Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

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Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials

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Lecture 8 – *April 18, 2013*

Kohn – Sham Equations

- Concept of Muffin-Tin Potential
- Linearized Augmented Plane-Wave (LAPW)
- Full-potential version FP-LAPW
- Muffin-Tin Orbital Method (& LMTO)

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The Kohn- Sham Method – The Kohn-Sham Equations

- Schrödinger-like equations with local potential

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta\rho} = \int d\vec{r}\,'\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \qquad \frac{\delta E_x[\rho]}{\delta\rho} \qquad \frac{\delta E_c[\rho]}{\delta\rho}$$

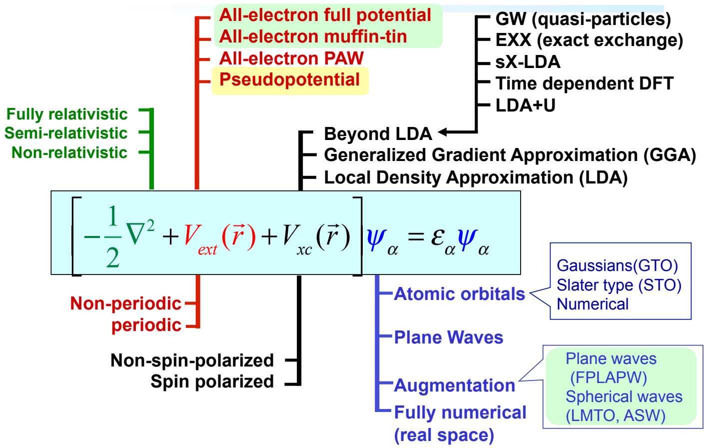
$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

$$\upsilon_{ext}(\vec{r}) = -e^2\sum_{s,n}\frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

- These equation are nonlinear and must be solved iteratively (self-consistently)

DFT: Implementations of the Kohn-Sham Method



All-electron full potential
All-electron muffin-tin
All-electron PAW
Pseudopotential

GW (quasi-particles)
EXX (exact exchange)
sX-LDA
Time dependent DFT
LDA+U

Fully relativistic
Semi-relativistic
Non-relativistic

Beyond LDA
Generalized Gradient Approximation (GGA)
Local Density Approximation (LDA)

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_{xc}(\vec{r})\right]\psi_\alpha = \varepsilon_\alpha\psi_\alpha$$

Non-periodic
periodic

Non-spin-polarized
Spin polarized

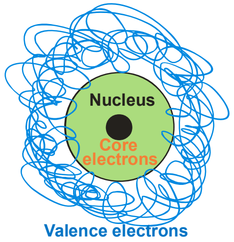
Atomic orbitals
Gaussians(GTO)
Slater type (STO)
Numerical

Plane Waves

Augmentation
Plane waves
(FPLAPW)
Spherical waves
(LMTO, ASW)

Fully numerical
(real space)

Plane Waves and Pseudopotentials



The basic idea of the pseudopotential theory:

- Core electrons are localized and therefore chemically inactive (inert)
- Valence electrons determine chemical properties of atoms and SOLIDS

⇒ **Describe valence states by smooth wavefunctions**

Features of the Pseudopotential Method

- *Pseudopotential is approximation to all-electron case, but…*

Very accurate
•Comparable accuracy to AE in most cases
•Simpler formalism

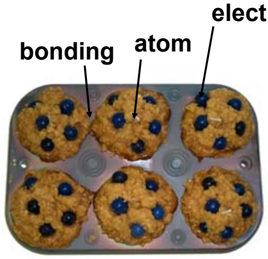
Low computational cost
•Perform calculations on ‘real-life’ materials

Allows full advantage of plane-wave basis sets
•Systematic convergence
•Easy to perform dynamics

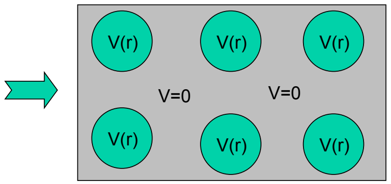
Basis Expansion around atom

- Previous lectures - delocalized basis set (*plane waves)*
- **Muffin tin approaches**
  - 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)

Muffin tin approaches

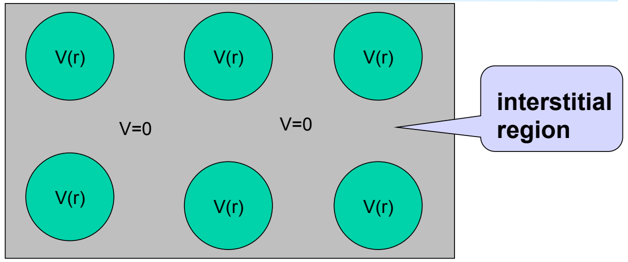


Every day life



Physical model

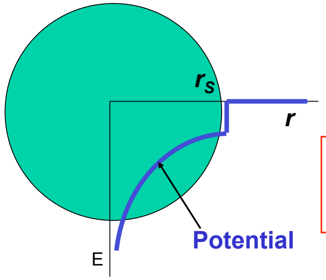
Muffin tin potential shape



Original approximation for the potential:

- spherically symmetric in spheres
- zero (or constant) outside

Muffin Tin Orbitals



Two sets of solutions

- Solve Schr. Eq. in sphere
- Solve Laplace Eq. in interstitial

for a given energy E

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

Main challenges

- Matching conditions at sphere boundary requires orbitals and first derivative to match at sphere boundary
- Needed - secular equation that is linear in energy

The original Augmented Plane Wave (APW) method (1)

- All APW descendent methods divide space into atomic centered spheres surrounded by an interstitial region
- The APW basis functions consist of ***planewaves*** in the interstitial region ***augmented into radial solutions*** of the Schrödinger equation inside the MT-spheres
- For a system with one atom per unit cell

Radial solution

$$\chi_{\mathbf{G}}^{\mathrm{APW}}(\mathbf{r},\mathbf{k}) = \begin{cases} e^{i\mathbf{k_G}\cdot\mathbf{r}} & \mathbf{r}\in \mathrm{I} \\ \sum_L a_L^{\mathbf{k_G}} u_l(r,E)Y_L(\hat{\mathbf{r}}) & \mathbf{r}\in \mathrm{MT}, \end{cases}$$

$$\mathbf{k_G} = \mathbf{k} + \mathbf{G}$$

reciprocal lattice vector

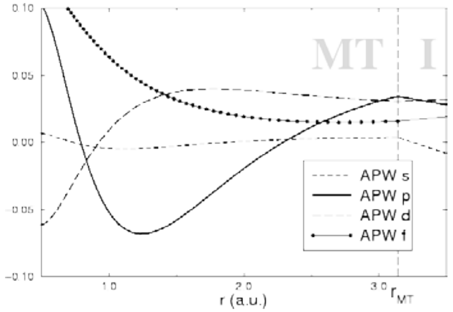
spherical harmonics

wave vector from BZ

$L \equiv \{l, m\}$

The original Augmented Planewave (APW) method (2)

Radial parts of an APW basis function for Ce



$\mathbf{k} = \frac{2\pi}{a}(0.101, 0.208, 0.107)$

$\mathbf{G} = \frac{2\pi}{a}(1, 1, 1)$

Energies: for s-states 0.3 Ry
all other 0.5 Ry

The original Augmented Planewave (APW) method (3)

- The coefficients $a_L^{\mathbf{k}_G}$ are found by expanding each planewave into Bessel functions $j_l(k_G r)$ at the MT-spheres, $r = r_{MT}$, requiring the basis functions to be continuous at the sphere boundaries

This yields $$a_L^{\mathbf{k}_G} = 4\pi i^l Y_L^*(\hat{\mathbf{k}}_G)\frac{j_l(k_G r_{MT})}{u_l(r_{MT},E)}.$$

- The planewaves are energy independent
- The radial solutions u_l depend on the energy at which the radial Schrödinger equation is evaluated

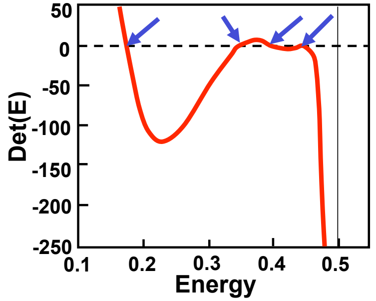
The original Augmented Planewave (APW) method (4)

- An eigenfunction $\Phi_i(\mathbf{r}) = \sum_{\mathbf{G}} C_{i\mathbf{G}}\chi_{\mathbf{G}}(\mathbf{r},\mathbf{k})$

  can only be efficiently described by orbital solutions u_l evaluated at the eigenenergy $\mathcal{E}_i$ of Φ_i
- A new set of APW basis functions must therefore be evaluated for each new energy treated.
- As the matrix elements representing operators depend on the choice of basis set the secular equation is non-linear in energy

$$\det[\underbrace{T_{\mathbf{GG'}}(E)}_{\textbf{kinetic energy operator}} + \underbrace{V_{\mathbf{GG'}}(E)}_{\textbf{Potential}} - E\underbrace{O_{\mathbf{GG'}}(E)}_{\textbf{Overlap}}] = 0,$$

The original Augmented Planewave (APW) method (5) – Finding the APW Eigenvalues



- **The APW determinant must be evaluated for a number of energies in order to find the energies corresponding to eigenvalues.**

The original Augmented Planewave (APW) method (6) – An asymptote problem

- The task of finding the APW eigenvalues becomes somewhat more troublesome, due to the ***asymptote problem***
- When going through a large number of energies, one might hit an energy for which $u_l(r_{MT},E)$ is very small or even equals zero.
- This yields very large or infinite coefficients a_L^i
- The determinant, involving matrix elements with summations over the coefficients will then go to infinity,

$$Det(E) \to \infty$$

- **Any routine used to find the eigenvalues must therefore be adjusted to handle the asymptotic behavior of the determinant at such energies**.

The original Augmented Planewave (APW) method (7)

$$\det[T_{\mathbf{GG'}}(E) + V_{\mathbf{GG'}}(E) - E\mathcal{O}_{\mathbf{GG'}}(E)] = 0,$$

- The procedure of evaluating the determinant for a number of different energies in order to find the energy eigenvalues makes the APW method very time consuming.

- **If the basis functions, and thereby the matrix elements were independent on energy, the secular equation would turn into a *general eigenvalue problem***

➡ **Linearization procedure**

The Linearized Augmented Plane Wave (LAPW) method

- An energy independent basis set must be able to describe all eigen-functions of the different eigenenergies

- By introducing the energy derivatives $\dot{u}_l \equiv \partial u_l / \partial E$ of the radial solutions u_l

  Andersen constructed an ***energy independent LAPW basis set***

O.K. Andersen, Phys. Rev. B 12, 3060 (1975)

$$\chi_{\mathbf{G}}^{\mathrm{LAPW}}(\mathbf{r},\mathbf{k}) = \begin{cases} e^{i\mathbf{k_G}\cdot\mathbf{r}} & \mathbf{r} \in \mathrm{I} \\ \sum_L R_L^{\mathrm{LAPW}}(r) Y_L(\hat{\mathbf{r}}) & \mathbf{r} \in \mathrm{MT} \end{cases}$$

$$R_L^{\mathrm{LAPW}}(r) = a_L^{\mathbf{k_G}} u_l(r, \mathcal{E}_1) + b_L^{\mathbf{k_G}} \dot{u}_l(r, \mathcal{E}_1)$$

linearization energy

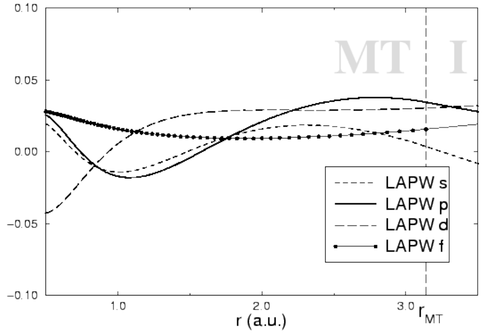
The Linearized Augmented Planewave (LAPW) method

- $\chi_{\mathbf{G}}^{\mathrm{LAPW}}$ provides a sufficient basis for eigenfunctions in an energy range around the linearization energy $\mathcal{E}_1$

- The two coefficients $a_L^{\mathbf{k_G}}$ and $b_L^{\mathbf{k_G}}$ are determined by forcing each basis function to be continuously differentiable, i.e., continuous with continuous first derivative, at the surfaces of the MT-spheres.

The Linearized Augmented Planewave (LAPW) method

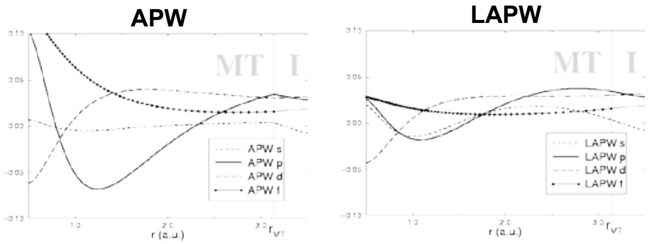
Radial parts of an LAPW basis function for Ce



The k and G as for APW basis functions
Reference energies: 0.3 Ry for s-states, 0.5 Ry for other

The Linearized Augmented Plane-wave (LAPW) method

Radial parts of an LAPW basis function for Ce



- The linear combinations of $u_l(r,\mathcal{E}_1)$ and $\dot{u}_l(r,\mathcal{E}_1)$ smoothly connected to the Bessel expansion at $r = r_{MT}$ differ considerably from the original APW solutions $u_l(r,\mathcal{E}_1)$

[2nd, or 3rd order expansion of $u_l(r,E)$?]

The Linearized Augmented Planewave (LAPW) method

- Thereby the LAPW basis functions, although more flexible in describing eigenfunctions far from $\mathcal{E}_1$ provide a poorer basis set close to $\mathcal{E}_1$

⇒ **There is no free lunch!**

  - The poorer basis set requires a larger number of planewaves
  - It is easier to solve larger general eigenequation than to deal with smaller determinant

$$\underbrace{det[\hat{T} + (\hat{V} - \varepsilon_\alpha I)\hat{O}]}_{} = 0$$

The matrix is diagonalized,
giving all LAPW eigenenergies at one time

The APW (LAPW) + localized orbitals

- The **variational freedom can be improved** by using a complementary basis set consisting of ***local orbitals.***
- They are local in the sense that they are completely confined within the MT-spheres

$$\chi_L^{lo}(\mathbf{r},\mathbf{k}) = \begin{cases} 0 & \mathbf{r} \in \mathrm{I} \\ R_L^{lo}(r) Y_L(\hat{\mathbf{r}}) & \mathbf{r} \in \mathrm{MT}. \end{cases}$$

$$R_L^{lo}(r) = a_L^{lo} u_l(r,\mathcal{E}_1) + b_L^{lo} \dot{u}_l(r,\mathcal{E}_1)$$

is set to 1

is determined using the condition that localized orbital should vanish at $r = r_{MT}$

- Localized orbitals can be generated for another reference energy

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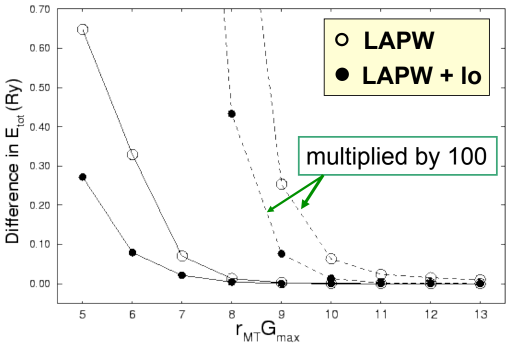
LAPW vs. LAPW+lo

Convergence of total energy for cerium (Z = 58)



Full potential LAPW (FP-LAPW)

- In its general form the LAPW (LAPW+lo) method expands the potential in the following form

$$V(\mathbf{r}) = \begin{cases} \sum\limits_{LM} V_{LM}(r) Y_{LM}(\hat{\mathbf{r}}) & \text{inside sphere} \\ \sum\limits_{\mathbf{K}} V_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} & \text{outside sphere} \end{cases}$$

- and the charge densities analogously.
- **Thus no shape approximations are made, a procedure frequently called a *``full-potential`` method***
  - The *``muffin-tin``* approximation used in early band calculations corresponds to retaining only the $l = 0$ component in the first expression and only the $K = 0$ component of the second
  - This (much older) procedure corresponds to taking the spherical average inside the spheres and the volume average in the interstitial region.

FP LAPW method - Summary

- The LAPW method is a variational expansion approach which solves the equations of DFT by approximating solutions as a finite linear combination of basis functions

- What distinguishes the LAPW method from others is the choice of basis.

- The LAPW basis is constructed to be particularly accurate and efficient for the solution of the ***all-electron** ab initio* electronic-structure problem, where solutions are rapidly varying and atomic-like (like isolated-atom solutions) near the atoms but more smoothly varying and not atomic-like throughout the rest of the cell

FP LAPW method - Summary

- The atomic-like nature of the LAPW basis in the vicinity of the atoms leads to an efficient representation, while the planewave nature in the interstitial region allows for highly accurate solutions for any atomic arrangement: close-packed or open, high-symmetry or low, surfaces or bulk

- An advantage of the ***LAPW method*** over the ***PPs based methods*** is that core and ***semicore electrons*** are explicitly included in the calculations.

- This can be especially important at high pressures, where outer core states may change substantially.

FP LAPW method - References

- D. Singh, ***Plane waves, pseudopotentials and the LAPW method***, Kluwer Academic, 1994

- G.K.H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, "*Efficient linearization of the augmented plane-wave method*," Phys. Rev. B **64, 195134 (2001).**

- P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka and J. Luitz, ***WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*** (Karlheinz Schwarz, Techn. Universität Wien, Austria), 2001. ISBN 3-9501031-1-2.

FP LAPW method - Codes

WIEN2k

http://www.wien2k.at

Peter Blaha, Karlheinz Schwarz & coworkers
Inst. f. Materials Chemistry, TU Vienna

The EXC!TING FP-LAPW Code (GNU – licence)

EXCITING is still in its beta state so check the consistency of your results carefully!

http://exciting.sourceforge.net

Claudia Ambrosch-Draxl
Karl-Franzes Universität Graz, Austria

FP LAPW method - Applications

Theoretical Mineral Physics

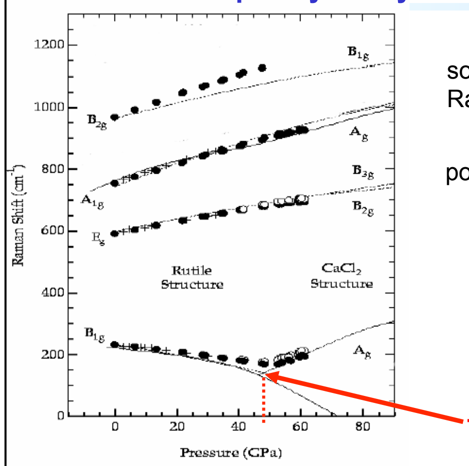
Ronald Cohen, Geophysical Laboratory, Carnegie Institution of Washington

The state-of-the-art in theoretical mineral physics uses first-principles methods.

- In 1992, a phase transition in stishovite (SiO_2) from the rutile structure to the $CaCl_2$ structure at 45 GPa was predicted using the LAPW method
- New Raman experiments found exactly what was predicted theoretically, with a best estimate of the phase transition pressure of 50 GPa.

FP LAPW method – Applications SiO_2

Raman frequency vs. hydrostatic pressure



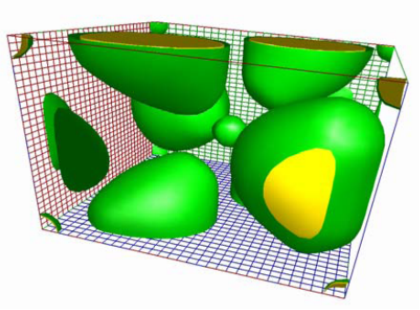
Transition

solid lines – predicted Raman frequencies

points – experimental data

FP LAPW method – Applications SiO_2

Valence charge density computed for SiO_2 stishovite.

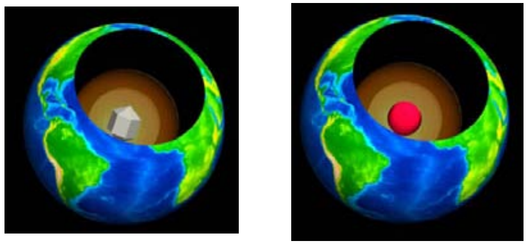


Insight into the nature of bonding

The oxygen ions are elongated towards the three surrounding silicon atoms.

Theoretical mineral physics

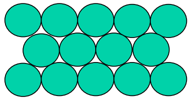
One of the most active areas in first-principles mineral physics is for properties of the Earth's core.



- Temperature of the core ?
- Composition ?

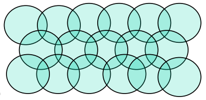
Muffin Tin Orbital Method

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

How to choose radius of spheres?

Solutions in 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 is zero as well

$$\boxed{\nabla^2\varphi(\mathbf{r},E)=0} \rightarrow \varphi(\mathbf{r})=R(r)Y_L(\hat{r}) \quad \textit{L=(l,m)}\ \ \textit{l=0,1,2,… |m|<l}$$

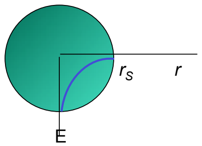
- **Take advantage of spherical symmetry** – express wavefunction in terms of spherical harmonics and radial portion

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

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

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

Solutions within the Atomic Spheres



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

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

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

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

Normalization function

Potential function obtained from matching conditions

Muffin Tin Orbitals

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

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

- **Where the *muffin tin orbitals* are given by:**

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

Muffin-tin Head

$$=K_L(\mathbf{r}_\mathbf{R}) \qquad \text{for } r_R>r_S$$

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

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

Structure constants – lattice info

Muffin Tin Orbitals

- **ASA gives particularly simple solutions in the interstitial region**

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

MT head

$$=K_L(\mathbf{r}_\mathbf{R}) \qquad r_R>r_S$$

MT tail in interstitial

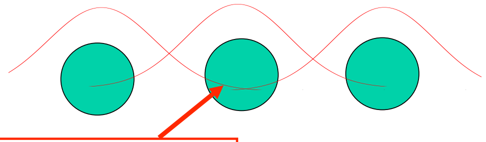
$$=-\sum_L S_{RL,R'L'}J_{L'}(\mathbf{r}_{\mathbf{R}'}) \qquad r_{R'}<r_{S'}\ \ (R'\neq R)$$

MT tail at other spheres

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

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

Canceling Muffin Tin Tails



Tail Cancellation needed

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

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

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

The Linearization of the problem

- Taylor expansion of the orbital…

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

with E_V being a reference energy for the problem

- This allows us to express the system in terms of ***linear muffin tin orbitals*** that depend on φ and $\dot{\varphi}$

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

chosen in such a way that the linear muffin tin orbitals and its derivatives match continuously to tail functions at muffin-tin sphere radius

⇨ **LMTO method**

Advantages of the LMTO over MTO

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

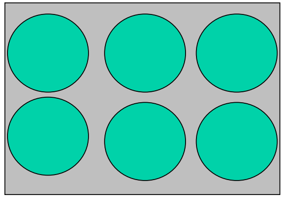
Accuracy: Eigenvalues correct up to third order in (E-E_v)

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

→Two reference energies often required

Full Potential Linear Muffin-Tin Orbital (FP-LMTO) method

- In a ***full potential*** method the idea is to describe the potentials and charge densities in the crystal without the approximation of regarding them as necessarily spherical.
- In FP-LMTO the unit cell is divided into non-overlapping muffin-tin spheres around the atoms and an interstitial region outside these spheres.



LMTO - Comparison with PPs and plane waves

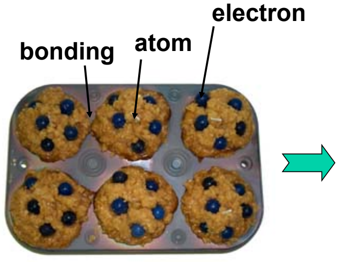
Comparison to PPs and plane waves

→ Very complicated formalism (and codes !) ☹
→No forces and stresses up to now ! ☹
→Problem to judge convergence of results ☹
→Relatively small secular matrices ☺
(standard diagonalization techniques efficient)
→All-electron technique ☺
(core electrons in spheres)
→Minimal basis, full analogy to atoms ☺
→Simple, approximative tight-binding version ☺

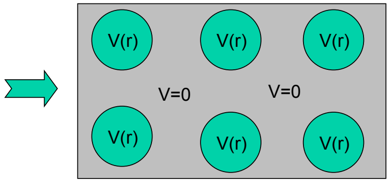
LMTO is commonly used, specially for metals

- ○ **Multiple Scattering Theory**
  &
- ○ **Basics of the alloy theory**

Muffin tin approaches (KKR & LMTO)



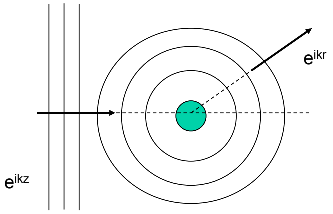
Every day life



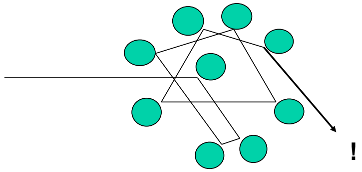
Physical model

Multiple Scattering Theory (MST)

- ***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 (KKR)
- 1960's – **first serious calculations using the approach – computers begin to catch up with the theory!**

Archives (http://www.aip.org/history/esva)

Multiple Scattering Theory – Basic Equation

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

-**H$_o$** is the free space Hamiltonian
-**V** is the perturbing potential
−Y is the electron wavefunction

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

- We can express the wavefunction at some position as a sum of the free space wavefunction, χ, 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

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

$$\boxed{G = G_o + G_o V G}$$

- We can expand this equation out to infinity…

$$\boxed{G = G_o + G_o V G_o + G_o V G_o V G_o + G_o V G_o V G_o V G_o + \ldots}$$

- 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$_o$*.

George Green's Mill
Nottingham, England

Introducing *T*-matrix

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

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

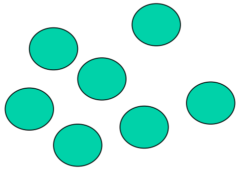
$$\boxed{G = G_o + G_o T G_o}$$

where

$$\boxed{T(V) = V + VG_oV + VG_oVG_oV + \ldots}$$

- 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 $\boldsymbol{T}$ 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 $\boldsymbol{t}$ matrix.

$$\boxed{t^i = V^i + V^i G_o V^i + V^i G_o V^i G_o V^i + \ldots}$$

Atomic *t*-matrix

- Solve the radial Schrodinger's equation for an isolated muffin tin potential and determine the regular and irregular solutions, Z and S.
- The atomic $\boldsymbol{t}$ matrix is diagonal in the angular momentum representation.

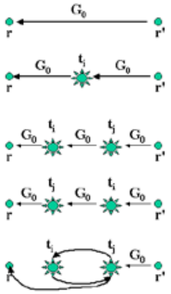
$$\boxed{t_l^\alpha = i \sin \delta_l e^{i\delta_l}}$$

- The phase shift, d, 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 matrices, t_i.

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



- 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 in between.

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

Getting the Band Structure Together

- In the ***MT*** formalism, the $\boldsymbol{T}$ 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 $\boldsymbol{T^{ij}}$ are the elements of its inverse.
- The matrix $\boldsymbol{m}$ is just the inverse of the cell $\boldsymbol{t}$ matrix.

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

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

Getting the Band Structure Together

- The poles of $M(E)$ determine the ***eigenenergies*** for the system for a given k through the following equation:

$$\boxed{\det\left[m(E)-\tilde{G}\left(E,\vec{k}\right)\right]=0} \Longrightarrow \boxed{\varepsilon(\vec{k})}$$

- **This allows us to calculate the system band structure**.
- **Possibility to calculate non-periodic systems (clusters)**

Problem with the KKR method

- 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)

Present Applications the KKR method

- **Practically only first-principles method for very important class of materials, i.e., random alloys on the market**

  Other methods → supercells

- **Coherent Potential Approximation (CPA) relatively easily implemented**

- **Virtual Crystal Approximation (VCA)**
  - **Potential of a Random Binary Alloy A_xB_{1-x}**

    $$V(A_xB_{1-x})=xV(A)+(1-x)V(B)$$

⇒ **Periodicity of the system restored**

Random Alloys

$$\langle G\rangle = G_0 + G_0\Sigma(G) = (G_0^{-1}-\Sigma)^{-1}$$

Self-energy

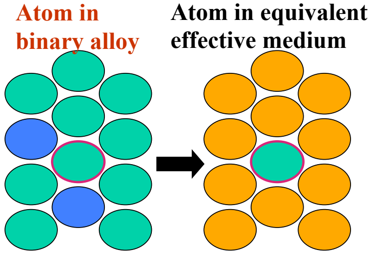
Configurationally averaged Green"s function

$$\langle G\rangle = G_0 + G_0\langle T\rangle G_0$$

$$\boxed{\Sigma = \langle T\rangle(1+G_0\langle T\rangle)^{-1}}$$

Coherent Potential Approximation (CPA)

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

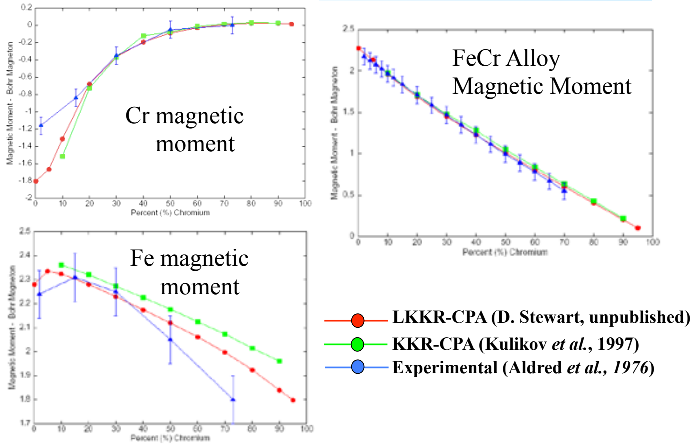


Scattering properties of alloy can be represented by an effective medium

How to determine 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).

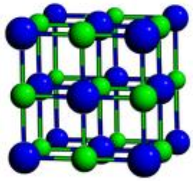
Application of KKR-CPA method- FeCr Alloys



Cluster expansion

Ortho-normal and complete set of basis functions are introduced.

s is the configuration variable (+/- 1 for binary systems)



Basis for M lattice sites is given as:

$$\Phi_{\alpha\nu}^{(M)}(\boldsymbol{\sigma}) = \Theta_{v_1}(\sigma_1)\Theta_{v_2}(\sigma_2)\cdots\Theta_{v_M}(\sigma_M).$$

Energy of the lattice (M sites) is given as:

$$E(\boldsymbol{\sigma}) = J_0 + \sum_{K=1}^{M}\sum_{\alpha_K}\sum_{\nu_K} J_{\alpha\nu}^{(K)}\Phi_{\alpha\nu}^{(K)}(\boldsymbol{\sigma}).$$

For all cluster sizes

For all clusters with number of atoms =K

$$J_{\alpha\nu}^{(K)} = \langle E(\boldsymbol{\sigma})|\Phi_{\alpha\nu}^{(K)}(\boldsymbol{\sigma})\rangle$$

Average of energies of all configurations projected onto the basis function

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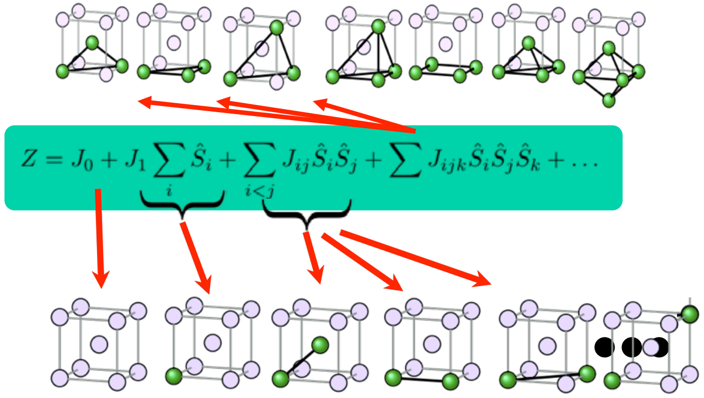
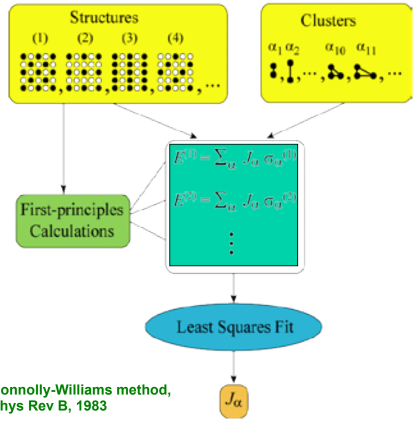
Cluster expansion

For binary system



$$Z = J_0 + J_1\underbrace{\sum_i \hat{S}_i} + \sum_{i<j}\underbrace{J_{ij}\hat{S}_i\hat{S}_j} + \sum J_{ijk}\hat{S}_i\hat{S}_j\hat{S}_k + \ldots$$

Cluster expansion fit



Connolly-Williams method,
Phys Rev B, 1983

- The cluster expansion is able to represent any function $E(s)$ of configuration s by an appropriate selection of the values of J_a.
- Converges rapidly using relatively compact structures (e.g. short-range pairs or small triplets).
- Unknown parameters of the cluster expansion is determined by fitting first-principles energies as shown.

Thank you !