The LMTO object of the CP-PAW code

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Chapter 1

Purpose and theoretical background of the LMTO Object

The LMTO object maps the wave functions expressed in augmented plane waves into a basiset of natural tight-binding orbitals. The natural tight-binding orbitals are a kind of LMTO's, screened such that the tails exhibit only scattering character in the context of nodeless wave functions[**?**].

1.0.1 Bare structure constants

The bare structure constants are the expansion constants for an off-site expansion of spherical Hankel functions.

$$|K_\alpha^\infty\rangle = |K_\alpha^\Omega\rangle - \sum_\beta |J_\beta^\Omega\rangle S_{\beta,\alpha}^\dagger + |K_\alpha^I\rangle \tag{1.1}$$

The index α denotes here an atomic site R and a set of angular momenta $L = (\ell, m)$.

In the following we will call $|K_\alpha^\Omega\rangle$ head function and $|J_\beta^\Omega\rangle$ tail functions.

1.0.2 Screened structure constants

The node-less scattering partial wave $|\dot{\bar{\phi}}_\alpha\rangle$ define the screening constants $\bar{Q}_\alpha$ such that the screened tail functions $|\bar{J}_\alpha\rangle$ match with value and derivative to the scattering partial wave

$$|\dot{\bar{\phi}}_\alpha\rangle \to |\bar{J}_\alpha^\Omega\rangle \stackrel{\text{def}}{=} |\bar{J}_\alpha^\Omega\rangle - |\bar{K}_\alpha^\Omega\rangle \bar{Q}_\alpha \tag{1.2}$$

A screened Hankel functions is a superposition of bare Hankel functions on a set of atomic positions withe the property that the tail functions are made entirely from screened bessel functions, i.e.

$$|\bar{K}_\alpha^\infty\rangle = |K_\alpha^\Omega\rangle - \sum_\beta |\bar{J}_\beta^\Omega\rangle \bar{S}_{\beta,\alpha}^\dagger + |\bar{K}_\alpha^I\rangle \tag{1.3}$$

The screened Hankel functions are defined by a superposition of bare Hankel functions

$$|\bar{K}_\alpha^\infty\rangle = \sum_\beta |K_\beta^\infty\rangle c_{\beta,\alpha} \tag{1.4}$$

By equating the two expressiones for the screened Hankel functions, namely Eq. 1.4 and Eq. 1.3, we can extract the screened structure constants and the superposition coeffcients.

$$\sum_\beta \Big[|K^\Omega_\beta\rangle - \sum_\gamma |J^\Omega_\gamma\rangle S^\dagger_{\gamma,\beta} + |K^I_\beta\rangle\Big] c_{\beta,\alpha} = |K^\Omega_\alpha\rangle - \sum_\beta \underbrace{\Big[|J^\Omega_\beta\rangle - |K^\Omega_\beta\rangle \bar{Q}_\beta\Big]}_{|\bar{J}^\Omega_\beta\rangle} \bar{S}^\dagger_{\beta,\alpha} + |\bar{K}^I_\alpha\rangle$$

$$\sum_\beta |K^\Omega_\beta\rangle c_{\beta,\alpha} - \sum_{\beta,\gamma} |J^\Omega_\gamma\rangle S^\dagger_{\gamma,\beta} c_{\beta,\alpha} = \sum_\beta |K^\Omega_\beta\rangle \Big[\delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha}\Big] - \sum_\beta |J^\Omega_\beta\rangle \bar{S}^\dagger_{\beta,\alpha} \quad (1.5)$$

By comparing the coefficients, we obtain

$$\begin{aligned} c_{\beta,\alpha} &= \delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha} \\ \bar{S}^\dagger_{\gamma,\alpha} &= \sum_\beta S^\dagger_{\gamma,\beta} c_{\beta,\alpha} \end{aligned} \quad (1.6)$$

which can be resolved to[1] the defining equation of the screened structure constants

$$\bar{\boldsymbol{S}}^\dagger = \boldsymbol{S}^\dagger \Big[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger\Big]^{-1} \quad (1.10)$$

and the expression of the screened Hankel functions

$$|\bar{K}^\infty_\alpha\rangle = \sum_\beta |K^\infty_\beta\rangle \Big[\delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha}\Big] . \quad (1.11)$$

[1]

$$\begin{aligned} \boldsymbol{c} = \mathbf{1} + \bar{\boldsymbol{Q}}\bar{\boldsymbol{S}}^\dagger = \mathbf{1} + \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger\boldsymbol{c} \quad &\Rightarrow \quad \sum_\gamma \Big[\delta_{\beta,\gamma} - \bar{Q}_\beta S^\dagger_{\beta,\gamma}\Big] c_{\gamma,\alpha} = \delta_{\beta,\alpha} \quad \Rightarrow \quad \boldsymbol{c} = [\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]^{-1} \\ \bar{\boldsymbol{S}}^\dagger = \boldsymbol{S}^\dagger\boldsymbol{c} = \boldsymbol{S}^\dagger[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]^{-1} \quad &\Leftrightarrow \quad [\mathbf{1} - \boldsymbol{S}\bar{\boldsymbol{Q}}]\bar{\boldsymbol{S}} = \boldsymbol{S} \end{aligned} \quad (1.7)$$

The calculation can be done on a cluster of atomic sites for a single screened Hankel function. That is, α in Eq. 1.6 may be a single fixed orbital index, while the indices β, γ can take any value on the cluster. Thus, $\bar{S}^\dagger$ and the coefficients c can be considered as vectors $\vec{s}$ and $\vec{c}$.

$$\begin{aligned} \vec{c}_\alpha = \vec{e}_\alpha + \bar{\boldsymbol{Q}}\vec{s}_\alpha = \vec{e}_\alpha + \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger\vec{c}_\alpha \quad &\Big[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger\Big]\vec{c}_\alpha = \vec{e}_\alpha \quad \Rightarrow \quad \boldsymbol{c}_\alpha = [\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]^{-1}\vec{e}_\alpha \\ \vec{s}_\alpha = \boldsymbol{S}^\dagger\vec{c}_\alpha = \boldsymbol{S}^\dagger[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]^{-1}\vec{e}_\alpha \end{aligned} \quad (1.8)$$

Thus we first evaluate $\boldsymbol{S}^\dagger$ on the cluster, and from that $[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]$. Then we solve the equation

$$[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]\vec{q}_\alpha = \vec{e}_\alpha \quad (1.9)$$

for $\vec{q}_\alpha$. Multiplication with te bare structure constants yields the screened structure constants as $\vec{s}_\alpha = \boldsymbol{S}^\dagger\vec{q}_\alpha$.

Chapter 2

Description of Subroutines

2.1 LMTO$STRUCTURECONSTANTS

```
subroutine lmto$structureconstants(r21,K2,L1x,L2x,S)
REAL(8)   ,INTENT(IN) :: R21(3) ! EXPANSION CENTER
INTEGER(4),INTENT(IN) :: L1X
INTEGER(4),INTENT(IN) :: L2X
REAL(8)   ,INTENT(IN) :: K2 ! 2ME/HBAR**2
REAL(8)   ,INTENT(OUT):: S((L1X+1)**2,(L2X+1)**2)
```

The bare structure constants are evaluated in `LMTO$STRUCTURECONSTANTS` as

$$S_{RL,R'L'} = (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}' - \vec{R}) \kappa^{\ell+\ell'-\ell''} \tag{2.1}$$

where

$$\kappa = \begin{cases} -i\sqrt{k^2} & \text{for } k^2 \geq 0 \\ \sqrt{k^2} & \text{for } k^2 < 0 \end{cases} \tag{2.2}$$

and where $H_L(k^2, \vec{R})$ is the solid Hankel function calculated in `LMTO$SOLIDHANKEL`. The solid Hankel function is the solution of the Helmholt equation[1]

$$\left[\vec{\nabla}^2 + k^2\right] H_L(\vec{r}) = -4\pi(-1)^\ell \mathcal{Y}(\vec{\nabla})\delta(\vec{r}) \tag{2.3}$$

Here $\mathcal{Y}_\ell(\vec{r}) = r^\ell Y_\ell(\vec{r})$ is a polynomial. With a gradient as argument it becomes a differential operator.

Near the origin the solid Hankel function behaves, irrespective of the value of k^2 like

$$H_\ell(\vec{r}) = (2\ell+1)!! \frac{1}{|\vec{r}|^{\ell+1}} Y_L(\vec{r}) \Big(1 + O(|\vec{r}|)\Big) \tag{2.4}$$

More information on the solid Hankel function can be found in appendix A.

[1] The factors and signs of the inhomogeneity need to be confirmed. The equation has been taken from the Methods book chapter "working with spherical Hankel and Bessel functions.

Appendix A

Definition of solid Hankel functions

The solid Hankel function has the form

$$H_L(\vec{R}) = Y_L(\vec{R}) \begin{cases} n_\ell(\sqrt{k^2}\cdot|\vec{R}|)\cdot\sqrt{k^2}^{\ell+1} & \text{for } k^2>0 \text{ (Abramovitz 10.1.26)} \\ m_\ell(\sqrt{-k^2}\cdot|\vec{R}|)\cdot\sqrt{\frac{2}{\pi}}\sqrt{-k^2}^{\ell+1} & \text{for } k^2<0 \text{ (Abramovitz 10.2.4)} \\ (2\ell-1)!!|\vec{R}|^{-\ell-1} & \text{for } k^2=0 \text{ (Abramovitz 10.2.5)} \end{cases} \tag{A.1}$$

The solid Hankel function is defined such that the boundary conditions at the origin are independent of k^2.

- the function

$$n_\ell(r) = r^\ell\Big(-\frac{1}{r}\partial_r\Big)^\ell\frac{1}{r}\cos(r) \tag{A.2}$$

  is the spherical Neumann function (see Eq. 8.175 of Cohen Tannoudhi Band 2), which is also called the spherical Bessel function of the second kind. Abramowitz defines $n_\ell(r) = -y_\ell(r)$ (compare Abramowitz Eq. 10.1.26)

  The spherical Neumann function obeys the radial Helmholtz equation (Abramowitz Eq. 10.1.1) for positive kinetic energy

$$\begin{aligned} & r^2\partial_r^2 n_\ell + 2r\partial_r n_\ell + \Big(r^2-\ell(\ell+1)\Big)n_\ell = 0 \\ \Rightarrow\quad & \Big[-\frac{1}{r}\partial_r r + \frac{\ell(\ell+1)}{r^2}\Big]n_\ell(r) = +n_\ell(r) \end{aligned} \tag{A.3}$$

  Note that the subroutine SPFUNCTION$NEUMANN returns the Neumann function with the opposite sign, namely what Abramowitz defines as Bessel function of the second kind. The minus sign is added in the calling routine.

- The function

$$m_\ell(r) = r^\ell\Big(-\frac{1}{r}\partial_r\Big)^\ell\frac{1}{r}\mathrm{e}^{-r} \tag{A.4}$$

  used for $k^2<0$ is obeys the radial Helmholtz equation (Abramowitz Eq. 10.2.1) for negative kinetic energy

$$\begin{aligned} & r^2\partial_r^2 m_\ell + 2r\partial_r m_\ell - \Big(r^2+\ell(\ell+1)\Big)m_\ell = 0 \\ \Rightarrow\quad & \Big[-\frac{1}{r}\partial_r r + \frac{\ell(\ell+1)}{r^2}\Big]m_\ell(r) = -m_\ell(r) \end{aligned} \tag{A.5}$$

They are solutions for negative energy and therefore they fall off exponentially. The solution $m_\ell(r)$ is proportional to the modified spherical Bessel functions of the third kind as defined by Abramowitz[1] in their Eq. 10.2.4.

$$m_\ell(r) = \frac{2}{\pi}\left[\sqrt{\frac{\pi}{2r}}K_{\ell+1}(r)\right] \tag{A.6}$$

which can be verified by comparing the defining equation Eq. A.4 with equations 10.2.24-25 and the definition Eq. 10.2.4 of Abramowitz.

Bibliography

[1] M. Abramowitz and I.A. Stegun, editors. Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables, volume 55 of Applied Mathematics Series. National Bureau of Standards, 1964.