1 Orthogonalized plane-wave method

Core states → localized orbitals

$$\phi_\alpha(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_m e^{i\mathbf{k}\mathbf{R}_m} w_\alpha(\mathbf{r}-\mathbf{R}_m) \tag{1}$$

$$\alpha = (n_c, \ell_c, m_c)$$

$$\int d^3r\, w_\alpha(\mathbf{r}-\mathbf{R}_m)^* \, w_{\alpha'}(\mathbf{r}-\mathbf{R}_n) = \delta_{nm}\delta_{\alpha\alpha'} \tag{2}$$

$$H|w_\alpha\rangle = \varepsilon_\alpha |w_\alpha\rangle \tag{3}$$

$$\Downarrow$$

$$\int d^3r\, \phi_\alpha(\mathbf{k},\mathbf{r})^* \, \phi_{\alpha'}(\mathbf{k}',\mathbf{r}) = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\alpha\alpha'} \tag{4}$$

$$H|\phi_\alpha(\mathbf{k})\rangle = \varepsilon_\alpha |\phi_\alpha(\mathbf{k})\rangle \tag{5}$$

Basis functions:

$$\underline{\phi_j(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G}_j)\mathbf{r}} - \sum_\alpha \mu_\alpha(\mathbf{k}+\mathbf{G}_j)\,\phi_\alpha(\mathbf{k},\mathbf{r})} \tag{6}$$

Condition (Gram-Schmidt type orthogonalization):

$$\langle\phi_j(\mathbf{k})|\phi_\alpha(\mathbf{k})\rangle = 0 \tag{7}$$

$$\Downarrow$$

$$\underline{\mu_\alpha(\mathbf{k}+\mathbf{G}_j)} = \frac{1}{\sqrt{V}}\int d^3r\, \phi_\alpha^*(\mathbf{k},\mathbf{r})\, e^{i(\mathbf{k}+\mathbf{G}_j)\mathbf{r}} \tag{8}$$

$$= \frac{1}{\sqrt{NV}}\sum_m \int d^3r\, w_\alpha^*(\mathbf{r}-\mathbf{R}_m)\, e^{i(\mathbf{k}+\mathbf{G}_j)(\mathbf{r}-\mathbf{R}_m)} \tag{9}$$

$$\underline{= \frac{1}{\sqrt{V_0}}\int d^3r\, w_\alpha^*(\mathbf{r})\, e^{i(\mathbf{k}+\mathbf{G}_j)\mathbf{r}}} \tag{10}$$

$$\Downarrow$$

$$\phi_j(\mathbf{k},\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G}_j)\mathbf{r}} - \sum_\alpha \phi_\alpha(\mathbf{k},\mathbf{r})\, \frac{1}{\sqrt{V}}\int d^3r\, \phi_\alpha^*(\mathbf{k},\mathbf{r})\, e^{i(\mathbf{k}+\mathbf{G}_j)\mathbf{r}} \tag{11}$$

By introducing the projector,

$$P = \sum_\alpha |\phi_\alpha(\mathbf{k})\rangle\langle\phi_\alpha(\mathbf{k})| \tag{12}$$

$$|\phi_j(\mathbf{k})\rangle = (1-P)\,|\mathbf{k}+\mathbf{G}_j\rangle \tag{13}$$

where

$$\langle\mathbf{r}|\mathbf{k}+\mathbf{G}_j\rangle = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G}_j)\mathbf{r}}\,. \tag{14}$$

Ansatz for eigenfunctions:

$$|\psi_n(\mathbf{k})\rangle = \sum_j |\phi_j(\mathbf{k})\rangle\, c_{jn}(\mathbf{k}) \tag{15}$$

$$H|\psi_n(\mathbf{k})\rangle = \varepsilon_{\mathbf{k}n}|\psi_n(\mathbf{k})\rangle \tag{16}$$

$$\sum_j \left(\langle\phi_i(\mathbf{k})|\,H\,|\phi_j(\mathbf{k})\rangle - \delta_{ij}\varepsilon_{\mathbf{k}n}\right) c_{jn}(\mathbf{k}) = 0 \tag{17}$$

Secular equation:

$$\boxed{\det\left(\underline{H}\left(\mathbf{k}\right)-\varepsilon_n\mathbf{k}\underline{I}\right)=0} \tag{18}$$

$$\phi_j\left(\mathbf{k},\mathbf{r}\right)=\frac{1}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{G}_j)\mathbf{r}}-\sum_\alpha\mu_\alpha\left(\mathbf{k}+\mathbf{G}_j\right)\phi_\alpha\left(\mathbf{k},\mathbf{r}\right) \tag{19}$$

$$\begin{aligned}\left\langle\phi_i\left(\mathbf{k}\right)\right|H\left|\phi_j\left(\mathbf{k}\right)\right\rangle &= \left\langle\mathbf{k}+\mathbf{G}_i\right|H\left|\mathbf{k}+\mathbf{G}_j\right\rangle+\sum_{\alpha,\alpha'}\mu^*_\alpha\left(\mathbf{k}+\mathbf{G}_i\right)\mu_{\alpha'}\left(\mathbf{k}+\mathbf{G}_j\right)\left\langle\phi_\alpha\left(\mathbf{k}\right)\right|H\left|\phi_{\alpha'}\left(\mathbf{k}\right)\right\rangle \\ &-\sum_\alpha\left(\mu^*_\alpha\left(\mathbf{k}+\mathbf{G}_i\right)\left\langle\phi_\alpha\left(\mathbf{k}\right)\right|H\left|\mathbf{k}+\mathbf{G}_j\right\rangle+\mu_\alpha\left(\mathbf{k}+\mathbf{G}_j\right)\left\langle\mathbf{k}+\mathbf{G}_i\right|H\left|\phi_\alpha\left(\mathbf{k}\right)\right\rangle\right)\end{aligned} \tag{20}$$

$$\left\langle\mathbf{k}+\mathbf{G}_i\right|H\left|\mathbf{k}+\mathbf{G}_j\right\rangle=\frac{\hbar^2}{2m}\left(\mathbf{k}+\mathbf{G}_i\right)^2\delta_{ij}+V_{ij} \tag{21}$$

$$\left\langle\phi_\alpha\left(\mathbf{k}\right)\right|H\left|\phi_{\alpha'}\left(\mathbf{k}\right)\right\rangle=\varepsilon_\alpha\delta_{\alpha\alpha'} \tag{22}$$

$$\left\langle\mathbf{k}+\mathbf{G}_i\right|H\left|\phi_\alpha\left(\mathbf{k}\right)\right\rangle=\varepsilon_\alpha\left\langle\mathbf{k}+\mathbf{G}_i|\phi_\alpha\left(\mathbf{k}\right)\right\rangle=\varepsilon_\alpha\mu^*_\alpha\left(\mathbf{k}+\mathbf{G}_i\right) \tag{23}$$

$$\Downarrow$$

$$\begin{aligned}\underline{\left\langle\phi_i\left(\mathbf{k}\right)\right|H\left|\phi_j\left(\mathbf{k}\right)\right\rangle} &= \frac{\hbar^2}{2m}\left(\mathbf{k}+\mathbf{G}_i\right)^2\delta_{ij}+V_{ij}+\sum_\alpha\varepsilon_\alpha\mu^*_\alpha\left(\mathbf{k}+\mathbf{G}_i\right)\mu_\alpha\left(\mathbf{k}+\mathbf{G}_j\right) \\ &-\sum_\alpha\varepsilon_\alpha\mu^*_\alpha\left(\mathbf{k}+\mathbf{G}_i\right)\mu_\alpha\left(\mathbf{k}+\mathbf{G}_j\right)-\sum_\alpha\varepsilon_\alpha\mu^*_\alpha\left(\mathbf{k}+\mathbf{G}_j\right)\mu_\alpha\left(\mathbf{k}+\mathbf{G}_i\right) \\ &\underline{=\frac{\hbar^2}{2m}\left(\mathbf{k}+\mathbf{G}_i\right)^2\delta_{ij}+\Gamma_{ij}}\end{aligned} \tag{24}$$

$$\underline{\Gamma_{ij}=V_{ij}-\sum_\alpha\varepsilon_\alpha\mu^*_\alpha\left(\mathbf{k}+\mathbf{G}_j\right)\mu_\alpha\left(\mathbf{k}+\mathbf{G}_i\right)} \tag{25}$$

2 Pseudopotentials

Similar to the OPW method, let us introduce the Bloch functions of the core-states, $\phi_\alpha\left(\mathbf{k},\mathbf{r}\right)$, and additional Bloch functions (not plane-waves), $\widetilde{\phi}_j\left(\mathbf{k},\mathbf{r}\right)$, such that the basis functions,

$$\underline{\phi_j\left(\mathbf{k},\mathbf{r}\right)=\widetilde{\phi}_j\left(\mathbf{k},\mathbf{r}\right)-\sum_\alpha\mu_{\alpha j}\left(\mathbf{k}\right)\phi_\alpha\left(\mathbf{k},\mathbf{r}\right)} \tag{26}$$

are required to be orthogonal to $\phi_\alpha\left(\mathbf{k},\mathbf{r}\right)$. This implies,

$$\mu_{\alpha j}\left(\mathbf{k}\right)=\int d^3r\,\phi^*_\alpha\left(\mathbf{k},\mathbf{r}\right)\widetilde{\phi}_j\left(\mathbf{k},\mathbf{r}\right) \tag{27}$$

$$=\frac{1}{\sqrt{N}}\int d^3r\,w^*_\alpha\left(\mathbf{r}\right)\widetilde{\phi}_j\left(\mathbf{k},\mathbf{r}\right)\ . \tag{28}$$

The eigenfunctions of the Hamiltonian are expanded with respect to $\phi_j\left(\mathbf{k},\mathbf{r}\right)$,

$$\left|\psi_n\left(\mathbf{k}\right)\right\rangle=\sum_j\left|\phi_j\left(\mathbf{k}\right)\right\rangle c_{jn}\left(\mathbf{k}\right) \tag{29}$$

$$=\sum_j\left[\left|\widetilde{\phi}_j\left(\mathbf{k}\right)\right\rangle-\sum_\alpha\mu_{\alpha j}\left(\mathbf{k}\right)\left|\phi_\alpha\left(\mathbf{k}\right)\right\rangle\right]c_{jn}\left(\mathbf{k}\right) \tag{30}$$

$$H\left|\psi_n\left(\mathbf{k}\right)\right\rangle=\varepsilon_{\mathbf{k}n}\left|\psi_n\left(\mathbf{k}\right)\right\rangle \tag{31}$$

We obtain the following equation,

$$H \sum_j \left| \widetilde{\phi}_j(\mathbf{k}) \right\rangle c_{jn}(\mathbf{k}) + \sum_j \sum_\alpha \left(\varepsilon_{\mathbf{k}n} - \varepsilon_{\mathbf{k}\alpha} \right) \mu_{\alpha j}(\mathbf{k}) \left| \phi_\alpha(\mathbf{k}) \right\rangle c_{jn}(\mathbf{k})$$
$$= \varepsilon_{\mathbf{k}n} \sum_j \left| \widetilde{\phi}_j(\mathbf{k}) \right\rangle c_{jn}(\mathbf{k}) \ . \tag{32}$$

By introducing the *pseudo-wavefunction*,

$$\underline{\left| \widetilde{\psi}_n(\mathbf{k}) \right\rangle = \sum_j \left| \widetilde{\phi}_j(\mathbf{k}) \right\rangle c_{jn}(\mathbf{k}) \ ,} \tag{33}$$

we get

$$\underline{H \left| \widetilde{\psi}_n(\mathbf{k}) \right\rangle + W \left| \widetilde{\psi}_n(\mathbf{k}) \right\rangle = \varepsilon_{\mathbf{k}n} \left| \widetilde{\psi}_n(\mathbf{k}) \right\rangle} \tag{34}$$

where W is a non-local *pseudopontential*,

$$W = \sum_\alpha \left(\varepsilon_{\mathbf{k}n} - \varepsilon_{\mathbf{k}\alpha} \right) \left| \phi_\alpha(\mathbf{k}) \right\rangle \left\langle \phi_\alpha(\mathbf{k}) \right| \tag{35}$$

or

$$\underline{W(\mathbf{r}, \mathbf{r}') = \sum_\alpha \left(\varepsilon_{\mathbf{k}n} - \varepsilon_{\mathbf{k}\alpha} \right) \phi_\alpha^*(\mathbf{k}, \mathbf{r}') \, \phi_\alpha(\mathbf{k}, \mathbf{r})} \tag{36}$$

and

$$\left\langle \mathbf{r} \right| W \left| \widetilde{\psi}_n(\mathbf{k}) \right\rangle = \int d^3 r' W(\mathbf{r}, \mathbf{r}') \, \widetilde{\psi}_n(\mathbf{k}, \mathbf{r}') \ . \tag{37}$$

Let us look at the local part of W,

$$W(\mathbf{r}, \mathbf{r}) = \sum_\alpha \left(\varepsilon_{\mathbf{k}n} - \varepsilon_{\mathbf{k}\alpha} \right) \left| \phi_\alpha(\mathbf{k}, \mathbf{r}) \right|^2 \ . \tag{38}$$

This is always (strongly) positive, since $\varepsilon_{\mathbf{k}n} \gg \varepsilon_{\mathbf{k}\alpha}$. Adding this to the Coulomb potential of the positively charged ion causes screening which can be approximated, e.g., by

$$V'(\mathbf{r}) = \begin{cases} const. & r < r_0 \\ A \frac{e^{-\kappa r}}{r} & r > r_0 \end{cases} \tag{39}$$

with suitably chosen parameters, A, $\varkappa$ and r_0.

3 Augmented plane-waves (APW)

Muffin-tin potential

$$V_c(\mathbf{r}) = \begin{cases} v_a(r) & r \leq r_{MT} \\ \sim const. & r > r_{MT} \end{cases} \tag{40}$$

The wafunction inside the muffin-tin ($r \leq r_{MT}$),

$$\phi(\mathbf{r}) = \sum_{\ell, m} C_{\ell m} R_\ell(r) \, Y_\ell^m(\vartheta, \varphi) \tag{41}$$

$$\left[-\frac{\hbar^2}{2m} \left(\partial_r^2 + \frac{2}{r} \partial_r \right) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} + v_a(r) - \varepsilon \right] R_\ell(r) = 0 \ . \tag{42}$$

Out of the muffin-tin ($r > r_{MT}$):

$$\phi_i(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k} + \mathbf{G}_i)\mathbf{r}} \tag{43}$$

Continuity at $r = r_{MT}$ implies,

$$\begin{aligned}\frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G}_i)\mathbf{r}} &= \frac{4\pi}{\sqrt{V}} \sum_{\ell,m} i^\ell \, j_\ell\left(\left|\mathbf{k}+\mathbf{G}_i\right| r\right) Y_\ell^m\left(\vartheta_k,\varphi_k\right)^* Y_\ell^m\left(\vartheta,\varphi\right) \\ &= \sum_{\ell,m} C_{\ell m}\left(\mathbf{k}+\mathbf{G}_i\right) R_\ell\left(r\right) Y_\ell^m\left(\vartheta,\varphi\right)\end{aligned}$$

with j_ℓ and Y_ℓ^m being the spherical Bessel functions and complex spherical harmonics, (ϑ_k, φ_k) and (ϑ, φ) are the azimuthal and polar angles of the vectors $\mathbf{k}$ and $\mathbf{r}$, respectively. From the above equation,

$$C_{\ell m}\left(\mathbf{k}+\mathbf{G}_i\right) = \frac{4\pi}{\sqrt{V}} i^\ell Y_\ell^m\left(\vartheta_k,\varphi_k\right)^* \frac{j_\ell\left(\left|\mathbf{k}+\mathbf{G}_i\right| r\right)}{R_\ell\left(r\right)} \, . \tag{44}$$

Note, however, that the derivative of these *augmented plane-waves* is not continuous at $r = r_{MT}$.

Ansatz for the eigenfunction:

$$\psi\left(\mathbf{k},\mathbf{r}\right) = \sum_j \phi_j\left(\mathbf{k},\mathbf{r}\right) c_j\left(\mathbf{k}\right) \tag{45}$$

Variational principle $\rightarrow c_j\left(\mathbf{k}\right)$

$$\min\left(\left\langle\psi\left(\mathbf{k}\right)\right| H \left|\psi\left(\mathbf{k}\right)\right\rangle - \varepsilon \left\langle\psi\left(\mathbf{k}\right)|\psi\left(\mathbf{k}\right)\right\rangle\right) \tag{46}$$

The integral should be taken over a Wigner-Seitz cell:

$$\left\langle\psi\left(\mathbf{k}\right)\right| H - \varepsilon \left|\psi\left(\mathbf{k}\right)\right\rangle = -\frac{\hbar^2}{2m}\int_{WS} d^3r \, \psi^*\left(\mathbf{k},\mathbf{r}\right) \Delta\psi\left(\mathbf{k},\mathbf{r}\right) + \int_{WS} d^3r \psi^*\left(\mathbf{k},\mathbf{r}\right)\left(V\left(\mathbf{r}\right)-\varepsilon\right)\psi\left(\mathbf{k},\mathbf{r}\right) \tag{47}$$

$$\int_{WS} d^3r \, \psi^*\left(\mathbf{k},\mathbf{r}\right) \Delta\psi\left(\mathbf{k},\mathbf{r}\right) = \int_{WS} d^3r \, \nabla\left(\psi^*\left(\mathbf{k},\mathbf{r}\right)\nabla\psi\left(\mathbf{k},\mathbf{r}\right)\right) - \int_{WS} d^3r \, \left|\nabla\psi\left(\mathbf{k},\mathbf{r}\right)\right|^2 \tag{48}$$

$$\int_{WS} d^3r \, \nabla\left(\psi^*\left(\mathbf{k},\mathbf{r}\right)\nabla\psi\left(\mathbf{k},\mathbf{r}\right)\right) = \int_{\Gamma_{WS}} d\mathbf{S} \, \psi^*\left(\mathbf{k},\mathbf{r}\right)\nabla\psi\left(\mathbf{k},\mathbf{r}\right) = 0 \tag{49}$$

since

$$\psi^*\left(\mathbf{k},\mathbf{r}+\mathbf{R}_m\right) = e^{-i\mathbf{k}\mathbf{R}_m}\psi^*\left(\mathbf{k},\mathbf{r}\right) \tag{50}$$

$$\nabla\psi\left(\mathbf{k},\mathbf{r}+\mathbf{R}_m\right) = e^{i\mathbf{k}\mathbf{R}_m}\nabla\psi\left(\mathbf{k},\mathbf{r}\right) \tag{51}$$

while the normal vektor of the surface of the Wigner-Seitz cell at $\mathbf{r}+\mathbf{R}_m$ is just the opposite the one at $\mathbf{r}$. Therefore, we conclude that

$$\left\langle\psi\left(\mathbf{k}\right)\right| H - \varepsilon \left|\psi\left(\mathbf{k}\right)\right\rangle = \frac{\hbar^2}{2m}\int_{WS} d^3r \, \left|\nabla\psi\left(\mathbf{k},\mathbf{r}\right)\right|^2 + \int_{WS} d^3r \psi^*\left(\mathbf{k},\mathbf{r}\right)\left(V\left(\mathbf{r}\right)-\varepsilon\right)\psi\left(\mathbf{k},\mathbf{r}\right) \, . \tag{52}$$

The ansatz for $\psi\left(\mathbf{k},\mathbf{r}\right)$ can now be substituted into the above equation, from wich a quadratic expression of $c_j\left(\mathbf{k}\right)$ can be obtained. Variation upon $c_j^*\left(\mathbf{k}\right)$ results then in a matrix equation,

$$\left(\left[\frac{\hbar^2}{2m}\left(\mathbf{k}+\mathbf{G}_i\right)^2 - \varepsilon\right]\delta_{ij} + M_{ij}^{APW}\left(\varepsilon,\mathbf{k}\right)\right) c_j\left(\mathbf{k}\right) = 0 \, , \tag{53}$$

where

$$\begin{aligned} M_{ij}^{APW}\left(\mathbf{k}\right) = -\frac{4\pi r_{MT}^2}{V_0}\frac{\hbar^2}{2m}\Bigg\{&\left[\left(\mathbf{k}+\mathbf{G}_i\right)\left(\mathbf{k}+\mathbf{G}_j\right) - \frac{2m}{\hbar^2}\right]\frac{j_\ell\left(\left|\mathbf{G}_i-\mathbf{G}_j\right| r_{MT}\right)}{\left|\mathbf{G}_i-\mathbf{G}_j\right|} \\ &-\sum_\ell\left(2\ell+1\right)P_\ell\left(\cos\vartheta_{ij}\right) j_\ell\left(\left|\mathbf{k}+\mathbf{G}_i\right| r_{MT}\right) j_\ell\left(\left|\mathbf{k}+\mathbf{G}_j\right| r_{MT}\right) L_\ell\left(\varepsilon\right)\Bigg\} \, , \end{aligned} \tag{54}$$

with the Legendre functions P_ℓ, the azimuthal angle ϑ_{ij} of the vector $\mathbf{G}_i - \mathbf{G}_j$ and

$$L_\ell(\varepsilon) = \frac{dR'_\ell(\varepsilon, r_{MT})}{dr} / R_\ell(\varepsilon, r_{MT}) \; . \tag{55}$$

The eigenenergies are obtained by solving the secular equation,

$$\underline{\det\left(\left[\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G}_i)^2 - \varepsilon\right]\delta_{ij} + M_{ij}^{APW}(\varepsilon, \mathbf{k})\right) = 0} \tag{56}$$

Note that this is not an ordinary matrix eigenvalue problem, since $M_{ij}^{APW}(\varepsilon, \mathbf{k})$ depends on ε. Thus, an exact solution can be achieved by itaration. Nevertheless, $L_\ell(\varepsilon)$ can well be approximated by $L_\ell(\varepsilon_\ell) + A_\ell(\varepsilon - \varepsilon_\ell)$, where ε_ℓ is a conveniently chosen energy (resonance) in the valence band. Thus we obtain a linear method, called *Linearized APW (LAPW)* method.