Secular matrices up to now

PW method

$$M_{s,t}^{PW} = \left[\frac{\hbar^2}{2m}\mathbf{k}_t^2 - E_\mathbf{k}\right]\,\delta_{s,t} + V(\mathbf{K}_s - \mathbf{K}_t)$$

OPW method

$$M_{s,t}^{OPW} = \left[\frac{\hbar^2}{2m}\mathbf{k}_t^2 - E_\mathbf{k}\right]\,\delta_{s,t} + V(\mathbf{K}_s - \mathbf{K}_t) - \sum_{j(Core)} (E_j - E_\mathbf{k})\,\mu^*_{\mathbf{k}_s,j}\,\mu_{\mathbf{k}_t,j}$$

APW method

$$\begin{aligned} M_{s,t}^{APW} \;=\; & \left[\frac{\hbar^2}{2m}\mathbf{k}_t^2 - E_\mathbf{k}\right]\Omega_0\delta_{s,t} - \\ & -4\pi r_{\mathrm{MT}}^2 \left\{ \left[\frac{\hbar^2}{2m}\mathbf{k}_s\cdot\mathbf{k}_t - E_\mathbf{k}\right] \frac{j_1(|\mathbf{k}_s - \mathbf{k}_t| r_{\mathrm{MT}})}{|\mathbf{k}_s - \mathbf{k}_t|} - \right. \\ & -\frac{\hbar^2}{2m}\sum_{l=0}^{\infty}(2l+1)\,P_l(\cos\vartheta_{s,t})\,j_l(k_s\,r_{\mathrm{MT}})\,j_l(k_t\,r_{\mathrm{MT}}) \\ & \left. \times \left[\frac{d}{dr}R_l(r;E)/R_l(r;E)\right]_{r=r_{\mathrm{MT}}} \right\} . \end{aligned}$$

mit $\mathbf{k}_i = \mathbf{k} + \mathbf{K}_i$.

KKR method

$$M_{lm;l'm'} \propto \cot\eta_l\,\sqrt{E}\,\delta_{l,l'}\delta_{m,m'} + A_{lm;l'n'}(E)$$

Variational ansatz for the APW method:

$$E \int\limits_{i+a} d^3r\, u^*\, u \;=\; \int\limits_{i+a} d^3r\, u^*\, \hat{H}\, u + \frac{\hbar^2}{2m}\frac{1}{2}\int\limits_{(S)} d\mathbf{s}\cdot\left[\nabla u_a^* + \nabla u_i^*\right](u_a - u_i) - \frac{\hbar^2}{2m}\frac{1}{2}\int\limits_{(S)} d\mathbf{s}\cdot\left[\nabla u_a - \nabla u_i\right](u_a^* + u_i^*)\,. \tag{1}$$

Taking under account that

$$\hat{H}u_t = E_t u_t \quad u_i = u_t + \delta u_i \quad u_a = u_t + \delta u_a$$

and

$$E = E_t + \delta E$$

one obtaines Eq. (15.5):

$$\delta E \int\limits_{i+a} d^3r\, u_t^* u_t = \int\limits_{i} d^3r\, u_t^* \hat{H}\delta u_i + \int\limits_{a} d^3r\, u_t^* \hat{H}\delta u_a + \frac{\hbar^2}{2m}\int_S d\mathbf{s}\cdot\left[u_t^*\nabla(\delta u_i) - \delta u_i \nabla u_t^*\right] - E_t\int_i d^3r\,\delta u_i\, u_t^* - \frac{\hbar^2}{2m}\int_S d\mathbf{s}\cdot\left[u_t^*\nabla(\delta u_a) - \delta u_a \nabla u_t^*\right] - E_t\int_a d^3r\,\delta u_i\, u_t^*\,.$$

The integrals that include the Hamiltonian $\hat{H}$ are reformulated by using the integral rule of Gauss:

$$\int\limits_V d^3r\; \nabla f(\mathbf{r}) = \int\limits_S d\mathbf{s}\, f(\mathbf{r}) \qquad :$$

One has

$$u_t^\star \hat{H} \delta u_i = -\frac{\hbar^2}{2m} u_t^\star \nabla^2 \delta u_i + u_t^\star V(\mathbf{r}) \delta u_i.$$

Using the identity

$$u_t^\star \nabla^2 \delta u_i \equiv \nabla(u_t^\star \nabla \delta u_i) - \nabla(\delta u_i \nabla u_t^\star) + (\delta u_i \nabla^2 u_t^\star)$$

one gets

$$u_t^\star \hat{H} \delta u_i = -\frac{\hbar^2}{2m} \nabla \left[u_t^\star \nabla \delta u_i - \delta u_i \nabla u_t^\star \right] + \delta u_i \hat{H} u_t^\star \,,$$

resulting to

$$\int\limits_i d^3 r\, u_t^* \hat{H} \delta u_i - \int\limits_i d^3 r\, \delta u_i \hat{H} u_t^* = -\frac{\hbar^2}{2m} \int\limits_S d\mathbf{s} \cdot [u_t^* \nabla \delta u - \delta u_i \nabla u_t^*] \neq 0 \,.$$

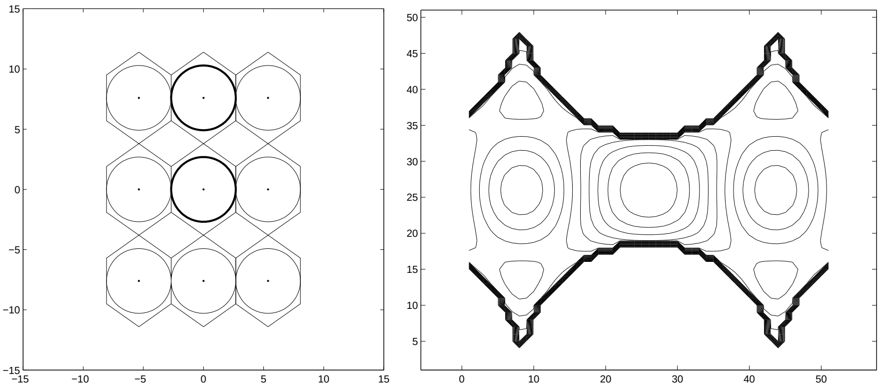
An equivalent treatment can be performed for the term $u_t^\star \hat{H} \delta u_a$:

$$\begin{aligned} \int\limits_i d^3 r\, u_t^\star \hat{H} \delta u_i &= -\frac{\hbar^2}{2m} \int\limits_S \mathrm{d}\mathbf{s} \cdot [u_t^\star \nabla \delta u_i - \delta u_i \nabla u_t^\star] + E_t \int\limits_i d^3 r\, \delta u_i u_t^\star \\ \int\limits_a d^3 r\, u_t^\star \hat{H} \delta u_a &= +\frac{\hbar^2}{2m} \int\limits_S \mathrm{d}\mathbf{s} \cdot [u_t^\star \nabla \delta u_a - \delta u_a \nabla u_t^\star] + E_t \int\limits_a d^3 r\, \delta u_a u_t^\star \end{aligned} \tag{2}$$

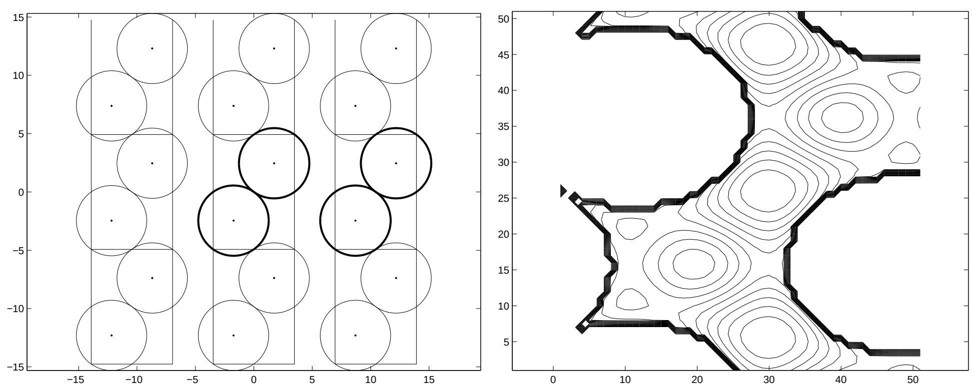
If these expressions are inserted into Eq. (15.5), one immediately obtains the *condition of stationarity*

$$\delta E \int d^3 r\, u_t^* u_t = 0 \,.$$

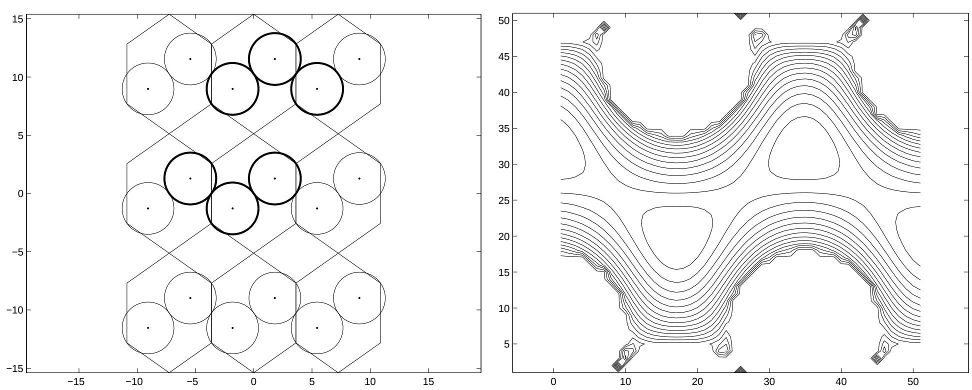
How good is the muffin-tin approximation?



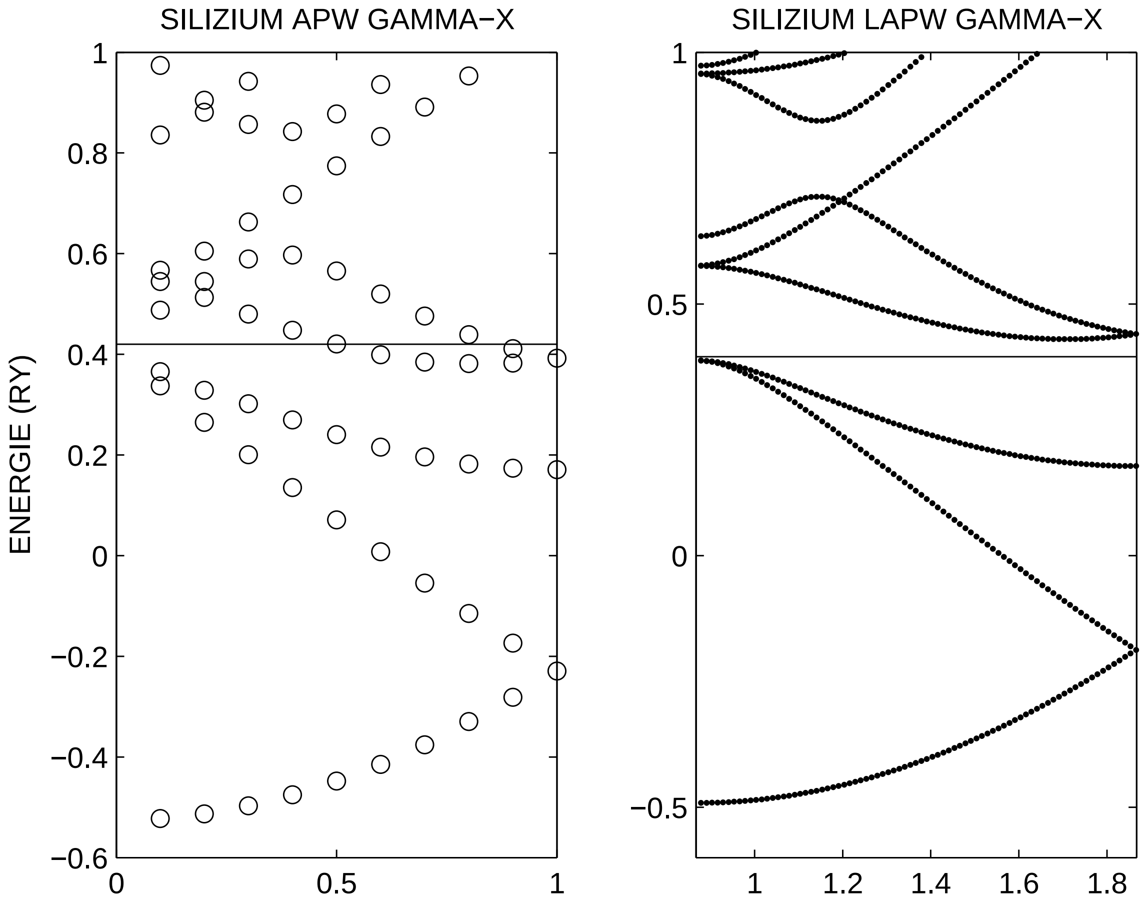
Structure of atomic spheres and interstitial region
for fcc copper



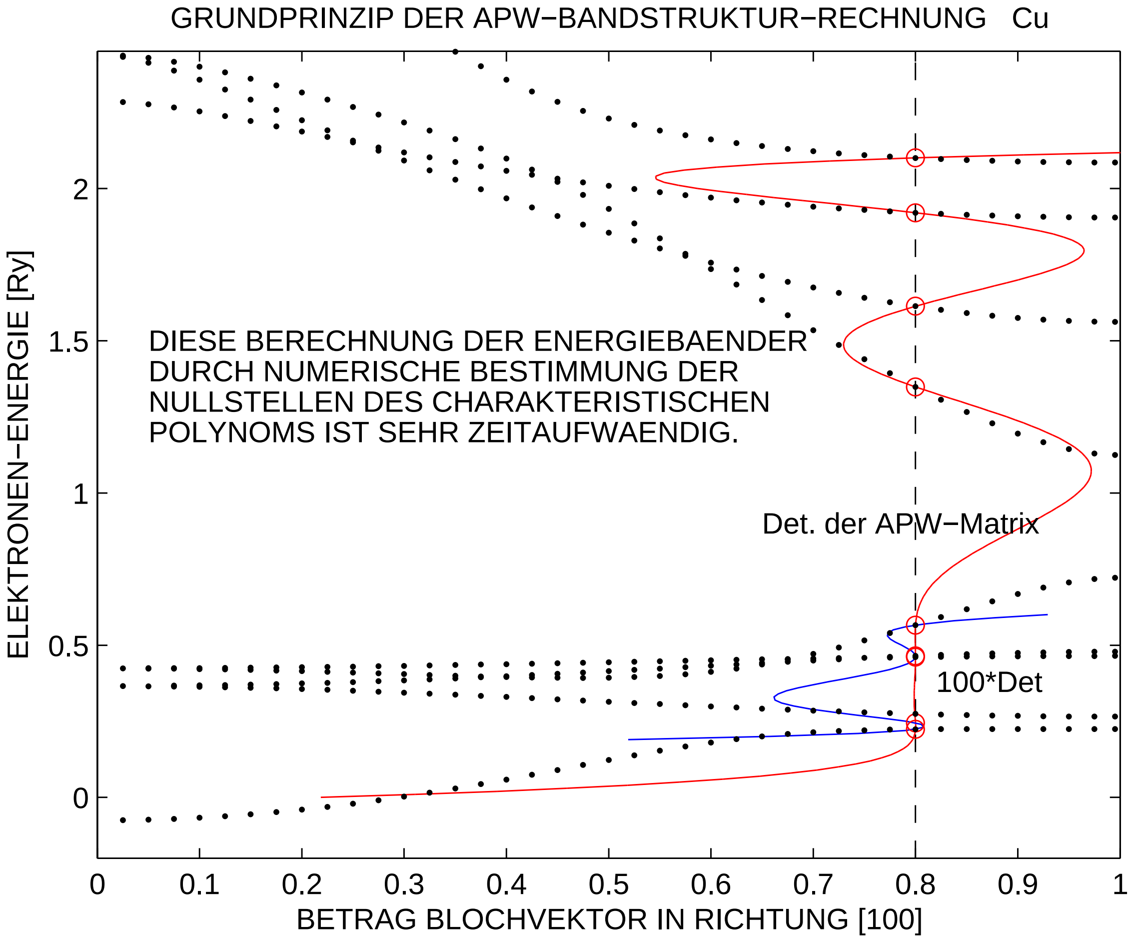
Structure of atomic spheres and interstitial region
for hcp magnesium

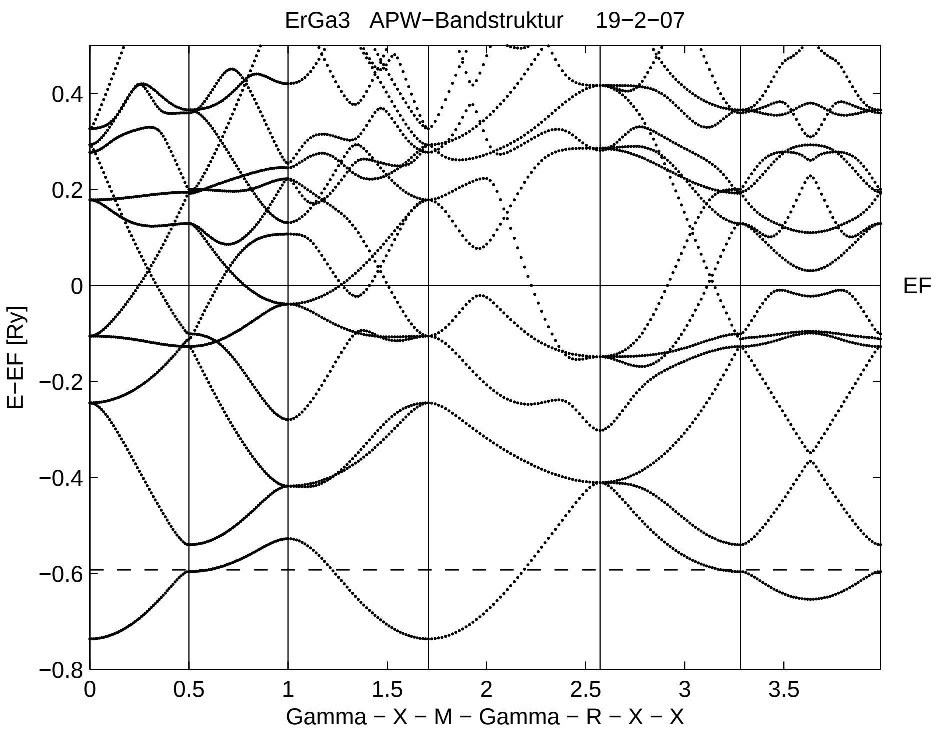


Structure of atomic spheres and interstitial region
for silicon (diamond structure)

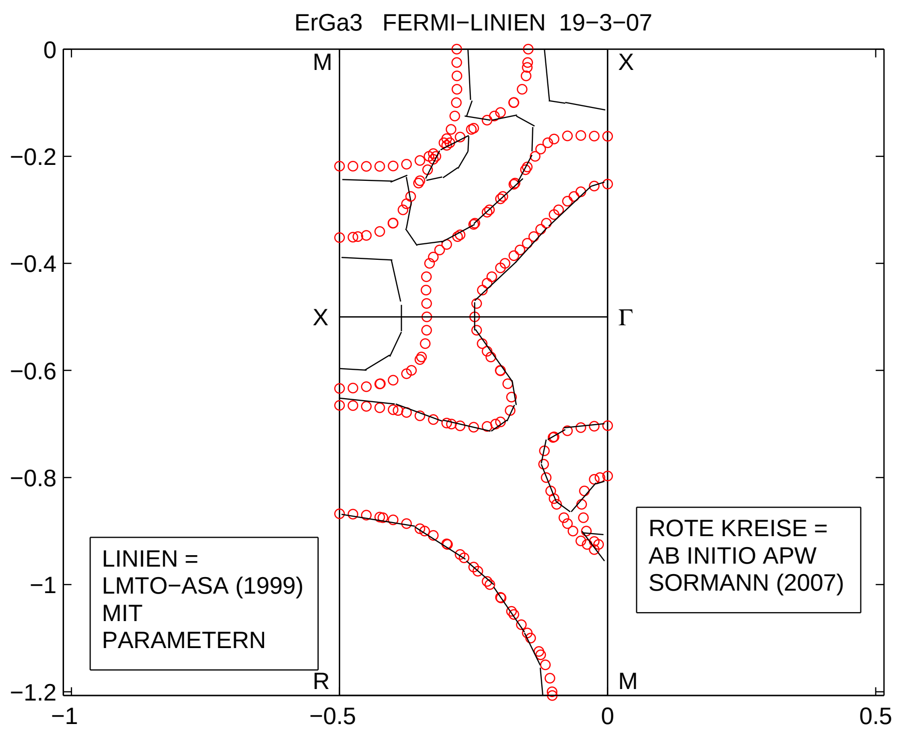

SILIZIUM APW GAMMA−X
SILIZIUM LAPW GAMMA−X
ENERGIE (RY)
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
0
0.5
1
0.5
0
−0.5
1
1.2
1.4
1.6
1.8

The main problem: APW → a non-linear Eigenvalue problem





APW-Bandstruktur für $ErGa_3$ (Sormann 2007).



„Fermi-Schnittlinien“ (*Fermi cuts*).