

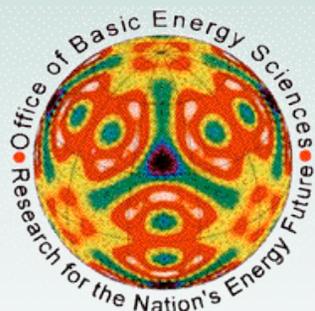
Introduction to the Layer-KKR Method

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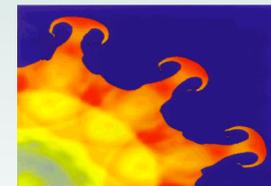
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UT-BATTELLE

History of Layer-KKR

- Multiple scattering theory began with Lord Rayleigh's article in *Phil. Mag.* 1892, "On the Influence of Obstacles in Rectangular Order upon the Properties of a Medium", focusing on the Laplace equation
- N. Kasterin extended Rayleigh's work to Helmholtz equation in 1892
- J. Koringa reasoned that Kasterin's method can be used to find bound electron states of solids from the Schrodinger equation in 1947
- W. Kohn and N. Rostoker rediscovered in 1950's
- Pendry used a layer formulation of KKR method for a dynamic theory of low energy electron diffraction (LEED) in early 1970's
- First version of Layer-KKR code in 1980's based on Pendry's LEED code
- Transport code developed at ORNL in 1990's

From Point Scatterers to Solids

- Many material properties are the result of the electronic density or structure within a solid (i.e. bulk modulus, electrical conductivity, magnetism, etc)
- *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
- Korringa Kohn Rostoker approach (KKR) provides a way to determine the electronic structure by separating potential effects due to individual scatterers from structural information of the crystal.

So your system has potential....

$$[H_0 + V]\psi(\vec{r}) = E\psi(\vec{r})$$

- H_0 is the free space Hamiltonian
- V is the perturbing potential
- Ψ is the electron wavefunction

$$\psi(\vec{r}) = \chi(\vec{r}) + \int G_0(\vec{r}, \vec{r}') V(\vec{r}') \psi(\vec{r}') d^3 r'$$

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_0 is the free electron propagator and describes motion in regions where no scattering from the potential occurs.

Letting Green do the expansion

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...

$$G = G_o + G_o V G_o + G_o V G_o V G_o + G_o V G_o V G_o V G_o + \dots$$

The Green function acts as the system propagator. This expansion shows the infinite number of scattering events that can occur through potential interactions.



George Green's Mill
Nottingham, England

Introducing the T matrix

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

$$\begin{aligned} G &= G_o + G_o (V + VG_o V + VG_o VG_o V + \dots) G_o \\ &= G_o + G_o T G_o \end{aligned}$$

where

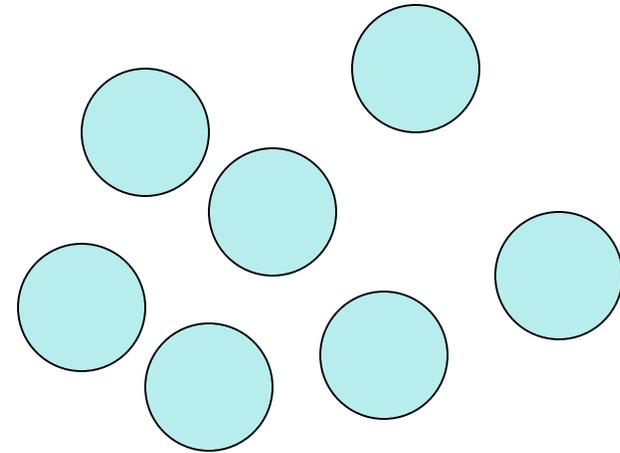
$$T(V) = V + VG_o V + VG_o VG_o V + \dots$$

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:

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

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

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

All the possible paths...

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

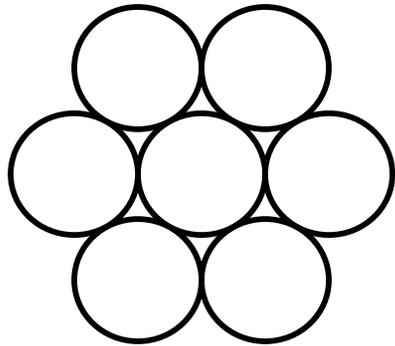
$$T\left(\sum_i V^i\right) = \sum_i t^i + \sum_i \sum_{j \neq i} t^i G_o t^j + \dots$$

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.

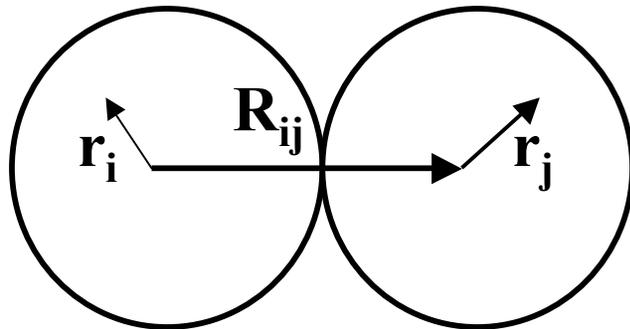
$$T = \sum_{ij} T^{ij} \quad \text{where} \quad T^{ij} = t^i \delta_{ij} + t^i G_o \sum_{k \neq i} T^{kj}$$

Muffin Tins Galore



In the muffin tin approximation:

- potentials at cells are spherically symmetric
- each scatterer can be surrounded by a sphere that doesn't intersect other spheres
- outside these spheres, the potential is zero or a constant



For MT we can expand the Green Function between sites using an angular momentum expansion

$$G_{ij} = \sum_{l,m} \langle \mathbf{r}_i | Y_{lm} | \mathbf{r}_j \rangle G_{lm}(\mathbf{r}_i, \mathbf{r}_j, E)$$

Getting the Band Together

In the MT formalism, the T matrix becomes:

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

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.

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

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:

$$\det [m - \tilde{G}(k)] = 0$$

This allows us to calculate the system band structure.

Layer upon layer...

In the layered version of the KKR approach, the work is divided up into three primary tasks:

- (1) Calculating the properties of the individual t matrices
- (2) Calculating the scattering properties of each layer
- (3) Embedding the layers between the two leads to get the total system.

Green mixes it up

$$G^{\alpha_i}(r, r'; E) = -2i\sqrt{2E} \sum_L Y_L^*(r') Z_L^{\alpha_i}(r_{<}; E) S_L^{\alpha_i}(r_{>}; E) Y_L(r) \\ - 2i\sqrt{2E} \sum_{LL'} Y_L^*(r') Z_L^{\alpha_i}(r_{<}; E) \Gamma_{LL'}^{\alpha_i}(E) Z_{L'}^{\alpha_i}(r; E) Y_{L'}(r)$$

Atomic contribution

**Embedding Contribution
Surrounding medium**

Z and S are the regular and irregular radial solutions to the Schrodinger's equation for site α .

Y are the complex spherical harmonics.

Γ contains all the information on the surrounding medium.

The effective medium revealed

$$\Gamma_{LL'}^{\alpha_i} = \left[\left(t^{\alpha_i} \right)^{-1} \left[\frac{1}{\Omega} \int_{\Omega} d^2 k \tau_i^{\alpha\alpha} (k) - t^{\alpha_i} \right] \left(t^{\alpha_i} \right)^{-1} \right]_{LL'}$$

Things that need to be calculated:

- (1) Single site t matrix
- (2) Scattering properties of a single layer, T_i
- (3) Reflectivity (R^{eff}) - backscattering from surrounding layers of a wave that started in layer i .

Atomic t matrix uncovered

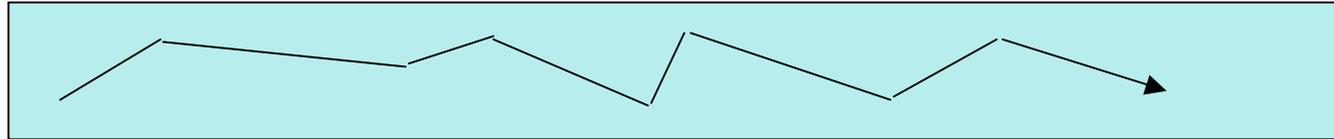
Solve the radial Schrodinger's equation for an isolated muffin tin potential and determine the regular and irregular solutions, Z and S.

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.

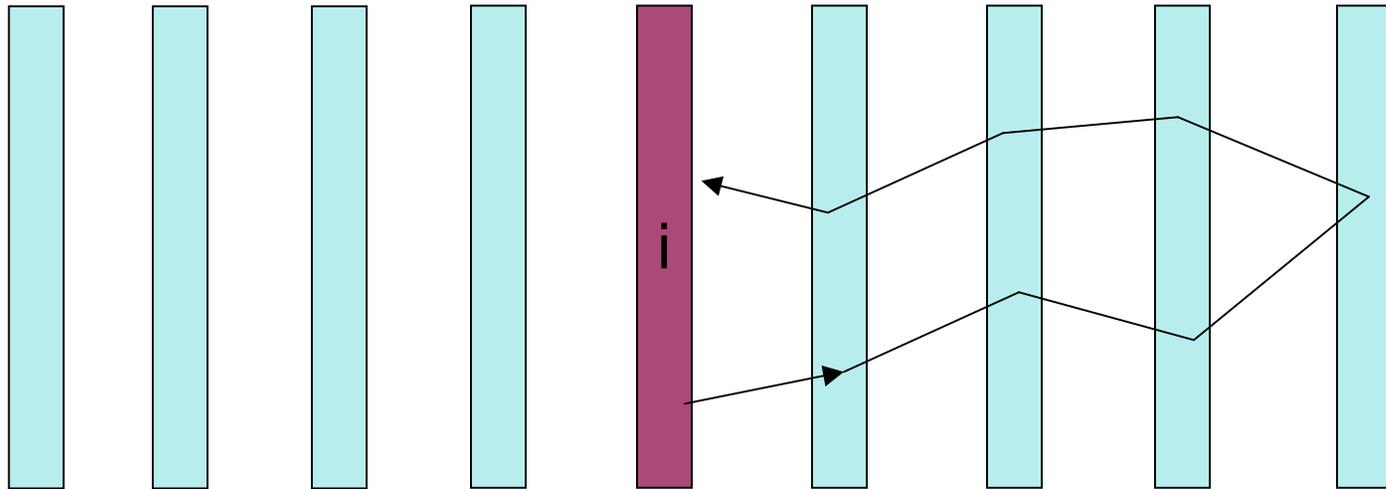
Scattering from a single layer



$$\left[T_i^{-1} \right]_{LL'}^{\alpha\beta} = \left(t_l^{\alpha_i} \right)^{-1} \delta_{LL'} \delta_{\alpha\beta} - g_{LL'}^{\alpha\beta}$$

Like the first discussion, we see that for a single layer the T matrix breaks down into potential scattering and structural information due to the propagator, $g_{LL'}$.

Reflecting on multiple layers



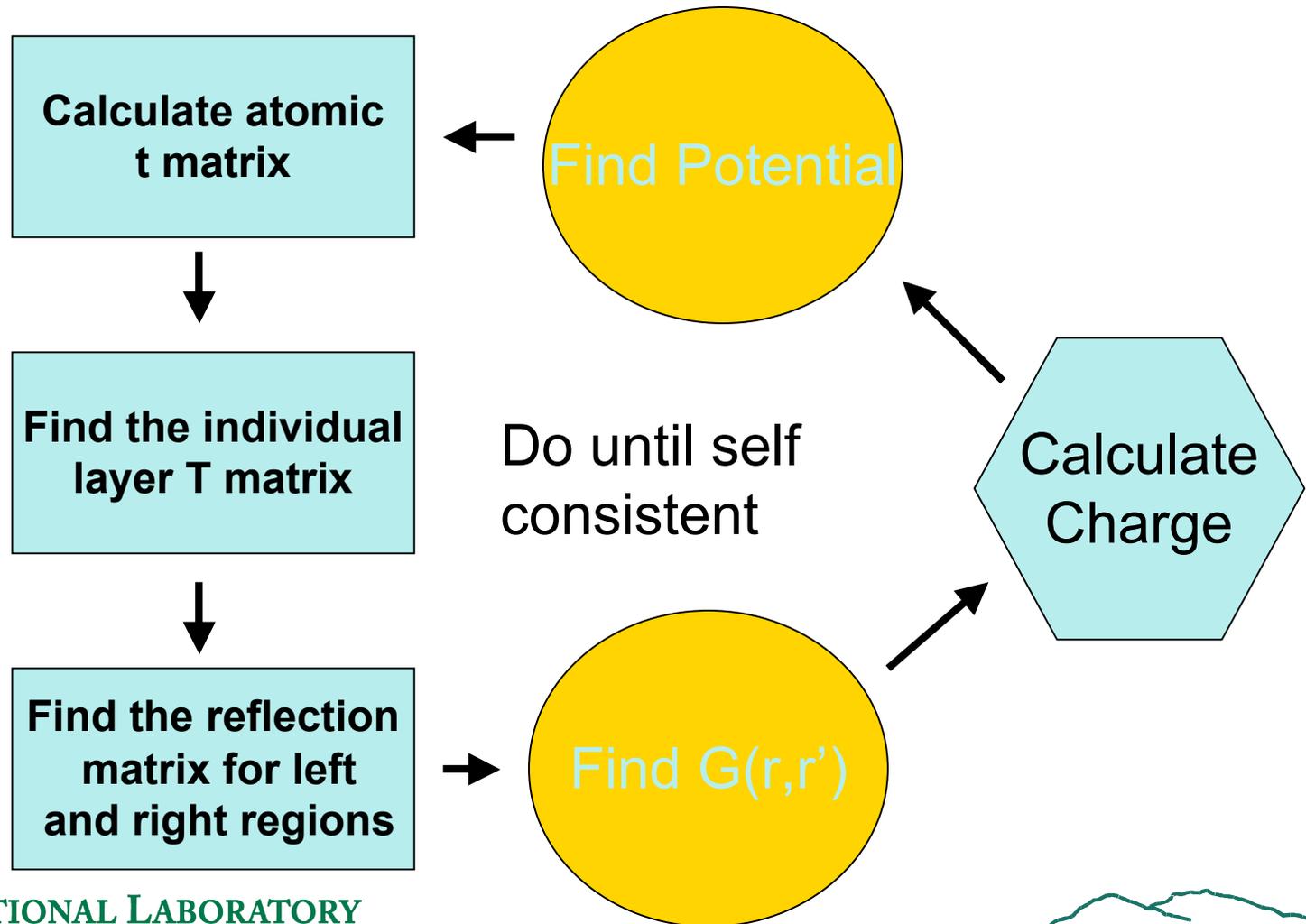
R_{eff} takes into account all possible paths that start at layer i and end back at layer i to determine the overall reflectivity.

A plane-wave basis is used to describe transport between layers.

As we move further away from layer i , the probability of the electron scattering back to layer i should decrease.

LKKR doubles layers until reflection converges.

Calculation Scheme Overview



General LKKR info

Input: atom positions and numbers

Key parameters: Number of energy points, number of k points, number of interlayer plane waves, angular momentum

Correspondence with Real World: The LKKR and other *ab-initio* techniques provide good information on crystal bond lengths, magnetic moments, valence band structure, resistance,...

Caveats: based on LDA so tendency to overbond, poor predictor of band gaps for semiconductors, difficult to converge for systems with closely separated layers, sparse structures need to be packed with empty spheres

LKRR can do

- Electronic structure and total energy
 - 1D, 2D, 3D band structures for bulk, surface, and interface
 - Surface work function
 - Stacking fault energy
 - Magnetic moment and configuration (bulk, surface and interface)
 - Magneto-crystalline anisotropy
 - Exchange coupling between layers
 - Noncollinear spins
- Electron scattering and transport
 - Linear response conductivity
 - Finite bias I-V curve
 - Transmission and reflection coefficients for Bloch states to use with semi-empirical models

LKKR cannot do

- Structural relaxations except volume changes
- Large 2D unit cells
 - Planar orientations with high Miller indices
 - Large molecules
 - Structural disorder
- Bulk solids with strongly ionic bonds
 - No intralayer dipole interaction
 - Exception: alternate layer-by-layer structure, e.g. MgO (100).

References

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