Density Functional Theory and the LMTO method
2017 Questaal Hands-On Course
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**Questaal** is the current CCP9 flagship (www.questaal.org)
It is an integrated electronic structure package that combines:
1. **DFT**
2. **GW, QSGW**
3. **DMFT**
4. **Analysis tools**
Outline of Talk

✔ How DFT works, general considerations
  Variants of functionals, self-consistency
✔ Different implementations of DFT, Survey
✔ All-electron methods; how augmentation works
✔ KKR Method
✔ Linearization ⇒ energy-independent basis
✔ The LMTO-ASA approximation
✔ Survey of some features of the ASA suite lm, lmgf, lmpg
✔ lmf : All-electron Full Potential method
Hohenberg and Kohn (1964) proved that the total energy $E$ can be determined solely from the density. The total energy is written:

$$E_{HK}[n] = T_s[n] + \int d^3r n(r)V_{\text{ext}}(r) + \int d^3r n(r)V_H(r) + E_{xc}[n]$$

where the density $n(r)$ is the basic variable. In Density-Functional Theory, $E=E[n(r)]$ --- functional of $n$ alone rather than the (vastly more complicated) $E=E[\{\psi_i\}]$.

They proved that $n(r)$ is determined by the variational principle:

$n(r)$ is the density where $E \to \text{min}$.

The proof is implicit $T[n]$ and $E_{xc}[n]$ are universal but unknown $T[n]$ is very pathological ... it must be to describe e.g. core levels.

⇒ Tractable theory: Kohn-Sham ansatz: Assume

$T[n]=T$ for a non-interacting system that generates $n$
Kohn-Sham Ansatz and the Variational Principle

\[ E_{KS} = T_s[n] + E_{\text{pot}}[n], \quad E_{\text{pot}}[n] = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_H[n] + E_{xc}[n] \]

Noninteracting ansatz provides a means for functional for \( T_{KS} \).

Assume a noninteracting auxiliary system exists which generates the same density. Its K.E. is known:

\[ H_{KS}^{\text{eff}} \psi_i = -\frac{1}{2} \nabla^2 \psi_i + V_{\text{eff}}^{\text{eff}}(\mathbf{r}) \psi_i = \varepsilon_i \psi_i, \quad V_{\text{eff}}^{\text{eff}}(\mathbf{r}) = \frac{\delta E_{\text{pot}}[n(\mathbf{r})]}{\delta n} \]

Multiply by \( \psi^* \) and integrate

\[ \langle \psi_i | -\frac{1}{2} \nabla^2 + V_{\text{eff}}^{\text{eff}} | \psi_i \rangle = \langle \psi_i | \varepsilon_i | \psi_i \rangle = \varepsilon_i \]

Sum over states \( i \) and note

\[ T_{KS} = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle \]

Then

\[ T_{KS} = \sum_i \varepsilon_i - \int d\mathbf{r} V^{\text{eff}}(\mathbf{r}) \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) = E_{bs} - \int d\mathbf{r} V^{\text{in}}(\mathbf{r}) n^{\text{out}}(\mathbf{r}) \]

\[ \text{Density } n(\mathbf{r}) \]

Thus we get at \( T_{KS} \) through a back door.
Kohn-Sham Ansatz in practice

DFT in practice: Kohn-Sham energy functional

\[ E_{KS} = T_s[n] + E_{\text{pot}}[n], \quad E_{\text{pot}}[n] = \int dr V_{\text{ext}}(r)n(r) + E_H[n] + E_{xc}[n] \]

Ansatz:

Get \( T_{KS} \) from orbitals \( \psi_i \) through \( H^{\text{eff}} \) where

\[ H_{KS}^{\text{eff}} \psi_i = -\nabla^2 \psi_i + V^{\text{eff}}(r)\psi_i = \varepsilon_i \psi_i, \quad V^{\text{eff}}(\mathbf{r}) = \frac{\delta E_{KS}[n(\mathbf{r})]}{\delta n} \]

- Tractable functional for the total energy and forces
- An effective non-interacting Schrödinger equation, with eigenfunctions \( \psi_i \) and eigenvalues \( \varepsilon_i \).
- A self-consistent electron density \( n(\mathbf{r}) = \sum_i n_{\text{occ}} |\psi_i(\mathbf{r})|^2 \)

- Ansatz is not controlled or rigorously defined.
- \( \psi_i \) and \( \varepsilon_i \) are fictitious
Self-consistency

Chicken-and egg problem: The density $n(r)$ generates $V_{\text{eff}}(r)$, while $V_{\text{eff}}(r)$ generates $n(r)$ through $V_{\text{eff}}(r) \rightarrow \psi(r) \rightarrow n(r)$. Need one to get the other.

Resolution: guess a trial $V_{\text{eff}}(r)$, and iterate until the $V_{\text{eff}}$ that generates $\psi$ is the same as the $V_{\text{eff}}$ generated by $\psi$.

\[ (-\nabla^2 + V_{\text{eff}})\psi = \varepsilon \psi \]

\[ \psi \]

\[ n = |\psi|^2 \]

\[ V_{\text{eff}}[n(r)] \]
The Harris-Foulkes Functional

The Kohn-Sham functional is then a functional of \( n_{\text{out}} \): 

\[
E_{\text{KS}}[V_{\text{in}}] = E_{bs} - \int d\mathbf{r} V_{\text{in}}(\mathbf{r}) n_{\text{out}}(\mathbf{r}) + E_{\text{pot}}[n_{\text{out}}] 
\]

\[E_{\text{KS}} = E_{\text{KS}}[V_{\text{in}}]\]

Alternative functional where \( n_{\text{in}} \) is the independent variable.

\[
E_{\text{HF}}[n_{\text{in}}] = E_{bs} - \int d\mathbf{r} V[n_{\text{in}}(\mathbf{r})] n_{\text{in}}(\mathbf{r}) + E_{\text{pot}}[n_{\text{in}}] 
\]

\[E_{\text{HF}} = E_{\text{HF}}[n_{\text{in}}]\]

Originally derived by Harris, but found independently and better explained by Foulkes and Haydock (PRB 39, 152520).

A Legendre transformation \([n_{\text{in}} \text{ and } V_{\text{in}} \text{ are conjugate variables}]\)


\( E_{\text{HF}} = E_{\text{KS}} \) at self-consistency, but differ when \( \Delta n \neq 0 \).

\( E_{\text{KS}} \) is variational \((E_{\text{KS}}[V_{\text{in}}] > E_{\text{KS}}[V_{\text{KS}}])\) while \( E_{\text{HF}} \) is only stationary:

Usually \( E_{\text{HF}} \to \text{max} \) while \( E_{\text{KS}} \to \text{min} \) (they bound solution).

Typically \( E_{\text{HF}} \) is better: it is less sensitive to \( \Delta n \).
Practical Implementations of the LDA

Single-particle orbitals $\psi_i$ are expanded in some basis set. Many ways to do this.

**Classification #1:** The $\psi_i$ expanded in plane waves (most common), or in short-range, atom-centered orbitals.

Questaal uses the latter.

**Classification #2:** orthogonalization to the core. *Either:*

- Replace the core by an effective (pseudo)potential, *or*
- Keep all electrons: Augment the wave functions in spheres around each nucleus with numerical solutions of the radial Schrodinger equation. Originally formulated by Slater

Questaal is an all-electron method.
Pseudopotentials

Add some artificial, or pseudo-potential $V^{PS}$ to $V^{LDA}$ ⇒ replace true wave function $\psi$ with smooth analog of $\psi^{PS}$, with the same eigenvalues.

No core!

$V^{PS}$ is not unique!

The envelope defines the basis.

Shown here as green.

Blue, red show augmentation region : region where $V^{PS} \neq 0$.

Can be Plane Waves, or Atom-centered functions
Augmentation

All-electron basis sets begin with envelope functions:

Far from nuclei $\psi$ is smooth and described by smooth envelopes. They can be either plane waves or local functions.

Valence $\psi$ must be orthogonal to core states $\Rightarrow$ many wiggles that envelope functions cannot well represent.

Solution: augment spheres around nucleus with numerical solutions of the Schrödinger equation (red, blue). Called partial waves.

At interface the augmented functions must match continuously and differentiably onto the envelopes.

Both value and slope must match $\Rightarrow$ quantization condition (see later).
Four basic variants

4 types depicted in figure.

Envelope functions are green. Blue, red show augmentation region

**Pseudo functions:**
- ✔ Very efficient
- ✗ Approximation can be an issue

**All-electron:**
- ✔ Most rigorous (e.g. semicores)
- ✗ More cumbersome

**Plane waves:**
- ✔ Readily made complete
- ✗ Not localized

**Atom centered functions:**
- ✔ Efficient, physical intuition
- ✗ Completeness can be an issue
Energy dependence

\[ \psi = \psi(E, r) \]. What about \( E \) dependence?

**Classification #3:** the basis can be

1. **Fixed (PP methods) -- simplest**
2. **potential-and-energy dependent (KKR, APW).**
   Accurate but expensive.
   (Nonlinear eigenvalue problem; see later)
3. **Potential dependent.**
   LAPW = linearized APW
   LMTO = linearized KKR

Linearization turns nonlinear secular matrix into linear algebraic eigenvalue problem, like fixed-basis case (later).
Modest loss of accuracy with large efficiency gains.
Muffin-tin potential and partial waves

Consider the MT part. $l$ and $m$ are good quantum numbers; use $L$ as a shorthand for compound $(l,m)$ indices. The SE separates and:

$$
\phi_l(\varepsilon, r) \text{ satisfies } (-\nabla^2 + V(r))\phi_l = \varepsilon \phi_l \quad \text{or equivalently:}
$$

$$
\begin{pmatrix}
-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} - \varepsilon \\
\end{pmatrix} r \phi_l(\varepsilon,r) = 0
$$

The $\phi_l(\varepsilon,r)$ are called partial waves.

MT potential: \textit{spherically symmetric} inside sphere (called “augmentation” sphere)

Constant in between

Cut and paste approach to Schrödinger equation

Construct basis function $\chi_j$ piecewise:
Numerics: logarithmic radial mesh

Inside $r_{MT}$,

$$\left(-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} - \epsilon\right) r\phi_l(\epsilon, r) = 0$$

Solution must be orthogonal to cores $\Rightarrow$ varies rapidly

Must be solved numerically on a radial mesh of points $r_i$:

Customary: use one of:

- logarithmic mesh $r_i = be^{ai}$  $\leftrightarrow$ Simpler, more common
- shifted logarithmic mesh $r_i = b[e^{a(i-1)} - 1]$  $\leftrightarrow$ Includes the origin

Questaal code adopts a shifted logarithmic mesh
Partial Waves and Boundary conditions

Consider a single muffin-tin. 

$l$ and $m$ are good quantum numbers. Consider only the valence state (suppress index $n$) and use $L$ as a shorthand for compound $l+m$ indices. The partial wave is then

$$\Phi_L(r) = Y_L(\hat{r}) \phi_l(r)$$

$\phi_l$ satisfies $$(-\nabla^2 + V(r)) \phi_l = \varepsilon \phi_l$$ or equivalently a 1D eqn in $u = r\phi$

$$\left(-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} - \varepsilon\right) u_l(\hat{U},r) = 0, \quad u_l(\hat{U},r) = r\phi_l(\hat{U},r)$$

$\Phi_l$ is only a partial wave (incomplete solution) because we have yet to specify the boundary condition both as $r \to 0$ and at $r = r_{MT}$

2nd order differential equation $\Rightarrow$ two solutions at any point. Restriction: $\phi_l(r)$ regular as $r \to 0$ eliminates one b.c.. The boundary condition at $r_{MT}$ will depend on the whole crystal.
Only one regular solution remains. Thus specifying $\varepsilon$ completely specifies the remaining degree of freedom of the partial wave.

At some energy $\varepsilon_0$ the slope is negative. As $\varepsilon$ increases, the curvature ($-\nabla^2$) increases. Between $\varepsilon_0$ and $\varepsilon_1$ slope $\phi'(r) \to 0$. At $\varepsilon_2$, $\phi(r) \to 0$. Above $\varepsilon_2$ an extra node is picked up.

This information is neatly encapsulated in the logarithmic derivative at $r_{MT}$

$$D\{\phi_l(\varepsilon)\} = \left. \frac{r \cdot d\phi_l(\varepsilon)}{\phi \cdot dr} \right|_{r_{MT}} = \left. \frac{d \ln \phi_l(\varepsilon)}{d \ln r} \right|_{r_{MT}}$$
Logarithmic Derivative II

\[ D\{\phi_l(\epsilon)\} = \frac{r \cdot d\phi_l(\epsilon)}{\phi \cdot dr} \bigg|_{r_{MT}} = \frac{d \ln \phi_l(\epsilon)}{d \ln r} \bigg|_{r_{MT}} \]

- \( \epsilon_0 \): \( \phi_l < 0 \) & \( \phi'_l < 0 \) \Rightarrow \( D > 0 \)
- \( \epsilon_1 \): \( \phi_l < 0 \) & \( \phi'_l > 0 \) \Rightarrow \( D < 0 \)
- \( \epsilon_2 \): \( \phi_l \to 0 \) & \( \phi'_l > 0 \) \Rightarrow \( D \to \pm\infty \)
- \( \epsilon_3 \): \( \phi_l > 0 \) & \( \phi'_l > 0 \) \Rightarrow \( D > 0 \)

\( D_l(\epsilon) \) is an ever-decreasing, cotangent-like function.

PP methods construct \( V^{ps} \) by making \( D^\text{pseudo}_l = D^\text{true}_l \).

The “center of gravity” \( C_l \) (natural resonance) occurs near the point \( D_l=-l \) (see later).
APW and KKR Methods

The $\phi_l(\varepsilon, r)$ join smoothly onto envelope functions in the interstitial.

Envelope function $\chi_j$ is “augmented” by $\phi_l(\varepsilon, r)$ in each augmentation sphere.

Envelopes can be any functions that are reasonably complete in the interstitial.

APW: Envelopes $\Rightarrow$ plane waves $\chi_G = e^{i(k+G).r}$ as in the PW-PP method except $\chi_G$ is augmented inside each MT sphere with partial waves.

KKR: If the potential really is a MT, it is solved exactly by

$$\nabla^2 + \varepsilon - V_{MT} \chi(\varepsilon, r) = 0, \quad r > r_{MT}$$

Helmholz equation: solns Hankels $H$ and Bessels $J$

Family of Hankel functions $H_{RL}(r) = H_L(r-R)$ at each site $R$: makes a nearly exact, minimal basis for the muffin-tin potential.

This is the KKR Method.
Spherical Hankel and Bessel Functions

Spherical Hankel and Bessel functions satisfy this equation:

\[
(\nabla^2 + \kappa^2) \{H_L, J_L\}(\kappa^2, r) = 0, \quad r \neq 0
\]

\[
\{H_L, J_L\}(\kappa, r) = \{h_l, j_l\}(\kappa^2, r)Y_L(\hat{r})
\]

Radial part

Factor out angular dependence

Hankels: singular as \( r \to 0 \), regular as \( r \to \infty \)

Bessels: regular as \( r \to 0 \), singular as \( r \to \infty \)

\[
h_l(\kappa^2, r) \to r^{-l-1}e^{-\kappa r} \quad \text{as} \quad r \to \infty
\]

\[
j_l(\kappa^2, r) \to r^l e^{\kappa r} \quad \text{as} \quad r \to \infty
\]

Hankels can be expanded as a linear combination of Bessels around a remote site. Called a one-center expansion:

\[
H_L(\kappa^2, r - \mathbf{R}) = \sum_{L'} S(\mathbf{R} - \mathbf{R}', \kappa)J_{L'}(\kappa^2, r)
\]

Structure constants
In the interstitial, solutions are linear combinations of atom-centered Hankel functions \( H_{RL} \) centered at each nucleus \( \mathbf{R} \).

For \( r < r_{MT} \),

\[
\Phi_{RL}(\mathbf{r}) = \sum_{RL} C_{RL} \phi_{RL}(\varepsilon, r) Y_L(r - \mathbf{R}),
\]

We have piecewise solutions of the SE, with kinks matching \( H_{RL} \) at \( r_{MT} \).

To satisfy boundary conditions, kinks must disappear.
Sum of all scattered waves becomes incoming spherical wave on any given sphere. Condition that they sustain each other without any original incoming plane wave. Condition gives Multiple-Scattering equations

\[ T_{ij} = t_i \delta_{ij} + t_i G_{ij}^0 t_j + t_i G_{ik}^0 t_k G_{kj}^0 t_j + \ldots \]

\[ = t_i \left[ \delta_{ij} + G_{ij}^0 t_j + G_{ik}^0 t_k G_{kj}^0 t_j + \ldots \right] \]

\[ = t_i \left[ \delta_{ij} - G_{ij}^0 t_j \right]^{-1} = \left[ t_i^{-1} \delta_{ij} - G_{ij}^0 \right]^{-1} \]

Outgoing wave \((H_{RL})\) becomes incoming wave \((J_{R'L'})\) at neighboring sites. \(H_{RL}\) scatters at each neighbor because of the MT potential there.

t=tan (phaseshift) = t-matrix of each scatterer separately

\(G^0\) is free electron propagator
Define an energy dependent MTO as an “Augmented Hankel function”

\[ \chi_{RL}(\varepsilon, r) = N_{RL}(\varepsilon)\Phi_{RL}(\varepsilon, r) + P_{RL}(\varepsilon)J_{RL}(\varepsilon, r), \quad r < r_{MT} \]
\[ = H_{RL}(\varepsilon - V_{MT}, r), \quad r > r_{MT} \]

\( H_{RL} \): exact soln of MT potential in interstitial
\( \Phi_{RL} \): exact soln of MT potential in sphere \( R \)

\( \chi_{RL} \) would be a solution if the \( J_{RL} \) “contaminates” the exact \( \Phi_{RL} \) ...

The eigenstate consists of a combination of \( H_{RL'} \) centered at all sites. Inside \( R \), \( H_{RL'} \) at \( R' \neq R \) extend to \( R \) and because of the expansion theory, can be expressed in terms of the \( J_{RL} \)

\[ H_{RL'}(\varepsilon, r) = \sum_{L'} S_{RL,R'L'}(\varepsilon)J_{RL}(\varepsilon, r) \quad \text{if } R' \neq R \]
\( \Phi_{RL} \) : Partial wave centred at \( R \)

\[
\chi_{RL}(\varepsilon, r) = N_{RL}(\varepsilon)\Phi_{RL}(\varepsilon, r) + P_{RL}(\varepsilon)J_{RL}(\varepsilon, r), \quad r < r_{MT}
\]

\[
= H_{RL}(\varepsilon, r), \quad r > r_{MT}
\]

\( H_{RL} \) : Hankel function centred at \( R \)

Idea: choose linear combinations \( \sum_{R'L'} [z_{R'L'}H_{R'L'}(\varepsilon, r)] \)

so that the tails from neighbors \( R' \neq R \) cancel the \( J_{RL} \) piece at \( R \)

added to make \( \chi_{RL} \) continuous.

Do this by defining the

“Potential function” \( P\{\phi_i(\varepsilon)\} = W\{\phi_i(\varepsilon), h_i\} / W\{\phi_i(\varepsilon), j_i\} \)

Wronskian at \( r_{MT} \)

\( P \) specifies how much \( J \) you must add to \( \chi_{RL} \) to make it continuous at \( r_{MT} \).
Properties of KKR

The “kink cancellation” condition can be written in this form:

\[ |P_{RL}(\varepsilon) - S_{RL,R'L'}(\varepsilon)| = 0 \]

Potential function = amount of \( J \) in the head
Structure Matrix = amount of \( J \) from neighbors

\( P_{RL} \) : parameterizes information about scattering at \( r_{MT} \).

All information about \( V(r) \) at site \( R \) is folded into \( P_{RL} \).

\( P_{RL} \) knows nothing about structure.

\( S_{R'L',RL} \) contains information about structure.

It knows nothing about potential.

KKR is elegant. Optimally compact for MT. (MT potential \( \equiv \) true potential in close-packed structures).

But ... solution involves a tedious energy search, with energy-dependent orbitals \( \Rightarrow \) inefficient, yields only \( G \), not \( \psi \).
Linear Methods in Band Theory

Problem ...
APW & KKR ⇒
energy dependent hamiltonians.
Resolved by linearization

Nearly all modern electronic structure methods use linearization in some way

Linearization

Key observation: partial wave $\phi_l(\varepsilon, r)$ in sphere varies **smoothly and slowly** with energy

$\phi_l(\varepsilon, r) = \phi_l(\varepsilon_v, r) + (\varepsilon - \varepsilon_v)\dot{\phi}_l(\varepsilon, r) + ...$

Energy dependence parameterized by log derivative function

Or by potential function (they are related)

$D\{\phi_l(\varepsilon)\} = d\ln\phi_l(\varepsilon) / d\ln r$

$P\{\phi_l(\varepsilon)\} = W\{\phi_l(\varepsilon), h_l\} / W\{\phi_l(\varepsilon), j_l\}$

Linearize $\phi_l(\varepsilon)$ kink-cancellation $\Rightarrow$ linear algebraic eigenvalue problem

APW $\rightarrow$ LAPW; KKR $\rightarrow$ LMTO

Gold standard Efficient
Parameterization of $D$ and $P$

It is not difficult to derive the connection between $P$ and $D$, and their properties when $\phi_l(\epsilon, r)$ is linearized. Skip derivation here: a bit tedious.

A particularly useful relation is:

$$P(\epsilon) = \frac{(\epsilon - C)}{\gamma(\epsilon - C) + \Delta} = \left( \frac{\Delta}{\epsilon - C} + \gamma \right)^{-1}$$

where the “potential parameters” are expressed in terms of Wronskians

$$\gamma = \frac{1}{P[D\{\phi\}]} = \frac{W\{J, \dot{\phi}\}}{W\{K, \dot{\phi}\}}$$
$$C = \epsilon_v - \frac{W\{K, \phi\}}{W\{K, \dot{\phi}\}}$$
$$\sqrt{\Delta} = -\left( \frac{2}{w} \right)^{1/2} \frac{2}{W\{J, \phi\}}$$

$C$ = “band center” = eigenvalue of isolated MT
$\Delta$ = “band width” = width of band, in absence of hybridization with other channels
$\gamma$ = “band distortion”

Most of the essential physics of the hamiltonian is contained in $C$, $\Delta$ and structure constants $S$. Note simple pole structure.
LMTO: Energy Linearization of KKR

By linearizing $\phi_l(\varepsilon)$:

$$
\phi_l(\varepsilon, r) = \phi_l(\varepsilon_v, r) + (\varepsilon - \varepsilon_v) \dot{\phi}_l(\varepsilon, r) + \ldots
$$

$P$ can be parameterized by a simple pole structure

$$
P^{-1} = \frac{\Delta}{\varepsilon - C} + \gamma
$$

Band width

Band “distortion”

Band center-of-gravity

The KKR condition

$$
0 = |P - S| = \left| \left( \frac{\Delta}{\varepsilon - C} + \gamma \right)^{-1} - S \right|
$$

can be written as

$$
|\varepsilon - C - \sqrt{\Delta} S^\gamma \sqrt{\Delta}| = 0, \quad (S^\gamma)^{-1} = S^{-1} - \gamma
$$

This is equivalent to the linear algebraic eigenvalue problem

$$
H\psi = \varepsilon\psi \quad \text{with} \quad H = C + \sqrt{\Delta} S^\gamma \sqrt{\Delta}
$$

Implemented in ASA part of Questaal package

See https://www.questaal.org/docs/code/asaoverview/
LAPW method and MT approximations

The envelope functions can be any complete basis.

Alternative to atom-centered $H_{RL}$: plane waves $\{e^{i(k+G)r}\}$

now $e^{i(k+G)r}$ is augmented inside each MT sphere with linear combinations of $\Phi_{RL}$ and $J_{RL}$ as before.

Similar “tail cancellation” condition ⇒ eigenfunctions.

But very expensive! Nonlinear eigenvalue problem. APW is rarely used today,

Linearization ⇒ LAPW method. Considered gold standard.

Traditionally KKR, APW, LMTO, LAPW (1980’s) approximated the true potential by the MT form.

Enlarge spheres to fill space ⇒ “Atomic Spheres Approximation”.

Geometry violation better than MT.

All methods can be recast to eliminate the MT approximation and can solve the SE to high accuracy.
ASA codes, lm, lmgf, lmpg

The Questaal package has three kinds of ASA codes. They are Noncollinear + with fully relativistic extensions.


lmgf: similar purpose for crystals, using a Green’s function technique (www.questaal.org/docs/code/lmgf/). Additional functionalities particularly useful for JMRAM:

- The coherent potential approximation for treating alloys and/or spin disorder
- Linear response capabilities for computing magnetic exchange interactions

lmpg: a layer Green’s function technique for transport through layered systems (www.questaal.org/docs/code/lmpg)
Attributes of the LMTO-ASA method

Positive attributes:

- Very fast and efficient: can study many systems parametrically, e.g. response of a system to an external field.
- The original LDA+U method, (nearly) the first noncollinear magnetism and magnetic exchange calculations, the first all-electron GW methods were built around it.
- Connection with GF enables linear response calculations of e.g. magnetic exchange interactions, and CPA alloy theory.
- Ideally suited for, e.g. spintronics.

Drawbacks:

- No forces
- Accuracy is limited; results often must be checked
- For many properties, other methods to do the same job better, or have functionality not in these methods.
Noncollinear Magnetism for large systems

ASA band code Im ... very versatile and efficient.

Noncollinear magnetism—good for spintronics, explained origins of INVAR (Nature 400, 46).

First description of LDA-based spin dynamics

Early paper on LDA calculations of Schottky barriers
Coherent Potential Approximation, Imgf

The CPA provides an elegant way to model disorder on a lattice.
Different constituents of an alloy, e.g. Fe and Ni in permalloy (PY=Fe$_{0.2}$Ni$_{0.8}$) occupy sites randomly (more or less)

Crystal: the kink condition is $|P - S| = 0$

Alloy: find a configurationally averaged “coherent potential function” $\mathcal{P}$ so the kink condition becomes $|\mathcal{P} - S| = 0$

Binary alloy: atoms A and B occupy a site with probabilities $c^A$ and $c^B = 1 - c^A$. Treat this site as an “impurity” embedded in an effective medium defined by the (as yet determined) coherent potential function $\mathcal{P}$
Coherent Potential Approximation II

From scattering theory, scattering from the impurity is given by the T-matrix. There is one for each atom $Q=1,2$:

$$t^Q = (P^Q - \mathcal{P}) \left[ 1 + (\mathcal{P} - S)^{-1} (P^Q - \mathcal{P}) \right]^{-1}$$  \hfill (1)

For there to be no net scattering on average (coherent potential), impose the condition

$$\sum_{Q=A,B} c^Q t^Q = 0 \tag{2}$$

(1) and (2) constitute two simultaneous (matrix) equations for $t$ and $\mathcal{P}$. They must be solved iteratively to self-consistency.

The CPA introduces an added complexity of an extra self-consistency step. $\mathcal{P}$ is now both complex and energy-dependent. Thus it cannot be converted to a linear algebraic eigenvalue problem. $\text{Im } \mathcal{P}$ is the alloy contribution to the quasiparticle lifetime, and is a direct measure of the alloy scattering rate.
CPA Energy Band Structure of Permalloy (lmgf)

Alloy scattering: \( k \) is not a good quantum number

In CPA, this gets reflected in a dynamical self-energy \( \Sigma(\omega, k) \).

\( \Sigma(\omega, k) \) has an imaginary component, which broadens the states.

Moderate scattering in majority channel, strong scattering in minority channel. Easily interpreted in terms of the potential parameters \( C \) and \( \Delta \).
Principal layer ASA-Green’s function code lmpg

Layer geometry: Active (Scattering) region $S$ cladded by semi-infinite leads $L$ and $R$.

Leads are assumed to be in equilibrium.

- Designed specifically for Landauer-Buttiker transport through layered systems:
- Periodic in 2 dimensions, not the third

lmpg has NEGF capability (non-equilibrium, Keldysh). NEGF enables:
(1) beyond linear response
(2) inelastic scattering
Spin Flip Scattering at Metallic Interfaces (Impg)

Spin-flip scattering at interfaces contributes to spin relaxation in metallic multilayers

Impg is designed to directly calculate spin-conserving and spin-flip transmission ($T_{\uparrow\uparrow}$ and $T_{\uparrow\downarrow}$) and reflectances ($R_{\uparrow\downarrow}$, $R_{\uparrow\uparrow}$)

In this Cu/Pd interface, the integrated spin flip probability was found to be approximately independent of surface intermixing.
All-electron, full-potential methods

Full-potential methods usually do the following:

- Construct the basis set as though \( V(r) \) were \( V^{MT}(r) \)
- Exploit the variational principle to determine energy states.

Additional requirements to surmount the ASA approximation:

- More accurate --- need more complete envelope functions.
  And
  - Ability to represent \( n(r) \) and \( V(r) \).

  Auxiliary basis for interstitial. We use plane waves.

- Matrix elements of the true potential: \( \langle \chi_i | V(r) - V^{MT}(r) | \chi_j \rangle \).
  Envelope functions should be smooth

Straightforward with LAPW; harder with LMTO
Smoothed Hankel Functions

Hankel functions:

- $\propto 1/r^{l+1}$ for small $r$ ... singularity a problem
- are "too stiff": real potentials are not flat in interstitial. Functions would be better if they satisfied a SE that approached a constant asymptotically, more like what real potentials do

Fourier transform of $H_L(E;r)$:

$$H_L(E; q) = \frac{-4\pi (iq)^l Y_L(iq)}{E - q^2}$$

FT of Gaussian w/ width $r_s$

$$g(r_s; r) = e^{-(r/r_s)^2}$$

Define smoothed Hankel as product of $H_L(E, q)$ and $g(r_s, q)$

$$H^s_L(E, r_s; q) = \frac{-4\pi (iq)^l Y_L(iq)e^{-4r_s^2q^2}}{E - q^2}$$
Smoothed Hankel Functions II

FT $H^s_L(E,r_s;q)$: to real space: result is a smoothed Hankel function.

Invented by M. Methfessel.

Properties thoroughly reviewed in J. Math. Phys. 39, 3393

Key features:
1. Smooth everywhere
2. Regular at the origin: $H^s \sim r^l$ as compared to $H \sim r^{-l-1}$.
3. Satisfy a Schrodinger equation

$$\nabla^2 H_L = (-E + V(r))H_L,$$

$$V(r) = -4\pi \frac{G_L(r_s;r)}{H_L(E,r_s;r)}$$
Augmentation

Standard LAPW and LMTO methods must augment (replace the envelope function) with radial solutions of the SE to very high $l$ ... something like $l=6$ or 8.

Curious ... because pseudopotential $l$-cutoffs are $\sim 2$. Yet there is a connection between augmentation and pseudopotentials. Why?

This code uses a unique form of augmentation.

The total density $n$ is a superposition of 3 densities:

1. Interstitial, or smooth density $n_i$. Not augmented ... extends everywhere in space (analogous to PP or PAW method)

2. True density inside augmentation sphere $R$, $n_{1RL}$

3. 1-center (local) representation of the interstitial density, $n_{2RL}$

$$n(r) = n_i(r) + \sum_{R,L}^{L_{\text{max}}} (n_{1RL}(r) - n_{2RL}(r))$$
Augmentation II

Properties of the “three-fold” representation of $n$:

1. A one-center expansion of $n_i$ at site $R$ becomes exactly to $\sum_L n_{2RL}$ in the limit $L_{\text{max}} \to \infty$ ... thus $n_i$ exactly cancels $n_{2R}$ and the remaining density is the true density $n_{1R}$. This establishes that the theory is exact if $L_{\text{max}} \to \infty$.

2. In general $n_i \neq n_{2R}$ inside the augmentation spheres. So for $L > L_{\text{max}}$ the density is carried by $n_i$, and also $n_i$ makes some nonzero contribution to $n$ for $L < L_{\text{max}}$.

3. For any $L_{\text{max}}$, the value and slope of $n_{1R}$ and $n_{1R}$ exactly match at $r_{MT}$. Thus the net local density vanishes there, value and slope, and $n$ is carried entirely by $n_i$. 

$$n(r) = n_i(r) + \sum_{RL}^{L_{\text{max}}} \left( n_{1RL}(r) - n_{2RL}(r) \right)$$
Augmentation III

The potential has a similar “three-fold” representation

\[ V(\mathbf{r}) = V_i(\mathbf{r}) + \sum_{RL}^{L_{\text{max}}} \left( V_{1RL}(\mathbf{r}) - V_{2RL}(\mathbf{r}) \right) \]

Each potential is computed (almost) independently of the others:

- \( V_i \) is calculated from \( n_i \) only
- \( V_{1R} \) is calculated from \( n_{1R} \) only
- \( V_{2R} \) is calculated from \( n_{2R} \) only

Why is this better?

- Cross terms are unwieldy
- \( L \) convergence much faster than standard LAPW
- Makes connection between PP and PAW methods, and all-electron methods.
Local orbitals

Recall energy linearization common to (nearly) all methods

\[ \Phi_{RL}(\varepsilon, \mathbf{r}) = \phi_{RL}(\varepsilon, \mathbf{r}) Y_{R_L}(\hat{\mathbf{r}}) \]

\[ \phi_{RL}(\varepsilon, \mathbf{r}) \approx \phi_{RL}(\varepsilon_v, \mathbf{r}) + (\varepsilon - \varepsilon_v) \frac{\partial \phi_{RL}}{\partial \varepsilon}(\varepsilon_v, \mathbf{r}) + ... \]

**Standard**: In the LMTO method (and LAPW) methods we add new augmentation orbitals \( \phi_{RL} = \phi_{RL}(\varepsilon_v, \mathbf{r}) \) and \( \partial \phi_{RL}/\partial \varepsilon \). Procedure:

1. Integrate \( \phi_{RL}(\varepsilon_z, \mathbf{r}) \) at some \( \varepsilon_z \)

2. Subtract \( a \times \phi_{RL} + b \times \partial \phi_{RL}/\partial \varepsilon \) from \( \phi_{RL}(\varepsilon_z, \mathbf{r}) \) to make both value, slope vanish at \( r_{MT} \). The resulting “local orbital” is completely confined to the augmentation sphere.

3. Add this orbital to the basis set. Extends range of energy window which solves SE, and the cost of a larger basis.
Questaal is the current CCP9 flagship (www.questaal.org) It is an integrated electronic structure package that combines:

**DFT**
- ASA
- Imf

**Outreach**
- Web site [www.questaal.org](http://www.questaal.org)
- Summer Schools
- Hands-on workshops
- Validation
- Visitors
- Repository [www.bitbucket.org/lmto/lm](http://www.bitbucket.org/lmto/lm)

**Funding sources**
- CCP9 EPSRC
- Simons Collaboration

**GW, QSGW**
- Imgw
- Imgwsc
- Imfdmft
- +CTQMC
- phonons
- Response functions

**DMFT**
- tbe
Descendant of the Stuttgart LMTO method

Problem ...

APW & KKR ⇒ energy dependent hamiltonians.

Resolved by linearization

Nearly all modern electronic structure methods use linearization in some way

Original LMTO-ASA was developed for the Stuttgart group.

Package formed the backbone of many developments:

- LDA+U (Anisimov)
- Exact exchange (Kotani)
- All-electron GW (Aryasetiawan)
- Electron-phonon interactions, superconductivity (Lichtenstein)

Full-potential version developed by Methfessel and MvS.

Full-Potential GW, QSGW developed by Kotani, Faleev, MvS.
Accessibility
Make Questaal easily accessible w/ relatively low barriers to use

- Comprehensive and well organized web site with tutorials
- Logical and transparent user interface
- Hands on workshops
- Code validation
- Visitors
- Technical support

Goal: competent nonspecialists should be able to perform routine calculations.
You are our test case!
Web site

Web site built in the last year
  by undergrads Kantor and Christensen
  supervised by Pashov

Modern, with many nice features.
  Each main code documented.
  Basic tutorials for functionality
  Many missing links; still far from complete.

We hope you will help us identify problems with the web site!
If there are mistakes or you can’t find something, let us know.

Web site built on Markdown (Kramdown) system
  Easily extended; intended for user community to add
  There is Style manual for uniform look and feel

We welcome contributions to the site (tutorials, new features)
Git repository for branching, history, version control
Modern, ninja-based build system
  Fast, parallel build
  One executable operates in both serial and MPI mode
Validation: several hundred code checks
Some links to emerging hardware architectures
  GW code has interface to Xeon Phi
Validation exercise (Jackson)
Repository has ticketing system
Stack exchange planned
We have a (limited) visitor scheme
Functionality

**DFT**
- Efficient basis set (Pashov)
- Magnetic linear response, CPA

**GW**
- Add diagrams (Gruening, Cunningham)
- Improve efficiency (Pashov, Lueders)
- Schemes to improve accuracy

**Phonons**
- Phonons, electron-phonon interaction in GW (Bononi, Laricchia)

**QSGW+DMFT**
- Acharya, in collaboration with Rutgers, Illinois, Paris

**Response functions**
- Optical response, some magnetic susceptibility in MBPT
- Magnetic susceptibility, some optical response, in DMFT
The GW approximation: Screened Hartree Fock

Hartree Fock: $e^-$ senses an attractive potential $V^x$ from antisymmetry that keeps $e^-$ apart.
Write $V^x$ in terms of Green's functions:

$$
\Sigma_x = V_x(r) = i \int G(r, r') \frac{1}{|r - r'|} d^3 r' = iGv
$$

$GW$: bare coulomb $v \rightarrow$ dynamically screened $W$:

$G =$ Green's Function, $W =$ screened coulomb interaction

$$
V_{\text{bare}}(r, r') = \frac{1}{|r - r'|} \rightarrow W(r, r', \omega) = \varepsilon^{-1}v; \quad \Sigma = iGW
$$

Dynamical screening is the essential difference between $GW$ and Hartree Fock. It make both qualitative and quantitative changes to the electronic structure.

More rigorously: $GW =$ the lowest order term in an exact expansion in $W$ (many-body perturbation theory)
All-electron GW: Eigenfunction Products

The LDA works with products of basis function pairs, e.g. to make potential matrix elements $\langle \chi_i | V | \chi_j \rangle$ or $n(r)$.

GW is more complicated. It requires integrals of 4 basis functions with two-point quantities, e.g. matrix elements of coulomb interaction $v(r, r') = 1/|r-r'|$.

Eigenfunction:

$$\psi_{kn}(r) = \sum_{Ru} \alpha_{Ru}^{kn} \Phi_{Ru}^k(r) + \sum_{G} \beta_{G}^{kn} P_{G}^k(r),$$

$$P_{G}^k(r) = \begin{cases} 0 & \text{if } r \in \text{any MT} \\ \exp(i(k + G) \cdot r) & \text{otherwise} \end{cases}$$

Interstitial:

$$P_{G_1}^{k_1}(r) \times P_{G_2}^{k_2}(r) = P_{G_1 + G_2}^{k_1 + k_2}(r)$$

$$e^{-i(k+G') \cdot r} \times e^{i(k+G) \cdot r} = e^{-i(G-G') \cdot r}$$

Augmentation

$$\Phi_L(r) \Phi_{L'}(r) = \phi_i(r) \phi_i(r) \times Y_{L'}(\hat{r}) Y_{L}(\hat{r})$$

Numerical solution

Products of $Y_L$

$$Y_{K}(\hat{r}) Y_{M}(\hat{r}) = \sum_{L} C_{KLM} Y_{L}(\hat{r})$$
**Product Basis**

**Interstitial:** use

\[ P_{G_1}^{k_1}(r) \times P_{G_2}^{k_2}(r) = P_{G_1+G_2}^{k_1+k_2}(r), \quad P_G^k = e^{i(k+G) \cdot r} \]

**Augmentation:** Construct complete set of product functions \( B_N(r) \):

\[ \{ \varphi_{Ru}(r) \times \varphi_{Ru'}(r) \} \]

spanned by \( B_N(r) \)

\( R \) is a site index; \( u \) is a compound index which contains : \( L \), label whether partial wave has \( \phi \), \( \phi \text{'dot} \), local orbital character.

In practice we must work with **Bloch sums** \( B_I^{(k)} \) of the \( B_I \).

Thus, the mixed basis completely spans the Hilbert space of basis function products

\[ \{ M_I^{k}(r) \} \equiv \{ P_G^k(r), B_{RN}^k(r) \} \]
Example: Coulomb Matrix Elements

The bare coulomb operator can be expanded in the mixed basis:

\[ v(r, r') = \sum_{k, l, j} |\tilde{M}^k_l(r)\rangle v_{lj}(k) \langle \tilde{M}^k_j(r')| \]

Similarly for all 2-point quantities, e.g. the dielectric function \( \varepsilon \) and screened coulomb interaction \( W \). The mixed basis functions are not orthogonal so we must define

\[ |\tilde{M}^k_l\rangle \equiv \sum_{l'} |M^k_{l'}\rangle (O^k)^{-1}_{l'l}, \quad O^k_{l'l} = \langle M^k_{l'} | M^k_l \rangle. \]

Complete information to generate the \( GW \) self-energy are matrix elements like this.
Quasiparticle self-Consistent GW: Optimal $G_0$

Start with some trial $V_{xc}$ (e.g. from LDA, or ...). Defines $G_0$:

$$H_0 = \frac{-1}{2m} \nabla^2 + V^{\text{ext}}(r) + V^H(r) + V^{xc}(r,r')$$

$$H_0 \psi_i = E_i \psi_i \rightarrow G_0(r,r',\omega) = \sum_i \frac{\psi_i(r)\psi_i^*(r')}{\omega - E_i}$$

GWA determines $\Delta V$ and thus $H$:

$$G_0 \xrightarrow{RPA} \varepsilon(iG_0G_0) \xrightarrow{GWA} \Sigma(r,r',\omega) = iG_0 W; \quad \Delta V = \Sigma - V^{xc}$$

Find a new $V_{xc}$ that minimizes norm $N$, a measure of $\Delta V G_0$.

$$V^{xc} = \frac{1}{2} \sum_{ij} \langle \psi_i | \text{Re}(\Sigma(E_i) + \Sigma(E_j)) | \psi_j \rangle$$  

(approximate) result of min $N$

Iterate to self-consistency.

At self-consistency, $E_i$ of $G$ matches $E_i$ of $G_0$ (real part).
Dual Nature of QSGW: both $G_0=(\omega-H_0)^{-1}$ and $G$

$E_i[G_0] = \text{Re } E_i[G] \Rightarrow \text{QSGW generates a nearly optimal noninteracting } G_0 \text{ or } H_0 \text{ for many kinds of materials classes ...}$

But ... as a many-body theory QSGW is limited ...

Primary many-body effect is a plasmon. Superconductivity, Kondo physics, spin fluctuations ... not captured.
**Questaal’s Implementation of QSGW+DMFT**

Questaal has an interface to Kristjian Haule’s **CTQMC**
(CTQMC = Continuous time Quantum Monte Carlo for DMFT)

Limited experience so far:
- Self-energies in QSGW+DMFT in a few compounds, e.g. $\text{La}_2\text{CuO}_4$.
- Special QSGW + "Magnetic DMFT" – Applied to Ni
- Ability to make two-particle quantities, e.g. spin susceptibilities.

Big challenges:
- $G_0$ is not constructed from diagrams
- What is local effective interaction $U$?
- Double counting