DFT Electronic Structure Calculations by Muffin Tin Orbital Based Basis

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Plan

- Introduction to Basis Sets.
- Muffin-Tin Approximation.
- Muffin Tin Orbitals.
  - Envelope function.
  - Screening.
  - Augmentation.
- Tail cancellation and KKR.
- Linearization: Linear Muffin Tin Orbital (LMTO).
- Improved LMTO – N-th order MTO (NMTO) Method.
  - Applications of NMTO in deriving few band Hamiltonians.

Electronic Structure Calculations:

- Electrons at the microscopic level govern the behavior of materials.

- Good description of many macroscopic properties are obtained in terms of -

Born-Oppenheimer Approximation

Nuclei and the electrons to a good approximation may be treated separately.

One-electron Approximation

Each electron behaves as an independent particle moving in the mean field of the other electrons plus the field of the nuclei.

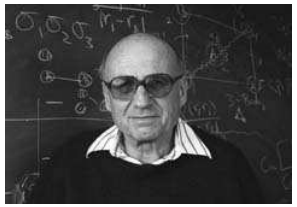
LDA

Most satisfactory foundation of the one electron picture is provided by the local approximation to the Hohenberg-Kohn-Sham density functional formalism

$\equiv$ **LDA**

$\Downarrow$

- LDA leads to an effective one electron potential which is a function of local electron density.
- Leads to Self consistent solution to an one electron Schrödinger Eqn.
  - **1998 Nobel Prize to Walter Kohn for DFT**



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Flow-chart for LDA self-consistency

First principles information: atomic no., crystal structure

$\Downarrow$

Choose initial electron density $\rho(r)$

Calculate effective potential through LDA:

$$V_{eff}(r) = V_{ion}(r) + \int d^3r' V_{ee}(r-r')\rho(r') + \frac{\delta E_{xc}[\rho]}{\delta r}$$

Solve K-S eqns:

$$[-\Delta + V_{ion}(r) + + \int d^3r' V_{ee}(r-r')\rho(r') + \frac{\delta E_{xc}[\rho]}{\delta r}]\phi_i(r) = \epsilon_i \phi_i(r)$$

Needs to expand K-S wavefunctions in terms of basis, Φ_{ilm}

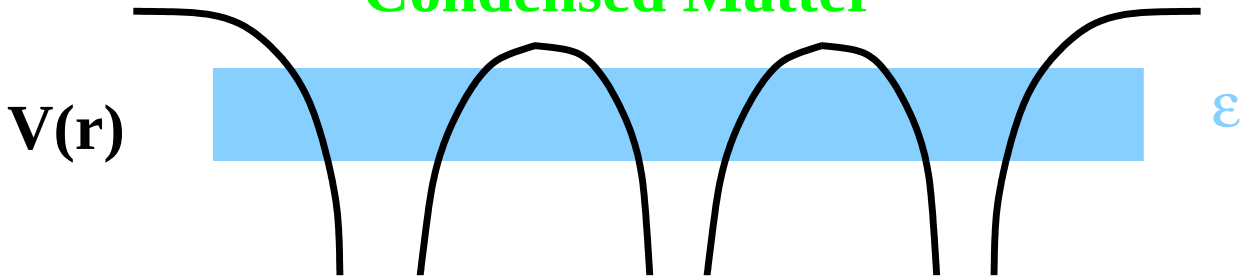
Calculate charge density: $\rho(r) = \sum |\phi_i(r)|^2$

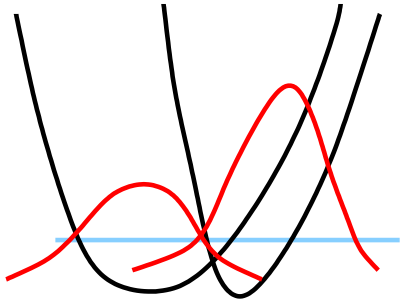
Iterate to selfconsistency

$\Downarrow$

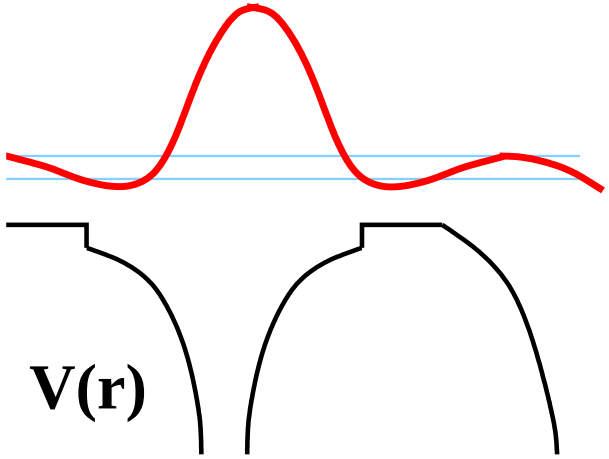
Total energy, inter-atomic forces, stress or pressure, band structure, . . .

Condensed Matter

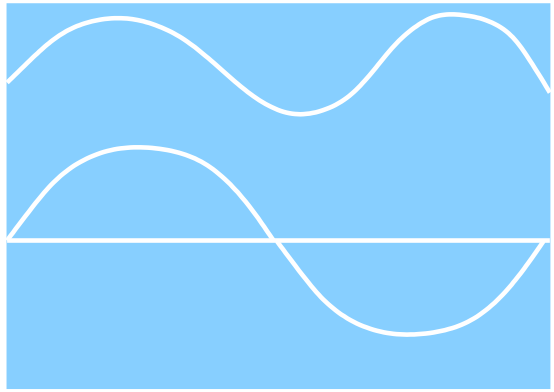




Gaussians



Muffin Tin Orbitals



Plane Waves

Existing Methods:

(A) Fixed Basis Set Methods:

$\Rightarrow$ The wave-function is determined as an expansion in some set of fixed basis functions, like linear combination of atomic orbitals (LCAO), plane waves, Gaussian orbitals etc.

$\Rightarrow$ One has to solve the eigenvalue problem : $(H - E O).a = 0$

Disadvantages : The basis set may be large to be reasonably complete.

Advantages : Computationally simple

Existing Methods:

(B) Partial Wave Methods:

$\Rightarrow$ The wave-function is expanded in a set of energy and potential dependent partial waves like the cellular method, the augmented plane wave method and the Korringa-Kohn-Rostoker method.

$\Rightarrow$ One has to solve set of eqns of the form : M(E).b =0 with complicated non-linear energy dependence .

Advantages :

$\odot$ The basis set is minimal.

$\odot$ Partial waves apply equally well to any atom in the periodic table.

$\odot$ Offers solution of arbitrary accuracy for closed packed systems.

Disadvantages : Computationally heavy

LMTO $\equiv$ Linearized version of KKR

$\longrightarrow$ *Combines the desirable features of the fixed basis method and that of partial waves.*

Summary on Foundations

- Density functional theory
- Kohn, Sham $\Rightarrow$ *reduction to effective non-interacting system.*
- Self consistent solution to an one electron Schrödinger eqn.

How do you do it ?

Matter is made from atoms ; Atoms are round

$\rightarrow$ Plane wave basis sets are easy to use, but are not chemical (Needs to post-processed in terms of construction of Wannier functions, charge densities etc.)

$\rightarrow$ LMTO basis, on the other hand, reflects the spherical and orbital character of constituent atoms .

- minimal basis.
- chemical.

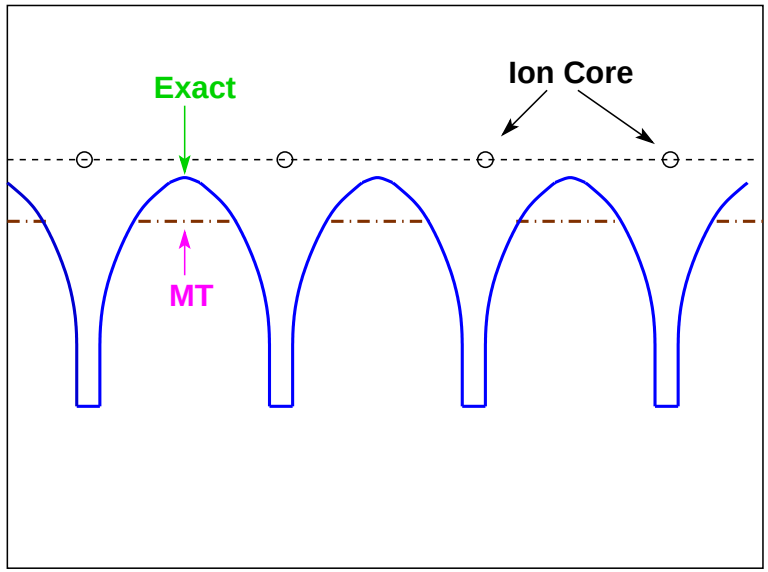
Ultimate goal is to understand.

Muffin-Tin

Potentials in a Solid: Muffin Tin Approximation

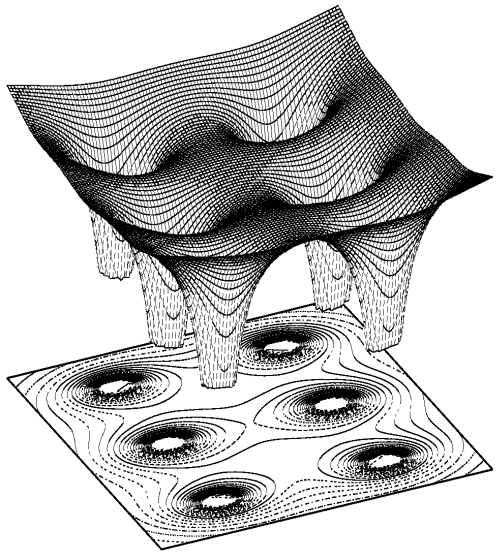
- Potential is assumed to be spherically symmetric close to nuclei/ion-core $\Rightarrow$ Muffin tin sphere.
- Potential is assumed to be flat in between $\Rightarrow$ Interstitial

$$v(\mathbf{r}-\mathbf{R}) = \begin{cases} v(r_{\mathbf{R}}) \text{ for } r_{\mathbf{R}} \leq s_{\mathbf{R}} \\ -v_0 \text{ for } r_{\mathbf{R}} > s_{\mathbf{R}} \end{cases} \qquad r_{\mathbf{R}} = |\mathbf{r}-\mathbf{R}|$$

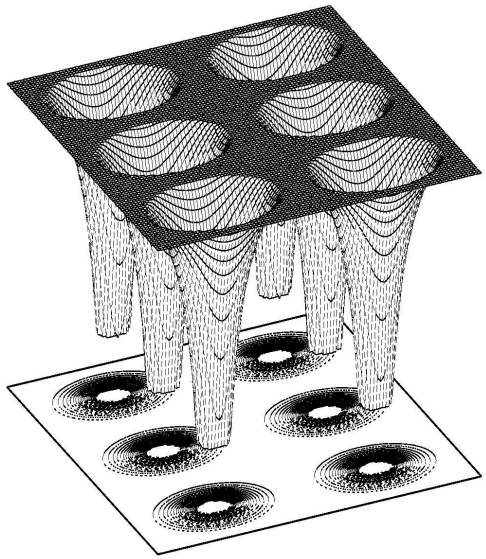


MT Approximation

THE FULL POTENTIAL



THE MUFFIN-TIN POTENTIAL



MT orbital based basis: Basics

- Based on scattering theory.
- Spherical symmetry of the potential inside MT sphere allows for working with Spherical Harmonics.
- The solutions of Schödinger equation inside MT sphere are nothing but partial waves.

$$[\frac{d^2}{dr_R^2} - v(r_R) + \frac{l(l+1)}{r_R^2} - \epsilon] r_R \phi_{RL}(r_R, \epsilon) = 0$$

- The solutions of Schödinger equation outside MT sphere are nothing but plane waves which can be expanded as spherical Neumann and Bessel functions $\rightarrow$ solution of radial equation with a constant potential.
- The solution at the entire space is obtained by matching the two solutions.

Envelope Functions

- Take an unscreened Neumann function

$\| K^o_{\mathbf{RL}} >= K^o_{\mathbf{R}}(r_{\mathbf{R}}) Y_L(\hat{r}_{\mathbf{R}})$

Non-zero in all space, sited at $\mathbf{R}$ and has angular momentum character $L(lm)$.

- This can be expanded about a set of points $\{\mathbf{R}^{'}\}$ as

$\| K^o_{RL} >= |K^o_{RL} > - \sum_{R'L'} |J^o_{R'L'} > S^o_{R'L',RL} + |K^o_{RL} >^i$

$| > \rightarrow$ truncated outside the MT sphere, $| >^i \rightarrow interstitial$
R and L summation is over the entire crystal and spd angular momentums respectively.

Introduction of Structure Matrix: $S_{R'L',RL} \rightarrow$ depends only on the lattice structure; characterized by an energy κ^2 $(E - V_0)$.

For κ^2 = 0, these functions become solutions of Laplace Equation.

Screening

We wish to screen each Neumann function by adding other Neumann functions at all sites.

- In this way we hope to localize them.
- The structure constants will then fall off rapidly with increasing distance (*localized structure matrix*).

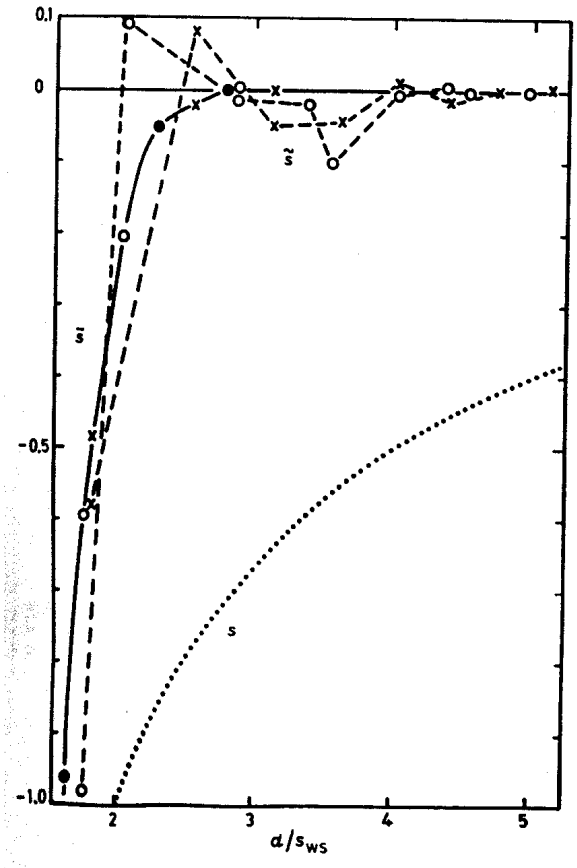
$$\| K^{\alpha}_{RL} >= \sum_{R'L'} \| K^{o}_{R'L'} > (\delta_{R'L',RL} + \alpha_{R'L'} S^{\alpha}_{R'L',RL})$$

$$S^{\alpha} = S^{o}(1 - \alpha S^{o})^{-1}$$

$\Rightarrow K^{\alpha}_{RL}$ can be viewed as the field of a 2^l-pole at R, screened by multi-poles at the neighboring site.

Transformation is characterized by the diagonal matrix α (screening constant)

Screening



$$|K^{\alpha}_{RL}\rangle = |K^{0}_{RL}\rangle - \sum_{R'L'} |J^{\alpha}_{R'L'}\rangle S^{\alpha}_{RL,R'L'} + |K^{\alpha}_{RL}\rangle$$

$$|J^{\alpha}_{RL}\rangle = |J^{0}_{RL}\rangle - \alpha |K^{0}_{RL}\rangle$$

SUITABILITY FOR REAL−SPACE TECHNIQUES $\Rightarrow$

Recursion techniques

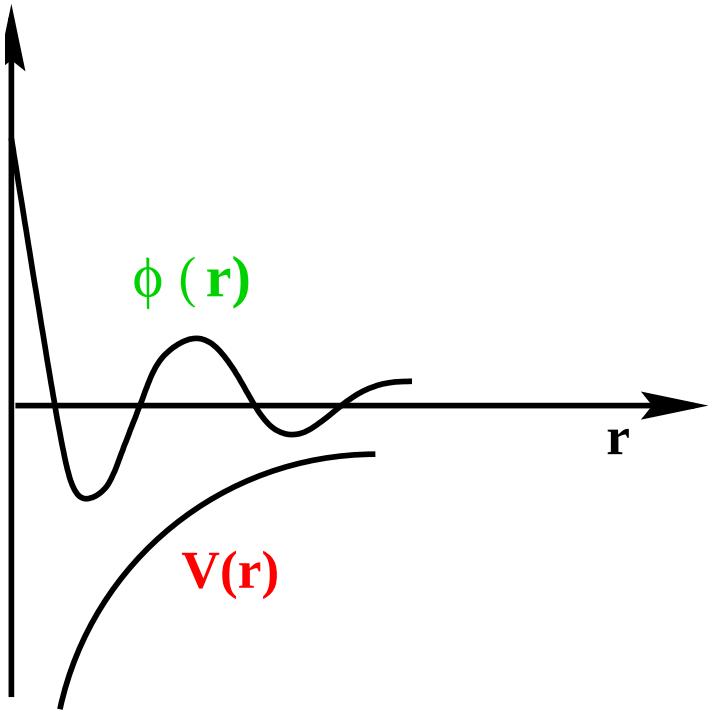
This gives us suitable envelope functions which we can then

(A) Augment to give MTO's

(B) Linearize to give LMTO's

Augmentation

- Inside each MT sphere we have a spherical potential.
- We solve Schrödinger Equation for this potential.
- Pick an energy E and angular momentum l and integrate out from r = 0 the radial equation. $\Rightarrow$ this gives *partial waves*, $|\phi_{\mathbf{R}L}(E) >$.



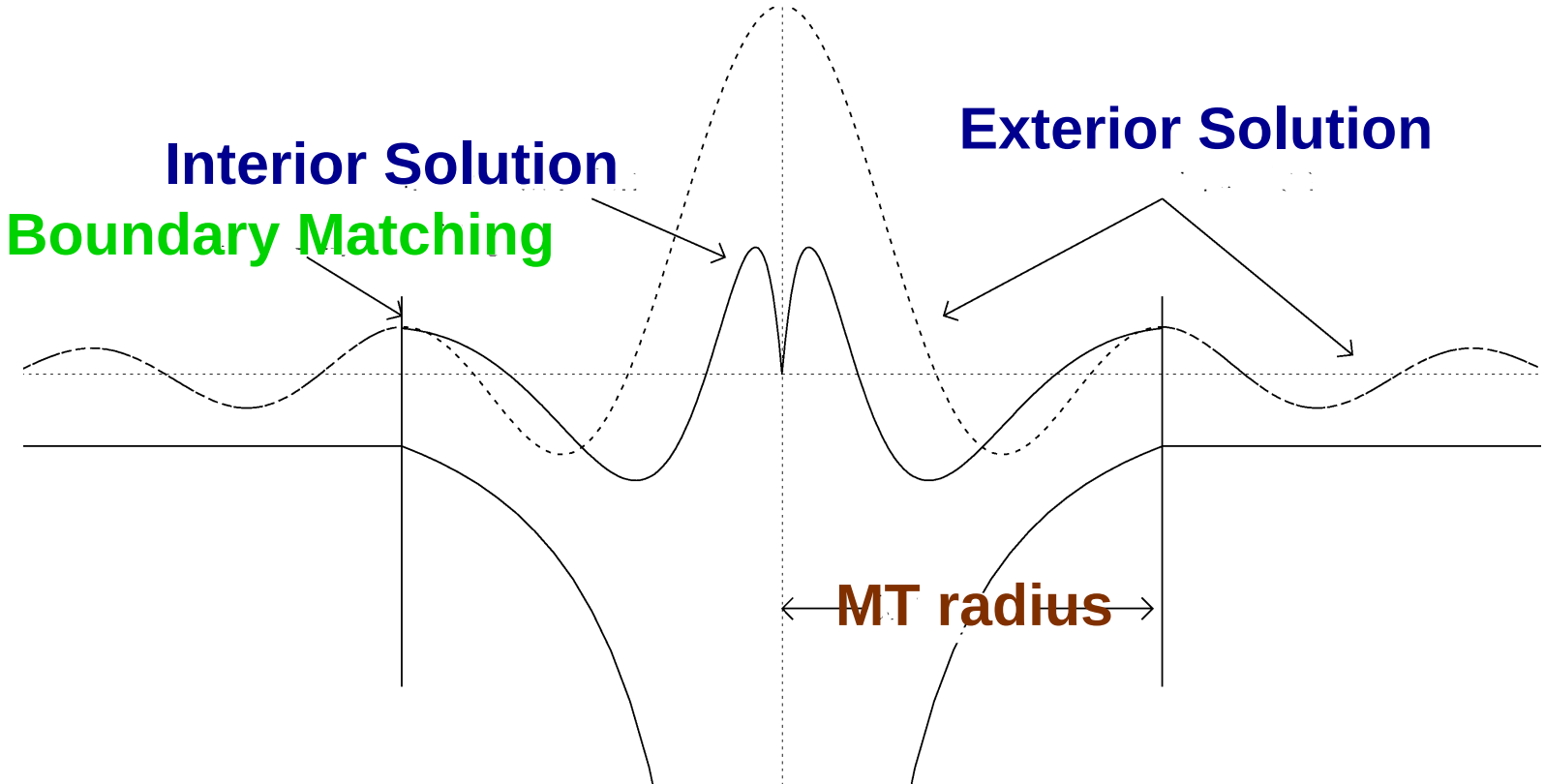
| ϕ > is the soln. in the spheres and | K$^{\alpha}$> in the interstitial. We therefore need to join them and this join should be smooth!

Augmentation

Augmentation involves replacing the $|K^o>$ inside each sphere by some other functions, matching continuously and differentiably the angular momentum components at the surface of the sphere.

$$|K^o_{RL}> \Rightarrow |\phi_{RL}(E)> N^\alpha_{RL}(E) + |J^\alpha_{RL}> P^\alpha_{RL}(E)$$

N(E): normalization function; P(E): potential function



Augmentation

- N and P should be chosen to make the join smooth.
- Need to use Wronskians.

$W\{f,g\} = s^2[f\frac{\partial g}{\partial r} - \frac{\partial f}{\partial r}g]_{r=s}$

$W\{f,g\} = sf(s)g(s)[D(g) - D(f)]$, where $D(f) = \frac{\partial ln(f)}{\partial ln(r)}$

The normalization and potential functions:

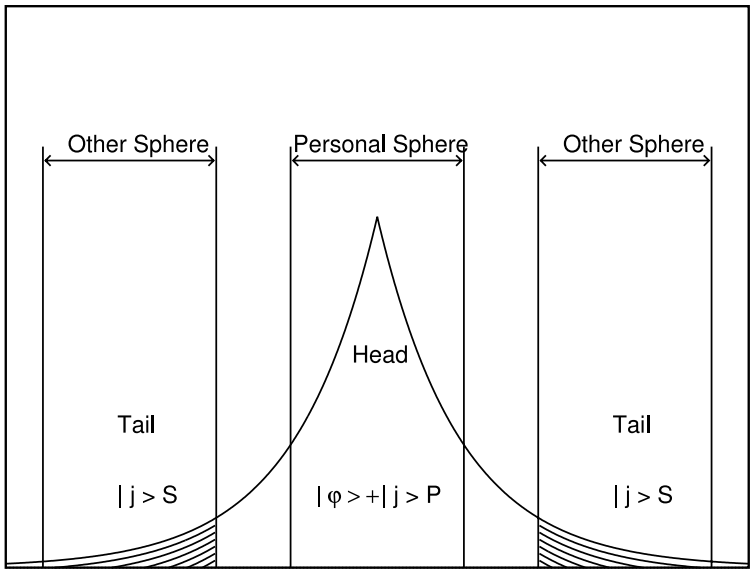
$$N^\alpha(E) = \frac{W\{J^\alpha, K\}}{W\{J^\alpha, \phi\}}$$

$$P^\alpha(E) = \frac{W\{\phi, K\}}{W\{\phi, J^\alpha\}}$$

Muffin Tin Orbital (MTO)

The augmented envelope function is the MTO

$$\| \chi^{\alpha}_{RL}(E) > \quad = \quad |\phi_{RL}(E) > N^{\alpha}_{RL}(E) + \sum_{R'L'} |J^{\alpha}_{R'L'} > [P^{\alpha}_{R'L'}(E)\delta_{R'L',RL} - S^{\alpha}_{R'L',RL}] + |\chi^{\alpha}_{RL} >^{i}$$



* **Head contains all informations about potential.**
* **Tail contains information only about the constant potential outside the MT sphere.**

Muffin Tin Orbital (MTO)

MTO's are energy dependent inside the spheres, because the partial waves as defined are energy dependent.

($*$) Find a soln. using the energy dependent MTO's $\Rightarrow$ leads to KKR eqns.

($*$) First linearize the MTO's to give an energy independent basis set, the LMTO's. One can then use them to make the matrix elements of the Hamiltonian which gives an eigenvalue problem [*Easier to Solve*]

KKR

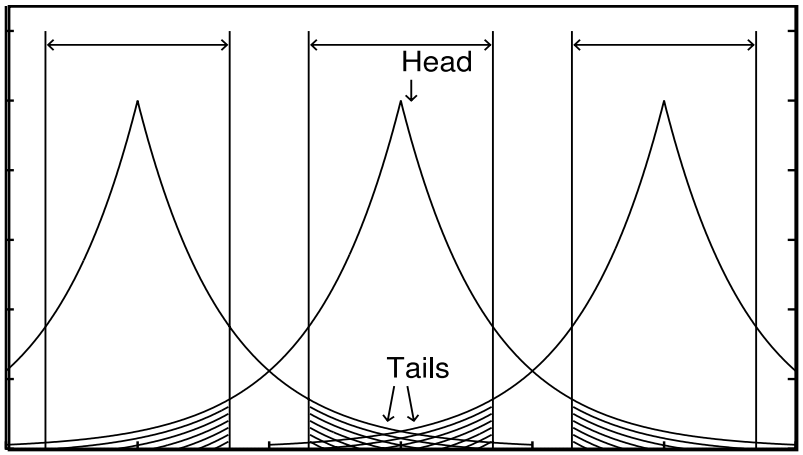
Consider linear superposition of the MTO's :

$$\| \Psi(E) >= \sum_{RL} \chi^{\alpha}_{RL}(E) > [N^{\alpha}_{RL}]^{-1} u_{RL}(E)$$

This will be a solution of the SE if inside each sphere all the J's in the tails from the different $\| \chi^{\alpha}_{RL} >$'s cancel.

Tail cancellation :

$$\sum_{RL}(P^{\alpha}_{R'L'}(E)\delta_{R'L',RL} - S^{\alpha}_{R'L',RL})[N^{\alpha}_{RL}(E)]^{-1} u_{RL}(E) = 0$$



KKR

- A solution can only by found at certain discrete energies, the eigenvalues.
- This equation is hard to solve because it is a complicated function of E.

The LMTO's

Andersen 1975

- Pick an energy E_ν.
- Augment the $|J^\alpha>$'s in such a way that the MTO does not change to 1st order in energy about E_ν.
- We can then use $|\chi(E_\nu)>$ as an *energy independent basis sets* $\Rightarrow$ LMTOs.
- With these we take matrix elements of the Hamiltonian.
- The resulting eigenvalue problem gives the solutions to SE in the region around E_ν.

The LMTO's

Differentiating the expansion for the MTO w.r.t energy we obtain:

$$\| \dot{\chi}^{\alpha}_{\mathbf{R}L} >= |\dot{\phi}^{\alpha}(E) > N^{\alpha}_{RL}(E) + |J^{\alpha}_{RL} > \dot{P}^{\alpha}_{RL}(E)$$

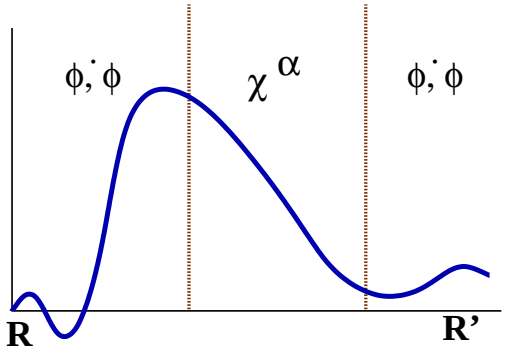
where $|\dot{\phi}^{\alpha}(E) >= \frac{1}{N^{\alpha}_{RL}} \frac{\partial}{\partial E}[|\phi(E) > N^{\alpha}_{RL}(E)]$ = $|\dot{\phi} > +o^{\alpha}|\phi >$

This implies, $|J^{\alpha}_{RL} > \rightarrow -|\dot{\phi}^{\alpha}_{RL}(E_\nu) > N^{\alpha}_{RL}(E_\nu)[\dot{P}^{\alpha}_{RL}(E_\nu)]^{-1}$

LMTO :

$$\| \chi^{\alpha}_{RL} > \quad = \quad |\phi_{RL}(E_\nu) > N^{\alpha}_{RL}(E_\nu) - \sum_{R'L'} |\dot{\phi}^{\alpha}_{RL}(E_\nu) > N^{\alpha}_{RL}(E_\nu)$$

$$[\dot{P}^{\alpha}_{RL}(E_\nu)]^{-1}[P^{\alpha}_{R'L'}(E_\nu)\delta_{R'L',RL} - S^{\alpha}_{R'L',RL}] + |\chi^{\alpha}_{RL} >^{i}$$



LMTO is made up of $\phi, \dot{\phi}$ and χ^{α}

The LMTO Hamiltonian

Starting with LMTO expression,

$$\| \chi^{\alpha}_{RL} > = |\phi_{RL}(E_\nu) > N^{\alpha}_{RL}(E_\nu) - \sum_{R'L'} |\dot{\phi}^{\alpha}_{RL}(E_\nu) > N^{\alpha}_{RL}(E_\nu)$$
$$[\dot{P}^{\alpha}_{RL}(E_\nu)]^{-1}[P^{\alpha}_{R'L'}(E_\nu)\delta_{R'L',RL} - S^{\alpha}_{R'L',RL}] + |\chi^{\alpha}_{RL} >^{i}$$

one can easily show that,

$$\| \chi^{\alpha}_{RL} > [N^{\alpha}_{RL}]^{-1} = |\phi_{RL} > - \sum_{R'L'} |\dot{\phi}^{\alpha}_{RL} > \sqrt{\frac{w}{2}}[\dot{P}^{\alpha}_{RL}]^{-1/2}[P^{\alpha}_{R'L'}\delta_{R'L',RL}$$
$$-S^{\alpha}_{R'L',RL}]\sqrt{\frac{2}{w}}[\dot{P}^{\alpha}_{RL}]^{-1/2} + |\chi^{\alpha}_{RL} >^{i} [N^{\alpha}_{RL}]^{-1}$$
$$= |\phi_{RL} > - \sum_{R'L'} h^{\alpha}_{R'L'} |\dot{\phi}^{\alpha}_{RL} > + |\chi^{\alpha}_{RL} >^{i} [N^{\alpha}_{RL}]^{-1}$$

The LMTO Hamiltonian

where, $h^\alpha = -(\dot{P}^\alpha)^{-1/2}[P^\alpha - S^\alpha](\dot{P}^\alpha)^{-1/2} = C^\alpha - E_\nu + \sqrt{\Delta^\alpha} S^\alpha \sqrt{\Delta^\alpha}$

$C^\alpha = E_\nu - \frac{P^\alpha}{\dot{P}^\alpha}$; $\sqrt{\Delta^\alpha} = \frac{1}{\dot{P}^\alpha}$ are the potential parameters.

$$h^\alpha + E_\nu = C^\alpha + \sqrt{\Delta^\alpha} S^\alpha \sqrt{\Delta^\alpha}$$ *: Division of Chemistry and Geometry*

With ASA approximation (replace the MT spheres by space-filling spheres):

$$\| \chi^\alpha_{RL} > [N^\alpha_{RL}]^{-1} = |\phi_{RL}(E_\nu) > - \sum_{R'L'} h^\alpha_{R'L'} |\dot{\phi}^\alpha_{RL}(E_\nu) >$$

Define function φ, $|\phi(E)>$ = $N(E)N^{-1}|\varphi(E)>$

so that $|\phi>$ = $|\varphi>$ and $|\dot{\phi}>$ = $\dot{\varphi}$ + $o|\phi>$

This gives, $\| \chi >$ = $\Pi\varphi + h\dot{\varphi}$, where $\Pi = I + ho$

Finally orthogonalizing the LMTOs $\| \tilde{\chi} >$ = $\Pi^{-1} \| \chi >$, gives the Hamiltonian form (neglecting few small terms),

$$H = E_\nu + h(I + ho)^{-1} = E_\nu + h - hoh - \ldots$$

Steps to LMTO

Envelope function, $\| K >$

$\Downarrow$

Screen to localize them:
$\| K^{\alpha} >= |K^{o} > - |J^{\alpha} > S^{\alpha} + |K^{\alpha} >^{i}$

$\Downarrow$

Replace $|K^{o} >$ by $|\phi(E) > N(E) + |J^{\alpha} > P^{\alpha}(E)$ $\Rightarrow$ **Defines MTO**

$\Downarrow$

Linearization [MTO does not change to (E - E_{ν})]
$|J^{\alpha} > \rightarrow$ - $|\dot{\phi}^{\alpha} > N^{\alpha}[\dot{P}^{\alpha}]^{-1}$

$\Downarrow$

Defines LMTO $\rightarrow$ leads to eigenvalue problem

DOWNFOLDING

Procedure to get few band Hamiltonian starting from many band complicated Hamiltonian.

LMTO's are divided into 2 sets :

Lower : Kept in the basis $\rightarrow$ dimension ldim

Intermediate : Downfolded $\rightarrow$ dimension idim

- Removed from the Hamiltonian but information is retained in the Structure matrix.
- Downfolded orbitals are provided by the tails of LMTO

DOWNFOLDING

* Take the KKR eqns.
* Shuffle the rows and columns so that they are grouped in order into *low* and *intermediate*.
* This leaves:

$$\begin{pmatrix} P^{\alpha}_{ll} - S^{\alpha}_{ll} & -S^{\alpha}_{li} \\ -S^{\alpha}_{il} & P^{\alpha}_{ii} - S^{\alpha}_{ii} \end{pmatrix} \begin{pmatrix} (N^{\alpha}_{l})^{-1}\, u_l \\ (N^{\alpha}_{i})^{-1}\, u_i \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

* If we linearize at this point we get ldim+idim solution, so instead we first eliminate the u_i . From the lower eq. :

$$[N^{\alpha}_{i}]^{-1} u_i = [P^{\alpha}_{ii} - S^{\alpha}_{ii}]^{-1} S^{\alpha}_{il} [N^{\alpha}_{l}]^{-1} u_l$$

* This gives in the upper eqn :

$$(P^{\alpha}_{ll} - S^{\alpha}_{ll} - S^{\alpha}_{li}(P^{\alpha}_{ii} - S^{\alpha}_{ii})^{-1} S^{\alpha}_{il})(N^{\alpha}_{l})^{-1} u_l = 0$$

If we now linearize and solve this eqn. we get ldim solns.

Disadvantages:

- The basis is complete to (E- E_ν) (*i.e.1st order*) inside the sphere while it is only complete to to (E- $E_\nu)^0$ = 1 (*0-th order*) in the interstitial $\Rightarrow$ INCONSISTENT

  Can be made consistent by removing the interstitial $\Rightarrow$ ASA

- The non-ASA corrections (*combined correction*) may of course be included in the Hamiltonian and in the Overlap matrices. BUT,

  (i) This makes the formalism heavy
  (ii) Basis must often be increased by multi-panel calculation.

- The expansion of the Hamiltonian H in the orthogonal representation as a power series in the two-centered tight-binding Hamiltonian h :

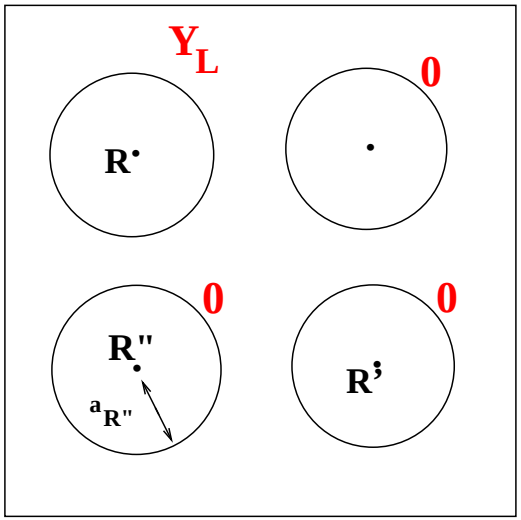
$$< \tilde{\chi}|(H - E_\nu)|\tilde{\chi} >= h - hoh + \ldots$$

  is obtained only within ASA and excluding downfolding.

Improved LMTO – NMTO Method:

- Still has a Muffin tin potential.
- Still use the partial waves, ϕ in the atomic sphere.
- Instead of Neumann function use Screened spherical waves (SSW) in the interstitial region.
- Define the kinked partial waves (KPWs) out of partial waves and screened spherical waves.
- Construct energy-independent NMTOs, which are superpositions of KPW's evaluated at N+1 energy points.

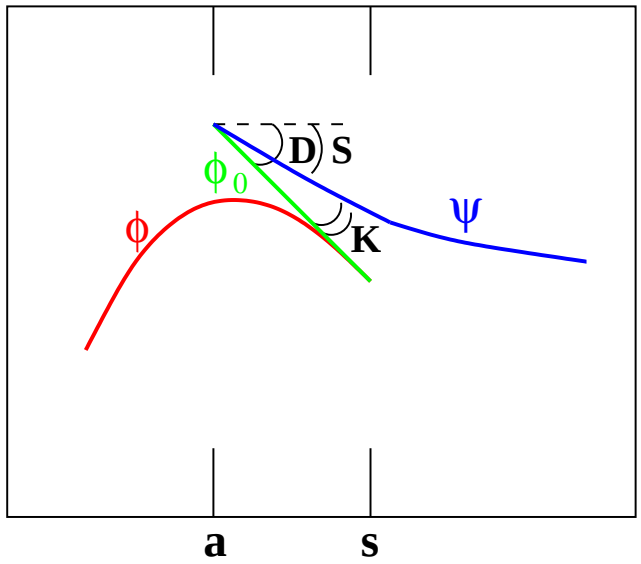
Screened Spherical Waves: SSW's



- Position a spherical wave $Y_L(\theta,\phi)\eta_l(\kappa r)$ at site R
- Screen at all other sites R$'$.
  a_R = hard core radii (*non-overlapping*) $<$ MT radii
- Mathematical definition : $\bigtriangledown^2|\psi>=-\kappa^2|\psi>(Soln.of wave eqn)$

  With boundary conditions: $|\psi_{RL}(a_{R'})>=\delta_{R,R'}\delta_{L,L'}Y_L$
- The specific b.c.(hard spheres) and energy-independent normalization chosen for SSWs reduces their energy dependence to a minimum.

Augmentation of a SSW



- The partial wave $|\phi>$ form soln. of SE inside the MT sphere. $\rightarrow$ *$|\phi>$ is given by numerical integration of SE out to the MT sphere s in the potential $v(r)$.*
- Continue the integration, but now backwards to the screening sphere a and using the flat interstitial potential $V_{MTZ} \Rightarrow$ defines $|\phi_o>$.
- Attach the screened spherical wave $|\psi>$ at the screening sphere, continuously but not differentially.

Augmentation of a SSW: KPW

$$\Downarrow$$

Kinked Partial Wave : $|\bar{\psi}>=|\phi>-|\phi_o>+|\psi>$

Soln to SE at energy E for its own MT potential and for the flat interstitial potential

but

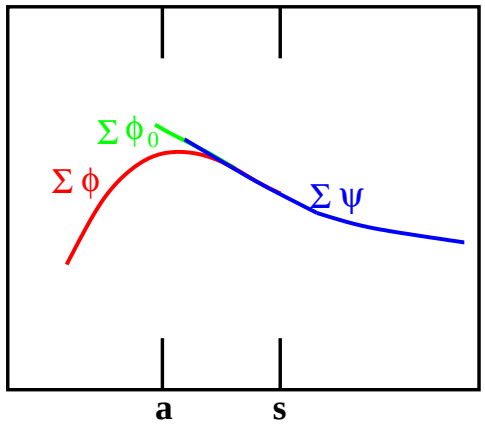
Has a kink (*discontinuous spatial derivative*) at all screening spheres.

Kink Matrix and Kink Cancellation

Kink Matrix: K = a [D - S]; $D = \frac{a}{\phi_o(a)} \frac{d\phi_o(a)}{dr}$

Kink matrix K contains the values of the kinks of all the $|\bar{\psi} >$ at all screening spheres.

Kink Cancellation:



$|\psi(E) >= \sum_i |\bar{\psi}_i(E) > v_i$ solution of SE in all space at E

$|\psi >$ must be differentiable, so the sum of the kinks of $|\bar{\psi} >$ must vanish : $K.v = 0$

$\boxed{a[D - S].v = 0}$ *c.f. tail cancellation condition :* $[P - S].v = 0$

NMTOs

• The members (labeled by $R'L'$) of the NMTO basis set for the energy mesh $\epsilon_0, ..., \epsilon_N$ are superpositions,

$$\chi^{(N)}_{R'L'}(\mathbf{r}) = \sum_{n=0}^{N} \sum_{RL \in A} \phi_{RL}(\epsilon_n, \mathbf{r})\ L^{(N)}_{nRL,R'L'}$$

of the kinked partial waves, $\phi_{RL}(\varepsilon, \mathbf{r})$, at the $N+1$ points (labeled by n) of the energy mesh.

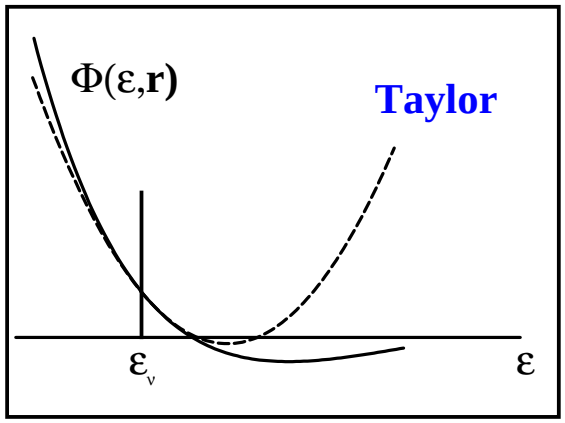
NMTOs

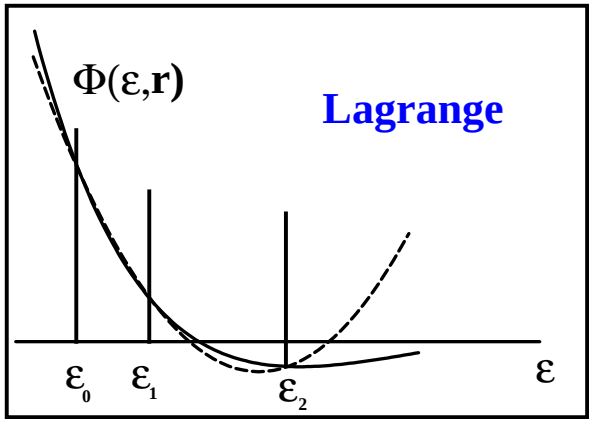
• The expression is the energy-quantized form of Lagrange interpolation,

$$\chi^{(N)}(\varepsilon) \approx \sum_{n=0}^{N} \phi(\epsilon_n)\, l_n^{(N)}(\varepsilon), \quad l_n^{(N)}(\varepsilon) \equiv \prod_{m=0,\neq n}^{N} \frac{\varepsilon - \epsilon_m}{\epsilon_n - \epsilon_m},$$

Nth-degree polynomial, $l_n^{(N)}(\varepsilon) \rightarrow$ matrix with elements, $L^{(N)}_{nRL,R'L'}$

$\phi(\varepsilon) \rightarrow \phi_{RL}(\varepsilon, \mathbf{r})$, $\chi^{(N)}(\varepsilon) \rightarrow \chi^{(N)}_{R'L'}(\mathbf{r})$





NMTOs

- By virtue of the variational principle, the errors of the energies ε_i is proportional to $(\varepsilon_i - \epsilon_0)^2 ... (\varepsilon_i - \epsilon_N)^2$.

- The Lagrange coefficients, $L_n^{(N)}$, as well as the Hamiltonian and overlap matrices in the *N*MTO basis are expressed solely in terms of the KKR resolvent, $K(\varepsilon)^{-1}$, and its first energy derivative, $\dot{K}(\varepsilon)^{-1}$, evaluated at the energy mesh, $\varepsilon = \epsilon_0, ..., \epsilon_N$.

This method gives rise to an energetically accurate and compact formalism for intelligible electronic structure calculation.

What we have done ?

Constructed an NMTO basis that is complete to $(\varepsilon_i - \epsilon_0) \ldots (\varepsilon_i - \epsilon_N)$ EVERYWHERE.

What is new (improvements) ?

- A consistent description both inside and outside MT.
- Error in the eigenvalue is of order $(\varepsilon_i - \epsilon_0)^2 \ldots (\varepsilon_i - \epsilon_N)^2$ rather than $(\varepsilon_i - \epsilon_\nu)^2$. $\Rightarrow$ Leads to improved accuracy in energy (*Needed for massive downfolding purpose*).
- The tight-binding Hamiltonian representation can be obtained both in presence of downfolding (Imp for generation of effective hopping interactions, onsite energies) and moving beyond ASA (Imp for handling complex systems).

NMTO: truly minimal set and Wannier functions

- The energy selective and localized nature of NMTO basis makes the NMTO set flexible and may be chosen as truly minimal($\equiv$ span selected bands with as few basis functions as there are bands).

- If these bands are isolated, the NMTO set spans the Hilbert space of the Wannier functions and the orthonormalized NMTOs are the Wannier functions.

- Even if the bands overlap with other bands, it is possible to pick out those few bands and their corresponding Wannier-like functions with NMTO method.

- The NMTO method can thus be used for direct generation of Wannier or Wannier-like functions.

Scheme to Get Few Band, TB Description

- Start with full LMTO band structure keeping all the orbitals of all the constituent atoms.

  $\mapsto$ This is the truth but complicated to analysis. Total no. of bands is at least 9 $\times$ N, [*N is the no. of atoms in a unit cell*].

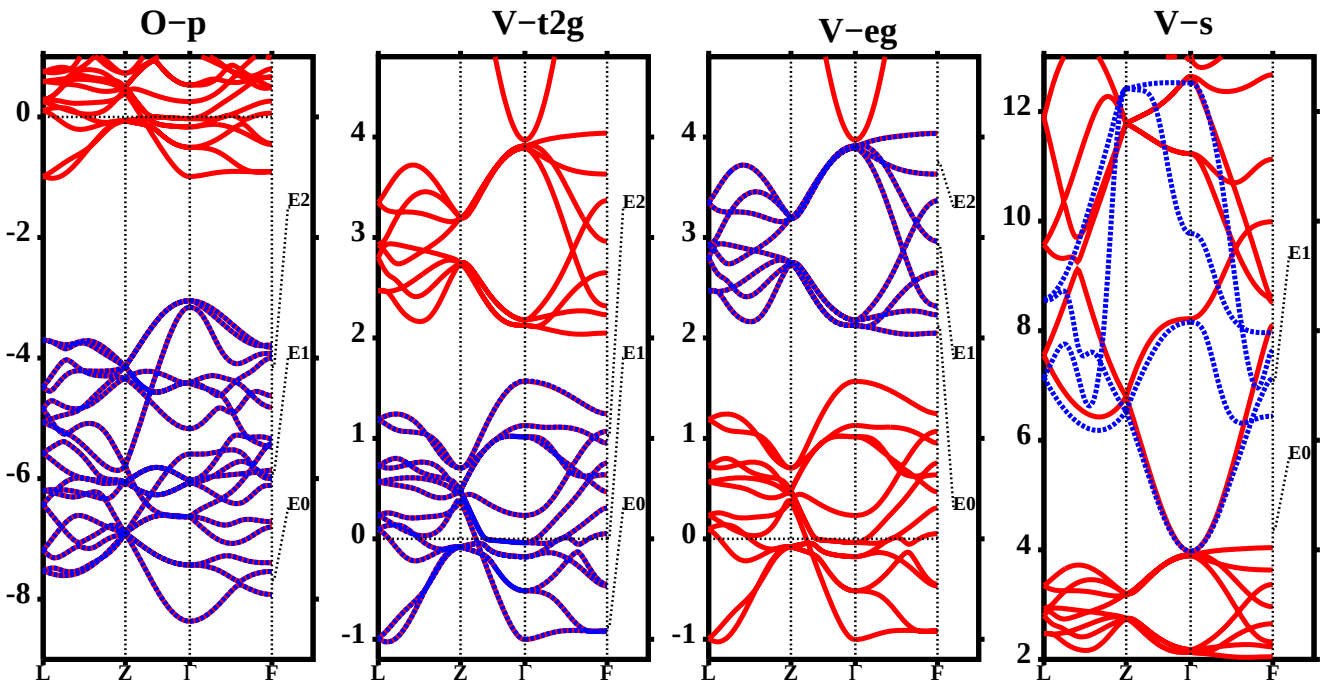
  $\mapsto$ We want to reproduce it over an energy window with a simple tight-binding Hamiltonian.

- Import the LMTO potentials to NMTO code (NOTE: NMTO IS STILL NON-SCF!). We want to take adv. of higher energy accuracy in NMTO.

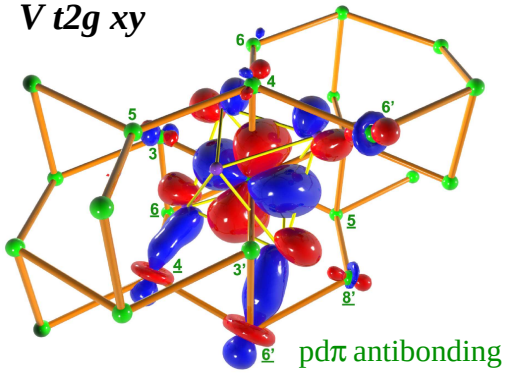
- Apply downfolding procedure keeping only the relevant orbitals and integrating out all other high energy degrees of freedom to get few-orbital band structure.

- Make the FT to extract the tight-binding parameters.

V2O3: *Corundum Structure*

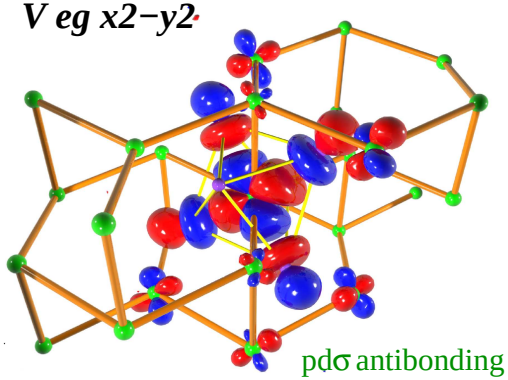


V t2g xy



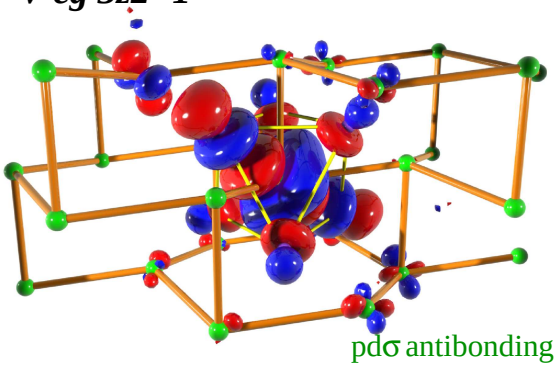
pdπ antibonding

V eg x2−y2



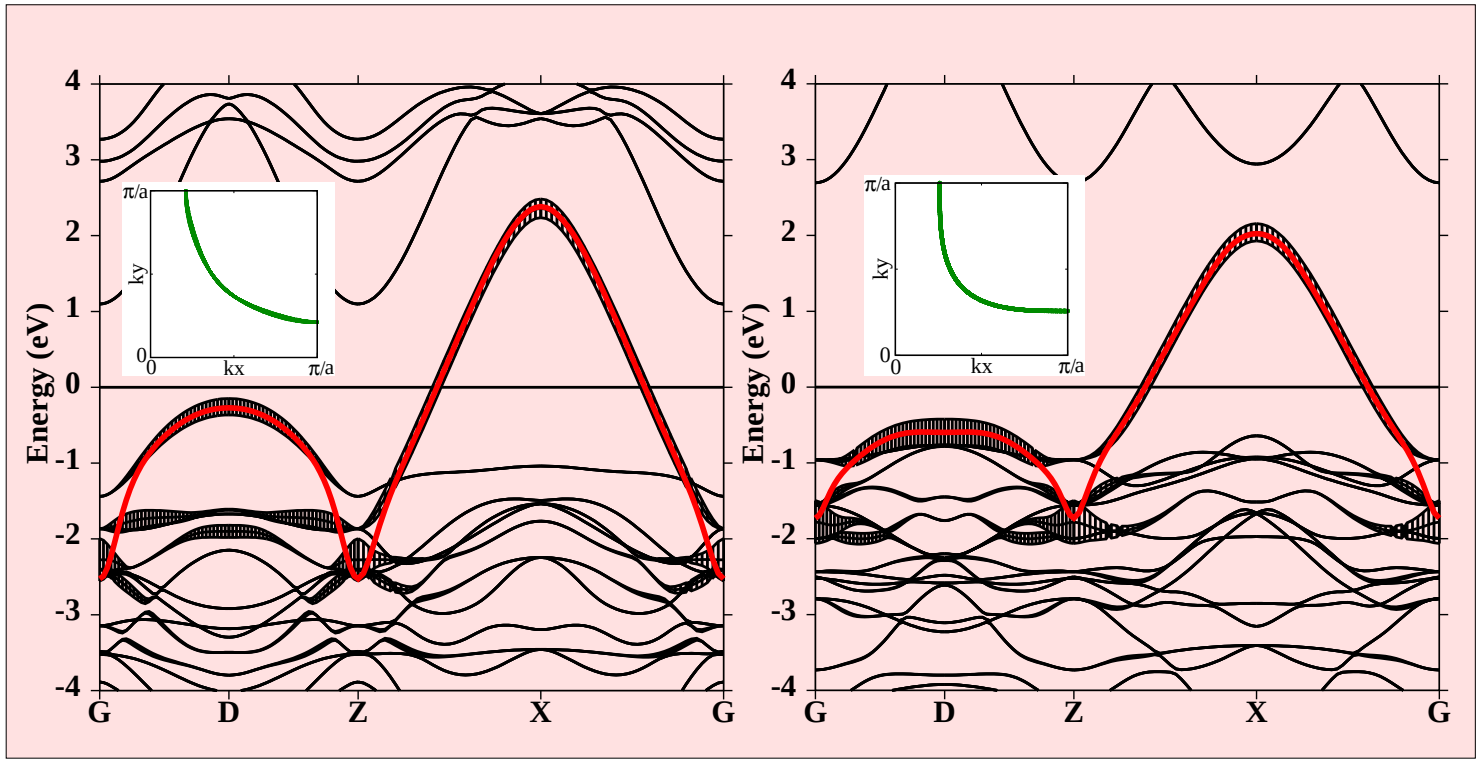
pdσ antibonding

V eg 3z2−1



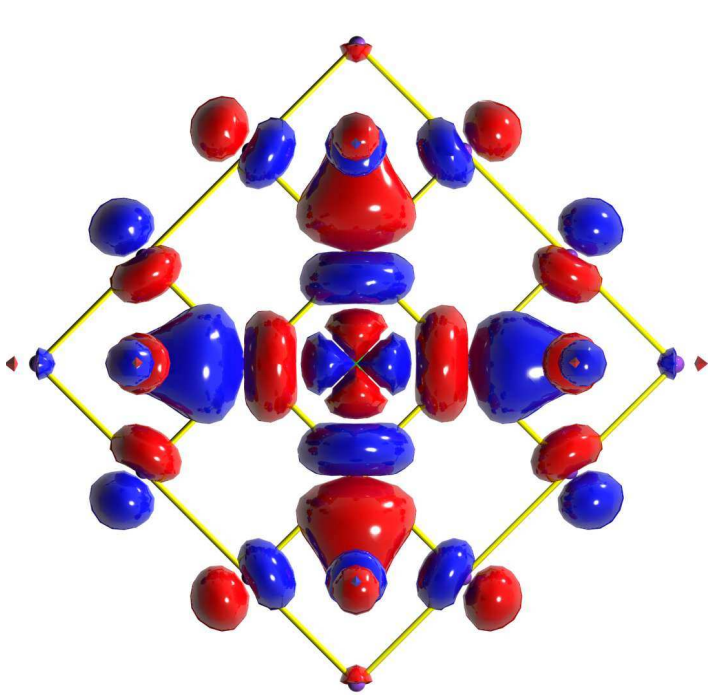
pdσ antibonding

HTSC



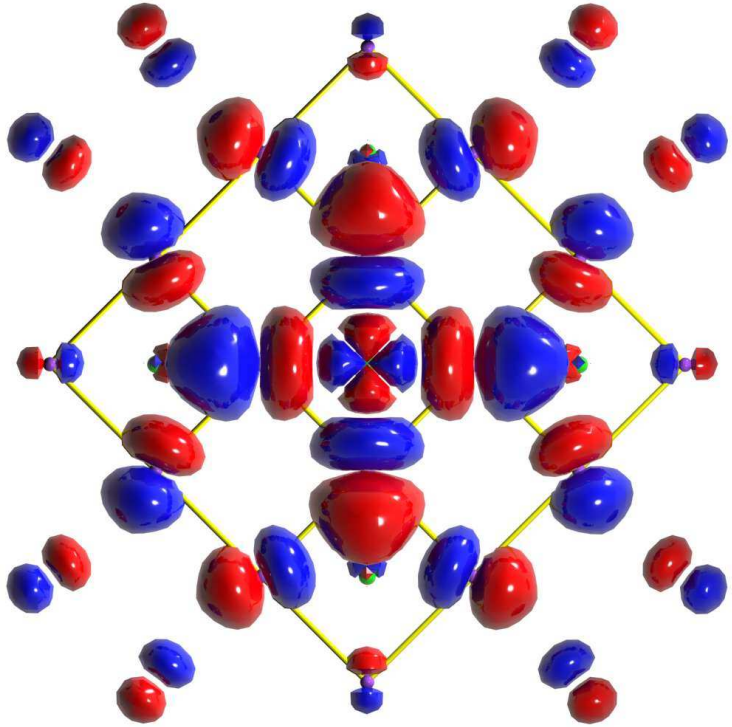
HTSC- Wannier-like functions

La_2CuO_4



Tc = 40 K

$HgBa_2CuO_4$



Tc = 90 K

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