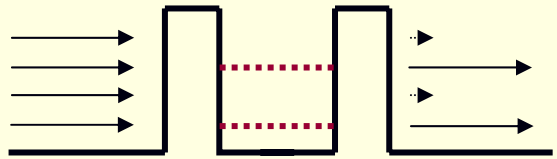
Muffin Tins, Green's Functions, and Nanoscale Transport

$$G^R = \left[E - H - \Sigma^R\right]^{-1}$$



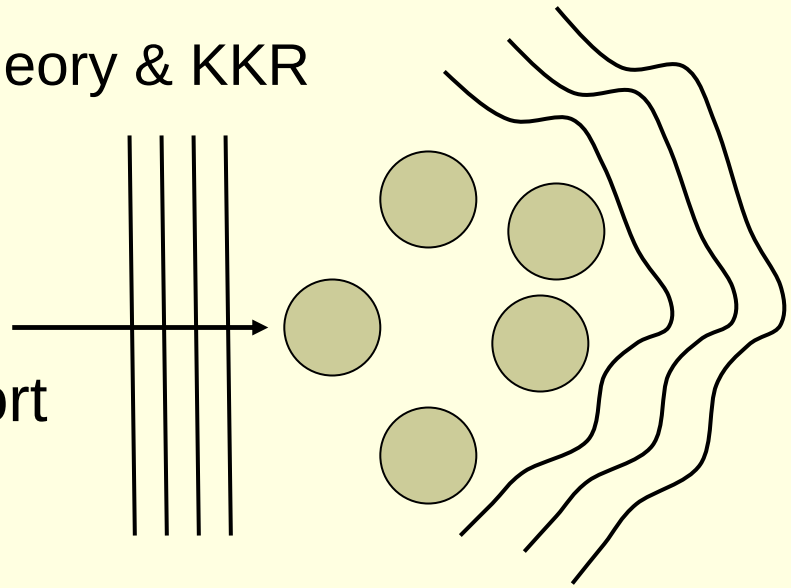
Derek Stewart

CNF Fall Workshop

Cooking Lesson #1

Talk Overview

- A more localized approach
  - Origins: Multiple Scattering Theory & KKR
  - Linear Muffin Tin Orbitals

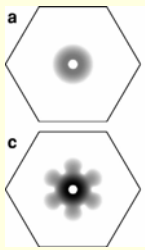


- Green's functions and Transport
  - Green's Function basics

$$G^R = \left[E - H - \Sigma^R\right]^{-1}$$

  - Tight binding models

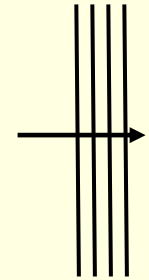
  - Transport



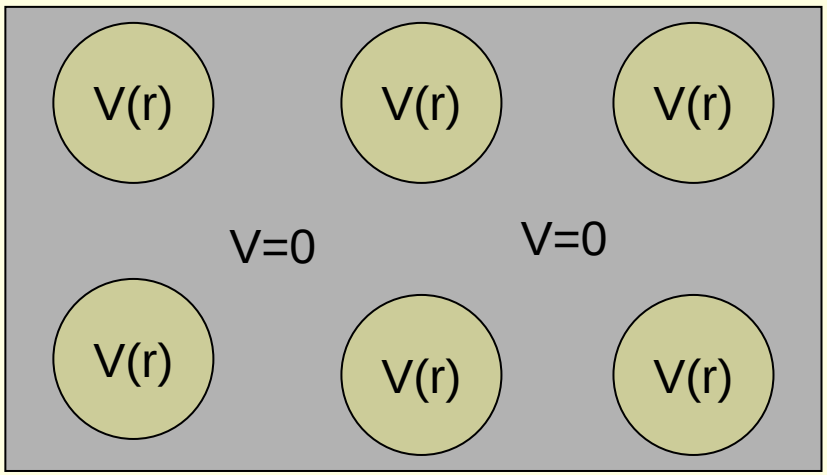
Basis expansion around atoms…

- In the previous talk this morning, you learned about a delocalized basis set (*plane waves*)

$$e^{ik \bullet r}$$



- Muffin tin approaches (KKR & LMTO)
  - Spherical potentials around each atom
  - Wavefunction expanded in spherical waves (s, p, d, f character)
  - Potential is zero in space between atoms
  - Solution of different sites connected together (multiple scattering, cancellation of orbital tails)



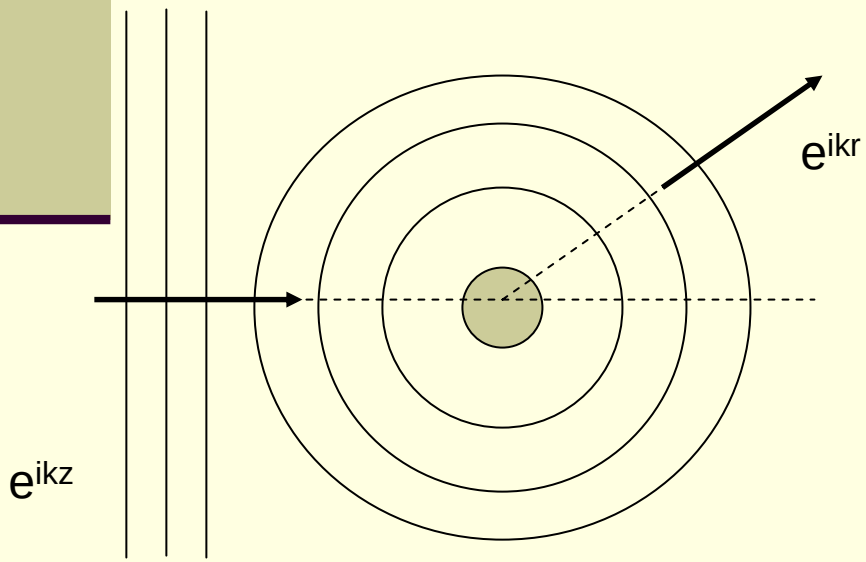
?

Multiple Scattering Theory (MST)

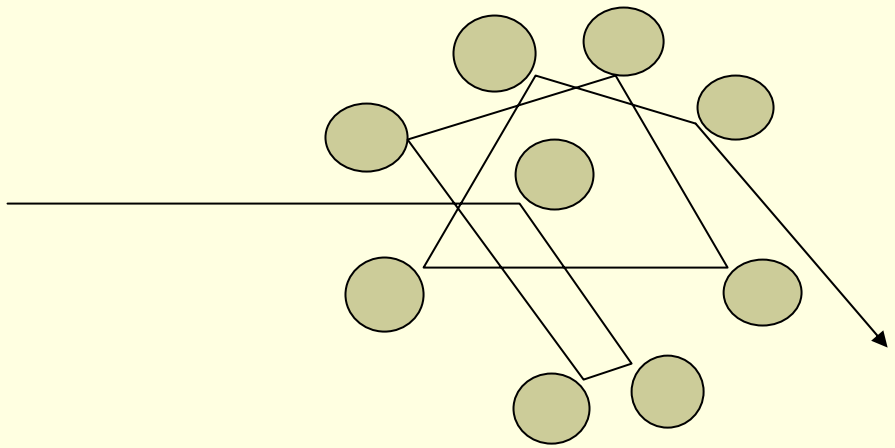
From Point Scatterers to Solids

- *Multiple scattering techniques* determine electronic structure by accounting for the scattering events an electron wavefunction experiences within a solid.

- This is tougher than it looks
  - single scatterer, single scattering event – analytic solution
  - two or more scatterers, *infinite* number of possible scattering events, recursive solutions required for wavefunctions



Single site



Multiple sites

!

Short History of MST

Lord Rayleigh (1892) "*On the Influence of Obstacles in Rectangular Order upon the Properties of a Medium*" Phil Mag. – Laplace Equation

- N. Kasterin (1897) – extends MST to Helmholtz equation (*scattering of sound waves by collection of spheres*)
- Korringa (Physica, 1947) – first use to find electronic states in solids (computational facilities however not up to the task)

Kohn and Rostoker

– rediscover in 1950's (Phys. Rev.)

- This leads to the Korringa Kohn Rostoker approach - *aka* - KKR
- 1960's – first serious calculations using the approach – computers begin to catch up with the theory!

*Images courtesy of Emilio Segré Visual Archives (http://www.aip.org/history/esva)

So your system has potential….

$$\left[H_o + V\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

- $\mathbf{H_o}$ is the free space Hamiltonian
- **V** is the perturbing potential
- Ψ is the electron wavefunction

$$\psi(\vec{r}) = \chi(\vec{r}) + \int G_o(\vec{r}, \vec{r}\,')\mathrm{V}(\vec{r}\,')\psi(\vec{r}\,')d^3r'$$

We can express the wavefunction at some position as a sum of the free space wavefunction, χ, with no perturbing potential, and contributions from the perturbing potential, ***V***, at different sites.

In this case, G_o is the free electron propagator and describes motion in regions where no scattering from the potential occurs.

Letting Green do the expansion

George Green's Mill
Nottingham, England

In analogy to the previous wave function equation, we can do a similar expansion for the system Green function.

$$G = G_o + G_o V G$$

We can expand this equation out to infinity…

$$G = G_o + G_o V G_o + G_o V G_o V G_o + G_o V G_o V G_o V G_o + \ldots$$

The total Green function acts as the system propagator. This expansion shows the infinite number of scattering events that can occur through potential interactions. Electron propagation in free space is described by G_o.

Introducing the T matrix

We can rearrange the last equation to isolate the effects of the potential.

$$G = G_o + G_o\left(V + VG_oV + VG_oVG_oV + \ldots\right)G_o$$
$$= G_o + G_oTG_o$$

where

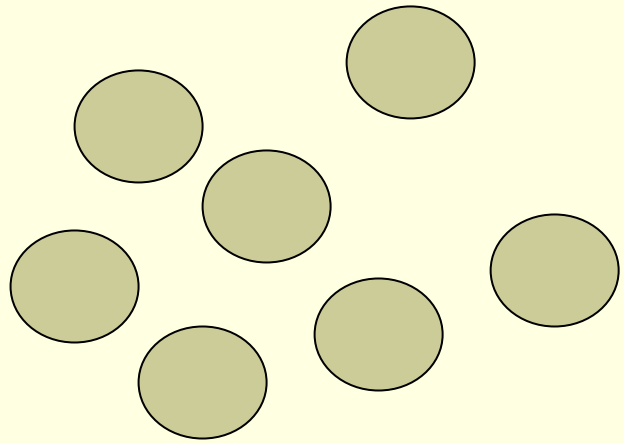
$$T\left(V\right) = V + VG_oV + VG_oVG_oV + \ldots$$

The scattering matrix, T, completely describes scattering within the potential assembly. It contains all possible scattering paths.

Multiple Scattering Sites

Assume the potential is made up of a sum of terms due to different cells or atoms.

$$V = \sum_i V^i$$



The T matrix in this case becomes:

$$T = T\left(\sum_i V^i\right) = \sum_i V^i + \sum_i V^i G_o \sum_j V^j + \ldots$$

We can separate out the sequences where the scattering always involves the same cell or atom into the cell t matrix.

$$t^i = V^i + V^i G_o V^i + V^i G_o V^i G_o V^i + \ldots$$

Atomic *t* matrix uncovered

Solve the radial Schrodinger's equation for an isolated muffin tin potential and determine the regular and irregular solutions, Z and S.

The atomic *t* matrix is diagonal in the angular momentum representation.

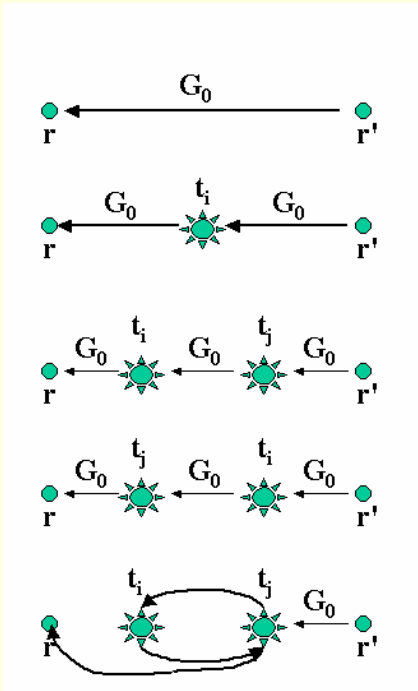
$$t_l^{\alpha} = i \sin \delta_l e^{i\delta_l}$$

The phase shift, δ, can be found from the atomic wavefunction.

All the possible paths…

We can now write the T matrix in terms of the single site scattering matrix, *t*.

$$T\left(\sum_i V^i\right) = \sum_i t^i + \sum_i \sum_{j \neq i} t^i G_o t^j + \ldots$$



This equation shows that the scattering matrix of an scattering assembly is made up of all possible scattering sequences.

Each scattering sequence involves scattering at individual cells with free electron propagation between.

$$T = \sum_{ij} T^{ij} \quad \text{where} \quad T^{ij} = t^i \delta_{ij} + t^i G_o \sum_{k \neq i} T^{kj}$$

Getting the Band Together

In the MT formalism, the T matrix becomes:

$$T^{ij} = t^i \delta_{ij} + t^i \sum_{k \neq i} \widetilde{G}^{ik} T^{kj}$$

There exists a matrix M such that T^{ij} are the elements of its inverse. The matrix m is just the inverse of the cell t matrix.

$$M^{ij} = m^i \delta_{ij} - \widetilde{G}^{ij} \left(1 - \delta_{ij}\right)$$

*The inverse of the T matrix is cleanly separated into **potential** scattering components, m^i, and **structural** components, G^{ij}.*

The poles of M determine the eigenenergies for the system for a given k through the following equation:

$$\det\left[m - \widetilde{G}(k)\right] = 0$$

This allows us to calculate the system band structure.

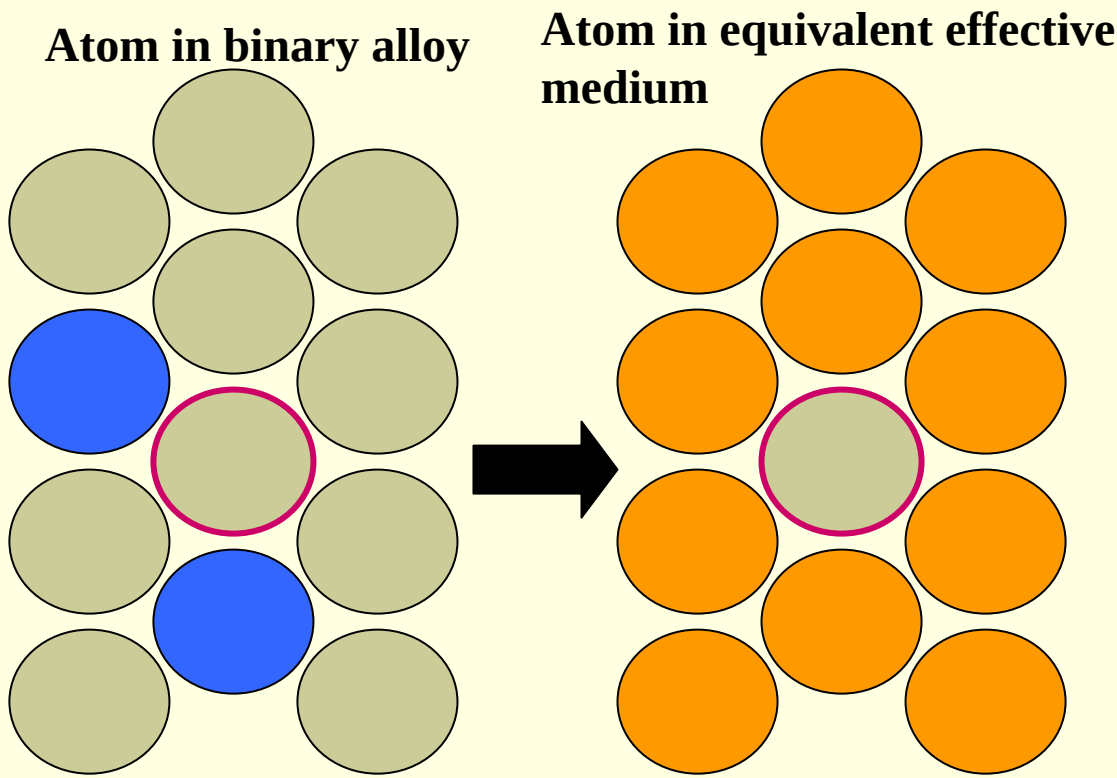
Coherent Potential Approximation (CPA)

Best *single-site* solution for describing scattering in substitutional alloys

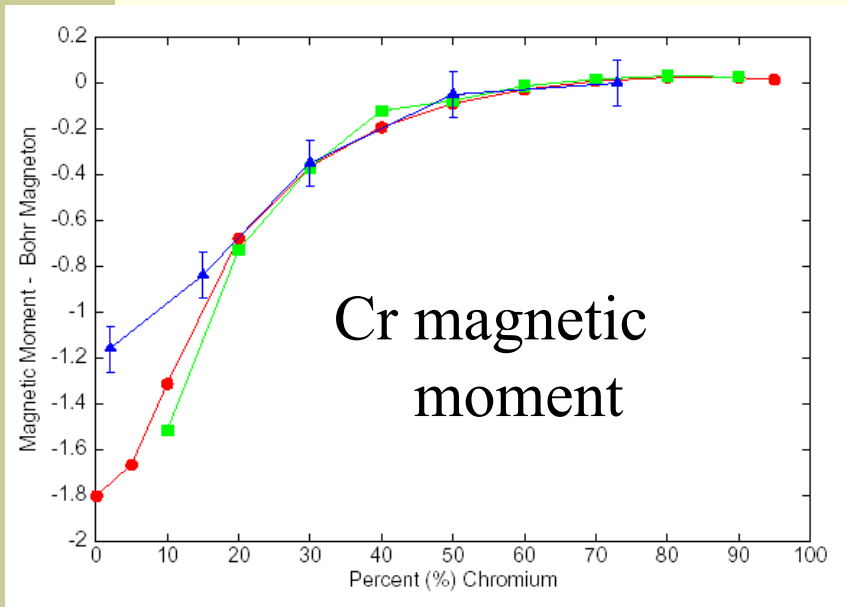
Scattering properties of alloy can be represented by an effective medium

Treat scattering by atom as an impurity in the effective medium.

Introduction of atom should give no scattering in the correct effective medium (iterative solution).



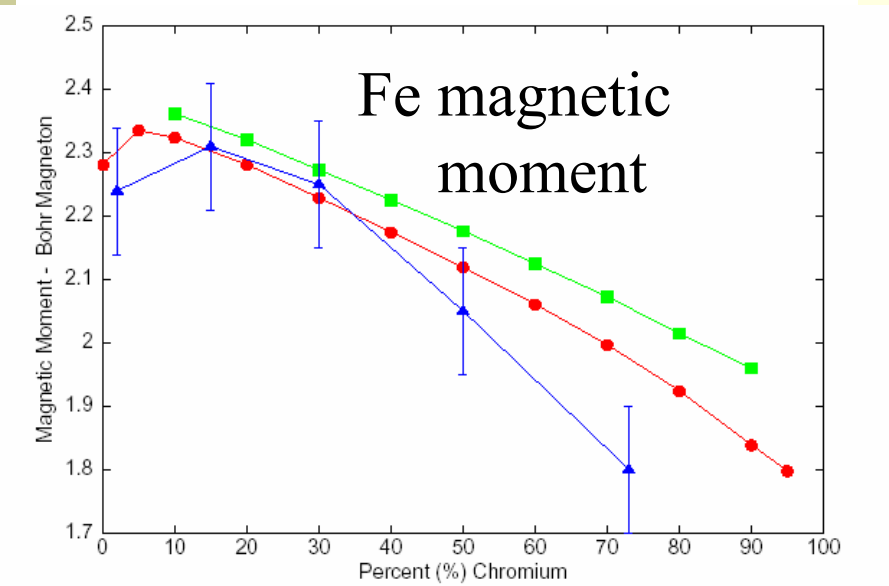
FeCr Alloys

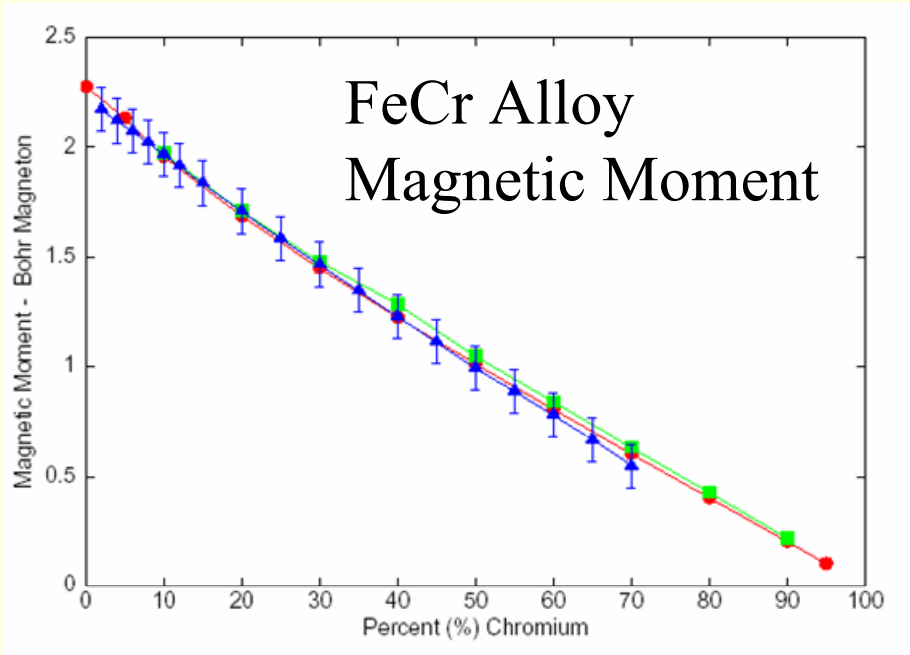


LKKR-CPA (D. Stewart, unpublished)

KKR-CPA (Kulikov *et al.*, 1997)

Experimental (Aldred *et al.*, *1976*)



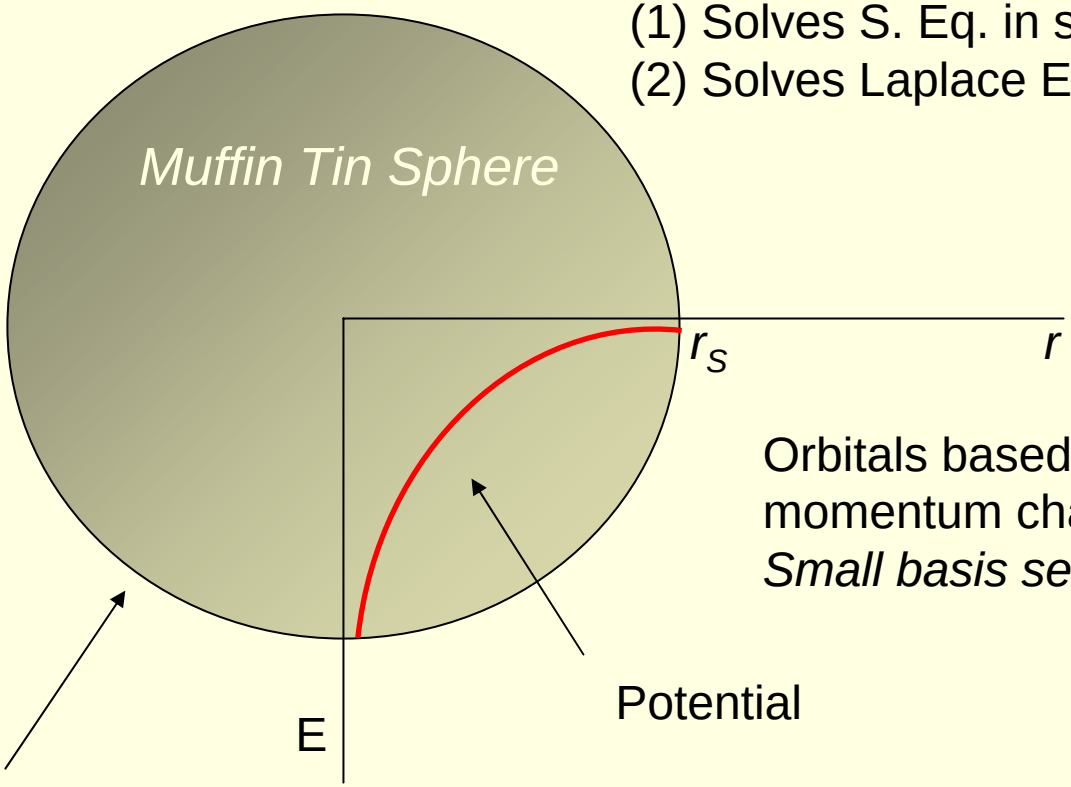


Problems with the KKR approach

- Linking interstitial region (V=0) with spherical regions with muffin tin potentials can be difficult
- Determinant used to find band structure is a non-linear function of energy (energy dependence carried in the site *t* matrices) – *this can not be reduced to a standard matrix eigenvalue problem*
- *The Solution – Linearize the equation* – LMTO approach (Andersen, PRB, 1975 – 1370 citations)

Linear Muffin Tin Orbitals

Two sets of solutions
(1) Solves S. Eq. in sphere
(2) Solves Laplace Eq. in interstitial



Orbitals based on angular momentum character – *s, p, d, f*
Small basis set!

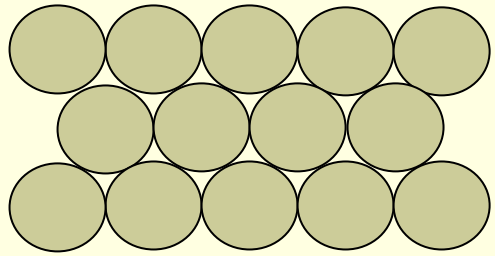
Potential

Need orbitals and 1st derivatives to match at sphere boundary

Main challenges
(1) Matching conditions at sphere boundary
(2) Need an equation that is linear in energy

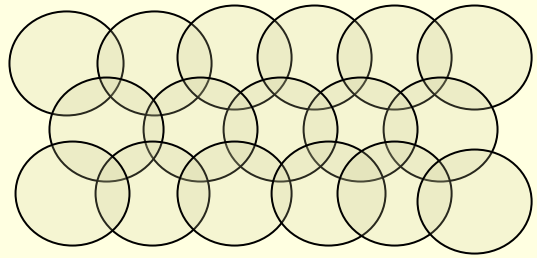
Making Life Easier with ASA
Atomic Sphere Approximation

Many crystals are close-packed systems
(fcc, bcc, and hcp)



Most of the space is filled by atomic spheres

What if we cheat a little…
and have the spheres overlap.



Doing this, we remove the interstitial region and our integration over space becomes an integration of atomic spheres.

This approach works best when the system is close packed,
Otherwise we have to pack the system with empty spheres to fill space

Solving for the Interstitial Region

$$-\nabla^2\varphi(\mathbf{r},E)+\left[V_R(r)-E\right]\varphi(\mathbf{r},E)=0$$

Potential in interstitial region is zero
Interstitial region has no space, electron kinetic energy in region zero as well

$$\nabla^2\varphi(\mathbf{r},E)=0 \longrightarrow \varphi(\mathbf{r})=R(r)Y_L(\hat{r}) \qquad L=(l,m)\ \ l=0,1,2,\ldots\ |m|<l$$

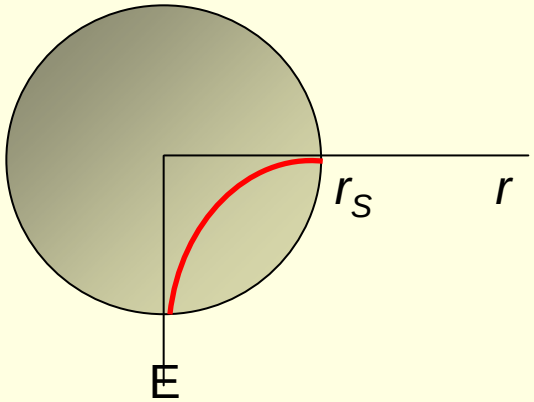
Take advantage of spherical symmetry – express wavefunction in terms of spherical harmonics and radial portion

$$J_L(\mathbf{r})=J_\ell(r)Y_L(\hat{r}), \qquad J_\ell(r)=\frac{1}{2(2\ell+1)}\left(\frac{r}{w}\right)^\ell$$

$$K_L(\mathbf{r})=K_\ell(r)Y_L(\hat{r}), \qquad K_\ell(r)=\left(\frac{w}{r}\right)^{\ell+1}$$

We get two solutions for Laplace's equation an regular one,
$J_L(\mathbf{r})$ (goes to zero at r=0) and irregular one, $K_L(\mathbf{r})$ (blows up at r=0)

Solving inside the Atomic Sphere



$$\varphi(\mathbf{r},E)=\varphi(r,E)Y_L(\hat{r})$$

$$-\nabla^2\varphi(\mathbf{r},E)+\left[V_R(r)-E\right]\varphi(\mathbf{r},E)=0$$

We need to match radial amplitude up with interstitial solutions, *J* and *K, at* r_S

$$\varphi(r,E)=\frac{1}{N_{R\ell}(E)}\left[K_\ell(r)-P_{R\ell}(E)J_\ell(r)\right]$$

Normalization function

Potential function

Muffin Tin Orbitals

We can define the total wavefunction as a superposition of muffin tin orbitals as

$$\psi(\mathbf{r}) = \sum_{RL} a_{RL} \Psi_{RL}(\mathbf{r}, E)$$

Where the muffin tin orbitals are given by:

$$\Psi(r, E) = N_{RL}(E)\varphi_{RL}(\mathbf{r}_\mathbf{R}, E) + P_{R\ell}(E) J_L(\mathbf{r}_\mathbf{R}) \qquad \text{for } r_R < r_S \longleftarrow \text{Muffin-tin Head}$$

$$= K_L(\mathbf{r}_\mathbf{R}) \qquad \text{for } r_R > r_S \longleftarrow \text{Muffin-tin Tail}$$

We also need to make sure solutions work in other atomic spheres…
Expansion theorem used to link solutions centered at different spheres

$$K_L(\mathbf{r}_\mathbf{R}) = -\sum_{L'} S_{RL,R'L'} J_{L'}(\mathbf{r}_{\mathbf{R}'})$$

Structure constants – lattice info

Canceling Muffin Tin Tails

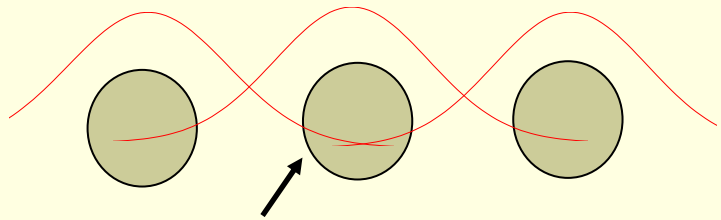
$$\Psi(r,E) = N_{RL}(E)\varphi_{RL}(\mathbf{r_R},E) + P_{R\ell}(E)J_L(\mathbf{r_R}) \qquad r_R < r_S$$ MT head

$$= K_L(\mathbf{r_R}) \qquad r_R > r_S$$ MT tail in interstitial

$$= -\sum_L S_{RL,R'L'} J_{L'}(\mathbf{r_{R'}}) \qquad r_{R'} < r_{S'} \ \ (R' \neq R)$$ MT tail at other spheres

The form of the muffin-tin orbitals does not guarantee that it solves the Schrodinger equation. We must insure that it does

$$\psi(\mathbf{r}) = \sum_{RL} a_{RL}\Psi_{RL}(\mathbf{r},E)$$



Tail Cancellation needed

$$\sum_{RL} a_{RL}\left[P_{RL}(E)\delta_{RL,R'L'} - S_{RL,R'L'}\right] = 0 \quad \rightarrow \quad \det\left[P_{RL}(E)\delta_{RL,R'L'} - S_{RL,R'L'}\right] = 0$$

For periodic systems, we can write this in k-space and get the band structure!

The Linear Approximation

Taylor expansion of the orbital…

$$\varphi_{R\ell}(r,E) = \varphi_{R\ell}(r,E_\nu) + (E - E_\nu)\dot{\varphi}_{RL}(r,E_\nu)$$

This allows us to express the system in terms of linear muffin tin orbitals that depend on φ and $\dot{\varphi}$ in a tight binding form (TB-LMTO)

$$\Psi_{RL}(\mathbf{r_R}) = \varphi_{RL}(\mathbf{r_R}) + \sum_{R'L'} \dot{\varphi}_{R'L'}(\mathbf{r_R}) h_{R'L',RL}$$

where $H_{RL,R'L'} = E_{\nu,RL}\delta_{RL,R'L'} + h_{R'L',RL}$

Speed Improvement: *Removal of non-linearity in determinant equation, accelerates calculations.*

Accuracy: Eigenvalues correct up to third order in ($E-E_\nu$)

Limitations: Can run into problems with semi-core d-states outside of the effective energy window.

Making everything self-consistent

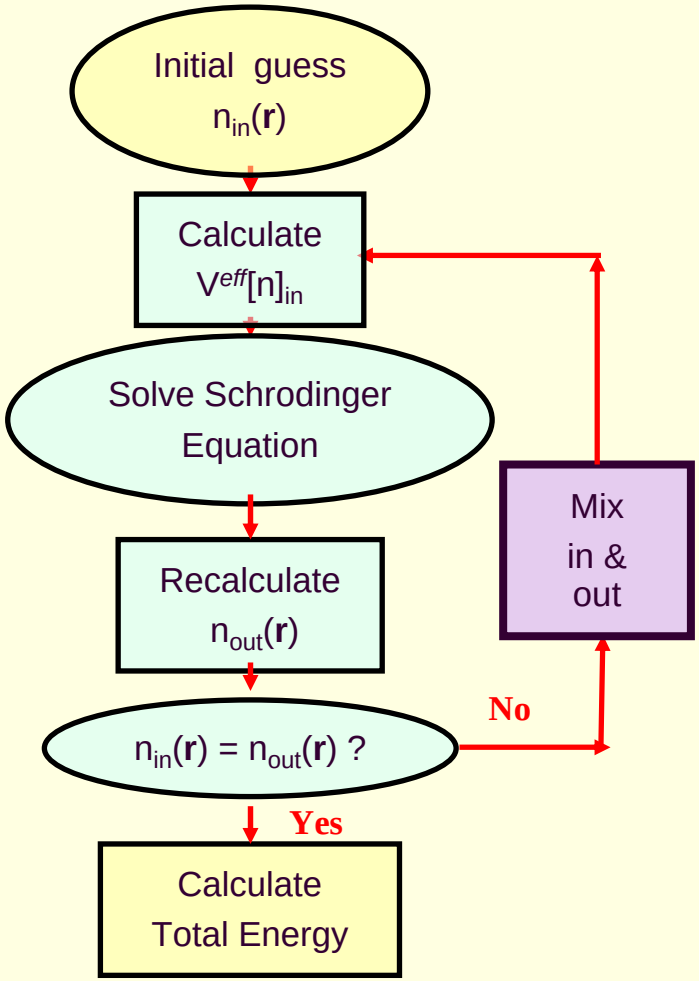


*Diagram courtesy Xiaoguang Zhang (ORNL)

Coming up this afternoon

- LMTO commands
- Running LMTO calculations
  - Silicon – role of empty spheres
  - Magnetic properties – Nickel
  - Density of states, band structure, etc

An Introduction to Green's Functions

Move over Wavefunctions

$$G^R = \left[E - H\right]^{-1}$$ ⟵ Off diagonal terms give you electron propagation,

$$T = \mathrm{Tr}\left[\Gamma_L G^R_{1N} \Gamma_R G^A_{N1}\right]$$

Diagonal elements give

$$\rho(r) = -\frac{1}{\pi}\int f\left(E - \varepsilon_F\right)\mathrm{Im}\,G(\mathbf{r},\mathbf{r},E)\,dE$$ Charge density

$$n(E) = -\frac{1}{\pi}\int \mathrm{Im}\,G(\mathbf{r},\mathbf{r},E)\,d^3\mathbf{r}$$ Density of states

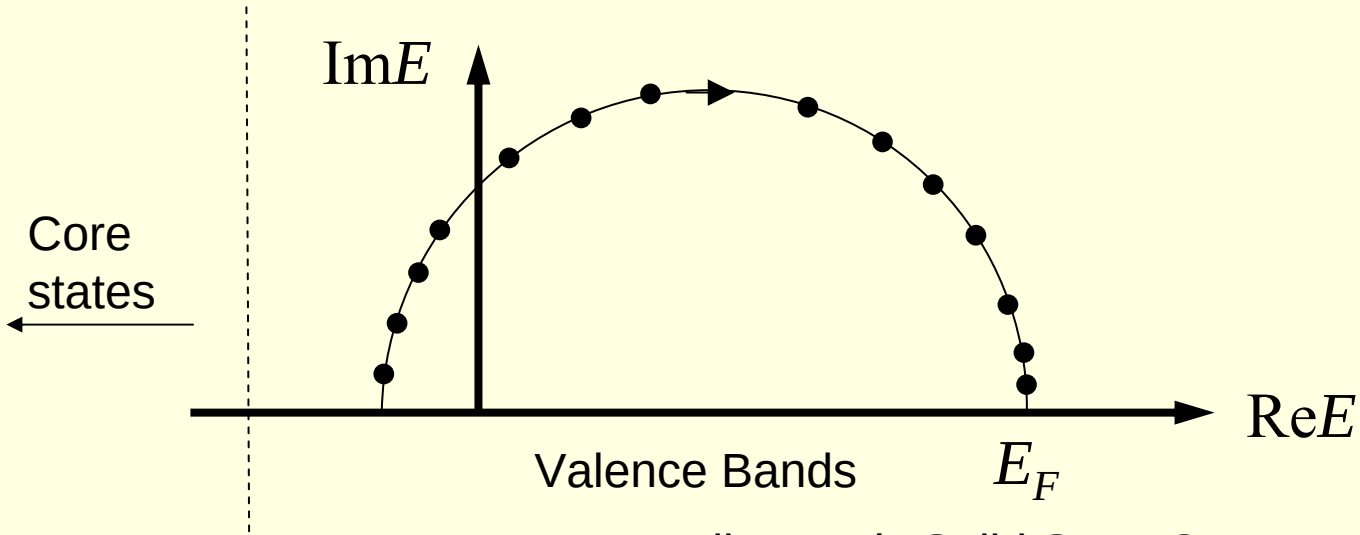
From the charge, we can calculate the potential and perform self-consistent calculations

Integration in the Complex Plane

Charge density is determined by integrating the Green's function over energy.

However, on the real axis, Green's function is a very sharp function.
If we move off the real axis, the Green's function becomes much smoother.

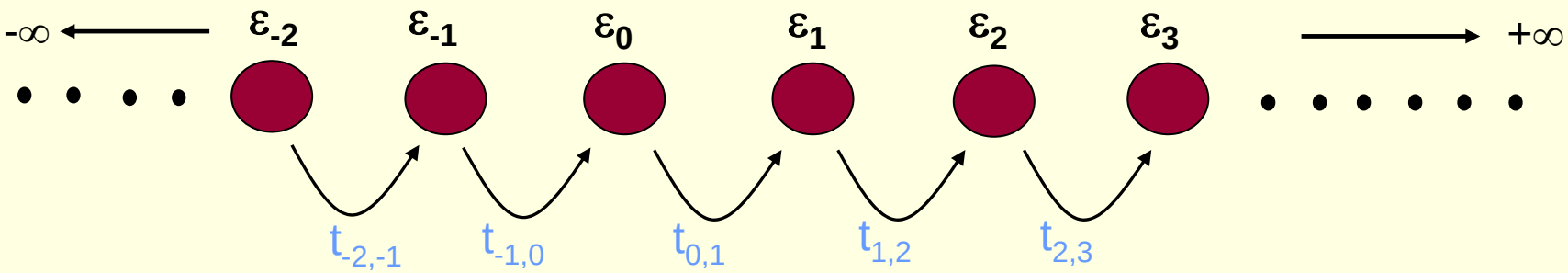
30 data points able to do the work of 1000's!



Zeller *et al.*, Solid State Comm., **44**, 993 (1982)

Tight Binding Models

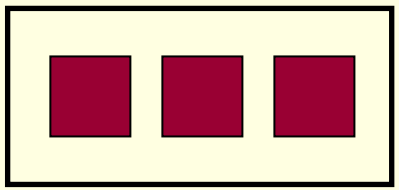
Tight-binding model (*results generalize to any first principles approach with screening or short range interactions*) – Take an infinite chain



$$H = \begin{bmatrix} \ldots & t_{-3,-2} & 0 & 0 & 0 & 0 & 0 \\ t_{-2,-3} & \varepsilon_{-2} & t_{-2,-1} & 0 & 0 & 0 & 0 \\ 0 & t_{-1,-2} & \varepsilon_{-1} & t_{-1,0} & 0 & 0 & 0 \\ 0 & 0 & t_{0,-1} & \varepsilon_{0} & t_{0,1} & 0 & 0 \\ 0 & 0 & 0 & t_{1,0} & \varepsilon_{1} & t_{1,2} & 0 \\ 0 & 0 & 0 & 0 & t_{2,1} & \varepsilon_{2} & t_{2,3} \\ 0 & 0 & 0 & 0 & 0 & t_{3,2} & \ldots \end{bmatrix}$$

tridiagonal matrix (very nice for inversion)

Isolated and Periodic Systems

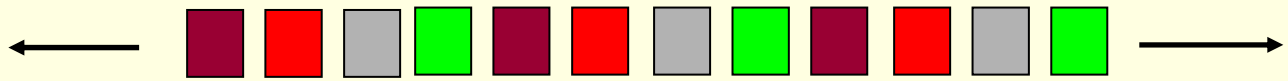


Isolated system (finite Hamiltonian – sharp energy levels)

$$G = [E - H]^{-1} = \begin{bmatrix} E-\varepsilon_1 & t_{12} & 0 \\ t_{21} & E-\varepsilon_2 & t_{23} \\ 0 & t_{32} & E-\varepsilon_3 \end{bmatrix}^{-1}$$

Applications: molecules, quantum wells, finite nanowires/tubes

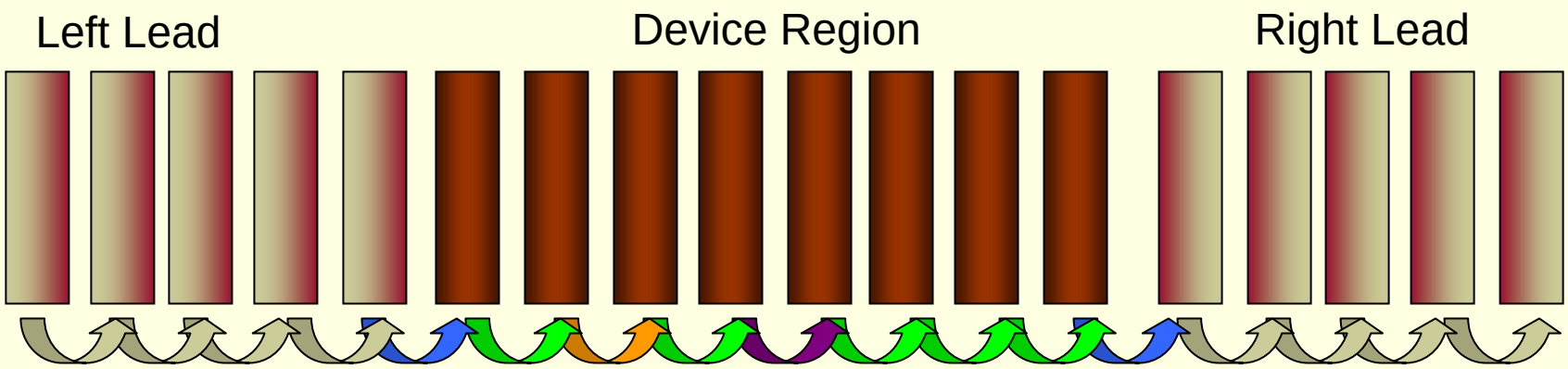
Infinite periodic system – still finite matrix!
(Period *N=4* here, coupling between layer *1* and layer *N*)



$$G = [E - H]^{-1} = \begin{bmatrix} E-\varepsilon_1 & t_{12} & 0 & t_{14} \\ t_{21} & E-\varepsilon_2 & t_{23} & 0 \\ 0 & t_{32} & E-\varepsilon_3 & t_{34} \\ t_{41} & 0 & t_{43} & E-\varepsilon_4 \end{bmatrix}^{-1}$$

Applications:
Multilayers, Bulk Systems

Device Geometry



Semi-infinite leads –

coupling between layers in leads must be identical or periodic

Device region –

no constraints on coupling between layers

Coupling between device and leads –

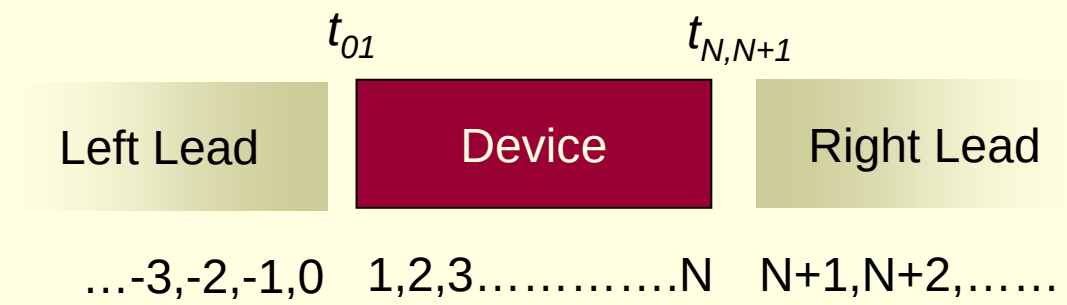
this coupling determines how easy it is for electrons to enter and leave the device region. This is critical for device performance.

Green's Function for Open System

How do we take an infinite system and reduce it to a manageable size?

$$H = \begin{bmatrix} H_L & t_{LD} & 0 \\ t_{DL} & H_D & t_{DR} \\ 0 & t_{RD} & H_R \end{bmatrix}$$

No interaction between leads



We can fold the information about the leads into self energies in the device region.

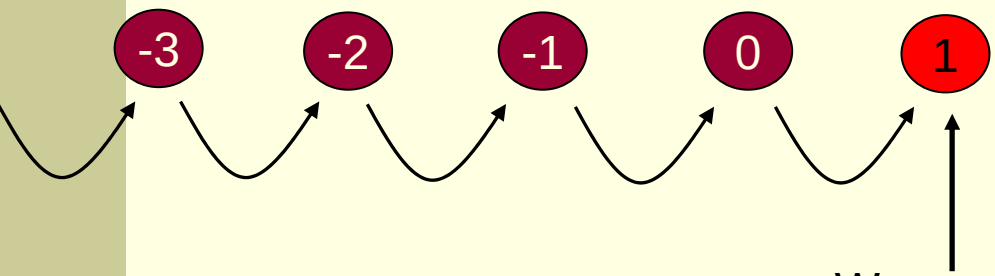
$$G^R(E) = \left[E - H - \Sigma_L - \Sigma_R\right]^{-1} \qquad \Sigma^{RB}_{1,1} = t_{1,0} g^R_{0,0} t_{0,1} \qquad \Sigma^{RB}_{\mathrm{N,N}} = t_{N,N+1} g^R_{N+1,N+1} t_{N+1,N}$$

Leads provide a **source** and **sink** for electrons.

Surface Green's function

The self energies give the electrons in the device region a finite lifetime and broaden the energy levels (no longer an isolated quantum box).

Solving for Surface Green's Functions



Semi-infinite chain of atoms

We need the Green's function at the end of chain

$$g_1^R(E) = \left[E - \varepsilon_1 - t_{10} g_1^R(E) t_{01}\right]^{-1}$$

Several approaches for determining the surface Green's function have been devised (direct iterative, iterative with mixing, etc)

Most robust technique uses renormalization approach known as *layer doubling.* With each iteration, the algorithm doubles the size of the layer. After *n* iterations, the effective layer thickness is 2^n larger than the original thickness!

Rapid convergence at the price of more matrix operations:

M.P. Lopez-Sancho, J.M. Lopez Sancho, and J. Rubio,
J. Phys. F: Metal Phys. **15**, 851 (1985).

Ballistic Transport

Transport on length scales less than the scattering length for electrons,
no diffusive transport , concept of potential at positions in device is difficult

$$T = \mathrm{Tr}\left[\Gamma_L G^R_{LR} \Gamma_R G^A_{RL}\right]$$ Transmission

$$I = \int dE\left(f_L - f_R\right)\mathrm{Tr}\left[\Gamma_L G^R \Gamma_R G^A\right] = \int \mathrm{Re}\left\{\mathrm{Tr}\left[t_{L,L+1} G^<_{L+1,L}(E)\right]\right\} dE$$

Equilibrium G^R

Non-equilibrium $G^<$

Spin Polarized Tunneling from Co surface (LM Suite)

- Tunneling from oxidized and unoxidized Co surfaces to Al probe.
- Oxygen monolayer on Co flips the spin polarization of tunneling from negative (minority carriers) to positive (majority carriers).

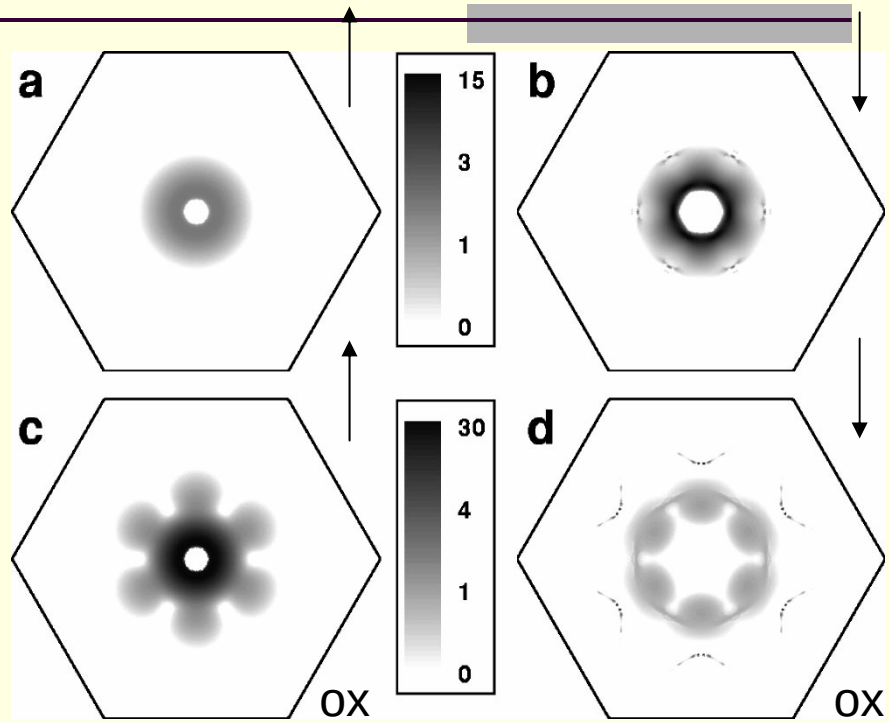
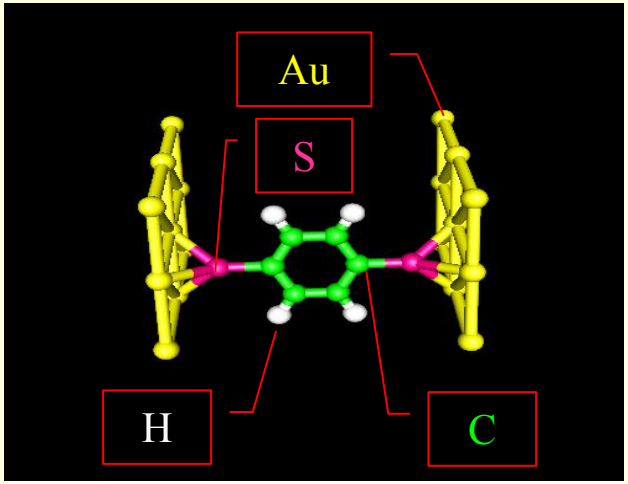
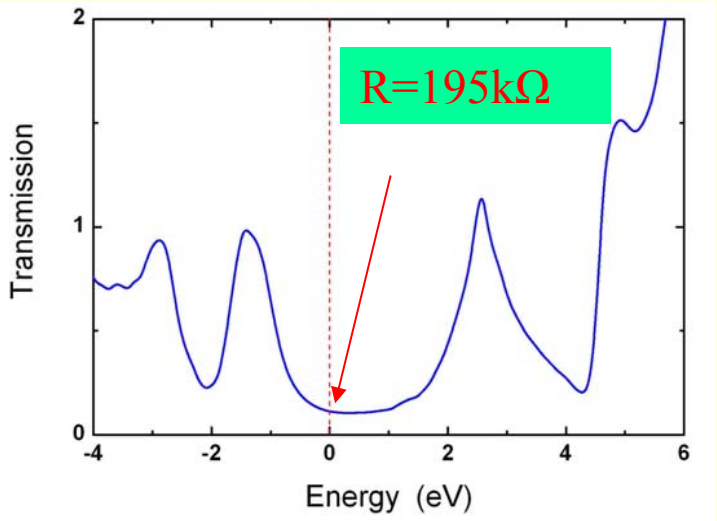


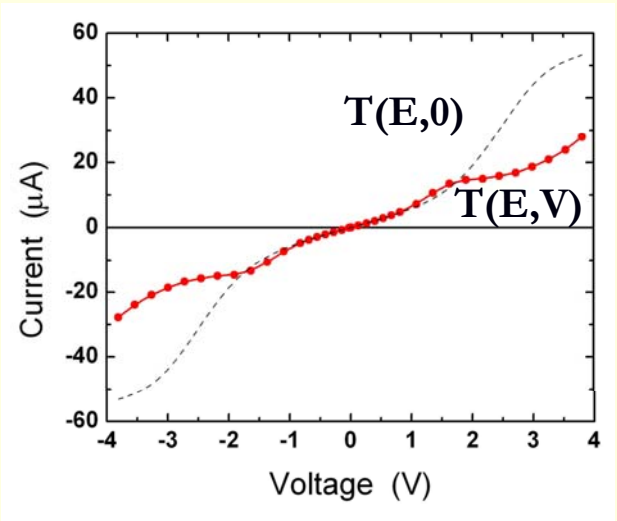
Figure: k resolved transmission from clean Co for (a) majority and (b) minority carriers and from oxidized Co for (c) majority and (d) minority carriers. Units 10^{-11} for (a,b) and 10^{-14} for (c,d).

Belashchenko et al., PRB, ***69****, 174408 (2004)*

Transport in Molecular Junctions (all-electron *ab-initio* calculation)







Faleev *et al., PRB, 71, 195422 (2005)*

Benefits of Green's Function Approach

- Capable of Handling Open Systems (something periodic DFT codes have trouble with)
- System Properties (electronic charge, density of states, etc) without using wavefunctions
- Ability to Handle Different Scattering Mechanisms through Self Energy Terms (not discussed here)
- Natural Formalism for Transport Calculations