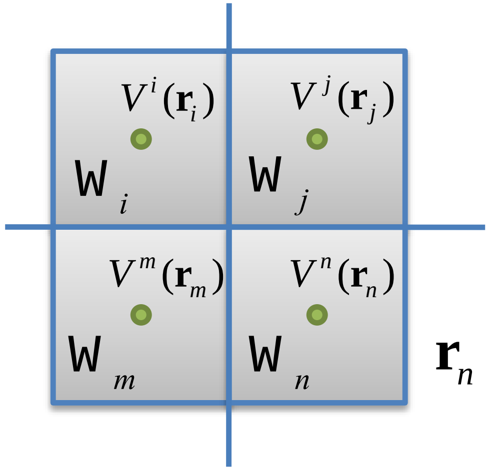
Solving Impurity Problems in the Framework of Multiple Scattering Theory

Multiple Scattering Theory (MST) Approach

- Also known as the KKR method, or Green function method
- The space is divided into non-overlapping domains, or atomic cells, each of which contains an atom
- The LDA/GGA potential is a collection of non-overlapping electronic scattering potentials centered at each atom
- Each atomic cell is considered as an electron scattering center
- The crystal wavefunction, or Bloch wave, is a standing wave solution of the multiple scattering problem
- Allows convenient calculation of the Green function of the Kohn-Sham equation

$$V^n(\mathbf{r}_n) = V_{\text{eff}}(\mathbf{r}), \quad \text{for } \mathbf{r} \in \Omega_n$$



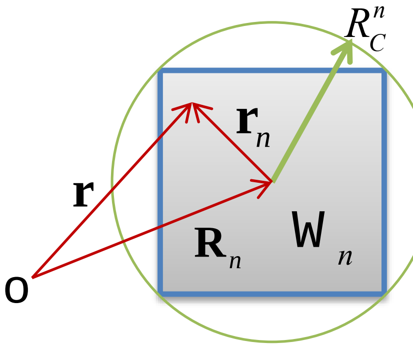
$$\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$$

$$V^n(\mathbf{r}_n) = 0, \quad \text{for } \mathbf{r} \notin \Omega_n$$

$$\rho(\mathbf{r}) = -\frac{2}{\pi} \operatorname{Im} \int_{-\infty}^{\varepsilon_F} G(\mathbf{r}_n, \mathbf{r}_n; \varepsilon) d\varepsilon.$$

$$G(\mathbf{r}_n, \mathbf{r}_n; \varepsilon) = \sum_{L,L'} Z_L^n(\mathbf{r}_n; \varepsilon) \tau_{LL'}^{nn}(\varepsilon) Z_{L'}^{n*}(\mathbf{r}_n; \varepsilon) - \sum_{L} Z_L^n(\mathbf{r}_n; \varepsilon) J_L^{n*}(\mathbf{r}_n; \varepsilon)$$

where $L = \{l, m\}$, $\mathbf{r}_n \in \Omega_n$. $Z_L^n(\mathbf{r}_n; \varepsilon)$ and $J_L^n(\mathbf{r}_n; \varepsilon)$ are the single site regular and irregular solutions, respectively, corresponding to $V^n(\mathbf{r}_n)$.



Single scattering is described by t-matrix, $\underline{t}_n$, which is determined by local potential $V^n(\mathbf{r}_n) \in \Omega_n$. If the potential spherical, $\underline{t}_n$ is given by the partial phase shifts δ_l.

Multiple scattering path matrix: $\underline{\tau}^{nm}$

Definition and iterative approach:

$$\underline{\tau}^{nm}(\varepsilon) = \underline{t}_n(\varepsilon)\delta_{nm} + \underline{t}_n(\varepsilon)\underline{g}^{nm}(\varepsilon)\underline{t}_m(\varepsilon) + \underline{t}_n(\varepsilon)\sum_{k=1}^{N}\underline{g}^{nk}(\varepsilon)\underline{t}_k(\varepsilon)\underline{g}^{km}(\varepsilon)\underline{t}_m(\varepsilon) + \dots$$

where $\underline{g}^{nm}(\varepsilon) = 0$ if $n = m$.

$$= \underline{t}_n(\varepsilon)\delta_{nm} + \underline{t}_n(\varepsilon)\sum_{k}\underline{g}^{nk}(\varepsilon)\underline{\tau}^{km}(\varepsilon)$$

$\underline{g}^{nm}(\varepsilon)$ is called real space structure constant matrix.

Matrix inverse approach:

$$\underline{\underline{M}}(\varepsilon) = \begin{bmatrix} \underline{t}_1^{-1}(\varepsilon) & -\underline{g}^{12}(\varepsilon) & \cdots & -\underline{g}^{1N}(\varepsilon) \\ -\underline{g}^{21}(\varepsilon) & \underline{t}_2^{-1}(\varepsilon) & \cdots & -\underline{g}^{2N}(\varepsilon) \\ \vdots & \vdots & \ddots & \vdots \\ -\underline{g}^{N1}(\varepsilon) & -\underline{g}^{N2}(\varepsilon) & \cdots & \underline{t}_N^{-1}(\varepsilon) \end{bmatrix}$$

$$\underline{\tau}^{nm}(\varepsilon) = \left[\underline{\underline{M}}(\varepsilon)\right]^{-1}_{nm}$$

A special case: periodic system

For periodic crystal, $\underline{t}_n(\varepsilon) = \underline{t}(\varepsilon)$, we take $\mathbf{k}$-space approach:

$$\underline{\tau}(\varepsilon;\mathbf{k}) = \left[\underline{t}^{-1}(\varepsilon) - \underline{g}(\mathbf{k};\varepsilon)\right]^{-1},$$

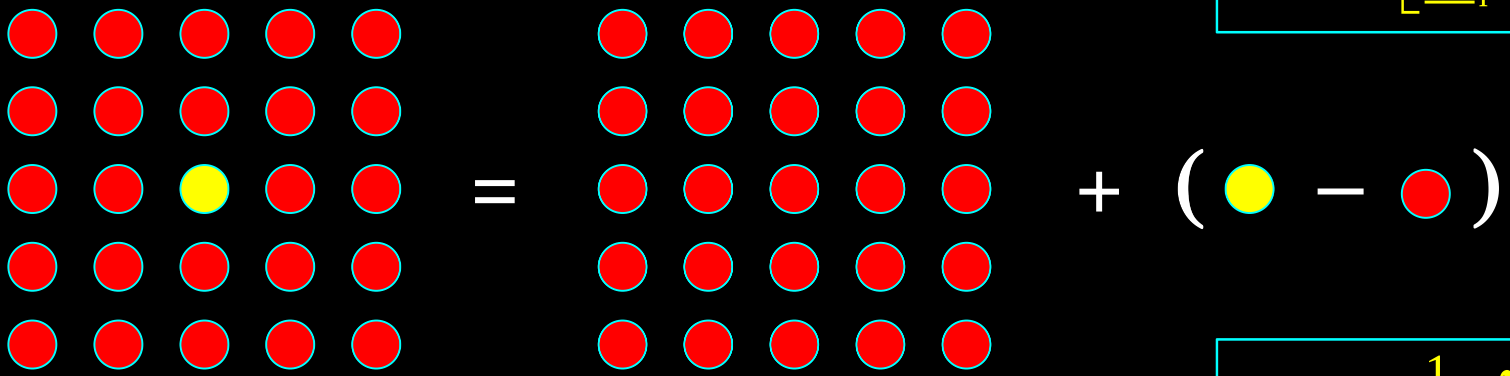
where $\underline{g}(\mathbf{k};\varepsilon)$ is a lattice Fourier transform of $\underline{g}^{nm}(\varepsilon)$.

The τ-matrix is given by: $\underline{\tau}^{nm}(\varepsilon) = \dfrac{1}{\Omega_{BZ}}\displaystyle\int_{BZ}\underline{\tau}(\varepsilon;\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m)}d^3\mathbf{k}.$

Our goal is to calculate $\underline{\tau}^{nn}(\varepsilon)$ so to calculate the Green function in Ω_n.

A Crystal With Single Impurity

$$\underline{\tau}_{\mathrm{I}}^{11}(\varepsilon)=\left[\underline{\underline{M}}_{\mathrm{I}}^{-1}(\varepsilon)\right]_{11}=\left[\underline{1}+\underline{\tau}_{\mathrm{H}}(\varepsilon)\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)\right]^{-1}\underline{\tau}_{\mathrm{H}}(\varepsilon)$$



t-matrix for host atom: $\underline{t}_{\mathrm{H}}$

t-matrix for the impurity: $\underline{t}_{\mathrm{I}}$

$$\underline{\tau}_{\mathrm{H}}(\varepsilon)=\frac{1}{\Omega_{BZ}}\int_{BZ}\left[\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)-\underline{g}(\mathbf{k};\varepsilon)\right]^{-1}d^3\mathbf{k}.$$

$$\underline{\underline{M}}_{\mathrm{I}}(\varepsilon)=\begin{bmatrix}\underline{t}_{\mathrm{I}}^{-1}(\varepsilon) & -\underline{g}^{12}(\varepsilon) & \cdots & -\underline{g}^{1N}(\varepsilon)\\ -\underline{g}^{21}(\varepsilon) & \underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & \cdots & -\underline{g}^{2N}(\varepsilon)\\ \vdots & \vdots & \ddots & \vdots\\ -\underline{g}^{N1}(\varepsilon) & -\underline{g}^{N2}(\varepsilon) & \cdots & \underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\end{bmatrix}=\begin{bmatrix}\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & -\underline{g}^{12}(\varepsilon) & \cdots & -\underline{g}^{1N}(\varepsilon)\\ -\underline{g}^{21}(\varepsilon) & \underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & \cdots & -\underline{g}^{2N}(\varepsilon)\\ \vdots & \vdots & \ddots & \vdots\\ -\underline{g}^{N1}(\varepsilon) & -\underline{g}^{N2}(\varepsilon) & \cdots & \underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\end{bmatrix}+\begin{bmatrix}\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & 0 & \cdots & 0\\ 0 & 0 & \cdots & 0\\ \vdots & \vdots & \ddots & \vdots\\ 0 & 0 & \cdots & 0\end{bmatrix}$$

$$\left[\underline{\underline{M}}_{\mathrm{I}}(\varepsilon)\right]_{11}^{-1}=\left[\underline{\underline{M}}_{\mathrm{H}}(\varepsilon)+\underline{\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)}\right]_{11}^{-1}=\left[\left[\underline{\underline{1}}+\underline{\underline{M}}_{\mathrm{H}}^{-1}(\varepsilon)\underline{\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)}\right]^{-1}\underline{\underline{M}}_{\mathrm{H}}^{-1}(\varepsilon)\right]_{11}=\left[\underline{1}+\underline{\tau}_{\mathrm{H}}(\varepsilon)\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)\right]^{-1}\underline{\tau}_{\mathrm{H}}(\varepsilon)$$

$$\underline{\underline{M}}_{\mathrm{H}}^{-1}(\varepsilon)=\begin{bmatrix}\underline{\tau}_{\mathrm{H}}(\varepsilon) & \underline{A}_{12}\\ \underline{A}_{21} & \underline{A}_{22}\end{bmatrix}$$

$$\left[\left[\underline{\underline{1}}+\underline{\underline{M}}_{\mathrm{H}}^{-1}(\varepsilon)\underline{\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)}\right]^{-1}\underline{\underline{M}}_{\mathrm{H}}^{-1}(\varepsilon)\right]_{11}=\left[\left[\begin{bmatrix}\underline{1} & \underline{0}\\ \underline{0} & \underline{1}\end{bmatrix}+\begin{bmatrix}\underline{\tau}_{\mathrm{H}}(\varepsilon) & \underline{A}_{12}\\ \underline{A}_{21} & \underline{A}_{22}\end{bmatrix}\begin{bmatrix}\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & \underline{0}\\ \underline{0} & \underline{0}\end{bmatrix}\right]^{-1}\begin{bmatrix}\underline{\tau}_{\mathrm{H}}(\varepsilon) & \underline{A}_{12}\\ \underline{A}_{21} & \underline{A}_{22}\end{bmatrix}\right]_{11}$$

$$=\left[\begin{bmatrix}\underline{1}+\underline{\tau}_{\mathrm{H}}(\varepsilon)\cdot\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right) & \underline{0}\\ \underline{A}_{21}\cdot\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right) & \underline{1}\end{bmatrix}^{-1}\begin{bmatrix}\underline{\tau}_{\mathrm{H}}(\varepsilon) & \underline{A}_{12}\\ \underline{A}_{21} & \underline{A}_{22}\end{bmatrix}\right]_{11}$$

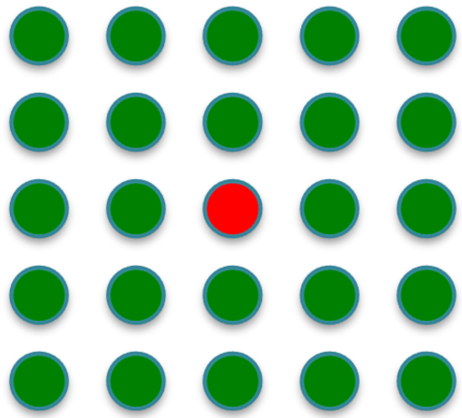
$$\begin{bmatrix}\underline{A} & \underline{0}\\ \underline{B} & \underline{1}\end{bmatrix}^{-1}=\begin{bmatrix}\underline{A}^{-1} & \underline{0}\\ -\underline{B}\cdot\underline{A}^{-1} & \underline{1}\end{bmatrix}$$

$$=\left[\begin{bmatrix}\left[\underline{1}+\underline{\tau}_{\mathrm{H}}(\varepsilon)\cdot\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)\right]^{-1} & \underline{0}\\ -\underline{A}_{21}\cdot\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)\left[\underline{1}+\underline{\tau}_{\mathrm{H}}(\varepsilon)\cdot\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)\right]^{-1} & \underline{1}\end{bmatrix}\cdot\begin{bmatrix}\underline{\tau}_{\mathrm{H}}(\varepsilon) & \underline{A}_{12}\\ \underline{A}_{21} & \underline{A}_{22}\end{bmatrix}\right]_{11}$$

$$=\left[\underline{1}+\underline{\tau}_{\mathrm{H}}(\varepsilon)\cdot\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)\right]^{-1}\underline{\tau}_{\mathrm{H}}(\varepsilon)$$

atom α : ● CPA medium: ●

Single impurity problem: atom α in a CPA medium host



Single site approximation: $\underline{\tau}^{11}_{\text{CPA}}(\varepsilon) = \sum_{\alpha=1}^{N_\alpha} c_\alpha \underline{\tau}^{11}_{\alpha}(\varepsilon),$ with N_α species in the alloy.

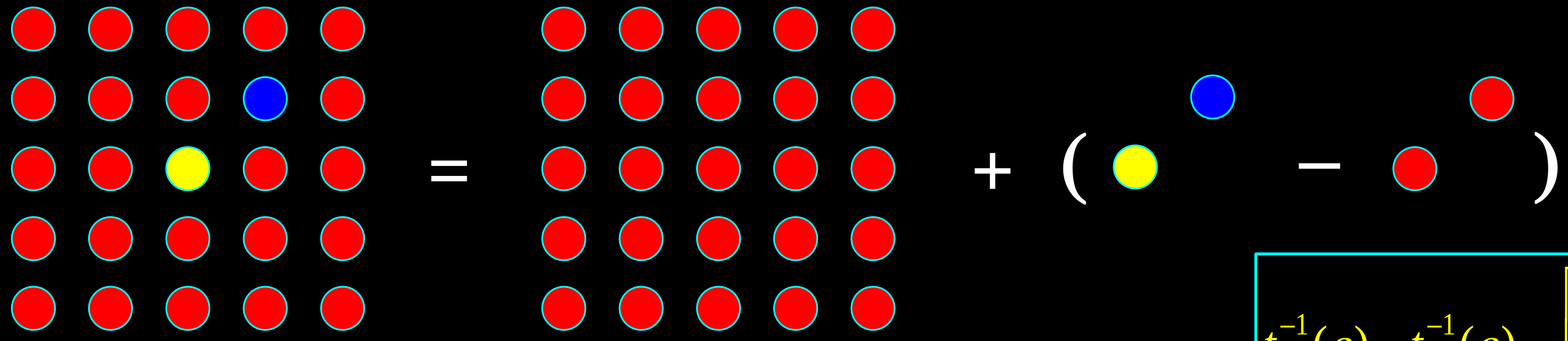
Single impurity problem: $\underline{\tau}^{11}_{\alpha}(\varepsilon) = \left[1 + \underline{\tau}^{11}_{\text{CPA}}(\varepsilon)\left(\underline{t}^{-1}_{\alpha}(\varepsilon) - \underline{t}^{-1}_{\text{CPA}}(\varepsilon)\right)\right]^{-1} \underline{\tau}^{11}_{\text{CPA}}(\varepsilon)$

Periodic system problem: $\underline{\tau}^{11}_{\text{CPA}}(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \left[\underline{t}^{-1}_{\text{CPA}}(\varepsilon) - \underline{g}(\varepsilon, \mathbf{k})\right]^{-1} d^3\mathbf{k}$

$\underline{t}_{\text{CPA}}(\varepsilon)$ is solved self-consistently by iterating the above equations.

$$G_\alpha(\mathbf{r},\mathbf{r};\varepsilon) = \sum_{L,L'} Z^{\alpha}_{L}(\mathbf{r};\varepsilon)\tau^{11}_{\alpha,LL'}(\varepsilon) Z^{\alpha *}_{L'}(\mathbf{r};\varepsilon) - \sum_{L} Z^{\alpha}_{L}(\mathbf{r};\varepsilon) J^{\alpha *}_{L}(\mathbf{r};\varepsilon) \quad \text{and} \quad \rho_\alpha(\mathbf{r}) = -\frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{\varepsilon_F} G_\alpha(\mathbf{r},\mathbf{r};\varepsilon) d\varepsilon$$

A Crystal With Double Impurities



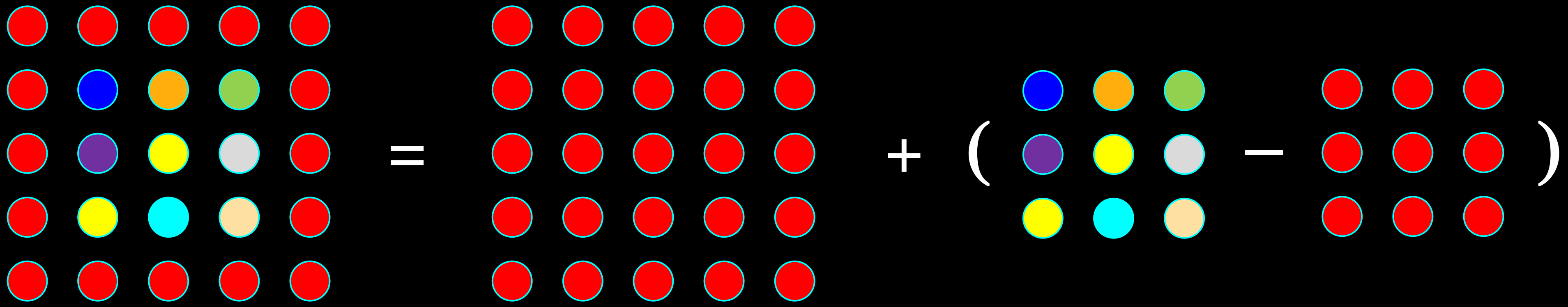
$$\underline{\underline{\tau}}_{\mathrm{H}}(\varepsilon)=\begin{bmatrix}\underline{\tau}_{\mathrm{H}}^{11}(\varepsilon) & \underline{\tau}_{\mathrm{H}}^{12}(\varepsilon)\\ \underline{\tau}_{\mathrm{H}}^{21}(\varepsilon) & \underline{\tau}_{\mathrm{H}}^{22}(\varepsilon)\end{bmatrix}$$

$$\underline{\underline{t}}_{\mathrm{C}}^{-1}(\varepsilon)-\underline{\underline{t}}_{\mathrm{H}}^{-1}(\varepsilon)=\begin{bmatrix}\underline{t}_{1}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & 0\\ 0 & \underline{t}_{2}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\end{bmatrix}$$

$$\underline{\underline{M}}_{\mathrm{C}}(\varepsilon)=\begin{bmatrix}\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & -\underline{g}^{12}(\varepsilon) & -\underline{g}^{13}(\varepsilon) & \cdots & -\underline{g}^{1N}(\varepsilon)\\ -\underline{g}^{21}(\varepsilon) & \underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & -\underline{g}^{23}(\varepsilon) & \cdots & -\underline{g}^{2N}(\varepsilon)\\ -\underline{g}^{31}(\varepsilon) & -\underline{g}^{32}(\varepsilon) & \underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & \cdots & -\underline{g}^{3N}(\varepsilon)\\ \vdots & \vdots & \vdots & \ddots & \vdots\\ -\underline{g}^{N1}(\varepsilon) & -\underline{g}^{N2}(\varepsilon) & -\underline{g}^{N3}(\varepsilon) & \cdots & \underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\end{bmatrix}+\begin{bmatrix}\underline{t}_{1}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & 0 & 0 & \cdots & 0\\ 0 & \underline{t}_{2}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & 0 & \cdots & 0\\ 0 & 0 & 0 & \cdots & 0\\ \vdots & \vdots & \vdots & \ddots & \vdots\\ 0 & 0 & 0 & \cdots & 0\end{bmatrix}$$

$$\underline{\tau}_{\mathrm{C}}^{11}(\varepsilon)=\left[\underline{\underline{M}}_{\mathrm{H}}(\varepsilon)+\underline{\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)}\right]_{11}^{-1}=\left[\left[\underline{\underline{1}}+\underline{\underline{M}}_{\mathrm{H}}^{-1}(\varepsilon)\underline{\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)}\right]^{-1}\underline{\underline{M}}_{\mathrm{H}}^{-1}(\varepsilon)\right]_{11}=\left[\left[\underline{\underline{1}}+\underline{\underline{\tau}}_{\mathrm{H}}(\varepsilon)\left(\underline{\underline{t}}_{\mathrm{C}}^{-1}(\varepsilon)-\underline{\underline{t}}_{\mathrm{H}}^{-1}(\varepsilon)\right)\right]^{-1}\underline{\underline{\tau}}_{\mathrm{H}}(\varepsilon)\right]_{11}$$

A Crystal With Cluster Embedding (i.e., Cluster Impurity)



$$\underline{\tau}_{\mathrm{C}}^{11}(\varepsilon)=\left[\underline{\underline{M}}_{\mathrm{C}}(\varepsilon)\right]_{11}^{-1}=\left[\underline{\underline{M}}_{\mathrm{H}}(\varepsilon)+\underline{\left(\underline{t}_{\mathrm{I}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon)\right)}\right]_{11}^{-1}=\left[\left[\underline{\underline{1}}+\underline{\underline{\tau}}_{\mathrm{H}}(\varepsilon)\left(\underline{\underline{t}}_{\mathrm{C}}^{-1}(\varepsilon)-\underline{\underline{t}}_{\mathrm{H}}^{-1}(\varepsilon)\right)\right]^{-1}\underline{\underline{\tau}}_{\mathrm{H}}(\varepsilon)\right]_{11}$$

N_{C} = the number of atoms in the cluster

$$\underline{\underline{t}}_{\mathrm{C}}^{-1}(\varepsilon)-\underline{\underline{t}}_{\mathrm{H}}^{-1}(\varepsilon)=\begin{bmatrix} \underline{t}_1^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & 0 & \cdots & 0 \\ 0 & \underline{t}_2^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \underline{t}_{N_{\mathrm{C}}}^{-1}(\varepsilon)-\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) \end{bmatrix}$$

$$\underline{\underline{\tau}}_{\mathrm{H}}(\varepsilon)=\begin{bmatrix} \underline{\tau}_{\mathrm{H}}^{11}(\varepsilon) & \underline{\tau}_{\mathrm{H}}^{12}(\varepsilon) & \cdots & \underline{\tau}_{\mathrm{H}}^{1N_{\mathrm{C}}}(\varepsilon) \\ \underline{\tau}_{\mathrm{H}}^{21}(\varepsilon) & \underline{\tau}_{\mathrm{H}}^{22}(\varepsilon) & \cdots & \underline{\tau}_{\mathrm{H}}^{2N_{\mathrm{C}}}(\varepsilon) \\ \vdots & \vdots & \ddots & \vdots \\ \underline{\tau}_{\mathrm{H}}^{N_{\mathrm{C}}1}(\varepsilon) & \underline{\tau}_{\mathrm{H}}^{N_{\mathrm{C}}2}(\varepsilon) & \cdots & \underline{\tau}_{\mathrm{H}}^{N_{\mathrm{C}}N_{\mathrm{C}}}(\varepsilon) \end{bmatrix}$$

Multiple scattering path matrix $\underline{\tau}^{nm}$ for the Host System

Recall the following expression in one of the previous slides

For periodic crystal, $\underline{t}_n(\varepsilon) = \underline{t}(\varepsilon)$, we take $\mathbf{k}$-space approach:

$$\underline{\tau}(\varepsilon;\mathbf{k}) = \left[\underline{t}^{-1}(\varepsilon) - \underline{g}(\mathbf{k};\varepsilon)\right]^{-1},$$

where $\underline{g}(\mathbf{k};\varepsilon)$ is a lattice Fourier transform of $\underline{g}^{nm}(\varepsilon)$.

The τ-matrix is given by: $\underline{\tau}^{nm}(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} \underline{\tau}(\varepsilon;\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_m)} d^3\mathbf{k}.$

Therefore,

For the host system, $\underline{t}_n(\varepsilon) = \underline{t}_{\mathrm{H}}(\varepsilon)$, we have:

$$\underline{\tau}_{\mathrm{H}}(\varepsilon;\mathbf{k}) = \left[\underline{t}_{\mathrm{H}}^{-1}(\varepsilon) - \underline{g}(\mathbf{k};\varepsilon)\right]^{-1}, \text{ and}$$

$$\underline{\tau}_{\mathrm{H}}^{nm}(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} \underline{\tau}_{\mathrm{H}}(\varepsilon;\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_m)} d^3\mathbf{k}, \text{ with } n, m = 1, 2, \ldots, N_{\mathrm{C}}.$$