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.

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 Structure constants

The concept of linear augmented waves is as follows:

1. At first a so-called envelope function is defined.
2. In a second step this envelope function is expanded about each atomic site into spherical harmonics.
3. In the third step the spherical-harmonics contributions are replaced differentially at some sphere radius by partial waves of the atomic potential.

2.1.1 Envelope functions

The envelope functions used here are solid Hankel functions, defined by the inhomogeneous Helmholtz equation

$$\left[\vec{\nabla}^2 + k^2\right] H_L(\vec{r}) = -4\pi(-1)^\ell \mathcal{Y}(\vec{\nabla})\delta(\vec{r}) \tag{2.1}$$

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.

2.1.2 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** $|J^{\Omega}_{\beta}\rangle$.

$$|K^{\infty}_{\alpha}\rangle = |K^{\Omega}_{\alpha}\rangle - \sum_{\beta} |J^{\Omega}_{\beta}\rangle S^{\dagger}_{\beta,\alpha} + |K^{I}_{\alpha}\rangle \tag{2.2}$$

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 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.

In the following we will call $|K^{\Omega}_{\alpha}\rangle$ **head function** and $|J^{\Omega}_{\beta}\rangle$ **tail functions**.

2.1.3 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

$$|\dot{\bar{\phi}}_{\alpha}\rangle \rightarrow |\bar{J}^{\Omega}_{\alpha}\rangle \stackrel{\text{def}}{=} |\bar{J}^{\Omega}_{\alpha}\rangle - |\bar{K}^{\Omega}_{\alpha}\rangle \bar{Q}_{\alpha} \tag{2.3}$$

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

$$|\bar{K}^{\infty}_{\alpha}\rangle = \sum_{\beta} |K^{\infty}_{\beta}\rangle c_{\beta,\alpha} \tag{2.4}$$

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

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

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

By equating the two expressiones for the screened Hankel functions, namely Eq. 2.4 and Eq. 2.5, we can extract the screened structure constants and the superposition coeffcients.

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

$$\sum_{\beta} |K^{\Omega}_{\beta}\rangle c_{\beta,\alpha} - \sum_{\beta,\gamma} |J^{\Omega}_{\gamma}\rangle S^{\dagger}_{\gamma,\beta} c_{\beta,\alpha} = \sum_{\beta} |K^{\Omega}_{\beta}\rangle \Big[\delta_{\beta,\alpha} + \bar{Q}_{\beta} \bar{S}^{\dagger}_{\beta,\alpha}\Big] - \sum_{\beta} |J^{\Omega}_{\beta}\rangle \bar{S}^{\dagger}_{\beta,\alpha} \tag{2.6}$$

By comparing the coefficients, we obtain

$$c_{\beta,\alpha} = \delta_{\beta,\alpha} + \bar{Q}_{\beta} \bar{S}^{\dagger}_{\beta,\alpha} \tag{2.7}$$

$$\bar{S}^{\dagger}_{\gamma,\alpha} = \sum_{\beta} S^{\dagger}_{\gamma,\beta} c_{\beta,\alpha} \tag{2.8}$$

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

SCREENED STRUCTURE CONSTANTS

$$\bar{\boldsymbol{S}}^{\dagger} = \boldsymbol{S}^{\dagger}\left[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}\right]^{-1} \tag{2.10}$$

and the expression of the screened Hankel functions

$$|\bar{K}^{\infty}_{\alpha}\rangle = \sum_{\beta} |K^{\infty}_{\beta}\rangle\left[\delta_{\beta,\alpha} + \bar{Q}_{\beta}\bar{S}^{\dagger}_{\beta,\alpha}\right] . \tag{2.11}$$

2.2 Calculate screened structure constants on 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. 2.8 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

$$\vec{c}_{\alpha} \overset{\text{Eq. } 2.7}{=} \vec{e}_{\alpha} + \bar{\boldsymbol{Q}}\vec{s}_{\alpha} \tag{2.12}$$

$$\vec{s}_{\alpha} \overset{\text{Eq. } 2.8}{=} \boldsymbol{S}^{\dagger}\vec{c}_{\alpha} \tag{2.13}$$

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

$$\begin{aligned} \left(\vec{c}_{\alpha}\right)_{\beta} &= c_{\beta,\alpha} \\ \left(\vec{s}_{\alpha}\right)_{\beta} &= \bar{S}^{\dagger}_{\beta,\alpha} \\ \left(\vec{e}_{\alpha}\right)_{\beta} &= \delta_{\beta,\alpha} \end{aligned} \tag{2.14}$$

$$\begin{aligned} & & \vec{c}_{\alpha} &\overset{\text{Eq. } 2.12}{=} \vec{e}_{\alpha} + \bar{\boldsymbol{Q}}\vec{s}_{\alpha} \overset{\text{Eq. } 2.13}{=} \vec{e}_{\alpha} + \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}\vec{c}_{\alpha} \\ \Rightarrow \quad & \left[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}\right]\vec{c}_{\alpha} &&= \vec{e}_{\alpha} \\ & \Rightarrow \quad \vec{c}_{\alpha} &&= [\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}]^{-1}\vec{e}_{\alpha} \\ & & \vec{s}_{\alpha} &\overset{\text{Eq. } 2.13}{=} \boldsymbol{S}^{\dagger}\vec{c}_{\alpha} = \boldsymbol{S}^{\dagger}[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}]^{-1}\vec{e}_{\alpha} \end{aligned} \tag{2.15}$$

[1]

$$\begin{aligned} \boldsymbol{c} = \mathbf{1} + \bar{\boldsymbol{Q}}\bar{\boldsymbol{S}}^{\dagger} = \mathbf{1} + \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}\boldsymbol{c} \quad &\Rightarrow \quad \sum_{\gamma}\left[\delta_{\beta,\gamma} - \bar{Q}_{\beta}S^{\dagger}_{\beta,\gamma}\right]c_{\gamma,\alpha} = \delta_{\beta,\alpha} \quad \Rightarrow \quad \boldsymbol{c} = [\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}]^{-1} \\ \bar{\boldsymbol{S}}^{\dagger} = \boldsymbol{S}^{\dagger}\boldsymbol{c} = \boldsymbol{S}^{\dagger}[\mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger}]^{-1} \quad &\Leftrightarrow \quad [\mathbf{1} - \boldsymbol{S}\bar{\boldsymbol{Q}}]\bar{\boldsymbol{S}} = \boldsymbol{S} \end{aligned} \tag{2.9}$$

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

$$\begin{aligned}[\mathbf{1}-\bar{\boldsymbol{Q}}\boldsymbol{S}^\dagger]\vec{c}_\alpha &= \vec{e}_\alpha \\ \vec{s}_\alpha &= \boldsymbol{S}^\dagger\vec{c}_\alpha \end{aligned} \tag{2.16}$$

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

$$\bar{S}^\dagger_{\gamma,\alpha} = \Big(\vec{s}_\alpha\Big)_\gamma \tag{2.17}$$

2.3 Augmentation and Potential parameters

2.3.1 Local orbitals

The local orbitals have the form

$$\begin{aligned}|\chi_\alpha\rangle = |\phi^K_\alpha\rangle &- |\phi^{\bar{J}}_{R,L}\rangle \bar{S}^\dagger_{R,L,R_\alpha,L_\alpha} \\ &+ |K^I_{R',L'}\rangle\Big[\delta_{R',L',R_{\alpha,\alpha}} - \bar{Q}_{R',L'}\bar{S}^\dagger_{R',L',R_\alpha,L_\alpha}\Big]\end{aligned} \tag{2.18}$$

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

$$\begin{aligned}|\phi^K_\alpha\rangle &= \overbrace{|\phi_\alpha\rangle \underbrace{\frac{W_\alpha[K,\dot{\bar{\phi}}]}{W_\alpha[\phi,\dot{\bar{\phi}}]}}_{Ktophi} - |\dot{\bar{\phi}}_\alpha\rangle \underbrace{\frac{W_\alpha[K,\phi]}{W_\alpha[\phi,\dot{\bar{\phi}}]}}_{-Ktophidot}}^{\rightarrow|K^\Omega_\alpha\rangle} \\ |\phi^{\bar{J}}_{R,L}\rangle &= \overbrace{|\dot{\bar{\phi}}_\beta\rangle \underbrace{\left(-\frac{W_\beta[\bar{J},\phi]}{W_\beta[\phi,\dot{\bar{\phi}}]}\right)}_{JBARtophidot}}^{\rightarrow|\bar{J}^\Omega_\beta\rangle}\end{aligned} \tag{2.19}$$

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

$$\begin{aligned}\langle\tilde{p}_\gamma|\tilde{\chi}_\alpha\rangle &= \langle\tilde{p}_\gamma|\tilde{\phi}^K_\alpha\rangle - \sum_{R',L'}\langle\tilde{p}_\gamma|\tilde{\phi}^{\bar{J}}_{R',L'}\rangle\bar{S}^\dagger_{R,L,R_\alpha,L_\alpha} \\ &= \langle\tilde{p}_\gamma|\tilde{\phi}^K_\alpha\rangle - \langle\tilde{p}_\gamma|\tilde{\phi}^{\bar{J}}_{R_\gamma,L_\gamma}\rangle\bar{S}^\dagger_{R_\gamma,L_\gamma,R_\alpha,L_\alpha}\end{aligned} \tag{2.20}$$

2.4 Coefficients of the tight-binding orbital

2.4.1 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

$$|\psi_n'\rangle = \sum_\alpha |\chi_\alpha\rangle q_\alpha \ , \tag{2.21}$$

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.

$$\begin{aligned} Q[\vec{q}] &:= \Big(\langle\tilde{\psi}_n| - \sum_\alpha q_\alpha^*\langle\tilde{\chi}_\alpha|\Big)\Big[\sum_{\delta,\gamma} |\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\langle\tilde{p}_\gamma|\Big]\Big(|\tilde{\psi}_n\rangle - \sum_\beta |\tilde{\chi}_\beta\rangle q_\beta\Big) \\ &= \sum_\gamma \Big[\sum_\delta \Big(\langle\tilde{\psi}_n|\tilde{p}_\delta\rangle - \sum_\alpha q_\alpha^*\langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\Big)\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\Big(\langle\tilde{p}_\gamma|\tilde{\psi}_n\rangle - \sum_\beta \langle\tilde{p}_\gamma|\tilde{\chi}_\beta\rangle q_\beta\Big) \end{aligned} \tag{2.22}$$

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

Minimization yields

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

$$\Rightarrow \qquad \sum_\gamma \Big[\sum_\delta \langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde{p}_\gamma|\tilde{\psi}_n\rangle = \sum_{\gamma,\beta}\Big[\sum_\delta \langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde{p}_\gamma|\tilde{\chi}_\beta\rangle q_\beta\Big)$$

$$\Rightarrow \qquad q_\beta = \sum_\beta \Big[\sum_{\gamma',\delta'} \langle\tilde{\chi}_\alpha|\tilde{p}_{\delta'}\rangle\langle\phi_{\delta'}|\theta_{\Omega_{R_\delta}}|\phi_{\gamma'}\rangle\langle\tilde{p}_{\gamma'}|\tilde{\chi}_\beta\rangle\Big]^{-1}\Big[\sum_{\gamma\delta} \langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde{p}_\gamma|\tilde{\psi}_n\rangle \tag{2.23}$$

This allows one to write the wave function in the form

$$|\psi_n\rangle \approx \sum_\alpha |\chi_\alpha\rangle\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle \tag{2.24}$$

with

$$\langle\tilde{\pi}_\alpha| = \sum_\gamma \Big[\sum_{\gamma',\delta'} \langle\tilde{\chi}_\alpha|\tilde{p}_{\delta'}\rangle\langle\phi_{\delta'}|\theta_{\Omega_{R_\delta}}|\phi_{\gamma'}\rangle\langle\tilde{p}_{\gamma'}|\tilde{\chi}_\beta\rangle\Big]^{-1}\Big[\sum_\delta \langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde{p}_\gamma| \tag{2.25}$$

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.

2.4.2 Transformation between local-orbital and partial-wave projections

In the previous section we derived in Eq. 2.25 a relation between orbital and partial wave projector functions.

$$\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle = \sum_\beta M_{\alpha,\beta}\langle\tilde{p}_\alpha|\tilde{\psi}_n\rangle \tag{2.26}$$

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

The derivatives are correspondingly derived as

$$\begin{aligned} dE &= \sum_{\alpha,n} \frac{\partial E}{\partial\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle} d\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle \\ &= \sum_{\alpha,\beta,n} \frac{\partial E}{\partial\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle} M_{\alpha,\beta}\, d\langle\tilde{p}_\alpha|\tilde{\psi}_n\rangle \\ &= \sum_{\beta,n}\left[\frac{1}{f_n}\sum_\alpha \frac{\partial E}{\partial\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle} M_{\alpha,\beta}\right] d\Big(\langle\tilde{p}_\alpha|\tilde{\psi}_n\rangle f_n\Big) \end{aligned} \tag{2.27}$$

Note, that the treatment of the occupations in the last step is only possible, because wave function and occupations always enter in a particular combination. **Note that f does not enter linearly. is the assumption used still correct?**

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

2.4.3 From local-orbital coefficients to the density matrix

Bloch theorem revisited

The Bloch states are eigenstates of the discrete lattice translation

$$\hat{S}(\vec{t}) = \int d^3r\ |\vec{r}+\vec{t}\rangle\langle\vec{r}| \tag{2.28}$$

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

$$\hat{S}(\vec{t})|\psi_{\vec{k}}\rangle = |\psi_{\vec{k}}\rangle e^{i\vec{k}\vec{r}} \tag{2.29}$$

This eigenvalue equation can be recast into the form

$$\langle\vec{r}-\vec{t}|\psi_{\vec{k}}\rangle = \langle\vec{r}|\psi_{\vec{k}}\rangle e^{i\vec{k}\vec{t}} \tag{2.30}$$

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

$$\langle\vec{r}|\psi_{\vec{k}}\rangle = u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}} \tag{2.31}$$

with

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{t}) \tag{2.32}$$

Bloch theorem in a local orbital basis

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

$$\begin{aligned}
\hat{S}(\vec{t}) \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} &= \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\int d^3r\ |\vec{r}+\vec{t}\rangle\langle\vec{r}| \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} &= \int d^3r\ |\vec{r}\rangle\langle\vec{r}| \sum_\alpha |\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\sum_\alpha \langle\vec{r}-\vec{t}|\chi_\alpha\rangle q_{\alpha,n} &= \sum_\alpha \langle\vec{r}|\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\sum_\alpha \langle\vec{r}|\chi_{\alpha+\vec{t}}\rangle q_{\alpha,n} &= \sum_\alpha \langle\vec{r}|\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
\sum_{\alpha'} \langle\vec{r}|\chi_{\alpha'}\rangle q_{\alpha'-\vec{t},n} &= \sum_\alpha \langle\vec{r}|\chi_\alpha\rangle q_{\alpha,n} e^{i\vec{k}_n\vec{t}} \\
q_{\alpha+\vec{t},n} &= q_{\alpha,n} e^{-i\vec{k}_n\vec{t}}
\end{aligned} \tag{2.33}$$

Density matrix

$$\rho_{\alpha,\beta+\vec{t}} = \sum_n \langle\pi_\alpha|\psi_n\rangle f_n \langle\psi_n|\pi_\beta\rangle e^{+i\vec{k}_n\vec{t}} \tag{2.34}$$

2.5 Core-valence exchange

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

$$\hat{\tilde{v}}_{x,cv} = \sum_{\alpha,\beta} |\tilde{p}_\alpha\rangle M_{\alpha,\beta} \langle\tilde{p}_\beta| \tag{2.35}$$

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

$$\begin{aligned}
\langle\chi_\alpha|\hat{v}_{x,cv}|\chi_\beta\rangle &= \sum_{\gamma,\delta} \langle\chi_\alpha|p_\gamma\rangle M_{\gamma,\delta} \langle p_\delta|\chi_\beta\rangle \\
&= \sum_{\gamma,\delta} \langle\tilde{\phi}^K_\alpha|\tilde{p}_\gamma\rangle M_{\gamma,\delta} \langle\tilde{p}_\delta|\tilde{\phi}^K_\beta\rangle \\
&- \sum_{\gamma,\delta,\beta'} \langle\tilde{\phi}^K_\alpha|\tilde{p}_\gamma\rangle M_{\gamma,\delta} \langle\tilde{p}_\delta|\tilde{\phi}^{\bar{J}}_{\beta'}\rangle \bar{S}^\dagger_{\beta',\beta} \\
&- \sum_{\gamma,\delta,\alpha',\alpha} \bar{S}_{\alpha,\alpha'} \langle\tilde{\phi}^{\bar{J}}_{\alpha'}|\tilde{p}_\gamma\rangle M_{\gamma,\delta} \langle\tilde{p}_\delta|\tilde{\phi}^K_\beta\rangle \\
&+ \sum_{\gamma,\delta,\alpha',\alpha} \bar{S}_{\alpha,\alpha'} \langle\tilde{\phi}^{\bar{J}}_{\alpha'}|\tilde{p}_\gamma\rangle M_{\gamma,\delta} \langle\tilde{p}_\delta|\tilde{\phi}^{\bar{J}}_{\beta'}\rangle \bar{S}^\dagger_{\beta',\beta}
\end{aligned} \tag{2.36}$$

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

As usual we build the expanded density matrix

$$\begin{pmatrix} \boldsymbol{\rho} & -\boldsymbol{\rho}\bar{\boldsymbol{S}}^{\dagger} \\ -\bar{\boldsymbol{S}}\boldsymbol{\rho} & \bar{\boldsymbol{S}}\boldsymbol{\rho}\bar{\boldsymbol{S}}^{\dagger} \end{pmatrix} \tag{2.37}$$

The matrix

$$\begin{pmatrix} \langle\tilde{\phi}^{K}|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^{K}\rangle & \langle\tilde{\phi}^{K}|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^{\bar{J}}\rangle \\ \langle\tilde{\phi}^{\bar{J}}|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^{K}\rangle & \langle\tilde{\phi}^{\bar{J}}|\tilde{p}\rangle\boldsymbol{M}\langle\tilde{p}|\tilde{\phi}^{\bar{J}}\rangle \end{pmatrix} \tag{2.38}$$

is calculated first using `potpar1(isp)%prok` and `potpar1(isp)%projbar`. [2]

[2] 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 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

$$S_{RL,R'L'} = (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}' - \vec{R}) \kappa^{\ell+\ell'-\ell''} \tag{3.1}$$

where

$$\kappa = \begin{cases} -i\sqrt{k^2} & \text{for } k^2 \geq 0 \\ \sqrt{-k^2} & \text{for } k^2 < 0 \end{cases} \tag{3.2}$$

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 Helmholtz equation[1]

$$\left[\vec{\nabla}^2 + k^2\right] H_L(\vec{r}) = -4\pi(-1)^\ell \mathcal{Y}(\vec{\nabla})\delta(\vec{r}) \tag{3.3}$$

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

$$H_\ell(\vec{r}) = (2\ell+1)!! \frac{1}{|\vec{r}|^{\ell+1}} Y_L(\vec{r}) \Big(1 + O(|\vec{r}|)\Big) \tag{3.4}$$

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.*

3.2 LMTO$SCREEN

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
```

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

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 Consistency checks

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

$$K^{\infty}_{\vec{0},L}(\vec{r}) = (2\ell-1)!!\frac{1}{|\vec{r}|^{\ell+1}}Y_L(\vec{r}) \tag{A.7}$$

$$J_{\vec{0},L}(\vec{r}) = \frac{1}{(2\ell+1)!!}|\vec{r}|^{\ell}Y_L(\vec{r}) \tag{A.8}$$

The explicit form of the first few is

$$K^{\infty}_{\vec{0},s}(\vec{r}) = \frac{1}{\sqrt{4\pi}}\frac{1}{|\vec{r}|} \tag{A.9}$$

$$K^{\infty}_{\vec{0},p_x}(\vec{r}) = \sqrt{\frac{3}{4\pi}}\frac{x}{|\vec{r}|^3} \tag{A.10}$$

$$J_{\vec{0},s}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \tag{A.11}$$

$$J_{\vec{0},p_x}(\vec{r}) = \frac{1}{3}\sqrt{\frac{3}{4\pi}}x \tag{A.12}$$

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

$$\begin{aligned} K^{\infty}_{\vec{0},s}(\vec{r}) = &-J_s(\vec{r}-\vec{R})S^{\dagger}_{\vec{R},s;\vec{0},s} \\ &-J_{p_x}(\vec{r}-\vec{R})S^{\dagger}_{\vec{R},p_x;\vec{0},s} - J_{p_y}(\vec{r}-\vec{R})S^{\dagger}_{\vec{R},p_y;\vec{0},s} - J_{p_z}(\vec{r}-\vec{R})S^{\dagger}_{\vec{R},p_z;\vec{0},s} \end{aligned} \tag{A.13}$$

$$K^{\infty}_{\vec{0},s}(\vec{R}) = \frac{1}{\sqrt{4\pi}}\frac{1}{|\vec{R}|} = -\underbrace{\frac{1}{\sqrt{4\pi}}}_{J_{\vec{R},s}(\vec{R})}\underbrace{\left(-\frac{1}{|\vec{R}|}\right)}_{S^{\dagger}_{\vec{R},s;\vec{0},s}} \tag{A.14}$$

$$\partial_x|_{\vec{R}}\, K^{\infty}_{\vec{0},s} = -\frac{1}{\sqrt{4\pi}}\frac{X}{|\vec{R}|^3} = -\underbrace{\frac{1}{3}\sqrt{\frac{3}{4\pi}}}_{\partial_x J_{\vec{R},p_x}(\vec{R})}\underbrace{\sqrt{3}\frac{X}{|\vec{R}|^3}}_{S^{\dagger}_{\vec{R},p_x,\vec{0},s}} \tag{A.15}$$

$$K_{\vec{0},p_x}(\vec{R}) = \sqrt{\frac{3}{4\pi}}\frac{X}{|\vec{R}|^3} = -\underbrace{\frac{1}{\sqrt{4\pi}}}_{J_{\vec{R},s}(\vec{R})}\underbrace{\left(-\sqrt{3}\frac{X}{|\vec{R}|^3}\right)}_{S^{\dagger}_{\vec{R},s,\vec{0},p_x}} \tag{A.16}$$

For $\kappa = 0$ the structure constants have the form

$$\begin{aligned} S_{RL,R'L'} &= (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}' - \vec{R}) \underbrace{\kappa^{\ell+\ell'-\ell''}}_{=1 \text{ for } \kappa=0} \\ S^{\dagger}_{RL,R'L'} &= (-1)^{\ell+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R} - \vec{R}') \underbrace{\kappa^{\ell+\ell'-\ell''}}_{=1 \text{ for } \kappa=0} \end{aligned} \tag{A.17}$$

The structure constants obtained from this equation are

$$\begin{aligned} S^{\dagger}_{\vec{R},s,\vec{0},s} &= (-1) 4\pi \frac{1}{\sqrt{4\pi}} \cdot \frac{1}{\sqrt{4\pi}} \frac{1}{|\vec{R}|} = -\frac{1}{|\vec{R}|} \\ S^{\dagger}_{\vec{R},p_x,\vec{0},s} &= 4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,p_x}} \sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3} = \sqrt{3} \frac{X}{|\vec{R}|^3} \\ S^{\dagger}_{\vec{R},s,\vec{0},p_x} &= (-1) 4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,s}} \sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3} = -\sqrt{3} \frac{X}{|\vec{R}|^3} \end{aligned} \tag{A.18}$$

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.