



# The Korringa-Kohn-Rostoker (KKR) Green function method

Phivos Mavropoulos

*Department of Physics*

*National and Kapodistrian University of Athens*

*Greece*

# Historical / general

Wave function method: Korringa (1947), Kohn and Rostoker (1954)

Green function method: Dupree (1961), Morgan (1966), Beeby (1967)

Mainly DFT method

Milestone:

Moruzzi, Janak and Williams (1978), *Calculated electronic properties of metals*

Worldwide development over the years (codes from several groups with different emphasis).

Oak Ridge, Bristol, München, Jülich, Dresden/Halle, Osaka, Budapest, Wien, ...

Emphasis: Magnetism (practically all groups),  
defects in crystals, disorder (KKR-CPA), transport (resistivity, Hall effects),  
many-body effects beyond DFT (KKR+DMFT), photoemission, spin dynamics,  
spin excitations, surfaces, large DFT-calculations (thousands of atoms),...

Good review: Ebert et al., Rep. Prog. Phys. 74 (2011) 096501

<http://stacks.iop.org/RoPP/74/096501>

Rydberg atomic units used here

$$\hbar = 1$$

$$m_e = \frac{1}{2}$$

$$e^2 = 2$$

# Green functions



# Green function: Definition

Time evolution operator

$$\psi(t) = e^{-iH(t-t')}\psi(t') \quad \longleftrightarrow$$

Retarded and advanced Green function

$$\begin{aligned} \psi(t) &= iG^R(t-t')\psi(t') & t' < t \\ \psi(t) &= -iG^A(t-t')\psi(t') & t < t' \end{aligned}$$

Fourier transform  $\rightarrow$  energy-dependent Green function:

$$G(E) = \int_{-\infty}^{\infty} G(t) e^{i(E+i\varepsilon)t} dt = (E + i\varepsilon - H)^{-1}$$

Spectral representation via eigenfunctions-eigenvalues:

$$G(E) = \sum_i \frac{|\psi_i\rangle\langle\psi_i|}{E - \epsilon_i}$$

$G(E)$  can be defined for complex  $E$   
(analytical continuation)

# Properties of the Green function I:

## Analytical properties

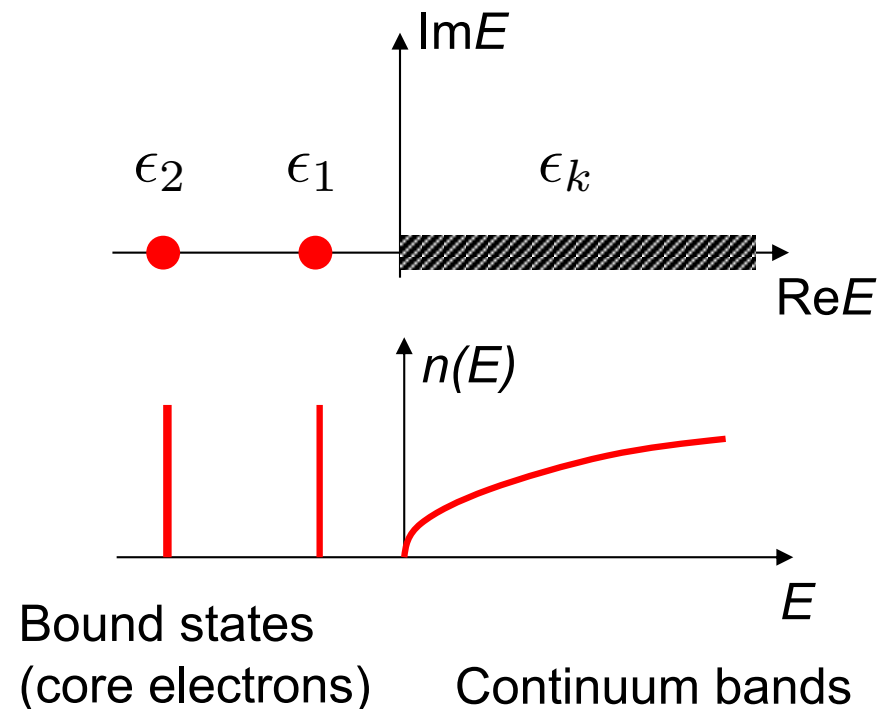
Analyticity in the physical sheet  $\text{Im}\sqrt{E} > 0$

Poles at the eigenvalues  $\epsilon_i$  and branch cut at the continuum  $\epsilon_k$

Find eigenvalues of  $H \Leftrightarrow$   
Locate singularities of  $G(E)$

Density of states:

$$n(E) = -\frac{1}{\pi} \text{Im Tr } G(E)$$



# Properties of the Green function II:

## Connection to physical properties

Definition:  $(E - H) G(E) = 1 \implies$

Real-space representation:  $(E - H) G(\vec{r}, \vec{r}'; E) = \delta(\vec{r} - \vec{r}')$

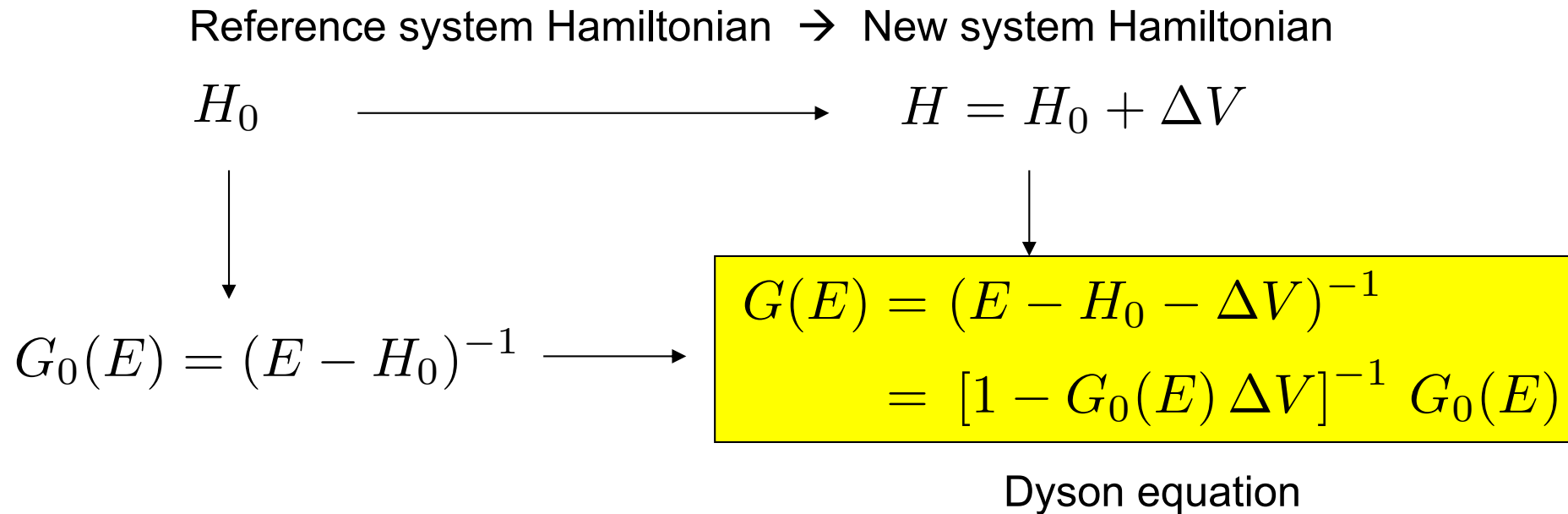
Expectation values of observables:

$$\begin{aligned}\langle \mathcal{O} \rangle &= -\frac{1}{\pi} \text{Im} \text{Tr} \int^{E_F} dE \mathcal{O} G(E) && \text{(General expression with Tr)} \\ &= -\frac{1}{\pi} \text{Im} \int^{E_F} dE \int d^3r d^3r' \mathcal{O}(\vec{r}, \vec{r}') G(\vec{r}', \vec{r}; E) && \text{(Real-space representation)}\end{aligned}$$

Charge density: 
$$\rho(\vec{r}) = -\frac{1}{\pi} \text{Im} \int^{E_F} dE G(\vec{r}, \vec{r}; E)$$

# Properties of the Green function III:

## Dyson equation



Example:

Free electrons  $\rightarrow$  Electrons in a crystal

$$H_0 = -\nabla^2 \quad H_{\text{cryst}} = H_0 + V_{\text{cryst}}(\vec{r})$$

Electrons in a crystal  $\rightarrow$  Electrons in a crystal + impurity

$$H_0 = H_{\text{cryst}} \quad H = H_{\text{cryst}} + \Delta V_{\text{imp}}$$

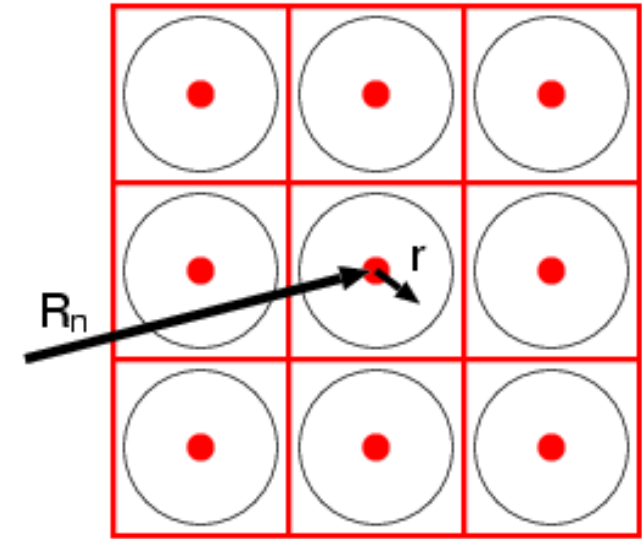
# Green functions in KKR

# Concept of KKR

Tessellation of space in atomic cells

Local scattering solution of Schrödinger's equation in each cell (spherical wave representation)

Multiple scattering of waves among atoms  
→ Coupling of local solutions



Starting point:

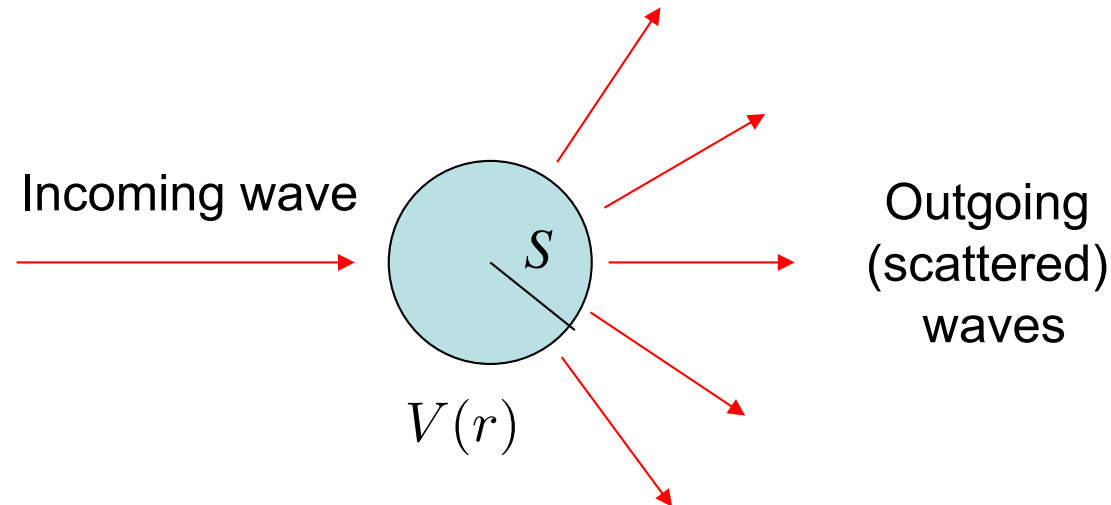
Free electron wave function

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} = 4\pi \sum_L i^l j_l(kr) Y_L(\hat{k}) Y_L(\hat{r}) \quad L \equiv (l, m)$$

Free electron Green function

$$g(\vec{r}, \vec{r}'; E) = -\frac{1}{4\pi} \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} = -i\sqrt{E} \sum_L j_l(r_{<}; E) h_l(r_{>}; E) Y_L(\vec{r}) Y_L(\vec{r}')$$

# Scattering from a single potential



Green  
function:

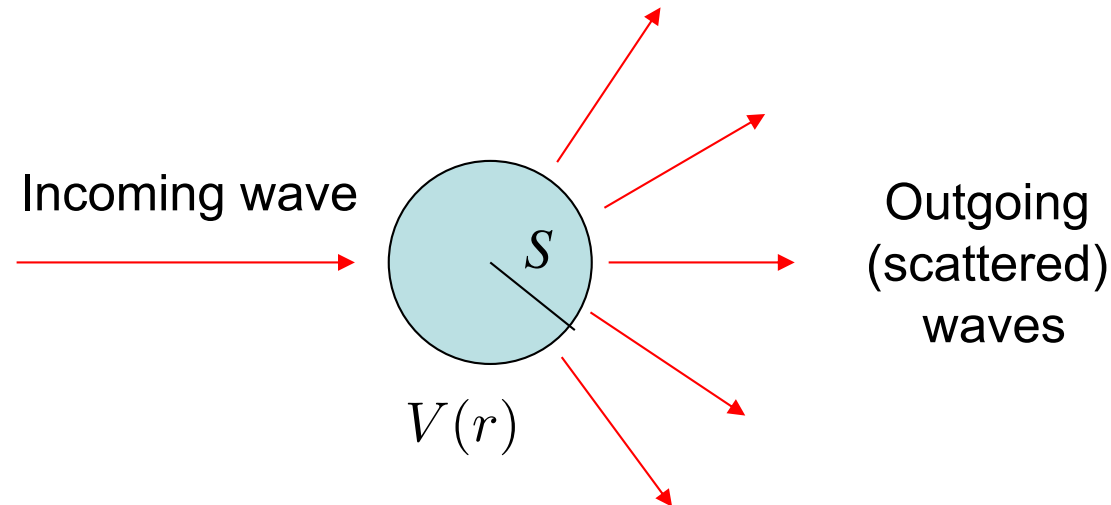
$$G(\vec{r}, \vec{r}'; E) = -i\sqrt{E} \sum_L \underbrace{R_l(r_{<}; E)}_{\substack{\text{Regular} \\ \text{solution} \\ \sim r^l}} \underbrace{H_l(r_{>}; E)}_{\substack{\text{Irregular} \\ \text{solution} \\ \sim 1/r^{l+1}}} Y_L(\vec{r}) Y_L(\vec{r}')$$

$L := (l, m)$

Free-space  
Green  
function:

$$g(\vec{r}, \vec{r}'; E) = -i\sqrt{E} \sum_L \underbrace{j_l(r_{<}; E)}_{\substack{\text{Bessel} \\ \text{function}}} \underbrace{h_l(r_{>}; E)}_{\substack{\text{Hankel} \\ \text{function}}} Y_L(\vec{r}) Y_L(\vec{r}')$$

# Scattering from a single potential



Green function:

$$G(\vec{r}, \vec{r}'; E) = -i\sqrt{E} \sum_L \underbrace{R_l(r_{<}; E)}_{\text{Regular solution}} \underbrace{H_l(r_{>}; E)}_{\text{Irregular solution}} Y_L(\vec{r}) Y_L(\vec{r}')$$

$$t_l(E) = \int_{\text{cell}} d^3r j_l(\sqrt{E}r) V(r) R_l(r; E)$$

Regular solution

Irregular solution

$$L := (l, m)$$

Free-space Green function:

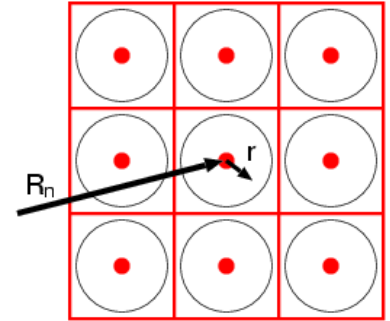
$$g(\vec{r}, \vec{r}'; E) = -i\sqrt{E} \sum_L \underbrace{j_l(r_{<}; E)}_{\text{Bessel function}} \underbrace{h_l(r_{>}; E)}_{\text{Hankel function}} Y_L(\vec{r}) Y_L(\vec{r}')$$



# KKR representation of GF

Crystal electron Green function:

$$(-\nabla^2 + V^n(\vec{r}) - E) G(\vec{r} + \vec{R}^n, \vec{r}' + \vec{R}^{n'}; E) = -\delta_{nn'} \delta(\vec{r} - \vec{r}')$$



Expanded as:

$$G(\vec{r} + \vec{R}^n, \vec{r}' + \vec{R}^{n'}; E) =$$

$$-i\sqrt{E} \sum_L R_L^n(\vec{r}_{<}; E) H_L^n(\vec{r}_{>}; E) \delta_{nn'}$$

“Single-site”

(atom in constant potential)

$$+ \sum_{LL'} R_L^n(\vec{r}; E) G_{LL'}^{nn'}(E) R_{L'}^{n'}(\vec{r}'; E)$$

“Back-scattering”

(contribution of all other atoms)

Structural Green functions

Free electrons:

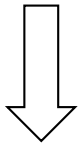
$$g = -i\sqrt{E} \sum_L j_L^n(\vec{r}_{<}; E) h_L^n(\vec{r}_{>}; E) \delta_{nn'}$$

$$+ \sum_{LL'} j_L^n(\vec{r}; E) g_{LL'}^{nn'}(E) j_{L'}^{n'}(\vec{r}'; E)$$

# Algebraic Dyson equation

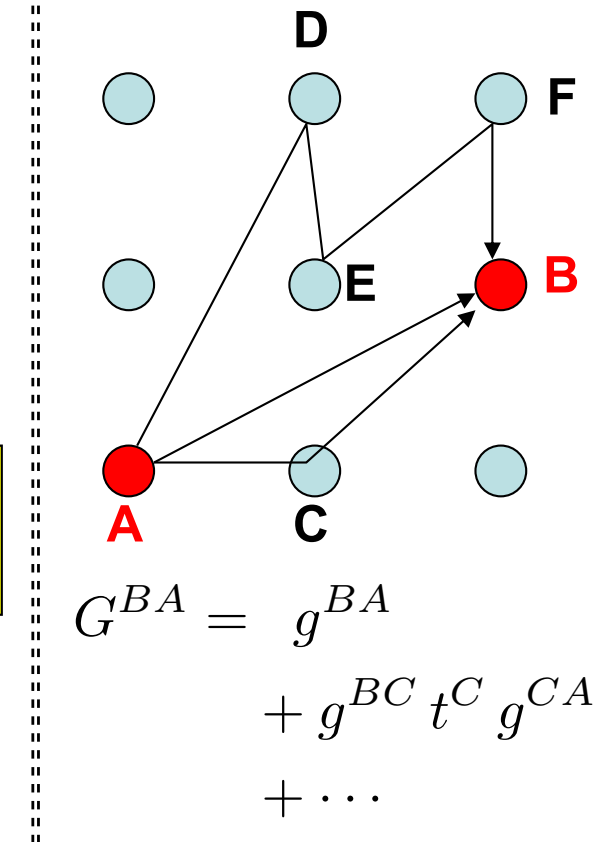
Dyson eq.: Green functions

$$G(E) = g(E) + g(E) V_{\text{cryst}} G(E)$$



Algebraic Dyson eq.: structural Green functions

$$G_{LL'}^{nn'}(E) = g_{LL'}^{nn'}(E) + \sum_{n'', L''} g_{LL''}^{nn''}(E) t_{l''}^{n''}(E) G_{L''L'}^{n''n'}(E)$$

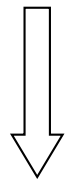


Interpretation: propagation over all scattering paths

$$G_{LL'}^{nn'} = g_{LL'}^{nn'} + \sum_{n'', L''} g_{LL''}^{nn''} t_{l''}^{n''} g_{L''L'}^{n''n'} + \sum_{n'', L''} \sum_{n''', L'''} g_{LL''}^{nn''} t_{l''}^{n''} g_{L''L'''}^{n''n'''} t_{l'''}^{n'''} g_{L'''L'}^{n'''n'} + \dots$$

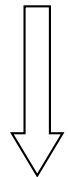
# Solution in $k$ -space for periodic systems

$$G_{LL'}^{nn'}(E) = g_{LL'}^{nn'}(E) + \sum_{n'', L''} g_{LL''}^{nn''}(E) t_{l''}^{n''}(E) G_{L''L'}^{n''n'}(E)$$



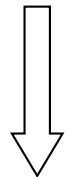
Fourier transformation of  $G, g$

$$G_{LL'}(\vec{k}; E) = g_{LL'}(\vec{k}; E) + \sum_{L''} g_{LL''}(\vec{k}; E) t_{l''}(E) G_{L''L'}(\vec{k}; E)$$



Matrix inversion

$$G_{LL'}(\vec{k}; E) = \left[ \left( 1 - \mathbf{g}(\vec{k}; E) \mathbf{t}(E) \right)^{-1} \mathbf{g}(\vec{k}; E) \right]_{LL'}$$



On-site term for charge density

$$G_{LL'}^{nn}(E) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k G_{LL'}(\vec{k}; E)$$

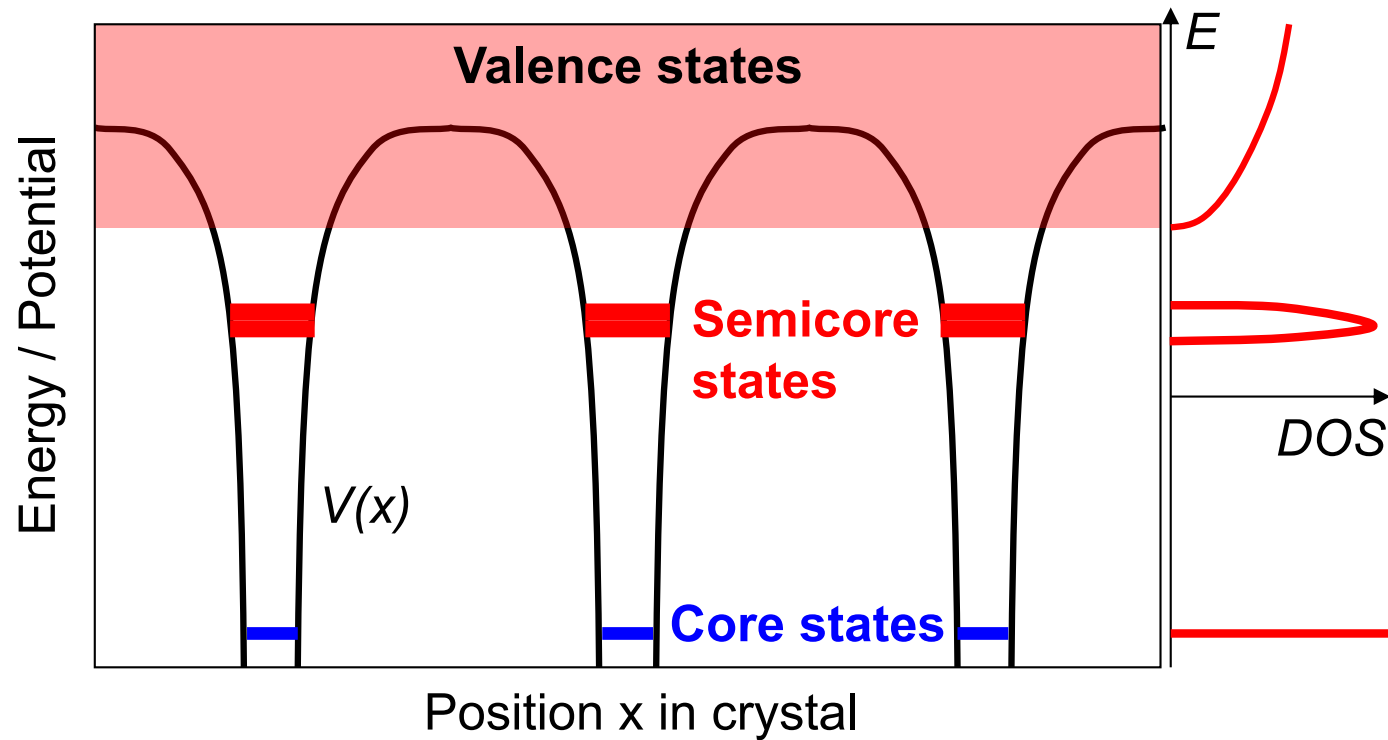
$$[G] = [g] + [g] \cdot [t] \cdot [G]$$

# Electronic structure calculations

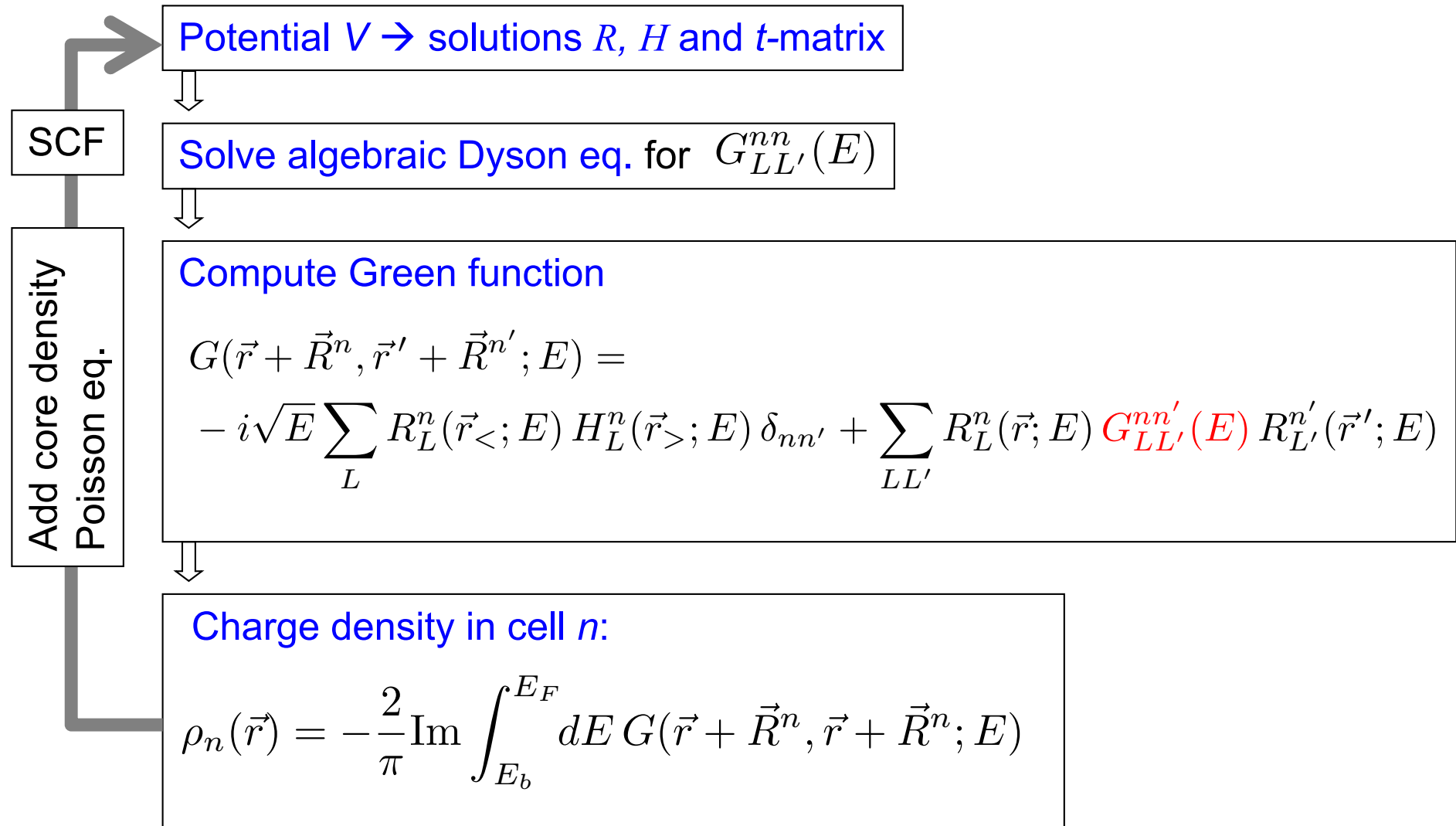
# Framework:

## One-electron states in a crystal

Self-consistent field  $V(x)$ ; density-functional theory



# Summary of algorithm for valence-electron charge density



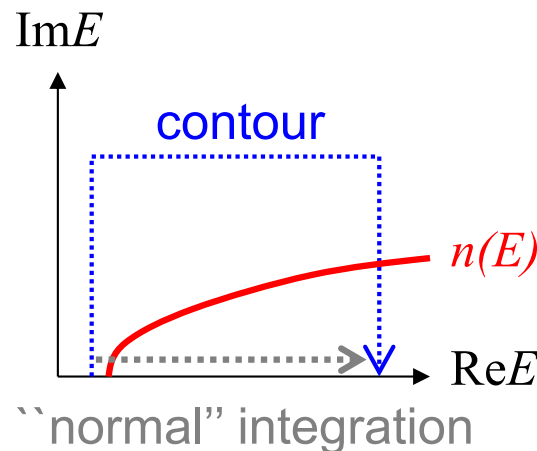
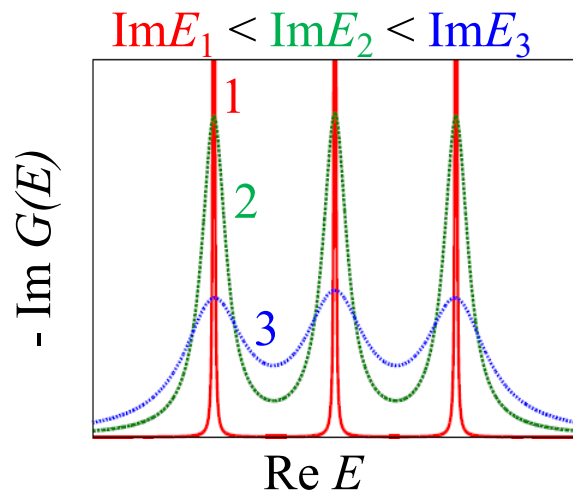
# Complex energy contour

$$\rho_n(\vec{r}) = -\frac{2}{\pi} \text{Im} \int_{E_b}^{E_F} dE G(\vec{r} + \vec{R}^n, \vec{r} + \vec{R}^n; E)$$

Integration:  
a lot of  $E$ -points

$$G(E) = \sum_{n\vec{k}} \frac{|\psi_{n\vec{k}}\rangle \langle \psi_{n\vec{k}}|}{\boxed{E - \epsilon_{n\vec{k}}}} \quad \text{Poles} \quad \rightarrow \quad n(E) = \sum_{n\vec{k}} \delta(E - \epsilon_{n\vec{k}})$$

$$G(E + i\varepsilon) = \sum_{n\vec{k}} \frac{|\psi_{n\vec{k}}\rangle \langle \psi_{n\vec{k}}|}{E + i\varepsilon - \epsilon_{n\vec{k}}} \quad \rightarrow \quad n(E + i\varepsilon) = \sum_{n\vec{k}} \frac{\varepsilon}{\varepsilon^2 + (E - \epsilon_{n\vec{k}})^2}$$



Lorentzian broadening  
→ Less  $E$ -points for integration

$G(E)$  is analytical  
→ Integral is the same.

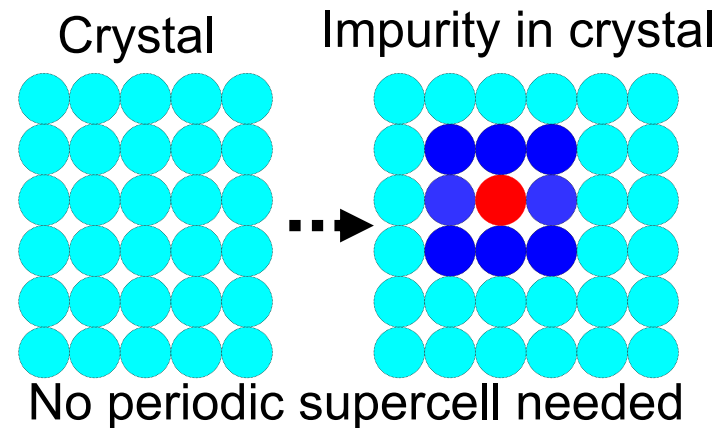
Exceptional in KKR: defects in crystals



# Impurity atoms in crystals

Dyson eq.: Reference system  $\rightarrow$  New system

$$\begin{aligned} G(E) &= (E - H_0 - \Delta V)^{-1} \\ &= [1 - G_0(E) \Delta V]^{-1} G_0(E) \end{aligned}$$



Computational effort depends on the number of *perturbed atomic potentials*  $N$  :  $O(N^3)$

$$\begin{aligned} G &= G_0 + G_0 \Delta V G \\ &= G_0 + G_0 \Delta V G_0 + G_0 \Delta V G_0 \Delta V G_0 + G_0 \Delta V G_0 \Delta V G_0 \Delta V G_0 + \dots \\ &= G_0 + G_0 [\Delta V + \Delta V G \Delta V] G_0 \\ &:= G_0 + G_0 T G_0 \end{aligned}$$

$T$  is confined in the perturbed region

# Impurity atoms in crystals

Green function and Dyson equation for the impurity system

$$G(\vec{r} + \vec{R}^n, \vec{r}' + \vec{R}^{n'}; E) = \\ - i\sqrt{E} \sum_L R_L^n(\vec{r}_{<}; E) H_L^n(\vec{r}_{>}; E) \delta_{nn'} + \sum_{LL'} R_L^n(\vec{r}; E) G_{LL'}^{nn'}(E) R_{L'}^{n'}(\vec{r}'; E)$$

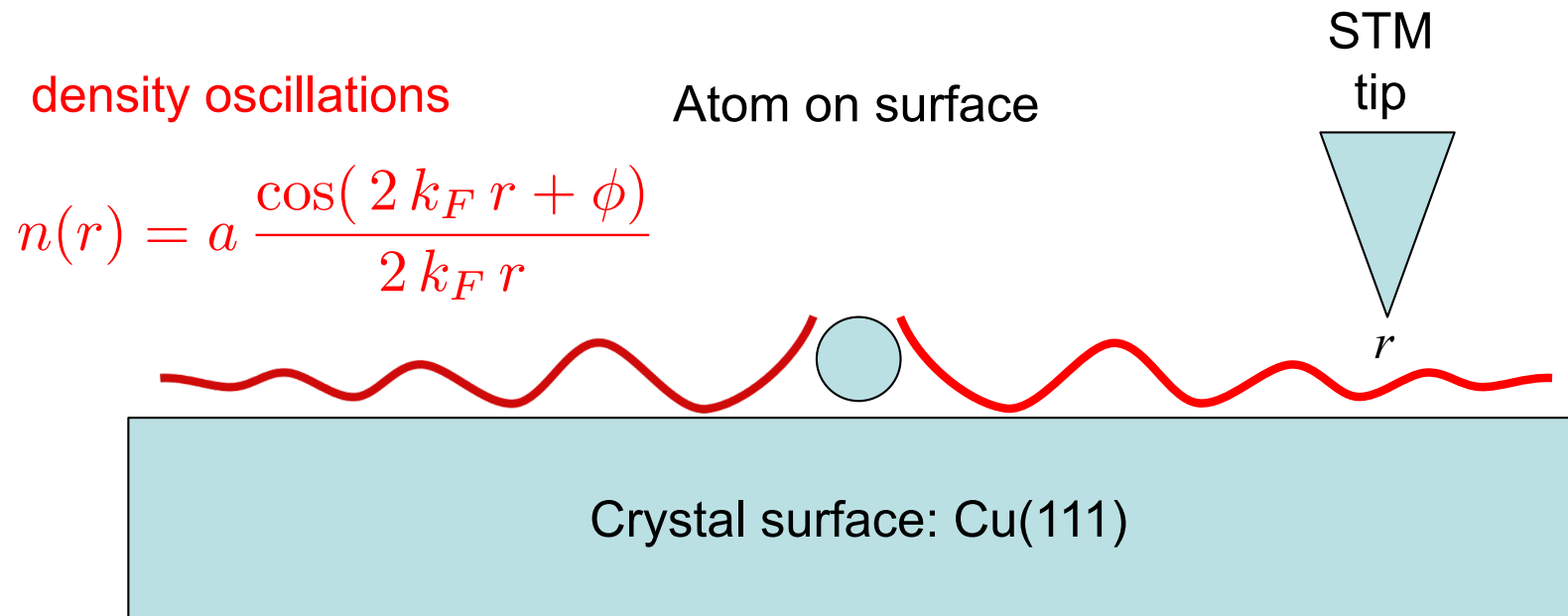
Summation only for the sites where t-matrix differs (impurities & surrounding atoms)

$$G_{LL'}^{nn'}(E) = G_{0;LL'}^{nn'}(E) + \sum_{n'', L''} G_{0;LL''}^{nn''}(E) [t_{l''}^{n''}(E) - t_{0;l''}^{n''}(E)] G_{L''L'}^{n''n'}(E)$$

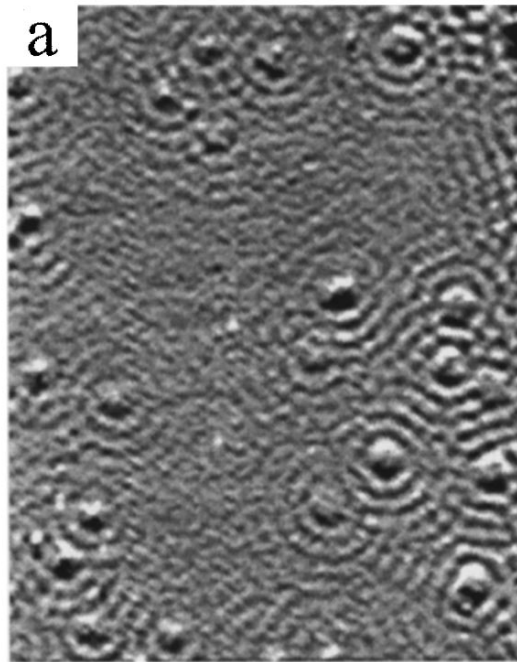
Size of linear system to solve:  $\text{DIMENSION} = N_{\text{at}} \times (2l + 1)^2$

$$G_{LL'}^{nn'}(E) = \left[ [\mathbf{1} - \mathbf{G}_0(\mathbf{t} - \mathbf{t}_0)]^{-1} \mathbf{G}_0 \right]_{LL'}^{nn'}$$

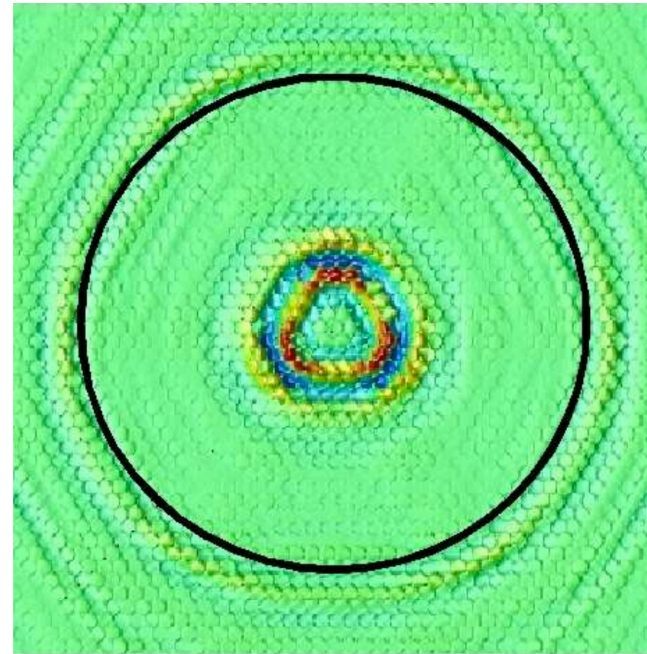
# Application: Density oscillations



# Application: Density oscillations



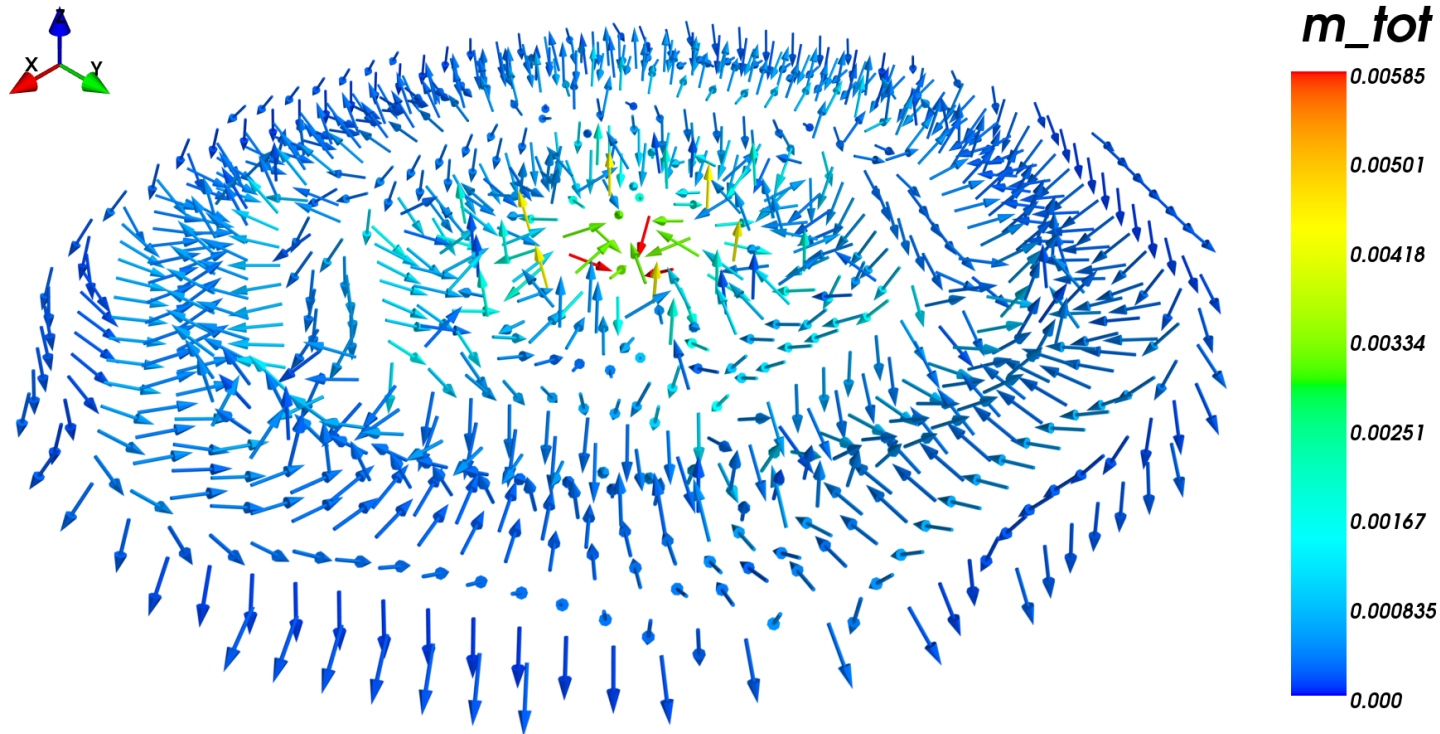
Exp.: Cu (111) surface  
Petersen et al., PRB **57**,  
R6858 (1998)



KKR calculation (Co in Cu surface)  
Samir Lounis, PhD thesis (RWTH Aachen)

# Application: Spin density oscillations

Fe atom on Au(111)



# Wave functions in KKR

# Secular equation

Tessellation of space in atomic cells

Local solution of Schrödinger's equation in each cell  
(spherical wave representation)

$$R_l(\vec{r}; E) Y_L(\hat{r})$$

In a sense: “optimal basis functions”

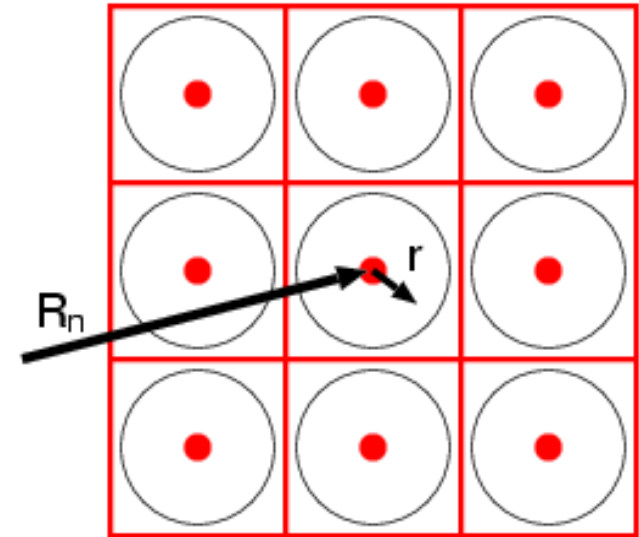
General solution:

$$\Psi_{\vec{k}}(\vec{r}) = \sum_L c_L(\vec{k}; E) R_l(\vec{r}; E) Y_L(\hat{r})$$

Insert into Schrödinger's eq. to obtain coefficients  $c_L$

$$\sum_{L'} \left[ \delta_{LL'} - t_l(E) g_{LL'}(\vec{k}; E) \right] c_{L'}(\vec{k}; E) = 0$$

Fourier-transformed coefficients of free-space Green function



# Multiple scattering

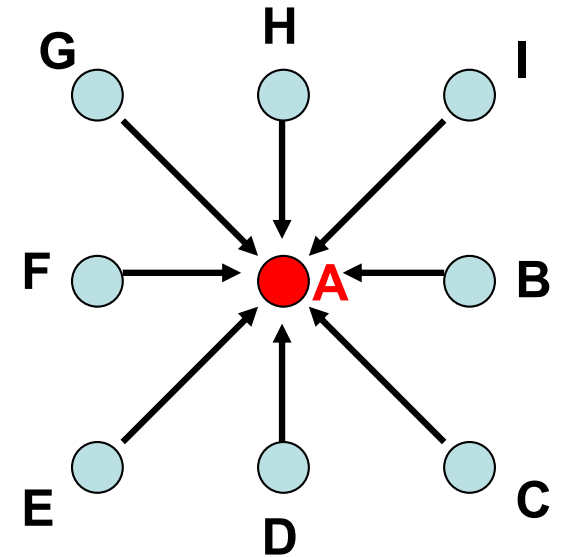
Bookkeeping:

$$1. \quad (\text{Incoming wave})_A = \sum_{n \in \{B, C, \dots\}} (\text{Outgoing waves})_n$$

$$2. \quad \psi_{\vec{k}}^{\text{sc}(n)}(\vec{r}) = \sum_L b_{\vec{k}L}^{\text{sc}(n)} h_L(\vec{r}; E)$$

$$\psi_{\vec{k}}^{\text{inc}(n')}(\vec{r}') = \sum_L b_{\vec{k}L}^{(n')} j_L(\vec{r}'; E)$$

← related by  $t$ -matrix ←



3. Transformation of Hankel functions:

$$h_L(\vec{r}' + \vec{R}^{n'} - \vec{R}^n; E) = \frac{i}{\sqrt{E}} \sum_{L'} g_{LL'}^{nn'}(E) j_{L'}(\vec{r}'; E)$$

4. Periodic system  $\rightarrow$  Bloch property  $\rightarrow k$ -space

$$\sum_{L'} \left( \delta_{LL'} - g_{LL'}(\vec{k}; E) t_{l'}(E) \right) c_{\vec{k}L'}^{(n')} = 0 \quad \Psi_{\vec{k}}(\vec{r}) = \sum_L c_{\vec{k}L} R_L(\vec{r}; E)$$

$$\text{KKR secular equation} \rightarrow E = E(\vec{k})$$



# Fermi surfaces, scattering off impurities

Lippmann-Schwinger equation

$$\Psi_{\vec{k}}^{\text{imp}}(\vec{r}) = \Psi_{\vec{k}}(\vec{r}) + \int d^3r' G_0(\vec{r}, \vec{r}'; E) [V^{\text{imp}}(\vec{r}) - V^{\text{cryst}}(\vec{r})] \Psi_{\vec{k}}^{\text{imp}}(\vec{r})$$

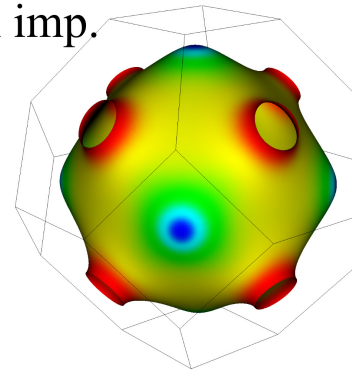
*t*-matrix (transition amplitude)

$$T_{\vec{k}\vec{k}'} = (\Psi_{\vec{k}}, V_{\text{imp}} \Psi_{\vec{k}'}^{\text{imp}})$$

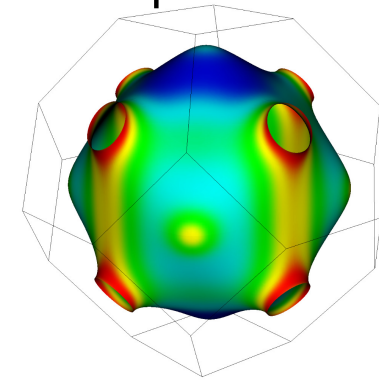
Scattering rate

$$w_{\vec{k}\vec{k}'} = 2\pi |T_{\vec{k}\vec{k}'}|^2 \delta(E_{\vec{k}} - E_{\vec{k}'})$$

Crystal momentum  
Zn imp.



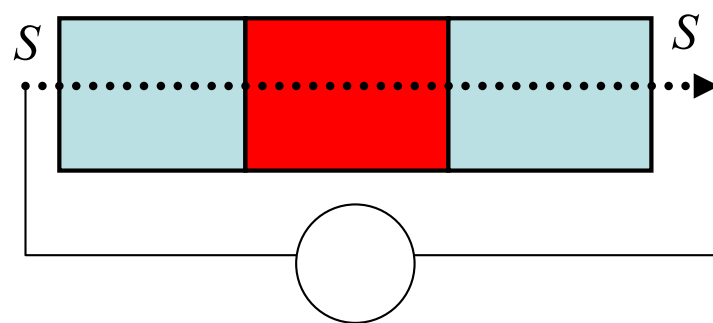
Spin



Finite lifetime (ps) of Fermi surf. states  
in fcc Cu due to scattering off 1% Zn  
impurities.

# Other applications

Conductance in a junction:



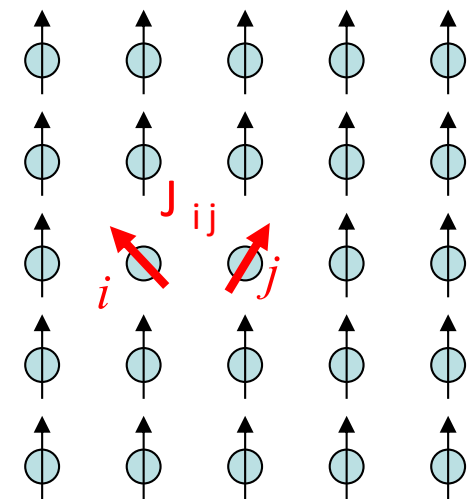
$$J = \Gamma \Delta U$$

$$\Gamma = -\frac{e^2 \hbar^3}{8\pi m^2} \int_S dS \int_{S'} dS' G(\mathbf{r}, \mathbf{r}'; E_F) \overleftrightarrow{\nabla}_z \overleftrightarrow{\nabla}'_z G^*(\mathbf{r}, \mathbf{r}'; E_F)$$

Exchange constants in ferromagnets

Heisenberg model: 
$$E = - \sum_{i,j} J_{ij} \hat{e}_i \cdot \hat{e}_j$$

$$J_{ij} = -\frac{1}{4\pi} \text{Im} \int^{E_F} dE \text{Tr}_L \Delta t_{(\uparrow-\downarrow)}^i G_{\uparrow}^{ij}(E_F) \Delta t_{(\uparrow-\downarrow)}^j G_{\downarrow}^{ji}(E_F)$$



# Summary

Green function method: Alternative to the Schrödinger equation

KKR Green function: Expansion in site-dependent scattering waves with single-site and multiple-scattering part

$$G(\vec{r} + \vec{R}^n, \vec{r}' + \vec{R}^{n'}; E) = -i\sqrt{E} \sum_L R_L^n(\vec{r}_{<}; E) H_L^n(\vec{r}_{>}; E) \delta_{nn'} + \sum_{LL'} R_L^n(\vec{r}; E) G_{LL'}^{nn'}(E) R_{L'}^{n'}(\vec{r}'; E)$$

Impurity problem: Dyson equation  
Only perturbed sites need recalculation

$$\begin{aligned} G(E) &= (E - H_0 - \Delta V)^{-1} \\ &= [1 - G_0(E) \Delta V]^{-1} G_0(E) \end{aligned}$$

Large systems > 10000 atoms: Sparse matrices allow for O(N) calculations  
(KKR-nano method by R. Zeller et al.)

Thank you for your attention!