

Introduction to Multiple Scattering Theory

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1 Formal Scattering Theory

1.1 Resolvents

Spectrum of Hermitean operator, \mathcal{H} , over a Hilbert space, \mathbf{H}

Discrete spectrum

Continuous spectrum

$$\begin{aligned} \mathcal{H}\varphi_n &= \varepsilon_n\varphi_n \\ (\varphi_n \in \mathbf{H}) \end{aligned}$$

$$\begin{aligned} \mathcal{H}\varphi_\alpha(\varepsilon) &= \varepsilon\varphi_\alpha(\varepsilon) \\ (\varphi_\alpha(\varepsilon) = \lim_{n \rightarrow \infty} \chi_n, \quad \chi_n \in \mathbf{H}) \end{aligned}$$

$$\langle \varphi_n | \varphi_m \rangle = \delta_{nm}$$

$$\langle \varphi_\alpha(\varepsilon) | \varphi_{\alpha'}(\varepsilon') \rangle = \delta_{\alpha\alpha'} \delta(\varepsilon - \varepsilon')$$

The (generalized) eigenfunctions form a complete set,

$$\sum_n |\varphi_n\rangle\langle\varphi_n| + \int d\varepsilon \sum_\alpha |\varphi_\alpha(\varepsilon)\rangle\langle\varphi_\alpha(\varepsilon)| = \mathcal{I} \quad . \quad (1)$$

Notation: $Sp(\mathcal{H}), \varrho(\mathcal{H}) = \mathbb{C} \setminus Sp(\mathcal{H})$

Units: $\hbar = 1, m = 1/2, e^2 = 2 \Rightarrow a_0 = \hbar^2/me^2 = 1, Ryd = \hbar^2/2ma_0^2 = 1$

The free-particle Hamiltonian,

$$\mathcal{H}_0 = \vec{p}^2 = -\Delta, \quad (2)$$

has no discrete spectrum over the Hilbert-space, $\mathbf{H} = \mathbf{L}^2(\mathbb{R}^3)$. However,

$$\mathcal{H}_0\varphi(\vec{p}) = p^2\varphi(\vec{p}), \quad \varphi(\vec{p}; \vec{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{p}\vec{r}}, \quad (3)$$

$$\varphi(\vec{p}) = \lim_{n \rightarrow \infty} \chi_n(\vec{p}), \quad \chi_n(\vec{p}; \vec{r}) = \frac{1}{(2\pi)^{3/2}} \exp(i\vec{p}\vec{r} - r^2/4n^2),$$

and $\chi_n(\vec{p}) \in \mathbf{L}^2(\mathbb{R}^3)$. Thus, the continuous spectrum of \mathcal{H}_0 covers the set of non-negative numbers.

The *resolvent* of \mathcal{H} is defined for any $z \in \rho(\mathcal{H})$ as

$$\mathcal{G}(z) = (z\mathcal{I} - \mathcal{H})^{-1} . \quad (4)$$

It obviously satisfies,

$$\mathcal{G}(z^*) = \mathcal{G}(z)^\dagger , \quad (5)$$

therefore, it is Hermitean only for $\varepsilon \in \rho(\mathcal{H}) \cap \mathbb{R}$. From the relation,

$$\mathcal{G}(z_1) - \mathcal{G}(z_2) = (z_2 - z_1) \mathcal{G}(z_1) \mathcal{G}(z_2) , \quad (6)$$

immediately follows that

$$\frac{d\mathcal{G}(z)}{dz} = -\mathcal{G}(z)^2 , \quad (7)$$

and, by noting that $\mathcal{G}(z)$ is bounded, it can be concluded that the mapping $z \rightarrow \mathcal{G}(z)$ is *analytic* for $z \in \rho(\mathcal{H})$. From Eq. (1) the *spectral resolution* of the resolvent can be written as

$$\mathcal{G}(z) = \sum_n \frac{|\varphi_n\rangle\langle\varphi_n|}{z - \varepsilon_n} + \int d\varepsilon \sum_\alpha \frac{|\varphi_\alpha(\varepsilon)\rangle\langle\varphi_\alpha(\varepsilon)|}{z - \varepsilon} . \quad (8)$$

Relationship between the eigenvalues of \mathcal{H} and the singularities of $\mathcal{G}(z)$:

$$\begin{aligned} \text{discrete spectrum of } \mathcal{H} &\longrightarrow \text{poles of first order of } \mathcal{G}(z) \\ \text{continuous spectrum of } \mathcal{H} &\longrightarrow \text{branch cuts of } \mathcal{G}(z) \end{aligned} . \quad (9)$$

Therefore, at the real axis the so-called *up-* and *down-side limits* of $\mathcal{G}(z)$ are introduced,

$$\mathcal{G}^\pm(\varepsilon) = \lim_{\delta \rightarrow +0} \mathcal{G}(\varepsilon \pm i\delta) \quad (\varepsilon \in \mathbb{R}) , \quad (10)$$

having the following relationship,

$$\mathcal{G}^\pm(\varepsilon) = \mathcal{G}^\mp(\varepsilon)^\dagger . \quad (11)$$

In particular, for $\varepsilon \in \rho(\mathcal{H}) \cap \mathbb{R}$

$$\mathcal{G}^+(\varepsilon) = \mathcal{G}^-(\varepsilon) = \mathcal{G}(\varepsilon) . \quad (12)$$

Using the identity,

$$\lim_{\delta \rightarrow +0} \frac{1}{\varepsilon - \varepsilon' \pm i\delta} = P \left(\frac{1}{\varepsilon - \varepsilon'} \right) \mp i\pi\delta(\varepsilon - \varepsilon') \quad ,$$

with P denoting the principal value distribution,

$$\begin{aligned} \operatorname{Re} \mathcal{G}^+ (\varepsilon) &= \operatorname{Re} \mathcal{G}^- (\varepsilon) \\ &= \sum_n |\varphi_n\rangle \langle \varphi_n| P \left(\frac{1}{\varepsilon - \varepsilon_n} \right) + \int d\varepsilon' \sum_\alpha |\varphi_\alpha (\varepsilon')\rangle \langle \varphi_\alpha (\varepsilon')| P \left(\frac{1}{\varepsilon - \varepsilon'} \right) \quad , \end{aligned} \quad (13)$$

and

$$\begin{aligned} \operatorname{Im} \mathcal{G}^+ (\varepsilon) &= -\operatorname{Im} \mathcal{G}^- (\varepsilon) \\ &= -\pi \left(\sum_n |\varphi_n\rangle \langle \varphi_n| \delta(\varepsilon - \varepsilon_n) + \int d\varepsilon' \sum_\alpha |\varphi_\alpha (\varepsilon')\rangle \langle \varphi_\alpha (\varepsilon')| \delta(\varepsilon - \varepsilon') \right) \quad , \end{aligned} \quad (14)$$

where the real and imaginary part of an operator, \mathcal{A} is defined as

$$\operatorname{Re} \mathcal{A} = \frac{1}{2} (\mathcal{A} + \mathcal{A}^\dagger) \quad \text{and} \quad \operatorname{Im} \mathcal{A} = \frac{1}{2i} (\mathcal{A} - \mathcal{A}^\dagger) \quad . \quad (15)$$

Generally, a given representation of the resolvent is called the *Green function*.

On the basis of the eigenfunctions of \mathcal{H} ,

$$G_{nn'} (z) = \langle \varphi_n | \mathcal{G} (z) | \varphi_{n'} \rangle = \sum_m \frac{\langle \varphi_n | \varphi_m \rangle \langle \varphi_m | \varphi_{n'} \rangle}{z - \varepsilon_m} = \delta_{nn'} \frac{1}{z - \varepsilon_n} \quad (16)$$

and, similarly,

$$G_{\alpha\alpha'} (z; \varepsilon, \varepsilon') = \delta_{\alpha\alpha'} \delta(\varepsilon - \varepsilon') \frac{1}{z - \varepsilon} \quad , \quad (17)$$

while in the *coordinate (real-space) representation*,

$$G (z; \vec{r}, \vec{r}') = \sum_m \frac{\varphi_n (\vec{r}) \varphi_n (\vec{r}')^*}{z - \varepsilon_n} + \int d\varepsilon \sum_\alpha \frac{\varphi_\alpha (\varepsilon; \vec{r}) \varphi_\alpha (\varepsilon; \vec{r}')^*}{z - \varepsilon} \quad . \quad (18)$$

The primary task of the Multiple Scattering Theory (or Korringa-Kohn-Rostoker method) is to give a general expression for $G (\vec{r}, \vec{r}'; z)$.

The Green function of free particles

$$G_0(z; \vec{r}, \vec{r}') = \frac{1}{(2\pi)^3} \int d^3k \frac{e^{i\vec{k}(\vec{r}-\vec{r}')}}{z - k^2}, \quad (19)$$

which can be evaluated as follows,

$$\begin{aligned} G_0(z; \vec{r}, \vec{r}') &= \frac{1}{(2\pi)^3} \int_0^\infty dk k^2 \frac{1}{z - k^2} \int d^2\hat{k} e^{i\vec{k}(\vec{r}-\vec{r}')} \\ &= -\frac{i}{8\pi^2 |\vec{r}' - \vec{r}'|} \left(\int_{-\infty}^\infty dk k \frac{e^{ik|\vec{r}-\vec{r}'|}}{z - k^2} - \int_{-\infty}^\infty dk k \frac{e^{-ik|\vec{r}-\vec{r}'|}}{z - k^2} \right). \end{aligned}$$

Obviously, the first and the second integral in the last expression can be closed in the upper and the lower complex semiplane, respectively. Thus, by choosing $p \in \mathbb{C}$, $\text{Im } p > 0$, such that $z = p^2$ yields

$$\begin{aligned} G_0(z; \vec{r}, \vec{r}') &= \frac{1}{4\pi |\vec{r}' - \vec{r}'|} \left[\text{Res}\left(\frac{ke^{ik|\vec{r}-\vec{r}'|}}{(p-k)(p+k)}, p\right) - \text{Res}\left(\frac{ke^{-ik|\vec{r}-\vec{r}'|}}{(p-k)(p+k)}, -p\right) \right] \\ &= -\frac{e^{ip|\vec{r}-\vec{r}'|}}{4\pi |\vec{r}' - \vec{r}'|}, \end{aligned} \quad (20)$$

while by choosing $p \in \mathbb{C}$, $\text{Im } p < 0$, such that $z = p^2$, one obtains

$$\begin{aligned} G_0(z; \vec{r}, \vec{r}') &= \frac{1}{4\pi |\vec{r}' - \vec{r}'|} \left[\text{Res}\left(\frac{ke^{ik|\vec{r}-\vec{r}'|}}{(p-k)(p+k)}, -p\right) - \text{Res}\left(\frac{ke^{-ik|\vec{r}-\vec{r}'|}}{(p-k)(p+k)}, p\right) \right] \\ &= -\frac{e^{-ip|\vec{r}-\vec{r}'|}}{4\pi |\vec{r}' - \vec{r}'|}. \end{aligned} \quad (21)$$

Clearly, independent of the choice of the square-root of z ($p_1 = -p_2$) the expression of $G_0(z; \vec{r}, \vec{r}')$ is unique. In particular,

$$G_0^\pm(\varepsilon; \vec{r}, \vec{r}') = -\frac{e^{\pm ip|\vec{r}-\vec{r}'|}}{4\pi |\vec{r}' - \vec{r}'|} \quad (\varepsilon > 0, p = \sqrt{\varepsilon}), \quad (22)$$

and

$$G_0^+(\varepsilon; \vec{r}, \vec{r}') = G_0^-(\varepsilon; \vec{r}, \vec{r}') = -\frac{e^{-p|\vec{r}-\vec{r}'|}}{4\pi |\vec{r}' - \vec{r}'|} \quad (\varepsilon < 0, p = \sqrt{-\varepsilon}). \quad (23)$$

1.2 Observables and Green functions

In a system of independent fermions, the measured value of a one-particle observable, say A , is given by

$$A = Tr (f (\mathcal{H}) \mathcal{A}) ,$$

where \mathcal{A} is the Hermitian operator related to A and, the Fermi-Dirac (density) operator is defined by

$$f (\mathcal{H}) = \left(I + e^{\beta(\mathcal{H}-\mu\mathcal{I})} \right)^{-1} ,$$

with $\beta = 1/k_B T$, T the temperature and μ the chemical potential. Evaluating the trace in the basis of the eigenstates of \mathcal{H} , the above expression reduces to

$$A = \sum_n f (\varepsilon_n) \langle \varphi_n | \mathcal{A} | \varphi_n \rangle + \int d\varepsilon \sum_\alpha f (\varepsilon) \langle \varphi_\alpha (\varepsilon) | \mathcal{A} | \varphi_\alpha (\varepsilon) \rangle , \quad (24)$$

where $f (\varepsilon) = 1 / (1 + e^{\beta(\varepsilon-\mu)})$. Recalling Eq. (8) one can write,

$$f (z) Tr (\mathcal{A} \mathcal{G} (z)) = \sum_n \frac{f (z) \langle \varphi_n | \mathcal{A} | \varphi_n \rangle}{z - \varepsilon_n} + \int d\varepsilon \sum_\alpha \frac{f (z) \langle \varphi_\alpha (\varepsilon) | \mathcal{A} | \varphi_\alpha (\varepsilon) \rangle}{z - \varepsilon} ,$$

which, in order to relate to Eq. (24), has to be integrated over a contour in the complex plane, \mathbb{C} comprising the spectrum of \mathcal{H} . In here, Cauchy's theorem is used, i.e., for a closed contour oriented clock-wise,

$$-\frac{1}{2\pi i} \oint dz \frac{g (z)}{z - a} = \begin{cases} g (a) & \text{if } a \text{ is within the contour} \\ 0 & \text{if } a \text{ is outside of the contour} \end{cases} ,$$

where it is supposed that the function g has no poles within the contour. Thus the poles of the Fermi-Dirac distribution,

$$f (z) \simeq k_B T \frac{1}{z - z_k} \quad \text{for } z \simeq z_k , \quad z_k = \mu + i (2k + 1) \pi k_B T \quad (k \in \mathbb{Z}) ,$$

have also to be taken into account,

$$A = -\frac{1}{2\pi i} \oint_{\mathbb{C}} dz f (z) Tr (\mathcal{A} \mathcal{G} (z)) - k_B T \sum_k Tr (\mathcal{A} \mathcal{G} (z_k)) , \quad (25)$$

where only the Matsubara poles, z_k , within the contour \mathbf{C} are considered in the sum of the *rhs*. By splitting the contour into (symmetric) upper and lower parts and making use of Eq. (5), Eq. (25) can further be transformed into

$$A = -\frac{1}{\pi} \text{Im} \int_{\mathcal{C}} dz f(z) \text{Tr}(\mathcal{A}\mathcal{G}(z)) - 2k_B T \sum_{\text{Im } z_k > 0} \text{Re} \text{Tr}(\mathcal{A}\mathcal{G}(z_k)) . \quad (26)$$

By deforming the contour to the real axis, the familiar expressions,

$$A = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) \text{Tr}(\mathcal{A}\mathcal{G}^+(\varepsilon)) = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) \text{Tr}(\mathcal{A}\mathcal{G}^-(\varepsilon)) , \quad (27)$$

can be deduced. In particular, the number of electrons can be calculated by taking $\mathcal{A} = \mathcal{I}$,

$$N = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) \text{Tr}\mathcal{G}^+(\varepsilon) = \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon) n(\varepsilon) , \quad (28)$$

where the *density of states* (DOS) is defined by

$$n(\varepsilon) = -\frac{1}{\pi} \text{Im} \text{Tr}\mathcal{G}^+(\varepsilon) = \frac{1}{\pi} \text{Im} \text{Tr}\mathcal{G}^-(\varepsilon) . \quad (29)$$

Thus, the discontinuity of the imaginary part of the Green function at the real axis is directly related to the density of states.

DOS of free particles

From Eq. (22) one immediately can derive for $\varepsilon > 0$,

$$\text{Im} \mathcal{G}_0^+(\varepsilon; \vec{r}, \vec{r}) = -\text{Im} \mathcal{G}_0^-(\varepsilon; \vec{r}, \vec{r}) = -\lim_{R \rightarrow 0} \frac{\sin(\kappa R)}{4\pi R} = -\frac{\kappa}{4\pi} ,$$

therefore, the density of states normalized to a unit volume can be written as

$$n_0(\varepsilon) = \Theta(\varepsilon) \frac{\sqrt{\varepsilon}}{4\pi^2} , \quad (30)$$

since for $\varepsilon < 0$ the Green function is real.

1.3 The T -operator

Defining the Hamiltonian, \mathcal{H} as a sum of the Hamiltonian of a reference system, \mathcal{H}_0 and the operator of perturbation, \mathcal{V}

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} , \quad (31)$$

the corresponding resolvents are coupled by

$$\begin{aligned} \mathcal{G}(z) &= (z\mathcal{I} - \mathcal{H}_0 - \mathcal{V})^{-1} \\ &= ((z\mathcal{I} - \mathcal{H}_0)(\mathcal{I} - \mathcal{G}_0(z)\mathcal{V}))^{-1} \\ &= (\mathcal{I} - \mathcal{G}_0(z)\mathcal{V})^{-1} \mathcal{G}_0(z) , \end{aligned} \quad (32)$$

or in terms of Dyson equations,

$$\mathcal{G}(z) = \mathcal{G}_0(z) + \mathcal{G}(z)\mathcal{V}\mathcal{G}_0(z) = \mathcal{G}_0(z) + \mathcal{G}_0(z)\mathcal{V}\mathcal{G}(z) , \quad (33)$$

which can be solved by successive iterations to yield the Born series,

$$\mathcal{G}(z) = \mathcal{G}_0(z) + \mathcal{G}_0(z)\mathcal{V}\mathcal{G}_0(z) + \mathcal{G}_0(z)\mathcal{V}\mathcal{G}_0(z)\mathcal{V}\mathcal{G}_0(z) + \dots . \quad (34)$$

By reformulating Eq. (34) as

$$\mathcal{G}(z) = \mathcal{G}_0(z) + \mathcal{G}_0(z)(\mathcal{V} + \mathcal{V}\mathcal{G}_0(z)\mathcal{V} + \dots)\mathcal{G}_0(z) , \quad (35)$$

it is worth to define the so-called T -operator,

$$\mathcal{T}(z) = \mathcal{V} + \mathcal{V}\mathcal{G}_0(z)\mathcal{V} + \mathcal{V}\mathcal{G}_0(z)\mathcal{V}\mathcal{G}_0(z)\mathcal{V} + \dots , \quad (36)$$

such that

$$\mathcal{G}(z) = \mathcal{G}_0(z) + \mathcal{G}_0(z)\mathcal{T}(z)\mathcal{G}_0(z) . \quad (37)$$

The subsequent relationships between the resolvents and the T -operator can easily be proved:

$$\mathcal{T}(z) = \mathcal{V} + \mathcal{V}\mathcal{G}(z)\mathcal{V}, \quad (38)$$

$$\mathcal{T}(z) = \mathcal{V} + \mathcal{V}\mathcal{G}_0(z)\mathcal{T}(z) = \mathcal{V} + \mathcal{T}(z)\mathcal{G}_0(z)\mathcal{V}, \quad (39)$$

$$\mathcal{G}_0(z)\mathcal{T}(z) = \mathcal{G}(z)\mathcal{V}, \quad (40)$$

as well as

$$\mathcal{T}(z)\mathcal{G}_0(z) = \mathcal{V}\mathcal{G}(z). \quad (41)$$

Since \mathcal{V} is Hermitean, similar to the resolvents the T -operator satisfies

$$\mathcal{T}(z^*) = \mathcal{T}(z)^\dagger, \quad (42)$$

and, in particular, for the side-limits

$$\mathcal{T}^+(\varepsilon)^\dagger = \mathcal{T}^-(\varepsilon). \quad (43)$$

From Eqs. (38), (7), (40) and (41):

$$\begin{aligned} \frac{d\mathcal{T}(z)}{dz} &= \mathcal{V}\frac{d\mathcal{G}(z)}{dz}\mathcal{V} = -\mathcal{V}\mathcal{G}(z)\mathcal{G}(z)\mathcal{V} \\ &= -\mathcal{T}(z)\mathcal{G}_0(z)^2\mathcal{T}(z) \\ &\quad \Downarrow \\ \frac{d\mathcal{T}(z)}{dz} &= \mathcal{T}(z)\frac{d\mathcal{G}_0(z)}{dz}\mathcal{T}(z). \end{aligned} \quad (44)$$

1.4 Scaling transformation of the resolvents

In general, we are not restricted to choosing the system of free particles as reference. Let us consider the Hamiltonian,

$$\mathcal{H}' = \mathcal{H}_0 + \mathcal{U} , \quad (45)$$

with the corresponding perturbation,

$$\mathcal{V}' = \mathcal{V} - \mathcal{U} , \quad (46)$$

such that

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} = \mathcal{H}' + \mathcal{V}' . \quad (47)$$

From Eqs. (34-39) immediately follows, that the resolvent $\mathcal{G}(z)$ can be expressed in terms of the resolvent of the new reference system,

$$\mathcal{G}'(z) = (z\mathcal{I} - \mathcal{H}')^{-1} . \quad (48)$$

or

$$\mathcal{G}'(z) = \mathcal{G}_0(z) + \mathcal{G}_0(z)\mathcal{U}\mathcal{G}'(z) , \quad (49)$$

and a new T -operator,

$$\mathcal{T}'(z) = \mathcal{V}' + \mathcal{V}'\mathcal{G}'(z)\mathcal{T}'(z) , \quad (50)$$

as

$$\mathcal{G}(z) = \mathcal{G}'(z) + \mathcal{G}'(z)\mathcal{T}'(z)\mathcal{G}'(z) . \quad (51)$$

Eqs. (49-51) represent the formal background to the so-called Screened Korringa-Kohn-Rostoker (SKKR) theory to be discussed later.

1.5 The Lippmann-Schwinger equation

Suppose $\varphi_\alpha(\varepsilon)$ is a generalized eigenfunction of \mathcal{H}_0 ,

$$(\varepsilon\mathcal{I} - \mathcal{H}_0)\varphi_\alpha(\varepsilon) = 0 . \quad (52)$$

Let us seek for a generalized eigenfunction of \mathcal{H} ,

$$(\varepsilon\mathcal{I} - \mathcal{H}_0)\psi_\alpha(\varepsilon) = \mathcal{V}\psi_\alpha(\varepsilon) , \quad (53)$$

in the form of

$$\psi_\alpha(\varepsilon) = \varphi_\alpha(\varepsilon) + \delta\psi_\alpha(\varepsilon) . \quad (54)$$

Clearly, for vanishing perturbation, $\mathcal{V} = 0$, $\delta\psi_\alpha(\varepsilon) = 0$ is expected. By substituting Eq. (54) into (53) we get

$$(\varepsilon\mathcal{I} - \mathcal{H}_0)(\varphi_\alpha(\varepsilon) + \delta\psi_\alpha(\varepsilon)) = (\varepsilon\mathcal{I} - \mathcal{H}_0)\delta\psi_\alpha(\varepsilon) = \mathcal{V}\varphi_\alpha(\varepsilon) + \mathcal{V}\delta\psi_\alpha(\varepsilon) , \quad (55)$$

where we made use of Eq. (52), from which

$$(\varepsilon\mathcal{I} - \mathcal{H})\delta\psi_\alpha(\varepsilon) = \mathcal{V}\varphi_\alpha(\varepsilon) \quad (56)$$

can be deduced. Since, over the spectrum of \mathcal{H} , the inverse of $\varepsilon\mathcal{I} - \mathcal{H}$ is defined through two different side-limits, two different solutions exist,

$$\psi_\alpha^\pm(\varepsilon) = \varphi_\alpha(\varepsilon) + \mathcal{G}^\pm(\varepsilon)\mathcal{V}\varphi_\alpha(\varepsilon) , \quad (57)$$

or by using Eq. (40)

$$\psi_\alpha^\pm(\varepsilon) = \varphi_\alpha(\varepsilon) + \mathcal{G}_0^\pm(\varepsilon)\mathcal{T}^\pm(\varepsilon)\varphi_\alpha(\varepsilon) . \quad (58)$$

Moreover, from Eqs. (39) and (58) it follows that

$$\mathcal{V}\psi_\alpha^\pm(\varepsilon) = (\mathcal{V} + \mathcal{V}\mathcal{G}_0^\pm(\varepsilon)\mathcal{T}^\pm(\varepsilon))\varphi_\alpha(\varepsilon) = \mathcal{T}^\pm(\varepsilon)\varphi_\alpha(\varepsilon) , \quad (59)$$

therefore,

$$\psi_\alpha^\pm(\varepsilon) = \varphi_\alpha(\varepsilon) + \mathcal{G}_0^\pm(\varepsilon)\mathcal{V}\psi_\alpha^\pm(\varepsilon) . \quad (60)$$

1.6 The optical theorem

In general, energy conservation requires to use only the so-called *on-the-energy shell matrixelements* of the T -operator,

$$T_{\alpha\alpha'}^{\pm}(\varepsilon) = \langle \varphi_{\alpha}(\varepsilon) | \mathcal{T}^{\pm}(\varepsilon) | \varphi_{\alpha'}(\varepsilon) \rangle . \quad (61)$$

Eq. (43) implies the relationship,

$$T_{\alpha\alpha'}^{+}(\varepsilon) = T_{\alpha'\alpha}^{-}(\varepsilon)^{*} . \quad (62)$$

Starting from Eq. (38) the matrixelements of $\mathcal{T}^{\pm}(\varepsilon)$ can be expressed as

$$T_{\alpha\alpha'}^{\pm}(\varepsilon) = V_{\alpha\alpha'}(\varepsilon) + \langle \varphi_{\alpha}(\varepsilon) | \mathcal{V} \mathcal{G}^{\pm}(\varepsilon) \mathcal{V} | \varphi_{\alpha'}(\varepsilon) \rangle , \quad (63)$$

where

$$V_{\alpha\alpha'}(\varepsilon) = \langle \varphi_{\alpha}(\varepsilon) | \mathcal{V} | \varphi_{\alpha'}(\varepsilon) \rangle . \quad (64)$$

Taking the difference,

$$T_{\alpha\alpha'}^{+}(\varepsilon) - T_{\alpha\alpha'}^{-}(\varepsilon) = \langle \varphi_{\alpha}(\varepsilon) | \underbrace{\mathcal{V}(\mathcal{G}^{+}(\varepsilon) - \mathcal{G}^{-}(\varepsilon))\mathcal{V}}_{2i \operatorname{Im} \mathcal{G}^{+}(\varepsilon)} | \varphi_{\alpha'}(\varepsilon) \rangle , \quad (65)$$

the spectral resolution of $\operatorname{Im} \mathcal{G}^{+}(\varepsilon)$, Eq. (14), can be used to give,

$$T_{\alpha\alpha'}^{+}(\varepsilon) - T_{\alpha\alpha'}^{-}(\varepsilon) = -2\pi i \sum_{\beta} \langle \varphi_{\alpha}(\varepsilon) | \mathcal{V} | \psi_{\beta}^{+}(\varepsilon) \rangle \langle \psi_{\beta}^{+}(\varepsilon) | \mathcal{V} | \varphi_{\alpha'}(\varepsilon) \rangle , \quad (66)$$

which by employing Eqs. (59) and (62) can be written as

$$T_{\alpha\alpha'}^{+}(\varepsilon) - T_{\alpha\alpha'}^{-}(\varepsilon) = -2\pi i \sum_{\beta} T_{\alpha\beta}^{+}(\varepsilon) T_{\beta\alpha'}^{-}(\varepsilon) , \quad (67)$$

referred to as the *generalized optical theorem*.

Using matrix notation,

$$T^\pm(\varepsilon) = \{T_{\alpha\alpha'}^\pm(\varepsilon)\} ,$$

Eq. (67) can be rewritten into the compact form,

$$T^+(\varepsilon) - T^-(\varepsilon) = -2\pi i T^+(\varepsilon) T^-(\varepsilon) , \quad (68)$$

or

$$T^+(\varepsilon)^{-1} - T^-(\varepsilon)^{-1} = 2\pi i I . \quad (69)$$

Multiplying the above equation with $T^+(\varepsilon)$ from the left and with $T^-(\varepsilon)$ from the right, it also follows that

$$T^+(\varepsilon) - T^-(\varepsilon) = -2\pi i T^-(\varepsilon) T^+(\varepsilon) , \quad (70)$$

consequently, the operators $T^+(\varepsilon)$ and $T^-(\varepsilon)$ commute with each other,

$$T^+(\varepsilon) T^-(\varepsilon) = T^-(\varepsilon) T^+(\varepsilon) . \quad (71)$$

1.7 The S -matrix

In order to get more insight into the physical meaning of the optical theorem we introduce the so-called S -matrix as

$$\psi_\alpha^+(\varepsilon) = \sum_{\alpha'} \psi_{\alpha'}^-(\varepsilon) S_{\alpha'\alpha}(\varepsilon) , \quad (72)$$

or

$$S_{\alpha'\alpha}(\varepsilon) = \langle \psi_{\alpha'}^-(\varepsilon) | \psi_\alpha^+(\varepsilon) \rangle , \quad (73)$$

which has to be unitary, since both sets of the functions, $\{\psi_\alpha^+(\varepsilon)\}$ and $\{\psi_\alpha^-(\varepsilon)\}$, should be complete. Making use of Eq. (59), the S -matrix can be expressed in terms of the T -matrices:

$$\mathcal{V}\psi_\alpha^+(\varepsilon) = \sum_{\alpha'} \mathcal{V}\psi_{\alpha'}^-(\varepsilon) S_{\alpha'\alpha}(\varepsilon)$$

↓

$$\begin{aligned}
T^+(\varepsilon) \varphi_\alpha(\varepsilon) &= \sum_{\alpha'} T^-(\varepsilon) \varphi_{\alpha'}(\varepsilon) S_{\alpha'\alpha}(\varepsilon) \\
&\Downarrow \\
T_{\beta\alpha}^+(\varepsilon) &= \sum_{\alpha'} T_{\beta\alpha'}^-(\varepsilon) S_{\alpha'\alpha}(\varepsilon) \\
&\Downarrow \\
T^+(\varepsilon) &= T^-(\varepsilon) S(\varepsilon) ,
\end{aligned}$$

thus,

$$S(\varepsilon) = T^-(\varepsilon)^{-1} T^+(\varepsilon) = I - 2\pi i T^+(\varepsilon) , \quad (74)$$

where the last expression was derived from Eq. (69). Consequently,

$$\begin{aligned}
S(\varepsilon) S(\varepsilon)^\dagger &= (I - 2\pi i T^+(\varepsilon)) (I + 2\pi i T^-(\varepsilon)) \\
&= I + 2\pi i \underbrace{(T^-(\varepsilon) - T^+(\varepsilon) - 2\pi i T^+(\varepsilon) T^-(\varepsilon))}_{=0} = I , \quad (75)
\end{aligned}$$

i.e., the $S(\varepsilon)$ matrix is unitary as required. Note that this directly follows also from Eq. (71).

In a diagonal representation, the S -matrix obviously has the form,

$$S_{\alpha\alpha'}(\varepsilon) = \delta_{\alpha\alpha'} e^{i2\delta_\alpha(\varepsilon)} , \quad (76)$$

where $\delta_\alpha(\varepsilon) \in \mathbb{R}$ is called the (generalized) *phaseshift*.. From (74), therefore,

$$\begin{aligned}
e^{i2\delta_\alpha(\varepsilon)} &= 1 - 2\pi i T_{\alpha\alpha}^+(\varepsilon) \\
&\Downarrow \\
T_{\alpha\alpha}^\pm(\varepsilon) &= -\frac{1}{\pi} e^{\pm i\delta_\alpha(\varepsilon)} \sin \delta_\alpha(\varepsilon) . \quad (77)
\end{aligned}$$

1.8 Integrated density of states: the Lloyd formula

Substituting Eq. (37) into (29) yields

$$\begin{aligned} n(\varepsilon) &= -\frac{1}{\pi} \text{Im} \text{Tr} \left(\mathcal{G}_0^+(\varepsilon) + \mathcal{G}_0^+(\varepsilon) \mathcal{T}^+(\varepsilon) \mathcal{G}_0^+(\varepsilon) \right) \\ &= n_0(\varepsilon) + \delta n(\varepsilon) , \end{aligned} \quad (78)$$

with

$$n_0(\varepsilon) = -\frac{1}{\pi} \text{Im} \text{Tr} \left(\mathcal{G}_0^+(\varepsilon) \right) , \quad (79)$$

and

$$\begin{aligned} \delta n(\varepsilon) &= -\frac{1}{\pi} \text{Im} \text{Tr} \left(\mathcal{G}_0^+(\varepsilon) \mathcal{T}^+(\varepsilon) \mathcal{G}_0^+(\varepsilon) \right) \\ &= -\frac{1}{\pi} \text{Im} \text{Tr} \left(\mathcal{G}_0^+(\varepsilon)^2 \mathcal{T}^+(\varepsilon) \right) \\ &= \frac{1}{\pi} \text{Im} \text{Tr} \left(\frac{d\mathcal{G}_0^+(\varepsilon)}{d\varepsilon} \mathcal{T}^+(\varepsilon) \right) , \end{aligned} \quad (80)$$

where we made use of Eq. (7). Employing Eq. (44) one can derive,

$$\begin{aligned} \delta n(\varepsilon) &= \frac{1}{\pi} \text{Im} \text{Tr} \left(\mathcal{T}^+(\varepsilon)^{-1} \frac{d\mathcal{T}^+(\varepsilon)}{d\varepsilon} \right) \\ &= \frac{d}{d\varepsilon} \left(\frac{1}{\pi} \text{Im} \text{Tr} \ln \mathcal{T}^+(\varepsilon) \right) \\ &= \frac{d}{d\varepsilon} \left(\frac{1}{\pi} \text{Im} \ln \det \mathcal{T}^+(\varepsilon) \right) . \end{aligned} \quad (81)$$

The integrated DOS,

$$N(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' n(\varepsilon') , \quad (82)$$

can then be directly expressed as

$$N(\varepsilon) = N_0(\varepsilon) + \delta N(\varepsilon) , \quad (83)$$

where

$$N_0(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' n_0(\varepsilon') \quad (84)$$

and

$$\delta N(\varepsilon) = \frac{1}{\pi} \text{Im} \ln \det T^+(\varepsilon) , \quad (85)$$

referred to as the *Lloyd formula*.

Quite trivially,

$$\delta N(\varepsilon) = -\frac{1}{\pi} \text{Im} \ln \det T^-(\varepsilon) , \quad (86)$$

therefore,

$$\begin{aligned} \delta N(\varepsilon) &= \frac{1}{2\pi} \text{Im} \ln \det \left(T^-(\varepsilon)^{-1} T^+(\varepsilon) \right) \\ &= \frac{1}{2\pi} \text{Im} \ln \det S(\varepsilon) . \end{aligned} \quad (87)$$

In diagonal representation, see Eq. (76), this reduces to

$$\delta N(\varepsilon) = \frac{1}{2\pi} \text{Im} \ln \prod_{\alpha} e^{i2\delta_{\alpha}(\varepsilon)} = \frac{1}{\pi} \sum_{\alpha} \delta_{\alpha}(\varepsilon) , \quad (88)$$

known as the famous *Friedel sum-rule*. The excess DOS caused by the perturbation can then be written as

$$\delta n(\varepsilon) = \frac{1}{\pi} \sum_{\alpha} \frac{d\delta_{\alpha}(\varepsilon)}{d\varepsilon} , \quad (89)$$

having sharp peaks at *resonances*, i.e., at rapid changes of the phaseshifts when crossing $\frac{\pi}{2}$.

2 The Korringa-Kohn-Rostoker Green function method

2.1 Characterization of the potential

Let us divide the configurational space, Ω (isomorphic to \mathbb{R}^3) into disjunct domains, Ω_n

$$\Omega = \cup_{n \in \mathbb{N}} \Omega_n ,$$

$$\Omega_n \cap \Omega_m = 0 .$$

The potential \mathcal{V} can then be written as a sum of *single-domain* potentials, \mathcal{V}_n ,

$$V(\vec{r}) = \sum_{n \in \mathbb{N}} V_n(\vec{r}) \quad (90)$$

$$V_n(\vec{r}) = \begin{cases} V(\vec{r}) & \text{for } \vec{r} \in \Omega_n \\ 0 & \text{for } \vec{r} \in \Omega \setminus \Omega_n \end{cases} . \quad (91)$$

The center of a particular domain, Ω_n defined by the position vector, \vec{R}_n is usually associated with the position of the atomic nucleus, regarded for simplicity to be point-like. For open systems or surfaces, the centers of the so-called empty spheres, describing the interstitial region or the vacuum, are, however, not related to singularities of the potential. In electronic structure calculations, first the atomic positions, \vec{R}_n are fixed and the domains (cells) are most commonly determined in terms of the Wigner-Seitz construction. In order to present a simple derivation of the Multiple Scattering Theory (MST), we shall restrict our discussion to single-cell potentials confined to spherical domains,

$$V_n(\vec{r}) = 0 \quad \text{for } |\vec{r}_n| \geq S_n \quad \left(\vec{r}_n \equiv \vec{r} - \vec{R}_n \right) , \quad (92)$$

where S_n is usually termed as the *muffin-tin* radius. It is important to note that by preserving the formalism we are going to derive, MST is valid also for *space-filling* potentials.

2.2 Single-site and multi-site scattering: operator formalism

The case when only a single potential, \mathcal{V}_n of type (91) is present, is referred to as the single-site scattering. The corresponding *single-site T-operator*, t^n (see Eq. (39)),

$$t^n = \mathcal{V}_n + \mathcal{V}_n \mathcal{G}_0 t^n , \quad (93)$$

can formally be expressed as

$$t^n = (\mathcal{I} - \mathcal{V}_n \mathcal{G}_0)^{-1} \mathcal{V}_n . \quad (94)$$

(Note that we dropped the energy argument of the corresponding operators.) Inserting Eq. (90) into Eq. (38) yields

$$\mathcal{T} = \sum_n \mathcal{V}_n + \sum_{nm} \mathcal{V}_n \mathcal{G}_0 \mathcal{V}_m + \sum_{nmk} \mathcal{V}_n \mathcal{G}_0 \mathcal{V}_m \mathcal{G}_0 \mathcal{V}_k + \dots = \sum_n \mathcal{Q}^n , \quad (95)$$

where we introduced the operators,

$$\begin{aligned} \mathcal{Q}^n &= \mathcal{V}_n + \sum_m \mathcal{V}_n \mathcal{G}_0 \mathcal{V}_m + \sum_{mk} \mathcal{V}_n \mathcal{G}_0 \mathcal{V}_m \mathcal{G}_0 \mathcal{V}_k + \dots \\ &= \mathcal{V}_n + \mathcal{V}_n \mathcal{G}_0 \sum_m \left(\mathcal{V}_m + \sum_k \mathcal{V}_m \mathcal{G}_0 \mathcal{V}_k + \dots \right) \\ &= \mathcal{V}_n + \mathcal{V}_n \mathcal{G}_0 \sum_m \mathcal{Q}^m . \end{aligned} \quad (96)$$

Separating the term n on the right-hand side of Eq. (96) and taking it to the left-hand side, we get

$$(\mathcal{I} - \mathcal{V}_n \mathcal{G}_0) \mathcal{Q}^n = \mathcal{V}_n + \mathcal{V}_n \mathcal{G}_0 \sum_{m(\neq n)} \mathcal{Q}^m , \quad (97)$$

which, by using Eq. (94), can be transformed to

$$\mathcal{Q}^n = t^n + t^n \mathcal{G}_0 \sum_{m(\neq n)} \mathcal{Q}^m . \quad (98)$$

The above Dyson-equation can be solved by successive iterations resulting in

$$\begin{aligned} \mathcal{Q}^n = & t^n + \sum_{m(\neq n)} t^n \mathcal{G}_0 t^m + \sum_{m(\neq n)} \sum_{k(\neq m)} t^n \mathcal{G}_0 t^m \mathcal{G}_0 t^k + \\ & \sum_{m(\neq n)} \sum_{k(\neq m)} \sum_{j(\neq k)} t^n \mathcal{G}_0 t^m \mathcal{G}_0 t^k \mathcal{G}_0 t^j + \dots , \end{aligned} \quad (99)$$

therefore,

$$\begin{aligned} \mathcal{T} = & \sum_n t^n + \sum_{n,m} t^n \mathcal{G}_0 (1 - \delta_{nm}) t^m + \sum_{n,m,k} t^n \mathcal{G}_0 (1 - \delta_{nm}) t^m \mathcal{G}_0 (1 - \delta_{mk}) t^k \\ & + \sum_{n,m,k,j} t^n \mathcal{G}_0 (1 - \delta_{nm}) t^m \mathcal{G}_0 (1 - \delta_{mk}) t^k \mathcal{G}_0 (1 - \delta_{kj}) t^j + \dots . \end{aligned} \quad (100)$$

The operator comprising all the scattering events between two particular sites is called the *scattering path operator* (SPO),

$$\begin{aligned} \tau^{nm} = & t^n \delta_{nm} + t^n \mathcal{G}_0 (1 - \delta_{nm}) t^m + \sum_k t^n \mathcal{G}_0 (1 - \delta_{nk}) t^k \mathcal{G}_0 (1 - \delta_{km}) t^k \\ & + \sum_{k,j} t^n \mathcal{G}_0 (1 - \delta_{nk}) t^k \mathcal{G}_0 (1 - \delta_{kj}) t^j \mathcal{G}_0 (1 - \delta_{jm}) t^m + \dots . \end{aligned} \quad (101)$$

Obviously,

$$\mathcal{T} = \sum_{nm} \tau^{nm} \quad (102)$$

and the following Dyson equations apply,

$$\tau^{nm} = t^n \delta_{nm} + \sum_k t^n \mathcal{G}_0 (1 - \delta_{nk}) \tau^{km} , \quad (103)$$

or

$$\tau^{nm} = t^n \delta_{nm} + \sum_k \tau^{nk} \mathcal{G}_0 (1 - \delta_{km}) t^m . \quad (104)$$

Inserting (102) into Eq. (37) yields

$$\mathcal{G} = \mathcal{G}_0 + \sum_{nm} \mathcal{G}_0 \tau^{nm} \mathcal{G}_0 , \quad (105)$$

which will be our starting point to evaluate the configurational space Green function.

It is useful to introduce also the *structural resolvent operator* as

$$\mathcal{G}^{nm} = \mathcal{G}_0 (1 - \delta_{nm}) + \sum_{k,j} \mathcal{G}_0 (1 - \delta_{nk}) \tau^{kj} \mathcal{G}_0 (1 - \delta_{jm}) . \quad (106)$$

The SPO, τ^{nm} , is obviously related to \mathcal{G}^{nm} by (see Eq. (101))

$$\tau^{nm} = t^n \delta_{nm} + t^n \mathcal{G}^{nm} t^m . \quad (107)$$

Comparing expressions (103) and (104) with (107), the following useful identities can be derived,

$$\sum_k \mathcal{G}_0 (1 - \delta_{nk}) \tau^{km} = \mathcal{G}^{nm} t^m , \quad (108)$$

and

$$\sum_k \tau^{nk} \mathcal{G}_0 (1 - \delta_{km}) = t^n \mathcal{G}^{nm} . \quad (109)$$

2.3 The angular momentum representation

The spherical harmonics, $Y_L(\hat{r})$, where $L \in \mathbb{N}$ stands for the composite index (ℓ, m) , satisfy the orthogonality and completeness relations,

$$\int d^2\hat{r} Y_L(\hat{r})^* Y_{L'}(\hat{r}) = \delta_{LL'} , \quad (110)$$

and

$$\sum_L Y_L(\hat{r}) Y_{L'}(\hat{r}')^* = \delta(\hat{r} - \hat{r}') \equiv \frac{1}{\sin\vartheta} \delta(\vartheta - \vartheta') \delta(\phi - \phi') , \quad (111)$$

respectively. Note also the identity,

$$\sum_{m=-\ell}^{\ell} Y_L(\hat{r})^* Y_L(\hat{r}') = \sum_{m=-\ell}^{\ell} Y_L(\hat{r}) Y_L(\hat{r}')^* . \quad (112)$$

The well-known solutions of the Schrödinger equation for free particles are

$$\begin{aligned} j_L(\varepsilon; \vec{r}) &\equiv j_\ell(pr) Y_L(\hat{r}) \\ n_L(\varepsilon; \vec{r}) &\equiv n_\ell(pr) Y_L(\hat{r}) \quad (p = \sqrt{\varepsilon}) , \\ h_L^\pm(\varepsilon; \vec{r}) &\equiv h_\ell^\pm(pr) Y_L(\hat{r}) \end{aligned} \quad (113)$$

where $j_\ell(x)$, $n_\ell(x)$ and $h_\ell^\pm(x) = j_\ell(x) \pm i n_\ell(x)$ are the spherical Bessel, Neumann and Hankel-functions, respectively.

An orthonormal, complete set of basisfunctions is formed by

$$\varphi_L(\varepsilon; \vec{r}) = \frac{\varepsilon^{1/4}}{\pi^{1/2}} j_L(\varepsilon; \vec{r}) \quad (\varepsilon > 0, L \in \mathbb{N}) , \quad (114)$$

since,

$$\int d^3r \varphi_L(\varepsilon; \vec{r})^* \varphi_{L'}(\varepsilon'; \vec{r}) = \delta_{LL'} \delta(\varepsilon - \varepsilon') \quad (115)$$

and

$$\int_0^\infty d\varepsilon \sum_L \varphi_L(\varepsilon; \vec{r}) \varphi_L(\varepsilon; \vec{r}')^* = \delta(\vec{r} - \vec{r}') . \quad (116)$$

Using the spectral resolution of the resolvent the Green function of free particles can then be written as

$$G_0(z; \vec{r}, \vec{r}') = \int_0^\infty d\varepsilon \sum_L \frac{\sqrt{\varepsilon} j_L(\varepsilon; \vec{r}) j_L(\varepsilon; \vec{r}')^*}{\pi(z - \varepsilon)} . \quad (117)$$

2.4 One-center expansion of the free-particle Green function

In terms of contour integrations, it can be shown that by choosing $p = \sqrt{z}$ such that $\text{Im } p > 0$,

$$G_0(z; \vec{r}, \vec{r}') = -ip \sum_L j_\ell(pr_{<}) h_\ell^+(pr_{>}) Y_L(\hat{r}) Y_L(\hat{r}')^* , \quad (118)$$

where $r_{<} = \min(r, r')$ and $r_{>} = \max(r, r')$.

Introducing the functions with *complex energy* arguments,

$$f_L(z; \vec{r}) \equiv f_\ell(pr) Y_L(\hat{r}) \quad (f_\ell = j_\ell, n_\ell \text{ or } h_\ell^\pm, \quad p^2 = z, \text{Im } p > 0) \quad (119)$$

with the corresponding 'conjugation'

$$f_L(z; \vec{r})^\times \equiv f_\ell(pr) Y_L(\hat{r})^* , \quad (120)$$

Eq. (118) can simply be written as

$$G_0(z; \vec{r}, \vec{r}') = -ip \sum_L j_L(z; \vec{r}_{<}) h_L^+(z; \vec{r}_{>})^\times = -ip \sum_L h_L^+(z; \vec{r}_{>}) j_L(z; \vec{r}_{<})^\times , \quad (121)$$

called the one-center expansion of the free-particle Green function.

For later purposes it is useful to introduce a *vector notation* for the functions $f_L(z; \vec{r})$,

$$\mathbf{f}(z; \vec{r}) \equiv [f_1(z; \vec{r}), f_2(z; \vec{r}), f_3(z; \vec{r}), \dots] , \quad (122)$$

and the respective adjungate vector,

$$\mathbf{f}(z; \vec{r})^\times \equiv \begin{bmatrix} f_1(z; \vec{r})^\times \\ f_2(z; \vec{r})^\times \\ f_3(z; \vec{r})^\times \\ \vdots \end{bmatrix} . \quad (123)$$

Eq. (121) can then be compactly written as

$$G_0(z; \vec{r}, \vec{r}') = -ip \mathbf{j}(z; \vec{r}_{<}) \mathbf{h}^+(z; \vec{r}_{>})^\times = -ip \mathbf{h}^+(z; \vec{r}_{>}) \mathbf{j}(z; \vec{r}_{<})^\times . \quad (124)$$

2.5 Single-site scattering

Let us first note that, according to Eqs. (38) and (91), $t^n(z)$ is zero outside Ω_n ,

$$t^n(z; \vec{r}, \vec{r}') = 0 \quad \text{for} \quad |\vec{r}_n| \geq S_n \quad \text{or} \quad |\vec{r}'_n| \geq S_n. \quad (125)$$

Because of traditional reasons, in the Lippmann-Schwinger equation the functions $j_L(\varepsilon; \vec{r})$, rather than those in Eq. (114), are considered as eigenfunctions of the free-particle Hamiltonian \mathcal{H}_0 ,

$$R_L^n(\varepsilon; \vec{r}_n) = j_L(\varepsilon; \vec{r}_n) + \int_{|\vec{x}_n| \leq S_n} d^3x_n \int_{|\vec{y}_n| \leq S_n} d^3y_n G_0(\varepsilon; \vec{r}_n, \vec{x}_n) t^n(\varepsilon; \vec{x}_n, \vec{y}_n) j_L(\varepsilon; \vec{y}_n), \quad (126)$$

where we shifted the origin of our coordinate system to \vec{R}_n . For $|\vec{r}_n| > S_n$ the one-center expansion of the free-particle Green function, Eq. (121) can be used to yield

$$R_L^n(\varepsilon; \vec{r}_n) = j_L(\varepsilon; \vec{r}_n) - ip \sum_{L'} h_{L'}^+(\varepsilon; \vec{r}_n) t_{L'L}^n(\varepsilon), \quad (127)$$

where the matrixelements of $t^n(\varepsilon)$ (single-site t -matrix) are defined as

$$t_{L'L}^n(\varepsilon) = \int_{|\vec{x}_n| \leq S_n} d^3x_n \int_{|\vec{y}_n| \leq S_n} d^3y_n j_{L'}(\varepsilon; \vec{x}_n)^\times t^n(\varepsilon; \vec{x}_n, \vec{y}_n) j_L(\varepsilon; \vec{y}_n). \quad (128)$$

By using the shorthand notations (122) and (123), the t -matrix,

$$\underline{t}^n(\varepsilon) \equiv \{t_{L'L}^n(\varepsilon)\}, \quad (129)$$

can be expressed as

$$\underline{t}^n(\varepsilon) = \int_{|\vec{x}_n| \leq S_n} d^3x_n \int_{|\vec{y}_n| \leq S_n} d^3y_n \mathbf{j}(\varepsilon; \vec{x}_n)^\times t^n(\varepsilon; \vec{x}_n, \vec{y}_n) \mathbf{j}(\varepsilon; \vec{y}_n) \quad (130)$$

and the normalization (127) as

$$R^n(\varepsilon; \vec{r}_n) = \mathbf{j}(\varepsilon; \vec{r}_n) - ip \mathbf{h}^+(\varepsilon; \vec{r}_n) \underline{t}^n(\varepsilon) \quad (|\vec{r}_n| > S_n). \quad (131)$$

Note that the functions $R_L^n(\varepsilon; \vec{r}_n)$ are regular at the origin ($\vec{r}_n = 0$). Frequently, a different kind of regular scattering wavefunctions,

$$\mathbf{Z}^n(\varepsilon; \vec{r}_n) = \mathbf{R}^n(\varepsilon; \vec{r}_n) \underline{t}^n(\varepsilon)^{-1}, \quad (132)$$

are used, which for $|\vec{r}_n| > S_n$ are normalized as

$$\begin{aligned} \mathbf{Z}^n(\varepsilon; \vec{r}_n) &= \mathbf{j}(\varepsilon; \vec{r}_n) \underline{t}^n(\varepsilon)^{-1} - ip \mathbf{h}^+(\varepsilon; \vec{r}_n) \\ &= \mathbf{j}(\varepsilon; \vec{r}_n) \left(\underline{t}^n(\varepsilon)^{-1} - ip \underline{I} \right) + p \mathbf{n}(\varepsilon; \vec{r}_n). \end{aligned} \quad (133)$$

Because of the definition (128) the optical theorem, Eq. (68), takes the form,

$$\underline{t}^n(\varepsilon)^{-1} - \left[\underline{t}^n(\varepsilon)^\dagger \right]^{-1} = 2ip \underline{I}, \quad (134)$$

implying that the *reactance matrix*,

$$\underline{K}^n(\varepsilon) = \left(\underline{t}^n(\varepsilon)^{-1} - ip \underline{I} \right)^{-1} \quad (135)$$

is Hermitean. Clearly, Eq. (133) can be written as

$$\mathbf{Z}^n(\varepsilon; \vec{r}_n) = \mathbf{j}(\varepsilon; \vec{r}_n) \underline{K}^n(\varepsilon)^{-1} + p \mathbf{n}(\varepsilon; \vec{r}_n). \quad (136)$$

As we shall see, in the explicit expression of the Green function, scattering solutions that are irregular at the origin and normalized for $|\vec{r}_n| > S_n$ as

$$\mathbf{H}^n(\varepsilon; \vec{r}_n) = -ip \mathbf{h}^+(\varepsilon; \vec{r}_n) \quad (137)$$

or

$$\mathbf{J}^n(\varepsilon; \vec{r}_n) = \mathbf{j}(\varepsilon; \vec{r}_n), \quad (138)$$

occur. From the boundary conditions, Eqs. (131) and (137), it is straightforward to show that

$$\mathbf{J}^n(\varepsilon; \vec{r}_n) = \mathbf{R}^n(\varepsilon; \vec{r}_n) - \mathbf{H}^n(\varepsilon; \vec{r}_n) \underline{t}^n(\varepsilon). \quad (139)$$

From Eq. (135) the inverse of the t -matrix can be expressed as

$$\underline{t}^n(\varepsilon)^{-1} = \underline{K}^n(\varepsilon)^{-1} + ip\underline{I}, \quad (140)$$

which has to be inserted into Eq. (74),

$$\begin{aligned} \underline{S}^n(\varepsilon) &= \left[\underline{t}^n(\varepsilon)^\dagger \right]^{-1} \underline{t}^n(\varepsilon) \\ &= \left(\underline{K}^n(\varepsilon)^{-1} - ip\underline{I} \right) \left(\underline{K}^n(\varepsilon)^{-1} + ip\underline{I} \right)^{-1} \\ &= (\underline{I} - ip\underline{K}^n(\varepsilon)) (\underline{I} + ip\underline{K}^n(\varepsilon))^{-1}. \end{aligned} \quad (141)$$

From the above equation it is obvious that, since $\underline{K}^n(\varepsilon)$ is a Hermitean matrix, $\underline{S}^n(\varepsilon)$ is unitary as stated in Section 1.7.

For a spherical potential, the t -matrix is diagonal, therefore, (see also Eq. (77))

$$t_{L'L}^n(\varepsilon) = \delta_{LL'} t_\ell^n(\varepsilon), \quad (142)$$

where

$$t_\ell^n(\varepsilon) = -\frac{1}{p} e^{i\delta_\ell^n(\varepsilon)} \sin \delta_\ell^n(\varepsilon), \quad (143)$$

with $\delta_\ell^n(\varepsilon)$ the ℓ -like partial phaseshifts and the reactance matrixelement,

$$K_\ell^n(\varepsilon) = -\frac{1}{p} \tan \delta_\ell^n(\varepsilon), \quad (144)$$

is indeed real. By matching the regular solution at the muffin tin radius the familiar text-book formula

$$\tan \delta_\ell^n(\varepsilon) = \frac{L_\ell^n(\varepsilon) j_\ell^n(pS_n) - p j_\ell'^n(pS_n)}{L_\ell^n(\varepsilon) n_\ell^n(pS_n) - p n_\ell'^n(pS_n)}, \quad (145)$$

with $L_\ell^n(\varepsilon) = \frac{d}{dr} \ln \varphi_\ell^n(\varepsilon; r) |_{r=S_n}$, can be obtained.

2.6 Two-center expansion of the free-particle Green function

In order to define matrixelements of the SPO, Eq. (101), and the structural resolvent, Eq. (106), an expansion of the free-particle Green function, $G_0(\varepsilon; \vec{r}, \vec{r}')$ in terms of the spherical Bessel functions centered around two different sites is needed, i.e., for

$$n \neq m \quad \text{and} \quad |\vec{r}_n| < S_n, \quad |\vec{r}_m| < S_m, \quad (146)$$

$$G_0\left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m\right) = \sum_{LL'} j_L(\varepsilon; \vec{r}_n) G_{0,LL'}^{nm}(\varepsilon) j_{L'}(\varepsilon; \vec{r}'_m)^\times, \quad (147)$$

or

$$G_0\left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m\right) = j(\varepsilon; \vec{r}_n) \underline{G}_0^{nm}(\varepsilon) j(\varepsilon; \vec{r}'_m)^\times, \quad (148)$$

where the expansion coefficients

$$\underline{G}_0^{nm}(\varepsilon) = \{G_{0,LL'}^{nm}(\varepsilon)\} \quad (149)$$

are referred to as the *real-space, free (or bare) structure constants*.

The explicit expression for $G_{0,LL'}^{nm}(\varepsilon)$ reads,

$$G_{0,LL'}^{nm}(\varepsilon) = -4\pi p i \sum_{L'L''} i^{\ell-\ell'-\ell''} h_{L''}^+(\varepsilon; \vec{R}_{nm}) C_{LL''}^{L'} , \quad (150)$$

with the Gaunt coefficients,

$$C_{LL''}^{L'} = \int d^2k Y_L(\hat{k})^* Y_{L'}(\hat{k}) Y_{L''}(\hat{k}) = \int d^2k Y_L(\hat{k}) Y_{L'}(\hat{k}) Y_{L''}(\hat{k})^* . \quad (151)$$

Let us summarize the one- and the two-center expansion for the free-particle Green function as follows,

$$\begin{aligned} G_0\left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m\right) &= \\ &= \delta_{nm} j(\varepsilon; \vec{r}_<) (-ip) h^+(\varepsilon; \vec{r}_>)^\times + (1 - \delta_{nm}) j(\varepsilon; \vec{r}_n) \underline{G}_0^{nm}(\varepsilon) j(\varepsilon; \vec{r}'_m)^\times . \end{aligned} \quad (152)$$

2.7 Multi-site scattering

Matrices in site-angular momentum representation

Substituting Eq. (152) into Eq. (106) and performing the necessary integrations we obtain

$$G^{nm} \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}_m + \vec{R}_m \right) = \mathbf{j}(\varepsilon; \vec{r}_n) \underline{G}^{nm}(\varepsilon) \mathbf{j}(\varepsilon; \vec{r}_m)^\times, \quad (153)$$

where we introduced the *structural Green function matrix*,

$$\underline{G}^{nm}(\varepsilon) = \underline{G}_0^{nm}(\varepsilon) (1 - \delta_{nm}) + \sum_{k(\neq n)} \sum_{j(\neq m)} \underline{G}_0^{nk}(\varepsilon) \underline{\mathcal{T}}^{kj}(\varepsilon) \underline{G}_0^{jm}(\varepsilon), \quad (154)$$

and the *matrix of the SPO*,

$$\underline{\mathcal{T}}^{kj}(\varepsilon) = \int_{|\vec{x}_k| \leq S_k} d^3 x_k \int_{|\vec{y}_j| \leq S_j} d^3 y_j \mathbf{j}(\varepsilon; \vec{x}_k)^\times \tau^{kj}(\varepsilon; \vec{x}_k, \vec{y}_j) \mathbf{j}(\varepsilon; \vec{y}_j). \quad (155)$$

Note that the SPO, $\tau^{kj}(\varepsilon; \vec{x}_k + \vec{R}_k, \vec{y}_j + \vec{R}_j)$, is zero for $|\vec{x}_k| > S_k$ or $|\vec{y}_j| > S_j$. It is straightforward to show that the operator equations (101), (103), (104) and (107) imply the matrix equations,

$$\begin{aligned} \underline{\mathcal{T}}^{nm}(\varepsilon) &= \delta_{nm} \underline{t}^n(\varepsilon) + \underline{t}^n(\varepsilon) \underline{G}_0^{nm}(\varepsilon) (1 - \delta_{nm}) \underline{t}^m(\varepsilon) \\ &+ \sum_k \underline{t}^n(\varepsilon) \underline{G}_0^{nk}(\varepsilon) (1 - \delta_{nk}) \underline{t}^k(\varepsilon) \underline{G}_0^{km}(\varepsilon) (1 - \delta_{km}) \underline{t}^m(\varepsilon) + \dots, \end{aligned} \quad (156)$$

$$\underline{\mathcal{T}}^{nm}(\varepsilon) = \delta_{nm} \underline{t}^n(\varepsilon) + \sum_k \underline{t}^n(\varepsilon) \underline{G}_0^{nk}(\varepsilon) (1 - \delta_{nk}) \underline{\mathcal{T}}^{km}(\varepsilon), \quad (157)$$

$$\underline{\mathcal{T}}^{nm}(\varepsilon) = \delta_{nm} \underline{t}^n(\varepsilon) + \sum_k \underline{\mathcal{T}}^{nk}(\varepsilon) \underline{G}_0^{km}(\varepsilon) (1 - \delta_{km}) \underline{t}^m(\varepsilon), \quad (158)$$

and

$$\underline{\mathcal{T}}^{nm}(\varepsilon) = \delta_{nm} \underline{t}^n(\varepsilon) + \underline{t}^n(\varepsilon) \underline{G}^{mm}(\varepsilon) \underline{t}^m(\varepsilon). \quad (159)$$

It is very useful to introduce the matrices in *site-angular momentum representation*,

$$\mathbf{t}(\varepsilon) = \{\underline{t}^n(\varepsilon) \delta_{nm}\} = \{t_{LL'}^n(\varepsilon) \delta_{nm}\} , \quad (160)$$

$$\mathbf{G}_0(\varepsilon) = \{\underline{G}_0^{nm}(\varepsilon) (1 - \delta_{nm})\} = \{G_{0,LL'}^{nm}(\varepsilon) (1 - \delta_{nm})\} , \quad (161)$$

$$\boldsymbol{\tau}(\varepsilon) = \{\underline{\tau}^{nm}(\varepsilon)\} = \{\tau_{LL'}^{nm}(\varepsilon)\} , \quad (162)$$

and

$$\mathbf{G}(\varepsilon) = \{\underline{G}^{nm}(\varepsilon)\} = \{G_{LL'}^{nm}(\varepsilon)\} , \quad (163)$$

since Eqs. (154), as well as (156-159) can be rewritten as

$$\mathbf{G}(\varepsilon) = \mathbf{G}_0(\varepsilon) + \mathbf{G}_0(\varepsilon) \boldsymbol{\tau}(\varepsilon) \mathbf{G}_0(\varepsilon) , \quad (164)$$

$$\boldsymbol{\tau}(\varepsilon) = \mathbf{t}(\varepsilon) + \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) \mathbf{t}(\varepsilon) + \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) \mathbf{t}(\varepsilon) + \dots , \quad (165)$$

$$\boldsymbol{\tau}(\varepsilon) = \mathbf{t}(\varepsilon) + \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) \boldsymbol{\tau}(\varepsilon) , \quad (166)$$

$$\boldsymbol{\tau}(\varepsilon) = \mathbf{t}(\varepsilon) + \boldsymbol{\tau}(\varepsilon) \mathbf{G}_0(\varepsilon) \mathbf{t}(\varepsilon) , \quad (167)$$

and

$$\boldsymbol{\tau}(\varepsilon) = \mathbf{t}(\varepsilon) + \mathbf{t}(\varepsilon) \mathbf{G}(\varepsilon) \mathbf{t}(\varepsilon) , \quad (168)$$

respectively. In particular, the Dyson equation (166) or (167) can be solved in terms of the following matrix inversion,

$$\boldsymbol{\tau}(\varepsilon) = \left(\mathbf{t}(\varepsilon)^{-1} - \mathbf{G}_0(\varepsilon) \right)^{-1} . \quad (169)$$

By comparing Eqs. (165) and (168) we find,

$$\begin{aligned} \mathbf{G}(\varepsilon) &= \mathbf{G}_0(\varepsilon) + \mathbf{G}_0(\varepsilon) \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) \\ &\quad + \mathbf{G}_0(\varepsilon) \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) + \dots \\ &= \mathbf{G}_0(\varepsilon) + \mathbf{G}(\varepsilon) \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) , \end{aligned} \quad (170)$$

from which the equation,

$$\mathbf{G}(\varepsilon) = \mathbf{G}_0(\varepsilon) (\mathbf{I} - \mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon))^{-1} \quad (171)$$

can be obtained. *Eqs. (169) and (171) are called the fundamental equations of the Multiple Scattering Theory.*

Evaluation of the Green function

In this section it will be shown that the Green function, $G \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right)$, appears to have the form,

$$\begin{aligned} G \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) &= \\ &= \mathbf{R}^n \left(\varepsilon; \vec{r}_n \right) \underline{\mathcal{G}}^{nm} \left(\varepsilon \right) \mathbf{R}^m \left(\varepsilon; \vec{r}'_m \right)^\times + \delta_{nm} \mathbf{R}^n \left(\varepsilon; \vec{r}'_< \right) \mathbf{H}^n \left(\varepsilon; \vec{r}'_> \right)^\times , \end{aligned} \quad (172)$$

with $r_< = \min (r_n, r'_n)$, $r_> = \max (r_n, r'_n)$ and the scattering solutions, $\mathbf{R}^n \left(\varepsilon; \vec{r}_n \right)$ and $\mathbf{H}^n \left(\varepsilon; \vec{r}_n \right)$, as normalized according to Eqs. (131) and (137), respectively.

For a particular pair of sites, n and m , we split the operator expression (105) as

$$\mathcal{G} \left(\varepsilon \right) = \mathcal{G}^{(nm)} \left(\varepsilon \right) + \mathcal{G}^{(\bar{n}m)} \left(\varepsilon \right) + \mathcal{G}^{(n\bar{m})} \left(\varepsilon \right) + \mathcal{G}^{(\bar{n}\bar{m})} \left(\varepsilon \right) , \quad (173)$$

where (see also Eqs. (106-109))

$$\begin{aligned} \mathcal{G}^{(nm)} \left(\varepsilon \right) &= \mathcal{G}_0 \left(\varepsilon \right) \tau^{nm} \left(\varepsilon \right) \mathcal{G}_0 \left(\varepsilon \right) \\ &= \delta_{nm} \mathcal{G}_0 \left(\varepsilon \right) t^n \left(\varepsilon \right) \mathcal{G}_0 \left(\varepsilon \right) + \mathcal{G}_0 \left(\varepsilon \right) t^n \left(\varepsilon \right) \mathcal{G}^{nm} \left(\varepsilon \right) t^m \left(\varepsilon \right) \mathcal{G}_0 \left(\varepsilon \right) , \end{aligned} \quad (174)$$

$$\mathcal{G}^{(\bar{n}m)} \left(\varepsilon \right) = \sum_{i(\neq n)} \mathcal{G}_0 \left(\varepsilon \right) \tau^{im} \left(\varepsilon \right) \mathcal{G}_0 \left(\varepsilon \right) = \mathcal{G}^{nm} \left(\varepsilon \right) t^m \left(\varepsilon \right) \mathcal{G}_0 \left(\varepsilon \right) , \quad (175)$$

$$\mathcal{G}^{(n\bar{m})} \left(\varepsilon \right) = \sum_{j(\neq m)} \mathcal{G}_0 \left(\varepsilon \right) \tau^{nj} \left(\varepsilon \right) \mathcal{G}_0 \left(\varepsilon \right) = \mathcal{G}_0 \left(\varepsilon \right) t^n \left(\varepsilon \right) \mathcal{G}^{nm} \left(\varepsilon \right) , \quad (176)$$

$$\mathcal{G}^{(\bar{n}\bar{m})} \left(\varepsilon \right) = \sum_{i(\neq n)} \sum_{j(\neq m)} \mathcal{G}_0 \left(\varepsilon \right) \tau^{ij} \left(\varepsilon \right) \mathcal{G}_0 \left(\varepsilon \right) + \mathcal{G}_0 \left(\varepsilon \right) = \mathcal{G}^{nm} \left(\varepsilon \right) + \delta_{nm} \mathcal{G}_0 \left(\varepsilon \right) . \quad (177)$$

First, for the case of $|\vec{r}_n| > S_n$, $|\vec{r}'_m| > S_m$, we evaluate the configurational space representation of the above operators. By making use of the expressions (152) as well as (153), the corresponding integrations can easily be performed yielding,

$$G^{(nm)} \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) = \delta_{nm} (-ip)^2 \mathbf{h}^+ (\varepsilon; \vec{r}_n) \underline{t}^n (\varepsilon) \mathbf{h}^+ (\varepsilon; \vec{r}'_m)^\times + (-ip)^2 \mathbf{h}^+ (\varepsilon; \vec{r}_n) \underline{t}^n (\varepsilon) \underline{G}^{nm} (\varepsilon) \underline{t}^m (\varepsilon) \mathbf{h}^+ (\varepsilon; \vec{r}'_m)^\times, \quad (178)$$

$$G^{(\bar{n}m)} \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) = (-ip) \mathbf{j} (\varepsilon; \vec{r}_n) \underline{G}^{nm} (\varepsilon) \underline{t}^m (\varepsilon) \mathbf{h}^+ (\varepsilon; \vec{r}'_m)^\times, \quad (179)$$

$$G^{(n\bar{m})} \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) = (-ip) \mathbf{h}^+ (\varepsilon; \vec{r}_n) \underline{t}^n (\varepsilon) \underline{G}^{nm} (\varepsilon) \mathbf{j} (\varepsilon; \vec{r}'_m)^\times, \quad (180)$$

$$G^{(\bar{n}\bar{m})} \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) = \mathbf{j} (\varepsilon; \vec{r}_n) \underline{G}^{nm} \varepsilon \mathbf{j} (\varepsilon; \vec{r}'_m)^\times + \delta_{nm} \left(\mathbf{j} (\varepsilon; \vec{r}_n) (-ip) \mathbf{h}^+ (\varepsilon; \vec{r}'_n)^\times \Theta (r'_n - r_n) + (-ip) \mathbf{h}^+ (\varepsilon; \vec{r}_n) \mathbf{j} (\varepsilon; \vec{r}'_n)^\times \Theta (r_n - r'_n) \right). \quad (181)$$

After adding all the contributions, we find

$$G \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) = \left[\mathbf{j} (\varepsilon; \vec{r}_n) - ip \mathbf{h}^+ (\varepsilon; \vec{r}_n) \underline{t}^n (\varepsilon) \right] \underline{G}^{nm} (\varepsilon) \left[\mathbf{j} (\varepsilon; \vec{r}'_m) - ip \underline{t}^m (\varepsilon) \mathbf{h}^+ (\varepsilon; \vec{r}'_m) \right]^\times + \delta_{nm} \left(\left[\mathbf{j} (\varepsilon; \vec{r}_n) - ip \mathbf{h}^+ (\varepsilon; \vec{r}_n) \underline{t}^n (\varepsilon) \right] (-ip) \mathbf{h}^+ (\varepsilon; \vec{r}'_n)^\times \Theta (r'_n - r_n) + (-ip) \mathbf{h}^+ (\varepsilon; \vec{r}_n) \left[\mathbf{j} (\varepsilon; \vec{r}'_n) - ip \underline{t}^n (\varepsilon) \mathbf{h}^+ (\varepsilon; \vec{r}'_n) \right]^\times \Theta (r_n - r'_n) \right). \quad (182)$$

For real potentials, \mathcal{V} (in fact, for time-reversal invariant Hamiltonians), $\underline{t}^n (\varepsilon)$ turns to be symmetric. Note that this is still valid if an effective (exchange) field, interacting only with the spin of the system, is present. Moreover, making use of the definition of the t -matrix, Eq. (128) and the identity (112), it is easy to prove that

$$\mathbf{h}^+ (\varepsilon; \vec{r}_n) \underline{t}^n (\varepsilon) \mathbf{h}^+ (\varepsilon; \vec{r}'_n)^\times = \mathbf{h}^+ (\varepsilon; \vec{r}'_n) \underline{t}^n (\varepsilon) \mathbf{h}^+ (\varepsilon; \vec{r}_n)^\times, \quad (183)$$

such that we arrive at

$$\begin{aligned}
G\left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m\right) = & \\
& \left[\mathbf{j}(\varepsilon; \vec{r}_n) - ip \mathbf{h}^+(\varepsilon; \vec{r}_n) \underline{t}^n(\varepsilon) \right] \underline{G}^{nm}(\varepsilon) \left[\mathbf{j}(\varepsilon; \vec{r}'_m) - ip \mathbf{h}^+(\varepsilon; \vec{r}'_m) \underline{t}^m(\varepsilon) \right]^\times \\
& + \delta_{nm} \left[\mathbf{j}(\varepsilon; \vec{r}'_<) - ip \mathbf{h}^+(\varepsilon; \vec{r}'_<) \underline{t}^n(\varepsilon) \right] (-ip) \mathbf{h}^+(\varepsilon; \vec{r}'_>)^\times . \quad (184)
\end{aligned}$$

Obviously, outside the muffin-tin region, the Green function exhibits the form of (172). Since, however, the Green function satisfies the equation,

$$(-\Delta + V(\vec{r}) - \varepsilon) G(\varepsilon; \vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') , \quad (185)$$

in all space, it can readily be continued inside the muffin-tins by keeping the functions $\mathbf{R}^n(\varepsilon; \vec{r}_n)$ and $\mathbf{H}^n(\varepsilon; \vec{r}_n)$ solutions of the Schrödinger equation related to the muffin-tin indexed by n .

An alternative expression of the Green function can be obtained when we replace the regular scattering solutions $\mathbf{R}^n(\varepsilon; \vec{r}_n)$ by $\mathbf{Z}^n(\varepsilon; \vec{r}_n)$ (see Eq. (132)) in Eq. (172). Namely,

$$\begin{aligned}
\mathbf{R}^n(\varepsilon; \vec{r}_n) \underline{G}^{nm}(\varepsilon) \mathbf{R}^m(\varepsilon; \vec{r}'_m)^\times = & \\
= \mathbf{Z}^n(\varepsilon; \vec{r}_n) \underline{t}^n(\varepsilon) \underline{G}^{nm}(\varepsilon) \underline{t}^n(\varepsilon) \mathbf{Z}^m(\varepsilon; \vec{r}'_m)^\times & \\
= \mathbf{Z}^n(\varepsilon; \vec{r}_n) \underline{\mathcal{T}}^{nm}(\varepsilon) \mathbf{Z}^m(\varepsilon; \vec{r}'_m)^\times - \delta_{nm} \mathbf{Z}^n(\varepsilon; \vec{r}'_<) \underline{t}^n(\varepsilon) \mathbf{Z}^n(\varepsilon; \vec{r}'_>)^\times , &
\end{aligned}$$

where we exploited Eq. (159), and

$$\mathbf{R}^n(\varepsilon; \vec{r}'_<) \mathbf{H}^n(\varepsilon; \vec{r}'_>)^\times = \mathbf{Z}^n(\varepsilon; \vec{r}'_<) \underline{t}^n(\varepsilon) \mathbf{H}^n(\varepsilon; \vec{r}'_>)^\times . \quad (186)$$

Adding the above two expressions and utilizing Eqs. (132) and (139) we obtain

$$\begin{aligned}
G\left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m\right) = & \\
= \mathbf{Z}^n(\varepsilon; \vec{r}_n) \underline{\mathcal{T}}^{nm}(\varepsilon) \mathbf{Z}^m(\varepsilon; \vec{r}'_m)^\times - \delta_{nm} \mathbf{Z}^n(\varepsilon; \vec{r}'_<) \mathbf{J}^n(\varepsilon; \vec{r}'_>)^\times . & \quad (187)
\end{aligned}$$

In case of $\delta \rightarrow 0$ it can be shown that,

$$\text{Im } G^+ \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}_n + \vec{R}_n \right) = \mathbf{Z}^n (\varepsilon; \vec{r}_n) \text{Im } \underline{\mathcal{T}}^{nn} (\varepsilon) \mathbf{Z}^n (\varepsilon; \vec{r}_n)^\times, \quad (188)$$

where

$$\text{Im } \underline{\mathcal{T}}^{nn} (\varepsilon) = \frac{1}{2i} \left(\underline{\mathcal{T}}^{nn} (\varepsilon) - \underline{\mathcal{T}}^{nn} (\varepsilon)^+ \right). \quad (189)$$

Namely,

$$\begin{aligned} G \left(\varepsilon + i0; \vec{r}_n + \vec{R}_n, \vec{r}_n + \vec{R}_n \right) &= \mathbf{Z}^n (\varepsilon + i0; \vec{r}_n) \underline{\mathcal{T}}^{nn} (\varepsilon + i0) \mathbf{Z}^n (\varepsilon + i0; \vec{r}_n)^\times \\ &\quad - \mathbf{Z}^n (\varepsilon + i0; \vec{r}_n) \mathbf{J}^n (\varepsilon + i0; \vec{r}_n)^\times, \end{aligned} \quad (190)$$

and

$$\begin{aligned} G \left(\varepsilon + i0; \vec{r}_n + \vec{R}_n, \vec{r}_n + \vec{R}_n \right)^* &= \mathbf{Z}^n (\varepsilon - i0; \vec{r}_n) \underline{\mathcal{T}}^{nn} (\varepsilon - i0) \mathbf{Z}^n (\varepsilon - i0; \vec{r}_n)^\times \\ &\quad - \mathbf{Z}^n (\varepsilon - i0; \vec{r}_n) \mathbf{J}^n (\varepsilon - i0; \vec{r}_n)^\times, \end{aligned} \quad (191)$$

$$\underline{\mathbf{K}}^n (\varepsilon + i0) = \underline{\mathbf{K}}^n (\varepsilon - i0) \Rightarrow \mathbf{Z}^n (\varepsilon + i0; \vec{r}_n) = \mathbf{Z}^n (\varepsilon - i0; \vec{r}_n) \quad ,$$

$\mathbf{J}^n (\varepsilon + i0; \vec{r}_n) = \mathbf{J}^n (\varepsilon - i0; \vec{r}_n)$, therefore,

$$\begin{aligned} G \left(\varepsilon + i0; \vec{r}_n + \vec{R}_n, \vec{r}_n + \vec{R}_n \right) - G \left(\varepsilon + i0; \vec{r}_n + \vec{R}_n, \vec{r}_n + \vec{R}_n \right)^* &= \\ \mathbf{Z}^n (\varepsilon + i0; \vec{r}_n) \left[\underline{\mathcal{T}}^{nn} (\varepsilon + i0) - \underline{\mathcal{T}}^{nn} (\varepsilon - i0) \right] \mathbf{Z}^n (\varepsilon + i0; \vec{r}_n)^\times, \end{aligned} \quad (192)$$

which immediately leads to Eq. (188).

Let us, finally, write the Green functions (172) and (187) by explicitly indicating the summations with respect to the angular momentum indices,

$$\begin{aligned} G \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) &= \quad (193) \\ &= \sum_{LL'} R_L^n (\varepsilon; \vec{r}_n) G_{LL'}^{nm} (\varepsilon) R_{L'}^m (\varepsilon; \vec{r}'_m)^\times + \delta_{nm} \sum_L R_L^n (\varepsilon; \vec{r}'_<) H_L^n (\varepsilon; \vec{r}'_>)^\times, \end{aligned}$$

and

$$\begin{aligned} G \left(\varepsilon; \vec{r}_n + \vec{R}_n, \vec{r}'_m + \vec{R}_m \right) &= \quad (194) \\ &= \sum_{LL'} Z_L^n (\varepsilon; \vec{r}_n) \tau_{LL'}^{nm} (\varepsilon) Z_{L'}^m (\varepsilon; \vec{r}'_m)^\times - \delta_{nm} \sum_L Z_L^n (\varepsilon; \vec{r}'_<) J_L^n (\varepsilon; \vec{r}'_>)^\times. \end{aligned}$$

2.8 Density of states, charge density, dispersion relation

In this section we give some expressions for quantities to be usually computed in electronic structure calculations of solids. The density of states defined in Eq. (29) can be written as

$$\begin{aligned} n(\varepsilon) &= -\frac{1}{\pi} \int d^3r \operatorname{Im} G^+(\varepsilon; \vec{r}, \vec{r}) \\ &= -\frac{1}{\pi} \sum_i \int_{\Omega_i} d^3r_i \operatorname{Im} G^+(\varepsilon; \vec{r}_i + \vec{R}_i, \vec{r}_i + \vec{R}_i) , \end{aligned} \quad (195)$$

therefore, the *local DOS* (LDOS), referenced to individual cells, can straightforwardly be defined as

$$n^i(\varepsilon) = -\frac{1}{\pi} \int_{\Omega_i} d^3r_i \operatorname{Im} G^+(\varepsilon; \vec{r}_i + \vec{R}_i, \vec{r}_i + \vec{R}_i) , \quad (196)$$

such that

$$n(\varepsilon) = \sum_i n^i(\varepsilon) . \quad (197)$$

Inserting expression (188) into Eq. (196) yields

$$\begin{aligned} n^i(\varepsilon) &= -\frac{1}{\pi} \int_{\Omega_i} d^3r_i \mathbf{Z}^i(\varepsilon; \vec{r}_i) \operatorname{Im} \underline{\mathcal{T}}^{ii}(\varepsilon) \mathbf{Z}^i(\varepsilon; \vec{r}_i)^\times \\ &= -\frac{1}{\pi} \operatorname{tr}(\underline{\mathbf{F}}^i(\varepsilon) \operatorname{Im} \underline{\mathcal{T}}^{ii}(\varepsilon)) , \end{aligned} \quad (198)$$

where now the trace has to be taken in angular momentum space and the matrix comprising the integrals of the scattering solutions, $\underline{\mathbf{F}}^i(\varepsilon)$ is defined as

$$\underline{\mathbf{F}}^i(\varepsilon) = \int_{\Omega_i} d^3r_i \mathbf{Z}^i(\varepsilon; \vec{r}_i)^\times \mathbf{Z}^i(\varepsilon; \vec{r}_i) , \quad (199)$$

or

$$F_{LL'}^i(\varepsilon) = \int_{\Omega_i} d^3r_i Z_L^i(\varepsilon; \vec{r}_i)^\times Z_{L'}^i(\varepsilon; \vec{r}_i) . \quad (200)$$

The case of spherical integration domains, i.e., the atomic sphere approximation (ASA)

Expanding the scattering solutions in terms of the spherical harmonics,

$$Z_L^i(\varepsilon; \vec{r}_i) = \sum_{L'} Y_{L'}(\hat{r}_i) Z_{L'L}^i(\varepsilon; r_i) , \quad (201)$$

Eq. (200) can be evaluated as follows,

$$\begin{aligned} F_{LL'}^i(\varepsilon) &= \sum_{L'', L'''} \int_{\Omega_i} d^3 r_i Z_{LL''}^i(\varepsilon; r_i) Y_{L''}(\hat{r}_i)^* Z_{L'L'''}^i(\varepsilon; r_i) Y_{L'''}(\hat{r}_i) \\ &= \sum_{L'', L'''} \left(\int_0^{S_i^{ASA}} r_i^2 dr_i Z_{LL''}^i(\varepsilon; r_i) Z_{L'L'''}^i(\varepsilon; r_i) \right) \underbrace{\int d^2 \hat{r}_i Y_{L''}(\hat{r}_i)^* Y_{L'''}(\hat{r}_i)}_{\delta_{L''L'''}} \\ &= \sum_{L''} \int_0^{S_i^{ASA}} r_i^2 dr_i Z_{LL''}^i(\varepsilon; r_i) Z_{L'L''}^i(\varepsilon; r_i) . \end{aligned} \quad (202)$$

In the diagonal (spherical symmetric) case this further reduces to

$$F_{LL'}^i(\varepsilon) = \delta_{LL'} \underbrace{\int_0^{S_i^{ASA}} r_i^2 dr_i Z_\ell^i(\varepsilon; r_i)^2}_{F_\ell^i(\varepsilon)} , \quad (203)$$

and the LDOS can be determined by the simple expression,

$$n^i(\varepsilon) = -\frac{1}{\pi} \sum_{\ell} F_\ell^i(\varepsilon) \sum_{m=-\ell}^{\ell} \text{Im} \tau_{\ell m, \ell m}^{ii}(\varepsilon) . \quad (204)$$

Quite naturally, the partial local DOS, $n_\ell^i(\varepsilon)$, can also be defined as

$$n_\ell^i(\varepsilon) = -\frac{1}{\pi} F_\ell^i(\varepsilon) \sum_{m=-\ell}^{\ell} \text{Im} \tau_{\ell m, \ell m}^{ii}(\varepsilon) , \quad (205)$$

such that

$$n^i(\varepsilon) = \sum_{\ell} n_\ell^i(\varepsilon) . \quad (206)$$

The *charge (or particle) density*,

$$\rho(\vec{r}) = -\frac{1}{\pi} \int_{-\infty}^{\varepsilon_F} d\varepsilon \operatorname{Im} G^+(\varepsilon; \vec{r}, \vec{r}) , \quad (207)$$

plays an essential role in electronic structure calculations based on the Density Functional Theory. Here we are restricted to $T = 0$, and the Fermi energy is denoted by ε_F . Similar to the DOS, the charge density can also be decomposed into local components,

$$\rho(\vec{r}) = \sum_i \rho^i(\vec{r}_i) , \quad (208)$$

where

$$\rho^i(\vec{r}_i) = -\frac{1}{\pi} \sum_{LL'} \int_{-\infty}^{\varepsilon_F} d\varepsilon Z_L^i(\varepsilon; \vec{r}_i) [\operatorname{Im} \mathcal{T}^{ii}(\varepsilon)]_{LL'} Z_{L'}^i(\varepsilon; \vec{r}_i)^\times , \quad (209)$$

which for spherically symmetric potentials reduces to

$$\rho^i(\vec{r}_i) = -\frac{1}{\pi} \sum_{LL'} \int_{-\infty}^{\varepsilon_F} d\varepsilon Z_\ell^i(\varepsilon; r_i) Z_{\ell'}^i(\varepsilon; r_i) \operatorname{Im} \tau_{LL'}^{ii}(\varepsilon) Y_L(\hat{r}_i) Y_{L'}(\hat{r}_i)^* . \quad (210)$$

Using the expansion for the product of spherical harmonics,

$$Y_L(\hat{r}_i) Y_{L'}(\hat{r}_i)^* = \sum_{L''} C_{L'L''}^L Y_{L''}(\hat{r}_i) , \quad (211)$$

$C_{L'L''}^L$ being the Gaunt coefficients as defined in Eq. (151), the local charge density can be decomposed into multipole components,

$$\rho^i(\vec{r}_i) = \sum_L \rho_L^i(r_i) Y_L(\hat{r}_i) , \quad (212)$$

where

$$\rho_L^i(r_i) = -\frac{1}{\pi} \sum_{L'L''} C_{LL''}^{L'} \int_{-\infty}^{\varepsilon_F} d\varepsilon Z_{\ell'}^i(\varepsilon; r_i) Z_{\ell''}^i(\varepsilon; r_i) \operatorname{Im} \tau_{L'L''}^{ii}(\varepsilon) . \quad (213)$$

In case of *three-dimensional translation symmetry* (for brevity, let us discuss the case of a simple lattice only), the structure constants can be evaluated in terms of lattice Fourier transformation,

$$\underline{G}_0^{mn'}(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3k \underline{G}_0(\varepsilon; \vec{k}) e^{i\vec{k}(\vec{R}_n - \vec{R}_{n'})}, \quad (214)$$

where BZ denotes the Brillouin zone of volume Ω_{BZ} and the reciprocal space structure constants,

$$\underline{G}_0(\varepsilon; \vec{k}) = \sum_{\vec{R}_n} \underline{G}_0^{n0}(\varepsilon) e^{-i\vec{k}\vec{R}_n}, \quad (215)$$

can directly be calculated in terms of the so-called Ewald summation for slowly converging series. It is straightforward to show that the lattice Fourier transform of the SPO-matrix,

$$\underline{\tau}(\varepsilon; \vec{k}) = \sum_{\vec{R}_n} \underline{\tau}^{n0}(\varepsilon) e^{-i\vec{k}\vec{R}_n}, \quad (216)$$

can be calculated as

$$\underline{\tau}(\varepsilon; \vec{k}) = \left[\underline{t}(\varepsilon)^{-1} - \underline{G}_0(\varepsilon; \vec{k}) \right]^{-1}, \quad (217)$$

where $\underline{t}(\varepsilon)$ is the single-site t -matrix of the cells being now uniform for the entire system. The site-diagonal part of the SPO-matrix,

$$\underline{\tau}^{00}(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3k \underline{\tau}(\varepsilon; \vec{k}), \quad (218)$$

which enters the local DOS,

$$n(\varepsilon) = -\frac{1}{\pi} \sum_L F_L(\varepsilon) \text{Im} \tau_{LL}^{00}(\varepsilon), \quad (219)$$

has poles at the eigenvalues of the Hamiltonian of the system, $\varepsilon_\alpha(\vec{k})$, where α labels the bands. From Eq. (217) it is obvious that these poles can be found by the condition,

$$\det \left(\underline{t}(\varepsilon)^{-1} - \underline{G}_0(\varepsilon; \vec{k}) \right) = 0, \quad (220)$$

referred to as the *KKR-equation* which determines the *dispersion relation* in the bulk case. It should be noted that Eq. (220) represents a formally exact tool for searching the spectrum of a 3D translational invariant (effective) one-electron system. The ‘penalty’ one has to pay for this exactness is the non-linearity of Eq. (220), i.e., $\varepsilon_\alpha(\vec{k})$ can not be determined from a simple (generalized) eigenvalue problem of a Hamiltonian matrix as in the case of linearized band structure methods. A useful visualization of the dispersion relation can be obtained by decomposing the DOS into k -dependent contributions,

$$n(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} d^3k A(\varepsilon; \vec{k}), \quad (221)$$

where the quantity,

$$A(\varepsilon; \vec{k}) = -\frac{1}{\pi} \sum_L F_L(\varepsilon) \text{Im} \tau_{LL}^{00}(\varepsilon; \vec{k}), \quad (222)$$

called the *Bloch spectral function*, has δ -like sharp peaks at $\varepsilon = \varepsilon_\alpha(\vec{k})$. Obviously, a constant-energy surface in the Brillouin zone, in particular, the Fermi surface can be constructed by connecting the peak positions of $A(\varepsilon; \vec{k})$ for the given energy, ε .

3 Generalization of multiple scattering theory

Referring to section 1.4, in the final section of this course we show how an arbitrary reference system can be used within the KKR Green function method. There are essentially two practical ways for doing this, depending on which of the fundamental equations, Eq. (169) or (171), is considered as starting point. It should be noted that both techniques are restricted to the case when the scatterers in the different systems are of the same geometrical arrangements, i.e., the position vectors \vec{R}_i are not changed. In order to handle structural relaxations, different techniques have to be used, the discussion of which extends the scope of this course.

3.1 The embedding technique

We start with Eq. (169) which for the system of interest (marked by index s) and the reference system (r) reads as

$$\boldsymbol{\tau}^s(\varepsilon) = \left(\mathbf{t}^s(\varepsilon)^{-1} - \mathbf{G}_0(\varepsilon) \right)^{-1}, \quad (223)$$

and

$$\boldsymbol{\tau}^r(\varepsilon) = \left(\mathbf{t}^r(\varepsilon)^{-1} - \mathbf{G}_0(\varepsilon) \right)^{-1}, \quad (224)$$

respectively. Performing simple algebraic manipulations,

$$\begin{aligned} \boldsymbol{\tau}^s(\varepsilon) &= \left(\mathbf{t}^r(\varepsilon)^{-1} - \Delta\mathbf{t}(\varepsilon)^{-1} - \mathbf{G}_0(\varepsilon) \right)^{-1} \\ &= \left(\mathbf{I} - \Delta\mathbf{t}(\varepsilon)^{-1} \left(\mathbf{t}^r(\varepsilon)^{-1} - \mathbf{G}_0(\varepsilon) \right)^{-1} \left(\mathbf{t}^r(\varepsilon)^{-1} - \mathbf{G}_0(\varepsilon) \right) \right)^{-1}, \end{aligned} \quad (225)$$

where

$$\Delta\mathbf{t}(\varepsilon)^{-1} = \mathbf{t}^r(\varepsilon)^{-1} - \mathbf{t}^s(\varepsilon)^{-1}, \quad (226)$$

it is straightforward to express $\boldsymbol{\tau}^s(\varepsilon)$ in terms of $\boldsymbol{\tau}^r(\varepsilon)$,

$$\boldsymbol{\tau}^s(\varepsilon) = \boldsymbol{\tau}^r(\varepsilon) \left(\mathbf{I} - \Delta \mathbf{t}(\varepsilon)^{-1} \boldsymbol{\tau}^r(\varepsilon) \right)^{-1}. \quad (227)$$

Therefore, once the t -matrices, $\mathbf{t}^r(\varepsilon)$ and $\mathbf{t}^s(\varepsilon)$, as well as the SPO matrix of the reference system, $\boldsymbol{\tau}^r(\varepsilon)$, are known, the SPO matrix, $\boldsymbol{\tau}^s(\varepsilon)$ can directly be calculated based on Eq. (227) and then the Green function of the system can be obtained from Eq. (194).

A particularly important application of the embedding technique refers to the case when only a finite number (say, a cluster) of scatterers differ from each other in the two systems, labelled by s and r . In this case, namely,

$$\Delta \underline{t}_i(\varepsilon)^{-1} = \begin{cases} \underline{t}_i^r(\varepsilon)^{-1} - \underline{t}_i^s(\varepsilon)^{-1} & \text{if } i \in C \\ \underline{0} & \text{if } i \notin C \end{cases}, \quad (228)$$

where C denotes the set of indices of the sites in the cluster. Rewriting formally Eq. (227),

$$\begin{aligned} \boldsymbol{\tau}^s(\varepsilon) &= \boldsymbol{\tau}^r(\varepsilon) + \boldsymbol{\tau}^r(\varepsilon) \Delta \mathbf{t}(\varepsilon)^{-1} \boldsymbol{\tau}^r(\varepsilon) \\ &+ \boldsymbol{\tau}^r(\varepsilon) \Delta \mathbf{t}(\varepsilon)^{-1} \boldsymbol{\tau}^r(\varepsilon) \Delta \mathbf{t}(\varepsilon)^{-1} \boldsymbol{\tau}^r(\varepsilon) + \dots, \end{aligned} \quad (229)$$

it is easy to express the projection of $\boldsymbol{\tau}^s(\varepsilon)$ onto the cluster, $\boldsymbol{\tau}_C^s(\varepsilon)$,

$$[\boldsymbol{\tau}_C^s(\varepsilon)]^{ij} = \underline{\tau}^{s,ij}(\varepsilon) \quad \text{for } i, j \in C, \quad (230)$$

as

$$\begin{aligned} \boldsymbol{\tau}_C^s(\varepsilon) &= \boldsymbol{\tau}_C^r(\varepsilon) + \boldsymbol{\tau}_C^r(\varepsilon) \Delta \mathbf{t}_C(\varepsilon)^{-1} \boldsymbol{\tau}_C^r(\varepsilon) \\ &+ \boldsymbol{\tau}_C^r(\varepsilon) \Delta \mathbf{t}_C(\varepsilon)^{-1} \boldsymbol{\tau}_C^r(\varepsilon) \Delta \mathbf{t}_C(\varepsilon)^{-1} \boldsymbol{\tau}_C^r(\varepsilon) + \dots, \end{aligned} \quad (231)$$

where $\boldsymbol{\tau}_C^r(\varepsilon)$ is the corresponding projection of the SPO matrix of the reference system and $\Delta \mathbf{t}_C(\varepsilon)^{-1}$ comprises the nonvanishing $\Delta \underline{t}_i^{-1}$ matrices (see Eq. (228)). Eq. (231) can then be written in a form similar to (227),

$$\boldsymbol{\tau}_C^s(\varepsilon) = \boldsymbol{\tau}_C^r(\varepsilon) \left(\mathbf{I} - \Delta \mathbf{t}_C(\varepsilon)^{-1} \boldsymbol{\tau}_C^r(\varepsilon) \right)^{-1}, \quad (232)$$

with the obvious difference that now one has to deal with matrices of dimension of $N \times (\ell_{\max} + 1)^2$, where N denotes the number of sites in the cluster and ℓ_{\max} is the angular momentum cut-off in the calculations. Specifically, for a single impurity at site i the above equation reduces to

$$\underline{\mathcal{T}}^{s,ii}(\varepsilon) = \underline{\mathcal{T}}^{r,ii}(\varepsilon) \left(\underline{\mathcal{I}} - \Delta \underline{\mathcal{t}}^i(\varepsilon)^{-1} \underline{\mathcal{T}}^{r,ii}(\varepsilon) \right)^{-1}. \quad (233)$$

Within the *single-site coherent potential approximation* for randomly disordered substitutional alloys, the reference system is associated with the (translational invariant) effective medium in which a particular constituent of the alloy (labelled by α) is immersed via

$$\underline{\mathcal{T}}^{\alpha,00}(\varepsilon) = \underline{\mathcal{T}}^{c,00}(\varepsilon) \left(\underline{\mathcal{I}} - \Delta \underline{\mathcal{t}}^\alpha(\varepsilon)^{-1} \underline{\mathcal{T}}^{c,00}(\varepsilon) \right)^{-1}. \quad (234)$$

Without going into details, the condition for self-consistently determining the t -matrix of the effective system, $\underline{\mathcal{t}}^c(\varepsilon)$, reads

$$\underline{\mathcal{T}}^{c,00}(\varepsilon) = \sum_{\alpha} c_{\alpha} \underline{\mathcal{T}}^{\alpha,00}(\varepsilon), \quad (235)$$

where c_{α} is the concentration of component α ($\sum_{\alpha} c_{\alpha} = 1$), while $\underline{\mathcal{T}}^{c,00}(\varepsilon)$ is calculated by using Eqs. (217) and (218) when replacing $\underline{\mathcal{t}}(\varepsilon)$ by $\underline{\mathcal{t}}^c(\varepsilon)$.

3.2 The Screened Korringa-Kohn-Rostoker method

In principal, an equivalent technique can be developed by focusing on the structural Green function matrix of the system (see Eq. (171)),

$$\mathbf{G}^s(\varepsilon) = \mathbf{G}_0(\varepsilon) (\mathbf{I} - \mathbf{t}^s(\varepsilon) \mathbf{G}_0(\varepsilon))^{-1} , \quad (236)$$

which by splitting the t -matrix into two parts,

$$\mathbf{t}^s(\varepsilon) = \mathbf{t}^r(\varepsilon) + \Delta\mathbf{t}(\varepsilon) , \quad (237)$$

with

$$\Delta\mathbf{t}(\varepsilon) = \mathbf{t}^s(\varepsilon) - \mathbf{t}^r(\varepsilon) , \quad (238)$$

can be related to the structural Green function matrix of the reference system,

$$\mathbf{G}^r(\varepsilon) = \mathbf{G}_0(\varepsilon) (\mathbf{I} - \mathbf{t}^r(\varepsilon) \mathbf{G}_0(\varepsilon))^{-1} , \quad (239)$$

as follows,

$$\begin{aligned} \mathbf{G}^s(\varepsilon) &= \mathbf{G}_0(\varepsilon) (\mathbf{I} - \mathbf{t}^r(\varepsilon) \mathbf{G}_0(\varepsilon) - \Delta\mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon))^{-1} \\ &= \mathbf{G}_0(\varepsilon) \left(\left[\mathbf{I} - \Delta\mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) (\mathbf{I} - \mathbf{t}^r(\varepsilon) \mathbf{G}_0(\varepsilon))^{-1} \right] (\mathbf{I} - \mathbf{t}^r(\varepsilon) \mathbf{G}_0(\varepsilon)) \right)^{-1} \\ &= \mathbf{G}_0(\varepsilon) (\mathbf{I} - \mathbf{t}^r(\varepsilon) \mathbf{G}_0(\varepsilon))^{-1} \left(\mathbf{I} - \Delta\mathbf{t}(\varepsilon) \mathbf{G}_0(\varepsilon) (\mathbf{I} - \mathbf{t}^r(\varepsilon) \mathbf{G}_0(\varepsilon))^{-1} \right)^{-1} \\ &\quad \Downarrow \\ \mathbf{G}^s(\varepsilon) &= \mathbf{G}^r(\varepsilon) (\mathbf{I} - \Delta\mathbf{t}(\varepsilon) \mathbf{G}^r(\varepsilon))^{-1} . \end{aligned} \quad (240)$$

The equivalence of Eqs. (227) and (240) can be proved directly!

Within the *Screened Korringa-Kohn-Rostoker method*, a reference system is used to obtain $\underline{G}^{r,ij}(\varepsilon)$ localized in real space. Obviously, a system formed by a uniform distribution of constant repulsive potentials (typically, $V_r=2-3$

Ryd) meets the above request, since the valence band of typical metals lies below V_r , thereby, no states of the reference system can be found in this region. This implies that, similar to $G_0(\varepsilon; \vec{r}, \vec{r}')$ for negative energies (see Eq. (23)), the Green function of the reference system exponentially decays in real space. For that reason, the matrices $\underline{G}^{r,ij}(\varepsilon)$ are referred to as the *screened structure constants*, used to define the *SPO in the screened representation*,

$$\boldsymbol{\tau}^{s(r)}(\varepsilon) = \left([\Delta \mathbf{t}(\varepsilon)]^{-1} - \mathbf{G}^r(\varepsilon) \right)^{-1}. \quad (241)$$

Obviously, once a real-space cut-off for $\underline{G}^{r,ij}(\varepsilon)$ is used,

$$\underline{G}^{r,ij}(\varepsilon) \simeq 0 \quad \text{for} \quad |\vec{R}_{ij}| > D, \quad (242)$$

sparse matrix techniques can be used to solve Eq. (241). Such a method has been developed to treat surfaces and interfaces of solids, where the translational invariance is broken normal to the planes and, therefore, a lattice Fourier transform does not apply with respect to this direction. The screened SPO is obviously related to the structural Green function matrix of the system by

$$\boldsymbol{\tau}^{s(r)}(\varepsilon) = \Delta \mathbf{t}(\varepsilon) + \Delta \mathbf{t}(\varepsilon) \mathbf{G}^s(\varepsilon) \Delta \mathbf{t}(\varepsilon), \quad (243)$$

and a similar expression holds for the *physical representation of the SPO*,

$$\boldsymbol{\tau}^s(\varepsilon) = \mathbf{t}^s(\varepsilon) + \mathbf{t}^s(\varepsilon) \mathbf{G}^s(\varepsilon) \mathbf{t}^s(\varepsilon), \quad (244)$$

Thus the transformation of the SPO from the screened to the physical presentation can be written as

$$\begin{aligned} \boldsymbol{\tau}^s(\varepsilon) &= \mathbf{t}^s(\varepsilon) [\Delta \mathbf{t}(\varepsilon)]^{-1} \boldsymbol{\tau}^{s(r)}(\varepsilon) [\Delta \mathbf{t}(\varepsilon)]^{-1} \mathbf{t}^s(\varepsilon) \\ &\quad - \mathbf{t}^s(\varepsilon) [\Delta \mathbf{t}(\varepsilon)]^{-1} \mathbf{t}^s(\varepsilon) + \mathbf{t}^s(\varepsilon), \end{aligned} \quad (245)$$

which does not imply any further numerical complication since the transformation is site-diagonal.

Literature

Gonis, A.: *Green functions for ordered and disordered systems* (North-Holland, Amsterdam) 1992

Messiah, A.: *Quantum mechanics* (North-Holland, Amsterdam) 1969

Newton, R.G.: *Scattering theory of waves and particles* (McGraw-Hill, New York) 1966

Taylor, J.R.: *Scattering theory* (John Wiley and Sons, New York) 1972

Weinberger, P.: *Electron scattering theory of ordered and disordered matter* (Clarendon, Oxford) 1990