KKR-CPA and Its Extension

The Self-consistent Process in an *Ab initio* Electronic Structure Calculation

$V_{\text{eff}}(\mathbf{r})$, crystal structure

One-electron Schrödinger Equation

$$[-\nabla^2 + V_{\text{eff}}(\mathbf{r})]\cdot\psi_\alpha(\mathbf{r};\varepsilon) = \varepsilon_\alpha \psi_\alpha(\mathbf{r};\varepsilon)$$

$$\rho(\mathbf{r}) = \sum_{\varepsilon_\alpha \le \varepsilon_F} \left|\psi_\alpha(\mathbf{r};\varepsilon)\right|^2$$

Is density converged?

No

LDA (or GGA) Potential

$$V_{\text{eff}}(\mathbf{r}) = \int_\infty \frac{2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' - \sum_{\mathbf{R}_n} \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|} + V_{\text{XC}}^{\text{LDA}}[\rho(\mathbf{r})]$$

$V_{\text{eff}}(\mathbf{r})$

Yes

ground state E, etc.

Atomic units:

$m_e = 1/2$

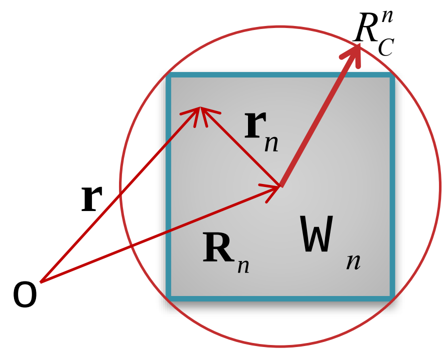
$\hbar = 1$

$\mu_{\text{B}} = e/c$

$e^2 = 2$

$$E[\rho] = \int_{-\infty}^{\varepsilon_F} \varepsilon\rho(\varepsilon)d\varepsilon - \int_\infty \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' - \int_\infty V_{\text{XC}}^{\text{LDA}}(\mathbf{r})\rho(\mathbf{r}) d^3\mathbf{r} + E_{\text{XC}}^{\text{LDA}}[\rho]$$

Green Function in Multiple Scattering Theory



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

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

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

$\underline{\underline{M}}(\varepsilon)$ matrix

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

$$\rho(\mathbf{r})=-\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\varepsilon_F}G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)d\varepsilon,$$

$$\rho(\varepsilon)=-\frac{1}{\pi}\mathrm{Im}\int_{\Omega_n}G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)d^3\mathbf{r}_n.$$

For periodic crystal, $\underline{t}^n(\varepsilon)=\underline{t}(\varepsilon)$, we take **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 $\underline{g}_{nm}(\varepsilon)$ and is called structure constant matrix.

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

There is no need for band structure ($\varepsilon_{n\mathbf{k}}$) and wave function ($\Psi_{n\mathbf{k}}(\mathbf{r})$) calculations

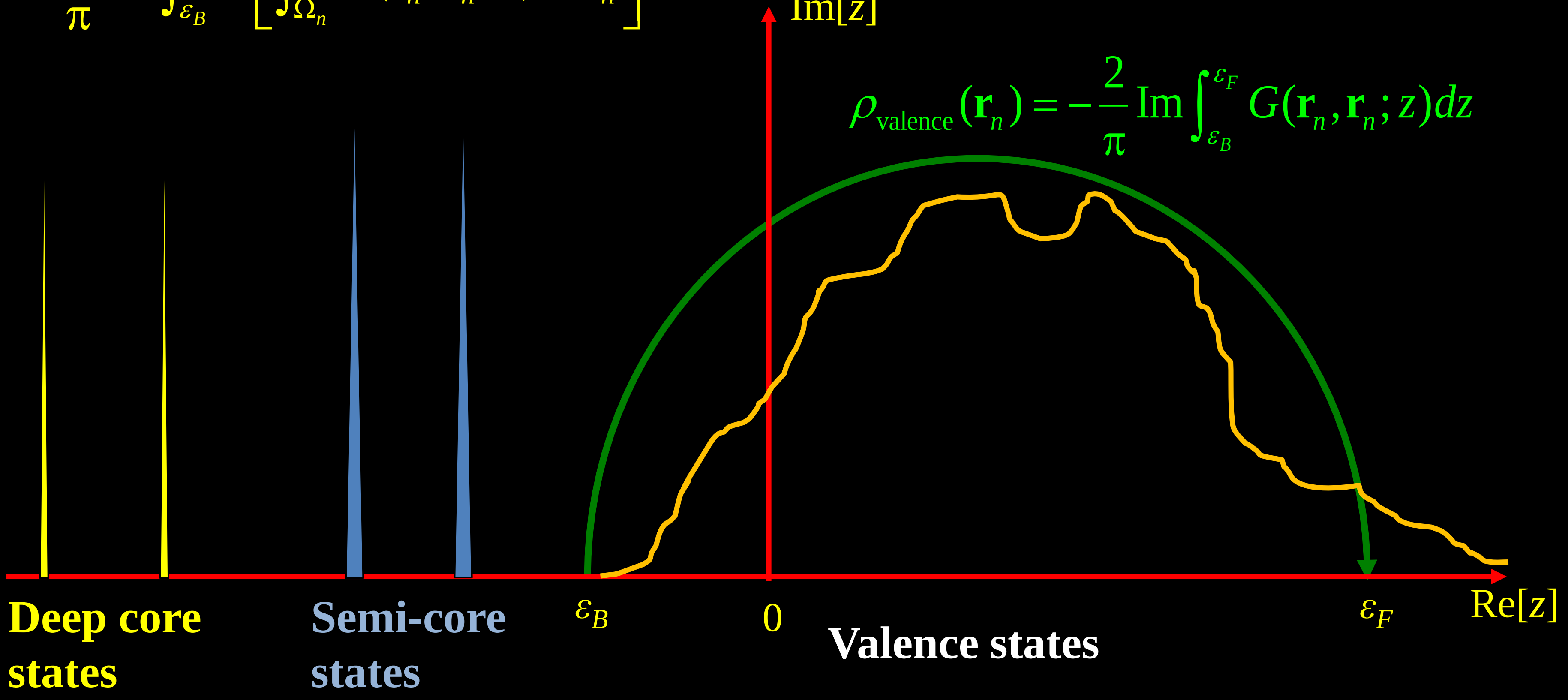
Green Function Method and Contour Integration

$$\rho(\mathbf{r}_n) = \rho_{\text{core}}(\mathbf{r}_n) + \rho_{\text{valence}}(\mathbf{r}_n)$$

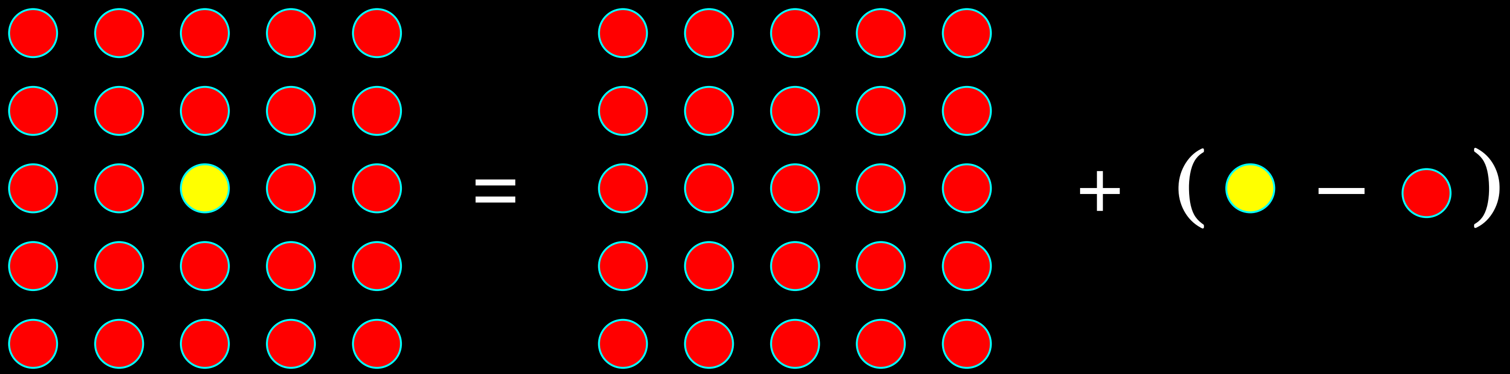
$$E = \sum_{\text{core}} \varepsilon_{\text{core}} + \sum_{n=1}^{N} \int_{\varepsilon_B}^{\varepsilon_F} \varepsilon \rho_n(\varepsilon) dz - \sum_{n=1}^{N} \int_{\Omega_n} \rho(\mathbf{r}_n) V_{\text{eff}}(\mathbf{r}_n) d^3\mathbf{r}_n + U[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

$$\int_{\varepsilon_B}^{\varepsilon_F} \varepsilon \rho_n(\varepsilon) dz = -\frac{2}{\pi} \operatorname{Im} \int_{\varepsilon_B}^{\varepsilon_F} z \left[\int_{\Omega_n} G(\mathbf{r}_n, \mathbf{r}_n; z) d^3\mathbf{r}_n \right] dz$$

$$\rho_{\text{valence}}(\mathbf{r}_n) = -\frac{2}{\pi} \operatorname{Im} \int_{\varepsilon_B}^{\varepsilon_F} G(\mathbf{r}_n, \mathbf{r}_n; z) dz$$



A Crystal With Single Impurity



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

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

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

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

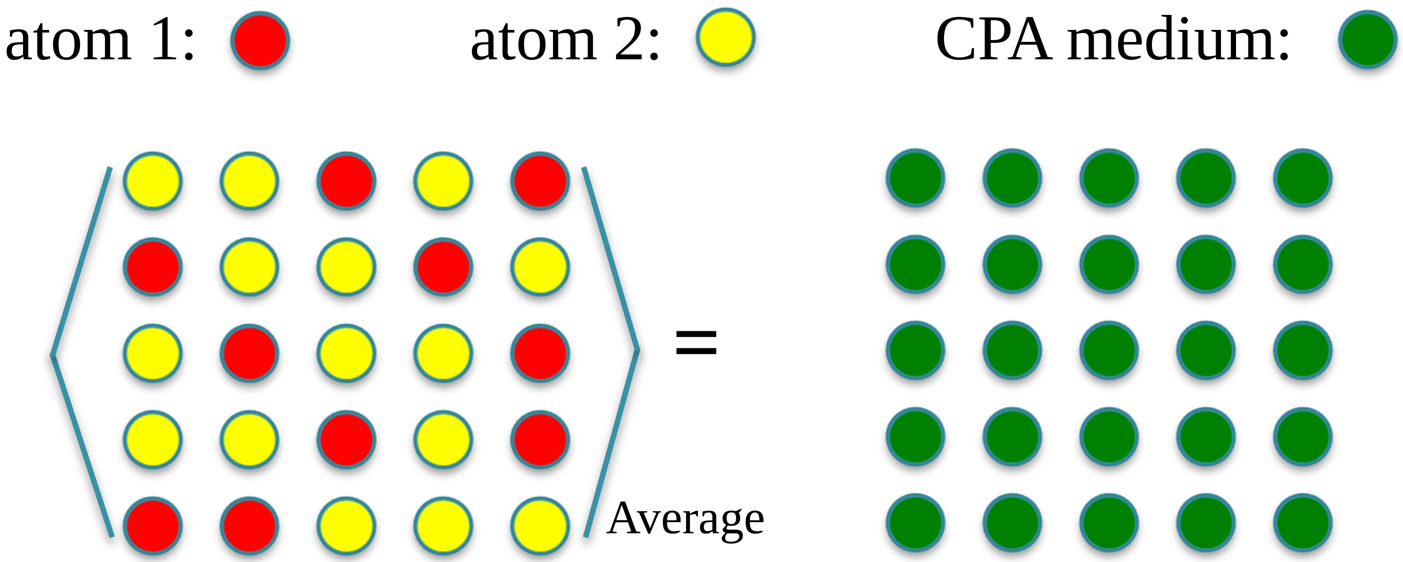
The extension to cluster embedding is straightforward, and the final expression for the τ-matrix is very much the same.

Ab initio Approaches to Random Alloys

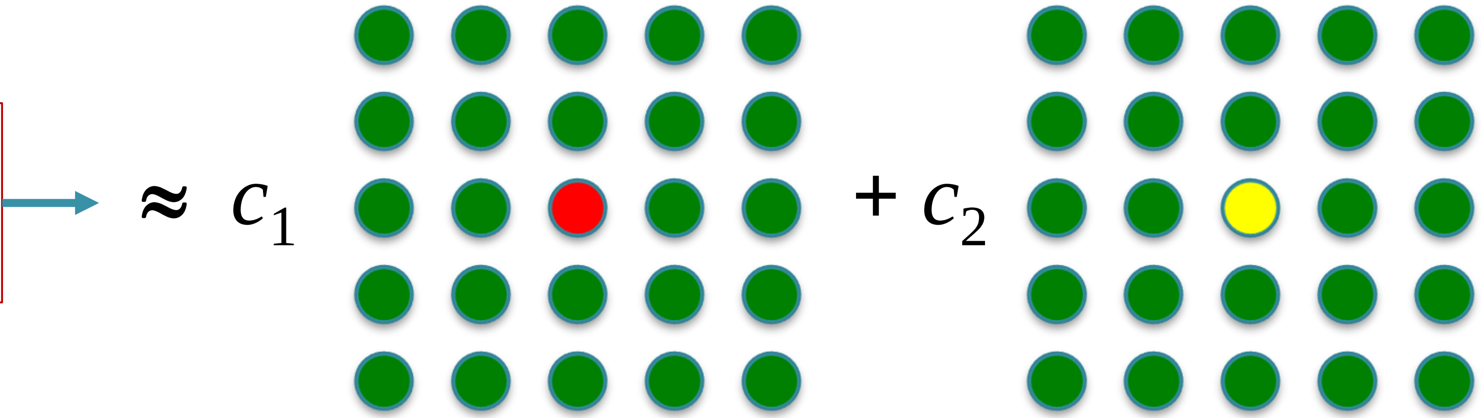
- Supercell approach: LSMS (linear scaling allow to study very large unit cell containing 10,000 atoms or more)
- Cluster expansion approach: KKR + SQS (special quasirandom structures)
- Effective medium approach: KKR-CPA

KKR-CPA Method

Coherent potential approximation (CPA) for obtaining the configuration average of the electron density for random alloys



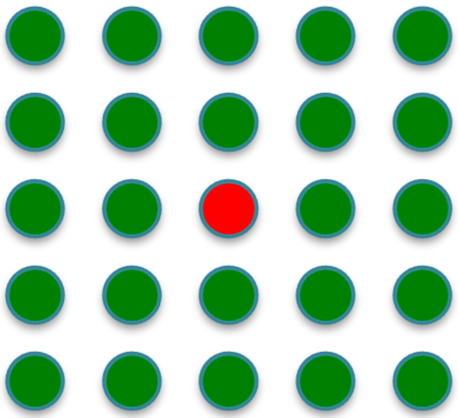
Single-site approximation



$$\langle G(\mathbf{r},\mathbf{r};\varepsilon)\rangle_{\text{ave}} = \sum_{\alpha=1}^{N_\alpha} c_\alpha G_\alpha(\mathbf{r},\mathbf{r};\varepsilon), \text{ and } \rho(\mathbf{r}) = -\frac{1}{\pi}\,\mathrm{Im}\sum_{\alpha=1}^{N_\alpha} c_\alpha \int_{-\infty}^{\varepsilon_F} G_\alpha(\mathbf{r},\mathbf{r};\varepsilon)\,d\varepsilon$$

atom α : CPA medium:

Single impurity problem:
atom α in a CPA medium host



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

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

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

$\underline{t}_{\mathrm{CPA}}(\varepsilon)$ is solved self-consistently by iterating the above equations with initial assumtion: $\underline{t}_{\mathrm{CPA}}(\varepsilon)=\sum_{\alpha=1}^{N_\alpha} c_\alpha \underline{t}_\alpha(\varepsilon)$, to start with.

Self-consistent Condition for the CPA Medium

In conventional KKR-CPA, for each energy point ε along the energy contour, we solve the multiple scattering τ-matrix for single impurity $\underline{t}_\alpha$, which is embedded in the CPA medium $\underline{t}_{\mathrm{CPA}}$.

The CPA medium is required to satisfy $\underline{\tau}_{\mathrm{CPA}}(\varepsilon) = \sum_{\alpha=1}^{N_\alpha} c_\alpha \underline{\tau}_\alpha(\varepsilon)$

$$\underline{t}_{\mathrm{CPA}}(\varepsilon) = \sum_{\alpha=1}^{N_\alpha} c_\alpha \underline{t}_\alpha(\varepsilon)$$

↓

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

$$\underline{\tau}_{\mathrm{CPA}}(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} \underline{\tau}_{\mathrm{CPA}}(\varepsilon;\mathbf{k})\, d^3\mathbf{k}.$$

→

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

$$\sum_{\alpha=1}^{N_\alpha} c_\alpha \underline{\tau}_\alpha(\varepsilon) \overset{?}{=} \underline{\tau}_{\mathrm{CPA}}(\varepsilon)$$

↓

Is $\underline{t}_{\mathrm{CPA}}(\varepsilon)$ converged?

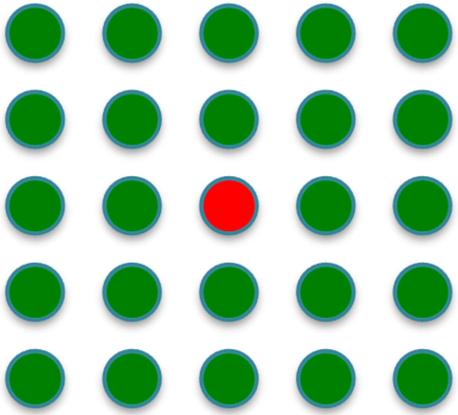
No → back to $\underline{\tau}_{\mathrm{CPA}}$ step

Yes ↓

This self-consistent CPA calculation is performed for each energy point along the energy contour, during each SCF iteration step for the charge self-consistency in DFT.

atom α :   CPA medium:

For atom α in the CPA medium host



$$G_\alpha(\mathbf{r},\mathbf{r};\varepsilon) = \sum_{L,L'} Z_L^\alpha(\mathbf{r};\varepsilon)\tau_{\alpha,LL'}(\varepsilon)Z_{L'}^{\alpha*}(\mathbf{r};\varepsilon) - \sum_L Z_L^\alpha(\mathbf{r};\varepsilon)J_L^{\alpha*}(\mathbf{r};\varepsilon)$$

$$\rho_\alpha(\mathbf{r}) = -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} G_\alpha(\mathbf{r},\mathbf{r};\varepsilon)d\varepsilon$$

$$\rho_\alpha(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\int_\Omega G_\alpha(\mathbf{r},\mathbf{r};\varepsilon)d^3\mathbf{r}$$

Net charge associated with atom α:

$$\Delta q_\alpha = \int_\Omega \rho_\alpha(\mathbf{r})d^3\mathbf{r} - Z_\alpha$$

Obviously, CPA medium is charge neutral: $\sum_{\alpha=1}^{N_\alpha} c_\alpha \Delta q_\alpha = 0.$

$$V_{\alpha,\mathrm{eff}}(\mathbf{r}) = V_{\alpha,\mathrm{Hartree}}(\rho_\alpha(\mathbf{r}),\rho_{\mathrm{CPA}}(\mathbf{r})) + V_{\mathrm{XC}}(\rho_\alpha(\mathbf{r}))$$

where $\rho_{\mathrm{CPA}}(\mathbf{r}) = \sum_{\alpha=1}^{N_\alpha} c_\alpha \rho_\alpha(\mathbf{r})$.

In conventional CPA method, the electrostatic potential, $V_{\alpha,\mathrm{Hartree}}(\rho_\alpha(\mathbf{r}),\rho_{\mathrm{CPA}}(\mathbf{r}))$, is calculated according to this picture: $\rho_\alpha(\mathbf{r})$ is surrounded by medium $\rho_{\mathrm{CPA}}(\mathbf{r})$ together with positive point charges on the atomic sites.

What is missing in conventional CPA method

- The effective medium is determined by requiring that the probability for a species occupying an atomic site is irrelevant to its local environment.
  - ✓ The short range ordering/clustering effect is missing
  - ✓ Efforts to improve: Molecular CPA, Non-local CPA (or DCA), Cluster Averaged CPA
- The effective medium site carries the same amount of charge, which is 0 in the single lattice case (e.g., FCC, BCC random alloys). It implies: $\langle \Delta q_\alpha \cdot V_\alpha \rangle = \langle \Delta q_\alpha \cdot V \rangle = \langle \Delta q_\alpha \rangle V$
  - ✓ The each chemical species carries a different amount of charges, due to charge transfer, but feels the same long range electrostatic potential (also known as the Madelung potential), arising from the charges on all the other atomic sites.
  - ✓ Supercell calculation shows that the long range electrostatic potential felt by a species depends linearly on the extra charge carried by the species. It implies: $\langle \Delta q_\alpha \cdot V_\alpha \rangle \neq \langle \Delta q_\alpha \rangle \langle V_\alpha \rangle$
  - ✓ Efforts to improve: local screening model or charge correlation model

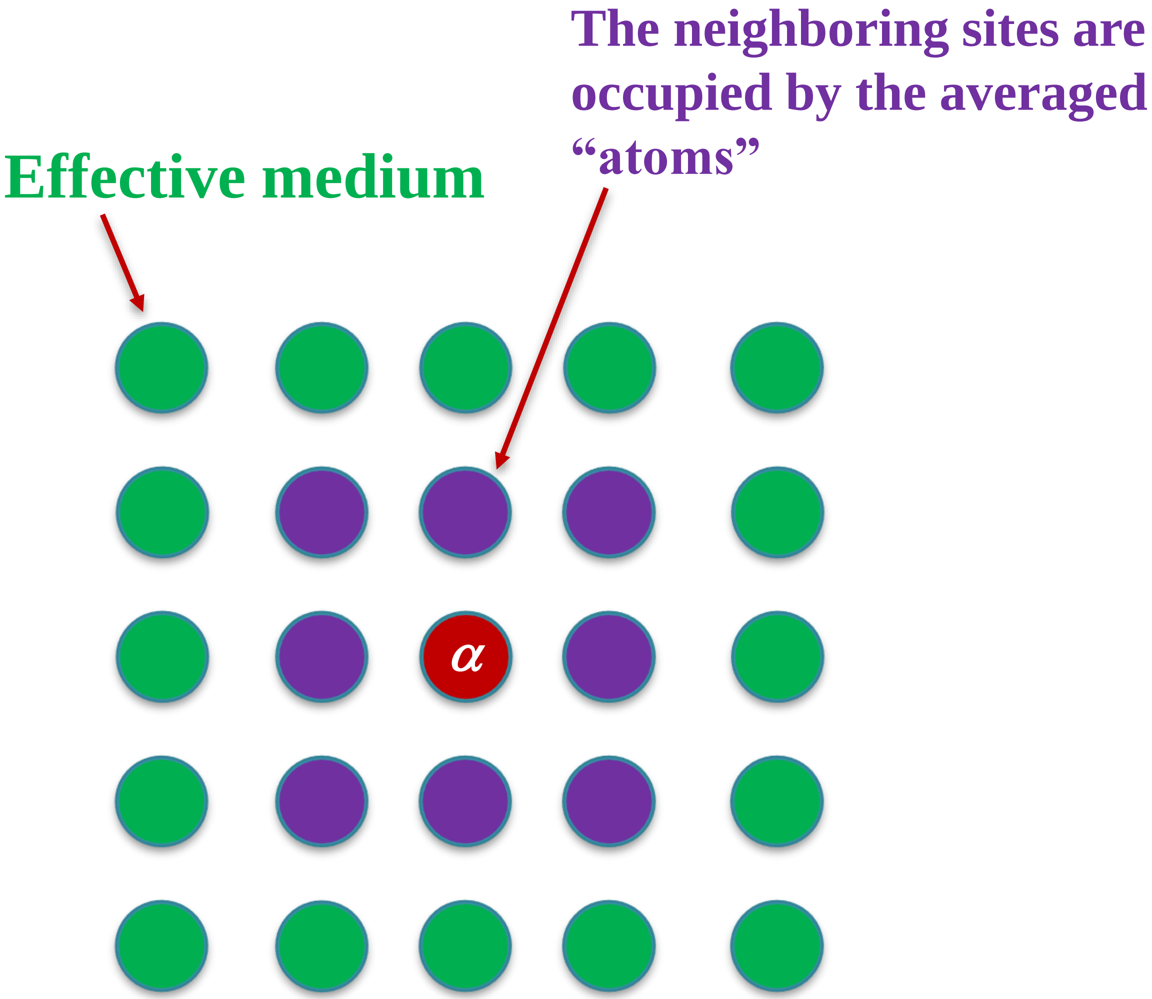
Cluster Averaged CPA

- Embedding a cluster, instead of single site, in the effective medium so to allow for including the short range correlation effects
- The neighboring "atoms" in the cluster are an averaged "atom" represented by the *t*-matrix determined as follows

$$\bar{\underline{t}}_{\alpha}(\varepsilon) = \sum_{\beta=1}^{N_{\beta}} P_{\alpha\beta}\, \underline{t}_{\beta}(\varepsilon)$$

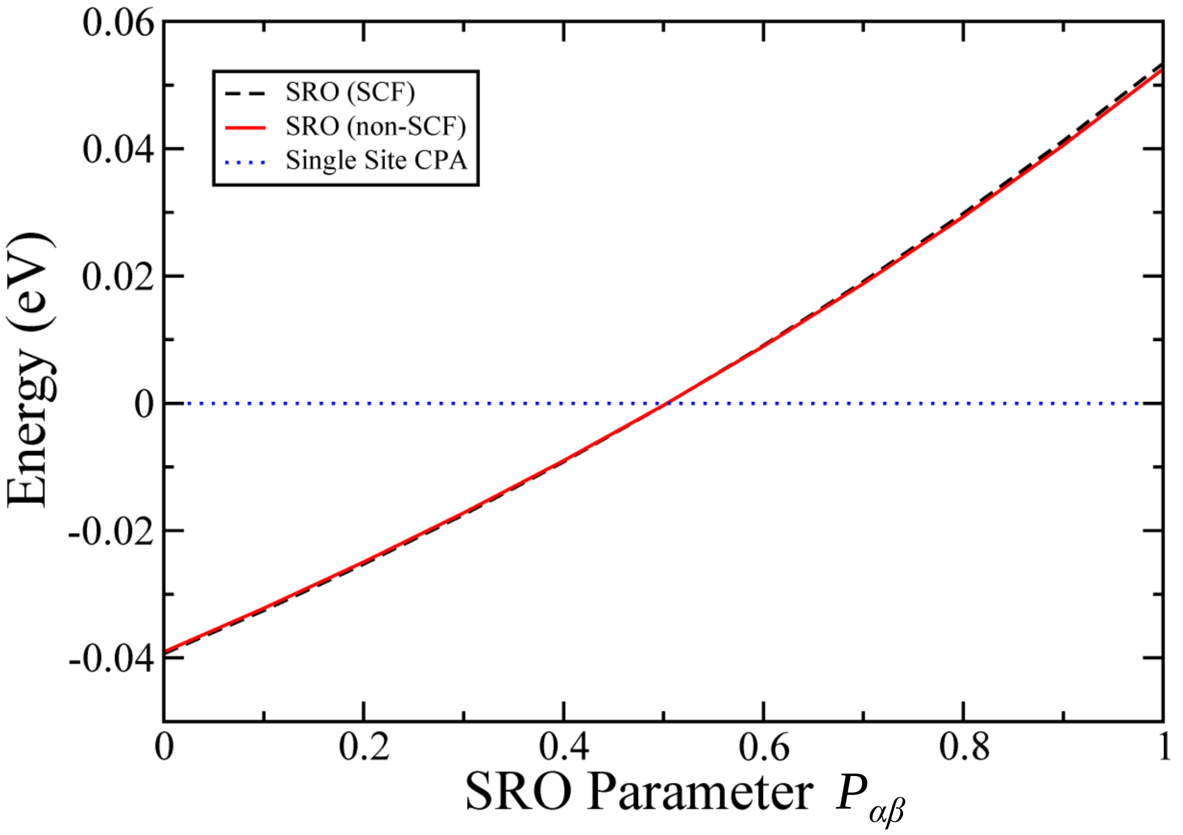
where $P_{\alpha\beta}$ is the conditional probability for a neighboring site occupied by species β if the central site is occupied by species α.

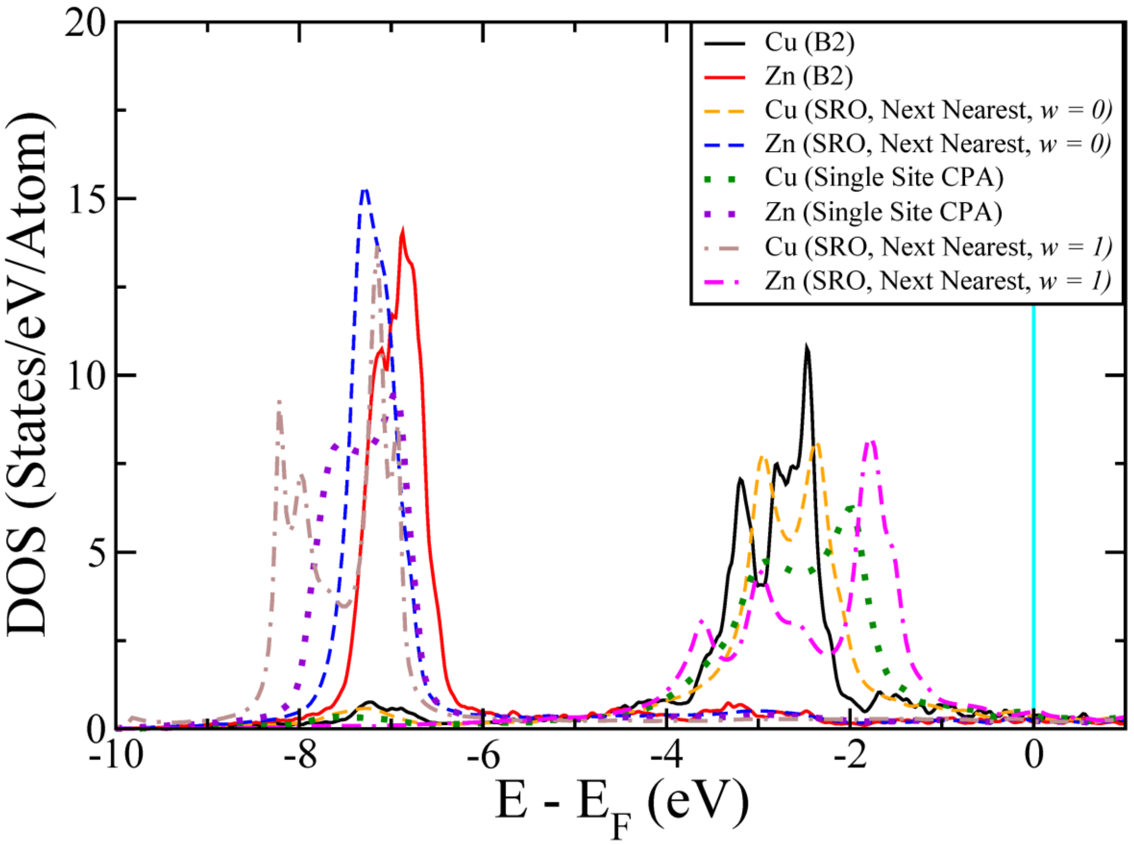
$$\underline{\tau}_{\alpha}(\varepsilon) = \left[\left[1+\underline{\underline{\tau}}_{\mathrm{CPA}}(\varepsilon)\left(\underline{\underline{t}}_{\alpha}^{-1}(\varepsilon)-\underline{\underline{t}}_{\mathrm{CPA}}^{-1}(\varepsilon)\right)\right]^{-1}\underline{\underline{\tau}}_{\mathrm{CPA}}(\varepsilon)\right]_{11}$$



A paper written by Vishnu Raghuraman: https://arxiv.org/abs/2006.09421, accepted for publication in PRB.

An Application of CA-CPA to CuZn





Warren-Cowley SRO parameter = $1 - P_{\alpha\beta} / c_\beta$

by *Vishnu Raghuraman*