

Augmented Plane Wave Method: (APW)

APW method is one of the most accurate - used to calculate the electronic structure of the materials.

The APW method was introduced by J. C. Slater - Phys. Rev. 51, 834 (1937)

It was constructed in a way that \bar{e} s are more or less free away from nucleus - which leads to pseudo-potential method. Plane waves are used to describe the propagation of free \bar{e} s - Basically plane waves are eigenfunction of a Hamiltonian with zero potential, $V=0$.

$$\psi(r, t) = A e^{i(\underline{k} \cdot \underline{r} - \omega t)}$$

Hence, in this method volume of the unit cell is divided into two regions

Close to the nuclei, e^- s behave as if they were in a free atom and therefore can be describe by atomic like wavefns.

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \cdot Y_{lm}(\theta, \phi)$$

$$R_{nl}(r) \text{ — Radial wavefns.} = \frac{U_{nl}(r)}{r}$$

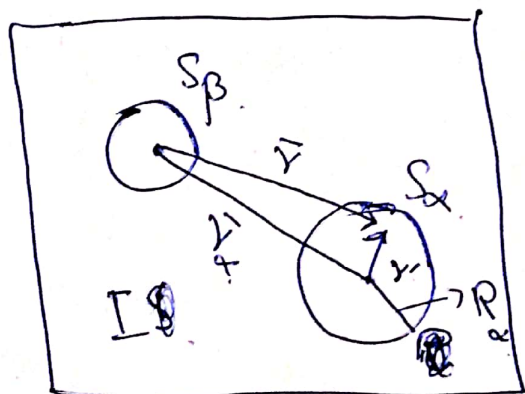
$$Y_{lm}(\theta, \phi) \text{ — Spherical Harmonics.}$$

$$= C_{lm} P_{lm}(\cos\theta) e^{im\phi}$$

$$= C_{lm} (1-g^2) \frac{d^m}{dg^m} P_l(g) e^{im\phi}$$

$$\Rightarrow g = \cos\theta, m = -l, \dots, +l$$

Hence, the volume of the unit cell is divided into two regions, see fig. below



A sphere with R_α radius (say it S_α) - called muffin-tin sphere, while the area outside the sphere is called the Interstitial region. (say it I). Potential of interstitial region is considered almost constant and in muffin-tin sphere it is spherically symmetric.

Within the APW method, the corresponding basis functions are defined as:

$$\phi_{\vec{k}}^{\vec{G}}(\vec{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} & \vec{r} \in I - \text{Plane wave (Interstitial region)} \\ \sum_{l,m} A_{lm}^\alpha(\vec{k} + \vec{G}) U_l^\alpha(\vec{r}, E) Y_{lm}(\theta, \phi) & \vec{r} \leq \bar{R}_\alpha \text{ (muffin-tin region)} \end{cases}$$

$\phi_{\vec{k}}^{\vec{G}}(S_\alpha + \vec{r}_\alpha)$

Here, Ω is the volume of unit cell, \vec{G} is the reciprocal lattice vector, S_α denotes the position vector of the atomic nucleus α and the radius of the corresponding muffin-tin sphere is $R_{MT} = R_\alpha$

The $U_l^\alpha(\bar{r}, E)$ is the radial function which is the regular solution of the radial part of the S.W.E.

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2m r^2} + V^\alpha(r) - E \right] r U_l^\alpha(\bar{r}, E) = 0.$$

with $V^\alpha(r)$ being the radial symmetric part of the potential in the atomic sphere, provided that $U_l^\alpha(\bar{r}, E)$ is the solution of that equation with energy eigenvalue of E . $Y_{lm}(\theta, \phi)$ are the spherical harmonics.

The co-efficient $A_{lm}^\alpha(\bar{K} + \bar{G})$ is determined for each atom by imposing the requirements that the values of the plane wave $(e^{i(\bar{K} + \bar{G}) \cdot \mathbf{r}})$ and the atomic-like orbital like wave function $(\psi_{lm}^\alpha(S_{\alpha} + \mathbf{r}))$ have to match each other on the sphere boundary.

It depends on E , which is a (3)
variational parameter in this scheme. Hence,
the APWs defined in muffin-tin region
are not simply a basis set, but gives
rise to several complications, such as,
most important, E has to be set equal to
the band energy. This requirement
makes the basis functions energy
dependent. Thus the solution of
the equation does not correspond
to a linear eigenvalue problem.

The main advantage of the APW
method is that it's ^{true} all electron method,
which means in principle, any core or
valence states can be expanded into
APWs i.e. for a given ^{all} values of l -
orbital angular momentum occupied and
un-occupied states (with different principle quantum
numbers) can be derived.

Although, in practice, the calculation of core and valence states is separated. As the former ones are confined within the atomic spheres, it allows for the reliable treatment of conduction bands, which is an important issue when optical properties are computed.

The main drawback of the APW method is wavefn. discontinuity at the boundary of muffin-tin sphere.

The other most disadvantages of APW method is the energy-dependence of the basis set — $U_l^a(\vec{r}, E)$.

⇒ Asymptotic Problem: Can not match energies where $U_l(r)$ is zero on the sphere boundary. This will in general happen at some energy states. Particular problem for 'd' and 'f' band materials.