Andersen’s LMTO method

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O. K. Andersen, PRB 12, 3060 (1975)
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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
Density Functional Theory (Hohenberg, Kohn, 1964, Kohn, Sham, 1965)

\[
(-\nabla^2 + V_{DFT}(r) - E_{kj})\psi_{kj}(r) = 0
\]

\(\psi_{kj}(r)\) describe one-electron Bloch states

\[
\psi_{kj}(r + R) = e^{ikR}\psi_{kj}(r)
\]

due to periodicity of the potential

\[
V_{DFT}(r + R) = V_{DFT}(r)
\]
Solving Schroedinger's equation for solids

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

\[-\nabla^2 \psi_{kj\omega}(r) + \int \Sigma(r, r', \omega) \psi_{kj\omega}(r') dr' = E_{kj\omega} \psi_{kj\omega}(r)\]

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

Bloch property is retained

\[\psi_{kj\omega}(r + R) = e^{ikR} \psi_{kj\omega}(r)\]

due to periodicity of the self-energy:

\[\Sigma(r + R, r' + R, \omega) = \Sigma(r, r', \omega)\]
Solving Schroedinger's equation for solids

Solution of differential equation is required

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

Properties of the potential \(V(r)\)
Solving Schroedinger's equation for solids

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

- Energy Bands
- Core Levels

$Ze^2/r$
Basis Sets & Variational Principle

Solving differential equation using expansion

\[ \psi_{kj}(r) = \sum_{\alpha} A_{\alpha}^{kj} \chi_{\alpha}^{k}(r) \]

where \( \chi_{\alpha}^{k}(r) \) is a basis set satisfying Bloch theorem

\[ \chi_{\alpha}^{k}(r + R) = e^{ikR} \chi_{\alpha}^{k}(r) \]

Two most popular examples:

• Plane waves, \( \chi_{\alpha}^{k}(r) \rightarrow e^{i(k+G)r}, \quad \alpha \rightarrow G \)

• Linear combinations of local orbitals

\[ \chi_{\alpha}^{k}(r) = \sum_{R} e^{ikR} \chi_{\alpha}(r - R) \]
Variational principle leads us to solve matrix eigenvalue problem

\[ \sum_{\beta} \langle \chi_{\alpha}^{k} | -\nabla^2 + V - E_{kj} | \chi_{\beta}^{k} \rangle A_{\beta}^{kj} = \]

\[ \sum_{\beta} \left( H_{\alpha\beta}^{k} - E_{kj} O_{\alpha\beta}^{k} \right) A_{\beta}^{kj} = 0 \]

where

\[ H_{\alpha\beta}^{k} = \langle \chi_{\alpha}^{k} | -\nabla^2 + V | \chi_{\beta}^{k} \rangle \] is hamiltonian matrix

\[ O_{\alpha\beta}^{k} = \langle \chi_{\alpha}^{k} | \chi_{\beta}^{k} \rangle \] is overlap matrix
Linear combinations of local orbitals will be considered.

\[ \chi^k_\alpha(r) = \sum_R e^{ikR} \chi_\alpha(r - R) \]
Smart choice of $\chi_\alpha(r)$ is important.

Linear Combination of Atomic Orbitals (LCAO)

$$\chi_\alpha(r) = \phi_l(r, E_{nlm}) i^l Y_{lm}(\hat{r})$$

Atomic potential

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

to be used in 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 interstials.

Muffin-tin potential

\[ V_{MT}(r) = V_{sph}(r), \quad r < S_{MT} \]

\[ V_{MT}(r) = V_{sph}(S_{MT}) = V_0, \quad r > S_{MT} \]
Solve radial Schroedinger equation inside the sphere

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

\[
(−\nabla^2_{rl} + V_{sph}(r) − E)\phi_l(r, E) = 0
\]

Solve Helmholtz equation outside the sphere

$$\phi_l(r, \kappa^2)i^l Y_{lm}(\hat{r})$$

\[
(−\nabla^2_{rl} + V_0 − E)\phi_l(r, \kappa^2) = 0
\]

$$\kappa^2 = E − V_0$$
Solution of Helmholtz equation outside the sphere

\[ \varphi_l(r, \kappa^2) = a_l j_l(\kappa r) + b_l h_l(\kappa r) \]

where coefficients \( a_l, b_l \) provide smooth matching with \( \varphi_l(r, E) \)

\[ a_l = W \{ j_l, \varphi_l \} \]
\[ b_l = W \{ h_l, \varphi_l \} \]
\[ W\{f, g\} = f'g - g'f \]
Linear combinations of local orbitals should be considered.

\[ \chi_L^k(r, E) = \sum_R e^{ikR} \chi_L(r - R, E) \]

\[ \chi_L(r, E) = \phi_l(r, E)i^l Y_L(\hat{r}), r < S_{MT} \]

\[ \chi_L(r, E) = \{a_l j_l(\kappa r) + b_l h_l(\kappa r)\}i^l Y_L(\hat{r}), r > S_{MT} \]

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

Consider instead:

\[ \chi_L(r, E) = \{\phi_l(r, E) - a_l j_l(\kappa r)\}i^l Y_L(\hat{r}), r < S_{MT} \]

\[ \chi_L(r, E) = b_l h_l(\kappa r)i^l Y_L(\hat{r}), r > S_{MT} \]
Basis Sets & Variational Principle

Bloch sum:

\[ \chi^k_L(r, E) = \sum_R e^{ikR} \chi_L(r - R, E) = \]

\[ \varphi_L(r, E) - a_l j_L(\kappa, r) + \sum_{R \neq 0} e^{ikR} b_l h_L(\kappa, r - R) = \]

\[ \varphi_L(r, E) - a_l j_L(\kappa, r) + \sum_{L'} j_{L'}(\kappa, r) S^k_{L'L}(\kappa) b_l = \]

\[ \varphi_L(r, E) + \sum_{L'} j_{L'}(\kappa, r)\{ S^k_{L'L}(\kappa) b_l - \delta_{L'L} a_l \} \]

where structure constants are:

\[ S^k_{L'L}(\kappa) = \sum_{R \neq 0} e^{ikR} \sum_{L''} C^{L''}_{LL'} h_{L''}(\kappa, R) \]
Basis Sets & Variational Principle

A single L-partial wave

\[ \chi_L^k(r, E) = \varphi_L(r, E) + \sum_{L'} j_{L'}(\kappa, r) \{ S_{L',L}^k(\kappa) b_l - \delta_{L',L} a_l \} \]

is not a solution:

\[ (-\nabla^2 + V_{MT}(r) - E)\chi_L^k(r, E) \neq 0 \]

However, a linear combination can be a solution

\[ \sum_L A_L^k \chi_L^k(r, E) = \sum_L A_L^k \varphi_L(r, E) = \psi_k(r) \]

Tail cancellation is needed

\[ \sum_L \{ S_{L',L}^k(\kappa) b_l(E) - \delta_{L',L} a_l(E) \} A_L^k = 0 \]

which occurs at selected \( E_{kj}, A_L^{kj} \)
Basis Sets & Variational Principle

\( \chi_L^k(r, E) \) 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

\[
\psi_{kj}(r) = \sum_L A_{L}^{kj} \chi_{L}^{k}(r, E_{kj})
\]

\[
\sum_L \langle \chi_{L}^{k} | -\nabla^2 + V_{MT} + V_{NMT} - E_{kj} | \chi_{L}^{k} \rangle A_{L}^{kj} = 0
\]

which solves the entire problem sufficiently accurate.

**Unfortunately, drawback: implicit E-dependence!**
Envelope Functions

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

\[
\varphi_l(r, E) = \varphi_l(r, E_{vl}) + (E - E_{vl})\dot{\varphi}_l(r, E_{vl})
\]

\[
\varphi_l(r, D) = \varphi_l(r, E_{vl}) + \dot{D}_{vl}^{-1}(D - D_{vl})\dot{\varphi}_l(r, E_{vl})
\]

\[
D_l(E) = S\varphi_l'(S, E)/\varphi_l(S, E)
\]

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

\[ h_L(r, E - V_0) = h_L(\kappa, r) \]

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

\[ \{ \phi_L(r, E) - a_l j_L(\kappa, r) \} / b_l \]

**Step 3.** Construct a Bloch sum

\[ \chi^k_L(r, E) = \sum_R e^{ikR} \chi_L(r - R, E) \]
Envelope Functions

Why take Hankel function as an envelope?

**Step 1.** Take ANY function $\Theta_{\alpha L}(r)$ which has one center expansion in terms of $\Xi_{\beta L}(r)$

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

$$a_{\alpha l} \varphi_L(r, E) - b_{\alpha l} \Xi_{\alpha L}(r)$$

**Step 3.** Construct a Bloch sum

$$\chi_{\alpha L}(r, E) = \sum_R e^{ikR} \chi_{\alpha L}(r - R, E)$$
Envelope functions can be Gaussians or Slater-type orbitals. They can be plane waves which generates augmented plane wave method (APW)

\[ e^{i(k+G)r} \]

\[ e^{i(k+G)r} = 4\pi \sum_{L} j_{l}(k + G | r)Y_{L}(r)Y_{L}^{*}(k + G) \]

\[ \chi_{k+G}(r, E) = 4\pi \sum_{L} \varphi_{l}(r, E)\alpha_{l}^{k+G}Y_{L}(r)Y_{L}^{*}(k + G) \]
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:

\[ \sum_G A_{k+G}^{kj} \chi_{k+G}(r, E_{kj}) = \psi_{kj}(r) \]

which solves the problem and delivers spectrum \( E_{kj}, \psi_{kj}(r) \)

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!**
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!
Linear Muffin-Tin Orbitals

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

\[ \phi_l(r, E) = \phi_l(r, E_{vl}) + (E - E_{vl}) \phi_l'(r, E_{vl}) \]

\[ \phi_l(r, D) = \phi_l(r, E_{vl}) + \dot{D}^{-1}_{vl}(D - D_{vl}) \phi_l(r, E_{vl}) \]

\[ D_l(E) = S\phi_l'(S, E) / \phi_l(S, E) \]

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.
Augmented plane waves:

$$\chi_{k+G}(r, E) = 4\pi \sum_L \varphi_l(r, E) a_l^{k+G} Y_L(r) Y^*_L(k + G), r \in S$$

$$\chi_{k+G}(r, E) = e^{i(k+G) \cdot r} 4\pi \sum_L j_l(|k + G| r) Y_L(r) Y^*_L(k + G), r \in \Omega_{\text{int}}$$

become \textbf{smooth} linear augmented plane waves:

$$\chi_{k+G}(r) = 4\pi \sum_L \{ \varphi_l(r, E_{vl}) a_l^{k+G} + \varphi_l(r, E_{vl}) b_l^{k+G} \} Y_L(r) Y^*_L(k + G), r \in S$$

$$\chi_{k+G}(r) = e^{i(k+G) \cdot r} = 4\pi \sum_L j_l(|k + G| r) Y_L(r) Y^*_L(k + G), r \in S, r \in \Omega_{\text{int}}$$
Consider local orbitals.

Energy-dependent muffin-tin orbital defined in all space:
\[ \chi_L(r, E) = \{ \varphi_l(r, E) - a_l j_l(\kappa r) \} / b_l i^l Y_L(\hat{r}), \ r < S_{MT} \]
\[ \chi_L(r, E) = h_l(\kappa r)i^l Y_L(\hat{r}), \ r > S_{MT} \]

becomes energy-independent
\[ \chi_L(r, E) = \{ a_l \varphi_l(r, E_{vl}) + b_l \dot{\phi}_l(r, E_{vl}) \} i^l Y_L(\hat{r}), \ r < S_{MT} \]
\[ \chi_L(r, E) = h_l(\kappa r)i^l Y_L(\hat{r}), \ r > S_{MT} \]

provided we also fix \( \kappa = \sqrt{E - V_0} \) to some number (say 0)
Linear Muffin-Tin Orbitals

Bloch sum should be constructed and one center expansion used:

\[
\sum_{R} e^{ikR} \chi_{L}(r - R) =
\]

\[
a_{l} \varphi_{L}(r, E_{vl}) + b_{l} \dot{\varphi}_{L}(r, E_{vl}) + \sum_{R \neq 0} e^{ikR} h_{L}(\kappa, r - R) =
\]

\[
a_{l} \varphi_{L}(r, E_{vl}) + b_{l} \dot{\varphi}_{L}(r, E_{vl}) + \sum_{L'} j_{L'}(\kappa, r) S_{L' L}^{k}(\kappa)
\]

Final augmentation of tails gives us LMTO:

\[
\chi_{L}^{k}(r) = a_{l}^{h} \varphi_{L}(r, E_{vl}) + b_{l}^{h} \dot{\varphi}_{L}(r, E_{vl}) + \sum_{L'} \{ a_{l}^{j} \varphi_{L'}(r, E_{vl'}) + b_{l}^{j} \dot{\varphi}_{L'}(r, E_{vl'}) \} S_{L' L}^{k}(\kappa)
\]
In more compact notations, LMTO is given by

$$\chi^k_L(r) = \Phi^h_L(r) + \sum_{L'} \Phi^j_{L'}(r) S^k_{L',L}(\kappa)$$

where we introduced radial functions

$$\Phi^h_L(r) = a^h_L \phi_L(r, E_{vl}) + b^h_L \phi_L'(r, E_{vl})$$

$$\Phi^j_L(r) = a^j_L \phi_L(r, E_{vl}) + b^j_L \phi_L'(r, E_{vl})$$

which match smoothly to Hankel and Bessel functions.
Another way of constructing LMTO. Consider envelope function as

$$\tilde{\chi}^k_L(r) = \sum_R e^{ikR} h_L(\kappa, r - R)$$

Inside every sphere perform smooth augmentation

$$\tilde{\chi}^k_L(r) = h_L(\kappa, r) + \sum_{L'} j_{L'}(\kappa, r) S^k_{L'LL}(\kappa)$$

⇓

$$\chi^k_L(r) = \Phi^h_{L'}(r) + \sum_{L'} \Phi^j_{L'}(r) S^k_{L'LL}(\kappa)$$

which gives again LMTO construction.
We could do the same trick for a single Hankel function

\[ \tilde{\chi}_L(r) = h_L(\kappa, r) \]

Inside every sphere perform one-Center expansion

\[ \tilde{\chi}_L(r) = h_L(\kappa, r)\delta_{R0} + (1 - \delta_{R0}) \sum_{L'} j_{L'}(\kappa, r - R)S_{L'L}(R) \]

and augmentation

\[ \chi_L(r) = \Phi^h_L(r)\delta_{R0} + (1 - \delta_{R0}) \sum_{L'} \Phi^j_{L'}(r - R)S_{L'L}(R) \]

Bloch summation is trivial.
Linear Muffin-Tin Orbitals

LMTO definition ($\kappa$ dependence is highlighted):

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

$$\chi_{L\kappa}^k (r) = \sum_R e^{ikR} h_L (\kappa, r - R), r \in \Omega_{int}$$

which should be used as a basis in expanding

$$\psi_{kj} (r) = \sum_{L\kappa} A_{L\kappa}^{kj} \chi_{L\kappa}^k (r)$$

Variational principle gives us matrix eigenvalue problem.

$$\sum_{L\kappa} \langle \chi_{L'\kappa'}^k | -\nabla^2 + V - E_{kj} | \chi_{L\kappa}^k \rangle A_{L\kappa}^{kj} = 0$$
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 \((\kappa^2 \text{ is fixed})\) 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.
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:

$$\chi_{\kappa L}^k(r) = \sum_R e^{ikR} \chi_{\kappa L}(r - R)$$

$$H_{\kappa' L' \kappa L}^k = \sum_R e^{ikR} H_{\kappa' L' \kappa L}(R)$$
Any linear combination of Hankel functions can be the envelope which is accurate for MT-potential

\[ h^{(\alpha)}_L(\kappa, r) = \sum_{RL'} A_{LL'}(R) h_{L'}(\kappa, r - R) \]

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)
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.
Exact LMTOs

LMTOs are linear combinations of phi’s and phi-dot’s inside the spheres, but only phi’s (Hankel functions at fixed $\kappa$) 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!
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.
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 \( K_{\kappa L}(r - R) = K_{\kappa LR} \) is no longer smooth!
Step 3. Take energy-derivative of the partial wave

\[ \dot{K}_{kLR} \]

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

Step 4. Consider a linear combination

\[ \chi_{kLR}(r) = K_{kLR}(r) + \sum_{L'R'} M_{LRL'R'} \dot{K}_{kL'R'}(r) \]

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

\[
\sum_{L\kappa} \langle \chi_{L',\kappa'}^k | -\nabla^2 + V - E_{kj} | \chi_{L\kappa}^k \rangle A_{L\kappa}^{kj} = 0
\]

with LMTOs defined in whole space as follows

\[
\chi_{L\kappa}^k (r) = \Phi_{L}^h (r) + \sum_{L'} \Phi_{L'}^j (r) S_{L',L}^{k} (\kappa), r \in \Omega_{MT}
\]

\[
\chi_{L\kappa}^k (r) = \sum_{R} e^{ikR} h_{L} (\kappa, r - R), r \in \Omega_{\text{int}}
\]
Ideas:

Use of plane wave Fourier transforms

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

\[
\rho(r) = \sum_{L} \rho_L(r) i^l Y_L(\hat{r}), \; r < S_{MT}
\]

\[
\rho(r) = \sum_{G} \rho_G e^{iGr}, \; r \in \Omega_{int}
\]

To design this method we need representation for LMTOs

\[
\chi_{kL}^k(r) = \sum_{L'} \chi_{kLL'}^k(r) i^l Y_{L'}(\hat{r}), \; r < S_{MT}
\]

\[
\chi_{kL}^k(r) = \sum_{G} \chi_{kL}(k + G) e^{i(k+G)r}, \; r \in \Omega_{int}
\]
**Problem:** Fourier transform of LMTOs is not easy since

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

**Solution:** Construct psuedoLMTO which is regualt everywhere

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

$$\tilde{\chi}_{Lk}^k(r) = \chi_{Lk}^k(r) = \sum_R e^{ikR} h_L(\kappa, r - R), r \in \Omega_{\text{int}}$$

and then perform Fourier transformation
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.
Weirich proposed to use linear combinations \( a_l j_l(\kappa r) + b_l j_l(\kappa r) \)

This gives \( \tilde{\chi}_{\kappa L}(k + G) \sim 1/G^4 \)

Wills proposed to match up to \( n \)th order
\[
a_l j_l(\kappa r) + b_l j_l(\kappa r) + b_l j_l(\kappa r) + c_l j_l(\kappa r) + \ldots
\]

This gives \( \tilde{\chi}_{\kappa L}(k + G) \sim n!!/G^{3+n} \)

with optimum \( n \) found near 10 to 12
Another idea (Savrasov 1996, Methfessel 1996) Smooth Hankel functions

\[
(-\nabla^2 - \kappa^2) \tilde{h}_l(\kappa r) i^l Y_L(r) = r^l e^{-\eta r^2} i^l Y_L(r)
\]

Parameter $\eta$ 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**

\[
\tilde{\chi}_{\kappa L}(k + G) \sim e^{-|k + G|^2 / 4\eta^2}
\]
Finally, we developed all necessary techniques to evaluate matrix elements

\[
\langle \chi_{L'k'}^k, -\nabla^2 + V | \chi_{Lk}^k \rangle_V = \langle \chi_{L'k'}^k, -\nabla^2 + V | \chi_{Lk}^k \rangle_{\Omega_{MT}} + \\
\langle \tilde{\chi}_{L'k'}^k, -\nabla^2 + \tilde{V} | \tilde{\chi}_{Lk}^k \rangle_V - \langle \tilde{\chi}_{L'k'}^k, -\nabla^2 + \tilde{V} | \tilde{\chi}_{Lk}^k \rangle_{\Omega_{MT}}
\]

where we have also introduced pseudopotential

\[
\tilde{V}(r) = \text{smooth, } r < S_{MT} \\
\tilde{V}(r) = V(r) = \sum_G \tilde{V}_G e^{i(k+G)r}, r \in \Omega_{\text{int}}
\]
Computer Programs available:

L m tA R T

(ASA-LMTO & FP LMTO methods)

http://physics.njit.edu/~savrasov
Advanced Topics: FP-LMTO Method

**LMART 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 magnetism.
- Tight-binding regime.
- Hopping integrals extraction regime.
- Optical Properties (e1, e2, reflectivity, electron energy loss spectra)
Computer Programs available:

**MindLab**

(Material Information & Design Laboratory)

Educational edition

MS Windows based software freely available on CDs during our Workshop, [http://physics.njit.edu/~savrasov](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.