15.4 Appendix: APW matrix elements

According to Eq. (15.8), the $(s,t)^{th}$ element of the APW secular matrix reads

$$\begin{aligned} M_{s,t} &= \left\langle s \left| \hat{H} - E \right| t \right\rangle + \left\langle s \left| \hat{S} \right| t \right\rangle \\ &= \int_{i+a} d^3r\, \phi_s^* \,(\hat{H} - E)\, \phi_t - \frac{\hbar^2}{2m} \int_{r_{\mathrm{MT}}} dS\, \phi_{a,s}^* \left[\frac{\partial}{\partial r}\phi_{a,t} - \frac{\partial}{\partial r}\phi_{i,t} \right] , \end{aligned}$$

where 'i' and 'a' mean integrations inside and outside the *muffin-tin* sphere with radius r_{MT}, respectively. $\phi_s(\mathbf{r};E)$ is the APW basis function which belongs to the Bloch vector $\mathbf{k}_s = \mathbf{k} + \mathbf{K}_s$:

$$\phi_s(\mathbf{r};E) = \begin{cases} 4\pi \sum_l \sum_m i^l\, j_l(k_s\, r_{\mathrm{MT}}) \frac{R_l(r;E)}{R_l(r_{\mathrm{MT}};E)}\; Y_{lm}(\vartheta,\varphi) Y_{lm}^*(\vartheta_{\mathbf{k}_s},\varphi_{\mathbf{k}_s}), \\ \text{für } |\mathbf{r}| \le r_{\mathrm{MT}} \\ e^{i\mathbf{k}_s\cdot\mathbf{r}} \;\text{ für } |\mathbf{r}| > r_{\mathrm{MT}} \end{cases} .$$

As a first step, one calculates the matrix element $\left\langle s \left| \hat{H} - E \right| t \right\rangle$:

$$\begin{aligned} \left\langle s \left| \hat{H} - E \right| t \right\rangle &= \int_{i+a} d^3r\, \phi_s^*(\mathbf{r};E)(\hat{H} - E)\phi_t(\mathbf{r};E) \\ &= \left[\frac{\hbar^2}{2m}\mathbf{k}_t^2 - E \right] \int_a d^3r\, \exp\left[i\mathbf{k}_{t,s}\cdot\mathbf{r} \right] \\ &= \left[\frac{\hbar^2}{2m}\mathbf{k}_t^2 - E \right] \left\{ \Omega_0 \delta_{s,t} - \int_i d^3r\, \exp\left[i\mathbf{k}_{t,s}\cdot\mathbf{r} \right] \right\} , \end{aligned}$$

with $\mathbf{k}_{t,s} = \mathbf{k}_t - \mathbf{k}_s$ and Ω_0 as the volume of the unit cell. By using

$$e \int_i d^3r\, \exp(i\mathbf{K}\cdot\mathbf{r}) = 4\pi \int_0^{r_{\mathrm{MT}}} dr\, r^2 \frac{\sin(Kr)}{Kr} = \frac{4\pi r_{\mathrm{MT}}^2\, j_1(K r_{\mathrm{MT}})}{K},$$

one obtains the following result of the integral to be investigated:

$$\int_{i+a} d^3r\, \phi_s^*(\mathbf{r};E)(\hat{H} - E)\phi_t(\mathbf{r};E) = \left[\frac{\hbar^2}{2m}\mathbf{k}_t^2 - E \right] \left[\Omega_0 \delta_{s,t} - 4\pi r_{\mathrm{MT}}^2 \frac{j_1(|\mathbf{k}_{t,s}|\, r_{\mathrm{MT}})}{|\mathbf{k}_{t,s}|} \right] .$$

Next, one has to determine the corresponding element of the structure matrix

$$\left\langle s \left| \hat{S} \right| t \right\rangle = -\frac{\hbar^2}{2m} \int_{r_{\mathrm{MT}}} dS\, \phi_{a,s}^* \left[\frac{\partial}{\partial r}\phi_{a,t} - \frac{\partial}{\partial r}\phi_{i,t} \right] .$$

To begin with, the plane wave in the interstitial region (a) is expanded into spherical Bessel functions and spherical harmonics:

$$\begin{aligned}\phi_{a,t}(\mathbf{r};E) &= \exp(i\mathbf{k}_t\cdot\mathbf{r}) \\ &= 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l\, j_l(k_t r) Y_{lm}^*(\vartheta_{k_t},\varphi_{k_t}) Y_{lm}(\vartheta_r,\varphi_r)\,.\end{aligned}$$

With

$$\phi_{i,t}(\mathbf{r};E) = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l\,\frac{j_l(k_t r_{\mathrm{MT}})}{R_l(r_{\mathrm{MT}};E)} R_l(r;E)\, Y_{lm}^*(\vartheta_{k_t},\varphi_{k_t})\, Y_{lm}(\vartheta_r,\varphi_r)$$

and

$$dS = r_{\mathrm{MT}}^2\, d\Omega_r = r_{\mathrm{MT}}^2\,\sin\vartheta_r d\vartheta_r\, d\varphi_r$$

one obtains the expression

$$\begin{aligned}&\left\langle s\left|\hat{S}\right|t\right\rangle = \\ &-\frac{\hbar^2}{2m} r_{\mathrm{MT}}^2 \int d\Omega_r\, 4\pi \sum_{l,l'=0}^{\infty}\sum_{m=-l}^{l}\sum_{m'=-l'}^{l'} (-i)^l\, j_l(k_s r_{\mathrm{MT}})\, Y_{lm}(\vartheta_{k_s},\varphi_{k_s}) \\ &\times Y_{lm}^*(\vartheta_r,\varphi_r)\, 4\pi\, i^{l'}\, Y_{l'm'}^*(\vartheta_{k_t},\varphi_{k_t})\, Y_{l'm'}(\vartheta_r,\varphi_r) \\ &\times\frac{\partial}{\partial r}\left[j_{l'}(k_t r) - \frac{j_{l'}(k_t r_{\mathrm{MT}})}{R_{l'}(r_{\mathrm{MT}};E)}\, R_{l'}(r;E)\right]_{r=r_{\mathrm{MT}}}\,.\end{aligned}$$

Using the orthogonality relation for the spherical harmonics $Y_{l,m}$, one obtains

$$\begin{aligned}&\left\langle s\left|\hat{S}\right|t\right\rangle = \\ &-(4\pi)^2\frac{\hbar^2}{2m} r_{\mathrm{MT}}^2 \sum_{l,l'=0}^{\infty}\sum_{m=-l}^{l}\sum_{m'=-l'}^{l'} (-i)^l\, i^{l'}\, Y_{lm}(\vartheta_{k_s},\varphi_{k_s})\, Y_{l'm'}^*(\vartheta_{k_t},\varphi_{k_t}) \\ &\times j_l(k_s r_{\mathrm{MT}})\, j_{l'}(k_t r_{\mathrm{MT}}) \left[\frac{1}{j_{l'}(k_t r_{\mathrm{MT}})}\frac{d}{dr} j_{l'}(k_t r) - \frac{1}{R_{l'}(r_{\mathrm{MT}};E)}\frac{d}{dr} R_{l'}(r;E)\right]_{r=r_{\mathrm{MT}}} \\ &\times \underbrace{\int d\Omega_r\, Y_{lm}^*(\vartheta_r,\varphi_r)\, Y_{l'm'}(\vartheta_r,\varphi_r)}_{=\delta_{ll'}\,\delta_{mm'}}\end{aligned}$$

and

$$\begin{aligned}\left\langle s\left|\hat{S}\right|t\right\rangle &= -\frac{\hbar^2}{2m}(4\pi)^2 r_{\mathrm{MT}}^2 \sum_{l=0}^{\infty}\underbrace{\sum_{m=-l}^{l} Y_{lm}(\vartheta_{k_s},\varphi_{k_s})\, Y_{lm}^*(\vartheta_{k_t},\varphi_{k_t})}_{=\frac{1}{4\pi}\,(2l+1)\,P_l(\cos\,\vartheta_{s;t})} \\ &\qquad\times j_l(k_s r_{\mathrm{MT}})\, j_l(k_t r_{\mathrm{MT}}) \left[\frac{1}{j_l(k_t r_{\mathrm{MT}})}\frac{d\, j_l(k_t r)}{dr}\right. \\ &\qquad\left. -\frac{1}{R_l(r_{\mathrm{MT}};E)}\frac{dR_l(r;E)}{dr}\right]_{r=r_{\mathrm{MT}}}\,,\end{aligned}$$

where the P_l represent Legendre polynomials, and $\vartheta_{s;t}$ means the angle between the vectors $\mathbf{k}_s$ and $\mathbf{k}_t$.

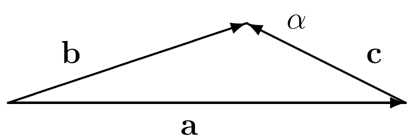
As a result, the above calculations yield the APW matrix elements by

$$\begin{aligned}
\langle s\,|\,M\,|\,t\rangle &= \left[\frac{\hbar^2}{2m}k_t^2 - E(\mathbf{k})\right]\left[\Omega_0\delta_{s,t} - 4\pi r_{\mathrm{MT}}^2 \frac{j_1(|\mathbf{k}_{t,s}|r_{\mathrm{MT}})}{|\mathbf{k}_{t,s}|}\right] \\
&\quad -\frac{\hbar^2}{2m}4\pi r_{\mathrm{MT}}^2 \sum_l (2l+1)P_l(\cos\vartheta_{s;t})j_l(k_s r_{\mathrm{MT}})j_l(k_t r_{\mathrm{MT}}) \\
&\quad \times \left[\frac{k_t}{r}\frac{1}{j_l(k_t r)}\frac{d}{dk_t}j_l(k_t r) - \frac{1}{R_l(r;E)}\frac{d}{dr}R_l(r;E)\right]_{r=r_{\mathrm{MT}}} .
\end{aligned}$$

The following term of the above expression, namely

$$\frac{\hbar^2}{2m}4\pi r_{\mathrm{MT}}^2 k_t \left[-\frac{1}{R}\sum_l (2l+1)P_l(\cos\vartheta_{s;t})j_l(k_s r_{\mathrm{MT}})\frac{d}{dk_t}j_l(k_t r_{\mathrm{MT}})\right],$$

shall now be transformed in a more comfortable equation. Starting with the relations



$$\mathbf{a} = \mathbf{b} - \mathbf{c}$$

$$a^2 = b^2 + c^2 - 2bc\cos\,\alpha.$$

one further gets

$$j_0(\lambda a) = \sum_{l=0}^{\infty}(2l+1)\,j_l(\lambda b)\,j_l(\lambda c)\,P_l(\cos\,\alpha).$$

By derivating this with respect of c, one has

$$\frac{\partial}{\partial c}j_0(\lambda a) = \underbrace{\frac{d}{dx}j_0(x)}_{=-j_1(x)}\,\lambda\,\frac{da}{dc} = -\lambda\,j_1(\lambda a)\frac{c - b\cos\alpha}{a},$$

and

$$\frac{c - b\cos\alpha}{a}\,j_1(\lambda a) = -\frac{1}{\lambda}\sum_l (2l+1)j_l(\lambda b)\,\frac{d}{dc}\,j_l(\lambda c)\,P_l(\cos\,\alpha).$$

Taking $\mathbf{b} = \mathbf{k}_s$; $\mathbf{c} = \mathbf{k}_t$; $\alpha = \vartheta_{s;t}$; $\lambda = r_{\mathrm{MT}}$ and $\mathbf{a} = \mathbf{k}_s - \mathbf{k}_t$ one finally gets

$$\begin{aligned}
\frac{k_t - k_s\cos\vartheta_{s;t}}{|\mathbf{k}_s - \mathbf{k}_t|}j_1(|\mathbf{k}_s - \mathbf{k}_t|r_{\mathrm{MT}}) &= \frac{k_t^2 - \mathbf{k}_s\cdot\mathbf{k}_t}{|\mathbf{k}_s - \mathbf{k}_t|k_t}j_1(|\mathbf{k}_s - \mathbf{k}_t|r_{\mathrm{MT}}) \\
&= -\frac{1}{r_{\mathrm{MT}}}\sum_l (2l+1)P_l(\cos\,\vartheta_{s;t})\,j_l(k_s r_{\mathrm{MT}}) \\
&\quad \times\frac{d}{dk_t}j_l(k_t r_{\mathrm{MT}}).
\end{aligned}$$

Using this identity, the final result for the matrix element $\langle s \,|\, M \,|\, t \rangle$ is

$$
\begin{aligned}
\langle s \,|\, M \,|\, t \rangle \;\; &= \;\; \left[\frac{\hbar^2}{2m} \mathbf{k}_t^2 - E(\mathbf{k}) \right] \Omega_0 \delta_{s,t} \\
&\quad -4\pi\, r_{\mathrm{MT}}^2 \left\{ \left[\frac{\hbar^2}{2m} \mathbf{k}_s \cdot \mathbf{k}_t - E(\mathbf{k}) \right] \frac{j_1(|\mathbf{k}_s - \mathbf{k}_t| r_{\mathrm{MT}})}{|\mathbf{k}_s - \mathbf{k}_t|} \right. \\
&\quad - \frac{\hbar^2}{2m} \sum_l (2l+1) P_l(\cos\vartheta_{s;t})\, j_l(|\mathbf{k}_s| r_{\mathrm{MT}}) \frac{j_l(|\mathbf{k}_t| r_{\mathrm{MT}})}{R_l(r_{\mathrm{MT}}; E)} \\
&\quad \left. \times \frac{d}{dr} R_l(r; E) \,|_{r=r_{\mathrm{MT}}} \right\}
\end{aligned}
$$

which is exactly the same equation like Eq. (15.9).