

# Linearized Augmented Plane Wave Method: (b)

As we know that the problem with APW method was that  $U_{\ell}^{\alpha}(\vec{r}, E)$  have to be constructed at the yet unknown - eigen-energy  $E = \epsilon_{\vec{k}}$ . If one could set  $E$  to a fixed parameter  $E_0$  - known quantity - then method called LAPW and basis radial function can be  $U_{\ell}^{\alpha}(\vec{r}, E_0)$ . can be modified - solve the matching problem at the muffin-tin boundary.

If we have calculated  $U_{\ell}^{\alpha}$  at some energy  $E_0$ , we could make Taylor expansion to find it at energies not far away from it:

$$U_{\ell}^{\alpha}(\vec{r}, \epsilon_{\vec{k}}^n) = U_{\ell}^{\alpha}(\vec{r}, E_0) + (E_0 - \epsilon_{\vec{k}}^n) \left. \frac{\partial U_{\ell}^{\alpha}(\vec{r}, E)}{\partial E} \right|_{E=E_0} + O(E_0 - \epsilon_{\vec{k}}^n)^2$$

Substituting the first two terms of the expansion in the APW for a fixed  $E_0$  gives the definition of an LAPW.

The energy difference  $(E_0 - E_{\vec{k}}^n)$  is yet unknown. Hence the basis functions inside the muffin-tin sphere are linear combinations of the already known radial functions  $U_l^\alpha(\bar{r}, E_0)$  and their energy derivatives  $U_l^{\alpha'}(\bar{r}, E_0)$  at the same energy  $E_0$ .

Within the LAPW method, the corresponding complete basis functions are defined as

$$\phi_{\vec{k}, \vec{G}}^{\vec{k}}(\bar{r}, E) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\vec{k} + \vec{G}) \cdot \bar{r}} & \bar{r} \in I \\ \sum_{l, m} \left( A_{lm}^{\alpha, \vec{k} + \vec{G}} U_l^\alpha(r, E_0) + B_{lm}^{\alpha, \vec{k} + \vec{G}} U_l^{\alpha'}(r, E_0) \right) & \bar{r} \in S_\alpha \end{cases} Y_m^l(\bar{r})$$

the

In order to determine both  $A_{\alpha, \bar{k}+\bar{G}}^{lm}$  and  $B_{\alpha, \bar{k}+\bar{G}}^{lm}$ , one will require that the function in the sphere matches the plane wave both in value and in slope at the sphere boundary. (5)

Above equation is not final definition of an LAPW yet. Let one want to describe an eigenstate  $\psi_{\bar{k}}^n$  that has predominantly p-character ( $l=1$ ) for atom  $\alpha$ . This means that in its expansion in LAPW's, the  $A_{\alpha, \bar{k}+\bar{G}}^{(l=1)m}$  are large. It is therefore advantageous to choose  $E_0$  near the centre of p-band. In this way the  $\mathcal{O}(E_0 - \epsilon_{\bar{k}}^n)^2$ -term will remain small, and cutting after the linear term is certainly allowed. This argument can be repeated for every physically important orbital angular momentum  $l$  (s-, p-, d-, and f-states, ...) and

for every atom. The drawback is, ~~one~~ one should not choose one universal  $E_0$ , but a set of well chosen  $E_{l,l}^\alpha$  up to  $l=3$ . Then the final definition of an LAPW is.

$$\Phi_{\vec{k}, \vec{G}}^{\vec{k}}(\vec{r}, E) = \left\{ \begin{array}{l} \frac{1}{\sqrt{\Omega}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \quad \vec{r} \in I \\ \sum_{l,m} \left( A_{lm}^{\alpha, \vec{k} + \vec{G}} U_l^\alpha(r, E_{l,l}^\alpha) + B_{lm}^{\alpha, \vec{k} + \vec{G}} \cdot \right. \\ \left. U_l^\alpha(r, E_{l,l}^\alpha) \right) \cdot Y_{lm}^l(\vec{r}) \quad \vec{r} \in S_\alpha \end{array} \right.$$

with the  $E_{l,l}^\alpha$  being fixed, the basis functions can be calculated once and for all.

## LAPW with Local Orbitals (LAPW+LO) ⑥

In the LAPW method, it was not clearly (explicitly) stated that which  $\bar{\epsilon}$ -states are going to be calculated.

For instance; can one calculate 1s orbital of Fe atom in bcc-Fe. — Answer. — No.

Because this  $\bar{\epsilon}$  is extremely well bound to the nucleus ( $-514 R_y$ ) —  $-6793.33 \text{ eV}$ .

This will act almost exactly — like ~~it~~ as if it were in a free Fe atom. Such a state is called a "core state", which ~~will~~ does not participate directly in chemical bonding with other atoms. Therefore, it must be contained entirely in the muffin-tin sphere. States that leak out of the muffin-tin sphere are called "valence states". Valence states participate in the chemical bonding, and these states are treated by LAPW. Core states are treated as in free atoms, but subject to the potential.

It frequently happens that states with the same " $l$ " but a different principal quantum number " $n$ " are both valence states. For instat, due to hybridization in bcc-Fe, the Fe have a non-negligible amount of 4p-character in its valence states that are about -0.2 Ry below the Fermi level. But 3p-states are around -4.2 Ry below the Fermi-level are not entirely confined in the core states too. Such low-lying valence states are called "semi-core states".

It is also not clear how  $E_{l,(l-1)}^{Fe}$  should be chosen: i.e. close to 3p, 4p — None of the choices is optimal (exclted). This problem is solved by adding an-other type of basis function to the LAPW basis set, called a local Orbital (LO), which is defined as,

$$\phi_{\alpha, LO}^{lm}(\vec{r}) = \begin{cases} 0 & \vec{r} \notin \Omega \\ \left[ A_{lm}^{\alpha, LO} U_l^{\alpha}(\vec{r}, E_{l,p}^{\alpha}) + B_{lm}^{\alpha, LO} U_l^{\alpha}(\vec{r}, E_{l,p}^{\alpha}) + C_{lm}^{\alpha, LO} U_l^{\alpha}(\vec{r}, E_{2,l}^{\alpha}) \right] Y_l^m(\vec{r}) & \vec{r} \in \Omega \end{cases}$$