

The Coherent Potential Approximation

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1 Green-function matrices in the TB formalism

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

$$\underline{\underline{H}} = \{ \underline{H}^{ij} \}, \quad (1)$$

where

$$\underline{H}^{ij} = \underline{\varepsilon}_i \delta_{ij} + \underline{\gamma}^{ij}. \quad (2)$$

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 $3d$ transition metals e.g., the hybridized $3d$ - $4s$ - $4p$ valence band spans a 9-dimensional space (18 including spin). In many cases the on-site energy blocks $\underline{\varepsilon}_i$ in Eq. (2) are themselves diagonal, but this is not necessary. The hopping integrals $\underline{\gamma}^{ij}$ are strictly site-off-diagonal.

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

$$\underline{\underline{G}}(z) := (z - \underline{\underline{H}})^{-1} \quad (3)$$

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

$$\underline{\underline{H}} \mathbf{c}_r = \varepsilon_r \mathbf{c}_r \quad (r \in \mathbb{N}) \quad (4)$$

are known, where \mathbf{c}_r are orthonormal column vectors,

$$\mathbf{c}_r^\dagger \mathbf{c}_s = \delta_{rs} \quad (5)$$

and form a full set of the Hilbert space,

$$\sum_r \mathbf{c}_r \mathbf{c}_r^\dagger = \underline{\underline{I}}. \quad (6)$$

The Hamiltonian matrix can then be written as

$$\underline{\underline{H}} = \sum_r \varepsilon_r \mathbf{c}_r \mathbf{c}_r^\dagger, \quad (7)$$

where n runs over all eigenvectors. This implies the spectral decomposition of the matrix $\underline{\underline{G}}(z)$,

$$\underline{\underline{G}}(z) = \sum_r \frac{\mathbf{c}_r \mathbf{c}_r^\dagger}{z - \varepsilon_r}. \quad (8)$$

The fundamental analytic property of the resolvent,

$$\underline{\underline{G}}(z^*) = \underline{\underline{G}}(z)^\dagger \quad (9)$$

is a consequence of this decomposition. Another fundamental identity can be derived from (3):

$$\frac{d\underline{\underline{G}}(z)}{dz} = -\underline{\underline{G}}(z)^2. \quad (10)$$

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

$$\underline{\underline{G}}^\pm(\varepsilon) = \sum_r \frac{\mathbf{c}_r \mathbf{c}_r^\dagger}{\varepsilon - \varepsilon_r \pm i0}, \quad (11)$$

for any $\varepsilon \in \mathbb{R}$. Note that $\underline{\underline{G}}^+(\varepsilon) \neq \underline{\underline{G}}^-(\varepsilon)$ if ε is in the spectrum of $\underline{\underline{H}}$. Equation (9) implies

$$[\underline{\underline{G}}^+(\varepsilon)]^\dagger = \underline{\underline{G}}^-(\varepsilon). \quad (12)$$

The well-known identity,

$$\frac{1}{\varepsilon - \varepsilon_r \pm i0} = \mathcal{P} \left(\frac{1}{\varepsilon - \varepsilon_r} \right) \mp i\pi \delta(\varepsilon - \varepsilon_r), \quad (13)$$

leads to the relationship,

$$\begin{aligned} \sum_r \delta(\varepsilon - \varepsilon_r) \mathbf{c}_r \mathbf{c}_r^\dagger &= -\frac{1}{2\pi i} [\underline{\underline{G}}^+(\varepsilon) - \underline{\underline{G}}^-(\varepsilon)] \\ &= -\frac{1}{2\pi i} [\underline{\underline{G}}^+(\varepsilon) - (\underline{\underline{G}}^+(\varepsilon))^\dagger]. \end{aligned} \quad (14)$$

By composing the trace of (14), the density of states of the system, $n(\varepsilon)$, can be expressed from the Green function as

$$\begin{aligned} n(\varepsilon) &= \sum_r \delta(\varepsilon - \varepsilon_r) = -\frac{1}{2\pi i} \text{Tr} [\underline{\underline{G}}^+(\varepsilon) - (\underline{\underline{G}}^+(\varepsilon))^\dagger] \\ &= -\frac{1}{2\pi i} [\text{Tr} \underline{\underline{G}}^+(\varepsilon) - (\text{Tr} \underline{\underline{G}}^+(\varepsilon))^*] \end{aligned} \quad (15)$$

↓

$$n(\varepsilon) = -\frac{1}{\pi} \text{Im Tr} \underline{\underline{G}}^+(\varepsilon) = \frac{1}{\pi} \text{Im Tr} \underline{\underline{G}}^-(\varepsilon). \quad (16)$$

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

$$\langle A \rangle = \int_{\varepsilon_b}^{\varepsilon_F} \sum_r \delta(\varepsilon - \varepsilon_r) \mathbf{c}_r^\dagger \underline{\underline{A}} \mathbf{c}_r d\varepsilon = \int_{\varepsilon_b}^{\varepsilon_F} \sum_r \delta(\varepsilon - \varepsilon_r) \text{Tr} [\mathbf{c}_r \mathbf{c}_r^\dagger \underline{\underline{A}}] d\varepsilon \quad (17)$$

↓

$$\langle A \rangle = -\frac{1}{\pi} \int_{\varepsilon_b}^{\varepsilon_F} \text{Im Tr} [\underline{\underline{G}}^+(\varepsilon) \underline{\underline{A}}] d\varepsilon = \frac{1}{\pi} \int_{\varepsilon_b}^{\varepsilon_F} \text{Im Tr} [\underline{\underline{G}}^-(\varepsilon) \underline{\underline{A}}] d\varepsilon, \quad (18)$$

so $\underline{\underline{G}}(z)$ and the spectrum of $\underline{\underline{H}}$ contain the same information.

2 Treating perturbations

Suppose now that $\underline{H} = \underline{H}_0 + \Delta\underline{H}$, and $\underline{G}_0(z) = (z - \underline{H}_0)^{-1}$ is the resolvent of the reference system. Then

$$\begin{aligned} (z - \underline{H}_0 - \Delta\underline{H}) \underline{G}(z) &= \underline{I} \\ (\underline{I} - \underline{G}_0(z) \Delta\underline{H}) \underline{G}(z) &= \underline{G}_0(z) \end{aligned} \quad (19)$$

↓

$$\underline{G}(z) = (\underline{I} - \underline{G}_0(z) \Delta\underline{H})^{-1} \underline{G}_0(z) = \underline{G}_0(z) (\underline{I} - \Delta\underline{H} \underline{G}_0(z))^{-1}. \quad (20)$$

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

$$\underline{G}(z) = \underline{G}_0(z) + \underline{G}_0(z) \Delta\underline{H} \underline{G}(z). \quad (21)$$

This equation can be solved iteratively:

$$\begin{aligned} \underline{G}^{(0)}(z) &= \underline{G}_0(z) \\ \underline{G}^{(1)}(z) &= \underline{G}_0(z) + \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) \\ \underline{G}^{(2)}(z) &= \underline{G}_0(z) + \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) + \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) \\ &\vdots \\ \underline{G}(z) &= \underline{G}_0(z) + \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) + \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) + \dots \end{aligned} \quad (22)$$

This Dyson-equation can be rearranged as

$$\begin{aligned} \underline{G}(z) &= \underline{G}_0(z) + \underline{G}_0(z) \left[\Delta\underline{H} + \Delta\underline{H} \underline{G}_0(z) \Delta\underline{H} + \dots \right] \underline{G}_0(z) \\ &= \underline{G}_0(z) + \underline{G}_0(z) \underline{T}(z) \underline{G}_0(z), \end{aligned} \quad (23)$$

where $\underline{T}(z)$ is the so-called scattering matrix,

$$\begin{aligned} \underline{T}(z) &= \Delta\underline{H} + \Delta\underline{H} \underline{G}_0(z) \Delta\underline{H} \\ &= \Delta\underline{H} + \Delta\underline{H} \underline{G}_0(z) \Delta\underline{H} + \Delta\underline{H} \underline{G}_0(z) \Delta\underline{H} \underline{G}_0(z) \Delta\underline{H} + \dots \\ &= \Delta\underline{H} + \Delta\underline{H} \underline{G}_0(z) \underline{T}(z). \end{aligned} \quad (24)$$

$\underline{T}(z)$ can be expressed as

$$\underline{T}(z) = \left[\underline{I} - \Delta\underline{H} \underline{G}_0(z) \right]^{-1} \Delta\underline{H} = \Delta\underline{H} \left[\underline{I} - \underline{G}_0(z) \Delta\underline{H} \right]^{-1}. \quad (25)$$

Furthermore,

$$\underline{T}(z) \underline{G}_0(z) = \Delta\underline{H} \underline{G}(z) \quad (26)$$

and

$$\underline{G}_0(z) \underline{T}(z) = \underline{G}(z) \Delta\underline{H}. \quad (27)$$

↓

$$\frac{d\underline{T}(z)}{dz} = \underline{\Delta H} \frac{d\underline{G}(z)}{dz} \underline{\Delta H} = -\underline{\Delta H} \underline{G}(z) \underline{\Delta H} \quad (28)$$

$$= -\underline{T}(z) \underline{G}_0(z) \underline{T}(z) = \underline{T}(z) \frac{d\underline{G}_0(z)}{dz} \underline{T}(z). \quad (29)$$

It can easily be shown that the \underline{T} matrix has similar analytical properties as the resolvent,

$$\underline{T}(z^*) = \underline{T}(z)^\dagger, \quad (30)$$

while

$$\underline{T}^\pm(\varepsilon) := \lim_{\delta \rightarrow 0} \underline{T}(\varepsilon \pm i\delta) \implies \underline{T}^-(\varepsilon) = \underline{T}^+(\varepsilon)^\dagger \quad (31)$$

at real energies ε .

By using equations (16) and (23), we get the density of states (DOS) of the perturbed system with respect to the reference system,

$$n(\varepsilon) = n_0(\varepsilon) - \frac{1}{\pi} \text{Im Tr} \left[\underline{G}_0^+(\varepsilon) \underline{T}^+(\varepsilon) \underline{G}_0^+(\varepsilon) \right]. \quad (32)$$

The second term on the right-hand side can be reformulated as follows:

$$\begin{aligned} \text{Tr} \left[\underline{G}_0^+(\varepsilon) \underline{T}^+(\varepsilon) \underline{G}_0^+(\varepsilon) \right] &= \text{Tr} \left[\underline{G}_0^+(\varepsilon)^2 \underline{T}^+(\varepsilon) \right] = -\text{Tr} \left[\frac{d\underline{G}_0^+(\varepsilon)}{d\varepsilon} \underline{T}^+(\varepsilon) \right] \\ &= -\text{Tr} \left[\underline{T}^+(\varepsilon)^{-1} \frac{d\underline{T}^+(\varepsilon)}{d\varepsilon} \right] = -\text{Tr} \frac{d \ln(\underline{T}^+(\varepsilon))}{d\varepsilon} \end{aligned}$$

leading to the Lloyd-formula, which gives the integrated DOS of the perturbed system,

$$N(\varepsilon) := \int_{-\infty}^{\varepsilon} n(\varepsilon') d\varepsilon' = N_0(\varepsilon) \pm \frac{1}{\pi} \text{Im Tr} \ln \underline{T}^\pm(\varepsilon). \quad (33)$$

3 On-site perturbations

Case of a single on-site impurity: $\underline{\Delta H}_i = \{\Delta H_i \delta_{in} \delta_{im}\}$,

$$\begin{aligned} \underline{T} &= \underline{\Delta H}_i + \underline{\Delta H}_i \underline{G}_0 \underline{\Delta H}_i + \dots \\ &= \left\{ \left[\Delta H_i + \Delta H_i \underline{G}_0^{ii} \Delta H_i + \dots \right] \delta_{in} \delta_{im} \right\} = \{t_i \delta_{in} \delta_{im}\}, \end{aligned} \quad (34)$$

with the single-site t -matrix

$$t_i = \Delta H_i + \Delta H_i \underline{G}_0^{ii} t_i = (I - \Delta H_i \underline{G}_0^{ii})^{-1} \Delta H_i. \quad (35)$$

Now let $\underline{\Delta H}$ be a sum of such on-site perturbations,

$$\underline{\Delta H} = \sum_i \underline{\Delta H}_i.$$

Then the T -matrix is given by

$$\begin{aligned}\underline{T} &= \left(\sum_i \Delta \underline{H}_i \right) + \left(\sum_i \Delta \underline{H}_i \right) \underline{G}_0 \left(\sum_i \Delta \underline{H}_i \right) + \dots \\ &= \sum_i \Delta \underline{H}_i + \sum_{i,j} \Delta \underline{H}_i \underline{G}_0 \Delta \underline{H}_j + \sum_{i,j,k} \Delta \underline{H}_i \underline{G}_0 \Delta \underline{H}_j \underline{G}_0 \Delta \underline{H}_k + \dots\end{aligned}\quad (36)$$

or written out in site-indices,

$$\begin{aligned}\underline{T}^{nm} &= \Delta \underline{H}_n \delta_{nm} + \Delta \underline{H}_n \underline{G}_0^{nm} \Delta \underline{H}_m + \sum_k \Delta \underline{H}_n \underline{G}_0^{nk} \Delta \underline{H}_k \underline{G}_0^{km} \Delta \underline{H}_m + \dots \\ &= \Delta \underline{H}_n \delta_{nm} + \sum_k \Delta \underline{H}_n \underline{G}_0^{nk} \underline{T}^{km}.\end{aligned}\quad (37)$$

The T -matrix can be rearranged as follows:

$$\underline{T} = \sum_i \underline{Q}_i \quad (38)$$

where

$$\underline{Q}_i := \Delta \underline{H}_i + \sum_j \Delta \underline{H}_i \underline{G}_0 \Delta \underline{H}_j + \sum_{j,k} \Delta \underline{H}_i \underline{G}_0 \Delta \underline{H}_j \underline{G}_0 \Delta \underline{H}_k + \dots \quad (39)$$

$$= \Delta \underline{H}_i + \Delta \underline{H}_i \underline{G}_0 \sum_j \underline{Q}_j \quad (40)$$

$$= \Delta \underline{H}_i + \Delta \underline{H}_i \underline{G}_0 \underline{Q}_i + \Delta \underline{H}_i \underline{G}_0 \sum_{j(\neq i)} \underline{Q}_j \quad (41)$$

↓

$$\left(\underline{I} - \Delta \underline{H}_i \underline{G}_0 \right) \underline{Q}_i = \Delta \underline{H}_i + \Delta \underline{H}_i \underline{G}_0 \sum_{j(\neq i)} \underline{Q}_j$$

↓

$$\underline{Q}_i = \underline{t}_i + \underline{t}_i \underline{G}_0 \sum_{j(\neq i)} \underline{Q}_j, \quad (42)$$

where \underline{t}_i is related to the single-site t -matrices introduced above,

$$\underline{t}_i = \left(\underline{I} - \Delta \underline{H}_i \underline{G}_0 \right)^{-1} \Delta \underline{H}_i = \{t_i \delta_{in} \delta_{jn}\}.$$

Solving equation (42) iteratively,

$$\begin{aligned}
\underline{\underline{Q}}_i^{(0)} &:= \underline{\underline{t}}_i & (43) \\
\underline{\underline{Q}}_i^{(1)} &= \underline{\underline{t}}_i + \sum_{j(\neq i)} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j \\
\underline{\underline{Q}}_i^{(2)} &= \underline{\underline{t}}_i + \sum_{j(\neq i)} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j + \sum_{\substack{j(\neq i) \\ k(\neq j)}} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j \underline{\underline{G}}_0 \underline{\underline{t}}_k \\
&\vdots \\
&\Downarrow \\
\underline{\underline{Q}}_i &= \underline{\underline{t}}_i + \sum_{j(\neq i)} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j + \sum_{\substack{j(\neq i) \\ k(\neq j)}} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j \underline{\underline{G}}_0 \underline{\underline{t}}_k + \sum_{\substack{j(\neq i) \\ k(\neq j) \\ l(\neq k)}} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j \underline{\underline{G}}_0 \underline{\underline{t}}_k \underline{\underline{G}}_0 \underline{\underline{t}}_l + \dots & (44)
\end{aligned}$$

Using equation (39), we arrive at the multiple-scattering expansion of the T -matrix,

$$\underline{\underline{T}} = \sum_i \underline{\underline{t}}_i + \sum_{i \neq j} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j + \sum_{i \neq j \neq k} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j \underline{\underline{G}}_0 \underline{\underline{t}}_k + \sum_{i \neq j \neq k \neq l} \underline{\underline{t}}_i \underline{\underline{G}}_0 \underline{\underline{t}}_j \underline{\underline{G}}_0 \underline{\underline{t}}_k \underline{\underline{G}}_0 \underline{\underline{t}}_l + \dots$$

Since for all $\underline{\underline{t}}_i = \{t_i \delta_{in} \delta_{im}\}$, the above equation can be rewritten in site-indices as

$$\underline{\underline{T}}^{nm} = \underline{\underline{t}}_n \delta_{nm} + (1 - \delta_{nm}) \underline{\underline{t}}_n \underline{\underline{G}}_0^{nm} \underline{\underline{t}}_m + \sum_{\substack{k \\ (k \neq n) \\ (k \neq m)}} \underline{\underline{t}}_n \underline{\underline{G}}_0^{nk} \underline{\underline{t}}_k \underline{\underline{G}}_0^{km} \underline{\underline{t}}_m + \dots \quad (45)$$

$$= \underline{\underline{t}}_n \delta_{nm} + \sum_k \underline{\underline{t}}_n \underline{\underline{G}}_0^{nk} (1 - \delta_{nk}) \underline{\underline{T}}^{km}. \quad (46)$$

Collecting all the single-site t -matrices into a site-diagonal matrix,

$$\underline{\underline{t}} = \{\underline{\underline{t}}_n \delta_{nm}\} = \begin{pmatrix} \underline{\underline{t}}_1 & 0 & 0 & \dots \\ 0 & \underline{\underline{t}}_2 & 0 & \dots \\ 0 & 0 & \underline{\underline{t}}_3 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (47)$$

and defining the site-off-diagonal part of the reference system's resolvent matrix,

$$\widehat{\underline{\underline{G}}}_0 := \{\underline{\underline{G}}_0^{nk} (1 - \delta_{nk})\} = \begin{pmatrix} 0 & \underline{\underline{G}}_0^{12} & \underline{\underline{G}}_0^{13} & \dots \\ \underline{\underline{G}}_0^{21} & 0 & \underline{\underline{G}}_0^{23} & \dots \\ \underline{\underline{G}}_0^{31} & \underline{\underline{G}}_0^{32} & 0 & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (48)$$

the T -matrix can be expressed as

$$\underline{\underline{T}} = \underline{\underline{t}} + \underline{\underline{t}} \widehat{\underline{\underline{G}}}_0 \underline{\underline{t}} + \underline{\underline{t}} \widehat{\underline{\underline{G}}}_0 \underline{\underline{t}} \widehat{\underline{\underline{G}}}_0 \underline{\underline{t}} \dots \quad (49)$$

or

$$\underline{\underline{T}} = \underline{\underline{t}} + \underline{\underline{t}} \widehat{\underline{\underline{G}}}_0 \underline{\underline{T}}, \quad (50)$$

that can be solved explicitly,

$$\underline{T} = \left[\underline{t}^{-1} - \widehat{\underline{G}}_0 \right]^{-1}. \quad (51)$$

For a periodic lattice with one atom per unit cell, $\underline{t}_i = \underline{t}_0$ ($\forall i$), the T -matrix can be evaluated via lattice Fourier transformation:

$$\underline{T}^{nm}(z) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k e^{i\vec{k}(\vec{R}_m - \vec{R}_n)} \underline{T}(z, \vec{k}), \quad (52)$$

where

$$\underline{T}(z, \vec{k}) = \left[\underline{t}_0(z)^{-1} - \underline{G}_0(z, \vec{k}) \right]^{-1}, \quad (53)$$

with

$$\underline{G}_0(z, \vec{k}) = \left(z\underline{I} - \underline{H}_0(\vec{k}) \right)^{-1}, \quad (54)$$

and

$$\underline{H}_0(\vec{k}) = \underline{\varepsilon}^0 + \underline{\gamma}(\vec{k}). \quad (55)$$

Here $\underline{\varepsilon}^0$ is the on-site energy matrix of the reference system and $\underline{\gamma}(\vec{k})$ is the lattice Fourier transform of the hopping integrals,

$$\underline{\gamma}(\vec{k}) = \sum_{\vec{R}_n \neq 0} e^{i\vec{k}\vec{R}_n} \underline{\gamma}(\vec{R}_n). \quad (56)$$

The resolvent matrix of the perturbed system can then be calculated by using Eq. (23). Equivalently, $\underline{G}^{mm}(z)$ can be evaluated as

$$\underline{G}^{mm}(z) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k e^{i\vec{k}(\vec{R}_m - \vec{R}_n)} \underline{G}(z, \vec{k}), \quad (57)$$

where

$$\underline{G}(z, \vec{k}) = \left(z\underline{I} - \underline{H}(\vec{k}) \right)^{-1} \quad (58)$$

and

$$\underline{H}(\vec{k}) = \underline{\varepsilon} + \underline{\gamma}(\vec{k}), \quad (59)$$

with $\underline{\varepsilon}$ being the on-site energy matrix of the perturbed system.

4 Chemically disordered systems

4.1 Binary alloys

Let's consider now a two-component (binary) random alloy, described by the random site-diagonal Hamiltonian,

$$\underline{H}_i(\xi_i) = \xi_i \underline{H}_i^A + (1 - \xi_i) \underline{H}_i^B, \quad (60)$$

where ξ_i are independent random variables with Bernoulli distribution:

$$\xi_i = \begin{cases} 1 & \text{with probability } \mathcal{P}_i(1) := c_i \\ 0 & \text{with probability } \mathcal{P}_i(0) = 1 - c_i \end{cases}, \quad (61)$$

and the two chemical components are labelled by A and B . By definition the expected values are

$$\mathbb{E} [\xi_i] \equiv \langle \xi_i \rangle = c_i, \quad (62)$$

thus the expected value of \underline{H}_i is

$$\langle \underline{H}_i \rangle = \langle \xi_i \rangle \underline{H}_i^A + \langle 1 - \xi_i \rangle \underline{H}_i^B = c_i \underline{H}_i^A + (1 - c_i) \underline{H}_i^B. \quad (63)$$

Independence means that the joint probability mass function of $\{\xi\}$ decomposes into the product of the individual probability mass functions:

$$\mathcal{P}(\{\xi\}) = \prod_{i=1}^N \mathcal{P}_i(\xi_i). \quad (64)$$

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

$$\sum_{\{\xi\}} \mathcal{P}(\{\xi\}) = \prod_i \left(\sum_{\xi_i=0}^1 \mathcal{P}_i(\xi_i) \right) = 1. \quad (65)$$

The configurational average of some physical quantity is then defined as

$$\langle F(\{\xi\}) \rangle := \sum_{\{\xi\}} \mathcal{P}(\{\xi\}) F(\{\xi\}) = \sum_{\xi_1} \dots \sum_{\xi_N} \mathcal{P}_1(\xi_1) \dots \mathcal{P}_N(\xi_N) F(\xi_1, \dots, \xi_N). \quad (66)$$

Since $\underline{G} = \underline{G}(\{\xi_1, \xi_2, \dots, \xi_N\}) \equiv \underline{G}(\{\xi\})$, the mean of a physical quantity A is

$$\langle A \rangle = \left\langle -\frac{1}{\pi} \text{Im} \int f(\varepsilon) \text{Tr} [\underline{A} \underline{G}(\{\xi\})] d\varepsilon \right\rangle \quad (67)$$

$$= -\frac{1}{\pi} \text{Im} \int f(\varepsilon) \text{Tr} [\underline{A} \langle \underline{G} \rangle] d\varepsilon \quad (68)$$

(where we suppressed the dependence of \underline{G} on the energy ε).

4.2 The Coherent Potential Approximation

Let us define an effective Hamiltonian \underline{H}_c (often noted as $\underline{\Sigma}_c$, the self-energy),

$$\underline{H}_c^{ij} = \underline{H}_{c,i} \delta_{ij} + \underline{\gamma}^{ij}, \quad (69)$$

such that

$$\langle \underline{G}(z) \rangle =: \underline{G}_c(z) = \left(z - \underline{H}_c \right)^{-1}. \quad (70)$$

called as the coherent potential approximation (CPA). Note that eqn. (70) can only be satisfied if $\underline{H}_c = \underline{H}_c(z)$ is a function of the energy, but it is (by definition) configuration-independent.

Choosing \underline{H}_c to be the Hamiltonian of the reference system,

$$\Delta \underline{H} = \{ \Delta \underline{H}_i \delta_{in} \delta_{im} \} = \{ (\underline{H}_i - \underline{H}_{c,i}) \delta_{in} \delta_{im} \}, \quad (71)$$

the \underline{T} matrix is defined as

$$\underline{T} = \underline{t} + \underline{t} \underline{\hat{G}} \underline{t} + \underline{t} \underline{\hat{G}} \underline{t} \underline{\hat{G}} \underline{t} + \dots \quad (72)$$

with

$$\underline{t} = \{\underline{t}_i \delta_{in} \delta_{im}\} \quad (73)$$

and

$$\underline{t}_i = \Delta \underline{H}_i + \Delta \underline{H}_i \underline{G}_c^{ii} \underline{t}_i = (\Delta \underline{H}_i^{-1} - \underline{G}_c^{ii})^{-1} . \quad (74)$$

Since, by definition, $\underline{G}_c = (z - \underline{H}_c)^{-1}$ is independent of the chemical configurations, the CPA condition (70) can be reformulated as

$$\langle \underline{G} \rangle = \underline{G}_c = \underline{G}_c + \underline{G}_c \langle \underline{T} \rangle \underline{G}_c \quad (75)$$

↓

$$\langle \underline{T} \rangle = 0 \quad (76)$$

↓

$$\langle \underline{t} \rangle + \langle \underline{t} \widehat{\underline{G}} \underline{t} \rangle + \langle \underline{t} \widehat{\underline{G}} \underline{t} \widehat{\underline{G}} \underline{t} \rangle + \dots = 0 , \quad (77)$$

or written out with respect to site indices,

$$\langle \underline{t}_n \rangle \delta_{nm} + \langle \underline{t}_n \underline{G}_c^{mm} \underline{t}_m \rangle (1 - \delta_{nm}) + \sum_{k(\neq n, m)} \langle \underline{t}_n \underline{G}_c^{nk} \underline{t}_k \underline{G}_c^{km} \underline{t}_m \rangle + \sum_{\substack{k(\neq n) \\ l(\neq k, m)}} \langle \underline{t}_n \underline{G}_c^{nk} \underline{t}_k \underline{G}_c^{kl} \underline{t}_l \underline{G}_c^{lm} \underline{t}_m \rangle + \dots = 0 . \quad (78)$$

Solving the above equation is quite cumbersome, therefore, the *single-site CPA (ss-CPA) condition* is introduced as follows,

$$\langle \underline{t}_n \rangle = 0 \quad (\forall n) . \quad (79)$$

The ss-CPA condition implies:

$$\langle \underline{t}_n \underline{G}_c^{mm} \underline{t}_m \rangle_{n \neq m} = \langle \underline{t}_n \rangle \underline{G}_c^{mm} \langle \underline{t}_m \rangle = 0 , \quad (80)$$

$$\sum_{k(\neq n, m)} \langle \underline{t}_n \underline{G}_c^{nk} \underline{t}_k \underline{G}_c^{km} \underline{t}_m \rangle = \sum_{k(\neq n, m)} \langle \underline{t}_n \underline{G}_c^{nk} \rangle \langle \underline{t}_k \rangle \underline{G}_c^{km} \langle \underline{t}_m \rangle = 0 . \quad (81)$$

thus, the condition set by eq. (78) is satisfied up to third order in \underline{t}_n ! In the sum contributing to eq. (78) in fourth order of the single-site t -matrices ,

$$\sum_{\substack{k(\neq n) \\ l(\neq k, m)}} \langle \underline{t}_n \underline{G}_c^{nk} \underline{t}_k \underline{G}_c^{kl} \underline{t}_l \underline{G}_c^{lm} \underline{t}_m \rangle$$

only those terms do not vanish by virtue of eq. (79), where each site index occurs at least twice, since averages like $\langle \dots \underline{t}_n \dots \underline{t}_n \dots \rangle$ do not vanish by (79). These terms are called *backscattering terms*. We can then state that the ss-CPA condition (79) implies the CPA condition (78) if *all the backscattering terms are disregarded*. Let's define this type of average as the *ss-CPA average*. Then we can write,

$$\langle \underline{t}_n \rangle = 0 \implies \langle \underline{T}^{nm} \rangle^{\text{ss-CPA}} = 0 \iff \langle \underline{G}^{nm} \rangle^{\text{ss-CPA}} = \underline{G}_c^{nm} . \quad (82)$$

4.2.1 Solving the ss-CPA condition

The ss-CPA can be solved iteratively. To initialize the iteration the average of the on-site energy matrices (termed as the virtual crystal approximaton, VCA) can be used,

$$\underline{\varepsilon}_c^{(0)} = c\underline{\varepsilon}_A + (1 - c)\underline{\varepsilon}_B. \quad (83)$$

1) Suppose that after the k^{th} step of the iteration the coherent-potential on-site energy matrix is $\underline{\varepsilon}_c^{(k)}$. As discussed before for periodic systems, the site-diagonal block of the CPA resolvent matrix can be evaluated as

$$\underline{G}_c^{ii(k)}(z) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k \underline{G}_c^{(k)}(z, \vec{k}), \quad (84)$$

where

$$\underline{G}_c^{(k)}(z, \vec{k}) = \left(z\underline{I} - \underline{\varepsilon}_c^{(k)} - \underline{\gamma}(\vec{k}) \right)^{-1}. \quad (85)$$

Note that $\underline{G}_c^{ii(k)}(z)$ is independent on the lattice sites, thus we denote it by $\underline{G}_c^{00(k)}(z)$.

2) The single-site CPA t -matrices for the two components are given by,

$$\underline{t}_\alpha^{(k)} = \left(\underline{I} - \Delta \underline{H}_\alpha^{(k)} \underline{G}_c^{00(k)} \right)^{-1} \Delta \underline{H}_\alpha^{(k)} \quad (\alpha = A, B) \quad (86)$$

with

$$\Delta \underline{H}_\alpha^{(k)} = \underline{\varepsilon}_\alpha - \underline{\varepsilon}_c^{(k)}. \quad (87)$$

3) According to eq. (79) we calculate

$$\underline{t}_c^{(k)} \equiv c\underline{t}_A^{(k)} + (1 - c)\underline{t}_B^{(k)}, \quad (88)$$

and check whether it is zero within a predefined accuracy. If not, we look for a next guess of the effective medium, $\underline{\varepsilon}_c^{(k+1)}$ and start again with step 1). A well-converging scheme to find $\underline{\varepsilon}_c^{(k+1)}$ is based on the notion that the new effective on-site energy matrix, $\underline{\varepsilon}_c^{(k+1)}$, provides the single-site t -matrix $\underline{t}_c^{(k)}$ with respect to $\underline{\varepsilon}_c^{(k)}$,

$$\underline{t}_c^{(k)} = \left(\underline{I} - (\underline{\varepsilon}_c^{(k+1)} - \underline{\varepsilon}_c^{(k)}) \underline{G}_c^{00(k)} \right)^{-1} (\underline{\varepsilon}_c^{(k+1)} - \underline{\varepsilon}_c^{(k)}) \quad (89)$$

↓

$$\underline{\varepsilon}_c^{(k+1)} = \underline{\varepsilon}_c^{(k)} + \left((\underline{t}_c^{(k)})^{-1} + \underline{G}_c^{(k)00} \right)^{-1} \quad (90)$$

$$= \underline{\varepsilon}_c^{(k)} + \left(\underline{I} + \underline{t}_c^{(k)} \underline{G}_c^{(k)00} \right)^{-1} \underline{t}_c^{(k)}. \quad (91)$$

Clearly, when the ss-CPA condition converges, $\underline{t}_c^{(k)} \rightarrow 0$, then $\underline{\varepsilon}_c^{(k)}$ also converges, $\underline{\varepsilon}_c^{(k+1)} - \underline{\varepsilon}_c^{(k)} \rightarrow 0$, and vica versa.

4.2.2 Restricted averages

Let us consider the average of the site-diagonal block of the resolvent matrix. Since any site is occupied by component A with probability c or component B with probability $1 - c$, this average can be written as

$$\langle \underline{G}^{mn} \rangle = c \langle \underline{G}^{mn} \rangle_{nA} + (1 - c) \langle \underline{G}^{mn} \rangle_{nB} , \quad (92)$$

where $\langle \underline{G}^{mn} \rangle_{n\alpha}$ denotes the so-called *restricted average*, when site n is occupied by component α , otherwise the random average over all the other sites is taken. In the relationship,

$$\langle \underline{G}^{mn} \rangle_{n\alpha} = \underline{G}_c^{mn} + \sum_{k,l} \underline{G}_c^{mk} \langle \underline{T}^{kl} \rangle_{n\alpha} \underline{G}_c^{ln} , \quad (93)$$

the restricted average of the T -matrix is evaluated as follows:

$$\langle \underline{T}^{kl} \rangle_{n\alpha} = \langle \underline{t}_k \rangle_{n\alpha} \delta_{kl} + \langle \underline{t}_k \underline{G}_c^{kl} \underline{t}_l \rangle_{n\alpha} (1 - \delta_{kl}) + \sum_{r(\neq k,l)} \langle \underline{t}_k \underline{G}_c^{kr} \underline{t}_r \underline{G}_c^{rl} \underline{t}_l \rangle_{n\alpha} + \sum_{\substack{r(\neq k) \\ s(\neq r,l)}} \langle \underline{t}_k \underline{G}_c^{kr} \underline{t}_r \underline{G}_c^{rs} \underline{t}_s \underline{G}_c^{sl} \underline{t}_l \rangle_{n\alpha} + \dots \quad (94)$$

$$\langle \underline{t}_k \rangle_{n\alpha} \delta_{kl} = \underline{t}_{n\alpha} \delta_{kn} \delta_{ln}$$

$$\begin{aligned} \langle \underline{t}_k \underline{G}_c^{kl} \underline{t}_l \rangle_{n\alpha} (1 - \delta_{kl}) &= \underline{t}_{n\alpha} \underline{G}_c^{ml} \langle \underline{t}_l \rangle_{n\alpha} \delta_{kn} (1 - \delta_{nl}) + \langle \underline{t}_k \rangle_{n\alpha} \underline{G}_c^{kl} \underline{t}_{n\alpha} \delta_{ln} (1 - \delta_{kn}) \\ &+ \langle \underline{t}_k \rangle_{n\alpha} \underline{G}_c^{kl} \langle \underline{t}_l \rangle_{n\alpha} (1 - \delta_{kl}) (1 - \delta_{nl}) (1 - \delta_{nk}) = 0 \end{aligned}$$

$$\begin{aligned} \sum_{r(\neq k,l)} \langle \underline{t}_k \underline{G}_c^{kr} \underline{t}_r \underline{G}_c^{rl} \underline{t}_l \rangle_{n\alpha} &= \delta_{nk} \delta_{nl} \sum_{r(\neq n)} \underline{t}_{n\alpha} \underline{G}_c^{mr} \langle \underline{t}_r \rangle_{n\alpha} \underline{G}_c^{rl} \underline{t}_{n\alpha} \\ &+ \delta_{nk} (1 - \delta_{nl}) \sum_{r(\neq n,l)} \underline{t}_{n\alpha} \underline{G}_c^{mr} \langle \underline{t}_r \rangle_{n\alpha} \underline{G}_c^{rl} \langle \underline{t}_l \rangle_{n\alpha} \\ &+ (1 - \delta_{nk}) \delta_{nl} \sum_{r(\neq k,n)} \langle \underline{t}_k \rangle_{n\alpha} \underline{G}_c^{kr} \langle \underline{t}_r \rangle_{n\alpha} \underline{G}_c^{rn} \underline{t}_{n\alpha} \\ &+ (1 - \delta_{nk}) (1 - \delta_{nl}) \sum_{r(\neq k,l)} \langle \underline{t}_k \underline{G}_c^{kr} \langle \underline{t}_r \rangle_{n\alpha} \underline{G}_c^{rl} \underline{t}_l \rangle_{n\alpha} \\ &= (1 - \delta_{nk}) (1 - \delta_{nl}) \langle \underline{t}_k \underline{G}_c^{kr} \underline{t}_{n\alpha} \underline{G}_c^{rl} \underline{t}_l \rangle_{n\alpha} , \end{aligned}$$

which is nonzero only for $k = l$. This is, however, a backscattering term which is neglected within the ss-CPA. Similarly, only the backscattering terms add contributions to the remaining sums in (94). Omitting these terms, we obtain

$$\langle \underline{T}^{kl} \rangle_{n\alpha}^{\text{ss-CPA}} = \underline{t}_{n\alpha} \delta_{kn} \delta_{ln} , \quad (95)$$

↓

$$\langle \underline{G}^{mn} \rangle_{n\alpha}^{\text{ss-CPA}} = \underline{G}_c^{mn} + \underline{G}_c^{mn} \underline{t}_{n\alpha} \underline{G}_c^{mn} = \underline{G}_c^{mn} \underline{D}_{n\alpha} = \tilde{\underline{D}}_{n\alpha} \underline{G}_c^{mn} \quad (96)$$

with the so-called *embedding matrices*

$$\underline{D}_{n\alpha} = \underline{I} + \underline{t}_{n\alpha} \underline{G}_c^{mn} \quad (97)$$

and

$$\tilde{\underline{D}}_{n\alpha} = \underline{I} + \underline{G}_c^{mn} \underline{t}_{n\alpha}. \quad (98)$$

The notation refers to the fact that $\underline{G}_c^{mn} \underline{D}_{n\alpha}$ or $\tilde{\underline{D}}_{n\alpha} \underline{G}_c^{mn}$ mean the site-diagonal block of the resolvent matrix for a system, when an atom α is embedded into the coherent medium at lattice site n . The ss-CPA condition can then be reformulated as

$$c \underline{D}_{nA} + (1 - c) \underline{D}_{nB} = c \tilde{\underline{D}}_{nA} + (1 - c) \tilde{\underline{D}}_{nB} = \underline{I}. \quad (99)$$

Later on we'll need the *two-site restricted average* of the site-off-diagonal blocks of the resolvent, $\langle \underline{G}^{nm} \rangle_{n\alpha, m\beta}$ for $n \neq m$. For this reason we need to calculate $\langle \underline{T}^{kl} \rangle_{n\alpha, m\beta}$. Similar considerations as in case of the one-site restricted average lead to the result,

$$\langle \underline{T}^{kl} \rangle_{n\alpha, m\beta}^{\text{ss-CPA}} = \underline{t}_{n\alpha} \delta_{kn} \delta_{ln} + \underline{t}_{m\beta} \delta_{km} \delta_{lm} + \underline{t}_{n\alpha} \underline{G}_c^{mm} \underline{t}_{m\beta} \delta_{kn} \delta_{lm} + \underline{t}_{m\beta} \underline{G}_c^{mn} \underline{t}_{n\alpha} \delta_{km} \delta_{ln}. \quad (100)$$

$\langle \underline{G}^{nm} \rangle_{n\alpha, m\beta}$ can then be evaluated as

$$\begin{aligned} \langle \underline{G}^{nm} \rangle_{n\alpha, m\beta} &= \underline{G}_c^{nm} + \sum_{k,l} \underline{G}_c^{mk} \langle \underline{T}^{kl} \rangle_{n\alpha, m\beta}^{\text{ss-CPA}} \underline{G}_c^{lm} \\ &= \underline{G}_c^{nm} + \underline{G}_c^{nn} \underline{t}_{n\alpha} \underline{G}_c^{nm} + \underline{G}_c^{mm} \underline{t}_{m\beta} \underline{G}_c^{nm} + \underline{G}_c^{nn} \underline{t}_{n\alpha} \underline{G}_c^{mm} \underline{t}_{m\beta} \underline{G}_c^{nm} + \underline{G}_c^{mm} \underline{t}_{m\beta} \underline{G}_c^{nn} \underline{t}_{n\alpha} \underline{G}_c^{nm}. \end{aligned} \quad (101)$$

According to the single-site CPA, we neglect the backscattering term $\underline{G}_c^{nm} \underline{t}_{m\beta} \underline{G}_c^{mm} \underline{t}_{n\alpha} \underline{G}_c^{nm}$ in the above formula and obtain the following compact result,

$$\langle \underline{G}^{nm} \rangle_{n\alpha, m\beta}^{\text{ss-CPA}} = (\underline{I} + \underline{G}_c^{nn} \underline{t}_{n\alpha}) \underline{G}_c^{nm} (\underline{I} + \underline{t}_{m\beta} \underline{G}_c^{mm}) = \tilde{\underline{D}}_{n\alpha} \underline{G}_c^{nm} \underline{D}_{m\beta}. \quad (102)$$

4.2.3 Bloch spectral functions for disordered alloys

In case of periodic solids the eigenstates of the Hamiltonian are Bloch functions characterized by \vec{k} vectors in the Brillouin zone and bands b ,

$$H(\vec{r}) \psi_b(\vec{k}, \vec{r}) = \varepsilon_b(\vec{k}) \psi_b(\vec{k}, \vec{r}) \quad (103)$$

where

$$\psi_b(\vec{k}, \vec{r} + \vec{R}_n) = e^{i\vec{k}\vec{R}_n} \psi_b(\vec{k}, \vec{r}). \quad (104)$$

Let us transform the Schrödinger equation (103) into the orthonormal tight-binding representation:

$$\sum_{m, \alpha'} \underbrace{\langle n, \alpha | H(\vec{r}) | m, \alpha' \rangle}_{H_{\alpha\alpha'}^{nm}} \underbrace{\langle m, \alpha' | \psi_b(\vec{k}, \vec{r}) \rangle}_{c_{b, \alpha'}^m(\vec{k})} = \varepsilon_b(\vec{k}) \underbrace{\langle n, \alpha | \psi_b(\vec{k}, \vec{r}) \rangle}_{c_{b, \alpha}^n(\vec{k})} \quad (105)$$

where n, m label sites, α, α' stand for orbitals, and the coefficients $c_{b, \alpha}^n(\vec{k})$ satisfy,

$$c_{b, \alpha}^n(\vec{k}) = e^{i\vec{k}\vec{R}_n} c_{b, \alpha}^0(\vec{k}). \quad (106)$$

Introducing the row-vector,

$$\mathbf{c}_b(\vec{k}) = \left\{ c_{b, \alpha}^0(\vec{k}) \right\}, \quad (107)$$

eq. (105) can be rewritten as

$$\sum_m \underline{H}^{nm} e^{i\vec{k}\vec{R}_m} \mathbf{c}_b(\vec{k}) = e^{i\vec{k}\vec{R}_n} \varepsilon_b(\vec{k}) \mathbf{c}_b(\vec{k}), \quad (108)$$

which can be reformulated in terms of the lattice Fourier transform of the Hamiltonian

$$\underline{H}(\vec{k}) = \sum_m e^{i\vec{k}(\vec{R}_m - \vec{R}_n)} \underline{H}^{nm} = \sum_n e^{i\vec{k}\vec{R}_n} \underline{H}^{0n} \quad (109)$$

↓

$$\underline{H}(\vec{k}) \mathbf{c}_b(\vec{k}) = \varepsilon_b(\vec{k}) \mathbf{c}_b(\vec{k}). \quad (110)$$

The resolvent in the \vec{k} -space can then be defined as,

$$\underline{G}(z, \vec{k}) = \sum_n e^{i\vec{k}\vec{R}_n} \underline{G}^{0n}(z) = \sum_b \frac{\mathbf{c}_b(\vec{k}) \mathbf{c}_b(\vec{k})^\dagger}{z - \varepsilon_b(\vec{k})}$$

which is related to the *Bloch spectral function (BSF)* by

$$\begin{aligned} A_B(\varepsilon, \vec{k}) &= \sum_b \delta(\varepsilon - \varepsilon_b(\vec{k})) = -\frac{1}{\pi} \text{Im Tr } \underline{G}^+(\varepsilon, \vec{k}) \\ &= -\frac{1}{\pi} \text{Im Tr } \sum_n e^{i\vec{k}\vec{R}_n} \underline{G}^{0n}(\varepsilon). \end{aligned} \quad (111)$$

The density of states of the system normalized to one atom can be expressed as

$$n(\varepsilon) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k \sum_b \delta(\varepsilon - \varepsilon_b(\vec{k})) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k A_B(\varepsilon, \vec{k}). \quad (112)$$

Calculating the BSF for a given energy ε with a small imaginary part δ , sharp peaks with a halfwidth of δ show up in the Brillouin zone at the eigenvalues of the Hamiltonian. This is the way to evaluate the energy dispersion of the Bloch electron (bandstructure) by using the resolvent (or Green's function).

In case of disordered alloys the BSF can at best be defined as an average of (111) in the configuration space,

$$A_B(\varepsilon, \vec{k}) = -\frac{1}{\pi} \text{Im Tr } \sum_{\vec{R}_n} e^{i\vec{k}\vec{R}_n} \langle \underline{G}^{0n}(\varepsilon) \rangle. \quad (113)$$

Next we decompose the BSF into two contributions,

$$A_B(\varepsilon, \vec{k}) = A_B^1(\varepsilon, \vec{k}) + A_B^2(\varepsilon, \vec{k}) \quad (114)$$

where

$$A_B^1(\varepsilon, \vec{k}) = -\frac{1}{\pi} \text{Im Tr } \langle \underline{G}^{00}(\varepsilon) \rangle \quad (115)$$

and

$$A_B^2(\varepsilon, \vec{k}) = -\frac{1}{\pi} \text{Im Tr } \sum_{\vec{R}_n(\neq 0)} e^{i\vec{k}\vec{R}_n} \langle \underline{G}^{0n}(\varepsilon) \rangle. \quad (116)$$

The first contribution can be evaluated by using the on-site restricted averages of the resolvent,

$$\langle \underline{G}^{00} \rangle = c \langle \underline{G}^{00} \rangle_{0A} + (1-c) \langle \underline{G}^{00} \rangle_{0B} = \underline{G}_c^{00}, \quad (117)$$

yielding

$$A_B^1(\varepsilon, \vec{k}) = -\frac{1}{\pi} \text{Im Tr } \underline{G}_c^{00}(\varepsilon). \quad (118)$$

For the second contribution we use the two-site restricted averages of the resolvent,

$$\begin{aligned} \langle \underline{G}^{0n} \rangle &= c^2 \langle \underline{G}^{0n} \rangle_{0A,nA} + c(1-c) \langle \underline{G}^{0n} \rangle_{0A,nB} + c(1-c) \langle \underline{G}^{0n} \rangle_{0B,nA} + (1-c)^2 \langle \underline{G}^{0n} \rangle_{0B,nB} \\ &= c^2 \underline{\tilde{D}}_A \underline{G}_c^{0n} \underline{D}_A + c(1-c) \underline{\tilde{D}}_A \underline{G}_c^{0n} \underline{D}_B + c(1-c) \underline{\tilde{D}}_B \underline{G}_c^{0n} \underline{D}_A + (1-c)^2 \underline{\tilde{D}}_B \underline{G}_c^{0n} \underline{D}_B \\ &= (c \underline{\tilde{D}}_A + (1-c) \underline{\tilde{D}}_B) \underline{G}_c^{0n} (c \underline{D}_A + (1-c) \underline{D}_B) = \underline{G}_c^{0n}, \end{aligned}$$

where we used the equality (99), resulting in

$$A_B^2(\varepsilon, \vec{k}) = -\frac{1}{\pi} \text{Im Tr } \sum_{\vec{R}_n(\neq 0)} e^{i\vec{k}\vec{R}_n} \underline{G}_c^{0n}(\varepsilon) = \frac{1}{\pi} \text{Im Tr } [\underline{G}_c^{00}(\varepsilon) - \underline{G}_c(\varepsilon, \vec{k})].$$

The Bloch spectral function of disordered alloys can thus be written within the ss-CPA in a similar way as for ordered systems, just by replacing $\underline{G}(\varepsilon, \vec{k})$ with $\underline{G}_c(\varepsilon, \vec{k})$,

$$A_B(\varepsilon, \vec{k}) = -\frac{1}{\pi} \text{Im Tr } \underline{G}_c(\varepsilon, \vec{k}). \quad (119)$$

We should emphasize again that this is the consequence of neglecting the backscattering terms in the restricted averages. Since

$$\underline{G}_c^{00}(\varepsilon) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k \underline{G}_c(\varepsilon, \vec{k}), \quad (120)$$

the average over the Brillouin zone of the BSF gives the averaged DOS per atom,

$$\frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k A_B(\varepsilon, \vec{k}) = -\frac{1}{\pi} \text{Im Tr } \underline{G}_c^{00}(\varepsilon) = \langle n(\varepsilon) \rangle. \quad (121)$$

The peaks of the BSF give a meaningful information on the bandstructure for disordered alloys as the positions of peaks $\varepsilon_b(\vec{k})$ can still be associated with the energies of the electrons. The peaks have, however, finite width even when approaching the imaginary part of the energy to zero. This refers to the fact that the Bloch states are not eigenstates of the system: the Bloch electrons are quasiparticles with finite lifetime being inversely proportional with the halfwidth of the peaks of the BSF. It is often useful to interpret the broadening of the peaks such that the bands of the pure ordered systems are mixed due to disorder. This mixing can be different in different parts of the Brillouin zone, thus the broadening of the peaks also varies in the BZ.

5 Description of the paramagnetic state - disordered local moments

Spin-polarized electrons are described within the tight-model by spin-dependent on-site energies,

$$\varepsilon_n = \varepsilon_n^{\text{nm}} + \underline{b}_n \vec{e}_n \cdot \vec{\sigma} \quad (122)$$

where now the single underline denotes matrices in orbital- and spin-space, i.e. a matrix of double size as before. In the above formula $\underline{\varepsilon}_n^{\text{nm}}$ and \underline{b}_n are matrices in orbital space related to the non-magnetic part of the Hamiltonian and the exchange splitting, respectively. The unit vector \vec{e}_n stands for the direction of the exchange field (within the local spin-density approximation of density functional theory it is identical with the direction of the magnetization) and $\vec{\sigma}$ denote the Pauli matrices. Note that spin-orbit coupling is not included in this description.

In the paramagnetic state the spin-orientations are distributed randomly over the unit sphere. We can choose these orientations as the independent continuous random variables with the distribution function,

$$\mathcal{P}(\{\vec{e}\}) = \prod_{n=1}^N \mathcal{P}(\vec{e}_n), \quad (123)$$

$$\mathcal{P}(\vec{e}_n) = \frac{1}{4\pi}, \quad \int d^2 e_n \mathcal{P}(\vec{e}_n) = 1, \quad (124)$$

where $\int d^2 e_n$ means integration on the surface of the unit sphere. The configurational averages can be calculated as

$$\langle F(\{\vec{e}\}) \rangle := \int d^2 e \mathcal{P}(\{\vec{e}\}) F(\{\vec{e}\}) = \int d^2 e_1 \dots \int d^2 e_N \mathcal{P}(\vec{e}_1) \dots \mathcal{P}(\vec{e}_N) F(\vec{e}_1, \dots, \vec{e}_N) \quad (125)$$

$$= \frac{1}{(4\pi)^N} \int d^2 e_1 \dots \int d^2 e_N F(\vec{e}_1, \dots, \vec{e}_N). \quad (126)$$

The Hamiltonian is then a function of the random variables,

$$\underline{H}(\{\vec{e}\}) = \left\{ \underline{\varepsilon}_n(\vec{e}_n) + \underline{\gamma}_{nm} \right\}, \quad (127)$$

where the hopping integrals are taken to be independent from the orientations of the local spin-variables. The mean of a physical quantity A can be calculated in terms of the resolvent,

$$\underline{G}(\{\vec{e}\}) = (z - \underline{H}(\{\vec{e}\}))^{-1},$$

as before,

$$\langle A \rangle = \left\langle -\frac{1}{\pi} \text{Im} \int f(\varepsilon) \text{Tr} [\underline{A} \underline{G}(\{\vec{e}\})] d\varepsilon \right\rangle \quad (128)$$

$$= -\frac{1}{\pi} \text{Im} \int f(\varepsilon) \text{Tr} [\underline{A} \langle \underline{G}(\{\vec{e}\}) \rangle] d\varepsilon, \quad (129)$$

thus, it is tempting to use the coherent-potential approximation to evaluate such averages,

$$\langle \underline{G}(\{\vec{e}\}) \rangle = \underline{G}_c. \quad (130)$$

Since \underline{G}_c describes a system with zero net magnetization, the effective on-site energy matrix $\underline{\varepsilon}_{c,n}$ should be unit matrix in spin space. The single-site t -matrices with respect to the effective medium are defined as

$$t_n = \Delta \underline{H}_n + \Delta \underline{H}_n \underline{G}_c^{nn} t_n = (\underline{I} - \Delta \underline{H}_n \underline{G}_c^{nn})^{-1} \Delta \underline{H}_n. \quad (131)$$

with

$$\Delta \underline{H}_n = \underline{\varepsilon}_n(\vec{e}_n) - \underline{\varepsilon}_{c,n}. \quad (132)$$

The single-site CPA condition then reads

$$\langle \underline{t}_n \rangle = \int d^2 e_n \underline{t}_n(\vec{e}_n) = 0. \quad (133)$$

It is straightforward to prove that $\underline{t}_n(\vec{e}_n)$ also takes the form of (122),

$$\underline{t}_n(\vec{e}_n) = \underline{t}_n^{\text{nm}} + \Delta \underline{t}_n \vec{e}_n \cdot \vec{\sigma}, \quad (134)$$

where the matrices $\underline{t}_n^{\text{nm}}$ and $\Delta \underline{t}_n$ are unit matrices in spin space. therefore, the condition (133) can be simplified to

$$\int d^2 e_n (\underline{t}_n^{\text{nm}} + \Delta \underline{t}_n \vec{e}_n \cdot \vec{\sigma}) = \underline{t}_n^{\text{nm}} + \Delta \underline{t}_n \underbrace{\int d^2 e_n \vec{e}_n \cdot \vec{\sigma}}_{=0} = \underline{t}_n^{\text{nm}} = 0. \quad (135)$$

Luckily, when solving the ss-CPA condition we got rid of the integration over continuous spin directions. We can calculate $\underline{t}_n^{\text{nm}}$ by using eq. (131) if we fix \vec{e}_n to \vec{e}_z and $-\vec{e}_z$,

$$\underline{t}_n(\pm \vec{e}_z) = \underline{t}_n^{\text{nm}} \pm \Delta \underline{t}_n \sigma_z \rightarrow \underline{t}_n^{\text{nm}} = \frac{1}{2} (\underline{t}_n(\vec{e}_z) + \underline{t}_n(-\vec{e}_z)), \quad (136)$$

where $\underline{t}_n(\pm \vec{e}_z)$ corresponds to impurities embedded into the effective medium with on-site energies,

$$\underline{\varepsilon}_n^\pm = \underline{\varepsilon}_n^{\text{nm}} \pm \underline{b}_n. \quad (137)$$

Thus the ss-CPA condition (135) can be reformulated in analogy of a binary alloy with $c = 0.5$, where the two components refer to the same magnetic atom with opposite (up and down) spin orientations,

$$\frac{1}{2} (\underline{t}_n^+ + \underline{t}_n^-) = 0. \quad (138)$$

This is the mean-field theory to calculate the electronic structure in the paramagnetic state called the picture of Disordered Local Moments (DLM).