Electrical Conductivity in Random Alloys using KKR-CPA

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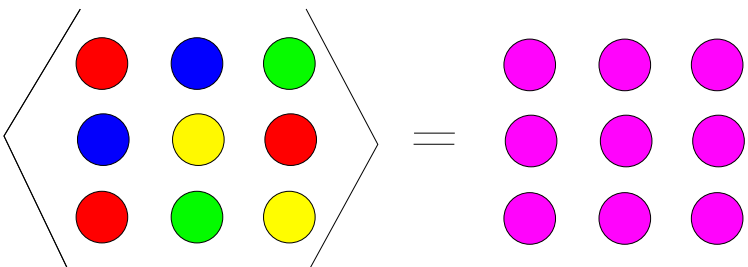
Agenda

- Brief introduction to Coherent Potential Approximation (CPA).
- Expressing Kubo-Greenwood Equation using Green's Functions.
- Obtaining a Kubo-Greenwood based conductivity expression within CPA formalism.
- CPA Results
- Cluster Averaged CPA (CA-CPA)
- CA-CPA conductivity
- Tests and limitations

Coherent Potential Approximation (CPA) [Györffy 1972, Stocks 1978]

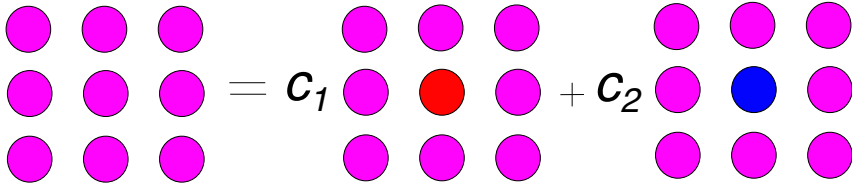
Replace random alloy with an effective medium that mimics the ensemble average



Multi-element alloy (several configurations) $\rightarrow$ Single element crystal (one configuration)

Single-Site Approximation

Assume complete randomness.
Species probability distribution $\equiv$ global concentration



In terms of t and τ-matrices

$$\tau^{nn}_{\mathrm{CPA}}(E) = \sum_{\alpha} c_\alpha \tau^{nn}_{\alpha}(E) \tag{1}$$

$$\tau^{nn}_{\alpha}(E) = \left[1 + \tau^{nn}_{\mathrm{CPA}}(E)(t^{-1}_{\alpha}(E) - t^{-1}_{\mathrm{CPA}}(E))\right]^{-1} \tau^{nn}_{\mathrm{CPA}}(E) \tag{2}$$

Single-Site CPA - A few more definitions

We can define

$$D_\alpha^{nn}(E) = \left[1 + \tau_{\mathrm{CPA}}^{nn}(E)(t_\alpha^{-1}(E) - t_{\mathrm{CPA}}^{-1}(E))\right]^{-1} \tag{3}$$

$$\tilde{D}_\alpha^{nn} = \left[1 + (t_\alpha^{-1}(E) - t_{\mathrm{CPA}}^{-1}(E))\tau_{\mathrm{CPA}}^{nn}(E)\right]^{-1} \tag{4}$$

The CPA condition can then be expressed as $\sum c_\alpha D_\alpha^{nn}(E) = 1$. Additionally,

$$D_\alpha^{nn}(E) = 1 + \tau_{\mathrm{CPA}}^{nn}(E) x_\alpha^{nn}(E) \tag{5}$$

$$\tilde{D}_\alpha^{nn}(E) = 1 + x_\alpha^{nn}(E)\tau_{\mathrm{CPA}}^{nn}(E) \tag{6}$$

The CPA condition can also be expressed as $\sum_\alpha c_\alpha x_\alpha^{nn}(E) = 0$, or $\langle x \rangle = 0$.

Conductivity from First Principles

There are different approches to calculating conductivity from first principles

- Boltzmann Transport Equation
- Landauer Formula
- Kubo-Greenwood Formula
- Non-equilibrium approaches

Kubo and Kubo-Greenwood Formulas [Kubo 1957]

Considering Hamiltonian $H = H_0 - e\sum_k E_k r_k$, and using linear response theory ($J_\mu = \mathrm{Re}\left[\sigma_{\mu\nu}(\omega) E_\nu^0 e^{i\omega t}\right]$), we can express the conductivity at $T = 0$ as

$$\sigma_{\mu\nu}(\omega) = \frac{V}{\hbar\omega}\int_0^\infty dt\ \left\langle [\hat{J}_\nu(0), \hat{J}_\mu(t)] \right\rangle_0 e^{-i\omega t} \tag{7}$$

where $\hat{J}$ is the current operator, V is the system volume and ω is the frequency of the E-field. For $\omega = 0$ (DC), it can be shown that

$$\sigma_{\mu\nu}(\epsilon_F) = \frac{\pi\hbar}{N\Omega}\left\langle \sum_{\alpha,\alpha'} \langle\alpha|j_\mu|\alpha'\rangle\langle\alpha'|j_\nu|\alpha\rangle \delta(\epsilon_F - \epsilon_\alpha)\delta(\epsilon_F - \epsilon_{\alpha'}) \right\rangle_{\text{ensemble}} \tag{8}$$

where $|\alpha\rangle, |\alpha'\rangle$ are eigenstates of the unperturbed Hamiltonian, the number of atoms is N and Volume per Atom is Ω.

Kubo-Greenwood Formula using Green's Functions

We want

$$\sigma_{\mu\nu}(\epsilon_F) = \frac{\pi\hbar}{N\Omega}\left\langle \sum_{\alpha,\alpha'} \langle\alpha|j_\mu|\alpha'\rangle\langle\alpha'|j_\nu|\alpha\rangle\delta(\epsilon_F-\epsilon_\alpha)\delta(\epsilon_F-\epsilon_{\alpha'})\right\rangle \tag{9}$$

in terms of Green's Functions. Let's use

$$\sum_\alpha |\alpha\rangle\langle\alpha|\delta(\epsilon_F-\epsilon_\alpha) = -\frac{1}{\pi}\lim_{\delta\to 0}\mathrm{Im}\ G(\epsilon_F+i\delta) \tag{10}$$

$$|\alpha\rangle\delta(\epsilon_F-\epsilon_\alpha) = -\frac{1}{\pi}\lim_{\delta\to 0}\mathrm{Im}\ G(\epsilon_F+i\delta)|\alpha\rangle \tag{11}$$

This gives us

$$\sigma_{\mu\nu}(\epsilon_F) = \frac{\hbar}{\pi N\Omega}\lim_{\delta\to 0}\mathrm{Tr}\,\langle j_\mu \mathrm{Im}G(\epsilon_F+i\delta) j_\nu \mathrm{Im}G(\epsilon_F+i\delta)\rangle \tag{12}$$

We now need to deal with the imaginary terms

Imaginary Part

Use

$$\lim_{\delta \to 0} \mathrm{Im}\ G(\epsilon_F + i\delta) = \frac{1}{2i} \lim_{\delta \to 0} [G(\epsilon_F + i\delta) - G(\epsilon_F - i\delta)] \tag{13}$$

This gives us

$$\sigma_{\mu\nu}(\epsilon_F) = -\frac{\hbar}{4\pi N\Omega} \lim_{\delta \to 0} [\tilde{\sigma}_{\mu\nu}(\epsilon_F + i\delta, \epsilon_F + i\delta) + \tilde{\sigma}_{\mu\nu}(\epsilon_F + i\delta, \epsilon_F - i\delta) \tag{14}$$

$$+\tilde{\sigma}_{\mu\nu}(\epsilon_F - i\delta, \epsilon_F + i\delta) + \tilde{\sigma}_{\mu\nu}(\epsilon_F - i\delta, \epsilon_F - i\delta)] \tag{15}$$

where

$$\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi N\Omega} \mathrm{Tr}\langle j_\mu G(z_1) j_\nu G(z_2)\rangle \tag{16}$$

From this point, whenever we refer to conductivity, we are talking about $\tilde{\sigma}$.

Calculating $\tilde{\sigma}$ - Position Basis

In position basis

$$\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi N \Omega} \int d^3\boldsymbol{r}\; d^3\boldsymbol{r}' \langle j_\mu(\boldsymbol{r}) G(\boldsymbol{r}, \boldsymbol{r}', z_1) j_\nu(\boldsymbol{r}') G(\boldsymbol{r}', \boldsymbol{r}, z_2) \rangle \tag{17}$$

Using

$$G(\boldsymbol{r_n}, \boldsymbol{r_n}, E) = \sum_{LL'} Z^n_L(\boldsymbol{r_n}, E) \tau^{nn}_{LL'}(E) Z^{n\bullet}_{L'}(\boldsymbol{r_n}, E),\; j_\mu(\boldsymbol{r}) = -\frac{i\hbar e}{m_e} \frac{\partial}{\partial r_\mu}, \tag{18}$$

we can write

$$\boxed{\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi N \Omega} \sum_{mn} \sum_{L_1 L_2 L_3 L_4} \langle J^{m\mu}_{L_4 L_1}(z_2, z_1) \tau^{mn}_{L_1 L_2}(z_1) J^{n\nu}_{L_2 L_3}(z_1, z_2) \tau^{nm}_{L_3 L_4}(z_2) \rangle} \tag{19}$$

where

$$J^{i\alpha}_{LL'}(z, z') = -\frac{i\hbar e}{m_e} \int_{\Omega_m} d^3\boldsymbol{r}\; Z^{m\bullet}_L(\boldsymbol{r}, z) \frac{\partial}{\partial r_\alpha} Z^m_{L'}(\boldsymbol{r}, z') \tag{20}$$

Solving Approaches [Butler 1985]

Reprinting expression

$$\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi N\Omega} \sum_{mn} \sum_{L_1 L_2 L_3 L_4} \langle J^{m\mu}_{L_4 L_1}(z_2, z_1) \tau^{mn}_{L_1 L_2}(z_1) J^{n\nu}_{L_2 L_3}(z_1, z_2) \tau^{nm}_{L_3 L_4}(z_2) \rangle \quad (21)$$

Now we have three approaches available to us

1. Calculate $\tilde{\sigma}$ for a supercell (computational intensive, impractical)
2. Using an effective medium (Coherent Potential Approximation)

CPA Conductivity - Translational Symmetry

We want to express

$$\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi N\Omega} \sum_{mn} \sum_{L_1 L_2 L_3 L_4} \langle J^{m\mu}_{L_4 L_1}(z_2, z_1) \tau^{mn}_{L_1 L_2}(z_1) J^{n\nu}_{L_2 L_3}(z_1, z_2) \tau^{nm}_{L_3 L_4}(z_2) \rangle \quad (22)$$

within CPA. First, we can write the sum as

$$\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi N\Omega} \left(\sum_{\substack{m=0 \\ n}} + \sum_{\substack{m=1 \\ n}} + \cdots \right) \langle J^{m\mu}_{L_4 L_1}(z_2, z_1) \tau^{mn}_{L_1 L_2}(z_1) J^{n\nu}_{L_2 L_3}(z_1, z_2) \tau^{nm}_{L_3 L_4}(z_2) \rangle \quad (23)$$

The CPA medium is uniform and has translation symmetry.

$$\boxed{\tilde{\sigma}_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi\Omega} \sum_{n} \sum_{L_1 L_2 L_3 L_4} \langle J^{0\mu}_{L_4 L_1}(z_2, z_1) \tau^{0n}_{L_1 L_2}(z_1) J^{n\nu}_{L_2 L_3}(z_1, z_2) \tau^{n0}_{L_3 L_4}(z_2) \rangle} \quad (24)$$

How to introduce CPA terms into $\tilde{\sigma}_{\mu\nu}$? Use

$$\tau = \tau_{\mathrm{CPA}} + \tau_{\mathrm{CPA}} T \tau_{\mathrm{CPA}} \tag{25}$$

where T, which represents excess scattering can be written in terms of the following series

$$T^{mn} = x^m \delta_{mn} + \sum_{p \neq m} x^m \tau^{mp}_{\mathrm{CPA}} T^{pn} \tag{26}$$

Averaging and ignoring some correlations

$$\langle T^{mn} \rangle = \langle x^m \rangle \delta_{mn} + \sum_{p \neq m} \langle x^m \rangle \tau^{mp}_{CPA} \langle T^{pn} \rangle \tag{27}$$

Note that $\langle x^m \rangle = 0$ for a CPA site and $\langle x^m \rangle = x^\alpha$ is site m is constrained to be of species α. This equation is applied repeatedly to get the final expression.

Final Expressions

We can write $\tilde{\sigma} = \tilde{\sigma}^0 + \tilde{\sigma}^1$, where

$$\tilde{\sigma}^1_{\mu\nu}(z_1, z_2) = -\frac{\hbar}{\pi\Omega} \sum_{\alpha\beta} c_\alpha c_\beta \tilde{J}^{\alpha\mu}_{L_4 L_1}(z_2, z_1) \left[\underbrace{(1 - \chi\omega)^{-1}}_{\text{Vertex Correction}} \chi \right]_{L_1 L_4 L_2 L_3} \tilde{J}^{\beta\nu}_{L_2 L_3}(z_1, z_2)$$

where

$$\chi_{(L_1 L_4),(L_2,L_3)}(z_1, z_2) = \frac{1}{\Omega_{\mathrm{BZ}}} \int d^3\boldsymbol{k}\ \tau_{L_1 L_2}(\boldsymbol{k}, z_1)\tau_{L_3 L_4}(\boldsymbol{k}, z_2) - \tau_{L_1 L_2}(z_1)\tau_{L_3 L_4}(z_2) \quad (28)$$

$$\omega_{(L_1 L_4),(L_2,L_3)}(z_1, z_2) = \sum_\alpha c_\alpha x^\alpha_{L_1 L_2}(z_1) x^\alpha_{L_3 L_4}(z_2) \quad (29)$$

$$\tilde{J}^{\alpha\mu}_{L_4 L_1} = \sum_{LL'} \tilde{D}^\alpha_{L_4 L} J^{\alpha\mu}_{LL'} D^\alpha_{L' L_1}, 1 \le L_i \le (l_{\max} + 1)^2 \quad (30)$$

Note that these are fourth order tensors and we need to express them in terms of second order.

Vertex Corrections [Butler 1985]

The ω matrix can also be approximated as

$$\omega_{(L_1L_4),(L_2L_3)}(z_1, z_2) = \langle x_{L_1L_2}(z_1)x_{L_3L_4}(z_2)\rangle \approx \langle x_{L_1L_2}(z_1)\rangle\langle x_{L_3L_4}(z_2)\rangle = 0 \tag{31}$$

This results in $(1 - \chi\omega)^{-1} \approx 1$ - the vertex correction term gets neglected in this approximation. Physical intuition for this can be gained by looking at the Boltzmann equation

$$eEv_q^\nu \frac{\partial f}{\partial \epsilon_q} = \sum_{qq'} P_{qq'}(g_q^\nu - g_{q'}^\nu) \tag{32}$$

Ignoring vertex corrections is the same as ignoring the "scattering-in" term (second on the RHS).

We can combine two angular momentum indices into 1 in order to simplify calculations

$$\tilde{\sigma}^1(z_1, z_2) = -\frac{\hbar}{\pi\Omega} \sum_{\alpha\beta} c_\alpha c_\beta \tilde{J}^{\alpha\mu}_{K_1^T}(z_2, z_1) \left[(1 - \chi\omega)^{-1}\chi\right]_{K_1 K_2} \tilde{J}^{\beta\nu}_{K_2}(z_1, z_2)$$

where $K_1^T = (L_4 L_1), K_1 = (L_1 L_4), K_2 = (L_2 L_3)$. Now the χ and ω matrices are second order tensors

$$\chi_{(L_1 L_4)(L_2, L_3)} \equiv \chi_{K_1 K_2} \ , \ \omega_{(L_1 L_4),(L_2 L_3)} \equiv \omega_{K_1 K_2} \tag{33}$$

where

$$1 \leq K_i \leq (l_{\max} + 1)^4 \tag{34}$$

$$K_1 = (l_{\max} + 1)^2 (L_1 - 1) + L_4, \ K_2 = (l_{\max} + 1)^2 (L_2 - 1) + L_3 \tag{35}$$

CuZn Resistivity

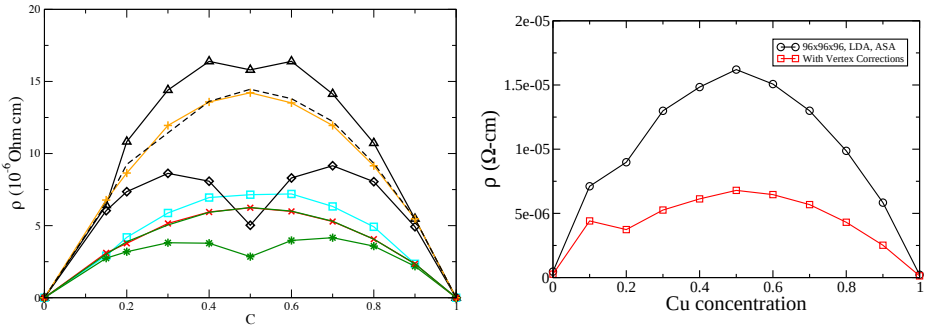
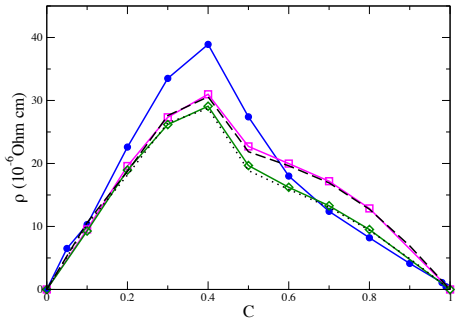


Figure 1: LHS is a numerically obtained plot from Tulip et al, 2008. The dashed black line is the single-site CPA resistivity. RHS is a MuST calculation, done at 96x96x96 Kpoints using LDA

AgPd Resistivity



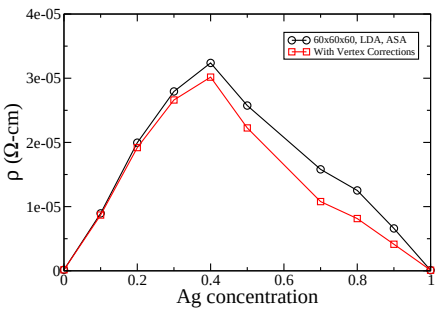


Figure 2: LHS is numerically obtained from Tulip et al, 2008 (except the blue line, which is experimental [Guenhault 1974]). The black dashed line is single-site resistivity. RHS is a MuST calculation at 60x60x60 Kpoints using LDA

AuPd Resistivity

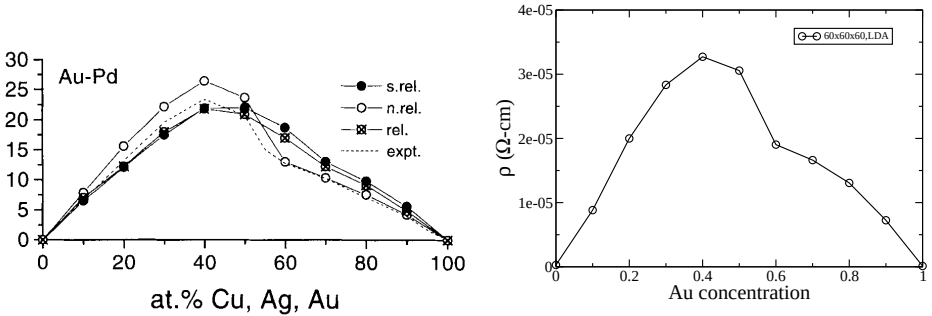


Figure 3: LHS is a plot taken from Banhart 1998. The line consisting of empty dots is the non-relativistic single-site CPA resistivity. RHS is a MuST calculation done at 60x60x60 Kpoints using LDA.

CuPd Resistivity

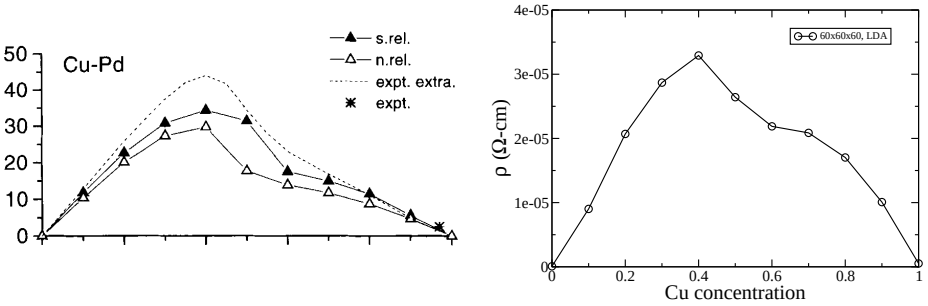


Figure 4: LHS is a plot taken from Banhart 1998. The line consisting of empty triangles is the non-relativistic single-site resistivity. RHS is a MuST calculation done at 60x60x60 Kpoints using LDA.

Cluster Averaged CPA*

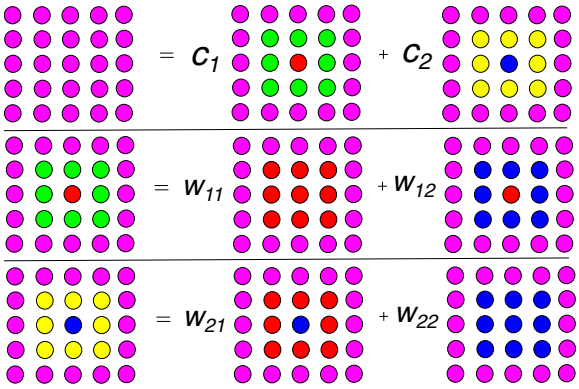
Embed an averaged cluster.

Cluster $\Rightarrow$ central atom + averaged neighbor atoms.

For central atom of species α,

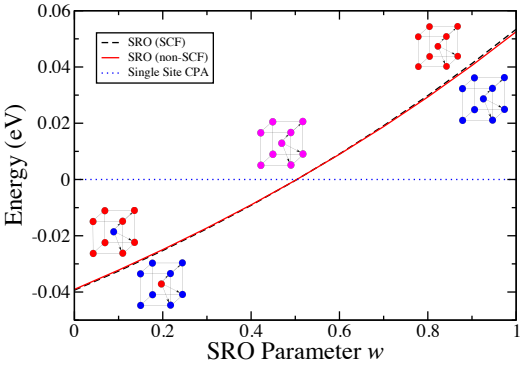
$$\bar{t}_\alpha(E) = \sum_\beta w_{\alpha\beta} t_\beta(E) \qquad (36)$$

$w_{\alpha\beta} \Rightarrow$ chemical SRO parameters



(* Alternative techniques include ECM-CPA, Non-Local CPA, and others)

Energy Analysis - CuZn



One independent SRO parameter $w = w_{\mathrm{Cu-Cu}}$. Parameter matrix

$$\boldsymbol{W} = \begin{bmatrix} w & 1-w \\ 1-w & w \end{bmatrix}. \quad (37)$$

Self-consistency does not significantly affect the energy in this case

CA-CPA Conductivity Expression

In this case, we can write $\tilde{\sigma} = \tilde{\sigma}^0 + \tilde{\sigma}^1$, where

$$\tilde{\sigma}^1(z_1, z_2) = -\frac{1}{\pi\Omega} \sum_{\alpha\beta, lmzr} c_\alpha c_\beta \tilde{J}^{\alpha\mu, ml}_{L_4 L_1}(z_2, z_1) \left[(1 - \chi\omega)^{-1}\chi\right]^{lmzr}_{L_1 L_4 L_2 L_3} \tilde{J}^{\beta\nu, zr}_{L_2 L_3}(z_1, z_2) \quad (38)$$

where

$$\chi^{lmzr}_{L_1 L_4, L_2 L_3}(z_1, z_2) = \frac{1}{\Omega_{\mathrm{BZ}}} \int d^3\boldsymbol{k}\ \tau_{L_1 L_2}(\boldsymbol{k}, z_1)\tau_{L_3 L_4}(\boldsymbol{k}, z_2) e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_l - \boldsymbol{R}_z + \boldsymbol{R}_r - \boldsymbol{R}_m)} - \tau^{lz}_{L_1 L_2}\tau^{rm}_{L_3 L_4}$$

$$\omega^{lmzr}_{L_1 L_4, L_2 L_3}(z_1, z_2) = \sum_\alpha c_\alpha x^{\alpha, lz}_{L_1 L_4}(z_1) x^{\alpha, rm}_{L_2 L_3}(z_2) \quad (39)$$

$$\tilde{J}^{\alpha\mu, ml}_{L_4 L_1}(z_1, z_2) = \sum_{L, L'} \tilde{D}^{\alpha, m0}_{L_4 L} J^{\alpha\mu}_{LL'}(z_1, z_2) D^{\alpha, 0l}_{L' L_1} \quad (40)$$

$$1 \le L_i \le (l_{\max} + 1)^2, 1 \le l, m, z, r \le N_\Gamma \quad (41)$$

The expression can be simplified into

$$\tilde{\sigma}^1(z_1,z_2) = -\frac{1}{\pi\Omega}\sum_{\alpha\beta} c_\alpha c_\beta \tilde{J}^{\alpha\mu}_{CK_1^T}(z_1,z_2)\left[(1-\chi\omega)^{-1}\chi\right]_{CK_1CK_2}\tilde{J}^{\beta\nu}_{CK_2}(z_1,z_2) \tag{42}$$

where $CK_1^T = ((m,l),(L_4L_1))$, $CK_1 = ((l,m),(L_1,L_4))$, $CK_2 = ((z,r),(L_2L_3))$

$$\chi^{lmzr}_{L_1L_4,L_2L_3} \equiv \chi_{CK_1,CK_2},\ \omega^{lmzr}_{L_1L_4,L_2L_3} \equiv \omega_{CK_1,CK_2} \tag{43}$$

The relationship between the two index styles are

$$CK_1 = (l_{\max}+1)^4(N_\Gamma(l-1)+m-1)+(l_{\max}+1)^2(L_1-1)+L_4 \tag{44}$$

$$CK_2 = (l_{\max}+1)^4(N_\Gamma(z-1)+r-1)+(l_{\max}+1)^2(L_2-1)+L_3 \tag{45}$$

$$1 \le CK_i \le N_\Gamma^2(l_{\max}+1)^4 \tag{46}$$

Comparison with NL-CPA conductivity expression

The conductivity expression for NL-CPA (which is another cluster based technique to incorporate SRO) is very similar to our expression

$$\chi^{I,K,L,J} = \frac{1}{\Omega_{BZ}} \sum_{\mathbf{K}_n} \int_{\Omega_t} d\tilde{\mathbf{k}} \hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}}) \times e^{i\mathbf{K}_n\cdot(\mathbf{R}_I-\mathbf{R}_K)} \hat{\tau}(\mathbf{K}_n;\tilde{\mathbf{k}}) e^{i\mathbf{K}_n\cdot(\mathbf{R}_L-\mathbf{R}_J)} - \hat{\tau}^{IK}\hat{\tau}^{LJ}. \tag{54}$$

Here, $L_{IJ}(0)$ is extracted by inverting a super matrix $[1 - w\chi]$, which has a dimension $N_c \times N_c \times N_\Lambda \times N_\Lambda$ (N_Λ specifying the number of angular momentum quantum numbers).

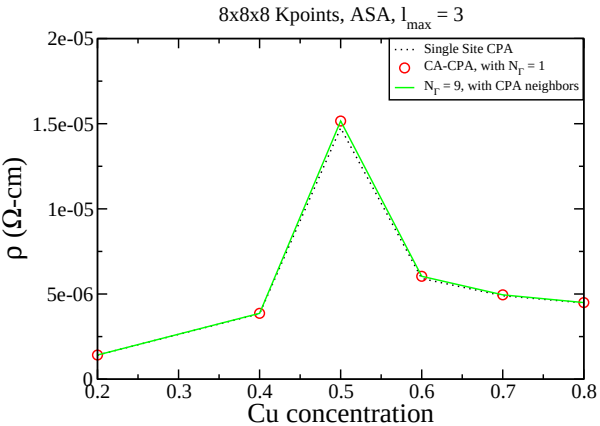
By comparing Eqs. (46) and (47) and using the definition $L^C_{IJ;\nu}=0$, the second term on the right hand side of Eq. (46) vanishes. We thus find the intercluster contribution to the conductivity to be

$$\tilde{\sigma}^1_{\mu\nu} = -\frac{4m^2}{\pi\hbar^3\Omega} \sum_{I,J,K,L} \sum_{\Lambda_1,\Lambda_2,\Lambda_3,\Lambda_4} J_{LI,\Lambda_1,\Lambda_2;\mu}([1 - \chi(\mathbf{0})w]^{-1}\chi(\mathbf{0}))^{IJKL}_{\Lambda_1,\Lambda_3,\Lambda_4,\Lambda_2} J_{JK,\Lambda_3,\Lambda_4;\nu}, \tag{55}$$

Sanity Check - CuZn

1. Set $N_\Gamma = 1$ and compare with single-site CPA
2. Set all neighbor atoms as CPA and compare with $N_\Gamma = 1$ case.

For further testing, we would want to set $w_{\alpha\beta} = c_\beta$ and see if it matches CPA conductivity



Computational Limitations

The SRO calculation is significantly more time consuming

CPA Calculation at 8x8x8	SRO Calculation at 8x8x8
$\sim$ 30 seconds	$\sim$ 14 hours

This is a problem as we need to use atleast a million kpoints to get convergent conductivity values for CuZn.
Additionally, memory usage is very high for SRO calculation. For $N_\Gamma = 9$, the program requires about 80 GB of memory (and 360 GB for $N_\Gamma = 13$, which is the first neighbor cluster for an FCC system)

Possible Approaches

1. Reduce cluster size - use $N_\Gamma = 3$ or 4, instead of using the entire first neighbor shell
2. Identify systems that need fewer K-points to get a converged conductivity value
3. There are many independent loops and can be parallelized to gain speed. Additionally, the large arrays can be broken up into smaller segments and stored on different processors.

Summary

1. The Kubo-Greenwood equation can be expressed in terms of Green's Functions and MS Path Operators.
2. The KG conductivity equation can be adapted to the CPA formalism.
3. CA-CPA can deal with SRO within CPA.
4. KG conductivity can be adapted to CA-CPA, but there are some computational limitations.

In the future, we plan to implement relativistic versions of the conductivity expressions, so that we can study spin transport (and exotic properties like anomalous hall effect)

Most of the single-site CPA conductivity theory comes from the following paper - W. H. Butler, Phys. Rev. B 31, 3260 (1985)

Thank you!

Any questions?

Appendix A: Kubo-Greenwood using Green's Functions

Starting with Kubo-Greenwood

$$\sigma_{\mu\nu}(\epsilon_F) = \frac{\pi\hbar}{N\Omega}\left\langle \sum_{\alpha}\langle\alpha|j_\mu\left(\sum_{\alpha'}|\alpha'\rangle\langle\alpha'|\delta(\epsilon_F-\epsilon_{\alpha'})\right)j_\nu\left[|\alpha\rangle\delta(\epsilon_F-\epsilon_\alpha)\right]\right\rangle \tag{47}$$

Simplifying

$$\sigma_{\mu\nu}(\epsilon_F) = \frac{\hbar}{\pi N\Omega}\lim_{\delta\to 0}\left\langle \sum_{\alpha}\langle\alpha|j_\mu \mathrm{Im}G(\epsilon_F+i\delta)j_\nu \mathrm{Im}G(\epsilon_F+i\delta)|\alpha\rangle\right\rangle \tag{48}$$

Replacing the sum with trace, we can write

$$\sigma_{\mu\nu}(\epsilon_F) = \frac{\hbar}{\pi N\Omega}\lim_{\delta\to 0}\mathrm{Tr}\left\langle j_\mu \mathrm{Im}G(\epsilon_F+i\delta)j_\nu \mathrm{Im}G(\epsilon_F+i\delta)\right\rangle \tag{49}$$

Appendix C: Species τ matrix (Obtaining CPA medium)

Previously it was mentioned that for the single-site approximation

$$\tau^{nn}_{\mathrm{CPA}}(\epsilon) = \sum_{\alpha} c_\alpha \tau^{nn}_{\alpha} \tag{50}$$

For a CPA medium with a single substitutional defect of species α, the τ-matrix can be written as

$$\tau^{nn}_{\alpha}(\epsilon) = \left[1 + \tau^{nn}_{\mathrm{CPA}}(\epsilon)(t^{-1}_{\alpha}(\epsilon) - t^{-1}_{\mathrm{CPA}}(\epsilon))\right]^{-1} \tau^{nn}_{\mathrm{CPA}}(\epsilon) \tag{51}$$

The CPA τ-matrix can be written as a fourier transform

$$\tau^{nm}_{\mathrm{CPA}}(\epsilon) = \frac{1}{\Omega_{\mathrm{BZ}}} \int d^3\boldsymbol{k} \left[t^{-1}_{\mathrm{CPA}}(\epsilon) - g(\boldsymbol{k}, \epsilon)\right]^{-1} e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_n - \boldsymbol{R}_m)} \tag{52}$$

(50), (51) and (52) can be solved self-consistently to get the single-site CPA medium

Appendix D: Performing CA-CPA calculations

The averaged cluster can be represented using block T-matrix. If the central atom is of species α, the matrices $\boldsymbol{T}_\alpha$ and $\boldsymbol{T}_{\mathrm{CPA}}$ is given by

$$\boldsymbol{T}_{\mathrm{CPA}}(E) = \begin{pmatrix} t_{\mathrm{CPA}}(E) & 0 & 0 & 0 & \cdots & 0 \\ 0 & t_{\mathrm{CPA}}(E) & 0 & 0 & \cdots & 0 \\ \vdots & 0 & t_{\mathrm{CPA}}(E) & 0 & \cdots & 0 \\ \vdots & \vdots & 0 & \ddots & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & t_{\mathrm{CPA}}(E) \end{pmatrix} \quad \boldsymbol{T}_\alpha(E) = \begin{pmatrix} \bar{t}_\alpha(E) & 0 & 0 & 0 & 0 & 0 & \cdots \\ 0 & \ddots & \ddots & \cdots & \cdots & \cdots & 0 \\ \vdots & \ddots & \bar{t}_\alpha(E) & 0 & \cdots & \cdots & 0 \\ \vdots & \vdots & 0 & \underline{t_\alpha(E)} & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & 0 & \bar{t}_\alpha(E) & \ddots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \bar{t}_\alpha(E) \end{pmatrix}$$

The τ-matrix for a cluster embedded CPA medium is given by

$$\tau^{nn}_{\mathrm{CPA}}(\epsilon) = \left(\left[1 + \boldsymbol{\tau}_{\mathrm{CPA}}(\epsilon)(\boldsymbol{T}^{-1}_\alpha(\epsilon) - \boldsymbol{T}^{-1}_{\mathrm{CPA}}(\epsilon)) \right]^{-1} \boldsymbol{\tau}_{\mathrm{CPA}}(\epsilon) \right)^{nn} \tag{53}$$

(53), (52) and (51) can be combined to form a self-consistent CA-CPA algorithm

Appendix E: Boltzmann Transport Equation [Kittel, Appendix F]

If the system has a distribution function $f_0(t, \boldsymbol{r}, \boldsymbol{p})$, and due to collisions, becomes $f(t + dt, \boldsymbol{r} + d\boldsymbol{r}, \boldsymbol{p} + d\boldsymbol{p})$, then

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \nabla_r f + \boldsymbol{a} \cdot \nabla_v f \approx -\frac{f - f_0}{\tau} \tag{54}$$

This is the Boltzmann Transport Equation. For a concentration gradient along i, we can write, in steady-state,

$$f = f_0 - \tau v_i \frac{\partial f}{\partial r_i} \approx f_0 - \tau v_i \frac{\partial f_0}{\partial r_i} \approx f_0 - \tau v_i \frac{\partial f_0}{\partial \mu} \frac{\partial \mu}{\partial r_i} \tag{55}$$

The particle flux density in direction j is given by

$$J_j = \int_0^\infty v_j f D(\epsilon) d\epsilon \approx -\frac{\partial \mu}{\partial r_i} \int_0^\infty \tau v_i v_j \frac{\partial f_0}{\partial \mu} D(\epsilon) d\epsilon \tag{56}$$

Appendix F: Simple Case - Drude Model

Consider $f_0 = e^{-\beta(\epsilon-\mu)}$, $i = j = x$, and τ constant, then current is given by

$$J_x = e\tau\beta\frac{\partial\mu}{\partial x}\int_0^\infty v_x^2 f_0 D(\epsilon)d\epsilon = e\tau\beta\frac{\partial\mu}{\partial x}\langle v_x^2\rangle \tag{57}$$

Here we want $\langle v_x^2\rangle$ for all particles in unit volume, so using Equipartition,

$$J_x = \frac{ne\tau}{m}\frac{\partial\mu}{\partial x} = \frac{ne^2\tau}{m}E = \sigma E \tag{58}$$

where σ is the Drude model conductivity. Here, to get real system conductivity, we need to account for τ not being constant, and $f_0 \equiv$ Fermi-Dirac distribution, in which case

$$J_x = eE\int_0^\infty \tau v_x^2\delta(\epsilon-\epsilon_F)D(\epsilon_F)d\epsilon \tag{59}$$

Appendix G: Drawback of this approach

To calculate conductivity using Boltzmann equation, we need the band structure $\epsilon(\boldsymbol{k})$. But for highly random alloys, the individual bands may not be well defined.

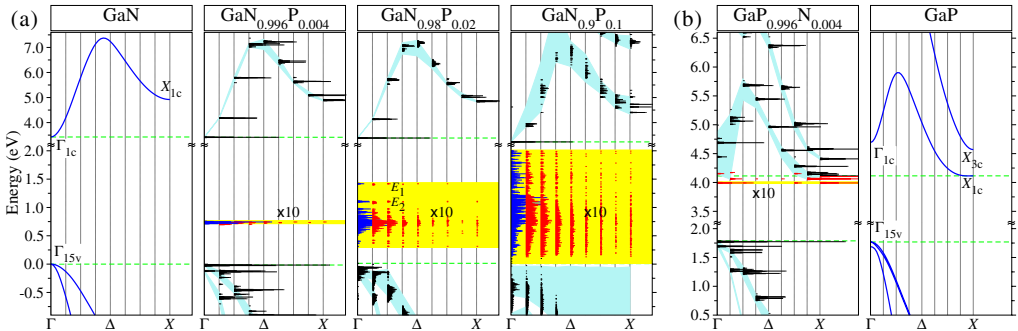


Figure 5: Random Ga(N, P) EBS taken from Popecu and Zunger, PRL 104, 236403 (2010)

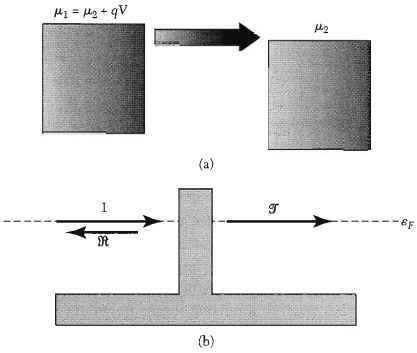


Figure 6: Applying a potential V

Consider a system where $L_x, L_y \ll L_z$. A potential ΔV has been applied to the system. The current can then be written as

$$I = e\Delta n v = e^2 \underbrace{D_R}_{\sim 1/\sqrt{\epsilon}} Vv = \frac{2e^2}{h} V \qquad (60)$$

The conductance for this system is constant, if we assume perfect transmission. Otherwise, we will have

$$G = \frac{2e^2}{h} \sum_{ij} T_{ij} \qquad (61)$$

where i, j represent the channels, or eigenstates