A case study: Aluminum bandstructure by OPW

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- In the following, the OPW method shall be applied to the fcc metal Al.

- What one needs to know: the reciprocal-lattice vectors $\mathbf{K}$ and the *crystal potential* of the Al metal, $V(\mathbf{r})$, with

$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R}) \qquad \rightarrow \quad V(\mathbf{K}) = \sum_{\mathbf{K}} V(\mathbf{K})\, \mathrm{e}^{i\mathbf{K}\cdot\mathbf{r}}\,.$$

- The OPW method is based on the *expanded eigenvalue problem*

$$\left(\hat{H} - E\,\hat{S}\right)\mathbf{a} = 0$$

with

$$H_{s,t} = H^{PW}_{s,t} - \sum_{l}^{core} \mu^{*}_{\mathbf{k}_s,j}\,\mu_{\mathbf{k}_t,j}\,E_j \tag{1}$$

and

$$S_{s,t} = H^{PW}_{s,t} - \sum_{l}^{core} \mu^{*}_{\mathbf{k}_s,j}\,\mu_{\mathbf{k}_t,j} \tag{2}$$

with $\mathbf{k}_s = \mathbf{k} + \mathbf{K}_s$ and $\mathbf{k}_t = \mathbf{k} + \mathbf{K}_t$.

The core parts contain energies and wave functions of the electron core states in Al:

$$E_j \quad \rightarrow \quad E_{nlm} \qquad \text{and} \quad w_j(\mathbf{r}) \quad \rightarrow \quad w_{nlm}(\mathbf{r})\,.$$

- Electronic structure of the Al atom (Z=13):

$1s^2 \quad 2s^2 \quad 2p^6 \qquad 3s^2 \quad 3p^1$

with the *core part* $|nlm>=|100>$, $|200>$, and $|21m>$
with $m = -1, 0, 1$.

The corresponding *atomic-like* Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(|\mathbf{r}|)\right)\, w_{nlm}(\mathbf{r}) = E_{nl}\, w_{nlm}(\mathbf{r})$$

with

$$w_{nlm}(\mathbf{r}) = R_{nl}(r)\, Y_{lm}(\tilde{\mathbf{r}})$$

where $\tilde{\mathbf{r}}$ means the unit vector in direction $\mathbf{r}$.

- The evaluation of the *core terms* in Eqs. (1) and (2) can be done as follows: one has

$$H_{s,t} = H_{s,t}^{PW} - \sum_{l}^{core} \mu^*_{\mathbf{k}_s,j}\, \mu_{\mathbf{k}_t,j}\, (E_j) \tag{3}$$

with

$$\begin{aligned} \mu_{\mathbf{k},nlm} &= \frac{4\pi}{\sqrt{\Omega_0}}\, i^l\, Y_{lm}(\tilde{\mathbf{k}}) \int_{r=0}^{\infty} dr\, r^2\, R_{nl}(r)\, j_l(|\mathbf{k}|r) \\ &= \frac{4\pi}{\sqrt{\Omega_0}}\, i^l\, Y_{lm}(\tilde{\mathbf{k}})\, I_{nl}(|\mathbf{k}|)\,. \end{aligned}$$

Including this expression into the sum in Eq. (3) leads to

$$\frac{(4\pi)^2}{\Omega_0} \sum_n \sum_{l=0}^{n-1} \underbrace{(-i)^l i^l}_{=1} (E_{nl})\, I_{nl}(|\mathbf{k}_s|) I_{nl}(|\mathbf{k}_t|) \sum_{m=-l}^{+l} Y^*_{lm}(\tilde{\mathbf{k}}_s)\, Y_{lm}(\tilde{\mathbf{k}}_t)$$

where the term in red gives the simple result

$$\frac{(2l+1)}{4\pi}\, P_l(\cos \angle[\mathbf{k}_s, \mathbf{k}_t])$$

with $P_l(x)$ as the l^{th}-order Legendre polynomial.
Using the abbreviation $x_{s,t} = \cos \angle[\mathbf{k}_s, \mathbf{k}_t]$, one gets for Al:

$$\frac{4\pi}{\Omega_0} \left\{ \left[(E_{10})\, I_{10}(k_s) I_{10}(k_t) + (E_{20})\, I_{20}(k_s) I_{20}(k_t) \right]\, P_0(x_{s,t}) + 3\, (E_{21})\, I_{21}(k_s) I_{21}(k_t)\, P_1(x_{s,t}) \right\}\,.$$

Taking into account that

$$P_0(x) = 1 \qquad \text{and} \quad P_1(x) = x\,,$$

The final result for the elements of the Hamilton and the structure matrix reads

$$H_{s,t} = H_{s,t}^{PW} - \frac{4\pi}{\Omega_0} \left\{ E_{10}\, I_{10}(k_s) I_{10}(k_t) + E_{20}\, I_{20}(k_s) I_{20}(k_t)\, + 3\, E_{21}\, I_{21}(k_s) I_{21}(k_t)\, x_{s,t} \right\}$$

and

$$S_{s,t} = \delta_{s,t} - \frac{4\pi}{\Omega_0} \left\{ I_{10}(k_s) I_{10}(k_t) + I_{20}(k_s) I_{20}(k_t)\, + 3\, I_{21}(k_s) I_{21}(k_t)\, x_{s,t} \right\}$$

with

$$I_{n0}(k) = \int_0^{\infty} dr\, r^2\, R_{n0}(r)\, \frac{sin(kr)}{kr}$$

and

$$I_{21}(k) = \int_0^{\infty} dr\, r^2\, R_{21}(r) \left[\frac{\sin(kr)}{(kr)^2} - \frac{\cos(kr)}{kr} \right]\,.$$

Finally, it is demonstrated how successful the OPW method works for Al. The following three figures show OPW band structures of Al (red circles), based on 9, 59, and 135 orthogonalized plane waves.
The corresponding APW band structure is drawn as black points.