The LMTO object of the CP-PAW code

Peter E. Blöchl

Institute of Theoretical Physics; Clausthal University of Technology;
D-38678 Clausthal Zellerfeld; Germany;
http://www.pt.tu-clausthal.de/atp/

Contents

Chapter 1

Todo

- lmto_overlapphi calculates the onsite overlap matrix of partial waves in a sphere.
- the core-valence exchange contribution differs from the old version, because it also includes the projection on the phidot functions.
- there has been a bug in `lmto$screen`, which has been fixed with version 3. It may be better to rewrite all structure constants routines with teh transposed structure constants.

Chapter 2

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[**?**].

2.1 Augmentation

The concept of linear augmented waves is as follows:

1. At first a so-called **envelope function** $|K^{\infty}_{\alpha}\rangle$ is defined.

2. In a second step, this envelope function is expanded about each atomic site into spherical harmonics. More generally, they are expanded into **head functions** $|K^{\Omega}_{\alpha}\rangle$ and **tail functions** $|J^{\Omega}_{\alpha}\rangle$. The head function is the dominant contribution and carries the quantum number of the final orbital, while the tail functions are the minor contributions with different quantum numbers. In practice, the head functions are solid Hankel functions and the tail functions are solid Bessel functions.

   The coefficients of the tail functions are called **structure constants**.

   The difference between the full envelope function and its expansion into head and tail functions is the interstitial contribution $|K^{I}_{\alpha}\rangle$.

3. In the third step the head and tail functions are replaced differentially at some sphere radius by partial waves of the atomic potential. For that purpose, we use a solution of the Schrödinger equation for some energy, denoted as $|\phi_{\alpha}\rangle$ and its energy derivative function $|\dot{\phi}_{\alpha}\rangle$.

   The matching parameters are called **potential parameters**.

2.2 Structure constants

2.2.1 Hankel functions as envelope function

In practice, we will use solid Hankel functions $H_L(\vec{r})$ as envelope functions, so that

$$\langle \vec{r}|K^{\infty}_{R,L}\rangle = H_L(\vec{r}-\vec{R}) \tag{2.1}$$

Solid Hankel functions are irregular solutions of the the inhomogeneous Helmholtz equation[1]

$$\left[\vec{\nabla}^2 + k^2\right] H_L(\vec{r}) = -4\pi(-1)^{\ell}\mathcal{Y}(\vec{\nabla})\delta(\vec{r}) \tag{2.2}$$

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.

Further detail about the Hankel and Bessel functions can be found in appendix A.

2.2.2 Hankel and Bessel functions as head and tail functions

By defining the envelope function via a isotropic and translationally invariant differential equation of second order, has the advantage that the solution can be expanded about different centers into regular solutions of the same differential equation with specific angular momenta. The regular solutions of the Helmholtz equation are the Bessel functions.

Hankel and Bessel functions are defined so that they behave at the origin as

$$K^{\Omega}_{R,L}(\vec{r}) = \left[(2\ell-1)!!\frac{1}{|\vec{r}-\vec{R}|^{\ell+1}} + \ldots\right] Y_L(\vec{r}-\vec{R})\theta_{\Omega_R}(\vec{r}) \tag{2.3}$$

$$J^{\Omega}_{R,L}(\vec{r}) = \left[\frac{1}{(2\ell+1)!!}|\vec{r}-\vec{R}|^{\ell+1} + \ldots\right] Y_L(\vec{r}-\vec{R})\theta_{\Omega_R}(\vec{r}) \tag{2.4}$$

$\theta_{\Omega_R}(\vec{r})$ is a step function that is one within the augmentation region Ω_R centered at site R, while it vanishes outside. The terms neglected are higher orders in $|\vec{r}-\vec{R}|$.

2.2.3 Bare structure constants

The **bare structure constants** $S^{\dagger}_{\beta,\alpha}$ are the expansion constants for an off-center expansion of solid spherical Hankel functions $|K^{\infty}_{\alpha}\rangle$ into **solid Bessel functions** $|J^{\Omega}_{\beta}\rangle$.

$$|K^{\infty}_{\alpha}\rangle = |K^{\Omega}_{\alpha}\rangle - \sum_{\beta}|J^{\Omega}_{\beta}\rangle S^{\dagger}_{\beta,\alpha} + |K^{I}_{\alpha}\rangle \tag{2.5}$$

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

The superscript ∞ denotes that the function extends over all space, a superscript Ω denotes that the function is truncated (set to zero) outside the augmentation sphere Ω_R centerd at the site denoted by the index. The superscript I denotes that the function is limited to the

[1] I am not sure whether also the three dimensional differential equation or only the one-dimensional differential equation for the radial part is called Helmholtz equation.

interstitial region, that is outside all augmentation spheres. If the augmentation spheres overlap, the function in the interstitial region is defined by subtraction of all sphere contributions.

BARE STRUCTURE CONSTANTS

The bare structure constants have the form

$$S_{RL,R'L'} = (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}'-\vec{R}) \begin{cases} (-ik)^{\ell+\ell'-\ell''} & \text{for } k^2>0 \\ \delta_{\ell+\ell'-\ell''} & \text{for } k^2=0 \\ \kappa^{\ell+\ell'-\ell''} & \text{for } k^2=-\kappa^2<0 \end{cases} \tag{2.6}$$

The bare structure constants are hermitean[2], i.e.

$$S_{RL,R'L'} = S_{R'L',RL} \tag{2.7}$$

This is however not true for each angular-momentum block individually, i.e. in general we have $S_{RL,R'L'} \neq S_{R,L',R'L}$.

2.2.4 Screened structure constants

The node-less scattering partial wave $|\bar{\dot{\phi}}_\alpha\rangle$ 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

$$|\bar{\dot{\phi}}_\alpha\rangle \to |\bar{J}^\Omega_\alpha\rangle \stackrel{\text{def}}{=} |J^\Omega_\alpha\rangle - |K^\Omega_\alpha\rangle\bar{Q}_\alpha \tag{2.8}$$

A screened solid Hankel function $|\bar{K}^\infty_\alpha\rangle$ is a superposition of bare solid Hankel functions on a set of atomic positions

$$|\bar{K}^\infty_\alpha\rangle = \sum_\beta |K^\infty_\beta\rangle c_{\beta,\alpha} \tag{2.9}$$

with the property that the tail functions are made entirely from screened Bessel functions $|\bar{J}^\Omega_\beta\rangle$, i.e.

$$|\bar{K}^\infty_\alpha\rangle = |K^\Omega_\alpha\rangle - \sum_\beta |\bar{J}^\Omega_\beta\rangle \bar{S}^\dagger_{\beta,\alpha} + |\bar{K}^I_\alpha\rangle \tag{2.10}$$

The expansion coefficients $\bar{S}$ are the screened structure constants.

By equating the two expressiones for the screened Hankel functions, namely Eq. 2.9 and Eq. 2.10, we can extract the screened structure constants and the superposition coeffcients.

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

$$\sum_\beta |K^\Omega_\beta\rangle c_{\beta,\alpha} - \sum_{\beta,\gamma} |J^\Omega_\gamma\rangle S^\dagger_{\gamma,\beta} c_{\beta,\alpha} = \sum_\beta |K^\Omega_\beta\rangle \Big[\delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha}\Big] - \sum_\beta |J^\Omega_\beta\rangle \bar{S}^\dagger_{\beta,\alpha} \tag{2.11}$$

[2] We use that $H_L(\vec{r}) = (-1)^\ell H_L(-\vec{r})$ and that the Gaunt coefficients $C_{L,L',L''}$ vanish unless $\ell+\ell'+''$ is even.

By comparing the coefficients, we obtain

$$c_{\beta,\alpha} = \delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha} \tag{2.12}$$

$$\bar{S}^\dagger_{\gamma,\alpha} = \sum_\beta S^\dagger_{\gamma,\beta} c_{\beta,\alpha} \tag{2.13}$$

which can be resolved to [3] the defining equation of the screened structure constants

SCREENED STRUCTURE CONSTANTS

$$\bar{\boldsymbol{S}}^\dagger = \boldsymbol{S}^\dagger \left[\mathbf{1} - \boldsymbol{S}^\dagger \bar{\boldsymbol{Q}}\right]^{-1} \tag{2.15}$$

and the expression of the screened Hankel functions

$$|\bar{K}^\infty_\alpha\rangle = \sum_\beta |K^\infty_\beta\rangle \left[\delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha}\right] . \tag{2.16}$$

Because, we calculate the screened structure constants on finite clusters, Eq. 2.15 should be considered of only formal value and should not be used in the actual calculations. Rather, the defining equations Eq. 2.13 shall be used as shown in the following section.

2.3 Screening on finite clusters

The screened structure constants are calculated on a cluster of atomic sites. The calculation can in principle be done for each single screened Hankel function independently. In practice we do the calculations for all atoms centered on a given site in one step.

We go back to the defining equation system Eq. 2.13 and rewrite it in terms of vectors, which are defined on the cluster B. The index α labeling the vectors correspond to the envelope functions centered at the central site.

The equations attain the form

$$\vec{c}_\alpha \overset{\text{Eq. 2.12}}{=} \vec{e}_\alpha + \bar{\boldsymbol{Q}} \vec{s}_\alpha \tag{2.17}$$

$$\vec{s}_\alpha \overset{\text{Eq. 2.13}}{=} \boldsymbol{S}^\dagger \vec{c}_\alpha \tag{2.18}$$

where the vectors $\vec{c}$, $\vec{s}_\alpha$ and $\vec{e}_\alpha$ are defined by its components

$$\left(\vec{c}_\alpha\right)_\beta = c_{\beta,\alpha}$$

$$\left(\vec{s}_\alpha\right)_\beta = \bar{S}^\dagger_{\beta,\alpha}$$

$$\left(\vec{e}_\alpha\right)_\beta = \delta_{\beta,\alpha} \tag{2.19}$$

[3]

$$\boldsymbol{c} = \mathbf{1} + \bar{\boldsymbol{Q}} \bar{\boldsymbol{S}}^\dagger = \mathbf{1} + \bar{\boldsymbol{Q}} \boldsymbol{S}^\dagger \boldsymbol{c} \quad \Rightarrow \quad \sum_\gamma \left[\delta_{\beta,\gamma} - \bar{Q}_\beta S^\dagger_{\beta,\gamma}\right] c_{\gamma,\alpha} = \delta_{\beta,\alpha} \quad \Rightarrow \quad \boldsymbol{c} = [\mathbf{1} - \bar{\boldsymbol{Q}} \boldsymbol{S}^\dagger]^{-1}$$

$$\bar{\boldsymbol{S}}^\dagger = \boldsymbol{S}^\dagger \boldsymbol{c} = \boldsymbol{S}^\dagger [\mathbf{1} - \bar{\boldsymbol{Q}} \boldsymbol{S}^\dagger]^{-1} \quad \Leftrightarrow \quad [\mathbf{1} - \boldsymbol{S} \bar{\boldsymbol{Q}}] \bar{\boldsymbol{S}} = \boldsymbol{S} \tag{2.14}$$

$$
\begin{aligned}
\vec{c}_\alpha &\overset{\text{Eq. 2.17}}{=} \vec{e}_\alpha + \bar{\boldsymbol{Q}}\vec{s}_\alpha \overset{\text{Eq. 2.18}}{=} \vec{e}_\alpha + \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger\vec{c}_\alpha \\
\Rightarrow \qquad \left[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger\right]\vec{c}_\alpha &= \vec{e}_\alpha \\
\Rightarrow \qquad \vec{c}_\alpha &= [\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]^{-1}\vec{e}_\alpha \\
\vec{s}_\alpha &\overset{\text{Eq. 2.18}}{=} \boldsymbol{S}^\dagger\vec{c}_\alpha = \boldsymbol{S}^\dagger[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]^{-1}\vec{e}_\alpha
\end{aligned}
\tag{2.20}
$$

Interestingly the vector on the right-hand side $\vec{e}_\alpha$ can not be simply ignored as the matrix form suggests. This is specific to the calculation on the cluster. Because of this we cannot identify the contribution of these vectors with a unit matrix.

CALCULATION OF SCREENED STRUCTURE CONSTANTS

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

$$
\begin{aligned}
[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]\vec{c}_\alpha &= \vec{e}_\alpha \\
\vec{s}_\alpha &= \boldsymbol{S}^\dagger\vec{c}_\alpha
\end{aligned}
\tag{2.21}
$$

for $\vec{c}_\alpha$ first using a standard routine for linear equation systems. From the result $\vec{c}_\alpha$, we obtain the screened structure constants $\vec{s}_\alpha$ by multiplication with the screened structure constants. Finally we obtain the screened structure constants as

$$
\bar{S}^\dagger_{\gamma,\alpha} = \left(\vec{s}_\alpha\right)_\gamma \tag{2.22}
$$

Note that the screened structure constants calculated on finite clusters are no more exactly hermitean.

2.4 Augmentation and Potential parameters

2.4.1 Local orbitals

The local orbitals have the form

$$
\begin{aligned}
|\chi_\alpha\rangle = &|\phi^K_\alpha\rangle - |\phi^J_{R,L}\rangle \bar{S}^\dagger_{R,L,R_\alpha,L_\alpha} \\
&+ |K^I_{R',L'}\rangle \left[\delta_{R',L',R_\alpha,\alpha} - \bar{Q}_{R',L'}\bar{S}^\dagger_{R',L',R_\alpha,L_\alpha}\right]
\end{aligned}
\tag{2.23}
$$

where, according to Eq. **??**,

$$
|\phi^K_\alpha\rangle = \overbrace{|\phi_\alpha\rangle \underbrace{\frac{W_\alpha[K,\bar{\dot\phi}]}{W_\alpha[\phi,\bar{\dot\phi}]}}_{Ktophi} - |\bar{\dot\phi}_\alpha\rangle \underbrace{\frac{W_\alpha[K,\phi]}{W_\alpha[\phi,\bar{\dot\phi}]}}_{-Ktophidot}}^{\rightarrow|K^\Omega_\alpha\rangle}
$$

$$
|\phi^{\bar J}_{R,L}\rangle = \overbrace{|\bar{\dot\phi}_\beta\rangle \underbrace{\left(-\frac{W_\beta[\bar J,\phi]}{W_\beta[\phi,\bar{\dot\phi}]}\right)}_{JBARtophidot}}^{\rightarrow|\bar J^\Omega_\beta\rangle} \tag{2.24}
$$

Note, that in the factor $JBARTOPHIDOT$ does not depend on the choice of $|\phi\rangle$.

Thus, the matrix elements $\langle\tilde p_\gamma|\tilde\chi_\alpha\rangle$ has the form

$$
\begin{aligned}
\langle\tilde p_\gamma|\tilde\chi_\alpha\rangle &= \langle\tilde p_\gamma|\tilde\phi^K_\alpha\rangle - \sum_{R',L'}\langle\tilde p_\gamma|\tilde\phi^{\bar J}_{R',L'}\rangle\bar S^\dagger_{R,L,R_\alpha,L_\alpha} \\
&= \langle\tilde p_\gamma|\tilde\phi^K_\alpha\rangle - \langle\tilde p_\gamma|\tilde\phi^{\bar J}_{R_\gamma,L_\gamma}\rangle\bar S^\dagger_{R_\gamma,L_\gamma,R_\alpha,L_\alpha}
\end{aligned} \tag{2.25}
$$

2.5 Coefficients of the tight-binding orbital

2.5.1 Introduction

In this section we describe how to determine the wave functions in terms of local orbitals, if the projections onto the pseudo wave functions are known.

The basic idea is to find a representation of the wave function in local orbitals

$$
|\psi'_n\rangle = \sum_\alpha |\chi_\alpha\rangle q_\alpha\ , \tag{2.26}
$$

such that the deviation from the true wave function $|\psi_n\rangle$ is as small as possible.

Ideally, this would amount to minimizing the mean square deviation of the orbital expansion from the wave function.

$$
Q'[\vec q] := \Big(\langle\psi_n| - \sum_\alpha q^*_\alpha\langle\chi_\alpha|\Big)\Big(|\psi_n\rangle - \sum_\beta|\chi_\beta\rangle q_\beta\Big)
$$

Because evaluating the mean square deviation as integral over all space is time consuming, we limit the integral to the augmentation spheres.

$$
\begin{aligned}
Q[\vec q] &:= \Big(\langle\tilde\psi_n| - \sum_\alpha q^*_\alpha\langle\tilde\chi_\alpha|\Big)\Big[\sum_{\delta,\gamma}|\tilde p_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\langle\tilde p_\gamma|\Big]\Big(|\tilde\psi_n\rangle - \sum_\beta|\tilde\chi_\beta\rangle q_\beta\Big) \\
&= \sum_\gamma\Big[\sum_\delta\Big(\langle\tilde\psi_n|\tilde p_\delta\rangle - \sum_\alpha q^*_\alpha\langle\tilde\chi_\alpha|\tilde p_\delta\rangle\Big)\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\Big(\langle\tilde p_\gamma|\tilde\psi_n\rangle - \sum_\beta\langle\tilde p_\gamma|\tilde\chi_\beta\rangle q_\beta\Big)
\end{aligned} \tag{2.27}
$$

where $\theta_{\Omega_{R_\delta}}$ is a step function that vanishes outside the augmentation sphere at R_δ.

Minimization yields

$$\frac{\partial Q}{\partial q^*_\alpha} = -\sum_\gamma \Big[\sum_\delta \langle\tilde\chi_\alpha|\tilde p_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\Big(\langle\tilde p_\gamma|\tilde\psi_n\rangle - \sum_\beta \langle\tilde p_\gamma|\tilde\chi_\beta\rangle q_\beta\Big) \stackrel{!}{=} 0$$

$$\Rightarrow \qquad \sum_\gamma \Big[\sum_\delta \langle\tilde\chi_\alpha|\tilde p_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde p_\gamma|\tilde\psi_n\rangle = \sum_{\gamma,\beta}\Big[\sum_\delta \langle\tilde\chi_\alpha|\tilde p_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde p_\gamma|\tilde\chi_\beta\rangle q_\beta\Big)$$

$$\Rightarrow \qquad q_\beta = \sum_\beta \Big[\sum_{\gamma',\delta'} \langle\tilde\chi_\alpha|\tilde p_{\delta'}\rangle\langle\phi_{\delta'}|\theta_{\Omega_{R_\delta}}|\phi_{\gamma'}\rangle\langle\tilde p_{\gamma'}|\tilde\chi_\beta\rangle\Big]^{-1}\Big[\sum_{\gamma\delta} \langle\tilde\chi_\alpha|\tilde p_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde p_\gamma|\tilde\psi_n\rangle \tag{2.28}$$

This allows one to write the wave function in the form

$$|\psi_n\rangle \approx \sum_\alpha |\chi_\alpha\rangle\langle\tilde\pi_\alpha|\tilde\psi_n\rangle \tag{2.29}$$

with

$$\langle\tilde\pi_\alpha| = \sum_\gamma \Big[\sum_{\gamma',\delta'} \langle\tilde\chi_\alpha|\tilde p_{\delta'}\rangle\langle\phi_{\delta'}|\theta_{\Omega_{R_\delta}}|\phi_{\gamma'}\rangle\langle\tilde p_{\gamma'}|\tilde\chi_\beta\rangle\Big]^{-1}\Big[\sum_\delta \langle\tilde\chi_\alpha|\tilde p_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde p_\gamma| \tag{2.30}$$

This expression works also if the number of local orbitals $|\chi_\alpha\rangle$ is smaller than the number of projector functions $\langle p_\gamma|$. Because of the inversion, this expression needs to be evaluated in reciprocal space.

2.5.2 Transformation between local-orbital and partial-wave projections

In the previous section we derived in Eq. 2.30 a relation between orbital and partial wave projector functions.

$$\langle\tilde\pi_\alpha|\tilde\psi_n\rangle = \sum_\beta M_{\alpha,\beta}\langle\tilde p_\alpha|\tilde\psi_n\rangle \tag{2.31}$$

This operation is performed in `lmto$projtontbo` with `ID='FWRD'`

The derivatives are correspondingly derived as

$$
\begin{aligned}
dE &= \sum_{\alpha,\beta} \underbrace{\frac{dE}{d\rho_{\alpha,\beta}}}_{=:h_{\beta,\alpha}} d\rho_{\alpha,\beta} \\
&= \sum_{\alpha,\beta} h_{\beta,\alpha} \Big[\sum_n \langle \pi_\alpha | d\psi_n \rangle f_n \langle \psi_n | \pi_\beta \rangle + \sum_n \langle \pi_\alpha | \psi_n \rangle f_n \langle d\psi_n | \pi_\beta \rangle \Big] \\
&= \sum_n \sum_\alpha f_n \underbrace{\sum_\beta \langle \psi_n | \pi_\beta \rangle h_{\beta,\alpha}}_{HTBC^\dagger_{n,\alpha}} \langle \pi_\alpha | d\psi_n \rangle + \sum_n \sum_\beta \langle d\psi_n | \pi_\beta \rangle \underbrace{\sum_\alpha h_{\beta,\alpha} \langle \pi_\alpha | \psi_n \rangle}_{HTBC_{\beta,n}} f_n \\
&= \sum_n \sum_\gamma f_n \underbrace{\sum_\alpha \underbrace{\sum_\beta \langle \psi_n | \pi_\beta \rangle h_{\beta,\alpha}}_{HTBC^\dagger_{n,\alpha}} M_{\alpha,\gamma}}_{HPROJ^\dagger_{n,\gamma}} \langle \tilde{p}_\gamma | d\tilde{\psi}_n \rangle \\
&+ \sum_n \sum_\gamma \langle d\tilde{\psi}_n | \tilde{p}_\gamma \rangle \underbrace{\sum_\beta M^\dagger_{\gamma,\beta} \underbrace{\sum_\alpha h_{\beta,\alpha} \langle \pi_\alpha | \psi_n \rangle}_{HTBC_{\beta,n}}}_{HPROJ_{\gamma,n}} f_n
\end{aligned}
\tag{2.32}
$$

Thus, we first define the Hamiltonian $\boldsymbol{h}$ (HAMIL)

$$
\begin{aligned}
\underbrace{h_{\alpha,\beta}}_{HAMIL} &= \frac{dE}{\rho_{\beta,\alpha}} \\
HTBC_{\beta,n} &= \sum_\alpha \underbrace{h_{\beta,\alpha}}_{HAMIL} \underbrace{\langle \tilde{\pi}_\alpha | \tilde{\psi}_n \rangle}_{TBC_{\alpha,n}} \\
HPROJ_{\gamma,n} &= \sum_\beta M^\dagger_{\gamma,\beta} \cdot HTBC_{\beta,n}
\end{aligned}
\tag{2.33}
$$

This operation is performed in `lmto$projtontbo` with `ID='BACK'`.

2.6 Core-valence exchange

The exchange term between core and valence electrons acts like a fixed, nonlocal potential acting on the electrons, of the form

$$
\hat{\tilde{v}}_{x,cv} = \sum_{\alpha,\beta} |\tilde{p}_\alpha\rangle M_{\alpha,\beta} \langle \tilde{p}_\beta| \tag{2.34}
$$

The core-valence exchange is furthermore diagonal in the site indices.

$$\begin{aligned}\langle\chi_\alpha|\hat{v}_{x,cv}|\chi_\beta\rangle &= \sum_{\gamma,\delta}\langle\chi_\alpha|p_\gamma\rangle M_{\gamma,\delta}\langle p_\delta|\chi_\beta\rangle \\ &= \sum_{\gamma,\delta}\langle\tilde{\phi}^K_\alpha|\tilde{p}_\gamma\rangle M_{\gamma,\delta}\langle\tilde{p}_\delta|\tilde{\phi}^K_\beta\rangle \\ &- \sum_{\gamma,\delta,\beta'}\langle\tilde{\phi}^K_\alpha|\tilde{p}_\gamma\rangle M_{\gamma,\delta}\langle\tilde{p}_\delta|\tilde{\phi}^{\bar{J}}_{\beta'}\rangle\bar{S}^\dagger_{\beta',\beta} \\ &- \sum_{\gamma,\delta,\alpha',\alpha}\bar{S}_{\alpha,\alpha'}\langle\tilde{\phi}^{\bar{J}}_{\alpha'}|\tilde{p}_\gamma\rangle M_{\gamma,\delta}\langle\tilde{p}_\delta|\tilde{\phi}^K_\beta\rangle \\ &+ \sum_{\gamma,\delta,\alpha',\alpha}\bar{S}_{\alpha,\alpha'}\langle\tilde{\phi}^{\bar{J}}_{\alpha'}|\tilde{p}_\gamma\rangle M_{\gamma,\delta}\langle\tilde{p}_\delta|\tilde{\phi}^{\bar{J}}_{\beta'}\rangle\bar{S}^\dagger_{\beta',\beta}\end{aligned} \tag{2.35}$$

Here we used the augmented Hankel and screened Bessel fucntions, respectively their pseudo versions.

As usual we build the expanded density matrix

$$\begin{pmatrix} \boldsymbol{\rho} & -\boldsymbol{\rho}\bar{\boldsymbol{S}}^\dagger \\ -\bar{\boldsymbol{S}}\boldsymbol{\rho} & \bar{\boldsymbol{S}}\boldsymbol{\rho}\bar{\boldsymbol{S}}^\dagger \end{pmatrix} \tag{2.36}$$

The matrix

$$\begin{pmatrix} \langle\tilde{\phi}^K|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^K\rangle & \langle\tilde{\phi}^K|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^{\bar{J}}\rangle \\ \langle\tilde{\phi}^{\bar{J}}|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^K\rangle & \langle\tilde{\phi}^{\bar{J}}|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^{\bar{J}}\rangle \end{pmatrix} \tag{2.37}$$

is calculated first using `potpar1(isp)%prok` and `potpar1(isp)%projbar`. [4]

[4] In the earlier version the contribution from the $\dot{\bar{\phi}}$ has been ignored!!! It has been verified by temporarily switching off the jbar contributiuon to potpar1(isp)%prok and potpar1(isp)%projbar. In this old version only potpar(isp)%ktophi is used to extract the ϕ contribution.

Chapter 3

Description of Subroutines

3.1 Workflow

```
---initialization-----
POTPAR = potential parameters
SBAR = screened structureconstants
<ptilde|chitilde>
tailed partial waves
  overlap (Onsite)
  utensor (Onsite)
  utensor (offsite)
...
----cycle-----------
TBC=<pi-tilde|psi> from PROJ=<ptilde|psitide>
DENMAT density matrix in local orbitals
...
total energy and derivatives
HAMIL hamiltonian matrix in tight-binding orbitals
...
HTBC = de/dtbc * 1/f
HPROJ = de/dproj * 1/f
```

3.2 LMTO$CLUSTERSTRUCTURECONSTANTS

LMTO\$CLUSTERSTRUCTURECONSTANTS calculates the screened structure constants SBAR ($\bar{\boldsymbol{S}}$) for a cluster of NAT atomic sites RPOS, of which the first site is called the central site of the cluster. The number of angular momenta on each site is defined by LX. The screening is defined by the vector QBAR ($\bar{Q}$). K2 ($\vec{k}^2 = -\kappa^2$) is the squared wave vector. (For envelope functions that fall off exponentially, this parameter is negative.)

```
SUBROUTINE LMTO$CLUSTERSTRUCTURECONSTANTS(K2,NAT,RPOS,LX,QBAR,NORB,N,SBAR)
REAL(8)   ,INTENT(IN) :: K2
INTEGER(4),INTENT(IN) :: NAT         ! NUMBER OF ATOMS ON THE CLUSTER
```

```
REAL(8)    ,INTENT(IN) :: RPOS(3,NAT) ! ATOMIC POSITIONS ON THE CLUSTER
INTEGER(4),INTENT(IN) :: LX(NAT)     ! X(ANGULAR MOMENTUM ON EACH CLUSTER)
INTEGER(4),INTENT(IN) :: N
REAL(8)    ,INTENT(IN) :: QBAR(N)
INTEGER(4),INTENT(IN) :: NORB
REAL(8)    ,INTENT(INOUT):: SBAR(NORB,N)
```

First, the bare structure constants are evaluates on the cluster using `LMTO\$STRUCTURECONSTANTS` and then the structure constants are screened using `LMTO\$SCREEN`.

3.2.1 LMTO$STRUCTURECONSTANTS

`LMTO\$STRUCTURECONSTANTS` calculates the bare structure constants for a pair of sites. The first site is at the origin, where the Hankel function is centered, and the second site at $\vec{R}$ specified by `R21`, is the center of the expansion into solid Bessel functions.

```
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

$$S_{RL,R'L'} \overset{\text{Eq. 2.6}}{=} (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}'-\vec{R}) \begin{cases} (-ik)^{\ell+\ell'-\ell''} & \text{for } k^2 > 0 \\ \delta_{\ell+\ell'-\ell''} & \text{for } k^2 = 0 \\ \kappa^{\ell+\ell'-\ell''} & \text{for } k^2 = -\kappa^2 < 0 \end{cases} \tag{3.1}$$

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 Helmholtz equation, Eq. 2.2.[1]

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

Remark: Because the Gaunt coefficients vanish for odd $\ell + \ell' - \ell''$, the structure constants are real even for $k^2 > 0$.

3.2.2 LMTO$SCREEN

I describe here what has been implemented as "version 3".

`LMTO$SCREEN` takes the bare structure constants $S_{RL,R'L'}$ connecting all orbitals on a specific cluster with each other and the screening constants $\bar{Q}$ for all orbitals on the cluster. It returns the screened structure constants connecting the orbitals on the central (first) site (1st index) with all orbitals (2nd index).

The structure constants are defined so that

$$\langle K_{RL}| = -\sum_{L'} S_{RL,R'L'} \langle J_{R'L'}| \qquad \text{for } R' \neq R \tag{3.2}$$

[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.*

First we evaluate

$$\boldsymbol{A} = \boldsymbol{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger \tag{3.3}$$

and the vectors $\vec{e}_\alpha$ defined by $(\vec{e}_\alpha)_\beta = \delta_{\beta,\alpha}$. Note that the number of vectors corresponds to the number of orbitals on the central site only. Therefore, these vectors do not build up a complete unit matrix.

Then we solve the equation system

$$\boldsymbol{A}\vec{c}_\alpha \overset{\text{Eq. 2.21}}{=} \vec{e}_\alpha \tag{3.4}$$

for $\vec{c}_\alpha$ and

$$\vec{s}_\alpha \overset{\text{Eq. 2.21}}{=} \boldsymbol{S}^\dagger\vec{c}_\alpha \tag{3.5}$$

$\left(\vec{s}_\alpha\right)_\beta = \bar{S}^\dagger_{\beta,\alpha}$ contains the transposed screened structure constants. After transposition, $\bar{S}$ is returned.

3.3 Waves object

The data exchange betweeen the waves object and the lmto object is determined by the local-orbital projections $\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle$ specified by the array THIS%TBC, which in turn is obtained from the partial-wave projections $\langle\tilde{p}|\tilde{\psi}_n\rangle$.

In waves$etot

```
CALL WAVES$TONTBO
-> CALL LMTO$PROJTONTBO('FWRD'...)
..
..
CALL LMTO$ETOT(LMNXX,NDIMD,NAT,DENMAT)
..
..
CALL WAVES$FROMNTBO()
-> CALL LMTO$PROJTONTBO('BACK'...)
..
..
CALL WAVES$FORCE
-> CALL WAVES_FORCE_ADDHTBC
...
CALL WAVES$HPSI
```

$$\begin{aligned}
\vec{F} &= -\sum_\alpha \frac{dE}{d\langle\tilde{p}_\alpha|\psi_n\rangle}\langle\vec{\nabla}_R\tilde{p}_\alpha|\psi_n\rangle + \text{c.c.} \\
&= -\sum_{\alpha,\beta} \frac{dE}{d\langle\tilde{\pi}_\beta|\psi_n\rangle}\frac{d\langle\tilde{\pi}_\beta|\psi_n\rangle}{d\langle\tilde{p}_\alpha|\psi_n\rangle}\langle\vec{\nabla}_R\tilde{p}_\alpha|\psi_n\rangle + \text{c.c.} \\
&= -\sum_{\alpha,\beta} \frac{dE}{d\langle\tilde{\pi}_\beta|\psi_n\rangle}\frac{d\langle\tilde{\pi}_\beta|\psi_n\rangle}{d\langle\tilde{p}_\alpha|\psi_n\rangle}\left[-\langle\vec{\nabla}_r\tilde{p}_\alpha|\psi_n\rangle\right] + \text{c.c.}
\end{aligned}$$

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.

A.1 Bare structure constants

This section is copied from Methods-book, Section "Working with spherical Hankel and Bessel functions", Peter Blöchl, private communication.

The bare structure constants have been determined first by Segall[2]. He uses the theorem[3] that supposedy goes back to Kasterin (N. Kasterin, Proc. Acad. Sci Amsterdam 6, 460 (1897/98)); see Seegall[2], Eq. B4)

$$h^{(1)}_\ell(\kappa r)Y_{\ell,m}(\vec r) = i^{-\ell}\mathcal{Y}_{\ell,m}(\vec\nabla_r)h^{(1)}_0(\kappa r) \tag{A.7}$$

where $h^{(1)}_\ell(x)$ i the spherical Hankel function of the first kind (see Eq. A.13 below) and where (Eq. B5 of Segall[2])

$$\mathcal{Y}_{\ell,m}(\vec\nabla) = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\left(\frac{1}{ik}\right)^{|m|}\Big(\partial_x \pm i\partial_y\Big)\mathcal{P}^{|m|}_\ell\left(\frac{1}{ik}\partial_z\right) \tag{A.8}$$

where the positive sign applies for nonzero m and the negative sign for negative m. Furthermore (see Segall[2] Eq. B5)

$$\mathcal{P}^{|m|}_\ell(z) = \frac{d^{|m|}P_\ell(z)}{dz^{|m|}}$$

where $P_\ell(z)$ is the conventional Legendre polynomial.

In addition Segall[2] refers in his Eq. B7 to Morse and Feshbach[4] (part II, p. 1574) for

$$h^{(1)}_0(\kappa|\vec r-\vec r'|) = 4\pi\sum_L\Big(h^{(1)}_\ell(\kappa|\vec r'|)Y_L(\vec r')\Big)j_\ell(\kappa|\vec r|)Y^*_L(\vec r) \tag{A.9}$$

which is valid for $|\vec r'| > |\vec r|$.

The two equations, Eq. A.7 and Eq. A.9, can be combined into

$$\begin{aligned}
h^{(1)}_\ell(\kappa|\vec r|)Y_{\ell,m}(\vec r) &\overset{\text{Eq. }A.7}{=} i^{-\ell}\mathcal{Y}_{\ell,m}(\vec\nabla_r)h^{(1)}_0(\kappa|\vec r|)\\
&= i^{-\ell}\mathcal{Y}_{\ell,m}(\vec\nabla_r)h^{(1)}_0(\kappa|(\vec r-\vec R)+\vec R|)\\
&\overset{\text{Eq. }A.9}{=} i^{-\ell}\mathcal{Y}_{\ell,m}(\vec\nabla_r)\left[4\pi\sum_{L'}\Big(h^{(1)}_{\ell'}(\kappa|\vec R|)Y_{L'}(-\vec R)\Big)j_{\ell'}(\kappa|\vec r-\vec R|)Y^*_{L'}(\vec r-\vec R)\right]\\
&\overset{\text{Eq. }A.11}{=} 4\pi\sum_{L'}\Big(i^{-\ell}\mathcal{Y}_{\ell,m}(\vec\nabla_R)h^{(1)}_{\ell'}(\kappa|\vec R|)Y_{L'}(-\vec R)\Big)j_{\ell'}(\kappa|\vec r-\vec R|)Y^*_{L'}(\vec r-\vec R)
\end{aligned}$$

Here we used that

$$\vec\nabla_r\big[f(\vec R)g(\vec r-\vec R)\big]=f(\vec R)\vec\nabla_r g(\vec r-\vec R)=-f(\vec R)\vec\nabla_R g(\vec r-\vec R) \quad (A.10)$$

$$=\underbrace{-\vec\nabla_R\overbrace{\big[f(\vec R)g(\vec r-\vec R)\big]}^{h(\vec r)}}_{=0}+\Big[\vec\nabla_R f(\vec R)\Big]g(\vec r-\vec R)\big] \quad (A.11)$$

We summarize the final result

CONDITION FOR STRUCTURE CONSTANTS (POSITIVE ENERGIES)

$$h^{(1)}_\ell(\kappa|\vec r|)Y_{\ell,m}(\vec r)=4\pi\sum_{L'}\Big(i^{-\ell}\mathcal{Y}_{\ell,m}(\vec\nabla_R)h^{(1)}_{\ell'}(\kappa|\vec R|)Y_{L'}(-\vec R)\Big)j_{\ell'}(\kappa|\vec r-\vec R|)Y^*_{L'}(\vec r-\vec R) \quad (A.12)$$

where $h^{(1)}(x)$ is the spherical Hankel function of the first kind defined in Abramowitz and Stegun (AS)[**?**]

$$h^{(1)}_\ell(x)\overset{AS10.1.1}{=}j_\ell(x)+iy_\ell(x)\overset{AS10.1.26}{=}x^\ell\Big(-\frac{1}{x}\partial_x\Big)^\ell\frac{\sin(x)-i\cos(x)}{x} \quad (A.13)$$

Expression for the structure constants

By comparing our notation to that of Daniel Grieger and using his expression for the Structure constants, we arrive at the following expression for the structure constants in our notation.

There was a misunderstanding with the sign of the structure constants. Here I follow the signconvention $K=-\sum JS$, which is opposite to the one I and Daniel had earlier.

$$S_{R',L',R,L}=-4\pi\sum_{L''}H^B_{L''}(\vec R'-\vec R)C_{L,L'',L}\left\{\begin{matrix}(-1)^{\ell'}(-ik)^{\ell+\ell'-\ell''}\\ (-1)^{\ell'}\delta_{\ell+\ell',\ell''}\\ (-1)^{\ell'}\kappa^{\ell+\ell'-\ell''}\end{matrix}\right\} \quad (A.14)$$

A.2 Consistency checks

We consider the case with $\kappa=0$, for which the solid Bessel and Hankel functions are

$$K^\infty_{\vec 0,L}(\vec r)=(2\ell-1)!!\frac{1}{|\vec r|^{\ell+1}}Y_L(\vec r) \quad (A.15)$$

$$J_{\vec 0,L}(\vec r)=\frac{1}{(2\ell+1)!!}|\vec r|^\ell Y_L(\vec r) \quad (A.16)$$

The explicit form of the first few is

$$K^{\infty}_{\vec{0},s}(\vec{r}) = \frac{1}{\sqrt{4\pi}}\frac{1}{|\vec{r}|} \tag{A.17}$$

$$K^{\infty}_{\vec{0},p_x}(\vec{r}) = \sqrt{\frac{3}{4\pi}}\frac{x}{|\vec{r}|^3} \tag{A.18}$$

$$J_{\vec{0},s}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \tag{A.19}$$

$$J_{\vec{0},p_x}(\vec{r}) = \frac{1}{3}\sqrt{\frac{3}{4\pi}}x \tag{A.20}$$

Now we extract the structure constants from the off-site expansion

$$\begin{aligned} K^{\infty}_{\vec{0},s}(\vec{r}) = &-S_{\vec{0},s;\vec{R},s}J_s(\vec{r}-\vec{R}) \\ &-S_{\vec{0},s;\vec{R},p_x}J_{p_x}(\vec{r}-\vec{R}) - S_{\vec{0},s;\vec{R},p_y}J_{p_y}(\vec{r}-\vec{R}) - S_{\vec{0},s;\vec{R},p_z}J_{p_z}(\vec{r}-\vec{R}) \end{aligned} \tag{A.21}$$

which allows us to evaluate the structure constants directly calculating value and derivatives at the second center and by exploiting selection rules[1]

$$K^{\infty}_{\vec{0},s}(\vec{R}) = \frac{1}{\sqrt{4\pi}}\frac{1}{|\vec{R}|} = -\underbrace{\left(-\frac{1}{|\vec{R}|}\right)}_{S_{\vec{0},s,\vec{R},s}}\underbrace{\frac{1}{\sqrt{4\pi}}}_{J_{\vec{R},s}(\vec{R})} \tag{A.22}$$

$$\partial_x|_{\vec{R}}\,K^{\infty}_{\vec{0},s} = -\frac{1}{\sqrt{4\pi}}\frac{X}{|\vec{R}|^3} = -\underbrace{\sqrt{3}\frac{X}{|\vec{R}|^3}}_{S_{\vec{0},s;\vec{R},px}}\underbrace{\frac{1}{3}\sqrt{\frac{3}{4\pi}}}_{\partial_x J_{\vec{R},px}(\vec{R})} \tag{A.23}$$

$$K_{\vec{0},p_x}(\vec{R}) = \sqrt{\frac{3}{4\pi}}\frac{X}{|\vec{R}|^3} = -\underbrace{\left(-\sqrt{3}\frac{X}{|\vec{R}|^3}\right)}_{S_{\vec{0},px;\vec{R},s}}\underbrace{\frac{1}{\sqrt{4\pi}}}_{J_{\vec{R},s}(\vec{R})}$$

$$\partial_x|_{\vec{R}}\,K^{\infty}_{\vec{0},p_x} = \sqrt{\frac{3}{4\pi}}\left(\frac{1}{|\vec{R}|^3} - 3\frac{X^2}{|\vec{R}|^5}\right) = -\underbrace{3\frac{3X^2-\vec{R}^2}{|\vec{R}|^2}}_{S_{\vec{0},px,\vec{R},px}}\underbrace{\frac{1}{3}\sqrt{\frac{3}{4\pi}}|\vec{R}|^{-3}}_{\partial_x|_{\vec{R}}J_{\vec{R},px}} \tag{A.24}$$

Thus, the matrix of structure constants in the (s,p$_x$) subspace is

$$\boldsymbol{S}_{\vec{0},\vec{R}} = \begin{pmatrix} -|\vec{R}|^{-1} & \sqrt{3}X/|\vec{R}|^3 \\ -\sqrt{3}X/|\vec{R}|^3 & 3[3X^2/R^2-1] \end{pmatrix} \tag{A.25}$$

We compare this result now for the one obtained from the direct formula for $\kappa = 0$. These structure constants have the form

$$S_{RL,R'L'} = (-1)^{\ell'+1}4\pi\sum_{L''}C_{L,L',L''}H_{L''}(\vec{R}'-\vec{R})\delta^{\ell+\ell'-\ell''} \tag{A.26}$$

[1]Only an s-function has a finite value at the origin, only a p-function has a finite first derivative at the center, etc.

The structure constants obtained from this equation are

$$S_{\vec{0},s;\vec{R},s} = (-1)4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{sss}} \cdot \underbrace{\frac{1}{\sqrt{4\pi}} \frac{1}{|\vec{R}|}}_{H_s(\vec{R})} = -\frac{1}{|\vec{R}|}$$

$$S_{\vec{0},s;\vec{R},p_x} = 4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,p_x}} \underbrace{\sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3}}_{H_{p_x}(\vec{R})} = \sqrt{3}\frac{X}{|\vec{R}|^3}$$

$$S_{\vec{0},p_x;\vec{R},s} = (-1)4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,s}} \sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3} = -\sqrt{3}\frac{X}{|\vec{R}|^3}$$

$$S_{\vec{0},p_x;\vec{R},p_x} = 4\pi \underbrace{\frac{1}{\sqrt{5\pi}}}_{C_{p_x,p_x,d_{3x^2-r^2}}} \underbrace{\overbrace{\sqrt{\frac{5}{16\pi}} \frac{3X^2-R^2}{|\vec{R}|^2}}^{Y_{3x^2-r^2}} \frac{3}{|\vec{R}|^3}}_{H_{3x^2-r^2}(\vec{R})} = 3\frac{3X^2-R^2}{|R^5|} \tag{A.27}$$

For Gaunt coefficients see footnote.[2]

[2]

$$Y_{p_x}Y_{p_x} = \frac{3}{4\pi}\frac{x^2}{r^2} = \frac{1}{4\pi}\frac{x^2}{r^2} + \frac{1}{4\pi}\frac{3x^2-r^2}{r^2} = \frac{1}{\sqrt{4\pi}}Y_s + \frac{1}{4\pi}\sqrt{\frac{16\pi}{5}}Y_{3x^2-r^2} = \frac{1}{\sqrt{4\pi}}Y_s + \sqrt{\frac{1}{5\pi}}Y_{3x^2-r^2}$$

$$\Rightarrow C_{p_x,p_x,s} = \frac{1}{\sqrt{4\pi}} \quad \text{and} \quad C_{p_x,p_x,d_{3x^2-r^2}} = \frac{1}{\sqrt{5\pi}} \tag{A.28}$$

Appendix B

Bloch theorem revisited

The Bloch states are eigenstates of the discrete lattice translation

$$\hat{S}(\vec{t}) = \int d^3r \; |\vec{r} + \vec{t}\rangle\langle\vec{r}| \tag{B.1}$$

for the discrete lattice vectors $\vec{t}$. The eigenvalue equation has the form

$$\hat{S}(\vec{t})|\psi_{\vec{k}}\rangle = |\psi_{\vec{k}}\rangle e^{i\vec{k}\vec{r}} \tag{B.2}$$

This eigenvalue equation can be recast into the form

$$\langle\vec{r} - \vec{t}|\psi_{\vec{k}}\rangle = \langle\vec{r}|\psi_{\vec{k}}\rangle e^{i\vec{k}\vec{t}} \tag{B.3}$$

This implies that the states can be written as product of a periodic function and a phase factor

$$\langle\vec{r}|\psi_{\vec{k}}\rangle = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}} \tag{B.4}$$

with

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{t}) \tag{B.5}$$

Bloch theorem in a local orbital basis

With $q_\alpha \stackrel{\text{def}}{=} \langle\pi_\alpha|\psi\rangle$, we obtain

$$\begin{aligned}
\hat{S}(\vec{t}) \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} &= \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\int d^3r \; |\vec{r} + \vec{t}\rangle\langle\vec{r}| \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} &= \int d^3r \; |\vec{r}\rangle\langle\vec{r}| \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\sum_\alpha \langle\vec{r} - \vec{t}|\chi_\alpha\rangle q_{\alpha,n} &= \sum_\alpha \langle\vec{r}|\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\sum_\alpha \langle\vec{r}|\chi_{\alpha+\vec{t}}\rangle q_{\alpha,n} &= \sum_\alpha \langle\vec{r}|\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\sum_{\alpha'} \langle\vec{r}|\chi_{\alpha'}\rangle q_{\alpha'-\vec{t},n} &= \sum_\alpha \langle\vec{r}|\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
q_{\alpha+\vec{t},n} &= q_{\alpha,n} e^{-i\vec{k}_n\vec{t}}
\end{aligned} \tag{B.6}$$

Density matrix

$$\rho_{\alpha,\beta+\vec{t}} = \sum_n \langle \pi_\alpha | \psi_n \rangle f_n \langle \psi_n | \pi_\beta \rangle \mathrm{e}^{+i\vec{k}_n \vec{t}} \tag{B.7}$$

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.

[2] B. Segall. Calculation of the band structure of "complex" crystals. Phys. Rev., 105:108, 1957.

[3] J. Korringa. On the calculation of the energy of a bloch wave in a metal. Physica, 13:392, 1947.

[4] P. M. Morse and H. Feshbach. Methods of Theoretical Physics. McGraw-Hill, NY, 1953.