1 Green-function matrices in the TB formalism

In the tight binding (TB) picture the matrix of a Hamiltonian $H$ is in the form

$$H = \{ H^{ij} \}, \text{ where}$$

$$H^{ij} = \delta_{ij} \varepsilon_{i} + \gamma^{ij},$$

(1)

(2)

Single and double underlines denote matrices in angular momentum space and site-angular momentum space, respectively. The size of each angular momentum block is determined by the dimension of the basis centered at each site $i$. In the case of 3$d$ transition metals e.g., the hybridized 3$d$-4$s$-4$p$ valence band spans a 9-dimensional space (18 including spin). In many cases the on-site energy blocks $\varepsilon_{i}$ in Eq. (2) are themselves diagonal, but this is not necessary. The hopping integrals $\gamma^{ij}$ are strictly site-off-diagonal.

The resolvent (or static Green-function) matrix of a given system described by the Hamiltonian $H$ can be defined as

$$G(z) := (z - H)^{-1}$$

(3)

for any $z \in \mathbb{C}$ (at least where the inversion can be performed). Supposing that the solutions of the eigenvalue equation,

$$H |i\rangle = \varepsilon_{i} |i\rangle,$$

(4)

are known, then the Hamiltonian matrix can be written as

$$H = \sum_{i} \varepsilon_{i} |i\rangle \langle i|,$$

(5)

where $i$ runs over all eigenfunctions. This implies the spectral decomposition of the matrix $G(z)$,

$$G(z) = \sum_{i} \frac{1}{z - \varepsilon_{i}} |i\rangle \langle i|.$$

(6)

The fundamental analytic property of the resolvent,

$$G(z^*) = G(z)^{j}$$

(7)
is a corollary of this decomposition. Another fundamental identity can be derived from definition:

$$\frac{dG(z)}{dz} = -G(z)^2.$$  \hspace{1cm} (8)

Since $G(z)$ is undefined at real energies, $\varepsilon_i$, we have to approach the real arguments from the imaginary direction,

$$G^\pm(\varepsilon) := \lim_{\delta \rightarrow 0} G(\varepsilon \pm i\delta)$$  \hspace{1cm} (9)

$$= \sum_i \frac{1}{\varepsilon - \varepsilon_i \pm i0} |i\rangle \langle i|,$$  \hspace{1cm} (10)

for any $\varepsilon \in \mathbb{R}$. Note that $G^+(\varepsilon) \neq G^-(\varepsilon)$ if $\varepsilon$ is in the spectrum of $H$. Equation (7) implies

$$[G^+(\varepsilon)]^\dagger = G^-(\varepsilon).$$  \hspace{1cm} (11)

The well-known identity of generalized functions,

$$\frac{1}{\varepsilon - \varepsilon_i \pm i0} = \mathcal{P} \left( \frac{1}{\varepsilon - \varepsilon_i} \right) \mp i\pi\delta(\varepsilon - \varepsilon_i),$$  \hspace{1cm} (12)

leads to the relationship,

$$\sum_i \delta(\varepsilon - \varepsilon_i) |i\rangle \langle i| = -\frac{1}{2\pi i} \left[ G^+(\varepsilon) - G^-(\varepsilon) \right]$$

$$= -\frac{1}{2\pi i} \left[ G^+(\varepsilon) - (G^+(\varepsilon))^\dagger \right].$$  \hspace{1cm} (13)

By composing the trace of (13), the density of states of the system, $n(\varepsilon)$, can be expressed from the Green function as

$$n(\varepsilon) = \sum_i \delta(\varepsilon - \varepsilon_i) = -\frac{1}{2\pi i} \text{Tr} \left[ G^+(\varepsilon) - (G^+(\varepsilon))^\dagger \right]$$

$$= -\frac{1}{2\pi i} \left[ \text{Tr} G^+(\varepsilon) - (\text{Tr} G^+(\varepsilon))^\dagger \right]$$

$$= -\frac{1}{\pi} \text{Im} \text{Tr} G^+(\varepsilon) = \frac{1}{\pi} \text{Im} \text{Tr} G^-(\varepsilon).$$  \hspace{1cm} (14)

The expectation value of an observable $A$ at zero temperature can be calculated as

$$\langle A \rangle = \int_{\varepsilon_b}^{\varepsilon_F} \sum_i \delta(\varepsilon - \varepsilon_i) \langle i| A |i\rangle \, d\varepsilon$$

$$= \int_{\varepsilon_b}^{\varepsilon_F} \text{Tr} \left( \sum_i \delta(\varepsilon - \varepsilon_i) |i\rangle \langle i| A \right) \, d\varepsilon$$

$$\langle A \rangle = -\frac{1}{\pi} \text{Im} \int_{\varepsilon_b}^{\varepsilon_F} \text{Tr} \left[ A G^+(\varepsilon) \right] \, d\varepsilon,$$  \hspace{1cm} (15)

so $G(z)$ and the spectrum of $H$ contain the same information.
2 Perturbations with respect to a reference system

Suppose now that $H = H_0 + \Delta H$, and $G_0 = (z - H_0)^{-1}$ is the resolvent of the reference system. Then

$$G(z) = (z - H)^{-1}$$

$$\left(z - H_0 - \Delta H\right) G(z) = I$$

$$\left(I - G_0(z) \Delta H\right) G(z) = G_0(z)$$

$$G(z) = \left(I - G_0(z) \Delta H\right)^{-1} G_0(z) = G_0(z) \left(I - \Delta H G_0(z)\right)^{-1}$$

On the other hand, from Eq. (19),

$$G(z) = G_0(z) + G_0(z) \Delta H G(z) .$$

This equation can be solved iteratively:

$$G_0^{(0)}(z) = G_0(z)$$

$$G_0^{(1)}(z) = G_0(z) + G_0(z) \Delta H G_0(z)$$

$$G_0^{(2)}(z) = G_0(z) + G_0(z) \Delta H G_0(z) + G_0(z) \Delta H G_0(z) \Delta H G_0(z)$$

$$\vdots$$

$$G(z) = G_0(z) + G_0(z) \Delta H G_0(z) + G_0(z) \Delta H G_0(z) \Delta H G_0(z) + \ldots$$

This Dyson-equation can be rearranged as

$$G(z) = G_0(z) + G_0(z) \Delta H G_0(z) \Delta H + \ldots \right] G_0(z)$$

$$= G_0(z) + G_0(z) T(z) G_0(z) ,$$

where $T(z)$ is the so-called scattering matrix,

$$T(z) = \Delta H + \Delta H G_0(z) \Delta H$$

$$= \Delta H + \Delta H G_0(z) \Delta H + \Delta H G_0(z) \Delta H G_0(z) \Delta H + \ldots$$

$$= \Delta H + \Delta H G_0(z) T(z) .$$

This can be rearranged to give

$$T(z) = \left(I - \Delta H G_0(z)\right)^{-1} \Delta H = \Delta H \left[I - G_0(z) \Delta H\right]^{-1} .$$

It can easily be shown that the $T$ matrix has similar analytical properties as the resolvent,

$$T(z^*) = T(z)$$

$$\frac{d}{dz} T(z) = T(z) \frac{d G_0(z)}{dz} T(z) ,$$

$$T^\pm(z) := \lim_{\delta \to 0} T(z \pm i \delta) .$$
at real energies \( \varepsilon \). By using equations (14) and (23), we get the density of states (DOS) of the perturbed system with respect to the reference system,

\[
n(\varepsilon) = n_0(\varepsilon) - \frac{1}{\pi} \text{ImTr} \left[ G_0^+(\varepsilon) T^+(\varepsilon) G_0^+(\varepsilon) \right].
\]

Using properties (8) and (27), then integrating with respect to energy, we arrive at the Lloyd-formula, which gives the integrated DOS of the perturbed system,

\[
N(\varepsilon) := \int_{-\infty}^{\varepsilon} n(\varepsilon') \, d\varepsilon' = N_0(\varepsilon) + \frac{1}{\pi} \text{ImTr} \ln T^+(\varepsilon).
\]

### 3 On-site impurities

Case of a single on-site impurity: \( \Delta H_{ii} = \{ \Delta H_{ii} \delta_{in}\delta_{im} \} \),

\[
T = \Delta H_{ii} + \Delta H_{ii} G_0 \Delta H_{ii} + \ldots
\]

\[
= \{ [\Delta H_{ii} + \Delta H_{ii} G_0^{ii} \Delta H_{ii} + \ldots] \delta_{in}\delta_{im} \}
\]

\[
= \{ t_i \delta_{in}\delta_{im} \}, \text{ thus}
\]

\[
t_i = \Delta H_{ii} + \Delta H_{ii} G_0^{ii} t_i.
\]

Now let \( \Delta H \) be a sum of such on-site differences: \( \Delta H = \sum_i \Delta H_{ii} \). Then

\[
T = \left( \sum_i \Delta H_{ii} \right) + \left( \sum_i \Delta H_{ii} \right) G_0 \left( \sum_i \Delta H_{ii} \right) + \ldots
\]

\[
= \sum_i \Delta H_{ii} + \sum_{i,j} \Delta H_{ii} G_0 \Delta H_{jj} + \sum_{i,j,k} \Delta H_{ii} G_0 \Delta H_{jj} G_0 \Delta H_{kk} + \ldots
\]

\[
T_{nm} = \Delta H_{n} \delta_{nm} + \Delta H_{n} G_0^{nm} \Delta H_{nm} + \sum_{k} \Delta H_{n} G_0^{nk} \Delta H_k G_0^{km} \Delta H_m + \ldots
\]

Both in operator and in matrix sense,

\[
T = \sum_i \Delta H_{ii} + \sum_{i,j} \Delta H_{ii} G_0 \Delta H_{jj} + \ldots
\]

\[
= \sum_i \left( \Delta H_{ii} + \sum_j \Delta H_{ii} G_0 \Delta H_{jj} + \ldots \right)
\]

\[
= \sum_i Q_i, \text{ where}
\]
\[ Q_n := \Delta H_n + \sum_m \Delta H_n G_0 \Delta H_m + \ldots \] (37)
\[ = \Delta H_n + \Delta H_n G_0 \sum_m \Delta Q_m \]
\[ = \Delta H_n + \Delta H_n G_0 Q_n + \Delta H_n G_0 \sum_{m(\neq n)} \Delta Q_m \]
\[
\left( I - \Delta H_n G_0 \right) Q_n = \Delta H_n + \Delta H_n G_0 \sum_{m(\neq n)} \Delta Q_m
\]
\[ Q_n = t_n + t_n G_0 \sum_{m(\neq n)} Q_m. \] (38)

where \( t_n \) is formally a single impurity \( T \)-matrix on the \( n \)-th site,

\[ t_n = \{ t_n \delta_{mn} \}. \] (39)

Solving equation (38) iteratively,

\[ Q_n^{(0)} := t_n \] (40)
\[ Q_n^{(1)} = t_n + \sum_{m(\neq n)} t_n G_0 t_m \]
\[ Q_n^{(2)} = t_n + \sum_{m(\neq n)} t_n G_0 t_m + \sum_{m(\neq n) k(\neq m)} t_n G_0 t_m G_0 t_k + \ldots \] (41)

Using equation (37), we arrive at the multiple scattering expansion of the \( T \) matrix,

\[ T = \sum_n t_n + \sum_{n \neq m} t_n G_0 t_m + \sum_{n \neq m \neq k} t_n G_0 t_m G_0 t_k + \ldots \] (42)

Since all \( t_n \) have the structure of \( \Delta H_n \),

\[ T^{nm} = t_n \delta_{nm} + (1 - \delta_{nm}) t_n G_0^{nm} t_m + \sum_{k(k \neq m)} t_n G_0^{nk} G_0^{km} t_m + \ldots \] (43)
\[ = t_n \delta_{nm} + \sum_k t_n G_0^{nk} (1 - \delta_{nk}) T^{km}. \] (44)

Defining the site-off-diagonal part of the reference system’s resolvent,

\[ \hat{G}_0 := \{ G_0^{nk} (1 - \delta_{nk}) \}; \] (45)
\[ T = t + t \hat{G}_0 T \]
\[
\downarrow
\quad T = \left[ t^{-1} + \hat{G}_0 \right]^{-1}
\] (46)
On the other hand,

\[ T = t + t \tilde{G} + t \tilde{G} t \tilde{G} t \tilde{G} \ldots, \]  

so

\[ G = G_0 + G_0 T G_0 \]  

is given in terms of \( G_0 \) and \( t \).

4 Chemically disordered systems

4.1 Binary alloys

Let’s consider now a two-state disordered system, e.g. a two-component (binary) random alloy:

\[ \Delta H_i = \xi_i \Delta H_i^A + (1 - \xi_i) \Delta H_i^B, \]  

where \( \xi_i \) are independent random variables with Bernoulli distribution:

\[ \xi_i = \begin{cases} 1 & \text{with probability } P_i(1) := c_i, \\ 0 & \text{with probability } P_i(0) = 1 - c_i. \end{cases} \]  

By definition the expected values are

\[ \mathbb{E} \xi_i \equiv \langle \xi_i \rangle = c_i, \]  

thus the expected value of \( \Delta H_i \) is

\[ \langle \Delta H_i \rangle = \langle \xi_i \rangle \Delta H_i^A + (1 - \xi_i) \Delta H_i^B = c_i \Delta H_i^A + (1 - c_i) \Delta H_i^B. \]  

Independence means that the joint probability mass function of \( \{ \xi \} \) decomposes to the product of the individual probability mass functions:

\[ P (\{ \xi \}) = \prod_{i=1}^{N} P_i (\xi_i). \]  

Of course \( P (\{ \xi \}) \) is a probability, since trivially

\[ \sum_{\{ \xi \}} P (\{ \xi \}) = \prod_{i=1}^{N} \left( \sum_{\xi_i=0}^{1} P_i (\xi_i) \right) = 1. \]  

The configurational average of some physical quantity is then defined as

\[ \langle F (\{ \xi \}) \rangle := \sum_{\{ \xi \}} P (\{ \xi \}) F (\{ \xi \}) = \sum_{\xi_1} \ldots \sum_{\xi_N} P_1 (\xi_1) \ldots P_N (\xi_N) F (\xi_1, \ldots, \xi_N). \]  

Since \( G = G (\{ \xi_1, \xi_2, \ldots, \xi_N \}) \equiv G (\{ \xi \}) \), the mean of a physical quantity \( A \) in the TB picture is

\[ \langle A \rangle = \left\langle -\frac{1}{\pi} \operatorname{Im} \int f(\varepsilon) \operatorname{Tr} [A G (\{ \xi \})] \, d\varepsilon \right\rangle \]  

\[ = -\frac{1}{\pi} \operatorname{Im} \int f(\varepsilon) \operatorname{Tr} [A G] \, d\varepsilon \]  

(where we suppressed the dependence of \( G \) on the energy \( \varepsilon \)).
4.2 Coherent Potential Approximation

\[ \langle G \rangle = G_0 + G_0 \langle T \rangle G_0 \]

\[ =: G_c = (z - H_c)^{-1}, \quad (57) \]

where we defined the effective Hamiltonian \( H_c \), often noted as \( \Sigma_c \), the self-energy. This assumption is the coherent potential approximation (CPA). The (57) CPA condition can only be satisfied if \( H_c = H_c(z) \) is a function of the energy, but it is (by definition) configuration-independent.

Let us now choose our reference system to be \( H_c \),

\[ T = t + \xi \hat{G} t + \xi \hat{G} t + \ldots \]

\[ \Delta H = H - H_c = \{ (H_i - H_{ci}) \delta_m \delta_{im} \} , \quad (59) \]

where \( H_{c,i} \) are to be determined. A condition is given by

\[ \langle G \rangle = G_c = G_c + G_c \langle T \rangle G_c \]

\[ \Downarrow \]

\[ \langle T \rangle = 0 \quad (61) \]

\[ \langle t \rangle + \langle t \hat{G} t \rangle + \ldots = 0. \]

Single-site CPA:

\[ \langle t \rangle := 0 \quad (63) \]

Considering this,

\[ \langle t_n \hat{G}^m t_m \rangle = \langle t_n \rangle \hat{G}^m \langle t_m \rangle = 0 \]

\[ \sum_{k \neq n} \langle t_n \hat{G}^k t_k \hat{G}^m t_m \rangle = \sum_{k \neq n} \langle t_n \hat{G}^k \langle t_k \rangle \hat{G}^m t_m \rangle = 0. \]

Thus eq. (63) satisfies the condition set by eq. (61) up to fourth order in \( t \). Since

\[ t_i = \xi_i t_A + (1 - \xi_i) t_B \]

eq. (63) reads as

\[ \langle t_i \rangle = c_t t_A + (1 - c_t) t_B = 0 \]

This is in fact a system of equations for \( H_c \), because

\[ t_i = (I - \Delta H_i \hat{G}_i^c) \Delta H_i^c, \quad (66) \]

\[ \Delta H_i^c = H_i^c - H_{c,i} \quad (\alpha = A, B) \]

and \( G_i^c \) can be determined from equation (57).