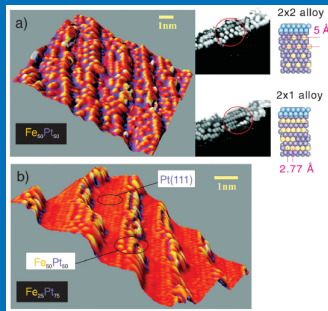
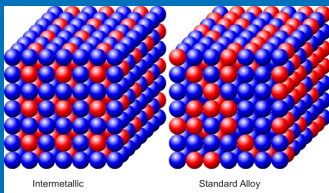


# Green Function DFT for alloys



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# Green Functions and Scattering Theory

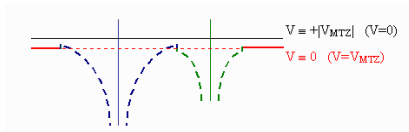
e.g. H.Ebert et al. Reports on Progress in Physics, **74**, 096501, (2011)

- DFT needs to solve the Kohn-Sham equation  $(-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}; [n]))\phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$  where  $V(\mathbf{r}; [n])$  is the effective potential.
- This can be framed in terms of the single electron Green function  $G(\mathbf{r}, \mathbf{r}'; \varepsilon)$ .
- Defined by  $(\varepsilon + \frac{\hbar^2 \nabla^2}{2m} - V(\mathbf{r}; [n]))G(\mathbf{r}, \mathbf{r}'; \varepsilon) = \delta(\mathbf{r} - \mathbf{r}')$ .
- Observables can be calculated from  $G$ , e.g. the electron density  $n(\mathbf{r}) = -\frac{1}{\pi} \text{Im} \int^{\varepsilon_F} G(\mathbf{r}, \mathbf{r}; \varepsilon) d\varepsilon$ .
- In terms of electron states

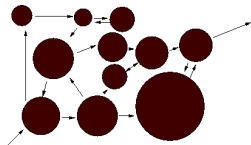
$$G(\mathbf{r}, \mathbf{r}'; \varepsilon) = \sum_i \frac{\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')}{(\varepsilon - \varepsilon_i)}$$

# Potentials and Scattering

- Effective Kohn-Sham DFT potentials in a solid, nuclear Coulombic and electronic screening contribution.



- Muffin-tin approximation



# Kohn-Sham Eqs. of DFT in terms of operators

- Begin with  $(\varepsilon - \hat{H})|\phi\rangle = 0$  where  $\hat{H} = \frac{-\hbar^2 \nabla^2}{2m} + V(\mathbf{r})$ . The Green function operator corresponding to  $\hat{H}$  is  $\hat{G}(\varepsilon) = (\varepsilon - \hat{H})^{-1}$  where  $\varepsilon$  has a small imaginary part.
- With no potential and so for the free electron  $(\varepsilon - \hat{H}_0)|\psi\rangle = 0$ ,  $\hat{G}_0 = (\varepsilon - \hat{H}_0)^{-1}$ .
- Get a Dyson equation (dropping hats)  
 $G = G_0 + G_0 V G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + \dots$ .
- In terms of the transition operator  $T$  such that  $T G_0 = V G$ ,  
 $G = G_0 + G_0 T G_0$ .
- $T$  describes all possible scattering in the system as it relates the free-electron  $G_0$  to the full scattering  $G$ . See  $|\phi\rangle = |\psi\rangle + G_0 V |\phi\rangle$  or  $|\phi\rangle = |\psi\rangle + G_0 T |\psi\rangle$ , (Lippmann-Schwinger Eq. which relates outgoing scattered wave to the incoming wave).

# Single site scattering

- $\phi(\mathbf{r}) = A \left( e^{i\mathbf{k}\cdot\mathbf{r}} + f(\theta, \phi) \frac{e^{ikr}}{r} \right)$
- $\phi(\mathbf{r}) = \sum_{L=l,m} a_L(\varepsilon) R_l(\varepsilon, r) Y_L(\hat{r})$  where  $R_l(\varepsilon, r)$  is the solution of the radial Schrödinger equation and  $Y_L(\hat{r})$  is a spherical harmonic ( $Y_L(\hat{r}) = Y_{l,m}(\theta, \phi)$ ).
- For  $r \rightarrow \infty$ ,  $R_l(\varepsilon, r) = \frac{1}{\sqrt{\varepsilon r}} \sin[\sqrt{\varepsilon} r - \frac{l\pi}{2} + \delta_l(\varepsilon)]$  where  $\delta_l(\varepsilon)$  is a **scattering phase shift** and leads to  $t^i$ .

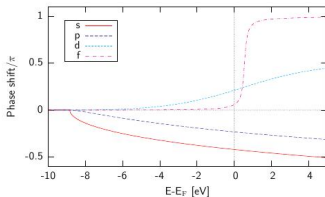
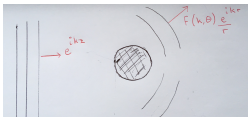


Figure 4.2: Phase shifts of electron states in Ce, obtained from LDA calculation.

- Localised electronic states are characterised by phase shifts with very sharp resonances, whereas band-like states have more slowly varying phase shifts.

# Multiple scattering and KKR formalism

- Multiple scattering theory describes a problem in terms of scattering properties of the individual sites.

- Some rearranging:

$$T = V + V G_0 T = \sum_i (V_i + V_i G_0 T) = \sum_i T^i \text{ with}$$
$$T^i = V_i + V_i G_0 T = V_i + V_i G_0^{ii} T^i + \sum_{j \neq i} V_i G_0^{ij} T^j.$$

- For a single potential, the transition operator

$$t^i = V_i + V_i G_0^{ii} t^i \text{ and we can write } T^i \text{ in terms of } t^i \text{'s i.e.}$$
$$T^i = t^i + \sum_{j \neq i} t^i G_0^{ij} T^j.$$

- If we write  $T = \sum_i T^i = \sum_i \sum_j \tau^{ij}$  we get

$$\tau^{ij} = t^i \delta_{ij} + \sum_{k \neq i} t^i G_0^{ik} \tau^{kj} =$$
$$t^i \delta_{ij} + \sum_{k \neq i} t^i G_0^{ik} t^k \delta_{kj} + \sum_{k \neq i} \sum_{l \neq k} t^i G_0^{ik} t^k G_0^{kl} t^l \delta_{lj} + \dots$$

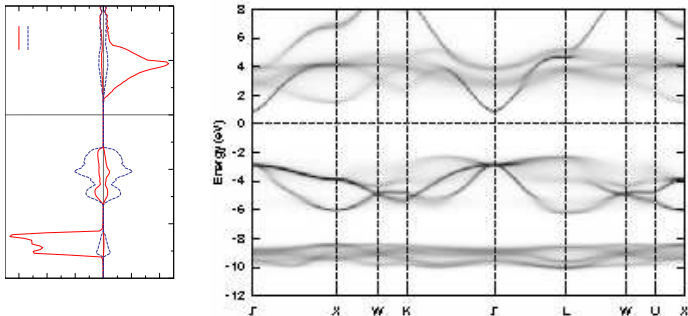
- $\tau^{ij}$  is the scattering path operator. It gives the scattered wave from site  $j$  owing to a wave incident on site  $i$ , taking into account all possible scatterings in between.

# Calculating properties from the KKR

- Inside the muffin-tin sphere the radial equation is solved numerically. At the muffin-tin boundary the solution matches to a combination of free-electron solutions and fixes the phase shifts and single site t-operator. Between sites electron propagates freely.
- Green function for DFT, spectra, response functions etc.  
$$G(\mathbf{r}, \mathbf{r}', \varepsilon) = Z^i(\mathbf{r}_i, \varepsilon) \tau^{ij}(\varepsilon) Z^j(\mathbf{r}'_j, \varepsilon) - \delta_{ij} Z^i(\mathbf{r}_{<}, \varepsilon) J^j(\mathbf{r}_{>}, \varepsilon)$$
where  $Z^n$  and  $J^n$  are solutions to the Schrödinger equation for a single site potential  $V_n$ . ( $\mathbf{r} = \mathbf{r}_i + \mathbf{R}_i$ ,  $\mathbf{r}' = \mathbf{r}'_j + \mathbf{R}_j$ ).
- Density for DFT:  $n(\mathbf{r}) = -\frac{1}{\pi} \int^{\varepsilon_F} \text{Im} G(\mathbf{r}, \mathbf{r}, \varepsilon) d\varepsilon$ .
- Density of states:  $n(\varepsilon) = -\frac{1}{\pi} \int \text{Im} G(\mathbf{r}, \mathbf{r}, \varepsilon) d\mathbf{r}$ .
- Spectral function:  
$$A_B(\mathbf{k}, \varepsilon) = -\frac{1}{\pi} \text{Im} \sum_{nm} e^{i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} \int d\mathbf{r} G(\mathbf{r} + \mathbf{R}_n, \mathbf{r} + \mathbf{R}_m, \varepsilon).$$
$$\rightsquigarrow A_B(\mathbf{k}, \varepsilon) = \sum_n \delta(\varepsilon - \varepsilon_n(\mathbf{k})).$$
In disordered systems peaks broaden but their positions give an effective band structure, with their width in energy interpreted as an inverse lifetime.

# Electronic structure of a paramagnetic transition metal oxide

The electronic structure for **MnO** in its paramagnetic (DLM) state. The loci of the peaks of the Bloch spectral function with the shading showing the spin fluctuation disorder broadening of these quasi-particle peaks.

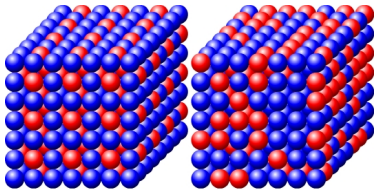


DOS for **MnO** on **Mn** and **O** sites (dashed). The left (right) panel shows the DOS associated with electrons with spins parallel (anti-parallel) to the local moment on the site. Note the sizeable gap of the paramagnetic state.

I.D.Hughes *et al.*, *New J.Phys.*10, 063010, (2008)



# Alloy Solid Solutions and Intermetallics



Intermetallic

Standard Alloy

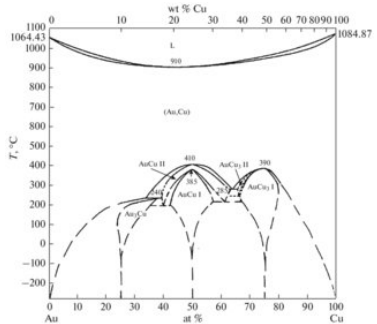
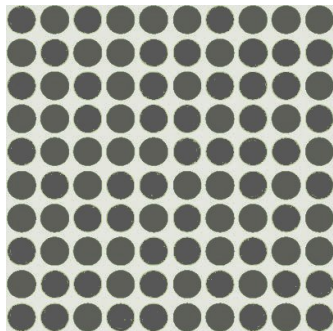
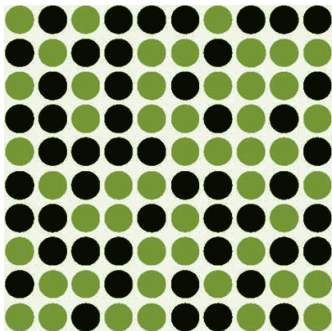


Fig. 1. Au-Cu phase diagram. Solid lines are borrowed from [12]; dashed lines are extrapolations.

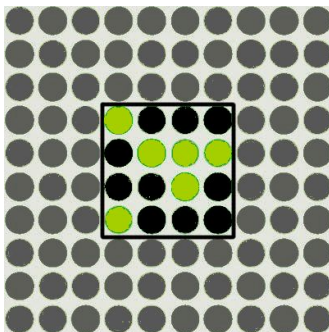
- Mixing of 2 metals (Hume Rothery Rules)
  - band filling (av. no. of electrons/atom).
  - atomic size difference.
  - electronegativity - arrangement of charge around a nucleus.
- Solid solution - each site with  $x(1-x)$  chance of A (B) atom.
- Ordered arrangement - intermetallic. Affects mechanical, electrical, thermal properties etc.

# Electrons and Disorder - An Effective Lattice



- $\langle G^{ij} \rangle = G_0^{ij} + \sum_{kl} G_0^{ik} \Xi^{kl} \langle G^{lj} \rangle$
- $\bar{G}(\mathbf{k}) = \frac{1}{N} \sum_j \langle G^{ij} \rangle e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} = (G_0^{-1}(\mathbf{k}) - \Xi(\mathbf{k}))^{-1}$
- $\Xi(\mathbf{k})$  is a *self energy*.

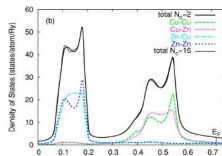
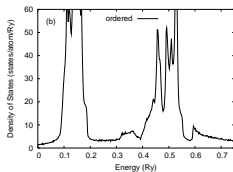
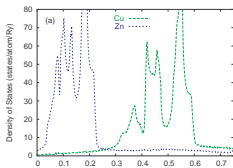
# Cluster Approximation



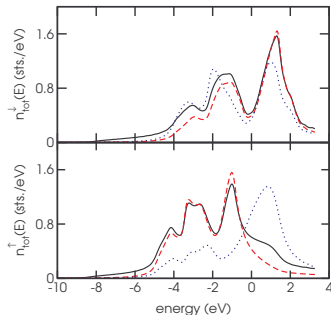
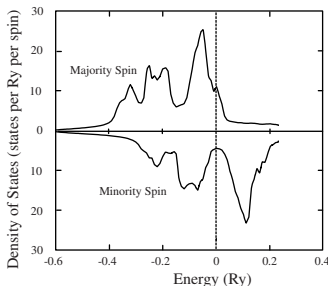
- $G_{IJ}^\eta = [\underline{G}^{0,-1} + \Xi - \underline{V}^\eta]_{IJ}^{-1}$
- $\sum_\eta P(\eta) G_{IJ}^\eta = \hat{G}_{IJ} \approx \langle G_{IJ} \rangle$
- $\hat{G}_{IJ} = \frac{1}{\Omega_{BZ}} \sum_{\mathbf{K}_n} \int [G^0(\mathbf{k}) - \Xi(\mathbf{K}_n)]^{-1} e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} d\mathbf{k}_n.$

# Electronic structure of disordered alloys - examples

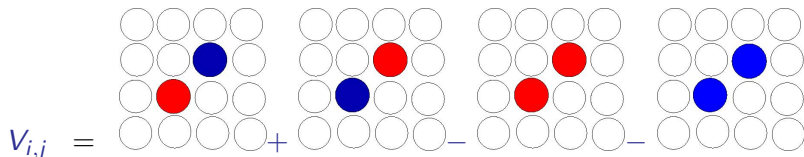
- Copper-Zinc alloy: pure **Cu** and **Zn**, B2-Cu-Zn, **Cu<sub>50</sub> Zn<sub>50</sub>**.



- Ferromagnetic b.c.c. **Fe** and **Fe<sub>80</sub>Cr<sub>20</sub>** alloy: spin-polarised DOS.



# Atom-atom interactions



- Atom swapping using  $V_{i,j}$ 's, and more complex cluster interactions. Effect of magnetism. Temperature dependence.
- Simulate alloy ordering, both long and short-ranged. Also defect energetics, elastic properties.

