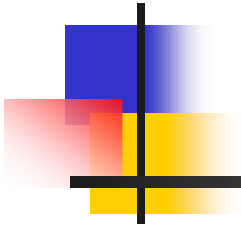
Andersen's LMTO method

S. Y. Savrasov
New Jersey Institute of Technology

O. K. Andersen, PRB 12, 3060 (1975)
O. K. Andersen, O. Jepsen, PRL 53, 2571 (1984)

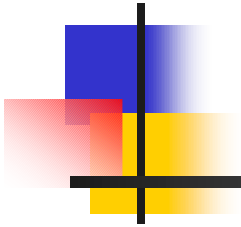
NJIT



Content

- Solving Schroedinger's equation for solids
- Basis sets & variational principle
- Envelope functions
- Linear muffin-tin orbitals
- Tight-binding LMTO representation
- Advanced topics

NJIT



Material Research

Computations of properties of materials

Ground state:

- Density, total energy, magnetization
- Volume & crystal structure
- Lattice dynamics, frozen magnons

Excitations:

- One-electron spectrum
- Photoemission & Optics
- Superconductivity
- Transport

Ab initio Material Design

NJIT

Solving Schroedinger equation for solids

Density Functional Theory (Hohenberg, Kohn, 1964
Kohn, Sham, 1965)

$$(-\nabla^2 + V_{DFT}(r) - E_{kj})y_{kj}(r) = 0$$

$y_{kj}(r)$ describe one-electron Bloch states

$$y_{kj}(r+R) = e^{ikR} y_{kj}(r)$$

due to periodicity of the potential

$$V_{DFT}(r+R) = V_{DFT}(r)$$

Solving Schroedingers equation for solids

Many-Body Theory (Hartree-Fock, GW, DMFT, etc.)

$$-\nabla^2 y_{kjw}(r) + \int \Sigma(r,r',w) y_{kjw}(r')dr' = E_{kjw} y_{kjw}(r)$$

where $\Sigma(r,r',w)$ is a non-hermitian complex frequency-dependent self-energy operator.

Bloch property is retained

$$y_{kjw}(r+R) = e^{ikR} y_{kjw}(r)$$

due to periodicity of the self-energy:

$$\Sigma(r+R,r'+R,w) = \Sigma(r,r',w)$$

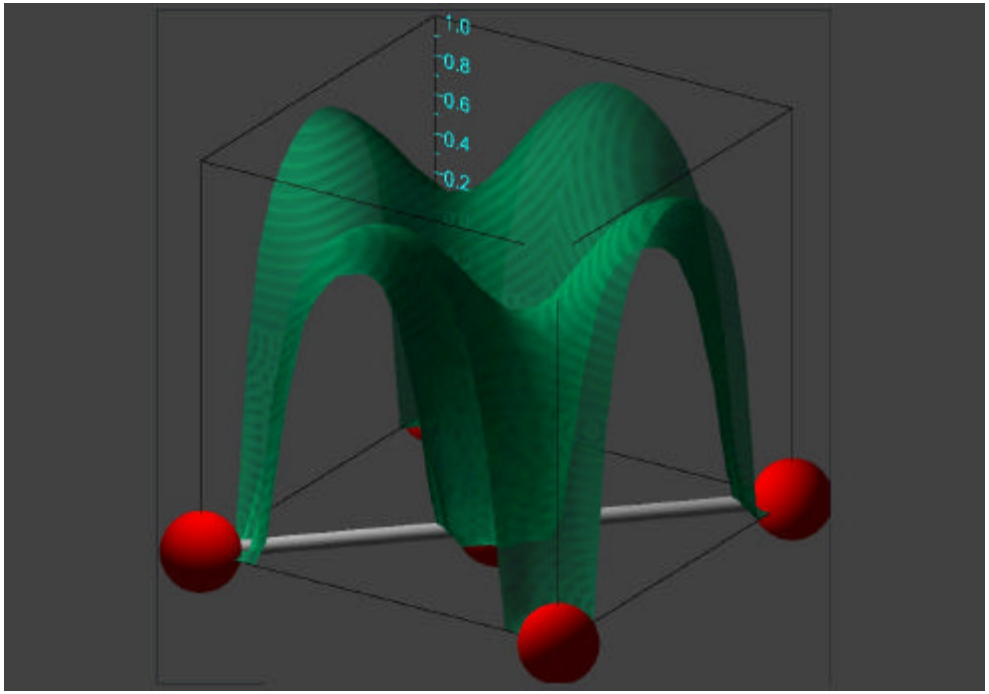
NJIT

Solving Schroedingers equation for solids

Solution of differential equation is required

$$(-\nabla^2 + V(r) - E_{kj}) y_{kj}(r) = 0$$

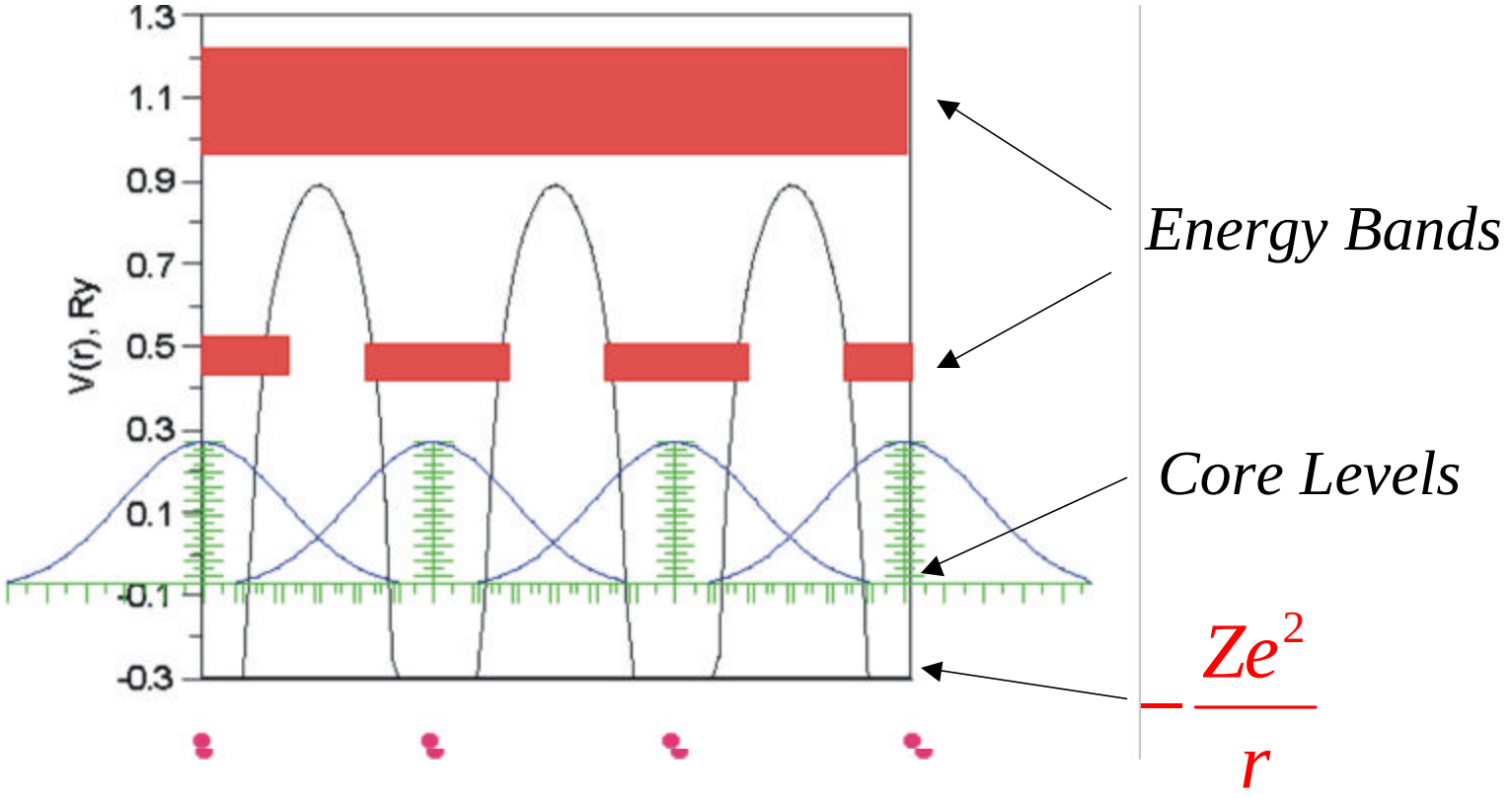
Properties of the potential $V(r)$



NJIT

Solving Schroedingers equation for solids

Properties of the solutions: $E_{kj}, y_{kj}(r)$



NJIT

Basis Sets & Variational Principle

Solving differential equation using expansion

$$y_{kj}(r) = \sum_a A_a^{kj} c_a^k(r)$$

where $c_a^k(r)$ is a basis set satisfying Bloch theorem

$$c_a^k(r+R) = e^{ikR} c_a^k(r)$$

Two most popular examples:

- Plane waves, $c_a^k(r) \to e^{i(k+G)r}$, $a \to G$
- Linear combinations of local orbitals

$$c_a^k(r) = \sum_R e^{ikR} c_a(r-R)$$

Basis Sets & Variational Principle

Variational principle leads us to solve matrix eigenvalue problem

$$\sum_b \langle c_a^k | -\nabla^2 + V - E_{kj} | c_b^k \rangle A_b^{kj} =$$

$$\sum_b (H_{ab}^k - E_{kj} O_{ab}^k) A_b^{kj} = 0$$

where

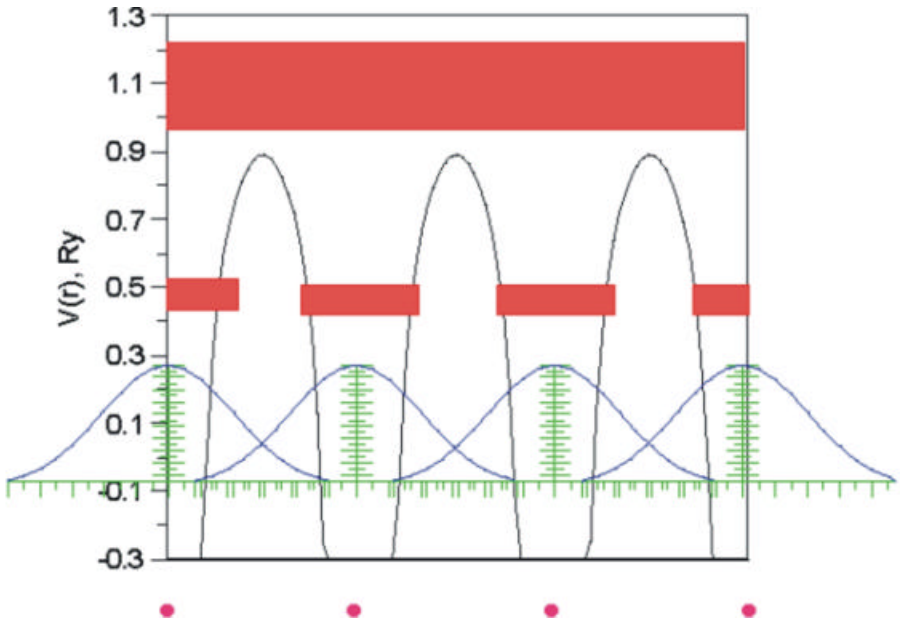
$H_{ab}^k = \langle c_a^k | -\nabla^2 + V | c_b^k \rangle$ is hamiltonian matrix

$O_{ab}^k = \langle c_a^k | c_b^k \rangle$ is overlap matrix

Basis Sets & Variational Principle

Linear combinations of local orbitals will be considered.

$$c_a^k(r) = \sum_R e^{ikR} c_a(r - R)$$



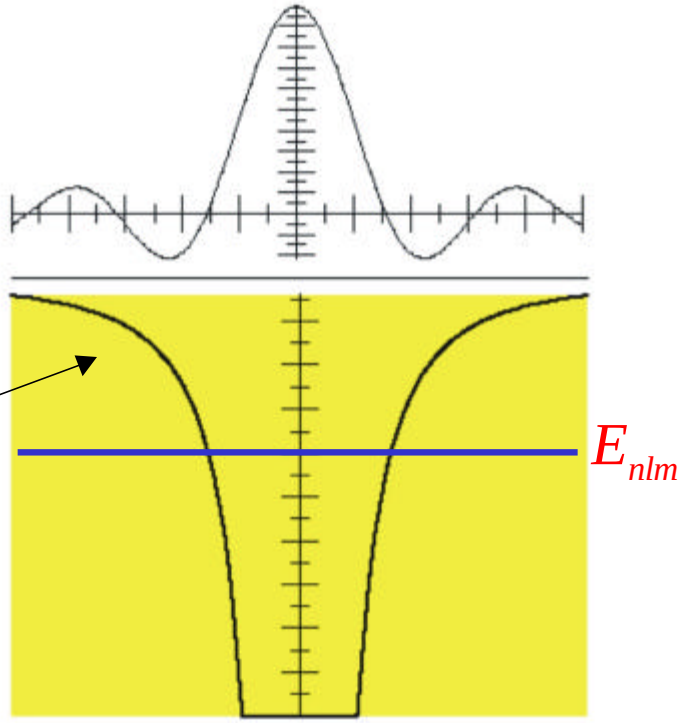
NJIT

Basis Sets & Variational Principle

Smart choice of $c_a(r)$ is important.

Linear Combination of Atomic Orbitals (LCAO)

$$c_a(r) = j_l(r, E_{nlm}) i^l Y_{lm}(\hat{r})$$



Atomic potential

$$c^{k}_{nlm}(r) = \sum_R e^{ikR} c_{nlm}(r - R)$$

to be used in variational principle

NJIT

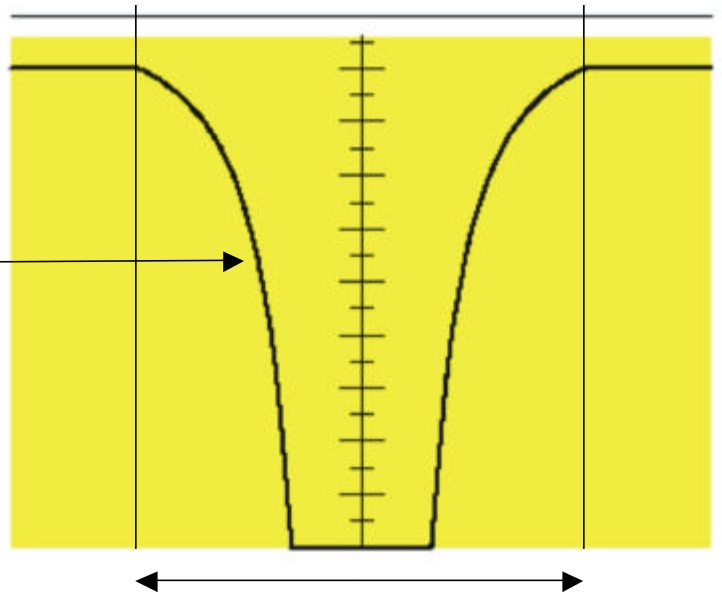
Basis Sets & Variational Principle

Muffin-tin Construction: Space is partitioned into non-overlapping spheres and interstitial region. potential is assumed to be spherically symmetric inside the spheres, and constant in the interstitials**.**

Muffin-tin potential

$$V_{MT}(r) = V_{sph}(r), r < S_{MT}$$

$$V_{MT}(r) = V_{sph}(S_{MT}) = V_0, r > S_{MT}$$



Basis Sets & Variational Principle

Solve radial Schroedinger equation inside the sphere

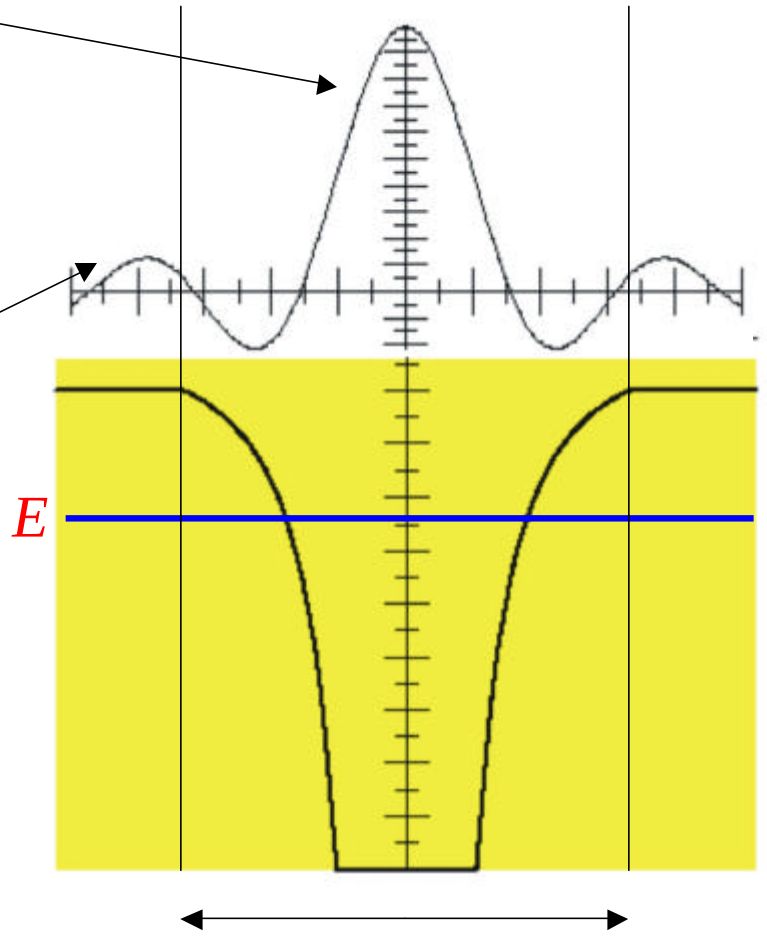
$$j_l(r,E)i^l Y_{lm}(\hat{r})$$

$$(-\nabla_{rl}^2 + V_{sph}(r) - E)j_l(r,E) = 0$$

Solve Helmholtz equation outside the sphere $j_l(r,k^2)i^l Y_{lm}(\hat{r})$

$$(-\nabla_{rl}^2 + V_0 - E)j_l(r,k^2) = 0$$

$$k^2 = E - V_0$$



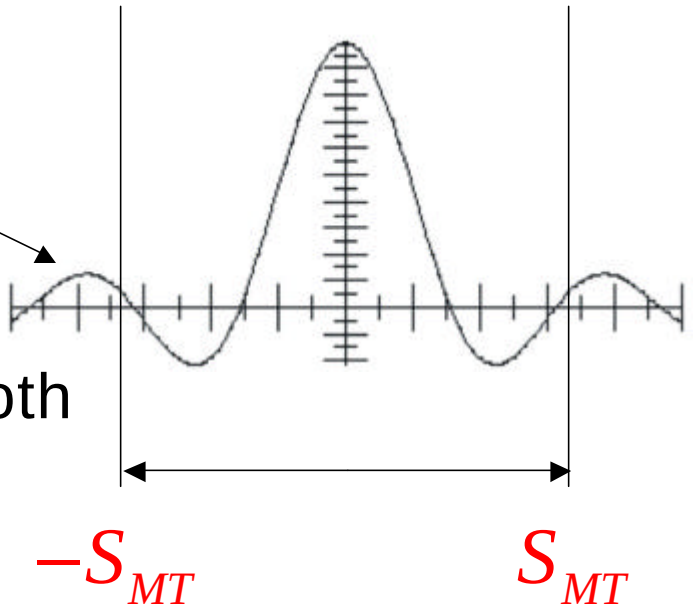
Muffin-tin sphere S_{MT}

NJIT

Basis Sets & Variational Principle

Solution of Helmholtz equation outside the sphere

$$j_l(r,k^2) = a_l j_l(kr) + b_l h_l(kr)$$



where coefficients a_l, b_l provide smooth matching with $j_l(r,E)$

$$a_l = W\{j_l, j_l\}$$

$$b_l = W\{h_l, j_l\}$$

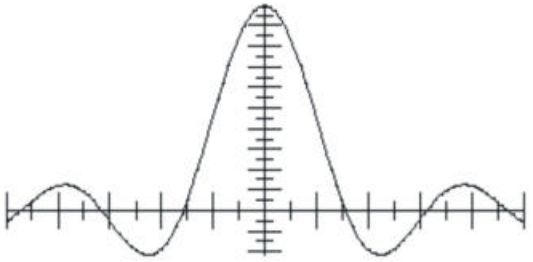
$$W\{f,g\} = f'g - g'f$$

NJIT

Basis Sets & Variational Principle

Linear combinations of local orbitals should be considered.

$$c_L^k(r,E) = \sum_R e^{ikR} c_L(r-R,E)$$



$$c_L(r,E) = j_l(r,E) i^l Y_L(\hat{r}), r < S_{MT}$$

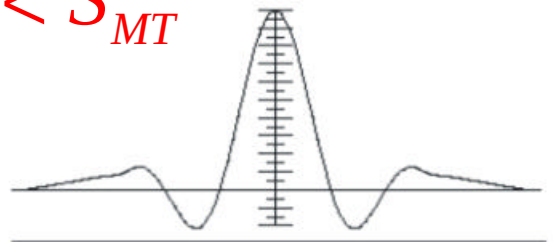
$$c_L(r,E) = \{a_l j_l(kr) + b_l h_l(kr)\} i^l Y_L(\hat{r}), r > S_{MT}$$

is a bad choice since Bessel does not fall off sufficiently fast.

Consider instead:

$$c_L(r,E) = \{j_l(r,E) - a_l j_l(kr)\} i^l Y_L(\hat{r}), r < S_{MT}$$

$$c_L(r,E) = b_l h_l(kr) i^l Y_L(\hat{r}), r > S_{MT}$$



NJIT

Basis Sets & Variational Principle

Bloch sum:

$$c_L^k(r,E) = \sum_R e^{ikR} c_L(r-R,E) =$$

$$j_L(r,E) - a_l j_L(k,r) + \sum_{R\neq 0} e^{ikR} b_l h_L(k, r-R) =$$

$$j_L(r,E) - a_l j_L(k,r) + \sum_{L'} j_{L'}(k,r) S^k_{L'L}(k) b_l =$$

$$j_L(r,E) + \sum_{L'} j_{L'}(k,r)\{S^k_{L'L}(k) b_l - d_{L'L} a_l\}$$

where structure constants are:

$$S^k_{L'L}(k) = \sum_{R\neq 0} e^{ikR} \sum_{L''} C^{L''}_{LL'} h_{L''}(k,R)$$

Basis Sets & Variational Principle

A single L-partial wave

$$c_L^k(r,E) = j_L(r,E) + \sum_{L'} j_{L'}(k,r)\{S_{L'L}^k(k)b_l - d_{L'L}a_l\}$$

is not a solution:

$$(-\nabla^2 + V_{MT}(r) - E)c_L^k(r,E) \neq 0$$

However, a linear combination can be a solution

$$\sum_L A_L^k c_L^k(r,E) = \sum_L A_L^k j_L(r,E) = y_k(r)$$

Tail cancellation is needed

$$\sum_L \{S_{L'L}^k(k)b_l(E) - d_{L'L}a_l(E)\}A_L^k = 0$$

which occurs at selected E_{kj}, A_L^{kj}

Basis Sets & Variational Principle

$c_L^k(r,E)$ is a good basis, basis of **MUFFIN-TIN ORBITALS (MTOs),** which solves Schroedinger equation for MT potential exactly!

For general (or full) potential it can be used with variational principle

$$y_{kj}(r) = \sum_L A_L^{kj} c_L^k(r, E_{kj})$$

$$\sum_L \langle c_{L'}^k | -\nabla^2 + V_{MT} + V_{NMT} - E_{kj} | c_L^k \rangle A_L^{kj} = 0$$

which solves the entire problem sufficiently accurate.
Unfortunately, drawback: implicit E-dependence!

NJIT

Envelope Functions

General idea to get rid of E-dependence: use Taylor series and get **LINEAR MUFFIN-TIN ORBITALS (LMTOs)**

$$j_l(r,E) = j_l(r,E_{nl}) + (E - E_{nl})\dot{j}_l(r,E_{nl})$$

$$j_l(r,D) = j_l(r,E_{nl}) + \dot{D}_{nl}^{-1}(D - D_{nl})\dot{j}_l(r,E_{nl})$$

$$D_l(E) = S j_l'(S,E) / j_l(S,E)$$

Before doing that, consider one more useful construction: **envelope function**.

In fact, concept of envelope functions is very general.

By choosing appropriate envelope functions, such as plane waves, Gaussians, spherical waves (Hankel functions) we will generate various electronic structure methods (**APW, LAPW, LCGO, LCMTO, LMTO**, etc.)

Envelope Functions

Algorithm, in terms of which we came up with the **MUFFIN-TIN ORBITAL** construction:

Step 1. Take a Hankel function

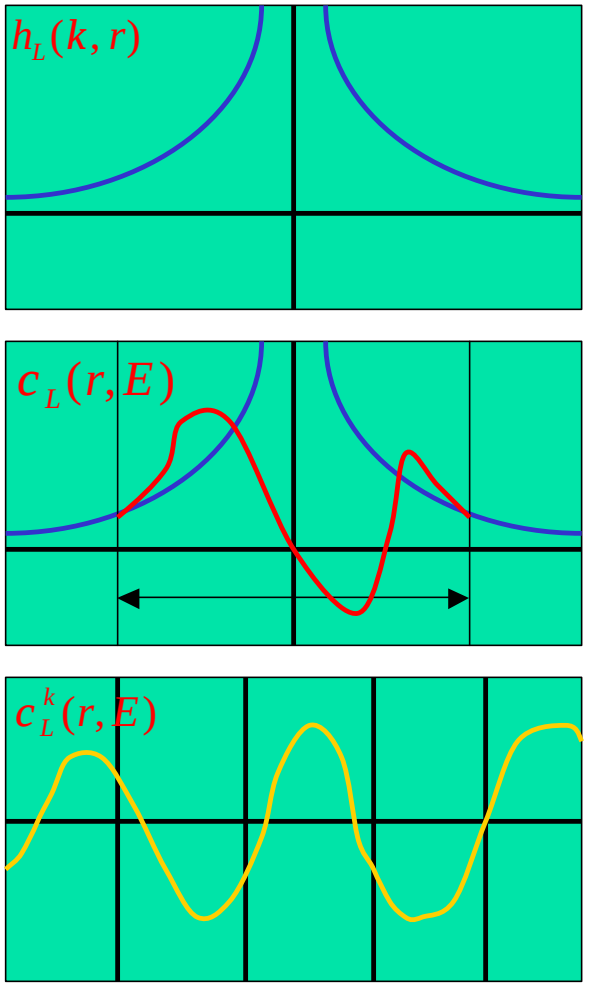
$$h_L(r, E - V_0) = h_L(k, r)$$

Step 2. Augment it inside the sphere by linear combination:

$$\{j_L(r, E) - a_l\, j_L(k, r)\} / b_l$$

Step 3. Construct a Bloch sum

$$c_L^k(r, E) = \sum_R e^{ikR}\, c_L(r - R, E)$$



NJIT

Envelope Functions

Why take Hankel function as an envelope?

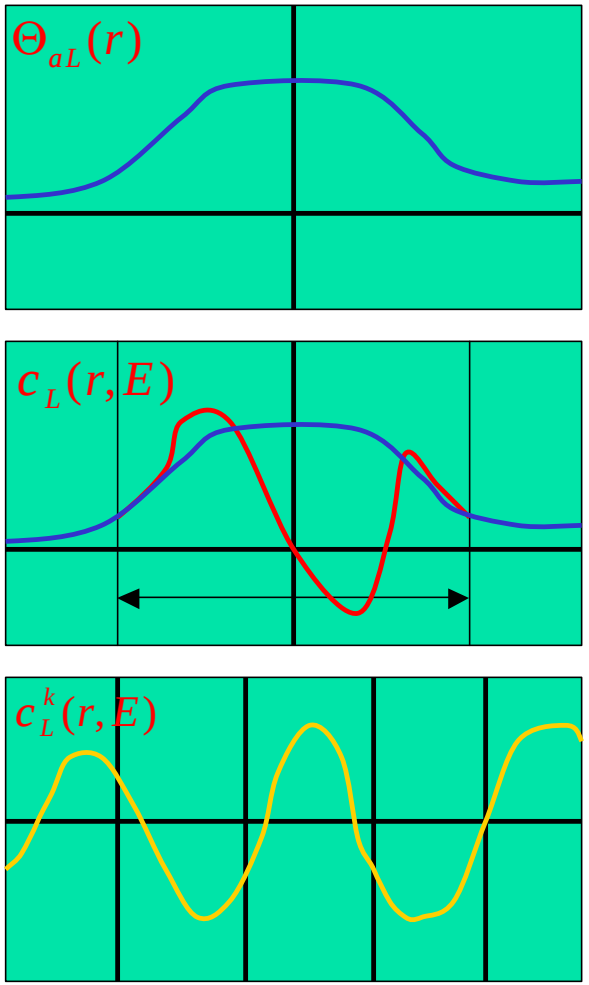
Step 1. Take ANY function $\Theta_{aL}(r)$ which has one center expansion in terms of $\Xi_{bL'}(r)$

Step 2. Augment it inside the sphere by linear combination:

$$a_{al} j_L(r,E) - b_{al} \Xi_{aL}(r)$$

Step 3. Construct a Bloch sum

$$c^k_{aL}(r,E) = \sum_R e^{ikR} c_{aL}(r-R,E)$$

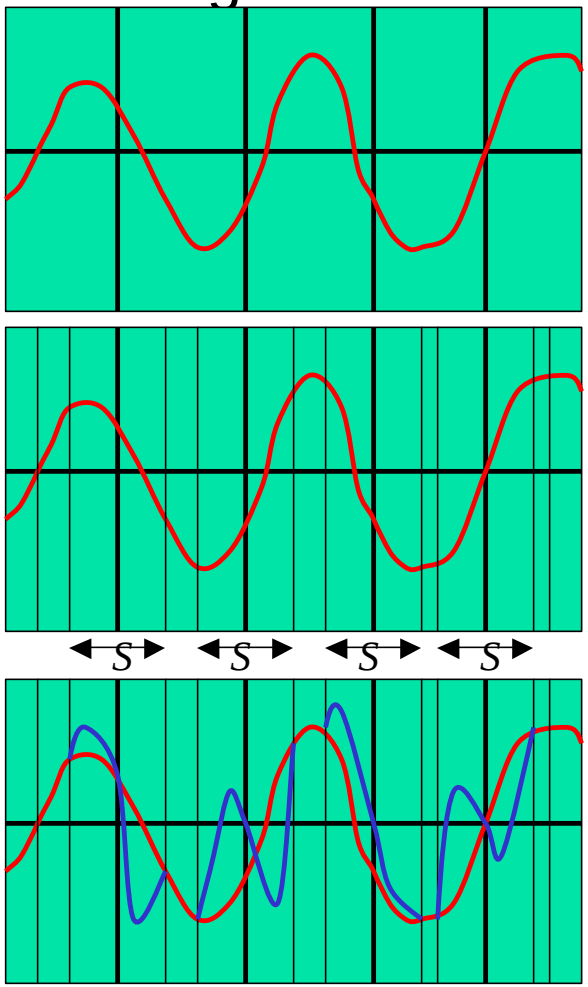


NJIT

Envelope Functions

Envelope functions can be Gaussians or Slater-type orbitals. They can be plane waves which generates augmented plane wave method (APW)

$$e^{i(k+G)r}$$



$$e^{i(k+G)r} =$$

$$4p \sum_L j_l(|k+G|r) Y_L(r) Y_L^*(k+G)$$

$$c_{k+G}(r,E) =$$

$$4p \sum_L j_l(r,E) a_l^{k+G} Y_L(r) Y_L^*(k+G)$$

Envelope Functions

Condition of augmentation – not necessarily smooth like with Hankel functions. APWs are not smooth but continuous.
We can require that linear combination of APWs is smooth:

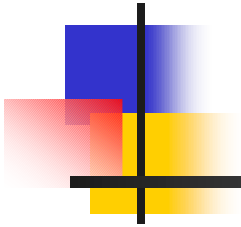
$$\sum_G A_{k+G}^{kj} c_{k+G}(r, E_{kj}) = y_{kj}(r)$$

which solves the problem and delivers spectrum $E_{kj}, y_{kj}(r)$

Another option – use APWs in the variational principle which takes into account discontinuity in the derivative of the basis functions (Slater, 1960)

In all cases so far implicit energy dependence is present!

NJIT



Envelope Functions

We learned how envelope functions augmented inside the spheres generate good basis functions.

The basis functions can be continuous and smooth like MTOs or simply continuous like APWs, in all cases either condition of tail cancellation or requirement of smoothness leads us to a set of equation which delivers the solution of the Schroedinger equation with MT potential.

Variational principle can be used for a full potential case. If basis functions are not smooth additional terms in the functional have to be included.

Implicit energy dependence complicates the problem!

NJIT

Linear Muffin-Tin Orbitals

General idea to get rid of E-dependence: use Teilor series and get read off the energy dependence.

$$j_l(r,E) = j_l(r,E_{nl}) + (E - E_{nl})\dot{j}_l(r,E_{nl})$$

$$j_l(r,D) = j_l(r,E_{nl}) + \dot{D}_{nl}^{-1}(D - D_{nl})\dot{j}_l(r,E_{nl})$$

$$D_l(E) = Sj_l'(S,E)/j_l(S,E)$$

Introduction of phi-dot function gives us an idea that we can always generate smooth basis functions by augmenting inside every sphere a linear combinations of phi's and phi-dot's

The resulting basis functions do not solve Schroedinger equation exactly but we got read of the energy dependence!

The basis functions can be used in the variational principle.

Linear Muffin-Tin Orbitals

Augmented plane waves:

$$c_{k+G}(r,E) = 4p\sum_L j_l(r,E)a_l^{k+G}Y_L(r)Y_L^*(k+G), r \in S$$

$$c_{k+G}(r,E) = e^{i(k+G)r}\,4p\sum_L j_l(|k+G|r)Y_L(r)Y_L^*(k+G), r \in \Omega_{\text{int}}$$

become **smooth** linear augmented plane waves:

$$c_{k+G}(r) = 4p\sum_L \{j_l(r,E_{ul})a_l^{k+G} + \dot{j}_l(r,E_{ul})b_l^{k+G}\}Y_L(r)Y_L^*(k+G), r \in S$$

$$c_{k+G}(r) = e^{i(k+G)r} = 4p\sum_L j_l(|k+G|r)Y_L(r)Y_L^*(k+G), r \in S, r \in \Omega_{\text{int}}$$

NJIT

Linear Muffin-Tin Orbitals

Consider local orbitals.

Energy-dependent muffin-tin orbital defined in all space:

$$c_L(r,E) = \{j_l(r,E) - a_l j_l(kr)\}/b_l i^l Y_L(\hat{r}), r < S_{MT}$$

$$c_L(r,E) = h_l(kr) i^l Y_L(\hat{r}), r > S_{MT}$$

becomes energy-independent

$$c_L(r,E) = \{a_l j_l(r,E_{nl}) + b_l \ddot{j}_l(r,E_{nl})\} i^l Y_L(\hat{r}), r < S_{MT}$$

$$c_L(r,E) = h_l(kr) i^l Y_L(\hat{r}), r > S_{MT}$$

provided we also fix $k = \sqrt{E - V_0}$ to some number (say 0)

Linear Muffin-Tin Orbitals

Bloch sum should be constructed and one center expansion used:

$$\sum_R e^{ikR} c_L(r-R) =$$

$$a_l j_L(r, E_{nl}) + b_l \dot{j}_L(r, E_{nl}) + \sum_{R\neq 0} e^{ikR} h_L(k, r-R) =$$

$$a_l j_L(r, E_{nl}) + b_l \dot{j}_L(r, E_{nl}) + \sum_{L'} j_{L'}(k, r) S^k_{L'L}(k)$$

Final augmentation of tails gives us LMTO:

$$c^k_L(r) = a^h_l j_L(r, E_{nl}) + b^h_l \dot{j}_L(r, E_{nl}) +$$

$$\sum_{L'} \{a^j_{l'} j_{L'}(r, E_{nl'}) + b^j_{l'} \dot{j}_{L'}(r, E_{nl'})\} S^k_{L'L}(k)$$

Linear Muffin-Tin Orbitals

In more compact notations, LMTO is given by

$$c_L^k(r) = \Phi_L^h(r) + \sum_{L'} \Phi_{L'}^j(r) S_{L'L}^k(k)$$

where we introduced radial functions

$$\Phi_L^h(r) = a_l^h j_L(r, E_{nl}) + b_l^h \ddot{j}_L(r, E_{nl})$$

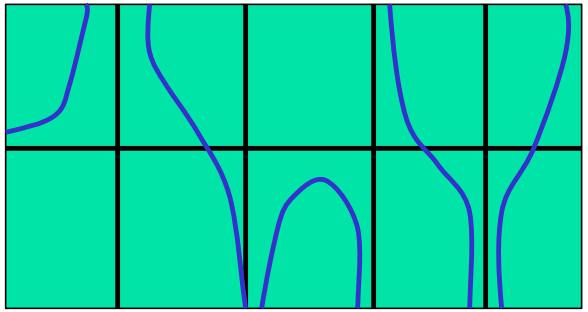
$$\Phi_L^j(r) = a_l^j j_L(r, E_{nl}) + b_l^j \ddot{j}_L(r, E_{nl})$$

which match smoothly to Hankel and Bessel functions.

Linear Muffin-Tin Orbitals

Another way of constructing LMTO.
Consider envelope function as

$$\tilde{c}_L^k(r) = \sum_R e^{ikR} h_L(k, r-R)$$

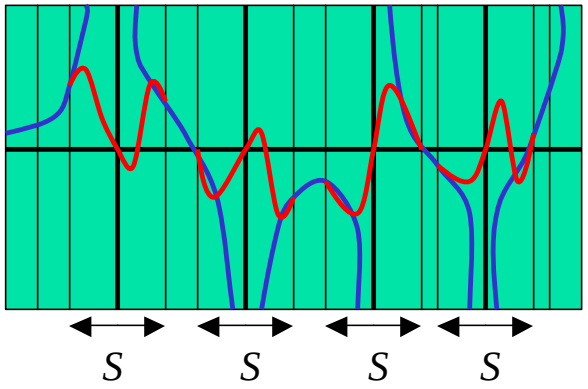


Inside every sphere perform smooth augmentation

$$\tilde{c}_L^k(r) = h_L(k,r) + \sum_{L'} j_{L'}(k,r) S_{L'L}^k(k)$$

$$\Downarrow$$

$$c_L^k(r) = \Phi_L^h(r) + \sum_{L'} \Phi_{L'}^j(r) S_{L'L}^k(k)$$

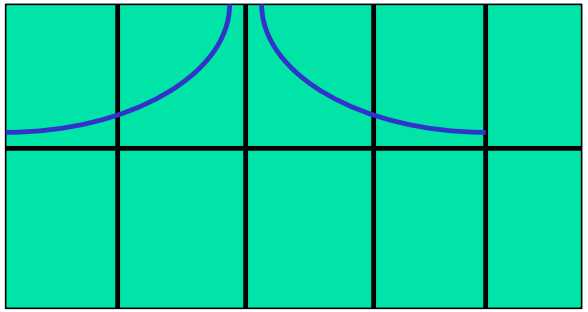


which gives again LMTO construction.

Linear Muffin-Tin Orbitals

We could do the same trick for a single Hankel function

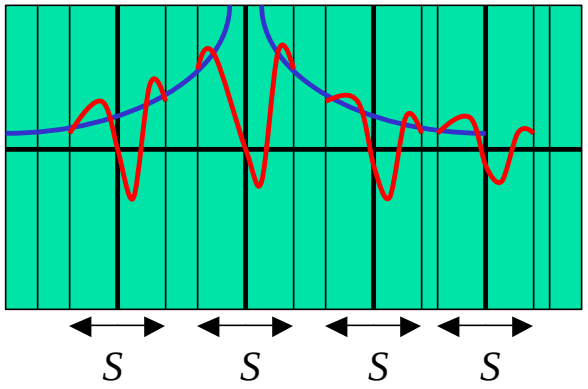
$$\tilde{c}_L(r) = h_L(k, r)$$



Inside every sphere perform one-Center expansion

$$\tilde{c}_L(r) = h_L(k, r) d_{R0} +$$

$$(1 - d_{R0}) \sum_{L'} j_{L'}(k, r - R) S_{L'L}(R)$$



and augmentation

$$c_L(r) = \Phi_L^h(r) d_{R0} +$$

$$(1 - d_{R0}) \sum_{L'} \Phi_{L'}^j(r - R) S_{L'L}(R)$$

Bloch summation is trivial.

NJIT

Linear Muffin-Tin Orbitals

LMTO definition (κ dependence is highlighted):

$$c_{Lk}^{k}(r) = \Phi_{L}^{h}(r) + \sum_{L'} \Phi_{L'}^{j}(r) S_{L'L}^{k}(k), r \in \Omega_{MT}$$

$$c_{Lk}^{k}(r) = \sum_{R} e^{ikR} h_{L}(k, r-R), r \in \Omega_{\text{int}}$$

which should be used as a basis in expanding

$$y_{kj}(r) = \sum_{Lk} A_{Lk}^{kj} c_{Lk}^{k}(r)$$

Variational principle gives us matrix eigenvalue problem.

$$\sum_{Lk} \langle c_{L'k'}^{k} | -\nabla^2 + V - E_{kj} | c_{Lk}^{k} \rangle A_{Lk}^{kj} = 0$$

Linear Muffin-Tin Orbitals

Accuracy and Atomic Sphere Approximation:

LMTO is accurate to first order with respect to $(E-E_\nu)$ within MT spheres.

LMTO is accurate to zero order (κ^2 is fixed) in the interstitials.

Atomic sphere approximation can be used: Blow up MT-spheres until total volume occupied by spheres is equal to cell volume. Take matrix elements only over the spheres.

ASA is a fast, accurate method which eliminates interstitial region and increases the accuracy.

Works well for close packed structures, for open structures needs empty spheres.

NJIT

Tight-Binding LMTO

Tight-Binding LMTO representation

LMTO decays in real space as Hankel function which depends on $\kappa^2=E-V_0$ and can be slow.

Can we construct a faster decaying envelope?

Advantage would be an access to the real space hoppings:

$$c^{k}_{kL}(r) = \sum_R e^{ikR} c_{kL}(r-R)$$

$$H^{k}_{k'L'kL} = \sum_R e^{ikR} H_{k'L'kL}(R)$$

NJIT

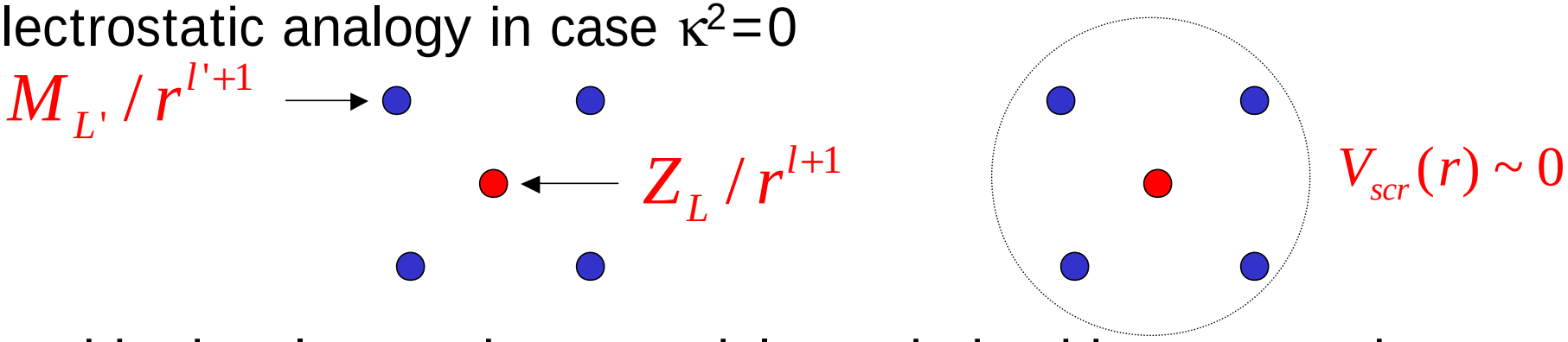
Tight-Binding LMTO

Any linear combination of Hankel functions can be the envelope which is accurate for MT-potential

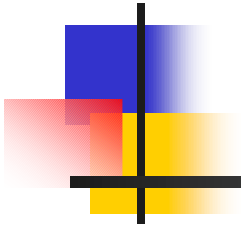
$$h_L^{(a)}(k,r) = \sum_{RL'} A_{LL'}(R) h_{L'}(k, r-R)$$

where A matrix is completely arbitrary. Can we choose A-matrix so that screened Hankel function is localized?

Electrostatic analogy in case $\kappa^2=0$



Outside the cluster, the potential may indeed be screened out. The trick is to find appropriate screening charges (multipoles)



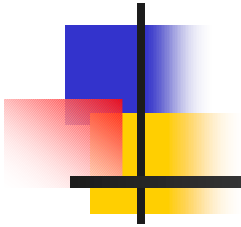
Tight-Binding LMTO

Once problem of screening is solved (*Andersen, Jepsen, 1984*) screened Hankel functions can be used as envelope functions and this leads us to so called:

Tight-Binding LMTO Representation.

Since mathematically it is just a transformation of the basis set, the obtained one-electron spectra are identical with original (long-range) LMTO representation.

However we gain access to short-range representation and access to hopping integrals, and building low-energy tight-binding models.



Advanced Topics

Exact LMTOs

LMTOs are linear combinations of phi's and phi-dot's inside the spheres, but only phi's (Hankel functions at fixed κ) in the interstitials.

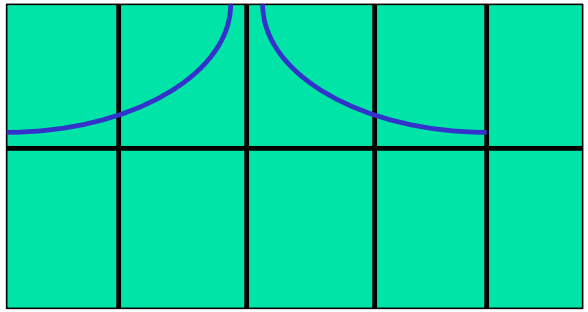
Can we construct the LMTOs so that they will be linear in energy both inside the spheres and inside the interstitials (Hankels and Hankel-dots)?

Yes, Exact LMTOs are these functions!

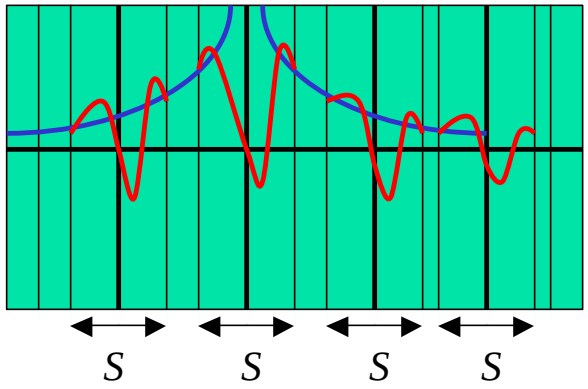
Advanced Topics

Let us revise the procedure of designing LMTO:

Step 1. Take Hankel function (possibly screened) as an envelope.



Step 2. Replace inside all spheres, the Hankel function by linear combinations of phi's and phi-dot's with the condition of smooth matching at the sphere boundaries.

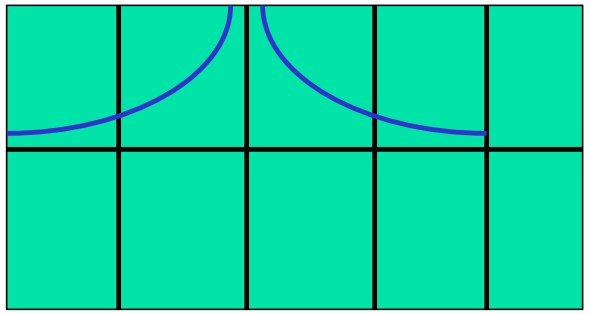


Step 3. Perform Bloch summation.

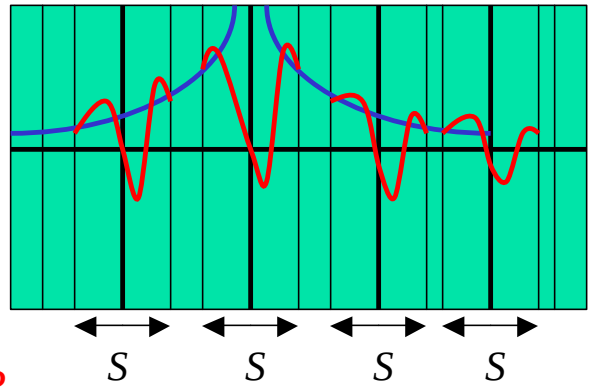
Advanced Topics

Design of exact LMTO (EMTO):

Step 1. Take Hankel function (possibly screened) as an envelope.



Step 2. Replace inside all spheres, the Hankel function by **only phi's** with the continuity condition at the sphere boundaries.



The resulting function $K_{kL}(r-R) = K_{kLR}$ is no longer smooth!

Advanced Topics

Step 3. Take energy-derivative of the partial wave

$$\dot{K}_{k\,LR}$$

So that it involves phi-dot's inside the spheres and Hankel-dot's in the interstitials.

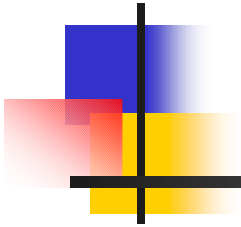
Step 4. Consider a linear combination

$$c_{kLR}(r) = K_{kLR}(r) + \sum_{L'R'} M_{LRL'R'} \dot{K}_{k\,L'R'}(r)$$

where matrix M is chosen so that the whole construction become smooth in all space (kink-cancellation condition)

This results in designing Exact Linear Muffin-Tin Orbital.

NJIT



Advanced Topics

Non-linear MTOs (NMTOs)

Do not restrict ourselves by phi's and phi-dot's, continue Tailor expansion to phi-double-dot's, etc.

In fact, more useful to consider just phi's at a set of additional energies, instead of dealing with energy derivatives.

This results in designing NMTOs which solve Schroedinger's equation in a given energy window even more accurately.

Advanced Topics: FP-LMTO Method

Problem:

Representation of density, potential, solution of Poisson equation, and accurate determination of matrix elements

$$\sum_{Lk} \langle c^{k}_{L'k'} | -\nabla^2 + V - E_{kj} | c^{k}_{Lk} \rangle A^{kj}_{Lk} = 0$$

with LMTOs defined in whole space as follows

$$c^{k}_{Lk}(r) = \Phi^{h}_{L}(r) + \sum_{L'} \Phi^{j}_{L'}(r) S^{k}_{L'L}(k), r \in \Omega_{MT}$$

$$c^{k}_{Lk}(r) = \sum_{R} e^{ikR} h_{L}(k, r-R), r \in \Omega_{\text{int}}$$

NJIT

Advanced Topics: FP-LMTO Method

Ideas:

Use of plane wave Fourier transforms
Weirich, 1984, Wills, 1987, Bloechl, 1986, Savrasov, 1996

Use of atomic cells and once-center spherical harmonics expansions
Savrasov & Savrasov, 1992

Use of interpolation in interstitial region by Hankel functions
Methfessel, 1987

Advanced Topics: FP-LMTO Method

At present, use of plane wave expansions is most accurate

$$r(r) = \sum_L r_L(r) i^l Y_L(\hat{r}), r < S_{MT}$$

$$r(r) = \sum_G r_G e^{iGr}, r \in \Omega_{\text{int}}$$

To design this method we need representation for LMTOs

$$c_{kL}^k(r) = \sum_{L'} c_{kLL'}^k(r) i^l Y_{L'}(\hat{r}), r < S_{MT}$$

$$c_{kL}^k(r) = \sum_G c_{kL}(k+G) e^{i(k+G)r}, r \in \Omega_{\text{int}}$$

Advanced Topics: FP-LMTO Method

Problem: Fourier transform of LMTOs is not easy since

$$c_{Lk}^{k}(r) = \sum_{R} e^{ikR} h_L(k, r-R), r \in \Omega_{\text{int}}$$

Solution: Construct psuedoLMTO which is regualt everywhere

$$\tilde{c}_{Lk}^{k}(r) = smooth, r < S_{MT}$$

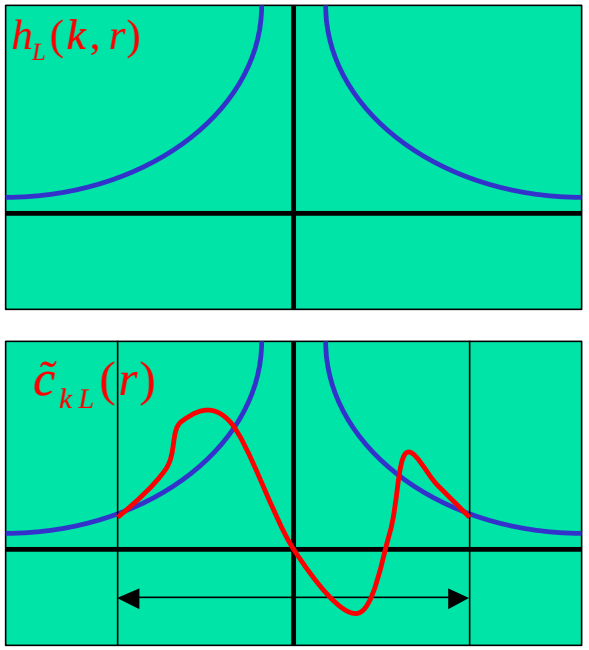
$$\tilde{c}_{Lk}^{k}(r) = c_{Lk}^{k}(r) = \sum_{R} e^{ikR} h_L(k, r-R), r \in \Omega_{\text{int}}$$

and then perform Fourier transformation

NJIT

Advanced Topics: FP-LMTO Method

The idea is simple – replace
the divergent part inside the spheres
by some regular function which matches
continuously and differentiably.



What is the best choice of these regular functions?

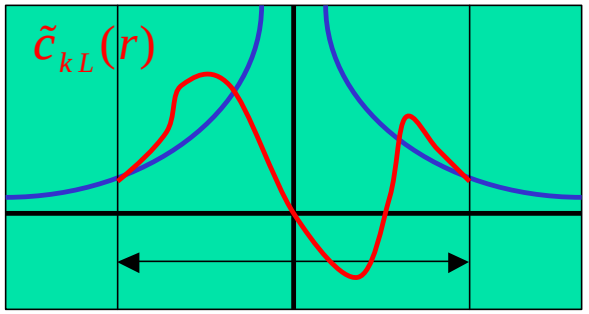
The best choice would be the one
when the Fourier transform is fastly
convergent.

The smoother the function the faster Fourier transform.

Advanced Topics: FP-LMTO Method

Weirich proposed to use linear combinations $a_l j_l(kr) + b_l \dot{j}_l(kr)$

This gives $\tilde{c}_{kL}(k+G) \sim 1/G^4$



Wills proposed to match up to nth order

$$a_l j_l(kr) + b_l \dot{j}_l(kr) + b_l \ddot{j}_l(kr) + c_l \dddot{j}_l(kr) + \ldots$$

This gives $\tilde{c}_{kL}(k+G) \sim n!!/G^{3+n}$

with optimum n found near 10 to 12

Advanced Topics: FP-LMTO Method

Another idea (*Savrasov 1996, Methfessel 1996*)
Smooth Hankel functions

$$(-\nabla^2 - k^2)\tilde{h}_l(kr)i^l Y_L(r) = r^l e^{-hr^2} i^l Y_L(r)$$

Parameter η is chosen so that the right-hand side is nearly zero when r is outside the sphere.

Solution of the equation is a generalized error-like function which can be found by some recurrent relationships.

It is smooth in all orders and gives Fourier transform decaying **exponentially** $\tilde{c}_{kL}(k+G) \sim e^{-|k+G|^2/4h^2}$

NJIT

Advanced Topics: FP-LMTO Method

Finally, we developed all necessary techniques to evaluate matrix elements

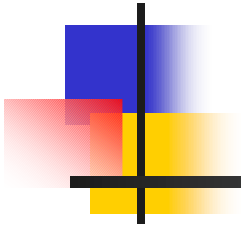
$$\langle c^{k}_{L'k'} | -\nabla^2 + V | c^{k}_{Lk} \rangle_V = \langle c^{k}_{L'k'} | -\nabla^2 + V | c^{k}_{Lk} \rangle_{\Omega_{MT}} +$$

$$\langle \tilde{c}^{k}_{L'k'} | -\nabla^2 + \tilde{V} | \tilde{c}^{k}_{Lk} \rangle_V - \langle \tilde{c}^{k}_{L'k'} | -\nabla^2 + \tilde{V} | \tilde{c}^{k}_{Lk} \rangle_{\Omega_{MT}}$$

where we have also introduced pseudopotential

$$\tilde{V}(r) = smooth, r < S_{MT}$$

$$\tilde{V}(r) = V(r) = \sum_G \tilde{V}_G e^{i(k+G)r}, r \in \Omega_{\text{int}}$$



Advanced Topics: FP-LMTO Method

Computer Programs available:

L m t A R T

(ASA-LMTO & FP LMTO methods)

http://physics.njit.edu/~savrasov

NJIT

Advanced Topics: FP-LMTO Method

L m t A R T features:

- Multiple-kappa LMTO basis sets and multi-panel technique.
- LSDA together with GGA91 and GGA96.
- Total energy and force calculations
- LDA+U method for strongly correlated systems.
- Spin-orbit coupling for heavy elements.
- Finite temperatures
- Full 3D treatment of magnetization in relativistic calculations.
- Non-collinear magnetizm.
- Tight-binding regime.
- Hopping integrals extraction regime.
- Optical Properties (e1,e2, reflectivity, electron energy loss spectra)

Advanced Topics: FP-LMTO Method

Computer Programs available:

M i n d L a b

(**M**aterial **In**formation & **D**esign **Lab**oratory)

Educational edition

MS Windows based software freely available on CDs

during our Workshop, http://physics.njit.edu/~savrasov

Conclusion

- LMTO, TB-LMTO, EMTO, NMTO is economical localized orbital basis set to solve the Schroedinger equation.
- It is physically transparent and allows readily to analyze the nature of bonding in solid-state and molecular systems.
- It is one of the most popular basis sets and widely used in density functional total energy calculations
- It provides a minimal basis for building correct models described by many-body Hamiltonians and further developments of combining electronic structure techniques with many-body dynamical mean-field methods.