Lecture on First-principles Computations (13): The KKR and LMTO method

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Recall: properties of transition metals

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Local density theory of metallic cohesion*

V. L. Moruzzi, A. R. Williams, and J. F. Janak
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 28 April 1976; revised manuscript received 21 June 1976)

We present the results of extensive numerical experiments designed to test the ability of the local-density theory of electronic exchange and correlation to describe binding in both simple and transition metals. Predicted nuclear separations, cohesive energies, and bulk moduli for 26 third- and fourth-row metals exhibit remarkable agreement with experiment. The only input to these calculations is the atomic number.

"Local density theory of metallic cohesion", PRB (1977)

- Equilibrium structure, cohesive energies, bulk moduli for *simple and transition m*etals
- Hedin-Lundqvist LDA, Korringa-Kohn-Rostocker (KKR) method

The KKR method

From the mathematical point of view, the most refined method of calculating energy band structures is the subtle procedure invented independently by Korringa, and by Kohn and Rostoker. This method is indeed so fundamental that it is to be found in all its essentials in a study by Rayleigh [in 1892] of the propagation of sound waves through an assembly of spheres.

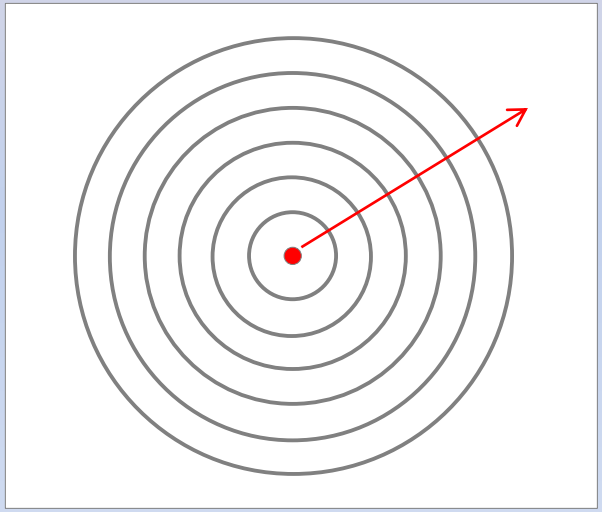
John M. Ziman in *Solid State Physics* (1971)

*Korringa, Physica **13**, 392 (1947)*
*Kohn & Rostoker, Phys. Rev. **94**, 1111 (1954)*

Green's function

Green's function (propagator) describes the propagation a particle from position $\boldsymbol{r}$ to $\boldsymbol{r}'$ at the energy E.

$$G = G(\boldsymbol{r}, \boldsymbol{r}', E)$$



Free propagator :

$$\left(-\frac{1}{2m}\nabla_{\boldsymbol{r}}^2 - E\right) G_0(\boldsymbol{r}, \boldsymbol{r}', E) = -\delta(\boldsymbol{r} - \boldsymbol{r}')$$

$$G_0(\boldsymbol{r}, \boldsymbol{r}', E) = -\frac{2m}{4\pi} \frac{e^{ik|\boldsymbol{r}-\boldsymbol{r}'|}}{|\boldsymbol{r} - \boldsymbol{r}'|}, \qquad k = \begin{cases} (2mE)^{1/2}, E \geq 0 \\ i(-2mE)^{1/2}, E < 0 \end{cases}$$

Spectral representation of Green's function

In general, given a single-particle Hamiltonian:

$$\hat{h} = -\frac{1}{2m}\nabla^2 + V(\boldsymbol{r})$$

We can define

$$\left(\hat{h} - E\right)G(\boldsymbol{r}, \boldsymbol{r}', E) = -\delta(\boldsymbol{r} - \boldsymbol{r})$$

If $\hat{h}\psi_n = \epsilon_n\psi_n$, then

$$G(\boldsymbol{r}, \boldsymbol{r}', E) = \sum_n \frac{\psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}')}{E - \epsilon_n} \qquad \left[\sum_n \psi_n(\boldsymbol{r})\psi_n^*(\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')\right]$$

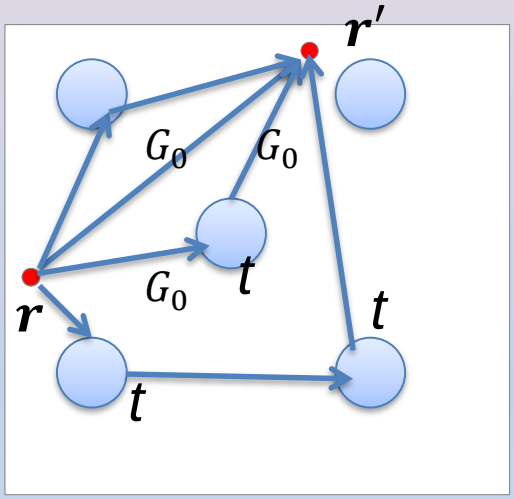
Poles!

Multiple scattering theory

Full Green's function:

$$G = G_0 + G_0 t G_0 + G_0 t G_0 t G_0 + \cdots$$

$$= G_0 + G_0 t G = G_0 + G_0 T G_0$$



(Dyson Equation)

$G = (G_0^{-1} - t)^{-1}$ (t: scattering matrix)

$T = t + t G_0 T = [t^{-1} - G_0]^{-1}$

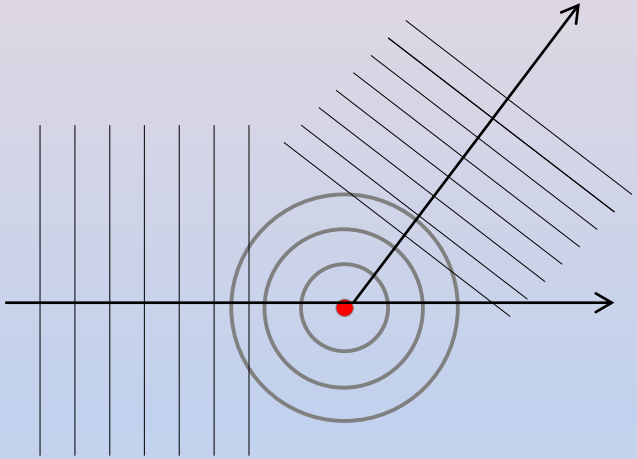
Stationary states of the system is given by the poles of G or T, or the zeros of the determinant,

$$\det\left(t^{-1}(E) - G_0(E)\right) = 0$$

The scattering matrix element

Consider spherically symmetric potential

$$\mathrm{V}(\mathbf{r}) = \begin{cases} V(r), & r \le R_c \\ 0, & r > R_c \end{cases}$$



The wave function:

$$\psi_L(\boldsymbol{r}) = i^l \psi_l(r) Y_{lm}(\hat{r})$$

$$r \le R_c: \quad \left[\frac{1}{2\mathrm{m}}\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2}\right) + V(r) - E\right] r\psi_l(r, E) = 0$$

$$r > R_c: \quad \psi_l(r, E) = C_l\left[j_l(kr) - \tan\left(\eta_l(E)\right) n_l(kr)\right], \qquad k = \sqrt{2mE}$$

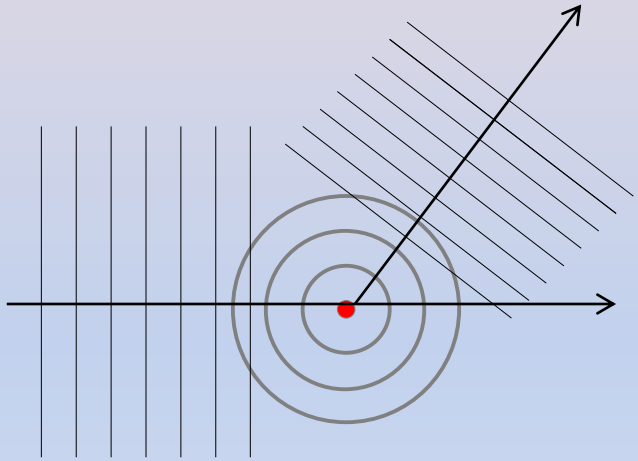
Spherical Bessel function

Spherical Neumann function

The scattering matrix element

Requiring $\psi_l(r,E)$ is continuously differentiable at R_c

Let $D_l(E) = r\dfrac{d}{dr}\ln\psi_l(r,E)|_{R_c}$, then



$$\tan\left(\eta_l(E)\right) = \frac{R_c j'_l(kr)|_{R_c} - D_l(E) j_l(kR_c)}{R_c n'_l(kr)|_{R_c} - D_l(E) n_l(kR_c)}$$

For positive energy $E > 0$,

$$r \gg R_c : \psi_l(\boldsymbol{r},E) \to \frac{C_l}{\kappa r}\sin\left(kr + \eta_l(E) - \frac{l\pi}{2}\right)$$

The full scattered wave function:

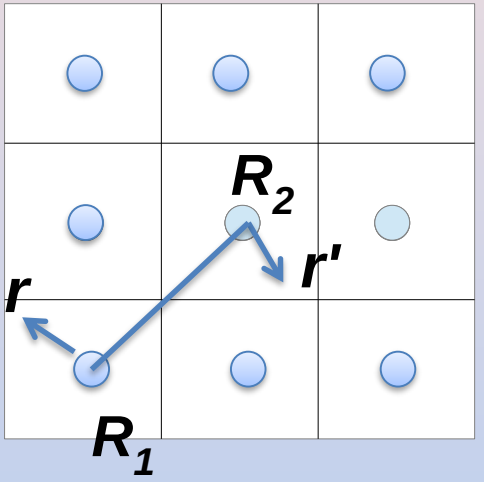
$$\psi_l(\boldsymbol{r},E) \to e^{i\boldsymbol{kr}} + i\frac{e^{i\boldsymbol{kr}}}{kr}\sum_l (2l+1)e^{\eta_l}\sin(\eta_l)P_l[\cos(\theta)]$$

The scattering matrix : $t_l(E) = -\dfrac{1}{\kappa}e^{i\eta_l(E)}\sin\left(\eta_l(E)\right)$

Green function in a lattice

Plane-wave expansion :

$$e^{i\mathbf{q}\cdot\mathbf{r}} = 4\pi \sum_{L} i^l j_l(q\mathbf{r}) Y_L^*(\hat{q}) Y_L(\hat{r})$$



Addition formula :

$$e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R_1})} = e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{R_2})} e^{i\boldsymbol{k}\cdot(\boldsymbol{R_1}-\boldsymbol{R_2})}$$

$$\Downarrow$$

$$G_0(|\,\boldsymbol{r}-\boldsymbol{r}'\,|, E) = -\frac{1}{\Omega}\sum_{\boldsymbol{k},\boldsymbol{G}} \frac{e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{\frac{|\boldsymbol{k}+\boldsymbol{G}|^2}{2m} - E}$$

$$G_0(|\,\boldsymbol{r}-\boldsymbol{r}'\,|, E) = \sum_{L,L'} i^l j_l(k|\,\boldsymbol{r}-\boldsymbol{R_1}\,|) Y_L\big(\widehat{\boldsymbol{r}-\boldsymbol{R_1}}\big) \times$$

$$B_{LL'}(\boldsymbol{R_2}-\boldsymbol{R_1}, E)(-i)^{l'} j_{l'}(k|\,\boldsymbol{r}'-\boldsymbol{R_2}\,|) Y_L^*\big(\widehat{\boldsymbol{r}'-\boldsymbol{R_2}}\big)$$

$$= \sum_{LL'} \phi_L(\boldsymbol{r}-\boldsymbol{R_1}) B_{LL'}(\boldsymbol{R_2}-\boldsymbol{R_1}, E) \phi_{L'}^*(\boldsymbol{r}'-\boldsymbol{R_2})$$

Green function in a lattice

$$G_0(|\,\boldsymbol{r}-\boldsymbol{r}'\,|,E)=\sum_{LL'}\phi_L\,(\boldsymbol{r}-\boldsymbol{R_1})B_{LL'}(\boldsymbol{R_2}-\boldsymbol{R_1},E)\phi^*_{L'}(\boldsymbol{r}'-\boldsymbol{R_2})$$

KKR structure factor

$$\phi_L(r)=i^l j_l(kr)Y_L(\hat{r})$$

$$B_{LL'}(\boldsymbol{R_2}-\boldsymbol{R_1},E)=-4\pi\kappa\sum_{L''}i^{l''}C^{L}_{L',L''}\,n_{l''}(k|\boldsymbol{R_2}-\boldsymbol{R_1}|)Y_{L''}(\widehat{\boldsymbol{R_2}-\boldsymbol{R_1}})$$

where

$$C^{L}_{L',L''}=\int d\theta d\varphi Y^*_L(\hat{r})\;Y_{L'}(\hat{r})Y_{L''}(\hat{r})$$

are Gaunt coefficients.

The scattering matrix: $t_{LL'}(\boldsymbol{R},\boldsymbol{R}',E)=t_l(E)\delta_{\boldsymbol{R},\boldsymbol{R}'}\delta_{L,L'}$

Band structure in a periodic lattice

$$[G_{LL'}(E,\boldsymbol{R},\boldsymbol{R}')]^{-1} = [B_{LL'}(\boldsymbol{R}-\boldsymbol{R}',E)\,]^{-1} - t_l(E)\,\delta_{\boldsymbol{R},\boldsymbol{R}'}\delta_{LL'}$$

Stable solutions exist when

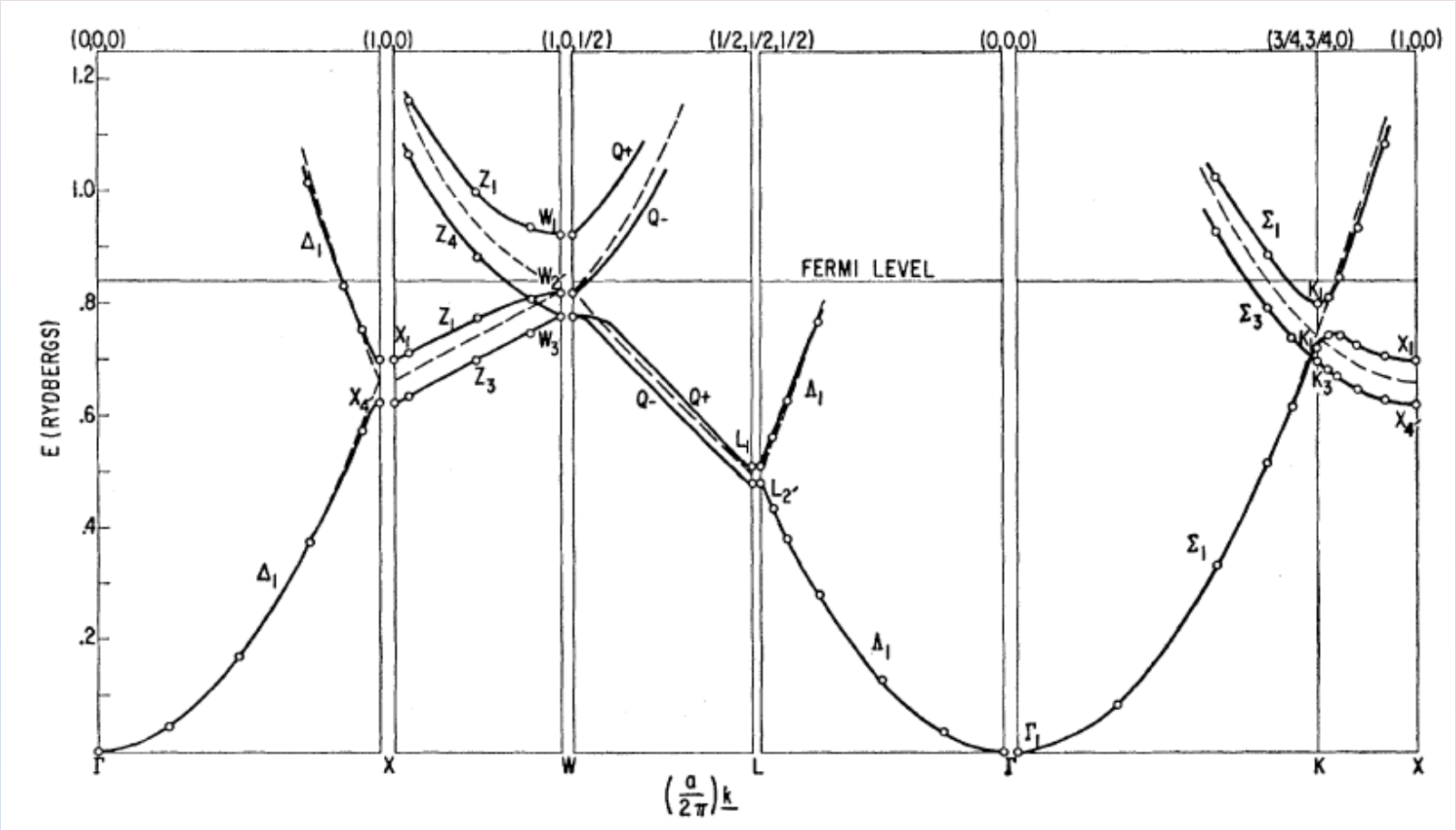
$$\det\left[t_l^{-1}(\boldsymbol{R},E)\delta_{\boldsymbol{R},\boldsymbol{R}'}\delta_{L,L'} - B_{LL'}(\boldsymbol{R}-\boldsymbol{R}',E)\right] = 0$$

For periodic lattices, Fourier transform to the ***k*** space

$$\det\left[t_l^{-1}(E)\delta_{L,L'} - B_{LL'}(\boldsymbol{k},E)\right] = 0 \Rightarrow$$

$E = E(\boldsymbol{k})$ The band structure is obtained.

The band structure of Al



B. Segall, Phys. Rev. (1961)

Solid lines : the KKR method

Dash lines : free electron bands

Density of states within the KKR method

Partial density of states (DOS)

$$D_L(E, \boldsymbol{k}) = -\frac{1}{\pi}\mathrm{Im}G_{LL}(E + i\delta, \boldsymbol{k})$$

Angular-resolved DOS

$$D(E, \boldsymbol{k}) = \sum_L n_L\,(E, \boldsymbol{k})$$

Total DOS

$$D(E) = \sum_{\boldsymbol{k}\in 1\mathrm{BZ}} \sum_L n_L\,(E, \boldsymbol{k})$$

Total density

$$n_{\boldsymbol{R}} = -\frac{1}{\pi}\sum_L \int_{-\infty}^{E_F} d\,E\mathrm{Im}G_{LL}(E + i\delta, \boldsymbol{R})$$

Key Features of the KKR method

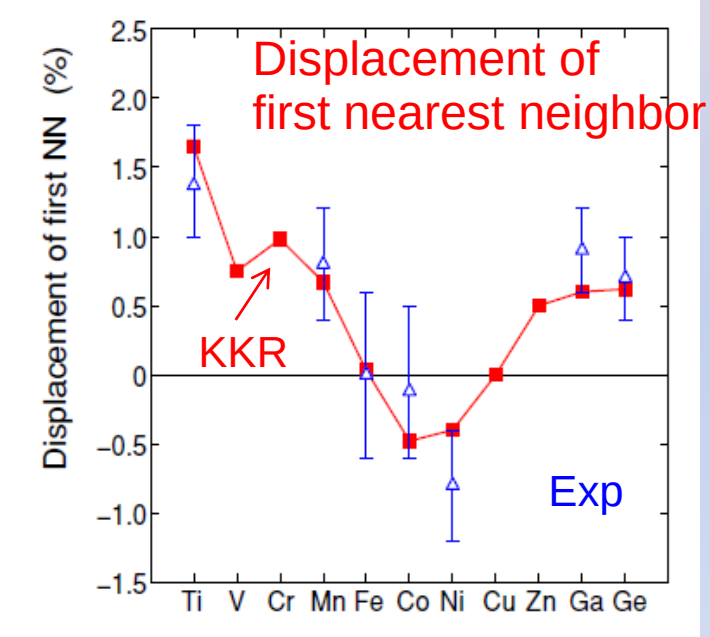
- Separation of the structure part (position of the atoms) and the scattering (chemical identity of atoms) part.

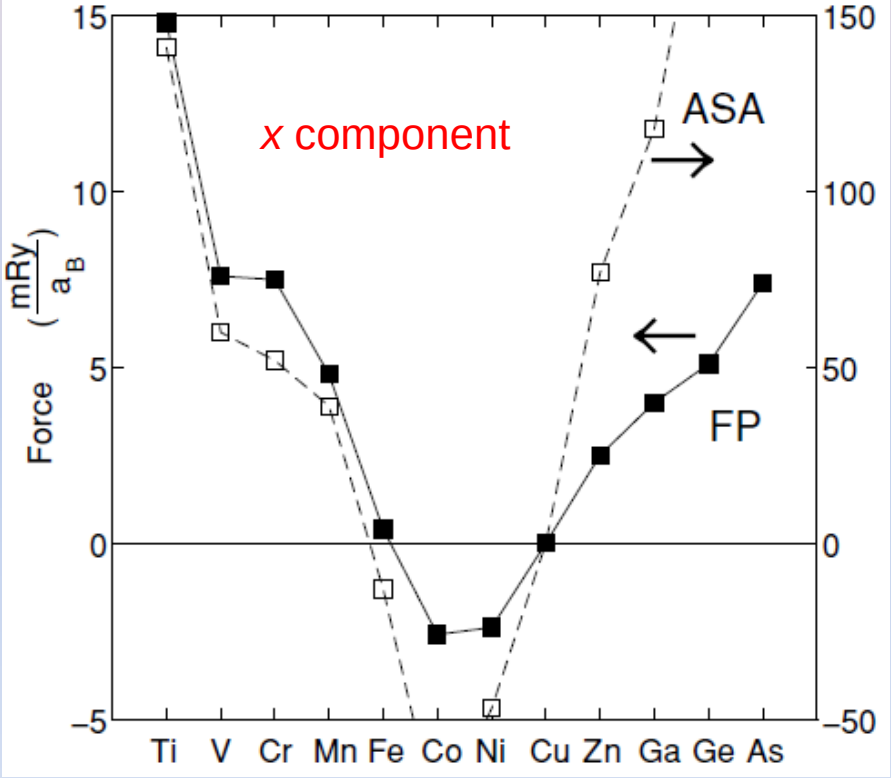
- Fast convergence with respect to angular momentum truncation (does not rely on a finite basis set for the expansion of the wave functions).

- Accurate: variational principle based on integral equations.

- Natural for low-symmetry systems (defects, surfaces, clusters, etc.) and disorder systems (alloys)

Extension from muffin-tin potential to full potential





Impurity in Cu host

Papanikolaou, Zeller, Dederichs, J. Phys. Condens Matter (2002)

Turning the KKR method into a orbital formalism

$$\chi_L(E,\boldsymbol{r}) = i^l Y_L(\hat{\boldsymbol{r}}) \begin{cases} \psi_l(E,r), & r \le R_{\mathrm{MT}} \\ C_l\left[j_l(\kappa r) - \tan\left(\eta_l(E)\right) n_l(kr)\right], & r > R_{\mathrm{MT}}, E > 0 \\ C_l\left[j_l(\kappa r) - \tan\left(\eta_l(E)\right) h_l^{(1)}(kr)\right], & r > R_{\mathrm{MT}}, E < 0 \end{cases}$$

$h_l^{(1)}(\kappa r) = j_l(\kappa r) + i n_l(\kappa r)$: Hankel functions.

Not a good basis, as $\chi_L(E,\boldsymbol{r})$ is not normalizable for $E < 0$

O.K. Andersen proposed the Muffin-tin orbitals (MTO)

$$\chi_L^{\mathrm{MTO}}(E,\mathrm{k},\boldsymbol{r}) = i^l Y_L(\hat{\boldsymbol{r}}) \begin{cases} \psi_l(E,r) + \kappa \cot\left(\eta_l(E)\right) j_l(kr), & r \le R_{\mathrm{MT}} \\ \kappa n_l(kr), & r > R_{\mathrm{MT}} \end{cases}$$

regular both at $r = 0$ and $r = \infty$, and normalizable for $E < 0$.

Now κ is an parameter independent of E.

The expansion theorem:

$$n_L(k, r - \boldsymbol{R}) = 4\pi \sum_{L'L''} C^L_{L'L''} n^*_{L''}(k, \boldsymbol{R} - \boldsymbol{R}') j_{L'}(k, r - \boldsymbol{R}')$$

The linearized MTO (LMTO) basis

Fixed reference energy

$$\chi_L^{\mathrm{LMTO}}(E_v, \mathrm{k}, r) = i^l Y_L(\hat{\boldsymbol{r}}) \begin{cases} \psi_l(E_v, r) + \kappa \cot\big(\eta_l(E_v)\big) J_l(kr), & r \le R_{\mathrm{MT}} \\ kN_l(kr), & r > R_{\mathrm{MT}} \end{cases}$$

Energy derivative of $\psi_l(E, r)$

$$J_l(kr) = -\frac{\dot{\psi}_l(E_v, r)}{k\frac{d}{E}\cot\big(\eta_l(E_v)\big)}, \; r \le R_{\mathrm{MT}}$$

$$N_L(k, \boldsymbol{r} - \boldsymbol{R}) = \begin{cases} n_l(kr), & \boldsymbol{r} \in I \\ 4\pi \sum_{L'L''} C^L_{L'L''} n^*_{L''}(k, \boldsymbol{R} - \boldsymbol{R}') J_{L'}(k, r - \boldsymbol{R}'), & |\boldsymbol{r} - \boldsymbol{R}'| \le R_{\mathrm{MT}}, \;\; \boldsymbol{R} \ne \boldsymbol{R}' \end{cases}$$

LMTO is a *minimal* basis, but can be quite accurate for closed packed structures.

A brief history overview

1937: Augmented plane waves

1940: Orthogonalized plane waves

1947, 1953: KKR (Korringa, Kohn, Rostoker)

1959: PKA (Phillips, Kleinman, Antoncik)

1975: The LAPW and LMTO methods

1979: Norm-conserving Pseudopotential

1990: Untrasoft Pseudopotential

1994: Projector augmented waves