

# 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

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

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

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  $\varepsilon_i$  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 static 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). Supposing that the solutions of the eigenvalue equation,

$$\underline{\underline{H}}|i\rangle = \varepsilon_i |i\rangle, \quad (4)$$

are known, then the Hamiltonian matrix can be written as

$$\underline{\underline{H}} = \sum_i \varepsilon_i |i\rangle \langle i|, \quad (5)$$

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

$$\underline{\underline{G}}(z) = \sum_i \frac{1}{z - \varepsilon_i} |i\rangle \langle i|. \quad (6)$$

The fundamental analytic property of the resolvent,

$$\boxed{\underline{\underline{G}}(z^*) = \underline{\underline{G}}(z)^\dagger} \quad (7)$$

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

$$\boxed{\frac{d\underline{\underline{G}}(z)}{dz} = -\underline{\underline{G}}(z)^2}. \quad (8)$$

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

$$\boxed{\underline{\underline{G}}^\pm(\varepsilon) := \lim_{\delta \rightarrow 0} \underline{\underline{G}}(\varepsilon \pm i\delta)} \quad (9)$$

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

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

$$[\underline{\underline{G}}^+(\varepsilon)]^\dagger = \underline{\underline{G}}^-(\varepsilon). \quad (11)$$

The well-known identity of generalized functions,

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

leads to the relationship,

$$\begin{aligned} \sum_i \delta(\varepsilon - \varepsilon_i) |i\rangle \langle i| &= -\frac{1}{2\pi i} [\underline{\underline{G}}^+(\varepsilon) - \underline{\underline{G}}^-(\varepsilon)] \\ &= -\frac{1}{2\pi i} [\underline{\underline{G}}^+(\varepsilon) - (\underline{\underline{G}}^+(\varepsilon))^\dagger]. \end{aligned} \quad (13)$$

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

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

$$\boxed{n(\varepsilon) = -\frac{1}{\pi} \text{Im} \text{Tr} \underline{\underline{G}}^+(\varepsilon) = \frac{1}{\pi} \text{Im} \text{Tr} \underline{\underline{G}}^-(\varepsilon)}. \quad (14)$$

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

$$\langle A \rangle = \int_{\varepsilon_b}^{\varepsilon_F} \sum_i \delta(\varepsilon - \varepsilon_i) \langle i| A |i\rangle d\varepsilon \quad (15)$$

$$= \int_{\varepsilon_b}^{\varepsilon_F} \text{Tr} \left( \sum_i \delta(\varepsilon - \varepsilon_i) |i\rangle \langle i| \underline{\underline{A}} \right) d\varepsilon \quad (16)$$

$$\boxed{\langle A \rangle = -\frac{1}{\pi} \text{Im} \int_{\varepsilon_b}^{\varepsilon_F} \text{Tr} [\underline{\underline{A}} \underline{\underline{G}}^+(\varepsilon)] d\varepsilon}, \quad (17)$$

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

## 2 Perturbations with respect to a reference system

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

$$\underline{G}(z) = (z - \underline{H})^{-1} \quad (18)$$

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

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

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,

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

This can be rearranged to give

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

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

$$\underline{T}(z^*) = \underline{T}(z)^\dagger, \quad (26)$$

$$\frac{d\underline{T}(z)}{dz} = \underline{T}(z) \frac{d\underline{G}_0(z)}{dz} \underline{T}(z), \text{ and} \quad (27)$$

$$\underline{T}^\pm(\varepsilon) := \lim_{\delta \rightarrow 0} \underline{T}(\varepsilon \pm i\delta) \quad (28)$$

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,

$$n(\varepsilon) = n_0(\varepsilon) - \frac{1}{\pi} \text{ImTr} \left[ \underline{\underline{G}}_0^+(\varepsilon) \underline{\underline{T}}^+(\varepsilon) \underline{\underline{G}}_0^+(\varepsilon) \right]. \quad (29)$$

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,

$$N(\varepsilon) := \int_{-\infty}^{\varepsilon} n(\varepsilon') d\varepsilon' = N_0(\varepsilon) + \frac{1}{\pi} \text{ImTr} \ln \underline{\underline{T}}^+(\varepsilon). \quad (30)$$

### 3 On-site impurities

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

$$\begin{aligned} \underline{\underline{T}} &= \Delta \underline{\underline{H}}_i + \Delta \underline{\underline{H}}_i \underline{\underline{G}}_0 \Delta \underline{\underline{H}}_i + \dots \\ &= \left\{ [\Delta \underline{\underline{H}}_i + \Delta \underline{\underline{H}}_i \underline{\underline{G}}_0^{ii} \Delta \underline{\underline{H}}_i + \dots] \delta_{in} \delta_{im} \right\} \end{aligned} \quad (31)$$

$$\begin{aligned} &= \{t_i \delta_{in} \delta_{im}\}, \text{ thus} \\ t_i &= \Delta \underline{\underline{H}}_i + \Delta \underline{\underline{H}}_i \underline{\underline{G}}_0^{ii} t_i. \end{aligned} \quad (32)$$

Now let  $\Delta \underline{\underline{H}}$  be a sum of such on-site differences:  $\Delta \underline{\underline{H}} = \sum_i \Delta \underline{\underline{H}}_i$ . Then

$$\begin{aligned} \underline{\underline{T}} &= \left( \sum_i \Delta \underline{\underline{H}}_i \right) + \left( \sum_i \Delta \underline{\underline{H}}_i \right) \underline{\underline{G}}_0 \left( \sum_i \Delta \underline{\underline{H}}_i \right) + \dots \\ &= \sum_i \Delta \underline{\underline{H}}_i + \sum_{i,j} \Delta \underline{\underline{H}}_i \underline{\underline{G}}_0 \Delta \underline{\underline{H}}_j + \sum_{i,j,k} \Delta \underline{\underline{H}}_i \underline{\underline{G}}_0 \Delta \underline{\underline{H}}_j \underline{\underline{G}}_0 \Delta \underline{\underline{H}}_k + \dots \end{aligned} \quad (33)$$

$$\begin{aligned} \underline{\underline{T}}^{nm} &= \Delta \underline{\underline{H}}_n \delta_{nm} + \Delta \underline{\underline{H}}_n \underline{\underline{G}}_0^{mm} \Delta \underline{\underline{H}}_m + \sum_k \Delta \underline{\underline{H}}_n \underline{\underline{G}}_0^{mk} \Delta \underline{\underline{H}}_k \underline{\underline{G}}_0^{km} \Delta \underline{\underline{H}}_m + \dots \\ &= \Delta \underline{\underline{H}}_n \delta_{nm} + \sum_k \Delta \underline{\underline{H}}_n \underline{\underline{G}}_0^{mk} \underline{\underline{T}}^{km}. \end{aligned} \quad (34)$$

Both in operator and in matrix sense,

$$\underline{\underline{T}} = \sum_i \Delta \underline{\underline{H}}_i + \sum_{i,j} \Delta \underline{\underline{H}}_i \underline{\underline{G}}_0 \Delta \underline{\underline{H}}_j + \dots \quad (35)$$

$$\begin{aligned} &= \sum_i \left( \Delta \underline{\underline{H}}_i + \sum_j \Delta \underline{\underline{H}}_i \underline{\underline{G}}_0 \Delta \underline{\underline{H}}_j + \dots \right) \\ &= \sum_i \underline{\underline{Q}}_i, \text{ where} \end{aligned} \quad (36)$$

$$\underline{Q}_{\underline{n}} := \Delta \underline{H}_{\underline{n}} + \sum_m \Delta \underline{H}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \Delta \underline{H}_{\underline{m}} + \dots \quad (37)$$

$$\begin{aligned} &= \Delta \underline{H}_{\underline{n}} + \Delta \underline{H}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \sum_m \Delta \underline{Q}_{\underline{m}} \\ &= \Delta \underline{H}_{\underline{n}} + \Delta \underline{H}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{Q}_{\underline{n}} + \Delta \underline{H}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \sum_{m(\neq n)} \Delta \underline{Q}_{\underline{m}} \end{aligned}$$

↓

$$\begin{aligned} \left( \underline{I} - \Delta \underline{H}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \right) \underline{Q}_{\underline{n}} &= \Delta \underline{H}_{\underline{n}} + \Delta \underline{H}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \sum_{m(\neq n)} \Delta \underline{Q}_{\underline{m}} \\ \underline{Q}_{\underline{n}} &= \underline{t}_{\underline{n}} + \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \sum_{m(\neq n)} \underline{Q}_{\underline{m}}, \end{aligned} \quad (38)$$

where  $\underline{t}_{\underline{n}}$  is formally a single impurity  $T$ -matrix on the  $n$ -th site,

$$\underline{t}_{\underline{n}} = \{ \underline{t}_{\underline{n}} \delta_{in} \delta_{jn} \}. \quad (39)$$

Solving equation (38) iteratively,

$$\underline{Q}_{\underline{n}}^{(0)} := \underline{t}_{\underline{n}} \quad (40)$$

$$\underline{Q}_{\underline{n}}^{(1)} = \underline{t}_{\underline{n}} + \sum_{m(\neq n)} \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{t}_{\underline{m}}$$

$$\underline{Q}_{\underline{n}}^{(2)} = \underline{t}_{\underline{n}} + \sum_{m(\neq n)} \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{t}_{\underline{m}} + \sum_{\substack{m(\neq n) \\ k(\neq m)}} \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{t}_{\underline{m}} \underline{G}_{\underline{0}} \underline{t}_{\underline{k}}$$

⋮

↓

$$\underline{Q}_{\underline{n}} = \underline{t}_{\underline{n}} + \sum_{m(\neq n)} \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{t}_{\underline{m}} + \sum_{\substack{m(\neq n) \\ k(\neq m)}} \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{t}_{\underline{m}} \underline{G}_{\underline{0}} \underline{t}_{\underline{k}} + \dots \quad (41)$$

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

$$\underline{T} = \sum_n \underline{t}_{\underline{n}} + \sum_{n \neq m} \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{t}_{\underline{m}} + \sum_{n \neq m \neq k} \underline{t}_{\underline{n}\underline{0}} \underline{G}_{\underline{0}} \underline{t}_{\underline{m}} \underline{G}_{\underline{0}} \underline{t}_{\underline{k}} + \dots \quad (42)$$

Since all  $\underline{t}_{\underline{n}}$  have the structure of  $\Delta \underline{H}_{\underline{n}}$ ,

$$\underline{T}^{nm} = \underline{t}_{\underline{n}} \delta_{nm} + (1 - \delta_{nm}) \underline{t}_{\underline{n}} \underline{G}_{\underline{0}}^{nm} \underline{t}_{\underline{m}} + \sum_{\substack{k \\ (k \neq n) \\ (k \neq m)}} \underline{t}_{\underline{n}} \underline{G}_{\underline{0}}^{nk} \underline{t}_{\underline{k}} \underline{G}_{\underline{0}}^{km} \underline{t}_{\underline{m}} + \dots \quad (43)$$

$$= \underline{t}_{\underline{n}} \delta_{nm} + \sum_k \underline{t}_{\underline{n}} \underline{G}_{\underline{0}}^{nk} (1 - \delta_{nk}) \underline{T}^{km}. \quad (44)$$

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

$$\widehat{\underline{G}}_{\underline{0}} := \{ \underline{G}_{\underline{0}}^{nk} (1 - \delta_{nk}) \}, \quad (45)$$

$$\underline{T} = \underline{t}_{\underline{n}} + \underline{t}_{\underline{n}} \widehat{\underline{G}}_{\underline{0}} \underline{T}$$

↓

$$\underline{T} = \left[ \underline{t}_{\underline{n}}^{-1} + \widehat{\underline{G}}_{\underline{0}} \right]^{-1} \quad (46)$$

On the other hand,

$$\underline{T} = \underline{t} + \underline{t} \widehat{G}_0 \underline{t} + \underline{t} \widehat{G}_0 \underline{t} \widehat{G}_0 \underline{t} \dots, \text{ so} \quad (47)$$

$$\underline{G} = \underline{G}_0 + \underline{G}_0 \underline{T} \underline{G}_0 \quad (48)$$

is given in terms of  $\underline{G}_0$  and  $\underline{t}$ .

## 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:

$$\Delta H_i = \xi_i \Delta H_i^A + (1 - \xi_i) \Delta H_i^B, \quad (49)$$

where  $\xi_i$  are independent random variables with Bernoulli distribution:

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

By definition the expected values are

$$\mathbb{E} \xi_i \equiv \langle \xi_i \rangle = c_i, \quad (50)$$

thus the expected value of  $\Delta H_i$  is

$$\langle \Delta H_i \rangle = \langle \xi_i \rangle \Delta H_i^A + \langle 1 - \xi_i \rangle \Delta H_i^B = c_i \Delta H_i^A + (1 - c_i) \Delta H_i^B. \quad (51)$$

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

$$\mathcal{P}(\{\xi\}) = \prod_{i=1}^N \mathcal{P}_i(\xi_i). \quad (52)$$

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

$$\sum_{\{\xi\}} \mathcal{P}(\{\xi\}) = \prod_i \left( \sum_{\xi_i=0}^1 \mathcal{P}_i(\xi_i) \right) = 1. \quad (53)$$

The configurational average of some physical quantity is then defined as

$$\langle F(\{\xi\}) \rangle := \sum_{\{\xi\}} \mathcal{P}(\{\xi\}) F(\{\xi\}) = \sum_{\xi_1} \dots \sum_{\xi_N} \mathcal{P}_1(\xi_1) \dots \mathcal{P}_N(\xi_N) F(\xi_1, \dots, \xi_N). \quad (54)$$

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

$$\langle A \rangle = \left\langle -\frac{1}{\pi} \text{Im} \int f(\varepsilon) \text{Tr} [\underline{A} \underline{G}(\{\xi\})] d\varepsilon \right\rangle \quad (55)$$

$$= -\frac{1}{\pi} \text{Im} \int f(\varepsilon) \text{Tr} [\underline{A} \langle \underline{G} \rangle] d\varepsilon \quad (56)$$

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

## 4.2 Coherent Potential Approximation

$$\begin{aligned}\langle \underline{G} \rangle &= \underline{G}_0 + \underline{G}_0 \langle \underline{T} \rangle \underline{G}_0 \\ &=: \underline{G}_c = \left( z - \underline{H}_c \right)^{-1},\end{aligned}\quad (57)$$

where we defined the effective Hamiltonian  $\underline{H}_c$  often noted as  $\underline{\Sigma}_c$ , the self-energy. This assumption is the coherent potential approximation (CPA). The (57) CPA condition 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.

Let us now choose our reference system to be  $\underline{H}_c$ ,

$$\underline{T} = \underline{t} + \underline{t} \widehat{\underline{G}}_c \underline{t} + \underline{t} \widehat{\underline{G}}_c \underline{t} \widehat{\underline{G}}_c \underline{t} + \dots \quad (58)$$

$$\Delta \underline{H} = \underline{H} - \underline{H}_c = \left\{ (\underline{H}_i - \underline{H}_{c,i}) \delta_{in} \delta_{im} \right\}, \quad (59)$$

where  $\underline{H}_{c,i}$  are to be determined. A condition is given by

$$\langle \underline{G} \rangle = \underline{G}_c = \underline{G}_c + \underline{G}_c \langle \underline{T} \rangle \underline{G}_c \quad (60)$$

↓

$$\boxed{\langle \underline{T} \rangle = 0} \quad (61)$$

$$\langle \underline{t} \rangle + \langle \underline{t} \widehat{\underline{G}}_c \underline{t} \rangle + \dots = 0. \quad (62)$$

Single-site CPA:

$$\boxed{\langle \underline{t} \rangle := 0}. \quad (63)$$

Considering this,

$$\langle \underline{t}_n \widehat{\underline{G}}_c^{nm} \underline{t}_m \rangle = \langle \underline{t}_n \rangle \widehat{\underline{G}}_c^{nm} \langle \underline{t}_m \rangle = 0 \quad (64)$$

$$\sum_{\substack{k \neq n \\ k \neq m}} \langle \underline{t}_n \widehat{\underline{G}}_c^{nk} \underline{t}_k \widehat{\underline{G}}_c^{km} \underline{t}_m \rangle = \sum_{\substack{k \neq n \\ k \neq m}} \langle \underline{t}_n \widehat{\underline{G}}_c^{nk} \rangle \langle \underline{t}_k \rangle \widehat{\underline{G}}_c^{km} \langle \underline{t}_m \rangle = 0. \quad (65)$$

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

$$\underline{t}_i = \xi_i \underline{t}_i^A + (1 - \xi_i) \underline{t}_i^B, \quad (66)$$

eq. (63) reads as

$$\boxed{\langle \underline{t}_i \rangle = c_i \underline{t}_i^A + (1 - c_i) \underline{t}_i^B = 0}. \quad (67)$$

This is in fact a system of equations for  $\underline{H}_c$ , because

$$\underline{t}_i^\alpha = \left( \underline{I} - \Delta \underline{H}_i^\alpha \underline{G}_c^{ii} \right)^{-1} \Delta \underline{H}_i^\alpha, \quad \text{where} \quad (68)$$

$$\Delta \underline{H}_i^\alpha = \underline{H}_i^\alpha - \underline{H}_{c,i}, \quad (\alpha = A, B) \quad (69)$$

and  $\underline{G}_c^{ii}$  can be determined from equation (57).