: Potentials, Diffusion and Waves.* Oxford University Press, Oxford,UK, first edition, 1989.

[4] R. G. Newton. *Scattering Theory of Waves and Particles.* Texts and Monographs in Physics. Springer Verlag, New York, second edition, 1982.

[5] N. Chernyavskaya and L. Shuster. Estimates for Green's function of the Sturm-Liouville operator. *J. Diff. Equat.*, 111:410–20, 1994.

[6] J. D. Jackson. *Classical Electrodynamics.* John Wiley and Sons, New York, second edition, 1975.

[7] A. Sommerfeld. *Partial Differential Equations in Physics.* Academic Press, New York, 1949.

[8] H. Isozaki. A generalization of the radiation condition of Sommerfeld for N-body Schrödinger operators. *Duke Math. J.*, 74(2):557–84, 1994.

[9] F.W. Byron Jr and R.W. Fuller. *Mathematics of Classical and Quantum Physics*, volume 2. Addison-Wesley, Reading, Massachusetts, 1970.

[10] F. Rellich. Die zulässigen Randbedingungen bei den singulären Eigenwertproblemen der mathematischen Physik. *Math. Zeitschrift*, 49:702–23, 1943.

[11] W. Bulla and F. Gesztesy. Deficiency indices and singular boundary conditions in quantum mechanics. *J. Math. Phys.*, 26(10):2520–8, 1985.

[12] A. M. Hinz. Regularity of solutions for singular Schrödinger equations. *Rev. Math. Phys.*, 4(1):95–161, 1992.

[13] Y. Joly. Finite-difference method for the calculation of low-energy positron diffraction. *Phys. Rev. B*, 53(19):13029–37, 1996.

[14] J. Korringa. Early history of multiple scattering theory for ordered systems. *Phys. Repts.*, 238(6):341–60, 1994.

[15] R.F.W. Bader. *Atoms in Molecules, A Quantum Theory.* Oxford University Press, Oxford,UK, first edition, 1990.

[16] D.D. Vvedensky. Theory of x-ray absorption fine structure. *Topics in Applied Physics*, 69:139–176, 1992. in Unoccupied Electronic State, F.C. Fuggle and J.E. Inglesfield, eds.

[17] R.V. Vedrinskiy and A.A. Novakovich. Method of Green's functions in the one-electron theory of x-ray spectra of disordered alloys. *Phys. Met. Metallogr.*, 39(1):1–8, 1975.

[18] M. Abramowitz and I.A. Stegun. *Handbook of Mathematical Functions.* Dover, New York, fifth edition, 1964.

[19] B. Friedman and J. Russek. Addition theorems for spherical waves. *Quart. Appl. Math.*, 12(1):13–23, 1954.

[20] S. Agmon. Spectral properties of Schrödinger operators and scattering theory. *Annali Scuola Normale Superiore Pisa, Classe di Scienze*, 2(2):151–218, 1975.

[21] P. Alsholm and G. Schmidt. Spectral and scattering theory for Schrödinger operators. *Arch. Rational Mech. Anal.*, 40:281–311, 1971.

[22] M. Horváth. Sur le développement spectral de l'opérateur de Schrödinger. *C. R. Acad. Sci. Paris A*, 311:499–502, 1990.

[23] B. Simon. Schrödinger semigroups. *Bull. Amer. Math. Soc.*, 7(3):447–???, 1982.