

# **The LMTO object of the CP-PAW code**

Peter E. Blöchl

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

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# Chapter 1

## Todo

### 1.1 Fixes

- `Imto_overlapphi` calculates the onsite overlap matrix of partial waves in a sphere.
- using only sp like tight-binding orbitals and local exchange lead to an increase of the band gap of silicon above 1.3 eV. After adding the d-orbitals to the HF term collapsed the band gap dramatically below the dft value. Core-valence exchange seems to have an important effect on the band gap too.
- The charge sumrule is not correct! The calculation for an H-atom yields  $Tr[\rho O] \approx 0.2$ . The problem is not the difference between tailed orbitals and the multicenter expansion, because  $(r * \chi)^2$  agrees quite well.

### 1.2 Ideas

- With the introduction of the tailed representation of the NTBO's we **switch from a multicenter expansion to a one-center expansion**. This, however, requires to increase the number of angular momenta for the tail functions beyond that used for the augmentation: Each (screening) Hankel function centered on the neighboring site contributes arbitrary many angular momenta at the central site.

The tail functions for the higher angular momenta behave, at the central site, like a bare Bessel function. Beyond the central site, we can add the same pairs of exponential tails as for the lower tailed partial waves.

(The following is probably no more true. please check!) Currently we use the following rule: Rule: (1) Each head function has exactly one tail function attributed to it. Thus we can identify the phidot function uniquely by looking for the tail function with the correct angular momentum. From (1) follows, that there is at most one tail function per site and angular momentum.

- Suggestion: the exponential functions for the tailed expansion are determined by trial and error. A more systematic approach for the tail function would be to (1) build a Hankel function on a neighboring site, which is augmented by (a) a bare Bessel function and (b) by

a screened scattering partial wave  $|\dot{\phi}\rangle$ . (1a) In order to make the formulation less dependent on the neighbor distance, we could also include the gradients of these functions. (2) These functions are expanded about the central site into an angular-momentum expansion. (3) a reasonably weighted least-square fit of the exponential tails to these functions will provide a “optimum shape” of the tails for each angular momentum.

- The orbitals in the tailed one-center expansion and as multicenter expansions can be compared using `LMTD_PLOTORBS`. Calculations for hydrogen suggest that a good choice is  $K2 = -1$ , and  $(\lambda_1, \lambda_2) = (4, 2)$ . The rationale for  $K2$  is that the energy of the hydrogen orbital is at  $-1Ry = -\frac{1}{2}H = \frac{1}{2}K2$ . (see [Dummy/Sitest/Test/Occtest/H2test](#))

## Chapter 2

# Purpose and theoretical background of the LMTO Object

The LMTO object maps the wave functions expressed in augmented plane waves onto 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].

### 2.1 Augmentation

The concept of linear augmented waves[2] is as follows:

1. At first, a so-called **envelope function**  $|K_\alpha^\infty\rangle$  is defined.<sup>1</sup>
2. In a second step, this envelope function is expanded about each atomic site  $R_\alpha$  into spherical harmonics. More generally, they are expanded into **head functions**  $|K_\alpha^\Omega\rangle$  and **tail functions**  $|J_\alpha^\Omega\rangle$ . 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.

$$|K_\alpha^\infty\rangle = |K_\alpha^\Omega\rangle - \sum_\beta |J_\beta^\Omega\rangle S_{\beta,\alpha}^\dagger + |K_\alpha^I\rangle \quad (2.1)$$

The coefficients  $S_{\alpha,\beta}$  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 envelope function**<sup>2</sup>  $|K_\alpha^I\rangle$ .

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<sup>1</sup>The superscript  $\infty$  denotes that the function extends over all space, a superscript  $\Omega$  denotes that the function is truncated (set to zero) outside the augmentation sphere  $\Omega_R$  centered at the site  $R_\alpha$  denoted by the index  $\alpha$ . The superscript  $I$  denotes that the function is non-zero only in 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. Similarly, the interstitial function contains terms from the higher angular momenta within the augmentation regions.

<sup>2</sup>The interstitial envelope function is confined mostly in the region in between the atoms, but it also accounts for the overlap of the atomic regions and so-called higher partial waves not taken care of in the regular partial-wave expansion.

3. In the third step, the head and tail functions are replaced differentiably at some sphere radius by **partial waves** of the atomic potential. For that purpose, we use as partial waves 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

$$\langle \vec{r} | K_\alpha^\infty \rangle = H_{L_\alpha}(\vec{r} - \vec{R}_\alpha) \quad (2.2)$$

Solid Hankel functions are irregular solutions of the the inhomogeneous Helmholtz equation<sup>3</sup>

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

Here  $\mathcal{Y}_L(\vec{r}) \stackrel{\text{def}}{=} r^\ell Y_L(\vec{r})$  is a polynomial. With a gradient as argument, it becomes a differential operator. With  $Y_L(\vec{r})$  we denote a spherical or real harmonic function and  $L \stackrel{\text{def}}{=} (\ell, m)$  is a composite index of angular momentum quantum number  $\ell$  and magnetic quantum number  $m$ .

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

### 2.2.2 Hankel and Bessel functions as head and tail functions

Defining the envelope function via an 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<sup>4</sup> so that they behave at the origin as

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

$$J_{R,L}^\Omega(\vec{r}) = \left[ \frac{1}{(2\ell + 1)!!} |\vec{r} - \vec{R}|^{\ell+1} + \dots \right] Y_L(\vec{r} - \vec{R}) \theta_{\Omega_R}(\vec{r}) \quad (2.5)$$

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

<sup>3</sup>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.

<sup>4</sup>This is our definition, not a generally accepted convention.

### 2.2.3 Bare structure constants

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

$$|K_\alpha^\infty\rangle = |K_\alpha^\Omega\rangle - \sum_\beta |J_\beta^\Omega\rangle S_{\beta,\alpha}^\dagger + |K_\alpha^I\rangle \quad (2.6)$$

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

The superscript  $\infty$  denotes that the function extends over all space, a superscript  $\Omega$  denotes that the function is truncated (set to zero) outside the augmentation sphere  $\Omega_R$  centered 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.

#### BARE STRUCTURE CONSTANTS

The bare structure constants have the form

$$S_{RL,R'L'} = (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}' - \vec{R}) \begin{cases} (-ik)^{\ell+\ell'-\ell''} & \text{for } k^2 > 0 \\ \delta_{\ell+\ell'-\ell''} & \text{for } k^2 = 0 \\ \kappa^{\ell+\ell'-\ell''} & \text{for } k^2 = -\kappa^2 < 0 \end{cases} \quad (2.7)$$

With  $C_{L,L',L''}$ , we denote the **Gaunt coefficients** defined by

$$Y_{L'}(\vec{r}) Y_{L''}(\vec{r}) = \sum_L Y_L(\vec{r}) C_{L,L',L''} \quad (2.8)$$

Note, that the Gaunt coefficients for spherical and real spherical harmonics differ.<sup>5</sup>

The bare structure constants are hermitean<sup>6</sup>, i.e.

$$S_{RL,R'L'} = S_{R'L',RL} \quad (2.9)$$

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

A so-called **screened LMTO representation** is defined by a set of screened scattering partial waves  $|\dot{\phi}_\alpha\rangle$ . In what we call the nodeless-representation, the scattering partial waves are defined as nodeless scattering wave functions.

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

$$|\dot{\phi}_\alpha\rangle \rightarrow |\bar{J}_\alpha^\Omega\rangle \stackrel{\text{def}}{=} |J_\alpha^\Omega\rangle - |K_\alpha^\Omega\rangle \bar{Q}_\alpha \quad (2.10)$$

<sup>5</sup>In practice, we use real spherical harmonics and the corresponding Gaunt coefficients.

<sup>6</sup>We use that  $H_L(\vec{r}) = (-1)^\ell H_L(-\vec{r})$  and that the Gaunt coefficients  $C_{L,L',L''}$  vanish unless  $\ell + \ell' + \ell''$  is even.



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

$$|\bar{K}_\alpha^\infty\rangle = \sum_{\beta} |K_\beta^\infty\rangle c_{\beta,\alpha} \quad (2.11)$$

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

$$|\bar{K}_\alpha^\infty\rangle = |K_\alpha^\Omega\rangle - \sum_{\beta} |\bar{J}_\beta^\Omega\rangle \bar{S}_{\beta,\alpha}^\dagger + |\bar{K}_\alpha^I\rangle \quad (2.12)$$

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

By equating the two expressions for the screened Hankel functions, namely Eq. 2.11 and Eq. 2.12, we can extract the screened structure constants  $\bar{S}_{\beta,\alpha}^\dagger$  and the superposition coefficients  $c_{\beta,\alpha}$ .

$$\begin{aligned} \sum_{\beta} \left[ |K_\beta^\Omega\rangle - \sum_{\gamma} |J_\gamma^\Omega\rangle S_{\gamma,\beta}^\dagger + |K_\beta^I\rangle \right] c_{\beta,\alpha} &= |K_\alpha^\Omega\rangle - \sum_{\beta} \underbrace{\left[ |J_\beta^\Omega\rangle - |K_\beta^\Omega\rangle \bar{Q}_\beta \right]}_{|\bar{J}_\beta^\Omega\rangle} \bar{S}_{\beta,\alpha}^\dagger + |\bar{K}_\alpha^I\rangle \\ \xRightarrow{\text{Eq. 2.11}} \sum_{\beta} |K_\beta^\Omega\rangle c_{\beta,\alpha} - \sum_{\beta,\gamma} |J_\gamma^\Omega\rangle S_{\gamma,\beta}^\dagger c_{\beta,\alpha} &= \sum_{\beta} |K_\beta^\Omega\rangle \left[ \delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}_{\beta,\alpha}^\dagger \right] - \sum_{\beta} |J_\beta^\Omega\rangle \bar{S}_{\beta,\alpha}^\dagger \end{aligned} \quad (2.13)$$

By comparing the coefficients, we obtain

$$c_{\beta,\alpha} = \delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}_{\beta,\alpha}^\dagger \quad (2.14)$$

$$\bar{S}_{\gamma,\alpha}^\dagger = \sum_{\beta} S_{\gamma,\beta}^\dagger c_{\beta,\alpha}, \quad (2.15)$$

which can be resolved to <sup>7</sup> the defining equation of the screened structure constants

#### SCREENED STRUCTURE CONSTANTS

$$\bar{S}^\dagger = \left[ \mathbf{1} - \mathbf{s}^\dagger \bar{\mathbf{Q}} \right]^{-1} \mathbf{s}^\dagger \quad (2.17)$$

and the expression of the screened Hankel functions

$$|\bar{K}_\alpha^\infty\rangle = \sum_{\beta} |K_\beta^\infty\rangle \left[ \delta_{\beta,\alpha} + \bar{Q}_\beta \bar{S}_{\beta,\alpha}^\dagger \right]. \quad (2.18)$$

Because we calculate the screened structure constants on finite clusters, Eq. 2.17 should be considered of only formal value and should not be used in the actual calculations. Rather, the defining equations Eq. 2.15 shall be used as shown in the following section.

$$\bar{S}^\dagger \stackrel{\text{Eq. 2.15}}{=} \mathbf{s}^\dagger \mathbf{c} \stackrel{\text{Eq. 2.14}}{=} \mathbf{s}^\dagger (\mathbf{1} + \bar{\mathbf{Q}} \bar{S}^\dagger) \Rightarrow (\mathbf{1} - \mathbf{s}^\dagger \bar{\mathbf{Q}}) \bar{S}^\dagger = \mathbf{s}^\dagger \Rightarrow \bar{S}^\dagger = (\mathbf{1} - \mathbf{s}^\dagger \bar{\mathbf{Q}})^{-1} \mathbf{s}^\dagger \quad (2.16)$$

## 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. 2.14, Eq. 2.15 and rewrite it in terms of vectors, which are defined on the cluster  $B$ . The index  $\alpha$  labeling the vectors counts the envelope functions centered at the central site. The dimension of the vectors and matrices defined below is given by angular momentum channels and sites with non-zero screening charge<sup>8</sup>  $\bar{Q}$ .

The equations attain the form

$$\vec{c}_\alpha \stackrel{\text{Eq. 2.14}}{=} \vec{e}_\alpha + \bar{Q} \vec{s}_\alpha \quad (2.19)$$

$$\vec{s}_\alpha \stackrel{\text{Eq. 2.15}}{=} \mathbf{S}^\dagger \vec{c}_\alpha \quad (2.20)$$

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

$$\begin{aligned} (\vec{c}_\alpha)_\beta &= c_{\beta,\alpha} \\ (\vec{s}_\alpha)_\beta &= \bar{S}_{\beta,\alpha}^\dagger \\ (\vec{e}_\alpha)_\beta &= \delta_{\beta,\alpha} \end{aligned} \quad (2.21)$$

In matrix form, all these quantities are non-square matrices.

$$\begin{aligned} \vec{c}_\alpha &\stackrel{\text{Eq. 2.19}}{=} \vec{e}_\alpha + \bar{Q} \vec{s}_\alpha \stackrel{\text{Eq. 2.20}}{=} \vec{e}_\alpha + \bar{Q} \mathbf{S}^\dagger \vec{c}_\alpha \\ \Rightarrow \quad [\mathbf{1} - \bar{Q} \mathbf{S}^\dagger] \vec{c}_\alpha &= \vec{e}_\alpha \\ \Rightarrow \quad \vec{c}_\alpha &= [\mathbf{1} - \bar{Q} \mathbf{S}^\dagger]^{-1} \vec{e}_\alpha \\ \vec{s}_\alpha &\stackrel{\text{Eq. 2.20}}{=} \mathbf{S}^\dagger \vec{c}_\alpha = \mathbf{S}^\dagger [\mathbf{1} - \bar{Q} \mathbf{S}^\dagger]^{-1} \vec{e}_\alpha \end{aligned} \quad (2.22)$$

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

<sup>8</sup>Inclusion of orbitals with vanishing screening charge does not affect the expansion coefficients  $c_{\alpha,\beta}$ . However, it also includes the structure constant matrix elements for the higher angular momenta with vanishing screening charge. The contribution of the higher angular momenta can be calculated after the screening has been done.

## CALCULATION OF SCREENED STRUCTURE CONSTANTS

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

$$[\mathbf{1} - \bar{\mathbf{Q}}\mathbf{S}^\dagger]\vec{c}_\alpha = \vec{e}_\alpha \quad (2.23)$$

$$\vec{s}_\alpha = \mathbf{S}^\dagger \vec{c}_\alpha \quad (2.24)$$

for  $\vec{c}_\alpha$  first from Eq. 2.23 using a standard routine for linear equation systems. Using the result for  $\vec{c}_\alpha$ , we obtain the screened structure constants  $\vec{s}_\alpha$  from Eq. 2.24 by multiplication with the bare structure constants.

Finally we obtain the screened structure constants as

$$\bar{S}_{\gamma,\alpha}^\dagger = \left( \vec{s}_\alpha \right)_\gamma \quad (2.25)$$

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

## 2.4 Derivatives

In order to evaluate forces, we need to investigate the derivatives of the structure constants with respect to changes of the atomic structure.

$$\begin{aligned} -\bar{\mathbf{Q}}d\mathbf{S}^\dagger\vec{c}_\alpha + [\mathbf{1} - \bar{\mathbf{Q}}\mathbf{S}^\dagger]d\vec{c}_\alpha &\stackrel{\text{Eq. 2.23}}{=} 0 \\ [\mathbf{1} - \bar{\mathbf{Q}}\mathbf{S}^\dagger]d\vec{c}_\alpha &= \bar{\mathbf{Q}}d\mathbf{S}^\dagger\vec{c}_\alpha \\ \Rightarrow d\vec{s}_\alpha &\stackrel{\text{Eq. 2.24}}{=} d\mathbf{S}^\dagger\vec{c}_\alpha + \mathbf{S}^\dagger d\vec{c}_\alpha = \bar{\mathbf{Q}}^{-1}d\vec{c}_\alpha \\ &= \bar{\mathbf{Q}}^{-1}[\mathbf{1} - \bar{\mathbf{Q}}\mathbf{S}^\dagger]^{-1}\bar{\mathbf{Q}}d\mathbf{S}^\dagger\vec{c}_\alpha \\ &= [\mathbf{1} - \mathbf{S}^\dagger\bar{\mathbf{Q}}]^{-1}d\mathbf{S}^\dagger\vec{c}_\alpha \end{aligned} \quad (2.26)$$

If this is correct, it implies that the screened structure constants depend only in second order on a displacement of the atoms.

### 2.4.1 Lower and higher angular momenta

The angular momentum expansion of a Hankel function  $|K_\alpha^\infty\rangle$  about a neighboring site has infinitely many angular momentum contributions  $|J_\alpha^\Omega\rangle$ . The Hankel functions  $|K_\alpha^\Omega\rangle$ , on the other hand, are limited to a subset. We call the angular momenta, for which the Hankel functions  $|K_\alpha^\Omega\rangle$  are taken into account, lower angular momenta, and those for which only the Bessel function  $|J_\alpha^\Omega\rangle$  are considered, the higher angular momenta. The distinction reflects directly to the values of  $\bar{\mathbf{Q}}$ , which are nonzero for the lower angular momenta and which vanish for the higher angular momenta.

To avoid the confusion between the choice of screening charges and the selection of tight-binding orbitals, we assume that there is an orbital considered for each non-zero screening charge. A truncation of the basisset is postponed. With this choice, the left index of the expansion coefficients  $c_{\beta,\alpha}$  in Eq. 2.11 runs over all sites in the cluster and angular momenta for which there is a non-zero screening charge  $\bar{Q}_\beta$ . The right index includes all orbital indices on the central site of the cluster.

If there are two orbitals with the same leading angular momentum, they will have, per definition, the same envelope function and the same tails.<sup>9</sup> Thus, we consider only the angular momenta during the construction and expand the structure-constant array after the screening has been completed.

A	indices of screened orbitals
B	indices of non-zero screening charges
C	indices of partial waves
D	indices of angular momenta considered one-center expansion of the tailed representation

Screened orbitals (A) can only be formed in channels with partial waves (C), because they require augmentation of the envelope function.

Non-zero screening charges (B) are only possible where partial waves (C) exist, because the irregular contribution must be augmented.

The number of screened orbitals (A) may be a subset of (B) the channels with non0zero screening charges.

## 2.5 Augmentation and Potential parameters

### 2.5.1 Local orbitals

The local orbitals have the form

$$\begin{aligned}
 |\chi_\alpha\rangle = & |\phi_\alpha^K\rangle - \sum_{R,L} |\phi_{R,L}^J\rangle \bar{S}_{R,L,R_\alpha,L_\alpha}^\dagger \\
 & + \sum_{R',L'} |K_{R',L'}^I\rangle \left[ \delta_{R',L',R_\alpha,L_\alpha} - \bar{Q}_{R',L'} \bar{S}_{R',L',R_\alpha,L_\alpha}^\dagger \right]
 \end{aligned} \tag{2.27}$$

<sup>9</sup>The difference between two such orbitals is thus confined to the augmentation region of the central site, and can probably be identified with a local orbital as they are used in LAPW.

where the new partial waves  $|\phi_\alpha^K\rangle$  and  $|\phi_\alpha^{\bar{J}}\rangle$  are superpositions of the valence and scattering partial waves that match differentiably to the head and tail functions  $|K_\alpha\rangle$  and  $|\bar{J}_\alpha\rangle$ .

$$\begin{aligned}
 |\phi_\alpha^K\rangle &= |\phi_\alpha\rangle \overbrace{\frac{W_\alpha[K, \dot{\phi}]}{W_\alpha[\phi, \dot{\phi}]} - |\dot{\phi}_\alpha\rangle \frac{W_\alpha[K, \phi]}{W_\alpha[\phi, \dot{\phi}]}}^{\rightarrow |K_\alpha^\Omega\rangle} \\
 &\quad \underbrace{\hspace{1.5cm}}_{Ktphi} \quad \underbrace{\hspace{1.5cm}}_{-Ktophidot} \\
 |\phi_{R,L}^{\bar{J}}\rangle &= |\dot{\phi}_\beta\rangle \overbrace{\left( -\frac{W_\beta[\bar{J}, \phi]}{W_\beta[\phi, \dot{\phi}]} \right)}^{\rightarrow |\bar{J}_\beta^\Omega\rangle} \\
 &\quad \underbrace{\hspace{1.5cm}}_{JBARTophidot}
 \end{aligned} \tag{2.28}$$

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

With  $W_\alpha[f, g]$  we denote the **Wronskian**

$$W_\alpha[f, g] \stackrel{\text{def}}{=} f_\alpha(\partial_r g_\alpha) - (\partial_r f_\alpha)g_\alpha = \det \begin{bmatrix} f & g \\ \partial_r f & \partial_r g \end{bmatrix} \tag{2.29}$$

which is used to match two functions differentiably to a third via

$$y(x) \rightarrow f(x) \frac{W[y, g]}{W[f, g]} + g(x) \frac{W[y, f]}{W[g, f]} \tag{2.30}$$

The matrix elements  $\langle \tilde{p}_\gamma | \tilde{\chi}_\alpha \rangle$ , which will be needed later, have the form

$$\begin{aligned}
 \langle \tilde{p}_\gamma | \tilde{\chi}_\alpha \rangle &= \langle \tilde{p}_\gamma | \tilde{\phi}_\alpha^K \rangle - \sum_{R', L'} \langle \tilde{p}_\gamma | \tilde{\phi}_{R', L'}^{\bar{J}} \rangle \bar{S}_{R, L, R_\alpha, L_\alpha}^\dagger \\
 &= \langle \tilde{p}_\gamma | \tilde{\phi}_\alpha^K \rangle - \langle \tilde{p}_\gamma | \tilde{\phi}_{R_\gamma, L_\gamma}^{\bar{J}} \rangle \bar{S}_{R_\gamma, L_\gamma, R_\alpha, L_\alpha}^\dagger
 \end{aligned} \tag{2.31}$$

## 2.6 Coefficients of the tight-binding orbital

### 2.6.1 Introduction

In this section, I describe how to determine the wave functions in terms of local orbitals, if the projections  $\langle \tilde{p}_\gamma | \tilde{\psi} \rangle$  onto the pseudo wave functions are known.

The basic idea is to find a representation of the wave function in terms of local orbitals  $|\chi_\alpha\rangle$

$$|\psi'_n\rangle = \sum_\alpha |\chi_\alpha\rangle q_\alpha, \tag{2.32}$$

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.

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

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

$$\begin{aligned} Q[\vec{q}] &:= \left( \langle \tilde{\psi}_n | - \sum_{\alpha} q_{\alpha}^* \langle \tilde{\chi}_{\alpha} | \right) \left[ \sum_{\delta, \gamma} |\tilde{p}_{\delta}\rangle \langle \phi_{\delta} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma}\rangle \langle \tilde{p}_{\gamma} | \right] \left( |\tilde{\psi}_n\rangle - \sum_{\beta} |\tilde{\chi}_{\beta}\rangle q_{\beta} \right) \\ &= \sum_{\gamma} \left[ \sum_{\delta} \left( \langle \tilde{\psi}_n | \tilde{p}_{\delta}\rangle - \sum_{\alpha} q_{\alpha}^* \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta}\rangle \right) \langle \phi_{\delta} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma}\rangle \right] \left( \langle \tilde{p}_{\gamma} | \tilde{\psi}_n\rangle - \sum_{\beta} \langle \tilde{p}_{\gamma} | \tilde{\chi}_{\beta}\rangle q_{\beta} \right) \end{aligned} \quad (2.33)$$

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

Minimization yields

$$\begin{aligned} \frac{\partial Q}{\partial q_{\alpha}^*} &= - \sum_{\gamma} \left[ \sum_{\delta} \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta}\rangle \langle \phi_{\delta} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma}\rangle \right] \left( \langle \tilde{p}_{\gamma} | \tilde{\psi}_n\rangle - \sum_{\beta} \langle \tilde{p}_{\gamma} | \tilde{\chi}_{\beta}\rangle q_{\beta} \right) \stackrel{!}{=} 0 \\ \Rightarrow \quad \sum_{\gamma} \left[ \sum_{\delta} \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta}\rangle \langle \phi_{\delta} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma}\rangle \right] \langle \tilde{p}_{\gamma} | \tilde{\psi}_n\rangle &= \sum_{\gamma, \beta} \left[ \sum_{\delta} \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta}\rangle \langle \phi_{\delta} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma}\rangle \right] \langle \tilde{p}_{\gamma} | \tilde{\chi}_{\beta}\rangle q_{\beta} \\ \Rightarrow \quad q_{\beta} &= \sum_{\gamma} \left[ \sum_{\gamma', \delta'} \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta'}\rangle \langle \phi_{\delta'} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma'}\rangle \langle \tilde{p}_{\gamma'} | \tilde{\chi}_{\beta}\rangle \right]^{-1} \left[ \sum_{\gamma \delta} \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta}\rangle \langle \phi_{\delta} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma}\rangle \right] \langle \tilde{p}_{\gamma} | \tilde{\psi}_n\rangle \end{aligned} \quad (2.34)$$

This allows one to write the wave function in the form

$$|\psi_n\rangle \approx \sum_{\alpha} |\chi_{\alpha}\rangle \langle \tilde{\pi}_{\alpha} | \tilde{\psi}_n\rangle \quad (2.35)$$

with

$$\langle \tilde{\pi}_{\alpha} | = \sum_{\gamma} \left[ \sum_{\gamma', \delta'} \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta'}\rangle \langle \phi_{\delta'} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma'}\rangle \langle \tilde{p}_{\gamma'} | \tilde{\chi}_{\beta}\rangle \right]^{-1} \left[ \sum_{\delta} \langle \tilde{\chi}_{\alpha} | \tilde{p}_{\delta}\rangle \langle \phi_{\delta} | \theta_{\Omega_{R_{\delta}}} | \phi_{\gamma}\rangle \right] \langle \tilde{p}_{\gamma} | \quad (2.36)$$

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, The multicenter expansion for the projector function is long-ranged so that this expression needs to be evaluated in a Bloch representation.

## 2.6.2 Transformation between local-orbital and partial-wave projections

In the previous section, I derived in Eq. 2.36 a relation between orbital and partial wave projector functions.

$$\langle \tilde{\pi}_{\alpha} | \tilde{\psi}_n\rangle = \sum_{\beta} M_{\alpha, \beta} \langle \tilde{p}_{\alpha} | \tilde{\psi}_n\rangle \quad (2.37)$$

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

The derivatives are correspondingly derived as

$$\begin{aligned}
 dE &= \sum_{\alpha,\beta} \underbrace{\frac{dE}{d\rho_{\alpha,\beta}}}_{=:h_{\beta,\alpha}} d\rho_{\alpha,\beta} \\
 &= \sum_{\alpha,\beta} h_{\beta,\alpha} \left[ \sum_n \langle \pi_\alpha | d\psi_n \rangle f_n \langle \psi_n | \pi_\beta \rangle + \sum_n \langle \pi_\alpha | \psi_n \rangle df_n \langle \psi_n | \pi_\beta \rangle + \sum_n \langle \pi_\alpha | \psi_n \rangle f_n \langle d\psi_n | \pi_\beta \rangle \right] \\
 &= \sum_n \sum_\alpha f_n \underbrace{\sum_\beta \langle \psi_n | \pi_\beta \rangle h_{\beta,\alpha} \langle \pi_\alpha | d\psi_n \rangle}_{HTBC_{n,\alpha}^\dagger} + \sum_n \sum_\beta \langle d\psi_n | \pi_\beta \rangle \underbrace{\sum_\alpha h_{\beta,\alpha} \langle \pi_\alpha | \psi_n \rangle f_n}_{HTBC_{\beta,n}} \\
 &\quad + \sum_n \sum_\beta \langle \psi_n | \pi_\beta \rangle \underbrace{\sum_\alpha h_{\beta,\alpha} \langle \pi_\alpha | \psi_n \rangle df_n}_{HTBC_{\beta,n}} \\
 &= \sum_n \sum_\gamma f_n \underbrace{\sum_\alpha \sum_\beta \langle \psi_n | \pi_\beta \rangle h_{\beta,\alpha} M_{\alpha,\gamma} \langle \tilde{\rho}_\gamma | d\tilde{\psi}_n \rangle}_{\underbrace{HTBC_{n,\alpha}^\dagger}_{HPROJ_{n,\gamma}^\dagger}} + \sum_n \sum_\gamma \langle d\tilde{\psi}_n | \tilde{\rho}_\gamma \rangle \underbrace{\sum_\beta M_{\gamma,\beta}^\dagger \sum_\alpha h_{\beta,\alpha} \langle \pi_\alpha | \psi_n \rangle f_n}_{\underbrace{HTBC_{\beta,n}}_{HPROJ_{\gamma,n}}} \\
 &\quad + \sum_n df_n \sum_\gamma \langle \tilde{\psi}_n | \tilde{\rho}_\gamma \rangle \underbrace{\sum_\beta M_{\gamma,\beta}^\dagger \sum_\alpha h_{\beta,\alpha} \langle \pi_\alpha | \psi_n \rangle}_{\underbrace{HTBC_{\beta,n}}_{HPROJ_{\gamma,n}}} \tag{2.38}
 \end{aligned}$$

Thus, we first define the Hamiltonian **h** (HAMIL)

$$\begin{aligned}
 \underbrace{h_{\alpha,\beta}}_{HAMIL} &= \frac{dE}{\rho_{\beta,\alpha}} \\
 HTBC_{\beta,n} &= \sum_\alpha \underbrace{h_{\beta,\alpha}}_{HAMIL} \underbrace{\langle \tilde{\pi}_\alpha | \tilde{\psi}_n \rangle}_{TBC_{\alpha,n}} \\
 HPROJ_{\gamma,n} &= \sum_\beta M_{\gamma,\beta}^\dagger \cdot HTBC_{\beta,n} \tag{2.39}
 \end{aligned}$$

This operation is performed in `lmtotoproj` with `ID='BACK'`.

Then the forces on the wave functions

$$\sum_\gamma \frac{1}{f_n} \frac{\delta \Delta E}{\delta \langle \psi_n |} = |\tilde{\rho}_\gamma \rangle HPROJ_{\gamma,n} \tag{2.40}$$

The forces acting on the occupations are, as usual, determined as

$$\frac{\partial E}{\partial f_n} = \langle \psi_n | \left[ \frac{1}{f_n} \frac{\delta E}{\delta \langle \psi_n |} \right] \tag{2.41}$$

## 2.7 Tailed representation of the natural tight-binding orbitals

The tailed representation replaces the multi-center expansion of the natural tight-binding orbitals by a one-center expansion. The underlying idea the short-ranged tails of the screened orbitals can be approximated by exponential tails, that are matched to the one-center expansion of the orbitals at the central site. Thus both the head and the tail functions centered on the central site are extended by a superposition of exponential tails.

## 2.8 How to choose the parameters

```
!CONTROL!DFT!NTBO
  MODUS='HYBRID' OFFSITE=F K2=-0.25 SCALERCUT=2. !END
!END!END!END
!STRUCTURE!SPECIES!NTBO
  NOFL=1 1 1 1 CV=T LHFWEIGHT=0.15
  TAILLAMBDA=4.0 2.0 RAUG/RCOV=0.9 RTAIL/RCOV=1.2
!END!END!END
```

### 2.8.1 Augmentation radius must be large for semi-core states

**Observation:** We had the problem that the total charge for core states of Ca has been much larger than one.

**Explanation:** This was apparently due to a augmentation radius that was chosen too small. The tail, represented by Hankel and Bessel functions decayed much slower than the real core state, so that the norm of the corresponding state was overestimated dramatically.

The augmentation radius specifies the matching radius of the Bessel and Hankel functions to the nodeless partial waves.<sup>10</sup> The kinetic energy of the Hankel and Bessel function is set by the parameter `k2`. Ideally it would approximate the kinetic energy of the partial waves at the augmentation radius.

**Remedy:** the augmentation radius must be chosen sufficiently large so that semi-core states are well represented by their partial wave alone, while the tail represented by Hankel and Bessel functions is negligible.<sup>11</sup>

<sup>10</sup>It is not related to the matching radius of all-electron, nodeless and pseudo partial waves, which defines the augmentation. The parameter here defines the shape of the natural tight-binding orbital.

<sup>11</sup>Special thanks to Robert Schade.



## Chapter 3

# Contributions to the Hamiltonian

### 3.1 Core-valence exchange

The exchange term between core and valence electrons acts like a fixed, nonlocal potential acting on the electrons, of the form<sup>1</sup>

$$\hat{v}_{x,cv} = \sum_{\alpha,\beta} |\tilde{p}_\alpha\rangle M_{\alpha,\beta} \langle \tilde{p}_\beta| \quad (3.1)$$

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

$$\begin{aligned} \langle \chi_\alpha | \hat{v}_{x,cv} | \chi_\beta \rangle &= \sum_{\gamma,\delta} \langle \chi_\alpha | p_\gamma \rangle M_{\gamma,\delta} \langle p_\delta | \chi_\beta \rangle \\ &= \sum_{\gamma,\delta} \langle \tilde{\phi}_\alpha^K | \tilde{p}_\gamma \rangle M_{\gamma,\delta} \langle \tilde{p}_\delta | \tilde{\phi}_\beta^K \rangle \\ &\quad - \sum_{\gamma,\delta,\beta'} \langle \tilde{\phi}_\alpha^K | \tilde{p}_\gamma \rangle M_{\gamma,\delta} \langle \tilde{p}_\delta | \tilde{\phi}_{\beta'}^J \rangle \bar{S}_{\beta',\beta}^\dagger \\ &\quad - \sum_{\gamma,\delta,\alpha',\alpha} \bar{S}_{\alpha,\alpha'} \langle \tilde{\phi}_{\alpha'}^J | \tilde{p}_\gamma \rangle M_{\gamma,\delta} \langle \tilde{p}_\delta | \tilde{\phi}_\beta^K \rangle \\ &\quad + \sum_{\gamma,\delta,\alpha',\alpha} \bar{S}_{\alpha,\alpha'} \langle \tilde{\phi}_{\alpha'}^J | \tilde{p}_\gamma \rangle M_{\gamma,\delta} \langle \tilde{p}_\delta | \tilde{\phi}_{\beta'}^J \rangle \bar{S}_{\beta',\beta}^\dagger \end{aligned} \quad (3.2)$$

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

As usual we build the expanded density matrix

$$\begin{pmatrix} \rho & -\rho \bar{S}^\dagger \\ -\bar{S} \rho & \bar{S} \rho \bar{S}^\dagger \end{pmatrix} \quad (3.3)$$

The matrix

$$\begin{pmatrix} \langle \tilde{\phi}^K | \tilde{p} \rangle \mathbf{M} \langle \tilde{p} | \tilde{\phi}^K \rangle & \langle \tilde{\phi}^K | \tilde{p} \rangle \mathbf{M} \langle \tilde{p} | \tilde{\phi}^J \rangle \\ \langle \tilde{\phi}^J | \tilde{p} \rangle \mathbf{M} \langle \tilde{p} | \tilde{\phi}^K \rangle & \langle \tilde{\phi}^J | \tilde{p} \rangle \mathbf{M} \langle \tilde{p} | \tilde{\phi}^J \rangle \end{pmatrix} \quad (3.4)$$

---

<sup>1</sup>Note that this matrix  $\mathbf{M}$  differs from the one with the same symbol in the previous section.

is calculated first using `potpar1(isp)%prok` and `potpar1(isp)%projbar`.<sup>2</sup>

## 3.2 U-tensor

## 3.3 Double-counting correction

The double-counting correction is that of Eq. 36 of the paper by Blöchl, Walther, Pruschke[3].

$$\begin{aligned} E_{xc}^{\hat{W}_R} &= \int d^3r n_R^x(\vec{r}) \epsilon_{xc}[n_{\sigma,\sigma'}^x(\vec{r})] \frac{n_R^x(\vec{r})}{n^x(\vec{r})} \\ &= \int d^3r \left( n^x(\vec{r}) \epsilon_{xc}[n_{\sigma,\sigma'}^x(\vec{r})] \right) \left( \frac{n_R^x(\vec{r})}{n^x(\vec{r})} \right)^2 \end{aligned} \quad (3.5)$$

The exchange correlation density is calculated with the correlated orbitals, but there is an additional factor, which cuts of the exchange correlation contribution at large radii, where the density vanishes.

For hybrid functionals only the scaled Hartree-Fock energy is added, so that the double counting is weighted as well and it is furthermore limited to the exchange term only. **This will be different, if also corrections for the correlation energies are added.**

Other double-counting schemes are discussed in appendix D.

Let us simplify the expression by introducing the symbols  $n_R = n_R^x(\vec{r})$  and  $n_t = n_{\sigma,\sigma'}^x(\vec{r})$ . With  $n_R^s$  and  $n_t^s$  we denote the spherical parts of the respective densities.

If the frozen-core density is employed, the contribution of the core must not be included in the double-counting term.

The expression above can be written in the following form:

$$\begin{aligned} E_{xc}^{\hat{W}_R} &= \int d^3r \left[ n_t(\vec{r}) \epsilon_{xc}[n_t(\vec{r})] - n^{core}(\vec{r}) \epsilon_{xc}[n^{core}(\vec{r})] \right] \left( \frac{n_R^s(\vec{r})}{n_t^s(\vec{r})} \right)^2 \\ &= \int d^3r f_{xc}(\vec{r}) \left( \frac{n_R^s(\vec{r})}{n_t^s(\vec{r})} \right)^2 \end{aligned} \quad (3.6)$$

With  $f_{xc} := n_t \epsilon_{xc}[n_t] - n^{core} \epsilon_{xc}[n^{core}]$  and  $\mu_{xc} := \frac{df_{xc}}{dn_t}$ , we obtain

$$\begin{aligned} dE_{xc}^{\hat{W}_R} &= \int d^3r \left( \frac{n_R^s}{n_t^s} \right)^2 \mu_{xc} dn_t + f_{xc} 2 \left( \frac{n_R^s}{n_t^s} \right)^2 \frac{dn_R^s}{n_R^s} - f_{xc} 2 \left( \frac{n_R^s}{n_t^s} \right)^2 \frac{dn_t^s}{n_t^s} \\ &= \int d^3r \left[ \left( \frac{n_R^s}{n_t^s} \right)^2 \mu_{xc} - 2f_{xc}^s \left( \frac{n_R^s}{n_t^s} \right)^2 \frac{1}{n_t^s} \right] dn_t + \left[ 2f_{xc}^s \left( \frac{n_R^s}{n_t^s} \right)^2 \frac{1}{n_R^s} \right] dn_R^s \end{aligned} \quad (3.7)$$

which yields the two potentials

$$\begin{aligned} v_t &\stackrel{\text{def}}{=} \left( \frac{n_R^s}{n_t^s} \right)^2 \left[ \mu_{xc} - \frac{2f_{xc}^s}{n_t^s} \right] \\ v_R &\stackrel{\text{def}}{=} \left( \frac{n_R^s}{n_t^s} \right)^2 \frac{2f_{xc}^s}{n_R^s} \end{aligned} \quad (3.8)$$

<sup>2</sup> In the earlier version the contribution from the  $\dot{\phi}$  has been ignored!!! It has been verified by temporarily switching off the jbar contributioun to `potpar1(isp)%prok` and `potpar1(isp)%projbar`. In this old version only `potpar(isp)%ktophi` is used to extract the  $\phi$  contribution.

For the cutoff function  $(n_R^s/n_t^s)^2$  we consider only the spherical contributions of the density and we ignore the spin contributions. This is accounted for in the derivations by only considering the spherical part  $f_{xc}^s$  of  $f_{xc}$ , while maintaining the non-spherical contributions to  $\mu_{xc}$ .

The total density  $n_t$  contains also the core density. If the core valence Fock term is included, they are part of the correlated electrons and need to be considered in the density  $n_R$ .

The double-counting correction has the negative sign, because the DFT-expression needs to be subtracted.<sup>3</sup> Its energy and the corresponding contributions to the auxiliary Hamiltonian are

$$E_{dc} = - \int d^3r \left( \frac{n_R^s}{n_t^s} \right)^2 f_{xc}^s$$

$$d\hat{H}_{dc} = -|\tilde{\pi}_\alpha\rangle\langle\chi_\alpha|\hat{v}_t|\chi_\beta\rangle\langle\tilde{\pi}_\beta| - |\tilde{\rho}_\alpha\rangle\langle\phi_\alpha|\hat{v}_R|\phi_\beta\rangle\langle\tilde{\rho}_\beta| \quad (3.9)$$

We start from two density matrices, which are the same at the moment.

see `lmto_simplifiedc_new`.

### Idea

$$E_{xc}^{\hat{W}_R} = \sum_{a,b,c,d} \int d^3r \chi_a^*(r)\chi_b(r)\chi_d^*(r)\chi_c(r) \frac{\epsilon_{xc}[n_{\sigma,\sigma'}^x(\vec{r})]}{n^x(\vec{r})} \quad (3.10)$$

---

<sup>3</sup>This subtraction is done outside the routine calculating the double-counting term.

## Chapter 4

# Description of Subroutines

### 4.1 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
```

### 4.2 LMTO\_POTPAR

All information that depends directly on the partial waves is stored in the structure POTPAR.

POTPAR Structure	
RAD	augmentation radius
Quantities connected to head functions	
NHEAD	number of head functions
LOFH(NHEAD)	angular momentum
ITAIL(NHEAD)	pointer to tail function
LNOFH(NHEAD)	pointer to partial wave $ \phi\rangle$ and projector $\langle p $
KTOPHI(NHEAD)	$ K^\Omega\rangle \rightarrow  \phi\rangle_{CKTOPHI} +  \dot{\phi}\rangle_{CKTOPHIDOT}$
KTOPHIDOT(NHEAD)	
Quantities connected to tail functions	
NTAIL(NTAIL)	number of tail functions
LOFT(NTAIL)	angular momentum
LNOFT(NTAIL)	pointer to partial wave $ \phi\rangle$ and projector $\langle p $
QBAR(NTAIL)	screening charge $ \bar{J}\rangle =  J\rangle -  K\rangle\bar{Q}$
JBARTOPHIDOT(NTAIL)	$ \bar{J}^\Omega\rangle \rightarrow  \dot{\phi}\rangle_{CJBARTOPHIDOT}$
Other stuff	
PROK(LNX,NHEAD)	$\langle \tilde{p}   \phi_{Cktopphi} + \dot{\phi}_{Cktophidot} \rangle$
PROJBAR(LNX,NTAIL)	$\langle \tilde{p}   \dot{\phi}_{Cjbartophidot} \rangle$
PHIOV(LNX,LNX)	$\langle \phi_\alpha   \theta_\Omega   \phi_\beta \rangle$
Tailed representation	
TAILED%GID	grid id for the radial grid
TAILED%LNX	
TAILED%LMNX	
TAILED%LOX(LNX)	
TAILED%AEF(NR,LNX)	
TAILED%PSF(NR,LNX)	
TAILED%NLF(NR,LNX)	
TAILED%U(LMNX,LMNX,LMNX,LMNX)	
TAILED%OVERLAP(LMNX,LMNX)	
TAILED%QLN(2,LNX,LNX)	

The variable lnx and lmnx in the substructure TAILED differ from the corresponding functions from the partial wave expansion.

### 4.3 LMTO\$CLUSTERSTRUCTURECONSTANTS

LMTO\$CLUSTERSTRUCTURECONSTANTS calculates the screened structure constants SBAR ( $\bar{S}$ ) 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 ( $\bar{k}^2 = -\kappa^2$ ) is the squared wave vector. (For envelope functions that fall off exponentially, this parameter is negative.)

```

SUBROUTINE LMT0$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 evaluated on the cluster using LMT0\$\\$STRUCTURECONSTANTS and then the structure constants are screened using LMT0\$\\$SCREEN.

#### 4.3.1 LMT0\$\\$STRUCTURECONSTANTS

LMT0\$\\$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 lmt0$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 LMT0\$\\$STRUCTURECONSTANTS as

$$S_{RL,R'L'} \stackrel{\text{Eq. 2.7}}{=} (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}' - \vec{R}) \begin{cases} (-ik)^{\ell+\ell'-\ell''} & \text{for } k^2 > 0 \\ \delta_{\ell+\ell'-\ell''} & \text{for } k^2 = 0 \\ \kappa^{\ell+\ell'-\ell''} & \text{for } k^2 = -\kappa^2 < 0 \end{cases} \quad (4.1)$$

where  $H_L(k^2, \vec{R})$  is the solid Hankel function calculated in LMT0\$\\$SOLIDHANKEL. The solid Hankel function is the solution of the Helmholtz equation, Eq. 2.3.<sup>1</sup>

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  $k^2 > 0$ .

#### 4.3.2 LMT0\$\\$SCREEN

*I describe here what has been implemented as “version 3”.*

LMT0\$\\$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

<sup>1</sup>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.”

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

$$\langle K_{RL} | = - \sum_{L'} S_{RL,R'L'} \langle J_{R'L'} | \quad \text{for } R' \neq R \quad (4.2)$$

First we evaluate

$$\mathbf{A} = \mathbf{1} - \bar{\mathbf{Q}}\mathbf{S}^\dagger \quad (4.3)$$

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

$$\mathbf{A}\vec{c}_\alpha \stackrel{\text{Eq. 2.23}}{=} \vec{e}_\alpha \quad (4.4)$$

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

$$\vec{s}_\alpha \stackrel{\text{Eq. 2.24}}{=} \mathbf{S}^\dagger \vec{c}_\alpha \quad (4.5)$$

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

## 4.4 Waves object

The data exchange between the waves object and the lmtot 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  $\langle \tilde{\rho} | \tilde{\psi}_n \rangle$ .

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
```

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

## 4.5 Offsite matrix elements

The offsite matrix elements are kept in the data type

```

TYPE OFFSITEX_TYPE
  INTEGER(4)      :: NDIS
  INTEGER(4)      :: NF
  REAL(8) , POINTER :: OVERLAP(:, :) ! OVERLAP MATRIX ELEMENTS
  REAL(8) , POINTER :: X22(:, :) !
  REAL(8) , POINTER :: X31(:, :)
  REAL(8) , POINTER :: BONDU(:, :)
  REAL(8) , POINTER :: DIS(:)
  REAL(8) , POINTER :: LAMBDA(:)
END TYPE OFFSITEX_TYPE

```

The matrix elements are initialized in LMT0\_initialize

```

LMT0_TAILEDGAUSSFIT()
  GAUSSIAN_FITGAUSS(GID, NR, W, L, AUX, NE, NPOW2, E, C(:NPOW2, :, LN))
  LMT0_TAILEDGAUSSORBTOLM()
LMT0_OFFXINT
  LMT0_OFFSITEOVERLAPSETUP !O(AB) ->OFFSITEX%OVERLAP
    LMT0_TWOCENTER
  LMT0_OFFSITEX22SETUP !U(AABB) ->OFFSITEX%X22
    LMT0_TWOCENTER
  LMT0_OFFSITEX31SETUP !U(AAAB) ->OFFSITEX%X31
    LMT0_TWOCENTER
  LMT0_TAILEDGAUSSOFFSITEU !U(ABAB) ->OFFSITEX%BONDU
    GAUSSIAN$ZDIRECTION_FOURCENTER(NIJKA, NEA, EA, LMNXA, ORBA &
    LMT0_OFFSITEXCONVERT()

```

The energy contribution is then calculated using offsite as follows

```

LMT0_OFFSITEXEVAL_NEW(EX)
  LMT0_EXPANDNONLOCAL
  LMT0_EXPANDLOCAL
  SPHERICAL$ROTATEYLM(LMX, ROT, YLMROT)
  LMT0_OFFSITEX22U(ISPA, ISPB, DIS, LMNXTA, LMNXTB, U22, DU22)

```



```

      lmtto_offsitexvalue
      LMTO_OFFSITEEX31U(ISPA,ISPB, DIS,LMNXTA,LMNXTB,U3A1B,DU3A1B)
      lmtto_offsitexvalue
      LMTO_OFFSITEEX31U(ISPB,ISPA,-DIS,LMNXTB,LMNXTA,U3B1A,DU3B1A)
      lmtto_offsitexvalue
      LMTO_OFFSITEEXBONDU(ISPA,ISPB,DIS,LMNXTA,LMNXTB,BONDU,DBONDU)
      lmtto_offsitexvalue

```

## 4.6 Matrix elements using Gaussians

LMTO\_TAILEDGAUSSOFFSITEU uses the gauss decomposition of the tailed orbitals in potpar%tailed%gaussnlf. In tailedgaussfit the following data structure is prepared.

```

POTPAR%TAILED%GAUSSNLF%NIJK
POTPAR%TAILED%GAUSSNLF%NORB
POTPAR%TAILED%GAUSSNLF%NPOW
POTPAR%TAILED%GAUSSNLF%NE
POTPAR%TAILED%GAUSSNLF%E
POTPAR%TAILED%GAUSSNLF%C

```

## 4.7 Matrix elements on an adaptive grid

```

lmtto_twocenter

MODULE LMTO_TWOCENTER_MODULE
LMTO_TWOCENTER
  ADAPT$EVALUATE
    ADAPTINI
    ADAPT_BASICRULE
    ADAPT_INTEGRAND
    LMTO_TWOCENTER_MYFUNC

```

## 4.8 Routines for reporting

```

LMTO$REPORT(NFIL)
...
LMTO$REPORTOVERLAP(NFIL)
LMTO$REPORTSBAR(NFIL)
LMTO$REPORTDENMAT(NFIL)
LMTO$REPORTHAMIL(NFIL)
LMTO$REPORTPERIODICMAT(NFIL,NAME,NNS,SBAR)
...
LMTO$WRITEPHI(FILE,GID,NR,NPHI,PHI)

```

## 4.9 Routines for plotting orbitals

There are a three routines that calculate the orbitals either in a spherical-harmonics expansion on radial grids or directly on an array of real-space points.

```

LMTO_TAILEDORBLM(IAT,IORB,NR,LMX,ORB)
LMTO_TAILED_NTBOOFR(IAT,iORB,NP,P,chi)
  LMTO_TAILEDORBLM(IAT,IORB,NR,LMX,ORB)
LMTO_NTBOOFR(IAT,iORB,NP,P,chi)

LMTO_PLOTTAILED() [OK]
  LMTO_TAILEDORBLM(IAT,IORB,NR,LMX,ORB)
LMTO_GRIDPLOT(type,iat) [ok]
  LMTO_GRIDORB_CUBEGRID(RO(: , IATO), RANGE, N1, N2, N3, ORIGIN, TVEC, P)
  LMTO_GRIDORB_STARGRID(RO(: , IATO), RANGE, NDIR, DIR, NRAD, X1D, P)
  LMTO_TAILED_NTBOOFR(TYPE, IAT, iORB, NP, P, chi)
    LMTO_TAILEDORBLM(IAT, IORB, NR, LMX, ORB)
    LMTO_NTBOOFR(IAT, iORB, NP, P, chi)
  LMTO_WRITECUBEFILE
..
LMTO_GRIDPLOT_UNTAILED(IATO)
  LMTO_GRIDORB_CUBEGRID(RO(: , IATO), RANGE, N1, N2, N3, ORIGIN, TVEC, P)
  LMTO_GRIDORB_STARGRID(RO(: , IATO), RANGE, NDIR, DIR, NRAD, X1D, P)
  LMTO_GRIDENVELOPE(RBAS, NAT, RO, IATO, LMX, NP, P, ENV, ENV1)
  LMTO_GRIDAUGMENT(RBAS, NAT, RO, IATO, LMX, NP, P, ORB1, ENV1)
  LMTO_GRIDGAUSS(RBAS, NAT, RO, IATO, LMX, NP, P, ORBG)
  LMTO_WRITECUBEFILE(NFIL, NATCLUSTER, ZCLUSTER, RCLUSTER &
LMTO_PLOTLOCORB(IATO)
  LMTO_GRIDENVELOPE(RBAS, NAT, RO, IATO, LM1X, NP, P, ENV, ENV1)
  LMTO_GRIDAUGMENT(RBAS, NAT, RO, IATO, LM1X, NP, P, ORB1, ENV1)
  LMTO_GRIDGAUSS(RBAS, NAT, RO, IATO, LM1X, NP, P, ORBG)
  LMTO_WRITECUBEFILE
LMTO_PLOTNTBO(TYPE, IATORB, LMNORB)
  LMTO_GRIDORB_CUBEGRID(CENTER, RADIUS, N1, N2, N3, ORIGIN, TVEC, P)
  LMTO_GRIDORB_STARGRID(CENTER, RADIUS, NDIR, DIR, NR, X1D, P)
  LMTO_TAILED_NTBOOFR(TYPE, IATORB, LMNORB, NP, P, ORB)
  LMTO_NTBOOFR(TYPE, IATORB, LMNORB, NP, P, ORB)
..
LMTO$PLOTWAVE(NFIL, IDIMO, IBO, IKPTO, ISPIN0, NR1, NR2, NR3)
  LMTO$PLOTWAVE_TAILED(NFIL, IDIMO, IBO, IKPTO, ISPIN0, NR1, NR2, NR3)
  WRITEWAVEPLOT(NFIL, TITLE, RBAS, NAT, RO, ZAT, Q, NAME, XK, NR1, NR2, NR3, WAVE)

```

- LMTO\_TAILEDORBLM(IAT, IORB, NR, LMX, ORB) calculates a specific orbital on radial grids in a spherical harmonics representation.
- LMTO\_PLOTTAILED() writes the tailed local orbitals in a spherical harmonics expansion to file, so that the componenst can be viewed by xmgrace. Each orbital is written to a file CHI5\_3.DAT where 5 is the atom index and 3 is the orbital index.

- `LMT0_TAILED_NTBOOFR(IAT,iORB,NP,P,chi)` calculates a specific tailed orbital on a set of real space points.
- `LMT0_GRIDPLOT_TAILED(IAT0)` writes the orbitals for the specified site to file. It supports a 3D representation with cube files, and one-dimensional representation on a star grid.

### Multicenter expansion

First the interstitial orbital is determined

$$\begin{aligned}
 |\bar{K}_\alpha^I\rangle &= |\bar{K}_\alpha^\infty\rangle - \left[ |K_\alpha^\Omega\rangle - \sum_\beta |J_\beta^\Omega\rangle \bar{S}_{\beta,\alpha}^\dagger \right] \\
 &= \sum_\beta |K_\beta^\infty\rangle (\delta_{\alpha,\beta} + \bar{Q}_\beta \bar{S}_{\beta,\alpha}^\dagger) - \left[ |K_\alpha^\Omega\rangle - \sum_\beta |J_\beta^\Omega\rangle \bar{S}_{\beta,\alpha}^\dagger \right] \\
 &= \sum_\beta |K_\beta^\infty\rangle (\delta_{\alpha,\beta} + \bar{Q}_\beta \bar{S}_{\beta,\alpha}^\dagger) - \left[ |K_\alpha^\Omega\rangle - \sum_\beta \left( |J_\beta^\Omega\rangle - |K_\beta^\Omega\rangle \bar{Q}_\beta \right) \bar{S}_{\beta,\alpha}^\dagger \right] \\
 &= \sum_\beta \left( |K_\beta^\infty\rangle - |K_\beta^\Omega\rangle \right) (\delta_{\alpha,\beta} + \bar{Q}_\beta \bar{S}_{\beta,\alpha}^\dagger) + \sum_\beta |J_\beta^\Omega\rangle \bar{S}_{\beta,\alpha}^\dagger
 \end{aligned} \tag{4.6}$$

This implies that within the sphere centered at  $R_\beta$  only the expansion into bare bessel functions survive, while outside only the bare Hankel function is considered.

## Chapter 5

# Benchmarks

### 5.1 Silicon

The files are in [~/Tree/Projects/SetupTests/Si](#).

I performed calculation for a silicon crystal. We used a mixing of the lcoal exchange of  $\alpha_X = 0.1$ . The local basiset included one s-type and one p-type tight-binding function.

The following dependencies have been explored:

- kinetic energy of the Hankel function:  $K2 = 0, \dots, -0.5$

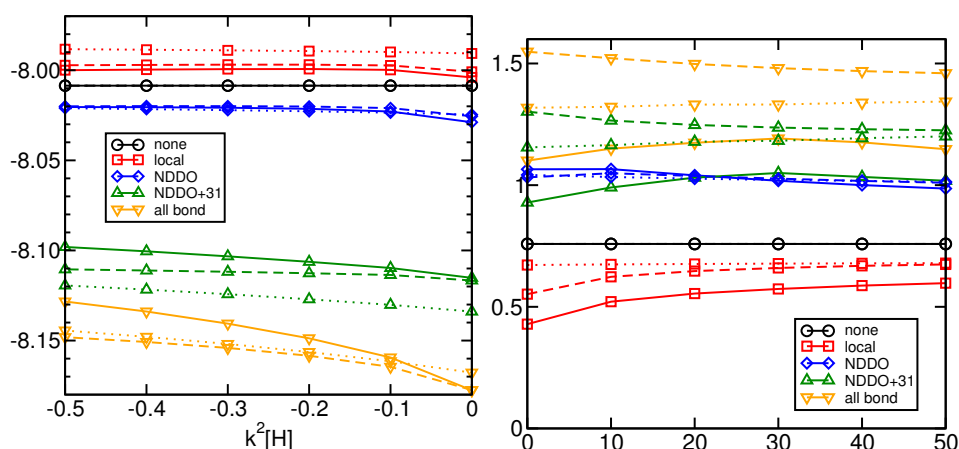


Fig. 5.1: Energy in Hartree and band gap in eV of the silicon crystal as function of the kinetic energy (times -0.01) of the envelope function for the PBE functional (black; none), local Hartree-Fock (red; onsite or local) NDDO-type exchange, i.e density of one site with the density on a bond partner (blue, NDDO), terms with three orbitals on one site and one on the bond partner (green NDDO+31) and the exchange of the bond density with itself (orange, all bond). The full line is the result for one s-type and one p-type orbital. For the dashed lines also d-type orbitals are included. The dotted lines are calculated with double orbitals for s,p and single orbitals for d.

- Augmentation radius. The augmentation radius is the radius at which the partial waves

are matched to the envelope function. It is also the radius for the sphere used to derive the projector function onto the local orbitals. The procedure apparently breaks down

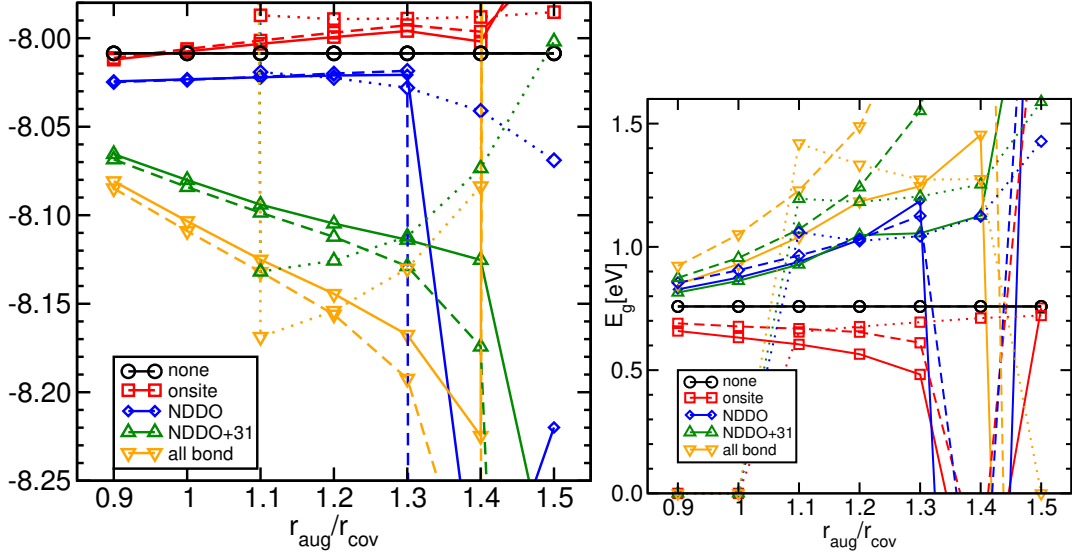
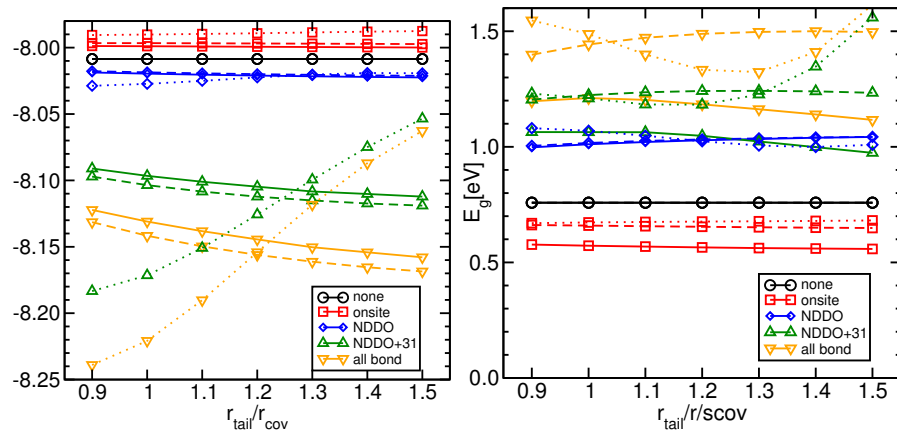
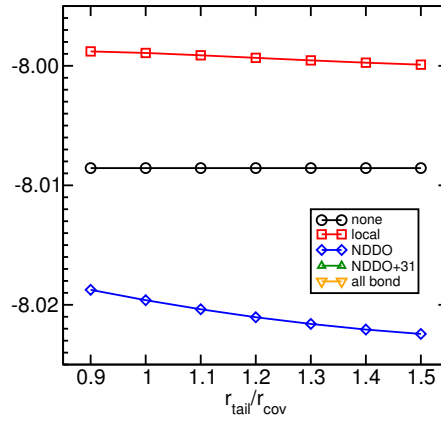


Fig. 5.2: Energy in Hartree and band gap in eV of the silicon crystal as function of the augmentation radius for the PBE functional (black; none), local Hartree-Fock (red; onsite or local) NDDO-type exchange, i.e. density of one site with the density on a bond partner (blue, NDDO), terms with three orbitals on one site and one on the bond partner (green NDDO+31) and the exchange of the bond density with itself (orange, all bond). The full line is the result for one s-type and one p-type orbital. For the dashed lines also d-type orbitals are included. The dotted lines are calculated with double orbitals for s,p and single orbitals for d.

completely, if the augmentation radius is too large. The dependency becomes stronger, if more non-local terms are included. This may be due to the fact that the double-counting term is only included for the local terms.

- tail matching radius





### 5.1.1 Summary

- The augmentation radius has the largest effects on the results both for the gap and for the total energy. Beyond a certain radius ( $> 1.2 r_{cov}$ ) the calculation becomes even unstable. For an “overcomplete TB-basisset  $2s+2p+1d$ ” the calculation also fails for ( $< 1.1 r_{cov}$ ).
- It becomes evident that the energy is rather insensitive to the parameters describing the local orbitals for local exchange and the NDDO terms. Additional terms such as “31” and “bondx”, which include the bond overlap density  $\chi_R(r)\chi_{R'}(r)$  lead to a very strong dependency on the choice of orbitals. Note that  $0.05 \text{ H} \approx 1.4 \text{ eV}$ !

This may be due to the poor description of the bond density by the exponential tails of the tailed orbitals.

It may also be due to the fact that these terms are not compensated by the double-counting term.

- It should be noted that the double-counting term is included only for local exchange.
- Choose value of  $-0.2 < k^2 < -0.5 \text{ H}$
- Choose value of  $r_{tail} = 1.2 r_{cov}$

## Appendix A

# Definition of solid Hankel functions

The solid Hankel function has the form

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

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

- the function

$$n_\ell(r) = r^\ell \left( -\frac{1}{r} \partial_r \right)^\ell \frac{1}{r} \cos(r) \quad (\text{A.2})$$

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

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

**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

$$m_\ell(r) = r^\ell \left( -\frac{1}{r} \partial_r \right)^\ell \frac{1}{r} e^{-r} \quad (\text{A.4})$$

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

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

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[4] in their Eq. 10.2.4.

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

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[5]. He uses the theorem[6] that supposedly goes back to Kasterin (N. Kasterin, Proc. Acad. Sci Amsterdam 6, 460 (1897/98)); see Segall[5], Eq. B4)

$$h_\ell^{(1)}(\kappa r) Y_{\ell,m}(\vec{r}) = i^{-\ell} \mathcal{Y}_{\ell,m}(\vec{\nabla}_r) h_0^{(1)}(\kappa r) \quad (\text{A.7})$$

where  $h_\ell^{(1)}(x)$  is the spherical Hankel function of the first kind (see Eq. A.13 below) and where (Eq. B5 of Segall[5])

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

where the positive sign applies for nonzero  $m$  and the negative sign for negative  $m$ . Furthermore (see Segall[5] Eq. B5)

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

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

In addition Segall[5] refers in his Eq. B7 to Morse and Feshbach[7] (part II, p. 1574) for

$$h_0^{(1)}(\kappa|\vec{r} - \vec{r}'|) = 4\pi \sum_L \left( h_\ell^{(1)}(\kappa|\vec{r}'|) Y_L(\vec{r}') \right) j_\ell(\kappa|\vec{r}|) Y_L^*(\vec{r}) \quad (\text{A.9})$$

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

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

$$\begin{aligned} h_\ell^{(1)}(\kappa|\vec{r}|) Y_{\ell,m}(\vec{r}) &\stackrel{\text{Eq. A.7}}{=} i^{-\ell} \mathcal{Y}_{\ell,m}(\vec{\nabla}_r) h_0^{(1)}(\kappa|\vec{r}|) \\ &= i^{-\ell} \mathcal{Y}_{\ell,m}(\vec{\nabla}_r) h_0^{(1)}(\kappa|\vec{r} - \vec{R}| + |\vec{R}|) \\ &\stackrel{\text{Eq. A.9}}{=} i^{-\ell} \mathcal{Y}_{\ell,m}(\vec{\nabla}_r) \left[ 4\pi \sum_{L'} \left( h_{\ell'}^{(1)}(\kappa|\vec{R}|) Y_{L'}(-\vec{R}) \right) j_{\ell'}(\kappa|\vec{r} - \vec{R}|) Y_{L'}^*(\vec{r} - \vec{R}) \right] \\ &\stackrel{\text{Eq. A.11}}{=} 4\pi \sum_{L'} \left( i^{-\ell} \mathcal{Y}_{\ell,m}(\vec{\nabla}_R) h_{\ell'}^{(1)}(\kappa|\vec{R}|) Y_{L'}(-\vec{R}) \right) j_{\ell'}(\kappa|\vec{r} - \vec{R}|) Y_{L'}^*(\vec{r} - \vec{R}) \end{aligned}$$



Here we used that

$$\vec{\nabla}_r [f(\vec{R})g(\vec{r} - \vec{R})] = f(\vec{R})\vec{\nabla}_r g(\vec{r} - \vec{R}) = -f(\vec{R})\vec{\nabla}_R g(\vec{r} - \vec{R}) \quad (\text{A.10})$$

$$= -\underbrace{\vec{\nabla}_R [f(\vec{R})g(\vec{r} - \vec{R})]}_{=0} + [\vec{\nabla}_R f(\vec{R})]g(\vec{r} - \vec{R}) \quad (\text{A.11})$$

We summarize the final result

CONDITION FOR STRUCTURE CONSTANTS (POSITIVE ENERGIES)

$$h_\ell^{(1)}(\kappa|\vec{r}|)Y_{\ell,m}(\vec{r}) = 4\pi \sum_{L'} \left( i^{-\ell} \mathcal{Y}_{\ell,m}(\vec{\nabla}_R) h_{\ell'}^{(1)}(\kappa|\vec{R}|) Y_{L'}(-\vec{R}) \right) j_{\ell'}(\kappa|\vec{r} - \vec{R}|) Y_{L'}^*(\vec{r} - \vec{R}) \quad (\text{A.12})$$

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

$$h_\ell^{(1)}(x) \stackrel{\text{AS10.1.1}}{=} j_\ell(x) + i y_\ell(x) \stackrel{\text{AS10.1.26}}{=} x^\ell \left( -\frac{1}{x} \partial_x \right)^\ell \frac{\sin(x) - i \cos(x)}{x} \quad (\text{A.13})$$

### 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.

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

## A.2 Consistency checks

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

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

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

The explicit form of the first few is

$$K_{0,s}^{\infty}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \frac{1}{|\vec{r}|} \quad (\text{A.17})$$

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

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

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

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

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

which allows us to evaluate the structure constants directly calculating value and derivatives at the second center and by exploiting selection rules<sup>1</sup>

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

$$\partial_x |_{\vec{R}} K_{0,s}^{\infty} = -\frac{1}{\sqrt{4\pi}} \frac{x}{|\vec{R}|^3} = - \underbrace{\sqrt{3} \frac{x}{|\vec{R}|^3}}_{S_{\vec{0},s;\vec{R},p_x}} \underbrace{\frac{1}{3} \sqrt{\frac{3}{4\pi}}}_{\partial_x J_{\vec{R},p_x}(\vec{R})} \quad (\text{A.23})$$

$$\begin{aligned} K_{0,p_x}^{\infty}(\vec{R}) &= \sqrt{\frac{3}{4\pi}} \frac{x}{|\vec{R}|^3} = - \underbrace{\left( -\sqrt{3} \frac{x}{|\vec{R}|^3} \right)}_{S_{\vec{0},p_x;\vec{R},s}} \underbrace{\frac{1}{\sqrt{4\pi}}}_{J_{\vec{R},s}(\vec{R})} \\ \partial_x |_{\vec{R}} K_{0,p_x}^{\infty} &= \sqrt{\frac{3}{4\pi}} \left( \frac{1}{|\vec{R}|^3} - 3 \frac{x^2}{|\vec{R}|^5} \right) = - \underbrace{3 \frac{3x^2 - \vec{R}^2}{|\vec{R}|^2}}_{S_{\vec{0},p_x;\vec{R},p_x}} \underbrace{\frac{1}{3} \sqrt{\frac{3}{4\pi}} |\vec{R}|^{-3}}_{\partial_x |_{\vec{R}} J_{\vec{R},p_x}} \end{aligned} \quad (\text{A.24})$$

Thus, the matrix of structure constants in the (s,p<sub>x</sub>) subspace is

$$\mathbf{S}_{\vec{0},\vec{R}} = \begin{pmatrix} -|\vec{R}|^{-1} & \sqrt{3}x/|\vec{R}|^3 \\ -\sqrt{3}x/|\vec{R}|^3 & 3[3x^2/R^2 - 1] \end{pmatrix} \quad (\text{A.25})$$

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

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

<sup>1</sup>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

$$\begin{aligned}
 S_{\vec{0},s;\vec{R},s} &= (-1)4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{sss}} \cdot \underbrace{\frac{1}{\sqrt{4\pi}} \frac{1}{|\vec{R}|}}_{H_s(\vec{R})} = -\frac{1}{|\vec{R}|} \\
 S_{\vec{0},s;\vec{R},p_x} &= 4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,p_x}} \underbrace{\sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3}}_{H_{p_x}(\vec{R})} = \sqrt{3} \frac{X}{|\vec{R}|^3} \\
 S_{\vec{0},p_x;\vec{R},s} &= (-1)4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,s}} \sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3} = -\sqrt{3} \frac{X}{|\vec{R}|^3} \\
 S_{\vec{0},p_x;\vec{R},p_x} &= 4\pi \underbrace{\frac{1}{\sqrt{5\pi}}}_{C_{p_x,p_x,d_{3x^2-r^2}}} \underbrace{\sqrt{\frac{5}{16\pi}} \frac{3X^2-R^2}{|\vec{R}|^2} \frac{3}{|\vec{R}|^3}}_{H_{3x^2-r^2}(\vec{R})} = 3 \frac{3X^2-R^2}{|\vec{R}|^5} \quad (\text{A.27})
 \end{aligned}$$

For Gaunt coefficients see footnote.<sup>2</sup>

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2

$$\begin{aligned}
 Y_{p_x} Y_{p_x} &= \frac{3}{4\pi} \frac{x^2}{r^2} = \frac{1}{4\pi} \frac{x^2}{r^2} + \frac{1}{4\pi} \frac{3x^2-r^2}{r^2} = \frac{1}{\sqrt{4\pi}} Y_s + \frac{1}{4\pi} \sqrt{\frac{16\pi}{5}} Y_{3x^2-r^2} = \frac{1}{\sqrt{4\pi}} Y_s + \sqrt{\frac{1}{5\pi}} Y_{3x^2-r^2} \\
 &\Rightarrow C_{p_x,p_x,s} = \frac{1}{\sqrt{4\pi}} \quad \text{and} \quad C_{p_x,p_x,d_{3x^2-r^2}} = \frac{1}{\sqrt{5\pi}} \quad (\text{A.28})
 \end{aligned}$$

## Appendix B

# Bloch theorem revisited

The Bloch states are eigenstates of the discrete lattice translation

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

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

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

This eigenvalue equation can be recast into the form

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

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

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

with

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

### Bloch theorem in a local orbital basis

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

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

**Density matrix**

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

## Appendix C

# Offsite matrix elements using Gaussian integrals

In LMTO\_INITIALIZE there are non-functional calls for doing the integrations in a representation of Gauss orbitals. The routines are no more present, except for

- LMTO\_TAILEDPRODUCTS. They have been removed in 7501a0g from Feb.2, 2013 (svn revision 1116 from Nov. 20, 2011). LMTO\_TAILEDPRODUCTS has been removed after 9803b02 on from Mar. 1, 2014.
- LMTO\_EXPANDPRODS

The routines related to Gaussians have been moved into the file `paw_lmto_stuffwithgaussians.f90`

```
!!$      CALL LMTO_TAILEDPRODUCTS()  
          gaussian_fitgauss  
!!$      CALL LMTO_GAUSSFITKPRIME()  
!!$      CALL LMTO_GAUSSFITKAUGMENT()  
!!$      CALL LMTO_GAUSSFITKJTails()  
!!$      CALL LMTO_ONSITEOVERLAP()
```

## Appendix D

# Double counting

### D.1 Other double-counting schemes

An excellent review of double-counting terms has been discussed by Nekrasov et al.[8].

#### Around-mean-field (AMF) and fully-localized limit (FLL)

In LDA+U, two double-counting schemes are in common use: one is called around mean-field (AMF)[9] and the other is called fully localized limit (FLL)[10].

In the Hubbard model, the two approximations have the form[8].

$$\begin{aligned}\hat{H}_{AMF}^{dc} &= \frac{1}{2}U \sum_{\sigma} \hat{n}_{d,\sigma}(\hat{n}_d - n_{\sigma}^0) - \frac{1}{2}J \sum_{\sigma} \hat{n}_{d,\sigma}(\hat{n}_{d,\sigma} - n_{\sigma}^0) \\ \hat{H}_{FLL}^{dc} &= \frac{1}{2}U n_d(n_d - 1) - \frac{1}{2}J \sum_{\sigma} \hat{n}_{d,\sigma}(\hat{n}_{d,\sigma} - 1)\end{aligned}\tag{D.1}$$

with

$$\begin{aligned}n_{d,\sigma} &= \sum_m \langle \hat{n}_{m,\sigma} \rangle \\ n_d &= \sum_{\sigma} n_{d,\sigma} \\ n_{\sigma}^0 &= \frac{1}{2(2\ell + 1)} \sum_{m,\sigma} n_{m,\sigma} \\ n^0 &= \sum_{\sigma} n_{\sigma}^0\end{aligned}\tag{D.2}$$

It is still unclear what are operators and what are numbers, but I believe all are numbers.

#### Nekrasov, Pavlov Sadovskii scheme

Nekrasov et al.[8] proposes a new scheme which amounts to removing the density of the correlated orbitals from the integral for the exchange-correlation term. The corresponding double-

counting energy would be

$$E^{DC} = E_{xc}[n_t - n_{corr}] - E_{xc}[n_t] \quad (D.3)$$

where  $n_t$  is the density of all orbitals, while  $n_{corr}$  is the density of the correlated orbitals only.

### Blöchl-Walther-Pruschke scheme

Our scheme[3] differs in that it divides the DFT exchange correlation energy based on a partitioning of the two-particle density, where  $n(\vec{r}) = \sum_R n_R(\vec{r})$

$$\begin{aligned} E_{xc} &= \int d^3r n(\vec{r}) \frac{1}{2} \int d^3r' \frac{e^2 \int_0^1 d\lambda h_\lambda(\vec{r}, \vec{r}')}{4\pi\epsilon|\vec{r} - \vec{r}'|} \\ &= \frac{1}{2} \sum_{R,R'} \int d^3r \int d^3r' \left( \frac{n_R(\vec{r})}{n(\vec{r})} \right) \left( n(\vec{r}) \frac{e^2 \int_0^1 d\lambda h_\lambda(\vec{r}, \vec{r}')}{4\pi\epsilon|\vec{r} - \vec{r}'|} \right) \left( \frac{n_{R'}(\vec{r}')}{n(\vec{r}')} \right) \end{aligned} \quad (D.4)$$

This formulation takes into account that the electrons are indistinguishable and that each electron contributes equally to the exchange correlation energy. Furthermore, the partitions of the expression add up to the total exchange-correlation energy (when also the inter-site terms are included).

The model rests on a well defined expression for the two-particle density, namely

$$n^{(2)}(\vec{r}, \vec{r}') = n^{(1)}(\vec{r})n^{(1)}(\vec{r}') + \frac{1}{2} \sum_{R,R'} \left( \frac{n_R(\vec{r})}{n(\vec{r})} \right) \left( n(\vec{r}) h_{\lambda=1}(\vec{r}, \vec{r}') \right) \left( \frac{n_{R'}(\vec{r}')}{n(\vec{r}')} \right) \quad (D.5)$$

and an expression for the kinetic-energy correction

$$T - T_s = \frac{1}{2} \sum_{R,R'} \int d^3r \int d^3r' \left( \frac{n_R(\vec{r})}{n(\vec{r})} \right) \left( n(\vec{r}) \frac{e^2 \int_0^1 d\lambda \left( h_\lambda(\vec{r}, \vec{r}') - h_{\lambda=1}(\vec{r}, \vec{r}') \right)}{4\pi\epsilon|\vec{r} - \vec{r}'|} \right) \left( \frac{n_{R'}(\vec{r}')}{n(\vec{r}')} \right) \quad (D.6)$$

Note, however, that only the total exchange-correlation energy including Coulomb and kinetic energy contributions is a density functional, whereas both contributions can be expressed individually as density-matrix functional.

Thus, a double-counting correction for a set of correlated orbitals, which contribute  $n_R$  to the total density would be

$$E_{dc} = -\frac{1}{2} \sum_R \int d^3r \int d^3r' \left( \frac{n_R(\vec{r})}{n(\vec{r})} \right) \left( n(\vec{r}) \frac{e^2 \int_0^1 d\lambda h_\lambda(\vec{r}, \vec{r}')}{4\pi\epsilon|\vec{r} - \vec{r}'|} \right) \left( \frac{n_R(\vec{r}')}{n(\vec{r}')} \right) \quad (D.7)$$

This integral can be approximated further as

$$E_{xc} = -\frac{1}{2} \sum_R \int d^3r n(\vec{r}) \epsilon[n(\vec{r})] \left( \frac{n_R(\vec{r})}{n(\vec{r})} \right)^2 \quad (D.8)$$



### D.1.1 Around mean field (AMF)

The original expression, AMF, for the double-counting term is derived from the mean-field approximation of the Hubbard model.

**This section is unfinished. It is an attempt to derive the AMF limit consistent with our U-tensor** We start out from the interaction

$$\hat{W} = \frac{1}{2} \sum_{i,j,k,l} W_{i,j,l,k} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l \quad (\text{D.9})$$

with

$$\begin{aligned} W_{i,j,k,l} &= \int d^4x \int d^4x' \frac{e^2 \chi_i^*(\vec{x}) \chi_j^*(\vec{x}') \chi_k(\vec{x}) \chi_l(\vec{x}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \\ &= \delta_{\sigma_i, \sigma_k} \delta_{\sigma_j, \sigma_l} \int d^3r \int d^3r' \frac{e^2 \phi_i^*(\vec{r}) \phi_j^*(\vec{r}') \phi_k(\vec{r}) \phi_l(\vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} = \delta_{\sigma_i, \sigma_k} \delta_{\sigma_j, \sigma_l} U_{i,j,k,l} \end{aligned} \quad (\text{D.10})$$

where the spin-orbitals  $\chi_i(\vec{r}, \sigma) = \phi_i(\vec{r}) \delta_{\sigma, \sigma_i}$  are decomposed into a outer product of a spatial orbital  $\phi_i(\vec{r})$  and a spinor. The interaction has the internal symmetry

$$W_{i,j,k,l} = W_{j,i,l,k} = W_{k,l,i,j}^* = W_{l,k,j,i}^* \quad (\text{D.11})$$

In order to arrive at the mean-field Hamiltonian, we express the wave function in terms of wave function of a non-interacting system, i.e. by Slater determinants. This non-interacting system is then optimized to minimize the expectation value of the Hamiltonian containing the interaction. (See Bogoljubov inequality) The result is the Hartree-Fock approximation.

The ground state is

$$|\Phi_0\rangle = \prod_n (\hat{a}_n^\dagger)^{\sigma_n} |\mathcal{O}\rangle \quad (\text{D.12})$$

where  $\vec{\sigma} \in \{0, 1\}^\infty$  is the occupation number representation of the Slater determinant. The orbitals making up the Slater determinant are  $|\phi_n\rangle$

$$\hat{a}_n^\dagger = \sum_j \hat{c}_j^\dagger \langle \pi_j | \psi_n \rangle \quad (\text{D.13})$$

with a complete set of one-particle orbitals and the bi-orthogonality condition this relationship can be inverted

$$\sum_n \hat{a}_n^\dagger \langle \psi_n | \chi_i \rangle = \sum_j \hat{c}_j^\dagger \langle \pi_j | \underbrace{\sum_n |\psi_n\rangle \langle \psi_n|}_{\substack{=1 \\ \delta_{i,j}}} | \chi_i \rangle = \hat{c}_i^\dagger \quad (\text{D.14})$$

$$\begin{aligned}
\langle \Phi | \hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_o \hat{a}_p | \Phi \rangle &= \delta_{m,o} \delta_{n,p} \langle \Phi | \hat{a}_m^\dagger \underbrace{\hat{a}_n^\dagger \hat{a}_m}_{\delta_{m,n} - \hat{a}_m \hat{a}_n^\dagger} \hat{a}_n | \Phi \rangle + \delta_{m,p} \delta_{n,o} \langle \Phi | \hat{a}_m^\dagger \underbrace{\hat{a}_n^\dagger \hat{a}_n \hat{a}_m}_{-(\delta_{m,n} - \hat{a}_m \hat{a}_n^\dagger) \hat{a}_n} | \Phi \rangle \\
&\quad - \delta_{m,p} \delta_{n,o} \delta_{m,n} \langle \Phi | \hat{a}_m^\dagger \hat{a}_m^\dagger \underbrace{\hat{a}_m \hat{a}_m}_{=0} | \Phi \rangle \\
&= \delta_{m,o} \delta_{n,p} \left[ \delta_{m,n} \langle \Phi | \hat{a}_m^\dagger \hat{a}_n | \Phi \rangle - \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle \right] \\
&\quad - \delta_{m,p} \delta_{n,o} \left[ \delta_{m,n} \langle \Phi | \hat{a}_m^\dagger \hat{a}_n | \Phi \rangle - \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle \right] \\
&= -\delta_{m,o} \delta_{n,p} \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle + \delta_{m,p} \delta_{n,o} \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle \\
&= f_m f_n \left[ \delta_{m,o} \delta_{n,p} - \delta_{m,p} \delta_{n,o} \right]
\end{aligned} \tag{D.15}$$

Here the occupations are those of the reference Slater determinant, the mean field.

Now we can evaluate the matrix elements for the interaction as

$$\begin{aligned}
\langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l | \Phi_0 \rangle &= \sum_{m,n,o,p} \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \langle \Phi_0 | \hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_o \hat{a}_p | \Phi_0 \rangle \langle \chi_k | \psi_o \rangle \langle \chi_l | \psi_p \rangle \\
&= \sum_{m,n,o,p} \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \left[ f_m f_n \left[ \delta_{m,o} \delta_{n,p} - \delta_{m,p} \delta_{n,o} \right] \right] \langle \chi_k | \psi_o \rangle \langle \chi_l | \psi_p \rangle \\
&= \sum_{m,n} f_m f_n \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \langle \chi_k | \psi_m \rangle \langle \chi_l | \psi_n \rangle - \sum_{m,n} f_m f_n \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \langle \chi_k | \psi_n \rangle \langle \chi_l | \psi_m \rangle \\
&= \underbrace{\sum_m \langle \chi_k | \psi_m \rangle f_m \langle \psi_m | \chi_i \rangle}_{\rho_{k,i}} \underbrace{\sum_m \langle \chi_l | \psi_n \rangle f_n \langle \psi_n | \chi_j \rangle}_{\rho_{l,j}} - \underbrace{\sum_m \langle \chi_l | \psi_m \rangle f_m \langle \psi_m | \chi_i \rangle}_{\rho_{l,i}} \underbrace{\sum_n \langle \chi_k | \psi_n \rangle f_n \langle \psi_n | \chi_j \rangle}_{\rho_{k,j}} \\
&= \rho_{k,i} \rho_{l,j} - \rho_{l,i} \rho_{k,j} \\
&= \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_k | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_l | \Phi_0 \rangle - \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_l | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_k | \Phi_0 \rangle
\end{aligned} \tag{D.16}$$

This is the expectation value of a Slater determinant which is the zero'th order term for an expansion in the deviation from these mean values.

The density matrix has the form

$$\rho_{i,j} = \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_i | \Phi_0 \rangle = \sum_{m,n} \langle \psi_m | \chi_j \rangle \langle \chi_i | \psi_n \rangle \underbrace{\langle \Phi_0 | \hat{a}_m^\dagger \hat{c}_n | \Phi_0 \rangle}_{\delta_{m,n} f_n} = \sum_n \chi_i | \psi_n \rangle f_n \langle \psi_n | \chi_j \rangle \quad (\text{D.17})$$

$$\begin{aligned}\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l &= \hat{c}_j^\dagger \hat{c}_i^\dagger \hat{c}_k \hat{c}_l \\ &= \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_k | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_l | \Phi_0 \rangle - \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_l | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_k | \Phi_0 \rangle\end{aligned}\quad (\text{D.18})$$

interaction in terms of products of one-particle operators  $\hat{c}_i^\dagger \hat{c}_j$ . There are two equivalent forms for this, namely

$$\begin{aligned}\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l &= \delta_{j,k} \hat{c}_i^\dagger \hat{c}_l - \hat{c}_i^\dagger \hat{c}_k \hat{c}_j^\dagger \hat{c}_l \\ &= \delta_{j,l} \hat{c}_j^\dagger \hat{c}_k - \hat{c}_j^\dagger \hat{c}_l \hat{c}_j^\dagger \hat{c}_k\end{aligned}\quad (\text{D.19})$$

Similarly the products of the field operators can be rewritten in a number of different ways

$$\begin{aligned}\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l &= -\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_l \hat{c}_k = -\hat{c}_j^\dagger \hat{c}_i^\dagger \hat{c}_k \hat{c}_l = \hat{c}_j^\dagger \hat{c}_i^\dagger \hat{c}_l \hat{c}_k \\ &= \delta_{j,k} \hat{c}_i^\dagger \hat{c}_l - \hat{c}_i^\dagger \hat{c}_k \hat{c}_j^\dagger \hat{c}_l =\end{aligned}\quad (\text{D.20})$$

$$\begin{aligned}&= \frac{1}{2} \sum_{i,j,k,l} W_{i,j,l,k} \frac{1}{2} \left[ -\left( \hat{c}_i^\dagger \hat{c}_k \hat{c}_j^\dagger \hat{c}_l - \delta_{k,j} \hat{c}_i^\dagger \hat{c}_l \right) + \left( \hat{c}_i^\dagger \hat{c}_l \hat{c}_j^\dagger \hat{c}_k - \delta_{j,l} \hat{c}_i^\dagger \hat{c}_k \right) \right] \\ &\stackrel{i \leftrightarrow l}{=} \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left( \hat{n}_{i,k} \hat{n}_{j,l} - \delta_{k,j} \hat{n}_{i,l} \right)\end{aligned}\quad (\text{D.21})$$

In the mean-field approximation, terms that are quadratic in  $\hat{n} - \langle \hat{n} \rangle$  are ignored.

$$\begin{aligned}\hat{W}_{MF} &= \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left( \langle \hat{n}_{i,k} \rangle \langle \hat{n}_{j,l} \rangle - \delta_{k,j} \langle \hat{n}_{i,l} \rangle \right) \\ &+ \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left( [\hat{n}_{i,k} - \langle \hat{n}_{i,k} \rangle] \langle \hat{n}_{j,l} \rangle + \langle \hat{n}_{i,k} \rangle [\hat{n}_{j,l} - \langle \hat{n}_{j,l} \rangle] - \delta_{k,j} [\hat{n}_{i,l} - \langle \hat{n}_{i,l} \rangle] \right) \\ &= \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left( \hat{n}_{i,k} \langle \hat{n}_{j,l} \rangle + \langle \hat{n}_{i,k} \rangle \hat{n}_{j,l} - \delta_{k,j} \hat{n}_{i,l} - \langle \hat{n}_{i,k} \rangle \langle \hat{n}_{j,l} \rangle \right)\end{aligned}\quad (\text{D.22})$$

The resulting Hamiltonian is a one-particle hamiltonian, which depends parametrically on the occupations., i.e the density matrix.

This Hamiltonian can be derived consistently<sup>1</sup> from the density-matrix functional with the density matrix  $\rho_{i,j} = \langle \hat{c}_i^\dagger \hat{c}_j \rangle$

$$E_{AMF}^{DC} = \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left( \rho_{i,k} \rho_{j,l} - \delta_{k,j} \rho_{i,l} \right) \quad (\text{D.23})$$

In order to arrive at the common expression, we consider the **density-density approximation**, that is we consider only density matrices that are diagonal in the orbital and spin coordinates

$$\begin{aligned}E_{AMF}^{DC} &\approx \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{i,j} \frac{W_{i,j,i,j} - W_{i,j,j,i}}{2} \rho_{i,i} \rho_{j,j} - \frac{1}{2} \sum_{i,j} \frac{W_{i,j,i,j} - W_{i,j,j,i}}{2} \rho_{i,i} \\ &= \frac{1}{2} \sum_{i \neq j} \frac{W_{i,j,j,i} - W_{i,j,i,j}}{2} \rho_{i,i} (\rho_{j,j} + 1)\end{aligned}\quad (\text{D.24})$$

<sup>1</sup>Both, the the total energy and the derived one-particle hamiltonian is consistent with the mean-field form of the interaction.

The terms with  $i = j$  cancel.

$$\begin{aligned}
E_{AMF}^{DC} &\approx \frac{1}{2} \sum_{m,m'} \frac{U_{m,m',m,m'} - U_{m,m',m',m} \delta_{\sigma,\sigma'}}{2} n_{m,\sigma} n_{m',\sigma'} \\
&\quad - \frac{1}{2} \sum_i \left( \sum_{m',\sigma'} \frac{U_{m,m',m',m} - U_{m,m',m,m'} \delta_{\sigma,\sigma'}}{2} \right) n_{m,\sigma} \\
&= \frac{1}{2} \sum_{\sigma} \sum_m \frac{U_{m,m,m,m}}{2} n_{m,\sigma} n_{m,\bar{\sigma}} \\
&\quad + \frac{1}{2} \sum_{m \neq m'} \sum_{\sigma,\sigma'} \frac{U_{m,m',m,m'} - U_{m,m',m',m} \delta_{\sigma,\sigma'}}{2} n_{m,\sigma} n_{m',\sigma'} \\
&\quad - \frac{1}{2} \sum_i \left( \sum_{m'} \frac{2U_{m,m',m',m} - U_{m,m',m,m'}}{2} \right) n_{m,\sigma} \tag{D.25}
\end{aligned}$$

### D.1.2 Definition of U and J parameters

The U- and J-parameters for one angular-momentum shell are defined by the U-tensor as follows[11] (see Eq. 5 of Shick et al.)

$$U := \frac{1}{(2\ell + 1)^2} \sum_{m_1, m_2} U_{m_1, m_2, m_1, m_2} \tag{D.26}$$

$$J := U - \frac{1}{2\ell(2\ell + 1)} \sum_{m_1, m_2} (U_{m_1, m_2, m_1, m_2} - U_{m_1, m_2, m_2, m_1}) \tag{D.27}$$

where the Coulomb matrix elements are

$$U_{i,j,k,l} = \int d^3r \int d^3r' \frac{e^2 \chi_i^*(\vec{r}) \chi_j^*(\vec{r}') \chi_k(\vec{r}) \chi_l(\vec{r}')}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \tag{D.28}$$

The indices used here are spatial-orbital indices.

## Appendix E

# Changelog, Bugfixes

- 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 `lmtoscreen`, which has been fixed with version 3. It may be better to rewrite all structure constants routines with the transposed structure constants.
- in `lmtomakestructureconstants`, the structure constants have not been calculated because the parallelization was wrong. in 13403f6.

```
-      IF (MOD(IAT1-1,NTASKS) .NE. THISTASK-1) THEN  
+      IF (MOD(IAT1-1,NTASKS) .eq. THISTASK-1) THEN
```

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