The Green Function Applied to Multiple Scattering Problem

The charge distribution for electrons can be written as:

\[ \rho(r) = e \sum_n \Psi_n^+(r) \Psi_n(r) \quad (1) \]

where \( e \) denotes elementary charge and the sum over \( n \) is over the occupied states. This reminds us of a form of Green function (in its purest and simplest form):

\[ G(r, r', E) = \sum_n \frac{\Psi_n(r) \Psi_n^+(r')}{E - E_n} \quad (2) \]

where \( \Psi_n \) and \( E_n \) are the eigenvector and eigenvalues of the Hamiltonian. The complete derivation of this form can be found in, for example, Paul Strange [1].

Having poles at physical energy levels, the Green function can be manipulated on the complex plane, and it is easy to obtain:

\[ G(r, r', E) = \sum_n \frac{\Psi_n(r) \Psi_n^+(r')}{E - E_n} = \lim_{\epsilon \to 0} \sum_n \frac{\Psi_n(r) \Psi_n^+(r')}{E - E_n + i\epsilon} \quad (3) \]

where it has become a standard trick to let \( \epsilon \) approach 0 to allow for simple calculations of the integral of the Green function using contour integral, and we shall see how some minor manipulation on the Green function can help us find the charge distribution of the atom.

Defining the fermi energy to be the energy of the highest occupied state in the ground state of the atom, we integrate the trace of the Green function up to the fermi energy:

\[ \int_{-\infty}^{\epsilon_f} Tr[G(r, r', E)] dE = \int_{-\infty}^{\epsilon_f} \lim_{\epsilon \to 0} \sum_n \frac{\Psi_n(r) \Psi_n^+(r')}{E - E_n + i\epsilon} dE \]

\[ = \sum_n \Psi_n^+(r) \Psi_n(r') \int_{-\infty}^{\epsilon_f} \frac{1}{E - E_n} - i\pi \delta(E - E_n) dE \]

\[ = \sum_n \Psi_n^+(r) \Psi_n(r') \int_{-\infty}^{\epsilon_f} \frac{1}{E - E_n} dE \quad (4) \]

and we have:

\[ \text{Im} \left( \int_{-\infty}^{\epsilon_f} Tr[G(r, r', E)] dE \right) = -i\pi \sum_n \Psi_n^+(r) \Psi_n(r') \quad (5) \]

and, easily, so:

\[ \rho(r) = -\frac{e}{\pi} \text{Im} \left( \int_{-\infty}^{\epsilon_f} Tr[G(r, r', E)] dE \right) = e \sum_n \Psi_n^+(r) \Psi_n(r') \quad (6) \]

which agrees with equation (1). While calculating the integral above can often be laborious, combining it with contour integral gives us a simple method of calculating the charge density without ever need integration.

For our purposes, suppose we want to find the charge density around a single pole of the Green function (i.e. finding the charge density of a certain energy level \( E_p \)):
\[ \rho(r) = -\frac{e}{\pi} \text{Im} \left( \int_{-\infty}^{\infty} \text{Tr}[G(r, r', E)] \, dE \right) \]
\[ = -\frac{e}{\pi} \text{Im} \left( \int_{-\infty}^{\infty} \lim_{\epsilon \to 0} \frac{\Psi(E, r) \psi^+(E, r')}{E - E_p + \epsilon} \, dE \right) \]
\[ = e^\Psi \left( E_p, r \right) \psi^+ \left( E_p, r' \right) \]

(7)

Notice that we have done the contour integral drawing a half circle around the pole at \( E_p \).

In our case, we have a more complicated Green function, and we replace the solutions \( \Psi_n(r) \) with the so-called regular solutions \( \phi_L(r, E) \) such that, when \( r \) goes to 0:
\[ \phi_L(r, E) \to j_L(\sqrt{\epsilon}r)Y_L(r) \]

(8)

where \( j_L \) is the spherical Bessel function and \( Y_L \) is the spherical harmonics with \( L \) standing for both \( l \) and \( m \). In our multiple scattering approach, the Green function takes the form:
\[ G(r, r', \epsilon) = \sqrt{\epsilon} \sum_{L,L'} \phi_L(r, \epsilon) \left( i s(\epsilon) - c(\epsilon) \right) (s^T(\epsilon))^{-1} \phi_{L'}(r, \epsilon) \]

(9)

where \( s = \sin \eta_l(\epsilon) \), and \( c = \cos \eta_l(\epsilon) \), and \( \eta_l \) is the phase shift of a scattering. This introduces the Jost matrix:
\[ J^+(\epsilon) = is(\epsilon) - c(\epsilon) \]

(10)

and so the expression for the Green function simplifies to:
\[ G(r, r', \epsilon) = \sqrt{\epsilon} \sum_{L,L'} \phi_L(r, \epsilon) J^+(\epsilon)^{-1} (s^T(\epsilon))^{-1} \phi_{L'}(r, \epsilon) \]

(11)

A derivation of this is beyond the scope of this paper, and we refer the readers to Xianglin for a detailed derivation [2]. Notice that the poles of the function has been integrated into the Jost matrix.

Finally, setting \( \epsilon = 1 \) and doing the integration, we will be find the charge density of the energy level \( p \):
\[ \rho(r) = -\frac{1}{\pi} \text{Im} \left( \int_{-\infty}^{\infty} \text{Tr}[G(r, r', \epsilon)] \, d\epsilon \right) \]
\[ = \sqrt{\epsilon_p} \text{Im} \left( \sum_{L,L'} \phi_L(r, \epsilon_p) H(\epsilon_p) (s^T(\epsilon_p))^{-1} \phi_{L'}(r, \epsilon_p) \right) \]

(12)

where \( H(\epsilon_p) \) is a function related to \( J^+(\epsilon)^{-1} \) by \( H(\epsilon_p) = x_p y_p J^{(2)}(\epsilon_0) \), the meaning of which we will discuss in the third Chapter.

Now we show how we could calculate the physical energy levels.

**Finding the energies levels from the Jost Matrix**

In fact, the Jost matrix is central to our theory. This derivation is based on the usual Quadratic Korringa-Kohn-Rostocker method (QKKR) as developed by Faulkner et al [3].

We start with a given scattering matrix:
\[ S_l(e) = e^{2i \Omega t} = \frac{J_l^-(e)}{J_l^+(e)} \]  
(13)

where \( J^+ \) is defined in the previous chapter, and \( J^-(e) = -is(e) - c(e) \). Observe that S has the same poles as the zeros of \( J^+ \), corresponding to the resonance and bound states of the system, depending on the sign of the zero.

To do this, we expand the Jost matrix (now we refer to \( J^+ \) as the Jost matrix and simply write it as \( J \)) around an energy \( e_0 \):

\[
J(e_0 + e) = J^{(0)}(e_0) + ef^{(1)}(e_0) + e^2f^{(2)}(e_0) \tag{14}
\]

Assuming the e is sufficiently small we keep up to the second order term. In this sense, the whole theory is a second order approximation on the energy.

To find \( f^{(1)}(e_0) \) and \( f^{(2)}(e_0) \), we expand the Jost matrix on three close energy values:

\[
J(e_0) = J^{(0)}(e_0) \tag{15a}
\]
\[
J(e_0 + e) = J^{(0)}(e_0) + ef^{(1)}(e_0) + e^2f^{(2)}(e_0) \tag{15b}
\]
\[
J(e_0 - e) = J^{(0)}(e_0) - ef^{(1)}(e_0) + e^2f^{(2)}(e_0) \tag{15c}
\]

and some algebra tells us:

\[
f^{(1)}(e_0) = \frac{1}{2e} [J(e_0 + e) - J(e_0 - e)] \tag{16a}
\]
\[
f^{(2)}(e_0) = \frac{1}{2e^2} [J(e_0 + e) + J(e_0 - e) - 2J(e_0)] \tag{16b}
\]

Then we are left to solve for the zeros, \( e_p \) of \( J \), which can be using the condition:

\[
\det(J(e_p)) = 0 \tag{17}
\]

To allow of easier math, we write equation (14) as in the form:

\[
A(e) = e^2 - B(e - D) \tag{18}
\]

where \( A(e) = f^{(2)}(e_0)^{-1}J(e_0 + e) \), and so on. Observe that \( A(e) \) has the same zeros as \( J(e_0 + e) \), so finding the zeros of \( J \) reduces to finding the zeros of \( A \):

\[
\det(A(e)) = 0 \tag{19}
\]

or equivalently (where I denotes the identity matrix of corresponding size):

\[
\det \begin{pmatrix} eI - D & I \\ -D^2 & eI - B + D \end{pmatrix} = 0 \tag{20}
\]

whose eigenvalues can be found by diagonalizing the following matrix:

\[
G = \begin{pmatrix} D & I \\ -D^2 & B - D \end{pmatrix} \tag{21}
\]

This method provides an easily implementable method to find the energies of a given scattering matrix, which can then be used to calculate the charge density using the method given in the previous chapter.

Finding Charge Density from the Green Function

Now we derive equation (12). In particular, we first show that, for a Jost matrix \( J \) with energy eigenvalue \( e_p \), its integral with a general function \( f(e) \) is given by:
\[
\text{Im} \left( \int_{-\infty}^{\infty} f(e)J^{-1}(e) \, de \right) = -\pi \text{Re} \left( f(e_p)x_py_p(J^{(2)}(e_0)) \right)
\]  
(22)

where \( J^{(2)}(e_0) \) is defined in (16b), and \( x_p \) and \( y_p \) are vectors we will define later. Now consider matrix \( H \) defined as:

\[
H = e - G = \begin{pmatrix}
e l - D & 1 \\
-D^2 & e l - B + D
\end{pmatrix}
\]  
(23)

where \( G \) is defined in (21).

References