The LMTO object of the CP-PAW code

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Chapter 1

Notes

- The variable `RAUG` must be large enough to enclose the semi-core states, because the decay of the envelope function is usually much too slow for them.
- The interpolation of the matrix elements on the distance grid must be investigated mor thoroughly. It is not clear why Gauss oscillation occur beyond the interpolation grid when the decay length is set too large. Tests have been done for the hydrogen atomic orbital but not for general orbitals.
- **The double counting term seems to work ok for the local exchange, but there is not such term for the non-local terms.!!!**

1.1 Fixes

- lmto_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 echange 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 quire well.

1.2 Ideas and remarks

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[**?**].

2.1 Augmentation: Overview

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

1. At first, a so-called **envelope function** $|K_\alpha^\infty\rangle$ is defined.[1]

2. In a second step, this envelope function is expanded about each atomic site R_α 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.

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

   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**[2] $|K_\alpha^I\rangle$.

[1] 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 centered at the site R_α denoted by the index α. 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 constains terms from the higher angular momenta within the augmentation regions.

[2] 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 Envelope functions and structure constants

2.2.1 Hankel functions as envelope function

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

$$\langle \vec{r}|K^\infty_\alpha\rangle = H_{L_\alpha}(\vec{r}-\vec{R}_\alpha) \tag{2.2}$$

Solid Hankel functions are irregular solutions of the the inhomogeneous Helmholtz equation[3]

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

Here $\mathcal{Y}_L(\vec{r}) \stackrel{\text{def}}{=} r^\ell Y_L(\vec{r})$ 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 ℓ and magnetic quantum number m.

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

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[4] so that they behave at the origin as

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

$$J^\Omega_{R,L}(\vec{r}) = \left[\frac{1}{(2\ell+1)!!}|\vec{r}-\vec{R}|^{\ell+1} + \ldots\right] Y_L(\vec{r}-\vec{R})\theta_{\Omega_R}(\vec{r}) \tag{2.5}$$

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

2.2.3 Bare structure constants

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

[3] 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.

[4] This is our definition, not a generally accepted convention.

ENVELOPE FUNCTION AND STRUCTURE CONSTANTS

$$|K_\alpha^\infty\rangle = |K_\alpha^\Omega\rangle - \sum_\beta |J_\beta^\Omega\rangle S^\dagger_{\beta,\alpha} + |K_\alpha^I\rangle \tag{2.6}$$

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 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

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

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

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

Note, that the Gaunt coefficients for spherical and real spherical harmonics differ.[5]

The bare structure constants are hermitean[6], i.e.

$$S_{RL,R'L'} = S_{R'L',RL} \tag{2.9}$$

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

The structure constants are evaluated by

```
LM1X=(L1X+1)**2
LM2X=(L2X+1)**2
CALL LMTO$STRUCTURECONSTANTS(R2-R1,K2,L1X,L2X,S(:LM1X,:LM2X))
```

2.2.4 Gradient of structure constants

See P. Blöchl, Methods: chapter *Working with spherical harmonics*, Section *Gradients of spherical harmonics*.

$$\partial_{r_j} Y_L(\vec{r}) = \sqrt{\frac{4\pi}{3}} \sum_{L'} C_{p_j,L,L'} \left[\frac{-\ell}{r} + \frac{2\ell+1}{r} \delta_{\ell',\ell-1} \right] Y_{L'}(\vec{r}) \tag{2.10}$$

[5] In practice, we use real spherical harmonics and the corresponding Gaunt coefficients.

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

For the product of a radial function $f(|\vec{r}|)$ and a spherical harmonics, I obtain

$$\partial_{r_j}\left[f(|\vec{r}|)Y_L(\vec{r})\right] = \sqrt{\frac{4\pi}{3}}\sum_{L'} C_{p_j,L,L'}\left[\frac{-\ell}{r}+\frac{2\ell+1}{r}\delta_{\ell',\ell-1}+\partial_r|_{r=\sqrt{\vec{r}^2}}\right] f(|\vec{r}|)Y_{L'}(\vec{r}) \quad (2.11)$$

I used

$$Y_{p_j}(\vec{r}) = \sqrt{\frac{3}{4\pi}}\frac{r_j}{|\vec{r}|} \quad (2.12)$$

2.3 Augmentation and Potential parameters

2.3.1 Local orbitals

LOCAL ORBITALS

Local orbitals are augmented Hankelfunctions

$$\begin{aligned}|\chi_\gamma\rangle &= \sum_\alpha \Bigg\{ \underbrace{|\phi^K_\alpha\rangle + |K^{\notin\Omega_\alpha}_\alpha\rangle}_{\text{R-independent}} \underbrace{-\sum_\beta \Big(|\phi^J_\beta\rangle - |J_\beta\rangle\Big) S^\dagger_{R_\beta,L_\beta,R_\alpha,L_\alpha}}_{\text{R-dependent and small}} \Bigg\} c_{\alpha,\gamma} \\ &= \sum_\alpha \Big\{ |\phi^K_\alpha\rangle - \sum_\beta |\phi^J_\beta\rangle S^\dagger_{R_\beta,L_\beta,R_\alpha,L_\alpha} + |K^I_\alpha\rangle \Big\} c_{\alpha,\gamma} \end{aligned} \quad (2.13)$$

Here, $|\phi^K_\alpha\rangle$ is a superposition of partial waves, which match at the augmentation radius to $|K_\alpha\rangle$, and which are set to zero outside the augmentation region. $|K^{\notin\Omega_\alpha}_\alpha\rangle$ is the Hankelfunction at site R_α and angular momentum L_α, which is set to zero inside its central augmentation region Ω_α.

The interstitial envelope function, which is zero in all augmentation regions is (see also Eq. 2.1)

$$|K^I_\alpha\rangle = |K^{\notin\Omega_\alpha}_\alpha\rangle - \sum_\beta |J_\beta\rangle S^\dagger_{R_\beta,L_\beta,R_\alpha,L_\alpha} \quad (2.14)$$

A suitable definition for $\boldsymbol{c}$ is a matrix that produces orthonormal states for an isolated atom. Thus, it is an onsite matrix. It is constructed by a onsite-Gram-Schmidt decomposition.

We introduce head and tail functions defined as

$$\begin{aligned}|\phi^H_\alpha\rangle &= \sum_{\beta;R_\beta=R_\alpha} |\phi^K_\beta\rangle c_{\beta,\alpha} \\ |\phi^T_\alpha\rangle &= |\phi^J_\alpha\rangle \end{aligned} \quad (2.15)$$

so that

$$
\begin{aligned}
|\chi_\gamma\rangle &= |\phi^H_\gamma\rangle - \sum_{\alpha,\beta} |\phi^J_\beta\rangle S^\dagger_{R_\beta,L_\beta,R_\alpha,L_\alpha} c_{\alpha,\gamma} + \sum_\alpha |K^I_\alpha\rangle c_{\alpha,\gamma} \\
&= |\phi^H_\gamma\rangle + \sum_\alpha \underbrace{\left(|K^I_\alpha\rangle - \sum_\beta |J^\Omega_\beta\rangle S^\dagger_{R_\beta,L_\beta,R_\alpha,L_\alpha}\right)}_{\text{Hankelfunction with central sphere cut out}} c_{\alpha,\gamma} \\
&\quad \underbrace{-\sum_{\alpha,\beta}\left(|\phi^J_\beta\rangle - |J_\beta\rangle\right) S^\dagger_{R_\beta,L_\beta,R_\alpha,L_\alpha} c_{\alpha,\gamma}}_{\text{small correction}}
\end{aligned}
\tag{2.16}
$$

2.3.2 Partial waves

The partial waves are constructed using the nodeless (or node reduced?) construction.

1. The node-reduced partial waves are matched to the envelope function.
2. the all-electron and pseudo local orbitals are constructed by adding and subtracting the difference of the corresponding partial wave minus the node-reduced partial waves. This construction allows the all-electron and pseudo orbitals to deviate from the envelope functuion also beyond the augmentation region.

2.3.3 Matching

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

$$
\begin{aligned}
|K_\alpha\rangle \to |\phi^K_\alpha\rangle &= \overbrace{|\phi_\alpha\rangle \underbrace{\frac{W_\alpha[K,\dot\phi]}{W_\alpha[\phi,\dot\phi]}}_{Ktophi} - |\dot\phi_\alpha\rangle \underbrace{\frac{W_\alpha[K,\phi]}{W_\alpha[\phi,\dot\phi]}}_{-Ktophidot}}^{\to |K^\Omega_\alpha\rangle} \\
|\phi^J_{R,L}\rangle &= \overbrace{|\dot\phi_\beta\rangle \underbrace{\left(-\frac{W_\beta[J,\phi]}{W_\beta[\phi,\dot\phi]}\right)}_{JBARtophidot}}^{\to |J^\Omega_\beta\rangle}
\end{aligned}
\tag{2.17}
$$

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

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

$$
W_\alpha[f,g] \stackrel{\text{def}}{=} f_\alpha(\partial_r g_\alpha) - (\partial_r f_\alpha) g_\alpha = \det \begin{bmatrix} f & g \\ \partial_r f & \partial_r g \end{bmatrix}
\tag{2.18}
$$

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

$$
y(x) \to f(x)\frac{W[y,g]}{W[f,g]} + g(x)\frac{W[y,f]}{W[g,f]}
\tag{2.19}
$$

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

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

2.3.4 Select phi and phidot

For each value of α a set of ϕ and $\dot{\phi}$ partial waves need to be selected. Let us consider one site and one specific angular momentum. There is a number n^ϕ_ℓ of partial waves plus one energy derivative function of the highest partial wave.

From the sequence of $n^\phi_\ell + 1$, we select the current and the next partial wave.

Remark: Another option is to use the current partial wave together with the last partial wave (the phidot function) in the sequence of $n^\phi_\ell + 1$ partial waves. In that case the effective potential defining the shape of the partial wave $|\Phi^K\rangle$ would behave very similar to the current partial wave, while it would raise sharply towards the boundary of the augmentation region.

2.3.5 Orthonormalization

The local orbitals are approximately orthonormalized: For an isolated atom, the orbitals shall be orthonormal.

The approximate orthonormalization is done by a Gram-Schmidt orthonormalization, so that the nature of the lowest states is almost preserved.

2.3.6 Coding: simplelmto_makechi1

The local orbitals are constructed in `simplelmto_makechi1`. Eq. 2.16 is used with the terms "small correction" ignored. They can later be integrated using local integrations.

The node-less partial waves are matched to the Hankel and Bessel functions. Then the differences of the all-electron and pseudo partial waves are added to the composite nodeless function. The following equation is only a sketch. Need to find a proper notation.

$$\begin{aligned}|\phi^{K,AE}\rangle &= |\phi^{K,NL}\rangle + \Big(|\phi^{AE}\rangle - |\phi^{NL}\rangle\Big) \\ |\phi^{K,PS}\rangle &= |\phi^{K,NL}\rangle + \Big(|\phi^{PS}\rangle - |\phi^{NL}\rangle\Big)\end{aligned} \tag{2.21}$$

This ensures that all partial waves are differentiable, and eventially become identical at large radii.

The nodeless head an tail functions are constructed such that they are

$$\begin{aligned}\langle\vec{r}|\phi^H\rangle &= \begin{cases}\sum_\beta\langle\vec{r}|\phi^K_\beta\rangle c_{\beta,\alpha} & \text{for } \vec{r}\in\Omega_\beta \\ \sum_\beta\langle\vec{r}|K^\infty_\beta\rangle c_{\beta,\alpha} & \text{for } \vec{r}\notin\Omega_\beta\end{cases} \\ \langle\vec{r}|\phi^T\rangle &= \begin{cases}\langle\vec{r}|\phi^J_\beta\rangle & \text{for } \vec{r}\in\Omega_\beta \\ \langle\vec{r}|J^\infty_\beta\rangle & \text{for } \vec{r}\notin\Omega_\beta\end{cases}\end{aligned} \tag{2.22}$$

The local orbitals are onsite orthonormal, i.e.

$$\langle \chi_\alpha | \chi_\beta \rangle = \delta_{\alpha,\beta} \qquad \text{for } R_\alpha = R_\beta \tag{2.23}$$

The projections are calculated on the radial grids as

$$\langle \tilde{p}_\alpha | \tilde{\phi}^H_\beta \rangle \qquad \text{and} \quad \langle \tilde{p}_\alpha | \tilde{\phi}^J_\beta \rangle \tag{2.24}$$

This accounts for cases where the projector function reached out of the augmentation sphere.

2.4 Coefficients of the tight-binding orbital

2.4.1 Equivalence of fitting and projection

In this section I show that fitting and projection lead to the same result, if the integrations are limited to the partial wave expansions. In this section, I use an implicit vector notation to make the the underlying content evident. However, this notation may not be unambigous.

Fitting

The projections are determined such that the square deviation between the original wave functions and the local orbital representation is minimized. The mean square deviation is approximated by the partial wave expansions in the augmentation regions.

$$F(\vec{q}) \overset{\text{def}}{=} \Big(\langle\tilde{\psi}| - q\langle\tilde{\chi}|\Big) \underbrace{\Big(|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\Big)}_{\approx\theta_\Omega} \Big(|\tilde{\psi}\rangle - |\tilde{\chi}\rangle q\Big) \overset{!}{=} \min \tag{2.25}$$

where θ_Ω is a function that is unity within the augmentation spheres. It acts only between partial waves centered in the samel augmentation sphere.

$$\begin{aligned}
\frac{dF}{dq^*} &= -\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\Big(\langle\tilde{p}|\tilde{\psi}\rangle - \langle\tilde{p}|\chi\rangle q\Big) \overset{!}{=} 0 \\
\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\psi}\rangle &= \langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\chi}\rangle q \\
q &= \Big(\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\chi}\rangle\Big)^{-1}\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\psi}\rangle \\
\langle\tilde{\pi}| &= \Big(\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\chi}\rangle\Big)^{-1}\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|
\end{aligned} \tag{2.26}$$

Projection

Here, I show that the fitting procedure described above is identical to a projection, with the integration limited to the partial wave expansion in the augmentation regions.

$$\begin{aligned}
\hat{P}^\chi|\Psi\rangle &= |\chi\rangle\Big(\langle\chi|\chi\rangle\Big)^{-1}\langle\chi|\Psi\rangle \\
&\approx |\chi\rangle\Big(\langle\chi|\Big(\sum_R \theta_{\Omega_R}\Big)|\chi\rangle\Big)^{-1}\langle\chi|\Big(\sum_R \theta_{\Omega_R}\Big)|\Psi\rangle \\
&\approx |\chi\rangle\Big(\langle\tilde{\chi}|\Big(|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\Big)|\tilde{\chi}\rangle\Big)^{-1}\langle\tilde{\chi}|\Big(|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\Big)|\tilde{\Psi}\rangle
\end{aligned} \tag{2.27}$$

Thus, I obtain the identical form for the projector function as found above in Eq. **??** for the fitting.

$$\langle\tilde{\pi}| = \Big(\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\chi}\rangle\Big)^{-1}\langle\tilde{\chi}|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}| \tag{2.28}$$

Thus the projectors obtained by fitting, Eq. 2.26, and by projection, Eq. 2.28, are identical.

2.4.2 Local-orbital projection (Explicit derivation)

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 $|\chi_\alpha\rangle$

$$|\psi'_n\rangle = \sum_\alpha |\chi_\alpha\rangle q_\alpha \ , \tag{2.29}$$

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.

$$\begin{aligned} Q[\vec{q}] &:= \Big(\langle\tilde{\psi}_n| - \sum_\alpha q^*_\alpha\langle\tilde{\chi}_\alpha|\Big)\Big[\sum_{\delta,\gamma}|\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\langle\tilde{p}_\gamma|\Big]\Big(|\tilde{\psi}_n\rangle - \sum_\beta|\tilde{\chi}_\beta\rangle q_\beta\Big) \\ &= \sum_\gamma\Big[\sum_\delta\Big(\langle\tilde{\psi}_n|\tilde{p}_\delta\rangle - \sum_\alpha q^*_\alpha\langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\Big)\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\Big(\langle\tilde{p}_\gamma|\tilde{\psi}_n\rangle - \sum_\beta\langle\tilde{p}_\gamma|\tilde{\chi}_\beta\rangle q_\beta\Big) \end{aligned} \tag{2.30}$$

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

Minimization yields

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

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

$$\Rightarrow \qquad q_\beta = \sum_\beta\Big[\sum_{\gamma',\delta'}\langle\tilde{\chi}_\alpha|\tilde{p}_{\delta'}\rangle\langle\phi_{\delta'}|\theta_{\Omega_{R_\delta}}|\phi_{\gamma'}\rangle\langle\tilde{p}_{\gamma'}|\tilde{\chi}_\beta\rangle\Big]^{-1}\Big[\sum_{\gamma\delta}\langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\Big]\langle\tilde{p}_\gamma|\tilde{\psi}_n\rangle \tag{2.31}$$

This allows one to write the wave function in the form

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$$|\psi_n\rangle \approx \sum_\alpha |\chi_\alpha\rangle\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle \tag{2.32}$$

with

$$\langle\tilde{\pi}_\alpha| = \sum_\gamma \underbrace{\left[\sum_{\gamma',\delta'}\langle\tilde{\chi}_\alpha|\tilde{p}_{\delta'}\rangle\langle\phi_{\delta'}|\theta_{\Omega_{R_\delta}}|\phi_{\gamma'}\rangle\langle\tilde{p}_{\gamma'}|\tilde{\chi}_\beta\rangle\right]^{-1}\left[\sum_\delta\langle\tilde{\chi}_\alpha|\tilde{p}_\delta\rangle\langle\phi_\delta|\theta_{\Omega_{R_\delta}}|\phi_\gamma\rangle\right]}_{=:\langle\tilde{\pi}_\alpha|\tilde{\phi}_\gamma\rangle:=\langle\pi_\alpha|\phi_\gamma\rangle}\langle\tilde{p}_\gamma| \tag{2.33}$$

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.

2.5 Transformation of density matrix and Hamiltonian

In the previous section, I derived in Eq. 2.33 a relation between orbital and partial wave projector functions. Here, the expressions for density matrix and Hamiltonian will be derived, assuming no further approximations.

$$\langle\tilde{\pi}_\alpha|\tilde{\psi}_n\rangle = \sum_\beta \underbrace{\langle\pi_\alpha|\phi_\beta\rangle}_{:=\langle\tilde{\pi}_\alpha|\tilde{\phi}_\beta\rangle}\langle\tilde{p}_\beta|\tilde{\psi}_n\rangle \tag{2.34}$$

This operation is performed in `simplelmto_denmatphitochi`

$$\hat{\rho} = \sum_n |\psi_n\rangle f_n\langle\psi_n| \approx \begin{cases}\sum_{\alpha,\beta}|\phi_\alpha\rangle\rho^{\varphi}_{\alpha,\beta}\langle\phi_\beta| \\ \sum_{\alpha,\beta}|\chi_\alpha\rangle\rho^{\chi}_{\alpha,\beta}\langle\chi_\beta|\end{cases} \tag{2.35}$$

where

$$\rho^{\varphi}_{\alpha,\beta} \stackrel{\text{def}}{=} \langle p_\alpha|\hat{\rho}|p_\beta\rangle = \langle\tilde{p}_\alpha|\tilde{\psi}_n\rangle f_n\langle\tilde{\psi}_n|\tilde{p}_\beta\rangle \tag{2.36}$$

$$\rho^{\chi}_{\alpha,\beta} \stackrel{\text{def}}{=} \langle\pi_\alpha|\hat{\rho}|\pi_\beta\rangle = \sum_{\gamma,\delta}\langle\pi_\alpha|\phi_\gamma\rangle\rho^{\varphi}_{\gamma,\delta}\langle\phi_\delta|\pi_\beta\rangle \tag{2.37}$$

The density matrix in the partial wave expansion is evaluated in k-space

$$\rho^{\varphi}_{\alpha,\vec{0},\beta,\vec{t}} = \frac{1}{\sum_k}\sum_k\sum_{n=1}^{nb}\langle\tilde{p}_{\alpha,0}|\psi_{n,k}\rangle f_{n,k}\langle\psi_{n,k}|\tilde{p}_{\beta,\vec{0}}\rangle e^{i\vec{k}\vec{t}} \tag{2.38}$$

The derivatives are correspondingly derived as

$$
\begin{aligned}
dE &= \sum_{\alpha,\beta} \underbrace{\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}}_{=:h^{\chi}_{\beta,\alpha}} d\rho^{\chi}_{\alpha,\beta} \\
&= \sum_{\alpha,\beta} \underbrace{\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}}_{=:h^{\chi}_{\beta,\alpha}} \sum_{\gamma,\delta} \Big(\Big(d\langle\pi_\alpha|\phi_\gamma\rangle \Big) \rho^{\varphi}_{\gamma,\delta} \langle\phi_\delta|\pi_\beta\rangle + \langle\pi_\alpha|\phi_\gamma\rangle d\rho^{\varphi}_{\gamma,\delta} \langle\phi_\delta|\pi_\beta\rangle + \langle\pi_\alpha|\phi_\gamma\rangle \rho^{\varphi}_{\gamma,\delta} \Big(d\langle\phi_\delta|\pi_\beta\rangle \Big) \Big) \\
&= \sum_{\gamma,\delta} \underbrace{\Big(\sum_{\alpha,\beta} \langle\phi_\delta|\pi_\beta\rangle \underbrace{\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}}_{=:h^{\chi}_{\beta,\alpha}} \langle\pi_\alpha|\phi_\gamma\rangle \Big)}_{h^{\varphi}_{\delta,\gamma}} d\rho^{\varphi}_{\gamma,\delta} \\
&\quad + \sum_{\alpha,\beta,\gamma,\delta} \rho^{\varphi}_{\gamma,\delta} \langle\phi_\delta|\pi_\beta\rangle \underbrace{\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}}_{=:h^{\chi}_{\beta,\alpha}} \Big(d\langle\pi_\alpha|\phi_\gamma\rangle \Big) + \sum_{\alpha,\beta,\gamma,\delta} \underbrace{\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}}_{=:h^{\chi}_{\beta,\alpha}} \langle\pi_\alpha|\phi_\gamma\rangle \rho^{\varphi}_{\gamma,\delta} \Big(d\langle\phi_\delta|\pi_\beta\rangle \Big) \\
&= \sum_{\gamma,\delta} h^{\varphi}_{\delta,\gamma} d\rho^{\varphi}_{\gamma,\delta} \\
&\quad + \sum_{\alpha,\beta,\gamma,\delta} \rho^{\varphi}_{\gamma,\delta} \langle\phi_\delta|\pi_\beta\rangle \underbrace{\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}}_{=:h^{\chi}_{\beta,\alpha}} \Big(d\langle\pi_\alpha|\phi_\gamma\rangle \Big) + \sum_{\alpha,\beta,\gamma,\delta} \underbrace{\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}}_{=:h^{\chi}_{\beta,\alpha}} \langle\pi_\alpha|\phi_\gamma\rangle \rho^{\varphi}_{\gamma,\delta} \Big(d\langle\phi_\delta|\pi_\beta\rangle \Big) \\
&= \sum_{\gamma,\delta} h^{\varphi}_{\delta,\gamma} d\rho^{\varphi}_{\gamma,\delta} + \sum_{j=1}^{3M} \underbrace{2\mathrm{Re}\Big\{ \sum_{\alpha,\beta,\gamma,\delta} \rho^{\varphi}_{\gamma,\delta} \langle\phi_\delta|\pi_\beta\rangle h^{\chi}_{\beta,\alpha} \frac{d\langle\pi_\alpha|\phi_\gamma\rangle}{dR_j} \Big\}}_{-F^{S}_{j}} dR_j \\
&= \sum_{\gamma,\delta} h^{\varphi}_{\delta,\gamma} d\rho^{\varphi}_{\gamma,\delta} - \sum_{j=1}^{3M} F^{S}_{j} dR_j
\end{aligned}
\tag{2.39}
$$

where

$$
\begin{aligned}
h^{\varphi}_{\beta,\alpha} &\stackrel{\mathrm{def}}{=} \sum_{\alpha,\beta} \langle\phi_\delta|\pi_\beta\rangle \frac{dE}{d\rho^{\chi}_{\alpha,\beta}} \\
h^{\varphi}_{\delta,\gamma} &\stackrel{\mathrm{def}}{=} \sum_{\alpha,\beta} \langle\phi_\delta|\pi_\beta\rangle h^{\chi}_{\beta,\alpha} \langle\pi_\alpha|\phi_\gamma\rangle \\
F^{S}_{j} &\stackrel{\mathrm{def}}{=} -2\mathrm{Re}\Big\{ \sum_{\alpha,\beta,\gamma,\delta} \rho^{\varphi}_{\gamma,\delta} \langle\phi_\delta|\pi_\beta\rangle h^{\chi}_{\beta,\alpha} \frac{d\langle\pi_\alpha|\phi_\gamma\rangle}{dR_j} \Big\}
\end{aligned}
\tag{2.40}
$$

2.6 Approximations

The key to efficiency is to limit the multicenter expansions. Therefore, I introduce a number of approximations.

Given the transformation matrix elements $\langle\pi|\phi\rangle$ and its derivatives with respect to atomic positions, we limit the multi-center expansion of the density matrix: We include only terms which are

- ρ^{χ} contains at most quadratic in the offsite terms of $\langle\pi|\phi\rangle$ and $\boldsymbol{\rho}^{\varphi}$
- Furthermore, terms in ρ^{χ}, which are quadratic in the off-site $\langle\pi|\phi\rangle$ terms are excluded
- For $\langle\pi|\phi\rangle$, only terms linear in the structure constants are considered. (This approximation will be described later.)

2.6.1 Transform of the density matrix from partial waves to local orbitals

The following describes the terms, where "forward" and "back" as well as "offsite" exclude onsite terms.

To be specific

$$\begin{aligned}\underbrace{\langle\pi_\alpha|\phi_\beta\rangle}_{\text{onsite}} &\overset{\text{def}}{=} \langle\pi_\alpha|\phi_\beta\rangle\delta_{R_\alpha,R_\beta}\\ \underbrace{\langle\pi_\alpha|\phi_\beta\rangle}_{\text{offsite}} &\overset{\text{def}}{=} \langle\pi_\alpha|\phi_\beta\rangle(1-\delta_{R_\alpha,R_\beta})\end{aligned} \tag{2.41}$$

I also use the terms "forward" and "back" as variants of "offsite" terms.

Now, I decompose the density matrix into terms that are limited to onsite terms and those involving all terms touchin a pair of sites. The terms quadratic in the off-site terms of $\langle\pi|\phi\rangle$ are marked in blue.

$$\begin{aligned}\underbrace{\rho^{\chi}_{\alpha,\beta}}_{\text{onsite}} &= \sum_{\gamma,\delta}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\\ &\quad+\sum_{\gamma,\delta}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{forward}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{back}}+\overbrace{\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{forward}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{back}}}^{\text{not included}}+\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{forward}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\\ \underbrace{\rho^{\chi}_{\alpha,\beta}}_{\text{offsite}} &= \sum_{\gamma,\delta}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{offsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}+\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{offsite}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}+\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{offsite}}\\ &\quad+\overbrace{\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{forward}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}}\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{forward}}}^{\text{not included}}\end{aligned} \tag{2.42}$$

Notice! The forward-back-forward is not yet carried through in the following.

2.6.2 Hamiltonian and forces

Forces and the Hamiltonian h^{φ} are obtained from the first variation of the total energy.

$$
\begin{aligned}
dE = & \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{d\rho^{\chi}_{\alpha,\beta}}_{\text{onsite}} + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{offsite}}\underbrace{d\rho^{\chi}_{\alpha,\beta}}_{\text{offsite}} \\
= & \Bigg\{ \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}} + \overbrace{\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{back}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{forward}}}^{\text{not included}} + \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{forward}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{back}} \\
& + \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{forward}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{back}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}} \Bigg\} \underbrace{d\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}} + \Bigg\{ \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{offsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}} + \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{offsite}} \\
& + \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{offsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}} \Bigg\} \underbrace{d\rho^{\varphi}_{\gamma,\delta}}_{\text{offsite}} + \sum_j 2\mathrm{Re}\Bigg[\Bigg\{ \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}} \\
& + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{forward}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}} + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{forward}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{back}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}} + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{forward}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}} \Bigg\} \underbrace{\frac{\langle\phi_\delta|\pi_\beta\rangle}{dR_j}}_{\text{onsite}} \\
& + \sum_j \Bigg\{ \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}} + \overbrace{\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{back}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}}^{\text{not included}} + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{back}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}} \Bigg\} \underbrace{\frac{\langle\phi_\delta|\pi_\beta\rangle}{dR_j}}_{\text{forward}} \Bigg] dR_j
\end{aligned}
\tag{2.43}
$$

Thus we obtain the Hamiltonian and forces as

$$h^{\varphi}_{\gamma,\delta} = \frac{dE}{d\rho^{\varphi}_{\delta,\gamma}} = \left(\frac{dE}{d\rho^{\varphi}}\right)^{\dagger}_{\gamma,\delta} = \frac{dE}{d\rho^{\varphi}_{\gamma,\delta}}$$

$$\underbrace{h^{\varphi}_{\gamma,\delta}}_{\text{onsite}} = \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}} + \overbrace{\underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{back}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{forward}}}^{\text{not included}} + \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{forward}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{back}}$$
$$+ \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{forward}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{back}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}$$

$$\underbrace{h^{\varphi}_{\gamma,\delta}}_{\text{offsite}} = \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{offsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}} + \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{offsite}} + \underbrace{\langle\phi_\delta|\pi_\beta\rangle}_{\text{onsite}}\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{offsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}$$

$$-F_j = 2\mathrm{Re}\Bigg[\Bigg\{\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}$$
$$+ \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{forward}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}} + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{forward}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{back}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}} + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{forward}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}}\Bigg\}\underbrace{\frac{\langle\phi_\delta|\pi_\beta\rangle}{dR_j}}_{\text{onsite}}$$
$$+ \sum_j\Bigg\{\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{back}} + \overbrace{\underbrace{h^{\chi}_{\beta,\alpha}}_{\text{onsite}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{back}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}}^{\text{not included}} + \underbrace{h^{\chi}_{\beta,\alpha}}_{\text{back}}\underbrace{\langle\pi_\alpha|\phi_\gamma\rangle}_{\text{onsite}}\underbrace{\rho^{\varphi}_{\gamma,\delta}}_{\text{onsite}}\Bigg\}\underbrace{\frac{\langle\phi_\delta|\pi_\beta\rangle}{dR_j}}_{\text{forward}}\Bigg] \tag{2.44}$$

the hamiltonian h^{φ} is calculated in `SIMPLELMTO_DENMATPHITOCHI2` with `ID='back'`.

Using the linearized form of $\langle\pi|\phi\rangle$ in the structure constants, the onsite terms of $d\langle\pi|\phi\rangle/dR$ vanish. The forces are calculated in the routine `SIMPLELMTO_FORCEPHITOCHI`.

2.6.3 Linearization of the transformation in the structure constants

To linear order in the structure constants, I obtain the projector as

$$\begin{aligned}
\langle\pi| &= \Big\{\langle\phi^H|\theta_\Omega|\phi^H\rangle - \boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|\theta_\Omega|\phi^H\rangle - \langle\phi^H|\theta_\Omega|\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c} + \boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|\theta_\Omega|\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c}\Big\}^{-1}\\
&\quad\times\Big(\langle\phi^H|p\rangle - \boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|p\rangle\Big)\langle\phi|\theta_\Omega|\phi\rangle\langle p|\\
&\approx \Big\{\Big(\langle\phi^H|\theta_\Omega|\phi^H\rangle\Big)^{-1} - \Big(\langle\phi^H|\theta_\Omega|\phi^H\rangle\Big)^{-1}\Big(-\boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|\theta_\Omega|\phi^H\rangle - \langle\phi^H|\theta_\Omega|\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c}\Big)\Big(\langle\phi^H|\theta_\Omega|\phi^H\rangle\Big)^{-1}\Big\}\\
&\quad\times\Big(\langle\phi^H|p\rangle - \boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|p\rangle\Big)\langle\phi|\theta_\Omega|\phi\rangle\langle p|\\
&\approx \Big(\langle\phi^H|\theta_\Omega|\phi^H\rangle\Big)^{-1}\Big\{\langle\phi^H|p\rangle - \boldsymbol{c}^\dagger\boldsymbol{S}\Big[\langle\phi^J|p\rangle - \langle\phi^J|\theta_\Omega|\phi^H\rangle\Big(\langle\phi^H|\theta_\Omega|\phi^H\rangle\Big)^{-1}\langle\phi^H|p\rangle\Big]\\
&\quad+\langle\phi^H|\theta_\Omega|\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c}\Big(\langle\phi^H|\theta_\Omega|\phi^H\rangle\Big)^{-1}\langle\phi^H|p\rangle\Big\}\langle\phi|\theta_\Omega|\phi\rangle\langle p|
\end{aligned} \tag{2.45}$$

We define the quantity

$$\langle\pi| = \langle\pi|\phi\rangle\langle p| \tag{2.46}$$

The following variables are constructed in `SIMPLELMTO_DEMATPHITOCHI2`. (translated from code)

$$\begin{aligned}
\text{PHIHHOV:} \quad & \langle\phi^H|\theta_\Omega|\phi^H\rangle = \langle\phi^H|p\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle p|\phi^H\rangle \\
\text{PHIHHOVINV:} \quad & \langle\phi^H|\theta_\Omega|\phi^H\rangle^{-1} \\
\text{PHIHTOV:} \quad & \langle\phi^H|\theta_\Omega|\phi^T\rangle = \langle\phi^H|p\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle p|\phi^T\rangle \\
\langle\pi|\phi\rangle &= \langle\phi^H|\theta_\Omega|\phi^H\rangle^{-1}\Big[\langle\tilde{\phi}^H|\tilde{p}\rangle\Big]\langle\phi|\theta_\Omega|\phi\rangle \qquad \text{for } R_\alpha = R_\beta \\
\langle\pi|\phi\rangle &= \langle\phi^H|\theta_\Omega|\phi^H\rangle^{-1}\Big[\boldsymbol{c}^\dagger\boldsymbol{S}\Big(\langle p|\phi^T\rangle - \langle p|\phi^H\rangle\langle\phi^H|\theta_\Omega|\phi^H\rangle^{-1}\langle\phi^H|\theta_\Omega|\phi^T\rangle\Big)^\dagger \\
&\quad + \langle\phi^H|\theta_\Omega|\phi^T\rangle\boldsymbol{S}^\dagger\boldsymbol{c}\langle\phi^H|\theta_\Omega|\phi^H\rangle^{-1}\langle\phi^H|p\rangle\Big]\langle\phi|\theta_\Omega|\phi\rangle \qquad \text{for } R_\alpha \neq R_\beta
\end{aligned} \tag{2.47}$$

2.7 Expressions

This section is too code specific and should be somewhere else

$$\begin{aligned}
\langle p_\alpha|\chi_\beta\rangle &= \langle p_\alpha|\phi^H_\beta\rangle - \sum_{\gamma,\delta}\langle p_\alpha|\phi^T_\gamma\rangle \underbrace{S^\dagger_{R_\gamma,L_\gamma,R_\delta,L_\delta}}_{S^*_{R_\delta,L_\delta,R_\gamma,L_\gamma}} c_{\delta,\beta} \\
\langle\chi_\alpha|p_\beta\rangle &= \langle\phi^H_\alpha|p_\beta\rangle - \sum_{\gamma,\delta} c^\dagger_{\alpha,\delta} S_{R_\delta,L_\delta,R_\gamma,L_\gamma}\langle\phi^T_\gamma|p_\beta\rangle
\end{aligned} \tag{2.48}$$

$$\begin{aligned}
\langle\pi| = &\Big\{\langle\phi^H|\theta_\Omega|\phi^H\rangle - \boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|\theta_\Omega|\phi^H\rangle - \langle\phi^H|\theta_\Omega|\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c} + \boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|\theta_\Omega|\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c}\Big\}^{-1} \\
&\times\Big(\langle\phi^H|p\rangle - \boldsymbol{c}^\dagger\boldsymbol{S}\langle\phi^J|p\rangle\Big)\langle\phi|\theta_\Omega|\phi\rangle\langle p|
\end{aligned} \tag{2.49}$$

where I used the short-hand notation

$$\begin{aligned}
\langle\phi^H|\theta_\Omega|\phi^H\rangle &= \langle\tilde{\phi}^H|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\phi}^H\rangle \\
\langle\phi^H|\theta_\Omega|\phi^J\rangle &= \langle\tilde{\phi}^H|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\phi}^J\rangle \\
\langle\phi^J|\theta_\Omega|\phi^J\rangle &= \langle\tilde{\phi}^J|\tilde{p}\rangle\langle\phi|\theta_\Omega|\phi\rangle\langle\tilde{p}|\tilde{\phi}^J\rangle
\end{aligned} \tag{2.50}$$

The following variables are calculated in `SIMPLELMTO_MAKECHI1` and supplied by the variable-sttructure `potpar` in the `simplelmto_module`.

$$\begin{aligned}
\text{AEPHIH:} \quad & \langle\vec{r}|\phi^H\rangle \\
\text{AEPHIT:} \quad & \langle\vec{r}|\phi^T\rangle = \langle\vec{r}|\phi^J\rangle \\
\text{AECHI:} \quad & \langle\vec{r}|\chi\rangle \\
\text{PROPHIH:} \quad & \langle\tilde{p}|\tilde{\phi}^H\rangle \\
\text{PROPHIT:} \quad & \langle\tilde{p}|\tilde{\phi}^T\rangle \\
\text{PHIOV:} \quad & \langle\phi|\theta_\Omega|\phi\rangle \\
\text{CMAT:} \quad & |\chi_\beta\rangle \leftarrow |K_\beta\rangle c_{\alpha,\beta}
\end{aligned} \tag{2.51}$$

The partial-wave overlap $\langle\phi|\theta_\Omega|\phi\rangle$ is calculated by integration up to the ASA radius. The latter is defined in the present code as the covalent radius of the element scaled up by the ratio between between the radii of volume filling and touching spheres.

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.[7] 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 neglegible.[8]

[7] 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.

[8] 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[1]

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

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

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

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

As usual we build the expanded density matrix

$$\begin{pmatrix} \boldsymbol{\rho} & -\boldsymbol{\rho}\bar{\boldsymbol{S}}^\dagger \\ -\bar{\boldsymbol{S}}\boldsymbol{\rho} & \bar{\boldsymbol{S}}\boldsymbol{\rho}\bar{\boldsymbol{S}}^\dagger \end{pmatrix} \tag{3.3}$$

The matrix

$$\begin{pmatrix} \langle\tilde{\phi}^K|\tilde{p}\rangle \boldsymbol{M} \langle\tilde{p}|\tilde{\phi}^K\rangle & \langle\tilde{\phi}^K|\tilde{p}\rangle \boldsymbol{M} \langle\tilde{p}|\tilde{\phi}^{\bar{J}}\rangle \\ \langle\tilde{\phi}^{\bar{J}}|\tilde{p}\rangle \boldsymbol{M} \langle\tilde{p}|\tilde{\phi}^K\rangle & \langle\tilde{\phi}^{\bar{J}}|\tilde{p}\rangle \boldsymbol{M} \langle\tilde{p}|\tilde{\phi}^{\bar{J}}\rangle \end{pmatrix} \tag{3.4}$$

[1] Note that this matrix $\boldsymbol{M}$ differs from the one with the same symbol in the previous section.

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

3.2 U-tensor

3.3 Double-counting correction

3.3.1 HSE-like

In the HSE functional[**?**], the double counting term exploits that the exchange-hole of the PBE functional is known.[**?**]. The procedure is described in the appendix of the HSE03 paper.[**?**]. A subroutine for the range separated exchange derived from the exchange hole is given in the Thesis of J. Heyd. (heyd04_thesis) An improved exchange-corrfelation hole has been determined by Bahmann and Ernzerhof[**?**].

See Kevin E. Riley et. al, Critical Assessement of the Performance of Density Functional Methods for Several Atomic and Molecular Properties, J. Chem. Theory Comput. 2007; 3(2): 407-433

The following does not belong here. It is obtained from Joost VandeVondele "Hybrid functionals in CP2K, A tutorial, Feb.10, 2011.https://www.cecam.org/upload/talk/presentation_5766.pdf Least square fit to the correct wave function under the constraint of orthonormality. They use the term Auxiliary density matrix method (ADMM): Guidon, Hutter and VandeVondele, J. Chem. Theory Comput., 6, 2348 (2010)

$$I = \min\Bigg[\sum_n f_n\Big(\langle\psi_n| - \sum_\alpha C^\dagger_{n,\alpha}\langle\chi_\alpha|\Big)\Big(\sum_{\gamma,\gamma'}|p_\gamma\rangle W_{\gamma,\gamma'}\langle p_{\gamma'}|\Big)\Big(|\psi_n\rangle - \sum_\beta |\chi_\beta\rangle C_{\beta,n}\Big) + \sum_{m,n}\Lambda_{n,m}\Big(\Big(\sum_{\alpha,\beta} C^\dagger_{m,\alpha}\langle\chi_\alpha|\chi_\beta\rangle C_{\beta,n}\Big) - \delta_{m,n}\Big)\Bigg] \tag{3.5}$$

$$\frac{dI}{dC^\dagger_{n,\alpha}} = \sum_\gamma\Big(\sum_{\gamma'}\langle\chi_\alpha|p_{\gamma'}\rangle W_{\gamma',\gamma}\Big)\Big(\langle p_\gamma|\psi_n\rangle - \sum_\beta\langle p_\gamma|\chi_\beta\rangle C_{\beta,n}\Big) f_n + \sum_m\sum_\beta\langle\chi_\alpha|\chi_\beta\rangle C_{\beta,m}\Lambda_{m,n} \stackrel{!}{=} 0 \tag{3.6}$$

$$\Rightarrow \sum_\beta\Big(\sum_{\gamma,\gamma'}\langle\chi_\alpha|p_{\gamma'}\rangle W_{\gamma',\gamma}\langle p_\gamma|\chi_\beta\rangle\Big) C_{\beta,n} - \sum_m\sum_\beta\langle\chi_\alpha|\chi_\beta\rangle C_{\beta,m}\Lambda_{m,n}\frac{1}{f_n} \stackrel{!}{=} \sum_\gamma\Big(\sum_{\gamma'}\langle\chi_\alpha|p_{\gamma'}\rangle W_{\gamma',\gamma}\Big)\langle p_\gamma|\psi_n\rangle \tag{3.7}$$

[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.

3.3.2 Blöchl, Walther, Pruschke

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

It is based on a partioning of the exchange correlation energy in the form using the functions

$$g_R(\vec{r}) = \frac{n_R^{\chi,s}(\vec{r})}{\sum_{R'} n_{R'}^{\chi,s}(\vec{r})} = \left[1 + \frac{\sum_{R';R'\neq R} n_{R'}(\vec{r})}{n_R(\vec{r})}\right]^{-1} \tag{3.8}$$

where $n_R^{\chi,s}(\vec{r})$ is the spherical part of the density from the local orbitals $|\chi\rangle$. The partitioning functions obey $\sum_R g_R(\vec{r}) = 1$, which allows to rewrite the exchange correlation energy in the form

$$E_{xc} = \sum_{R,R'} \int d^3r\; n(\vec{r})\epsilon_{xc}[n(\vec{r})]\; g_R(\vec{r}) g_{R'}(\vec{r}) \tag{3.9}$$

The resulting onsite terms are used for our double-counting term for an on-site interaction.

$$E_{xc}^{\hat{W}_R} = \int d^3r \left(n(\vec{r})\epsilon_{xc}[n]\right) g_R^2(\vec{r}) \tag{3.10}$$

The exchange correlation density is calculated with the partial wave expansion, and it is cut off by the squared partitioning function.

Other double-counting schemes are discussed in appendix E.

- 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.**
- Let us simplify the expression by introducing the symbols $n_R = n_R^{\chi}(\vec{r})$ and $n_t = n_{\sigma,\sigma'}^{\chi}(\vec{r})$. 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 be excluded in the double-counting term.
- In the denominator of the cutoff function $g_R(\vec{r})$, I replace the multicenter expansion of the density in terms of local orbitals, the one-center partial-wave expansion.

The expression above can be written in the following form:

$$\begin{aligned} E_{xc}^{\hat{W}_R} &= \int d^3r \left[n_t(\vec{r})\epsilon_{xc}[n_t(\vec{r})] - n^{core}(\vec{r})\epsilon_{xc}[n^{core}(\vec{r})]\right] \left(\frac{n_R^s(\vec{r})}{n_t^s(\vec{r})}\right)^2 \\ &= \int d^3r\; f_{xc}(\vec{r}) \left(\frac{n_R^s(\vec{r})}{n_t^s(\vec{r})}\right)^2 \end{aligned} \tag{3.11}$$

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

$$\begin{aligned} dE_{xc}^{\hat{W}_R} &= \int d^3r \left(\frac{n_R^s}{n_t^s}\right)^2 \mu_{xc} dn_t + f_{xc} 2 \left(\frac{n_R^s}{n_t^s}\right)^2 \frac{dn_R^s}{n_R^s} - f_{xc} 2 \left(\frac{n_R^s}{n_t^s}\right)^2 \frac{dn_t^s}{n_t^s} \\ &= \int d^3r \left[\left(\frac{n_R^s}{n_t^s}\right)^2 \mu_{xc} - 2f_{xc}^s \left(\frac{n_R^s}{n_t^s}\right)^2 \frac{1}{n_t^s}\right] dn_t + \left[2f_{xc}^s \left(\frac{n_R^s}{n_t^s}\right)^2 \frac{1}{n_R^s}\right] dn_R^s \end{aligned} \tag{3.12}$$

which yields the two potentials

$$v_t \stackrel{\text{def}}{=} \left(\frac{n_R^s}{n_t^s}\right)^2 \left[\mu_{xc} - \frac{2f_{xc}^s}{n_t^s}\right]$$
$$v_R \stackrel{\text{def}}{=} \left(\frac{n_R^s}{n_t^s}\right)^2 \frac{2f_{xc}^s}{n_R^s} \tag{3.13}$$

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 μ_{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.[3] Its energy and the corresponding contributions to the auxiliary Hamiltonian are

$$E_{dc} = -\int d^3r \left(\frac{n_R^s}{n_t^s}\right)^2 f_{xc}^s$$
$$d\hat{\tilde{H}}_{dc} = -|\tilde{\pi}_\alpha\rangle\langle\chi_\alpha|\hat{v}_t|\chi_\beta\rangle\langle\tilde{\pi}_\beta| - |\tilde{p}_\alpha\rangle\langle\phi_\alpha|\hat{v}_R|\phi_\beta\rangle\langle\tilde{p}_\beta| \tag{3.14}$$

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

Avoid singularities

In practice, the cutoff function is evaliuated as

$$g_R(\vec{r}) = \left(\frac{n_R^s(\vec{r})}{n_t^2(\vec{r}) + \Delta}\right)^2 \tag{3.15}$$

where

$$n_R^s = \rho^\chi_{\alpha,\beta}\chi^*_\beta(\vec{r})\chi_\alpha(\vec{r}) \tag{3.16}$$

is evaluated from the local orbitals from site R.

$$n_t^s(\vec{r}) = \rho^\phi_{\alpha,\beta}\phi^*_\beta(\vec{r})\phi_\alpha(\vec{r}) \tag{3.17}$$

is evaluated from the partial waves centered at this site. Δ, chosen as 10^{-2} a.u., avoids problems, when n_t^s becomes smaller than the true density at larger distances.

Idea

$$E_{xc}^{\hat{W}_R} = \sum_{a,b,c,d}\int d^3r\ \chi^*_a(r)\chi_b(r)\chi^*_d(r)\chi_c(r)\frac{\epsilon_{xc}[n^\chi_{\sigma,\sigma'}(\vec{r})]}{n^\chi(\vec{r})} \tag{3.18}$$

[3] 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)	$\|K^{\Omega}\rangle \rightarrow \|\phi\rangle c_{KTOPHI} + \|\dot{\bar{\phi}}\rangle c_{KTOPHIDOT}$
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)	$\|\bar{J}^{\Omega}\rangle \rightarrow \|\dot{\bar{\phi}}\rangle c_{JBARTOPHIDOT}$
Other stuff	
PROK(LNX,NHEAD)	$\langle\tilde{p}\|\phi c_{ktopphi} + \dot{\tilde{\phi}} c_{ktophidot}\rangle$
PROJBAR(LNX,NTAIL)	$\langle\tilde{p}\|\dot{\bar{\phi}} c_{jbartophidot}\rangle$
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` ($\vec{k}^2 = -\kappa^2$) is the squared wave vector. (For envelope functions that fall off exponentially, this parameter is negative.)

```
SUBROUTINE LMTO$CLUSTERSTRUCTURECONSTANTS(K2,NAT,RPOS,LX,QBAR,NORB,N,SBAR)
REAL(8)   ,INTENT(IN) :: K2
INTEGER(4),INTENT(IN) :: NAT          ! NUMBER OF ATOMS ON THE CLUSTER
REAL(8)   ,INTENT(IN) :: RPOS(3,NAT) ! ATOMIC POSITIONS ON THE CLUSTER
INTEGER(4),INTENT(IN) :: LX(NAT)      ! X(ANGULAR MOMENTUM ON EACH CLUSTER)
INTEGER(4),INTENT(IN) :: N
REAL(8)   ,INTENT(IN) :: QBAR(N)
INTEGER(4),INTENT(IN) :: NORB
REAL(8)   ,INTENT(INOUT):: SBAR(NORB,N)
```

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

4.3.1 LMTO$STRUCTURECONSTANTS

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

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

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

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

where $H_L(k^2, \vec{R})$ is the solid Hankel function calculated in `LMTO$SOLIDHANKEL`. The solid Hankel function is the solution of the Helmholtz equation, Eq. 2.3.[1]

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

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

4.3.2 LMTO$SCREEN

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

`LMTO$SCREEN` takes the bare structure constants $S_{RL,R'L'}$ connecting all orbitals on a specific cluster with each other and the screening constants $\bar{Q}$ for all orbitals on the cluster. It returns

[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.*

the screened structure constants connecting the orbitals on the central (first) site (1st index) with all orbitals (2nd index).

The structure constants are defined so that

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

First we evaluate

$$\boldsymbol{A} = \mathbf{1} - \bar{\boldsymbol{Q}}\boldsymbol{S}^{\dagger} \tag{4.3}$$

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

$$\boldsymbol{A}\vec{c}_\alpha \overset{\text{Eq. ??}}{=} \vec{e}_\alpha \tag{4.4}$$

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

$$\vec{s}_\alpha \overset{\text{Eq. ??}}{=} \boldsymbol{S}^{\dagger}\vec{c}_\alpha \tag{4.5}$$

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

4.4 Waves object

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

In `waves$etot`

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

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

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 `LMTO_initialize`

```
LMTO_TAILEDGAUSSFIT()
   GAUSSIAN_FITGAUSS(GID,NR,W,L,AUX,NE,NPOW2,E,C(:NPOW2,:,LN))
   LMTO_TAILEDGAUSSORBTOYLM()
LMTO_OFFXINT
    LMTO_OFFSITEOVERLAPSETUP  !O(AB)  ->OFFSITEX%OVERLAP
       LMTO_TWOCENTER
    LMTO_OFFSITEX22SETUP      !U(AABB) ->OFFSITEX%X22
       LMTO_TWOCENTER
    LMTO_OFFSITEX31SETUP      !U(AAAB) ->OFFSITEX%X31
       LMTO_TWOCENTER
    LMTO_TAILEDGAUSSOFFSITEU  !U(ABAB) ->OFFSITEX%BONDU
       GAUSSIAN$ZDIRECTION_FOURCENTER(NIJKA,NEA,EA,LMNXA,ORBA &
    LMTO_OFFSITEXCONVERT()
```

The energy contibution is then calculated using offsitex as follows

```
LMTO_OFFSITEXEVAL_NEW(EX)
    LMTO_EXPANDNONLOCAL
    LMTO_EXPANDLOCAL
    SPHERICAL$ROTATEYLM(LMX,ROT,YLMROT)
    LMTO_OFFSITEX22U(ISPA,ISPB, DIS,LMNXTA,LMNXTB,U22,DU22)
```

```
      lmto_offsitexvalue
   LMTO_OFFSITEX31U(ISPA,ISPB, DIS,LMNXTA,LMNXTB,U3A1B,DU3A1B)
      lmto_offsitexvalue
   LMTO_OFFSITEX31U(ISPB,ISPA,-DIS,LMNXTB,LMNXTA,U3B1A,DU3B1A)
      lmto_offsitexvalue
   LMTO_OFFSITEXBONDU(ISPA,ISPB,DIS,LMNXTA,LMNXTB,BONDU,DBONDU)
      lmto_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

```
lmto_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(R0(:,IAT0),RANGE,N1,N2,N3,ORIGIN,TVEC,P)
    LMTO_GRIDORB_STARGRID(R0(:,IAT0),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(IAT0)
    LMTO_GRIDORB_CUBEGRID(R0(:,IAT0),RANGE,N1,N2,N3,ORIGIN,TVEC,P)
    LMTO_GRIDORB_STARGRID(R0(:,IAT0),RANGE,NDIR,DIR,NRAD,X1D,P)
    LMTO_GRIDENVELOPE(RBAS,NAT,R0,IAT0,LMX,NP,P,ENV,ENV1)
    LMTO_GRIDAUGMENT(RBAS,NAT,R0,IAT0,LMX,NP,P,ORB1,ENV1)
    LMTO_GRIDGAUSS(RBAS,NAT,R0,IAT0,LMX,NP,P,ORBG)
    LMTO_WRITECUBEFILE(NFIL,NATCLUSTER,ZCLUSTER,RCLUSTER &
LMTO_PLOTLOCORB(IAT0)
    LMTO_GRIDENVELOPE(RBAS,NAT,R0,IAT0,LM1X,NP,P,ENV,ENV1)
    LMTO_GRIDAUGMENT(RBAS,NAT,R0,IAT0,LM1X,NP,P,ORB1,ENV1)
    LMTO_GRIDGAUSS(RBAS,NAT,R0,IAT0,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$PLOTWAVE(NFIL,IDIM0,IB0,IKPT0,ISPIN0,NR1,NR2,NR3)
    LMTO$PLOTWAVE_TAILED(NFIL,IDIM0,IB0,IKPT0,ISPIN0,NR1,NR2,NR3)
        WRITEWAVEPLOTC(NFIL,TITLE,RBAS,NAT,R0,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 expanion 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.

- `LMTO_TAILED_NTBOOFR(IAT,iORB,NP,P,chi)` calculates a specific tailed orbital on a set of real space points.
- `LMTO_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

$$\begin{aligned}
|\bar{K}^I_\alpha\rangle &= |\bar{K}^\infty_\alpha\rangle - \Big[|K^\Omega_\alpha\rangle - \sum_\beta |\bar{J}^\Omega_\beta\rangle \bar{S}^\dagger_{\beta,\alpha}\Big] \\
&= \sum_\beta |K^\infty_\beta\rangle \Big(\delta_{\alpha,\beta} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha}\Big) - \Big[|K^\Omega_\alpha\rangle - \sum_\beta |\bar{J}^\Omega_\beta\rangle \bar{S}^\dagger_{\beta,\alpha}\Big] \\
&= \sum_\beta |K^\infty_\beta\rangle \Big(\delta_{\alpha,\beta} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha}\Big) - \Big[|K^\Omega_\alpha\rangle - \sum_\beta \Big(|J^\Omega_\beta\rangle - |K^\Omega_\beta\rangle \bar{Q}_\beta\Big) \bar{S}^\dagger_{\beta,\alpha}\Big] \\
&= \sum_\beta \Big(|K^\infty_\beta\rangle - |K^\Omega_\beta\rangle\Big) \Big(\delta_{\alpha,\beta} + \bar{Q}_\beta \bar{S}^\dagger_{\beta,\alpha}\Big) + \sum_\beta |J^\Omega_\beta\rangle \bar{S}^\dagger_{\beta,\alpha}
\end{aligned} \tag{4.6}$$

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

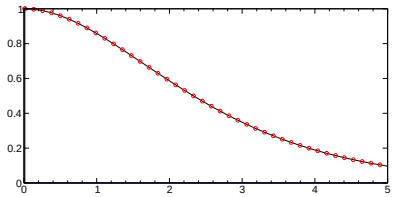
Chapter 5

Benchmarks

5.1 Hydrogen

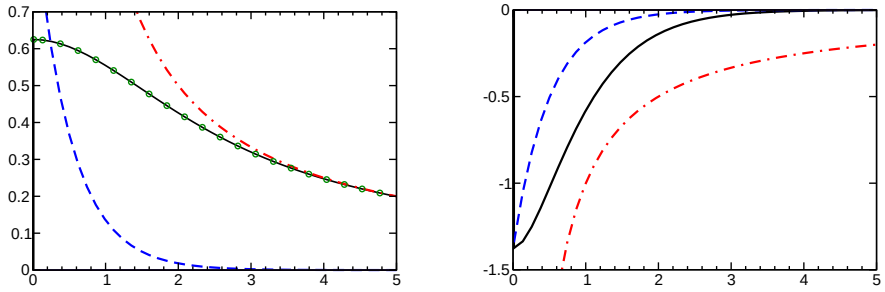
The hydrogen atom and the dihydrogen cation in a basisset of hydrogen orbitals, many of the integrals can be calculated analytically. The analytical results are in the appendix in section A.1 and the off-site matrix elements are in section A.2 The energies are then composed in section A.3.

1. In order to test the calculations of the integrals, the local orbital is overwritten by the exact atomic orbital of hydrogen in `simplelmto_makechi1` by setting the parameter `TH1S=.true.`.
2. in `simplelmto_offxint` the parameters for the distance grid are changed to `NDIS=100,dsmn=0.01d0,dsm`
3. `SIMPLELMTO_OFFSITEOVERLAPSETUP` is tested as follows:
   - I set `TPR=.true.`, which writes the integrals into the file XOV.DAT and terminates after writing.
   - run the code for a hydrogen atom or molecule with NPRO=1 and offsite exchange on.
   - inspect the file `XOV.DAT` and compare with analytical result.



4. `SIMPLELMTO_OFFSITEX22SETUP` is tested as follows:
   - I set `TPR=.true.`, which writes the integrals into the file X22.DAT and terminates after writing.
   - Switch the long-range correction off by selecting `TOFF=.true.` in `SIMPLELMTO_EXPLDISF`
   - run the code for a hydrogen atom or molecule with NPRO=1 and offsite exchange on.

- inspect the file `X22.DAT` and compare with analytical result.



The graph shows (left) the 22-matrix element and (right) the 22 matrix element with the long-range part subtracted. Also shown is (red,dash-dotted) the function $\pm d^{-1}$ and (blue,dashed) e^{-2r/a_0}. The green spheres are the analytic result.

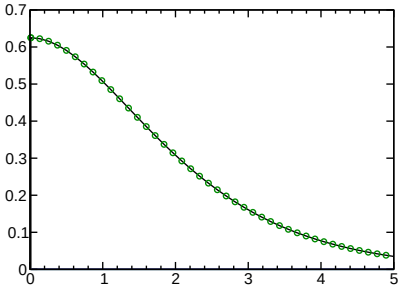
The numeric data are divided by 4π before printing. the agreement is good only when this factor is included. This factor is in order as shown by the U-matrix elements in `simplelmto_offsitexeval`, described below.

The agreement of analytic and with the code is perfect.

- undo the changes made for the test of `SIMPLELMTO_OFFSITEX22SETUP`.

5. `SIMPLELMTO_OFFSITEX31SETUP` is tested as follows:

- I set `TPR=.true.`, which writes the integrals into the file X22.DAT and terminates after writing.
- run the code for a hydrogen atom or molecule with NPRO=1 and offsite exchange on.
- inspect the file `X31.DAT` and compare with analytical result. I find precise agreement.
- undo the changes made for the test of `SIMPLELMTO_OFFSITEX31SETUP`



The graph shows the 31-matrix element. The green spheres are the analytic result.

The numeric data are divided by 4π before printing. the agreement is good only when this factor is included. This factor is in order as shown by the U-matrix elements in `simplelmto_offsitexeval`, described below.

The agreement of analytic and with the code is perfect. The matrix elements do not fall off to zero upt to 5 a_0.

6. The fitting of the data with interpolating data as described in section sec:interpolation4center is performed in `simplelmto_offsitexconvert`.

   This fitting is critical. I find strong Gauss oscillations, when the decay length becomes 0.5 a_0 or longer.

```
INTEGER(4),PARAMETER :: NDIS=25  !#(DISTANCE GRID POINTS)
REAL(8)   ,PARAMETER :: DSMN=0.01D0,DSMX=8.D0 !PARMS FOR DISTANCE GRID
                        !DISTANCE GRID WILL BE SCALED BY RCOV1+RCOV2
INTEGER(4),PARAMETER :: NF=10  !#(FIT FUNCTIONS 1<NF<NDIS!)
REAL(8)   ,PARAMETER :: DCAYMN=0.01D0,DCAYMX=0.3D0 !PARMS FOR FIT FUNCTION
```

7. We test in `simplelmto_offsitexeval` the accuracy of the interpolation and whether all factors are correct for the U-tensor and overlap matrix elements. Print statements are introduced right after `SIMPLELMTO_OFFSITEOVERLAP`, `SIMPLELMTO_OFFSITEX22U` and `SIMPLELMTO_OFFSITEX31U` two write the distance and the matrix element.

   The grid for the interpolation is defined in `simplelmto_offxint` as

```
INTEGER(4),PARAMETER :: NDIS=25  !#(DISTANCE GRID POINTS)
REAL(8)   ,PARAMETER :: DSMN=0.01D0,DSMX=8.D0 !PARMS FOR DISTANCE GRID
INTEGER(4),PARAMETER :: NF=10  !#(FIT FUNCTIONS 1<NF<NDIS!)
REAL(8)   ,PARAMETER :: DCAYMN=0.01D0,DCAYMX=0.3D0 !PARMS FOR FIT FUNCTIONS
```

   The matrix elements for the distance of $1.7007533934015353 a_0$ are compared with the analytic results for hydrogen.

	code	analytic	relative error
overlap	0.66909903193483400	0.6690200686	10^{-4}
I22	0.46359781572577707	0.4639919717	8×10^{-4}
I31	0.36493908697317334	0.3649471777	2×10^{-5}

8. In the structure file, I set `LHFWEIGHT=1.` to obtain the results similar to a full exchange calculation. (See also section A.3 for the dihydrogen cation at its equilibrium distance.)

   The atomic distance is $1.7007533934015353 a_0$.

onsite charge per site	0.48233	0.29957
onsite exchange per site	-0.03635	
double counting per site	0.03936	
offsite charge	0.64543	0.400846
offsite exchange	-0.22371	

$$
\begin{aligned}
|\psi\rangle = (|\chi_1\rangle + |chi_2\rangle)\,\frac{1}{\sqrt{2+2S}} &= (|\chi_1\rangle + |chi_2\rangle)\,c \\
c &= 0.5473362632 \\
S &= 0.6690200686 \\
d &= 1.7007533934015353 a_0 \\
\frac{n_{onsite}}{sites} &= c^2 = \frac{1}{2+2S} = 0.299576985 \\
n_{offsite} &= 2c^2 S = \frac{2S}{2+2S} = 0.4008460301 \\
E_{X,onsite} &= U_{onsite}\rho_{11}\rho_{11} \\
E_{X,31} &= \frac{1}{2}\left(l_{31}\rho_{11}\rho_{12} + l_{31}\rho_{22}\rho_{21}\right) \\
E_{X,22} &= \frac{1}{2}\left(l_{22}\rho_{12}\rho_{21} + l_{22}\rho_{21}\rho_{12}\right)
\end{aligned}
\tag{5.1}
$$

where S is the offsite overlap, d is the interatomic distance.

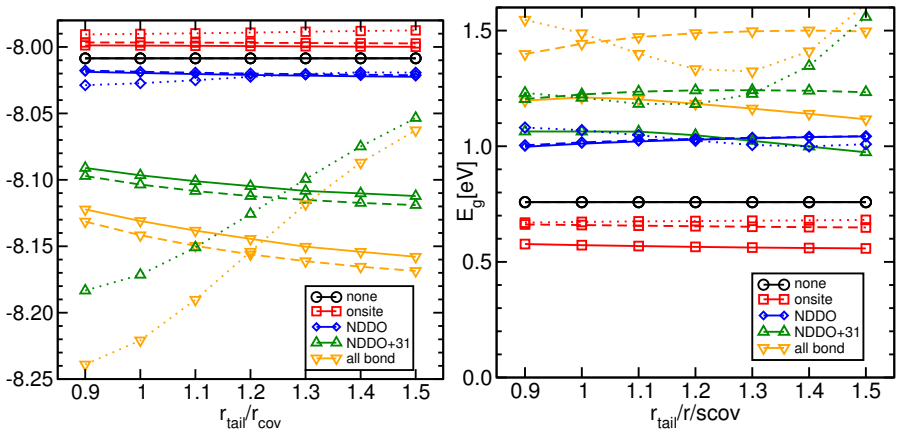
5.2 Silicon

The files are in `~/Tree/Projects/SetupTests/Si`.

I performed calculation for a silicon crystal. We used a mixing of the local 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: $K2 = 0, \ldots, -0.5$
- 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 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



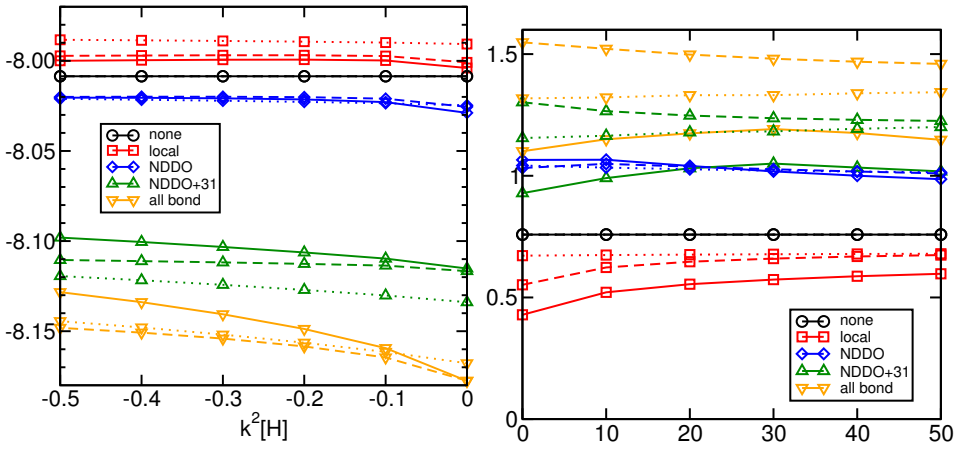
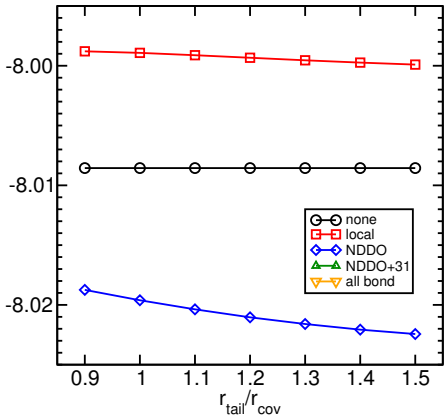


Fig. 5.1: Energy in Hartree and band gap in eV of the silicon crystal as function of the kinetic energy (times -0.01) of the envelope function for the PBE functional (black; none), local Hartree-Fock (red; onsite or local) NDDO-type exchange, i.e density of one site with the density on a bond partner (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 dashe4d lines also d-type orbitals are included. The dotted lines are calculated with double orbitals for s,p and single orbitals for d.



5.2.1 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 $2s+2p+1d$ teh calculationb 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 H≈1.4 eV!

  This may be due to the poor description of the bond density by the exponential tails ofg

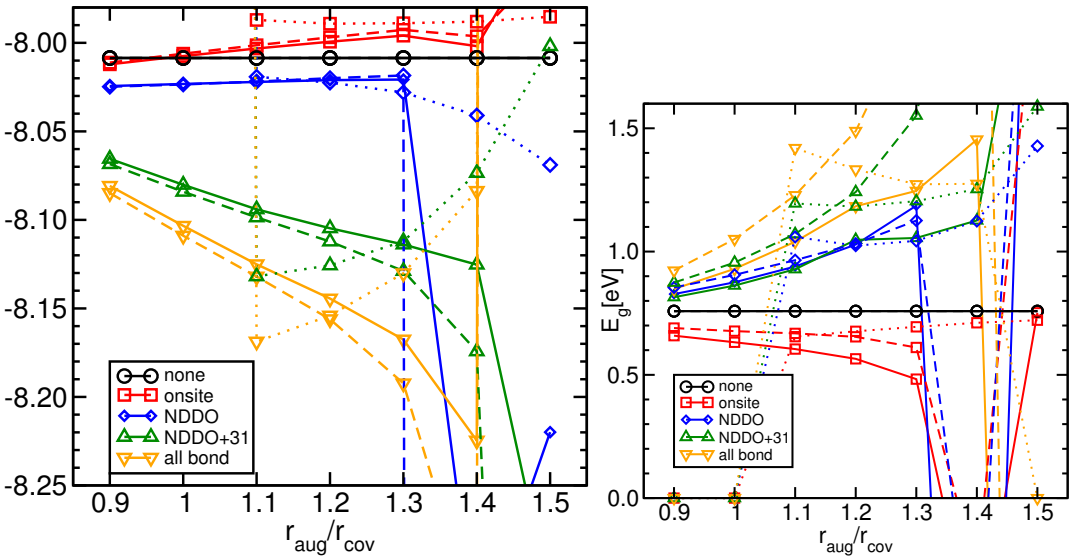


Fig. 5.2: Energy in Hartree and band gap in eV of the silicon crystal as function of the augmentation radius for the PBE functional (black; none), local Hartree-Fock (red; onsite or local) NDDO-type exchange, i.e density of one site with the density on a bond partner (blue, NDDO), terms with three orbitals 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 dashe4d lines also d-type orbitals are included. The dotted lines are calculated with double orbitals for s,p and single orbitals for d.

the tailed orbitals.

It may also be due to the fact the 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 $-0.2 < k^2 < -0.5$ H
- Choose value of $r_{tail} = 1.2 r_{cov}$

Chapter 6

Implementation of simpler orbitals

This is a description of a more recent development using simpler orbitals. The basic idea is to simplify the orbitals so that they do not change their shape but that are directly tied to the central atom. This can be accomplished by using envelope functions that fall of so rapidly, that they are almost zero at the nuclear site of the neighboring atoms.

6.1 Projector functions

Density matrix

Here, we use the expression for $\langle\phi|\pi\rangle$, which is approximated by the linear terms in the structure constants to evaluate the density matrix in the local orbitals. Consistent with the previous approximation, we retain only terms that are linear in the offsite terms of $\langle\phi|\pi\rangle$.

$$\rho^{\chi} = \langle\pi|\phi\rangle\rho^{\phi}\langle\phi|\pi\rangle \tag{6.1}$$

In the following, I break this expression up into on- and off-site terms. The indices j, k are site indices and not orbital indices. The objects are matrices related to the orbital indices of each site.

$$\begin{aligned}
\rho^{\chi}_{j,k} &= \langle\pi_j|\phi_k\rangle\rho^{\phi}_{kk}\langle\phi_k|\pi_k\rangle + \langle\pi_j|\phi_j\rangle\rho^{\phi}_{jk}\langle\phi_k|\pi_k\rangle + \langle\pi_j|\phi_j\rangle\rho^{\phi}_{jj}\langle\phi_j|\pi_k\rangle \quad \text{for } j \neq k \\
\rho^{\chi}_{j,j} &= \langle\pi_j|\phi_j\rangle\rho^{\phi}_{jj}\langle\phi_j|\pi_j\rangle + \sum_k \langle\pi_j|\phi_j\rangle\rho^{\phi}_{jk}\langle\phi_k|\pi_j\rangle + \sum_k \langle\pi_j|\phi_k\rangle\rho^{\phi}_{kj}\langle\phi_j|\pi_j\rangle
\end{aligned} \tag{6.2}$$

I define analogous potentials

$$\begin{aligned}
dE &= \sum_{\alpha,\beta} \frac{dE}{d\rho^{\chi}_{\alpha,\beta}} d\rho^{\chi}_{\alpha,\beta} = \sum_{\alpha,\beta} \left(\frac{dE}{d\rho^{\chi}_{\beta,\alpha}}\right)^* d\rho^{\chi}_{\alpha,\beta} = \mathrm{Tr}\left[\left(\frac{dE}{d\rho^{\chi}}\right)^* d\rho\right] = \mathrm{Tr}\left[v^{\chi} d\rho\right] \\
v^{\chi} &= \left(\frac{dE}{d\rho^{\chi}}\right)^* \\
v^{\phi} &= \left(\frac{dE}{d\rho^{\phi}}\right)^*
\end{aligned} \tag{6.3}$$

$$v^{\phi} = \langle\phi|\pi\rangle v^{\chi}\langle\pi|\phi\rangle \tag{6.4}$$

and split up into on- and off-site terms

$$\begin{aligned} v^{\phi}_{j,k} &= \langle\phi_j|\pi_j\rangle v^{\chi}_{j,k}\langle\pi_k|\phi_k\rangle + \langle\phi_j|\pi_k\rangle v^{\chi}_{k,k}\langle\pi_k|\phi_k\rangle + \langle\phi_j|\pi_j\rangle v^{\chi}_{j,j}\langle\pi_j|\phi_k\rangle \quad \text{for } j \neq k \\ v^{\phi}_{j,j} &= \sum_k \langle\phi_j|\pi_j\rangle v^{\chi}_{j,k}\langle\pi_k|\phi_j\rangle + \langle\phi_j|\pi_j\rangle v^{\chi}_{j,j}\langle\pi_j|\phi_j\rangle + \sum_k \langle\phi_j|\pi_k\rangle v^{\chi}_{k,j}\langle\pi_j|\phi_j\rangle \end{aligned} \tag{6.5}$$

6.2 Failed procedure

The procedure described here failed, probably doe to inverting a singular matrix.

The projector functions are determined so that

$$\langle p_\zeta|\psi\rangle = \sum_\gamma \langle p_\zeta|\chi_\alpha\rangle\langle\pi_\alpha|\psi\rangle \quad \Rightarrow \quad \langle\pi_\alpha| = \sum_\gamma \Big(\langle p|\chi\rangle\Big)^{-1}_{\alpha,\gamma}\langle p_\gamma| \tag{6.6}$$

$$\begin{aligned} \langle p_\zeta|\chi_\gamma\rangle &= \sum_\alpha \left\{ \langle p_\zeta|\phi^H_\alpha\rangle - \sum_\beta \langle p_\zeta|\phi^T_\beta\rangle S^{\dagger}_{R_\beta,L_\beta,R_\alpha,L_\alpha} c_{\alpha,\gamma} \right\} \\ &= \sum_\eta \left\{ \delta_{\zeta,\eta} - \underbrace{\sum_{\beta,\alpha,\mu} \langle p_\zeta|\phi^T_\beta\rangle S^{\dagger}_{R_\beta,L_\beta,R_\alpha,L_\alpha} c_{\alpha,\mu} \Big(\langle p|\phi^H\rangle\Big)^{-1}_{\mu,\eta}}_{=:Z^{\dagger}_{\zeta,\eta}} \right\} \langle p_\eta|\phi^H_\gamma\rangle \\ \langle p|\chi\rangle &= \Big(\mathbf{1} - \boldsymbol{Z}^{\dagger}\Big)\langle p|\phi^H\rangle \end{aligned} \tag{6.7}$$

with

$$\boldsymbol{Z}_{\zeta,\eta} \overset{\text{def}}{=} \Big(\langle p|\phi^H\rangle\Big)^{-1,\dagger}_{\zeta,\mu} \boldsymbol{c}^{\dagger}_{\mu,\alpha}\boldsymbol{S}_{\alpha,\beta}\Big(\langle p|\phi^J\rangle\Big)^{\dagger} . \tag{6.8}$$

Thus, we obtain the projector functions for the local orbitals as

$$\begin{aligned} \langle p|\chi\rangle\langle\pi| = \langle p| \quad &\overset{\text{Eq. 6.7}}{\Leftrightarrow} \quad \sum_{\beta,\gamma}\Big[\delta_{\alpha,\beta} - \big(Z^{\dagger}\big)_{\alpha,\beta}\Big]\langle p_\beta|\phi^H_\gamma\rangle\langle\pi_\gamma| = \langle p_\alpha| \\ \Rightarrow \quad \langle\pi_\gamma| &= \sum_{\alpha,\beta}\Big(\langle p|\phi^H\rangle\Big)^{-1}_{\gamma,\beta}\Big[\mathbf{1} - \boldsymbol{Z}^{\dagger}\Big]^{-1}_{\beta,\alpha}\langle p_\alpha| \end{aligned} \tag{6.9}$$

6.3 Code structure

Initialization

```
simplelmto$makepotpar1
  simplelmto$makechi1
  simplelmto$onsitematrixelements
  simplelmto$offxint
```

Iteration:

```
simplelmto$hybrid
  waves$getrspacemata('denmat')
  simplelmto$onsitedenmatextractadd('extract' denmat ->donsite)
  simplelmto$structureconstants
  simplelmto$zmat1
  SIMPLELMTO_DENMATPHITOCHI1('FWRD',
!
  SIMPLELMTO_HYBRIDENERGY:(denmat,donsite) ->(etot,hamil,honsite,F)
!
  SIMPLELMTO_DENMATPHITOCHI1('BACK')
  SIMPLELMTO_ONSITEDENMATEXTRACTADD('ADDBACK',hamil+honsite->hamil
  WAVES$SETRSPACEMATA('HAMIL',NND,HAMIL)
```

6.3.1 Local orbitals

In `simplelmto$makechi1` the local orbitals are constructed.

First the head and tail functions are constructed such that

- the nodeless head function matches to the solid Hankel function at the radius `RAUG` with value and derivative.
- the nodeless tail function matches to the solid Bessel function function at the radius `RAUG` with value and derivative.

With the same coefficients we determine the all-electron and pseudo head and tail functions. This implies that the all-electron and pseudo head and tail functions do not obey the matching conditions.

The local orbitals are composed form nodeless head function within the augmentation sphere and solid Hankel function beyond. In a second step we adds the difference of the all-electron and pseudo head function to obtain the corresponding local orbitals.

An on-site Gram-Schmidt-type orthonormalization is performed on the local orbitals. The matrix that changes the augmented Hankelfunctions to the normalized local orbitals is `CMAT`. It is required later to translate the structure constants for Hankel functions to those of local orbitals.

Alongside with the orbitals also the head functions are transformed.

6.3.2 Projections

In `simplelmto$makechi1` we also determine

$$\begin{aligned} \langle \tilde{p}_\alpha | \tilde{\phi}^H_\beta \rangle &= \texttt{PROPHIH} \\ \langle \tilde{p}_\alpha | \tilde{\phi}^T_\beta \rangle &= \texttt{PROPHIT} \end{aligned} \tag{6.10}$$

Later we will need the inverse of $\langle p|\phi^H\rangle$. $\langle p|\Phi^H\rangle$ is a $N^\phi \times N^\chi$ matrix and $\boldsymbol{c}$ is a $N^\chi \times N^\chi$ matrix. The inversion shall be done in the least-square sense, that is

$$\Big(\langle p|\Phi^H\rangle\Big)^{-1} = \Big(\langle \Phi^H|p\rangle\langle\phi|\phi\rangle\langle p|\Phi^H\rangle\Big)^{-1}\langle\Phi^H|p\rangle\langle\phi|\phi\rangle = \texttt{PROPHIHINV} \tag{6.11}$$

ZMAT

First the structure constants are calculated. The calculated structure constants are defined

$$|K_\alpha^\infty\rangle = -\sum_{\beta\in R'} |J_\beta\rangle S_{\alpha,\beta} \text{for } R' \neq R_\alpha \tag{6.12}$$

The object `ZMAT` is calculated in `SIMPLELMTO$ZMAT1`. It is constructed in each iteration because it takes the structure constants, which depend on the atomic structure.

WARNING!! I the code, the variable `ZMAT` is overloaded.

- the off-site terms contain

$$\texttt{Zmat} = \left(\langle p|\phi^H\rangle\right)^{-1,\dagger} \boldsymbol{c}^\dagger \boldsymbol{S} \left(\langle p|\phi^J\rangle\right)^\dagger \tag{6.13}$$

- the on-site terms contain

$$\texttt{Zmat} = \left(\mathbf{1} - \sum_{R'} \boldsymbol{Z}_{R,R'}\boldsymbol{Z}_{R',R}\right)^{-1} \tag{6.14}$$

The variable $\boldsymbol{Z}$ does not have non-zero on-site elements, because the on-site matrix elements of the bare structure constants vanish.

6.4 Transformation of density matrix and Hamiltonian

6.4.1 Formally correct derivation

Let me introduce symbols for the density matrix ρ^ϕ in terms of partial waves and the one ρ^χ in terms of local orbitals.

$$\begin{aligned}\rho^\phi_{\alpha,\beta} &:= \langle\tilde{p}_\alpha|\tilde{\psi}_n\rangle f_n \langle\tilde{\psi}_n|\tilde{p}_\beta\rangle \\ \rho^\chi_{\alpha,\beta} &:= \langle\pi_\alpha|\hat{\rho}|\pi_\beta\rangle\end{aligned} \tag{6.15}$$

We use the definition of the orbital projector functions Eq. 6.9 to transform the density matrix from a partial-wave to a local-orbital representation.

$$\boldsymbol{\rho}^\chi = \left(\langle p|\phi^H\rangle\right)^{-1} (\mathbf{1}-\boldsymbol{Z})^{-1,\dagger} \boldsymbol{\rho}^\phi (\mathbf{1}-\boldsymbol{Z})^{-1} \left(\langle p|\phi^H\rangle\right)^{\dagger,-1} \tag{6.16}$$

The Hamiltonian is then obtained from the derivatives.

$$\begin{aligned}
dE &= \sum_{\alpha,\beta} \frac{dE}{d\rho^{\chi}_{\alpha,\beta}} d\rho^{\chi}_{\alpha,\beta} = \sum_{\alpha,\beta} H^{\chi}_{\beta,\alpha} d\rho^{\chi}_{\alpha,\beta} = \sum_{\alpha,\beta} H^{\chi}_{\beta,\alpha} d\Big(\sum_n \langle\pi_\alpha|\psi_n\rangle f_n \langle\psi_n|\pi_\alpha\rangle\Big) \\
&= \sum_{\alpha,\beta} H^{\chi}_{\beta,\alpha} d\Big(\sum_n \langle\pi_\alpha|\psi_n\rangle f_n \langle\psi_n|\pi_\alpha\rangle\Big) \\
&= \mathrm{Tr}\Big(\langle p|\phi^H\rangle\Big)^{\dagger-1} \boldsymbol{H}^{\chi} \Big(\langle p|\phi^H\rangle\Big)^{-1} d\Big[\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{\dagger,-1}\Big(\sum_n \langle p|\psi_n\rangle f_n \langle\psi_n|p\rangle\Big)\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{-1}\Big] \\
&= \mathrm{Tr}\underbrace{\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{-1}\Big(\langle p|\phi^H\rangle\Big)^{\dagger-1} \boldsymbol{H}^{\chi} \Big(\langle p|\phi^H\rangle\Big)^{-1}\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{\dagger,-1}}_{\boldsymbol{H}^{\phi}} \\
&\quad \times \Big[d\boldsymbol{Z}^{\dagger}\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{\dagger,-1}\boldsymbol{\rho}^{\phi} + d\boldsymbol{\rho}^{\phi} + \boldsymbol{\rho}^{\phi}\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{-1} d\boldsymbol{Z}\Big] \\
&= \mathrm{Tr}\Big[\boldsymbol{H}^{\phi} d\boldsymbol{\rho}^{\phi}\Big] + 2\mathrm{Tr}\Big[\boldsymbol{H}^{\phi}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{-1} d\boldsymbol{Z}\Big]
\end{aligned} \tag{6.17}$$

The Hamiltonian $\boldsymbol{H}^{\phi}$ describes the correction to the Hamiltonian

$$d\hat{H} = \sum_{\alpha,\beta} |p_\alpha\rangle H^{\phi}_{\alpha,\beta} \langle p_\beta| \tag{6.18}$$

The second term depends on the atomic positions via the bare structure constants. With Eq. 6.8, we obtain

$$F_j = -\mathrm{Tr}\Big\{\Big(\langle p|\phi^T\rangle\Big)^{\dagger} \boldsymbol{H}^{\phi}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}-\boldsymbol{Z}\Big)^{-1}\Big(\langle p|\phi^H\rangle\Big)^{-1,\dagger} \boldsymbol{c}^{\dagger}\frac{d\boldsymbol{S}}{dR_j}\Big\} \tag{6.19}$$

6.4.2 Coding of direct inversion

First, I convert

$$\sum_{\vec{t}} \Big(\mathbf{1}-\boldsymbol{Z}\Big)_{\alpha,\vec{0},\beta,\vec{t}} \mathrm{e}^{-i\vec{k}\vec{t}} \tag{6.20}$$

then I invert the k-dependent matrix $\boldsymbol{X}_{\alpha,\beta}(\vec{k})$ and transform it back

$$X_{\beta,\vec{0},\alpha,\vec{t}} = \frac{1}{N_k}\sum_{\vec{k}} \mathrm{e}^{-i\vec{k}\vec{t}}\Big[\sum_{\vec{t}'}\Big(\mathbf{1}-\boldsymbol{Z}\Big)_{\alpha,\vec{0},\beta,\vec{t}'} \mathrm{e}^{-i\vec{k}\vec{t}'}\Big]^{-1}_{\beta,\alpha} \tag{6.21}$$

6.4.3 Approximate inversion

We start with Eq. 6.9

$$\langle\pi| = \Big(\langle p|\phi^H\rangle\Big)^{-1}\Big\{\mathbf{1}-\boldsymbol{Z}\Big\}^{-1,\dagger}\langle p| \tag{6.22}$$

The matrix Z is not hermitean, nor does it have the same dimensions for the two dimensions. According to the derivation Eq. 6.7, we need the left-handed inverse of $\mathbf{1}-\boldsymbol{Z}^{\dagger}$, respectively the transpose of the right-handed inverse of $\mathbf{1}-\boldsymbol{Z}$.

Instead of the complete inversion of $\mathbf{1}-\boldsymbol{Z}$, I approximate it by downfolding: For this purpose, I divide the system in an on-site term and the surrounding, which is then treated as bath.

$$\begin{pmatrix} \mathbf{1} & -\boldsymbol{Z}_{AB} \\ -\boldsymbol{Z}_{BA} & \boldsymbol{Y} \end{pmatrix} \begin{pmatrix} \boldsymbol{A}_{AA} & \boldsymbol{A}_{AB} \\ \boldsymbol{A}_{BA} & \boldsymbol{A}_{BB} \end{pmatrix} = \begin{pmatrix} \mathbf{1}_{AA} & \mathbf{0}_{AB} \\ \mathbf{0}_{BA} & \mathbf{1}_{BB} \end{pmatrix} \tag{6.23}$$

The matrix $\boldsymbol{Z}$ is not hermitean. The matrix $\boldsymbol{Y}$ is defined as

$$\boldsymbol{Y} := \mathbf{1}_{BB} - \boldsymbol{Z}_{BB} \tag{6.24}$$

Below, the approximations will be introduced by "tampering" with $\boldsymbol{Y}$. The onsite terms of $\boldsymbol{Z}$ are zero.

Before I work out $\boldsymbol{A}$, let me investigate which parts of $\boldsymbol{A}$ are actually required:

$$\begin{aligned} |p\rangle &= |\pi\rangle \Big(\langle p|\phi^H\rangle\Big)^\dagger (\mathbf{1}-\boldsymbol{Z}) \\ |p\rangle \boldsymbol{A} \Big(\langle p|\phi^H\rangle\Big)^{\dagger,-1} &= |\pi\rangle \underbrace{\Big(\langle p|\phi^H\rangle\Big)^\dagger \underbrace{(\mathbf{1}-\boldsymbol{Z})\boldsymbol{A}}_{\mathbf{1}} \Big(\langle p|\phi^H\rangle\Big)^{\dagger,-1}}_{\mathbf{1}} \\ \langle \pi| &= \Big(\langle p|\phi^H\rangle\Big)^{-1} \boldsymbol{A}^\dagger \langle p| \\ \langle \pi_A| &= \Big(\langle p_A|\phi^H_A\rangle\Big)^{-1} \Big(\boldsymbol{A}_{AA}\Big)^\dagger \langle p_A| + \Big(\langle p_A|\phi^H_A\rangle\Big)^{-1} \Big(\boldsymbol{A}_{BA}\Big)^\dagger \langle p_B| \end{aligned} \tag{6.25}$$

Now I work out $\boldsymbol{A}$, the inverse of $\mathbf{1}-\boldsymbol{Z}$ by resolving Eq. 6.23.

$$\begin{aligned} \boldsymbol{A}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{A}_{BA} &= \mathbf{1}_{AA} \\ \boldsymbol{A}_{AB} - \boldsymbol{Z}_{AB}\boldsymbol{A}_{BB} &= \mathbf{0}_{AB} \\ -\boldsymbol{Z}_{BA}\boldsymbol{A}_{AA} + \boldsymbol{Y}_{BB}\boldsymbol{A}_{BA} &= \mathbf{0}_{BA} \\ -\boldsymbol{Z}_{BA}\boldsymbol{A}_{AB} + \boldsymbol{Y}_{BB}\boldsymbol{A}_{BB} &= \mathbf{1}_{BB} \end{aligned} \tag{6.26}$$

The third equation links $\boldsymbol{A}_{BA}$ to $\boldsymbol{A}_{AA}$

$$\boldsymbol{A}_{BA} = \boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\boldsymbol{A}_{AA} \tag{6.27}$$

Insertion into the first equation produces an equation for $\boldsymbol{A}_{AA}$

$$\begin{aligned} &\Big(\mathbf{1}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)\boldsymbol{A}_{AA} = \mathbf{1}_{AA} \\ \Rightarrow \quad &\boldsymbol{A}_{AA} = \Big(\mathbf{1}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1} \end{aligned} \tag{6.28}$$

and $\boldsymbol{A}_{BA}$

$$\boldsymbol{A}_{BA} = \boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big(\mathbf{1}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1} \tag{6.29}$$

$$\begin{aligned}
\langle\pi_A| &= \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(\boldsymbol{A}_{AA}\Big)^\dagger\langle p_A| + \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(\boldsymbol{A}_{BA}\Big)^\dagger\langle p_B| \\
&= \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(\mathbf{1}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}\langle p_A| \\
&\quad + \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(\mathbf{1}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}\Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\langle p_B| \\
&= \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(\mathbf{1}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}\Big[\langle p_A| + \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\langle p_B|\Big] \qquad (6.30)
\end{aligned}$$

Test: I test the biorthogonality condition $\langle\pi_\alpha|\chi_\beta\rangle = \delta_{\alpha,\beta}$ using

$$|\chi\rangle = \Big(|\phi^K\rangle - |\phi^J\rangle\boldsymbol{S}^\dagger\Big)\boldsymbol{c} = |\phi^H\rangle - |\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c} \qquad (6.31)$$

$$\begin{aligned}
\langle\pi_A|\chi\rangle &= \Big\{\Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(1 - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger} \\
&\quad \times\Big[\langle p_A| + \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\langle p_B|\Big]\Big\}\Big\{|\phi^H\rangle - |\phi^J\rangle\boldsymbol{S}^\dagger\boldsymbol{c}\Big\} \\
&= \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(1 - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger} \\
&\quad \times\begin{cases}\langle p_A|\phi_A^H\rangle - \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\langle p_B|\phi_B^J\rangle\Big(\boldsymbol{S}_{AB}\Big)^\dagger\boldsymbol{c}_{AA} & \text{for } \chi\in A \\ -\langle p_A|\phi_A^J\rangle\Big(\boldsymbol{S}_{B,A}\Big)^\dagger\boldsymbol{c}_{BB} + \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\Big[\langle p_B|\phi_B^H\rangle - \langle p_B|\phi_B^J\rangle\Big(\boldsymbol{S}_{BB}\Big)^\dagger\boldsymbol{c}_{BB}\Big] & \text{for } \chi\in B\end{cases} \\
&= \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(1 - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger} \\
&\quad \times\begin{cases}\Big[\mathbf{1}_{AA} - \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\Big(\boldsymbol{Z}_{AB}\Big)^\dagger\Big]\langle p_A|\phi_A^H\rangle & \text{for } \chi\in A \\ -\Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\langle p_B|\phi_B^H\Big) + \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\Big[\langle p_B|\phi_B^H\rangle - \Big(\boldsymbol{Z}_{BB}\Big)^\dagger\Big(\langle p_B|\phi_B^H\Big)\Big] & \text{for } \chi\in B\end{cases} \\
&= \Big(\langle p_A|\phi_A^H\rangle\Big)^{-1}\Big(1 - \boldsymbol{Z}_{AB}\boldsymbol{Y}_{BB}^{-1}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger} \\
&\quad \times\begin{cases}\Big[\mathbf{1}_{AA} - \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\Big(\boldsymbol{Z}_{AB}\Big)^\dagger\Big]\langle p_A|\phi_A^H\rangle & \text{for } \chi\in A \\ \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big\{-\mathbf{1} + \Big(\boldsymbol{Y}_{BB}\Big)^{-1,\dagger}\Big[1 - \Big(\boldsymbol{Z}_{BB}\Big)^\dagger\Big]\Big\}\Big(\langle p_B|\phi_B^H\Big) & \text{for } \chi\in B\end{cases} \qquad (6.32)
\end{aligned}$$

We have purposely not used the identity $\boldsymbol{Y} = \Big(\mathbf{1}_{BB} - \boldsymbol{Z}_{BB}\Big)^{-1}$, because this identity will be violated when we approximate $\boldsymbol{Y}$.

If the identity holds one can show in a few additional steps that $\langle\pi_A|\chi_A\rangle = \mathbf{1}_{AA}$ and $\langle\pi_A|\chi_B\rangle = \mathbf{0}_{AB}$.

Approximating Y by the unit matrix

In the limit of vanishing orbital overlap, the off-site terms of $\boldsymbol{Z}$ vanish and $\boldsymbol{Y}_{22} = \mathbf{1}$.

$$\langle \pi_A| = \Big(\langle p_A|\phi^H_A\rangle\Big)^{-1}\Big(\mathbf{1}_{AA} - \boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}\Big[\langle p_A| + \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\langle p_B|\Big]$$
$$\Leftrightarrow \qquad \langle \pi| = \Big(\langle p|\phi^H\rangle\Big)^{-1}\Big(\mathbf{1} - \boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}\Big(\mathbf{1} + \boldsymbol{Z}\Big)^\dagger\langle p| \tag{6.33}$$

When the matrix $\boldsymbol{Y}_{22}$ is set equal to the unit matrix, we obtain

$$\begin{aligned}\langle \pi_A|\chi\rangle &= \Big(\langle p_A|\phi^H_A\rangle\Big)^{-1}\Big(\mathbf{1} - \boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger} \\ &\quad\times\begin{cases}\Big[\mathbf{1}_{AA} - \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big(\boldsymbol{Z}_{AB}\Big)^\dagger\Big]\langle p_A|\phi^H_A\rangle & \text{for } \chi\in A\\ \Big(\boldsymbol{Z}_{BA}\Big)^\dagger\Big\{-\mathbf{1} + \Big[\mathbf{1} - \Big(\boldsymbol{Z}_{BB}\Big)^\dagger\Big]\Big\}\Big(\langle p_B|\phi^H_B\Big) & \text{for } \chi\in B\end{cases} \\ &= \begin{cases}\mathbf{1}_{AA} & \text{for } \chi\in A\\ \Big(\langle p_A|\phi^H_A\rangle\Big)^{-1}\Big(\Big[\mathbf{0}_{BA} - \boldsymbol{Z}_{BB}\boldsymbol{Z}_{BA}\Big]\Big(\mathbf{1} - \boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1}\Big)^\dagger\langle p_B|\phi^H_B\rangle & \text{for } \chi\in B\end{cases}\end{aligned} \tag{6.34}$$

Approximating the conversion of the density matrix

As long as we do not approximate $\boldsymbol{Y}$, the bi-orthogonality is exactly obeyed. However, we need to evaluate the inverse of $\boldsymbol{Y} := \mathbf{1} - \boldsymbol{Z}_{BB}$. Secondly the conversion of the density matrix involves complicated multicenter sums, which produce long-ranged contributions. The goal is to truncate the multicenter sum, but in way that is as consistent as possible. This is probably better than just truncating the sum so that the neighborlist is filled up.

- We approximate $\boldsymbol{Y} \approx \mathbf{1}_{BB}$.
- Ontop of this approximation, when we convert the density matrix from a partial-wave representation into a local-orbital representation, we ignore
  - all onsite terms, that contain more than two off-site terms of $\boldsymbol{\rho}$ or $\boldsymbol{Z}$ in a product and we ignore
  - all off-site terms with more than one off-site term.

  This approximation limits all products to terms that exist only on one atom pair at a time. This seems to be consisten with the first approximation setting $\boldsymbol{Y} = \mathbf{1}$.

$$(\mathbf{1}+\boldsymbol{Z})^\dagger\boldsymbol{\rho}^\phi(\mathbf{1}+\boldsymbol{Z}) \approx \begin{cases}\boldsymbol{\rho}^\phi_{\text{onsite}} + \boldsymbol{Z}^\dagger\boldsymbol{\rho}^\phi_{\text{offsite}} + \boldsymbol{\rho}^\phi_{\text{offsite}}\boldsymbol{Z} + \boldsymbol{Z}^\dagger\boldsymbol{\rho}^\phi_{\text{onsite}}\boldsymbol{Z} & \text{onsite}\\ \boldsymbol{\rho}^\phi_{\text{offsite}} + \boldsymbol{Z}^\dagger\boldsymbol{\rho}^\phi_{\text{onsite}} + \boldsymbol{\rho}^\phi_{\text{on-site}}\boldsymbol{Z} & \text{offsite}\end{cases} \tag{6.35}$$

  Note that the onsite terms of $\boldsymbol{Z}$ are zero.

  The error terms have the form

$$\Delta \approx \begin{cases}\boldsymbol{Z}\boldsymbol{\rho}^\phi_{\text{offsite}}\boldsymbol{Z}^\dagger & \text{onsite}\\ \boldsymbol{Z}\Big(\boldsymbol{\rho}^\phi_{\text{onsite}} + \boldsymbol{\rho}^\phi_{\text{offsite}}\Big)\boldsymbol{Z}^\dagger & \text{offsite}\end{cases} \tag{6.36}$$

Transformation of density matrix and Hamiltonian

$$\boldsymbol{\rho}^{\chi} = \Big(\langle p|\phi^H\rangle\Big)^{-1}(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA})^{-1,\dagger}\underbrace{\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}+\boldsymbol{Z}\Big)}_{\text{special}}(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA})^{-1}\Big(\langle p|\phi^H\rangle\Big)^{\dagger,-1}$$

$$\begin{aligned}
dE &= \sum_{\alpha,\beta}\frac{dE}{d\rho^{\chi}_{\alpha,\beta}}d\rho^{\chi}_{\alpha,\beta} = \sum_{\alpha,\beta}H^{\chi}_{\beta,\alpha}d\rho^{\chi}_{\alpha,\beta} = \sum_{\alpha,\beta}H^{\chi}_{\beta,\alpha}d\Big(\sum_n\langle\pi_\alpha|\psi_n\rangle f_n\langle\psi_n|\pi_\alpha\rangle\Big)\\
&= \sum_{\alpha,\beta}H^{\chi}_{\beta,\alpha}d\Big(\sum_n\langle\pi_\alpha|\psi_n\rangle f_n\langle\psi_n|\pi_\alpha\rangle\Big)\\
&= \mathrm{Tr}\Big(\langle p|\phi^H\rangle\Big)^{\dagger-1}\boldsymbol{H}^{\chi}\Big(\langle p|\phi^H\rangle\Big)^{-1}d\Bigg[\Big(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}\underbrace{\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}+\boldsymbol{Z}\Big)}_{\text{special}}\Big(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1}\Bigg]\\
&= \mathrm{Tr}\underbrace{\Big(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1}\Big(\langle p|\phi^H\rangle\Big)^{\dagger-1}\boldsymbol{H}^{\chi}\Big(\langle p|\phi^H\rangle\Big)^{-1}\Big(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}}_{\bar{H}}\\
&\quad\times\Bigg[d\Big(\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{\dagger}\Big(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1,\dagger}\underbrace{\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}+\boldsymbol{Z}\Big)}_{\text{special}}+\underbrace{d\boldsymbol{Z}^{\dagger}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}+\boldsymbol{Z}\Big)}_{\text{special}}\\
&\quad+\underbrace{\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}d\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}+\boldsymbol{Z}\Big)}_{\text{special}}\\
&\quad+\underbrace{\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}\boldsymbol{\rho}^{\phi}d\boldsymbol{Z}}_{\text{special}}+\underbrace{\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}+\boldsymbol{Z}\Big)}_{\text{special}}\Big(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1}d\Big(\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)\Bigg]\\
&= \mathrm{Tr}\Bigg[\Big(\mathbf{1}+\boldsymbol{Z}\Big)\bar{H}\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}d\boldsymbol{\rho}^{\phi}\Bigg]+2\mathrm{Tr}\Bigg[\bar{\boldsymbol{H}}\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}\boldsymbol{\rho}^{\phi}d\boldsymbol{Z}\Bigg]\\
&\quad+2\mathrm{Tr}\Bigg[\bar{\boldsymbol{H}}\Big(\mathbf{1}+\boldsymbol{Z}\Big)^{\dagger}\boldsymbol{\rho}^{\phi}\Big(\mathbf{1}+\boldsymbol{Z}\Big)\Big(\mathbf{1}-\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)^{-1}d\Big(\boldsymbol{Z}_{AB}\boldsymbol{Z}_{BA}\Big)\Bigg]
\end{aligned}\tag{6.37}$$

6.4.4 Otherstuff

This is a suggestion for later: We will calculate the on-site matrix

$$\begin{aligned}
X_{\alpha,\beta}(\vec{R}_2-\vec{R}_1) &= \sum_{\gamma}\boldsymbol{Z}_{\alpha,\gamma}(\vec{R}_2-\vec{R}_1)\boldsymbol{Z}_{\gamma,\beta}(\vec{R}_1-\vec{R}_2)\\
&= \sum_{\eta,\mu\in R_1}\sum_{\gamma,\gamma'\in R_2}\Big[\langle p|\phi^H\rangle^{-1,\dagger}\boldsymbol{c}^{\dagger}\Big]_{\alpha,\eta}S_{R_\eta,L_\eta,R_\gamma,L_\gamma}\\
&\quad\times\Big[\langle p|\phi^J\rangle^{\dagger}\langle p|\phi^H\rangle^{-1,\dagger}\boldsymbol{c}^{\dagger}\Big]_{\gamma,\gamma'}S_{R_{\gamma'},L'_{\gamma},R_\mu,L_\mu}\Big[\langle p|\phi^J\rangle^{\dagger}\Big]_{\mu,\beta}\\
&= \sum_{\eta,\mu\in R_1}\sum_{\gamma,\gamma'\in R_2}\Big[\boldsymbol{c}\langle p|\phi^H\rangle^{-1}\Big]^{\dagger}_{\alpha,\eta}S_{R_\eta,L_\eta,R_\gamma,L_\gamma}\\
&\quad\times\Big[\boldsymbol{c}\langle p|\phi^H\rangle^{-1}\langle p|\phi^J\rangle\Big]^{\dagger}_{\gamma,\gamma'}S_{R_{\gamma'},L'_{\gamma},R_\mu,L_\mu}\Big[\langle p|\phi^J\rangle\Big]^{\dagger}_{\mu,\beta}
\end{aligned}\tag{6.38}$$

$$
\begin{aligned}
S_{RL,R'L'} &\overset{\text{Eq. 2.7}}{=} (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}'-\vec{R}) \begin{cases} (-ik)^{\ell+\ell'-\ell''} & \text{for } k^2>0 \\ \delta_{\ell+\ell'-\ell''} & \text{for } k^2=0 \\ \kappa^{\ell+\ell'-\ell''} & \text{for } k^2=-\kappa^2<0 \end{cases} \\
S_{R'L',RL} &= S_{RL,R'L'} \\
S_{RL,R'L'}S_{R'L',RL''} &= (-1)^{\ell'+\ell''}(4\pi)^2 \sum_{\bar{L}} \sum_{\bar{L}'} C_{L,L',\bar{L}} C_{L',L'',\bar{L}'} H_{\bar{L}}(\vec{R}'-\vec{R}) H_{\bar{L}'}(\vec{R}-\vec{R}') \\
&\quad \times \begin{cases} (-ik)^{2\ell+2\ell'-\bar{\ell}-\bar{\ell}'} & \text{for } k^2>0 \\ \delta_{\ell+\ell'-\bar{\ell}}\delta_{\ell+\ell'-\bar{\ell}'} & \text{for } k^2=0 \\ \kappa^{2\ell+2\ell'-\bar{\ell}-\bar{\ell}'} & \text{for } k^2=-\kappa^2<0 \end{cases} \\
&= (-1)^{\ell'+\ell''}(4\pi)^2 \sum_{\bar{L}} \sum_{\bar{L}'} C_{L,L',\bar{L}} C_{L',L'',\bar{L}'} H_{\bar{L}}(\vec{R}'-\vec{R}) H_{\bar{L}'}(\vec{R}-\vec{R}') \\
&\quad \times \begin{cases} (-ik)^{2\ell+2\ell'-\bar{\ell}-\bar{\ell}'} & \text{for } k^2>0 \\ \delta_{\ell+\ell'-\bar{\ell}}\delta_{\ell+\ell'-\bar{\ell}'} & \text{for } k^2=0 \\ \kappa^{2\ell+2\ell'-\bar{\ell}-\bar{\ell}'} & \text{for } k^2=-\kappa^2<0 \end{cases}
\end{aligned}
\tag{6.39}
$$

Let me denote the radial part of $H_L(\vec{R}) = h_\ell(|\vec{r}|)Y_L(\vec{R})$.

$$
\begin{aligned}
S_{RL,R'L'}S_{R'L',RL''} &= (-1)^{\ell'+\ell''}(4\pi)^2 \sum_{\bar{\ell},\bar{\ell}'} h_{\bar{\ell}}(|\vec{R}'-\vec{R}|) h_{\bar{\ell}'}(|\vec{R}'-\vec{R}|) \\
&\quad \times \sum_{\bar{m},\bar{m}'} C_{L,L',\bar{L}} C_{L',L'',\bar{L}'} Y_{\bar{L}}(\vec{R}'-\vec{R})(-1)^{\bar{\ell}'} Y_{\bar{L}'}(\vec{R}'-\vec{R}) \\
&\quad \times \begin{cases} (-ik)^{2\ell+2\ell'-\bar{\ell}-\bar{\ell}'} & \text{for } k^2>0 \\ \delta_{\ell+\ell'-\bar{\ell}}\delta_{\ell+\ell'-\bar{\ell}'} & \text{for } k^2=0 \\ \kappa^{2\ell+2\ell'-\bar{\ell}-\bar{\ell}'} & \text{for } k^2=-\kappa^2<0 \end{cases}
\end{aligned}
\tag{6.40}
$$

6.5 Analysis of the code structure in paw_lmto

PAW_WAVES

```
CALL LMTO$PROJTONTBO_NEW('FWRD',XK(:,IKPT),NDIM,NBH,NPRO,THIS\%PROJ &
  &                                        ,NORB,THIS\%TBC_NEW)
```

The subroutine lmto$etot is called from the paw_waves1 object.

```
LMTO$ETOT(LMNXX_,NDIMD_,NAT_,DENMAT_,DH_)
   LMTO_HYBRID()
      CALL LMTO_NTBODENMAT_NEW()
      CALL LMTO_HYBRIDENERGY()
      CALL LMTO_NTBODENMATDER_NEW()
      CALL LMTO_CLEANDENMAT_NEW()
```

6.6 Helmholtz equation

http://fortranwiki.org/fortran/show/Bessel+function

Yukawa Potential obeys the Helmholtz equation: In RPA without local field effects, the Energy looks like that of a Hartree Fock calculation, but with a modified exchange term. In the exchange, the interaction is changed to the screened interaction, which is represented by a Yukawa potential.

$$v(\vec{r}) = \int d^3r' \; \frac{e^2 n(\vec{r'})}{4\pi\epsilon_0 |\vec{r} - \vec{r'}| \exp(\lambda|\vec{r} - \vec{r'}|)} \tag{6.41}$$

The Yukawa potential satisfies the Helmholtz equation [1]

$$\left(\vec{\nabla}^2 - \lambda^2\right) \frac{\mathrm{e}^{-\lambda|\vec{r}|}}{|\vec{r}|} = -4\pi\delta(\vec{r}) \tag{6.44}$$

The Helmholtz equation has the form

$$\begin{aligned}
\left(\nabla^2 - \lambda^2\right) v(\vec{r}) &= \int d^3r' \; \frac{e^2 n(\vec{r'})}{\epsilon_0} \left(\nabla^2 - \lambda^2\right) \frac{1}{4\pi|\vec{r} - \vec{r'}| \exp(\lambda|\vec{r} - \vec{r'}|)} \\
&= -\int d^3r' \; \frac{e^2 n(\vec{r'})}{\epsilon_0} \delta(\vec{r} - \vec{r'}) \\
&= -\frac{e^2}{\epsilon_0} n(\vec{r})
\end{aligned} \tag{6.45}$$

[1]

$$\begin{aligned}
\vec{\nabla} \frac{1}{r} \mathrm{e}^{-\lambda r} &= \left(-\frac{1}{r^2} - \frac{1}{r}\lambda\right) \mathrm{e}^{-\lambda|\vec{r}|} \frac{\vec{r}}{r} = -\left(\lambda r + 1\right) \frac{\vec{r}}{r^3} \mathrm{e}^{-\lambda|\vec{r}|} \\
\vec{\nabla}^2 \frac{1}{|\vec{r}|} \mathrm{e}^{-\lambda|\vec{r}|} &= \vec{r}\left[-\lambda \frac{1}{r^3} \mathrm{e}^{-\lambda|\vec{r}|} + \left(\lambda r + 1\right) \frac{3}{r^4} \mathrm{e}^{-\lambda|\vec{r}|} + \left(\lambda r + 1\right) \frac{1}{r^3} \lambda \mathrm{e}^{-\lambda|\vec{r}|}\right] \frac{\vec{r}}{r} - \left(\lambda r + 1\right) \frac{3}{r^3} \mathrm{e}^{-\lambda|\vec{r}|} \\
&= \left(-\lambda r + 3\left(\lambda r + 1\right) + \left(\lambda r + 1\right)\lambda r - \left(\lambda r + 1\right) 3\right) \frac{1}{r^3} \mathrm{e}^{-\lambda|\vec{r}|} \\
&= \left(-\lambda r + 3\lambda r + 3 + (\lambda r)^2 + \lambda r - 3\lambda r - 3\right) \frac{1}{r^3} \mathrm{e}^{-\lambda|\vec{r}|} = \lambda^2 \frac{1}{r} \mathrm{e}^{-\lambda|\vec{r}|}
\end{aligned} \tag{6.42}$$

In order to verify that the inhomogeneity is a delta function we consider the integral

$$\begin{aligned}
\int_{r<r_c} d^3r \left(\vec{\nabla}^2 - \lambda^2\right) \frac{1}{r} \mathrm{e}^{-\lambda r} &= \int_{r=r_c} d\vec{A} \, \vec{\nabla} \frac{1}{r} \mathrm{e}^{-\lambda r} - \lambda^2 4\pi \int_0^{r_c} dr \; r^2 \frac{1}{r} \mathrm{e}^{-\lambda r} \\
&= -\underbrace{\int_{r=r_c} d\vec{A} \frac{\vec{r}}{r^3}}_{4\pi} \left(\lambda r + 1\right) \mathrm{e}^{-\lambda|r|} - \lambda^2 4\pi \int_0^{r_c} dr \; \underbrace{r \mathrm{e}^{-\lambda r}}_{\frac{-1}{\lambda^2}\partial_r(\lambda r+1)\mathrm{e}^{-\lambda r}} \\
&= -4\pi \left(\lambda r_c + 1\right) \mathrm{e}^{-\lambda r_c} + 4\pi\left(\left(\lambda r_c + 1\right)\mathrm{e}^{-\lambda r_c} - 1\right) = -4\pi
\end{aligned} \tag{6.43}$$

Radial Green function: In order to obtain the radial Green's function, we expand the density and potential in spherical harmonics

$$\begin{aligned}\Big(\nabla^2-\lambda^2\Big)v_L(|\vec{r}|)Y_L(\vec{r}) &= -\frac{e^2}{\epsilon_0}n_L(|\vec{r}|)Y_L(\vec{r})\\ \Big(\frac{1}{r}\partial_r^2 r-\frac{\ell(\ell+1)}{r^2}-\lambda^2\Big)v_L(|\vec{r}|) &= -\frac{e^2}{\epsilon_0}n_L(|\vec{r}|)\end{aligned} \tag{6.46}$$

Determine a radial Green's function

$$\Big(\frac{1}{r}\partial_r^2 r-\frac{\ell(\ell+1)}{r^2}-\lambda^2\Big)g_\ell(r,r')=\delta(r-r') \tag{6.47}$$

and make the following ansatz for the potential.

$$v_L(r)=\int_0^\infty dr'\; g_\ell(r,r')\frac{e^2 n_L(r')}{\epsilon_0} \tag{6.48}$$

Let $j_\ell(r)$ be the regular solution and $h_\ell(r)$ the irregular solution, which goes to zero at infinity. The $j_\ell(r)$ is, up to a constant factor, equal to the modified spherical Bessel function of the first kind with argument κr and $h_\ell(r)$ is, up to a constant factor, the modified bessel function of the third kind with argument κr. The factor is chosen so that they have the κ-independent limit for small arguments.

$$j_\ell(r)=\frac{1}{(2\ell+1)!!}r^\ell(1+O(r^2)) \quad \text{and} \quad h_\ell(r)=(2\ell-1)!!r^{-\ell-1}(1+O(r^2)) \tag{6.49}$$

In the following, I will refer to the $j_\ell(r)$ as Bessel functions and to the $h_\ell(r)$ as Hankel functions.

The Green's function must solve the homogeneous equation for $r\neq r'$, and it must no continuous but not differentiable for $r=r'$. This is accomplished with the ansatz

$$g_\ell(r,r')=A(r')\left[\theta(r'-r)\frac{j_\ell(r)}{j(\vec{r'})}+\theta(r-r')\frac{h_\ell(r)}{h_\ell(r')}\right] \tag{6.50}$$

The factor $A(r)$ is then determined by

$$\lim_{\epsilon\to 0}\int_{r'-\epsilon}^{r'+\epsilon} dr\;\frac{1}{r}\partial_r^2 r\; g_L(r,r')=1 \tag{6.51}$$

which leads to the following condition

$$\begin{aligned}1&=\lim_{\epsilon\to0}\frac{1}{r'}\Big[\partial_r r g_L(r,r')\Big]_{r'-\epsilon}^{r'+\epsilon}=\lim_{\epsilon\to0}\frac{1}{r'}\Big[g_L(r,r')+r\partial_r g_L(r,r')\Big]_{r'-\epsilon}^{r'+\epsilon}\\ &=\partial_r|_{r'+\epsilon}\,g_L(r,r')-\partial_r|_{r'-\epsilon}\,g_L(r,r')\\ &=A(r')\left[\delta(r-r')\frac{h_\ell(r)}{h_\ell(r')}+\theta(r'^{+}-r')\frac{\partial_r h_\ell(r'^{+})}{h_\ell(r')}-\delta(r'-r)\frac{j_\ell(r)}{j(\vec{r'})}-\theta(r'-r'^{-})\partial_r\frac{j_\ell(r'^{-})}{j(\vec{r'})}\right]\\ &=A(r')\left[\frac{\partial_r h_\ell(r')}{h_\ell(r')}-\frac{\partial_r j_\ell(r')}{j(\vec{r'})}\right]\\ &=A(r')\left[\frac{j(\vec{r'})\partial_r h_\ell(r')-h_\ell(r')\partial_r j_\ell(r')}{j(\vec{r'})h_\ell(r')}\right]\end{aligned} \tag{6.52}$$

The numerator can be simplified as follows: We can use the Helmholtz equation to show that the following integral vanishes. The origin has been excluded, because K_L is not differentiable, so that Gauss theorem cannot be applied there

$$\begin{aligned}
0 &= \int_{r_1<|\vec{r}|<r_2} d^3r \left(J_L \vec{\nabla}^2 K_L - K_L \vec{\nabla}^2 J_L \right) \\
&= \int_{r_1<|\vec{r}|<r_2} d^3r \, \vec{\nabla} \Big(J_L \vec{\nabla} K_L - K_L \vec{\nabla} J_L \Big) \\
&= \int_{|\vec{r}|=r_2} d\vec{A} \Big(J_L \vec{\nabla} K_L - K_L \vec{\nabla} J_L \Big) - \int_{|\vec{r}|=r_1} d\vec{A} \Big(J_L \vec{\nabla} K_L - K_L \vec{\nabla} J_L \Big)
\end{aligned} \tag{6.53}$$

Thus the surface integral is independent of the radius. I name its value C

$$\begin{aligned}
C &= \int_{|\vec{r}|=r_2} d\vec{A} \left(J_L \vec{\nabla} K_L - K_L \vec{\nabla} J_L \right) \\
&= \int_{|\vec{r}|=r_2} d\vec{A} \left[j_\ell Y_L \left(h_\ell \vec{\nabla} Y_L + Y_L \vec{\nabla} h_\ell \right) - h_\ell Y_L \left(j_\ell \vec{\nabla} Y_L + Y_L \vec{\nabla} j_\ell \right) \right] \\
&= \int_{|\vec{r}|=r_2} d\vec{A} \underbrace{Y_L Y_L}_{\sum_{L''} C_{L'',L,L} Y_{L''}} \left[j_\ell \vec{\nabla} h_\ell - h_\ell \vec{\nabla} j_\ell \right] \\
&= r^2 \left(j_\ell \partial_r h_\ell - h_\ell \partial_r j_\ell \right)
\end{aligned} \tag{6.54}$$

The Hankel and Bessel functions are defined[2] such that

$$\begin{aligned}
j_\ell(r) &= \frac{1}{(2\ell+1)!!} r^\ell + \dots \\
h_\ell(r) &= (2\ell-1)!! r^{-\ell-1} + \dots
\end{aligned} \tag{6.55}$$

so that

$$C = r^2 \frac{1}{2\ell+1} \Big((-\ell-1) r^{-2} - \ell r^{-2} \Big) = -1 \tag{6.56}$$

$$A(\vec{r'}) = \frac{j(\vec{r'}) h_\ell(r')}{j(\vec{r'}) \partial_r h_\ell(r') - h_\ell(r') \partial_r j_\ell(r')} = -r^2 j(\vec{r'}) h_\ell(r') \tag{6.57}$$

We insert this result into the expression for the Green function

$$\begin{aligned}
g_\ell(r, r') &= A(r') \left[\theta(r'-r) \frac{j_\ell(r)}{j(\vec{r'})} + \theta(r-r') \frac{h_\ell(r)}{h_\ell(r')} \right] \\
&= -r'^2 \left[\theta(r'-r) j_\ell(r) h(\vec{r'}) + \theta(r-r') h_\ell(r) j_\ell(r') \right]
\end{aligned} \tag{6.58}$$

[2] Methods, Section: Working with spherical Hankel and Bessel functions

In practice we calculate the following steps

$$
\begin{aligned}
v_l(r) &= \int_0^\infty dr'\; g_\ell(r,r')\frac{e^2 n_L(r')}{\epsilon_0} \\
&= -4\pi\frac{e^2}{4\pi\epsilon_0}\int_0^\infty dr'\; r'^2\left[j_\ell(r)\theta(r'-r)h_\ell(\vec{r'}) + h_\ell(r)\theta(r-r')j_\ell(r')\right] n_L(r') \\
&= j_\ell(r)\left[-4\pi\frac{e^2}{4\pi\epsilon_0}\int_0^\infty dr'\; r'^2\theta(r'-r)h_\ell(\vec{r'})\frac{e^2 n_L(r')}{\epsilon_0}\right] \\
&+ h_\ell(r)\left[-4\pi\frac{e^2}{4\pi\epsilon_0}\int_0^\infty dr'\; r'^2\theta(r-r')j_\ell(r')n_L(r')\right] \\
&= j_\ell(r)\left[-4\pi\frac{e^2}{4\pi\epsilon_0}\int_0^r dr'\; r'^2 h_\ell(\vec{r'})n_L(r')\right] + h_\ell(r)\left[-4\pi\frac{e^2}{4\pi\epsilon_0}\int_r^\infty dr'\; r'^2 j_\ell(r')n_L(r')\right] \\
&= j_\ell(r)\Big[a(\infty)-a(r)\Big] + h_\ell(r)b(r) \\
a(r) &= -4\pi\frac{e^2}{4\pi\epsilon_0}\int_0^r dr'\; r'^2 h_\ell(\vec{r'})n_L(r') \\
b(r) &= -4\pi\frac{e^2}{4\pi\epsilon_0}\int_0^r dr'\; r'^2 j_\ell(r')n_L(r')
\end{aligned}
\tag{6.59}
$$

I use the routines `SPFUNCTION$MODBESSEL(L,K*X,Y,DYDX)` (ABRAMOWITZ 10.2.4) and `SPFUNCTION$MODHANKEL(L,K*X,Y,DYDX)`(ABRAMOWITZ 10.2.4) (which is taken from routione `LMTO\$solidbessel` `LMTO\$solidhankel` in `paw\_lmtobasics`

Chapter 7

Off-site matrix elements NDDO

7.1 Interpolation of the four-center integrals

In order to make the code fasst. The four-center integrals are mapped onto a distance grid, with the distance pointing in the z-direction.

The functions to be interpolated have the property that their slope a the origibn vanishes, and that they fall off exponentially. Therefore, the fit functions are chosen as

$$g_j(x) = (1 + \lambda_j x)\mathrm{e}^{-\lambda_j x} \tag{7.1}$$

The least-square fit in the distance grid minimizes

$$I[\{c_j\}] \stackrel{\text{def}}{=} \int dx \left(f(x) - \sum_j g_j(x) c_j \right)^2 \tag{7.2}$$

so that

$$\frac{\partial I}{\partial c_j} = 2 \left[\left(\int dx \; g_k(x) g_j(x) \right) c_j - (g_k(x) f(x)) \right] \stackrel{!}{=} 0 \tag{7.3}$$

The integration is performed on a distance grid, which is necessarily finite. One consence is that the fit function may produce maxima beyond the distance grid. Because of this we augment the overlap integral of two fit functions by an analytic integral from the maximum grid point to

infinity.

$$\begin{aligned}
&\int_{x_{max}}^{\infty} dx\ g_k(x)g_j(x) \\
= &\int_{x_{max}}^{\infty} dx\ \left(1+(\lambda_j+\lambda_k)x+\lambda_j\lambda_k x^2\right)\mathrm{e}^{-(\lambda_j+\lambda_k)x} \\
= &\frac{1}{\lambda_1+\lambda_2}\int_{y_{max}}^{\infty} dy\ \Big(1+y+\underbrace{\frac{\lambda_j\lambda_k}{(\lambda_j+\lambda_k)^2}}_{:=K}y^2\Big)\mathrm{e}^{-y} \\
\overset{\text{Eq. A.11}}{=} &\frac{1}{\lambda_1+\lambda_2}\left[\left(-1-(1+y)-K(y^2+2y+2)y^2\right)\mathrm{e}^{-y}\right]_{y_{max}}^{\infty} \\
= &\frac{1}{\lambda_1+\lambda_2}\left[-\left(2+y+K(y^2+2y+2)\right)\mathrm{e}^{-y}\right]_{y_{max}}^{\infty} \\
= &\frac{1}{\lambda_1+\lambda_2}\left(2+y_{max}+K(y_{max}^2+2y_{max}+2)\right)\mathrm{e}^{-y_{max}} \\
&\text{with } y_{max}=(\lambda_j+\lambda_k)x_{max} \text{ and } K=\frac{\lambda_j\lambda_k}{(\lambda_j+\lambda_k)^2}
\end{aligned} \tag{7.4}$$

I do not include such an extension in the integral $\int_{x_{max}}^{\infty} dx\ g_k(x)f(x)$, which is the same as treating $f(x)=0$ for $x>x_{max}$.

Instead of the integral, I use a sum over grid points. That is, there is a factor x_{max}/N_x for the integrals up to x_{max} missing. Rather than scaling the integrations, I divide the integral beyond x_{max} by the same factor.

The fit produces Gauss oscillations beyond the grid, if the largest decay constant is larger than $\lambda = 0.4(r_{cov,1}+r_{cov,2})$.

Remark: The fit functions, that is the distribution of the decay constants, need to be investigated further to obtain the maximum flexibilit=y,

7.2 Exchange energy and U-tensor

The exchange energy with a screened interaction has the form

$$\begin{aligned}
E_{xc} &= -\frac{1}{2}\sum_{n,m} f_n f_m \int d^3r \int d^3r\ \psi_n^*(\vec{r})\psi_m(\vec{r})\frac{e^2\mathrm{e}^{-\lambda|\vec{r}-\vec{r'}|}}{4\pi|\vec{r}-\vec{r'}|}\psi_m^*(\vec{r'})\psi_n(\vec{r'}) \\
&= -\frac{1}{2}\sum_{n,m} f_n f_m \sum_{\alpha,\beta,\gamma,\delta}\langle\psi_n|\pi_\alpha\rangle\langle\pi_\gamma|\psi_m\rangle\langle\psi_m|\pi_\beta\rangle\langle\pi_\delta|\psi_n\rangle \\
&\quad\times\underbrace{\int d^3r\int d^3r\ \chi_\alpha^*(\vec{r})\chi_\gamma(\vec{r})\frac{e^2\mathrm{e}^{-\lambda|\vec{r}-\vec{r'}|}}{4\pi|\vec{r}-\vec{r'}|}\chi_\beta^*(\vec{r'})\chi_\delta(\vec{r'})}_{U_{\alpha,\beta,\gamma,\delta}} \\
&= -\frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\underbrace{\sum_n\langle\pi_\delta|\psi_n\rangle f_n\langle\psi_n|\pi_\alpha\rangle}_{\rho_{\delta,\alpha}}\underbrace{\sum_m\langle\pi_\gamma|\psi_m\rangle f_m\langle\psi_m|\pi_\beta\rangle}_{\rho_{\gamma,\beta}}U_{\alpha,\beta,\gamma,\delta} \\
&= -\frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\rho_{\delta,\alpha}\rho_{\gamma,\beta}U_{\alpha,\beta,\gamma,\delta}
\end{aligned} \tag{7.5}$$

with the density matrix

$$\rho_{\alpha,\beta} = \sum_n \langle \pi_\alpha | \psi_n \rangle f_n \langle \psi_n | \pi_\beta \rangle \tag{7.6}$$

and the screened U-tensor

$$U_{\alpha,\beta,\gamma,\delta} = \int d^3r \int d^3r' \; \chi^*_\alpha(\vec{r}) \chi^*_\beta(\vec{r'}) \frac{e^2 \cdot \mathrm{e}^{-\lambda|\vec{r'}-\vec{r}|}}{4\pi\epsilon_0 |\vec{r'}-\vec{r}|} \chi_\gamma(\vec{r}) \chi_\delta(\vec{r'}) \tag{7.7}$$

7.2.1 Division of exchange energy

The goal is to limit the set of matrix elements for which the Coulomb interaction is considered to

- onsite terms and
- terms which are restricted to a pairs of atoms.
- terms of the U-tensor with orbitals centered on more than two sites.

Of the terms which are restricted to a pair of distinct atoms the so-called two-center NDDO terms are dominant: These terms consist of U-tensor matrix elements that describe an interaction of a charge density $n_{\alpha,\gamma}(\vec{r})$ centered on one site, i.e $R_\alpha = R_\gamma$, with a density $n_{\beta,\delta}(\vec{r'})$ centered on another site, i.e. $R_\delta = R_\beta \neq R_\alpha$.

If the two orbitals are centered on two atoms, the density is located in the bond center and its contribution vanishes quickly with distance.

When we exclude terms for which one node is connected to orbitals from different sites there are only in-site and NDDO terms left. NDDO stands for **"Neglect of diatomic differential overlap"** and has been invented by Pople.

$$\begin{aligned} E_{xc} = & \underbrace{-\frac{1}{2} \sum_R \sum_{\alpha,\beta,\gamma,\delta \in R} \rho_{\delta,\alpha} \rho_{\gamma,\beta} U_{\alpha,\beta,\gamma,\delta}}_{\text{onsite}} \\ & \underbrace{-\frac{1}{2} \sum_{R \neq R'} \sum_{\alpha,\gamma \in R} \sum_{\delta\beta, \in R'} \rho_{\delta,\alpha} \rho_{\gamma,\beta} U_{\alpha,\beta,\gamma,\delta}}_{\text{NDDO-terms}} + \text{terms with off-site densities} \end{aligned} \tag{7.8}$$

When we include all terms centered on a bond, there is one contribution with one off-site density, the 31-term, and one with two off-site densities, which I call bond exchange "bondx".

$$\begin{aligned} \Delta E_{xc} = & \underbrace{-\frac{1}{2} \sum_{R \neq R'} 4 \sum_{\alpha \in R} \sum_{\beta,\gamma,\delta \in R'} \rho_{\delta,\alpha} \rho_{\gamma,\beta} U_{\alpha,\beta,\gamma,\delta}}_{\text{31-terms}} \\ & \underbrace{-\frac{1}{2} \sum_{R \neq R'} \sum_{\alpha,\beta \in R} \sum_{\delta\gamma, \in R'} \rho_{\delta,\alpha} \rho_{\gamma,\beta} U_{\alpha,\beta,\gamma,\delta}}_{\text{Bondx-terms}} \\ & + \text{terms on at least three sites} \end{aligned} \tag{7.9}$$

For the time being we concentrate on the NDDO terms.

7.2.2 Interaction

Let me abstract from the specific form of the interaction and describe it as $w(r)$. Later, we will require its value and derivatives which are computed here.

$$
\begin{aligned}
w(r) &= \frac{e^2}{4\pi\epsilon_0 r} \underbrace{\mathrm{e}^{-\lambda r}}_{\text{screening}} \\
\partial_r w(r) &= \frac{-e^2}{4\pi\epsilon_0 r^2} \underbrace{\Big(1+\lambda r\Big)\mathrm{e}^{-\lambda r}}_{\text{screening}} \\
\partial_r^2 w(r) &= \frac{-e^2}{4\pi\epsilon_0 r^2}\Big(1+\lambda r\Big)\mathrm{e}^{-\lambda r}\Big(-\frac{2}{r}\underbrace{-\lambda+\frac{\lambda}{1+\lambda r}}_{-\lambda^2 r/(1+\lambda r)}\Big) = \frac{+2e^2}{4\pi\epsilon_0 r^3}\underbrace{\Big(1+\lambda r\Big)\Big(1+\frac{1}{2}\frac{\lambda^2 r^2}{1+\lambda r}\Big)\mathrm{e}^{-\lambda r}}_{\text{screening}} \\
&= \frac{+2e^2}{4\pi\epsilon_0 r^3}\underbrace{\Big(1+\lambda r+\frac{1}{2}\lambda^2 r^2\Big)\mathrm{e}^{-\lambda r}}_{\text{screening}}
\end{aligned}
\tag{7.10}
$$

7.3 Thomas Fermi screening

Let us consider the static limit of screening of the Coulomb interaction by the olarization of the material.

$$
\begin{aligned}
\vec{\nabla}\vec{D} &= \rho \\
\vec{\nabla}^2\Phi = -\vec{\nabla}\vec{E} &= -\frac{1}{\epsilon_0}\rho(\vec{r})
\end{aligned}
\tag{7.11}
$$

where $D=\epsilon_0\vec{E}$, $\vec{E}=-\vec{\nabla}\Phi$.

If a charge density $\rho_{ind}(\vec{r})$ is induced by the potential produced by an external charge density $\rho_{ext}(\vec{r})$, one obtains

$$
\begin{aligned}
\vec{\nabla}^2\delta\Phi &= -\frac{1}{\epsilon_0}\underbrace{\frac{d\rho}{d\Phi}\delta\Phi}_{\rho_{ind}} - \frac{1}{\epsilon_0}\rho_{ext}(\vec{r}) = \lambda^2\delta\Phi - \frac{1}{\epsilon_0}\rho_{ext}(\vec{r}) \\
\lambda &= \sqrt{-\frac{1}{\epsilon_0}\frac{d\rho}{d\Phi}}
\end{aligned}
\tag{7.12}
$$

Note that $\frac{d\rho}{d\Phi}\leq 0$.

For a probe charge $\rho_{ext}(\vec{r})=-e\delta(\vec{r})$, we obtain

$$
\delta v(\vec{r}) = -e\delta\Phi(\vec{r}) \stackrel{?}{=} \frac{e^2}{4\pi\epsilon_0|\vec{r}|}\mathrm{e}^{-\lambda|\vec{r}|} \tag{7.13}
$$

$$
\vec{\nabla}^2\delta\Phi(\vec{r}) = \frac{-e}{4\pi\epsilon_0}\left(\frac{1}{r}\partial_r^2 r\right)\frac{1}{r}\mathrm{e}^{-\lambda r} = \lambda^2\delta\Phi(r) + \frac{-e}{4\pi\epsilon_0}4\pi\delta(\vec{r}) = \lambda^2\delta\Phi(r) + \frac{-e}{\epsilon_0}\delta(\vec{r}) q.e.d.
$$

When we introduce the electron density $n(\vec{r}) = \frac{1}{-e}\rho(\vec{r})$ and the electron potential $v(\vec{r}) = -e\Phi(\vec{r})$, we obtain

$$v(\vec{r}) = \int d^3r' \, \frac{e^2 n_{ext}(\vec{r'}}{4\pi\epsilon_0|\vec{r}-\vec{r'}|} e^{-\lambda|\vec{r}-\vec{r'}|} \qquad \text{with} \qquad \lambda = \sqrt{-\frac{e^2}{\epsilon_0}\frac{dn}{dv}} \tag{7.14}$$

Thus, in linear response and in the static case, the interaction is modified from a Coulomb potential into a Yukawa potential. In order to obtain the screening length λ^{-1}, one needs an estmate the response of the electron gas to an external potential.

7.3.1 Thomas Fermi: Free electron gas

Thomas Fermi theory considers for this purpose a free electron gas.

$$\epsilon(\vec{k},\sigma) = \frac{\hbar\vec{k}^2}{2m_e} + v \tag{7.15}$$

where Φ is the electrostatic potential.

The particle number N in the volume V is related to the Fermi wave vector, indicating the wave-vector of the highest occupied states.

$$\begin{aligned} N &= \sum_{\sigma\in\{\uparrow,\downarrow\}} \frac{V}{(2\pi)^3}\left(\frac{4\pi}{3}k_F^3\right) \qquad \Rightarrow \qquad k_F = 2\pi\sqrt[3]{\frac{3}{4\pi\sum_\sigma}n} \\ \mu &= \frac{\hbar^2 k_F^2}{2m_e} + v = \frac{\hbar^2}{2m_e}\left(2\pi\sqrt[3]{\frac{3}{4\pi\sum_\sigma}n}\right)^2 + v \end{aligned} \tag{7.16}$$

with $n = N/V$.

Now we fix the chemical potential, but introduce a perturbation in the electrostatic potential.

$$\begin{aligned} 0 &= \frac{\hbar^2}{2m_e}\left(2\pi\sqrt[3]{\frac{3}{4\pi\sum_\sigma}}\right)^2 \frac{2}{3}n^{-\frac{1}{3}}\delta n + \delta v \\ \frac{dn}{dv} &= -\left[\frac{\hbar^2}{2m_e}\left(2\pi\sqrt[3]{\frac{3}{4\pi\sum_\sigma}}\right)^2 \frac{2}{3}n^{-\frac{1}{3}}\right]^{-1} = -\frac{3m_e}{(2\pi\hbar)^2}\left(\frac{4\pi\sum_\sigma}{3}\right)^{\frac{2}{3}} n^{\frac{1}{3}} \end{aligned} \tag{7.17}$$

We can use Thomas Fermi screening with

$$\lambda = \sqrt{-\frac{e^2}{\epsilon_0}\frac{dn}{dv}} = \sqrt{\frac{e^2}{\epsilon_0}\frac{3m_e}{(2\pi\hbar)^2}\left(\frac{4\pi\sum_\sigma}{3}\right)^{\frac{2}{3}} n^{\frac{1}{3}}} = \sqrt{\frac{e^2 m_e}{4\pi\epsilon_0\hbar^2}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\left(4\sum_\sigma\right)^{\frac{2}{3}} n^{\frac{1}{3}}} \tag{7.18}$$

Test[1]

[1] Compare https://en.wikipedia.org/wiki/Electric-field_screening

$$\begin{aligned} \lambda &= \sqrt{\frac{me^2 k_F}{\epsilon_0\pi^2\hbar^2}} = \sqrt{\frac{me^2}{\epsilon_0\pi^2\hbar^2}2\pi\sqrt[3]{\frac{3}{4\pi\sum_\sigma}n}} \\ &= \sqrt{\frac{me^2}{4\pi\epsilon_0\hbar^2}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\left(8\sqrt[3]{\frac{1}{4\sum_\sigma}}\right)n^{\frac{1}{3}}} \end{aligned} \tag{7.19}$$

We can further use $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$

THOMAS FERMI SCREENING

$$\lambda = \left(\frac{3}{\pi}\right)^{\frac{1}{6}} \left(4\sum_{\sigma}\right)^{\frac{1}{3}} \left(n a_0^3\right)^{\frac{1}{6}} a_0^{-1} \approx 1,985 \times \left(n a_0^3\right)^{\frac{1}{6}} a_0^{-1} \tag{7.20}$$

	a_{lat}	N_e/a_{lat}^3	n	λ
Si diamond	5.431 Å	24	0.023 a_0^{-3}	1.061 a_0^{-1}
C diamond	3.567 Å	24	0.078 a_0^{-3}	1.298 a_0^{-1}
MgO halite	4.212 Å	24	0.023 a_0^{-3}	1.195 a_0^{-1}
MgO halite	4.212 Å	32	0.023 a_0^{-3}	1.253 a_0^{-1}
Al fcc	4.046 Å	12	0.027 a_0^{-3}	1.086 a_0^{-1}
Fe bcc	2.856 Å	16	0.102 a_0^{-3}	1.356 a_0^{-1}
$SrTiO_3$3	3.988 Å	24	0.056 a_0^{-3}	1.228 a_0^{-1}

Lattice constants from https://en.wikipedia.org/wiki/Lattice_constant.

Apparently, the Thomas-Fermi Screening length is for all dense materials fairly similar, namely $\lambda \approx 1.1 a_0^{-1} \approx 2.1$ Å^{-1}.

7.3.2 Relation to HSE06

The HSE06 functional uses a total energy of the form

$$E_{xc}^{HSE} = E_{xc}^{PBE} + a\left(E_X^{HF,SR} - E_X^{PBE,SR}\right) \tag{7.21}$$

where the shortranged parts are obtained with a screened Coulomb interaction

$$\frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{r'}|} \to \frac{e^2}{4\pi\epsilon_0|\vec{r}-\vec{r'}|}\left(1 - \mathrm{erf}(w|\vec{r}-\vec{r'}|)\right) \tag{7.22}$$

The parameter w is chosen between 0.11-0.2 a_0^{-1}. The mixing parameter is chosen as $a = \frac{1}{4}$.

We want to replace this description with the exponential screening. The comparison is shown in figure 7.1. The exponential form is more long ranged. A screening length of 3 a_0 seems to be comparable to the HSE parameter $\omega = 0.2 a_0^{-1}$.

7.4 Long-range expansions

When the Coulomb potential is placed on a radial grid, it is important to remove the long-ranged tail, which extends beyond the grid. This is important, in particular if the potential is interpolated.

On wikipedia, $\sum_\sigma = 2$ is used. The result is thus identical

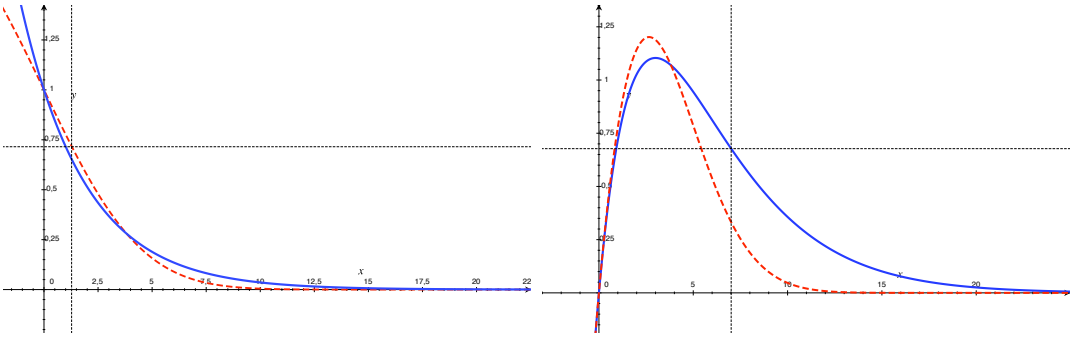


Fig. 7.1: Left: Comparison of the screening $\exp(-\frac{r}{3})$ in the Yukawa potential (solid blue) and that $1-\mathrm{erf}(r/5)$ of the HSE functional (red dashed). Right: potential multiplied with r^2.

7.4.1 Long-range expansion of the potential

Let me start with the potential of an electron density

$$\begin{aligned}
v(\vec{r}) &= \int d^3r'\; w(|\vec{r}-\vec{r'}|)n(\vec{r'}) \\
&= \int d^3r'\; n(\vec{r'})\left[w(|\vec{r}-\vec{R'}|) + (\vec{r'}-\vec{R'})\;\vec{\nabla}_{r'}w(|\vec{r}-\vec{r'}|)\Big|_{\vec{r'}=\vec{R'}} + \ldots\right] \\
&= \int d^3r'\; n(\vec{r'})\left[w(|\vec{r}-\vec{R'}|) \overset{!}{-} (\vec{r'}-\vec{R'})\vec{\nabla}_r w(|\vec{r}-\vec{R'}|) + \ldots\right] \\
&= w(|\vec{r}-\vec{R}|)\underbrace{\left[\int d^3r'\; n(\vec{r'})\right]}_{Q} - \Big(\vec{\nabla}w(|\vec{r}-\vec{R'}|)\Big)\underbrace{\left[\int d^3r'\; n(\vec{r'})(\vec{r'}-\vec{R'})\right]}_{\vec{D}} + \ldots \\
&= \int d^3r'\; \delta(\vec{r'}-\vec{R'})\left[Qw(|\vec{r}-\vec{r'}|) - \vec{D}\vec{\nabla}w(|\vec{r}-\vec{r'}|) + \ldots\right] \\
&= \int d^3r'\; w(|\vec{r}-\vec{r'}|)\left[Q\delta(\vec{r'}-\vec{R'}) - \vec{D}\vec{\nabla}'\delta(\vec{r'}-\vec{R'}) + \ldots\right]
\end{aligned} \tag{7.23}$$

This provides me with the multipole expansion of the potential, as well as a multipole representation of the density.

$$P(\vec{r}) = \sum_R Q\delta(\vec{r}-\vec{R}) - \vec{D}\vec{\nabla}\delta(\vec{r'}-\vec{R}) + \ldots \tag{7.24}$$

The multipole representation of the density is a density that vanishes everywhere except for a point, while it produces the same multipole expansion of the potential as the original density.

The long-ranged potential $v^{lr}(\vec{r})$ is the potential created by the multipole expansion.

$$v^{lr}(\vec{r}) = \int d^3r'\; w(|\vec{r}-\vec{r'}|)P(\vec{r'}) = \Big(Q - \vec{D}\vec{\nabla}\Big)w(|\vec{r}-\vec{R'}|) \tag{7.25}$$

It can be expressed in terms of real spherical harmonics as

$$v^{lr}(\vec{r}) = \left[\sqrt{4\pi}Qw(|\vec{r}-\vec{R'}|)\right]Y_s(\vec{r}-\vec{R'}) + \sum_i\left[\sqrt{\frac{4\pi}{3}}D_i\Big(\partial_r w|_{|\vec{r}-\vec{R'}|}\Big)\right]Y_{p_i}(\vec{r}-\vec{R'}) \tag{7.26}$$

7.4.2 Long-range expansion of the energy

Consider the electrostatic interaction of two multipole expansions

$$
\begin{aligned}
E^{lr} &= \int d^3r \int d^3r'\; P_1(\vec{r}) w(|\vec{r}-\vec{r'}|) P_2(\vec{r'}) \\
&= \int d^3r \left[Q_1 \delta(\vec{r}-\vec{R}_1) - \vec{D}_1 \left(\vec{\nabla}_r \delta(\vec{r}-\vec{R}_1) \right) \right] \\
&\qquad \times \int d^3r'\; w(|\vec{r}-\vec{r'}|) \Big[Q_2 \delta(\vec{r'}-\vec{R}_2) - \vec{D}_2 \vec{\nabla}_{r'} \delta(\vec{r'}-\vec{R}_2) \Big] \\
&= \int d^3r \left[Q_1 \delta(\vec{r}-\vec{R}_1) + \delta(\vec{r}-\vec{R}_1) \vec{D}_1 \vec{\nabla}_r \right] \Big[Q_2 w(|\vec{r}-\vec{R}_2|) - \vec{D}_2 \vec{\nabla}_r w(|\vec{r}-\vec{R}_2|) \Big] \\
&= Q_1 Q_2 w(|\vec{R}_1-\vec{R}_2|) + \vec{D}_1 Q_2 \vec{\nabla}_{R_1} w(|\vec{R}_1-\vec{R}_2|) - Q_1 \vec{D}_2 \vec{\nabla}_{R_1} w(|\vec{R}_1-\vec{R}_2|) \\
&\quad - \Big(\vec{D}_1 \vec{\nabla}_{R_1} \Big) \Big(\vec{D}_2 \vec{\nabla}_{R_1} \Big) w(|\vec{R}_1-\vec{R}_2) \\
&= Q_1 Q_2 w(|\vec{R}_1-\vec{R}_2|) + \Big(\vec{D}_1 Q_2 - Q_1 \vec{D}_2 \Big) \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \frac{\vec{R}_1-\vec{R}_2}{|\vec{R}_1-\vec{R}_2|} \\
&\quad - \Big(\vec{D}_1 \vec{\nabla}_{R_1} \Big) \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} \\
&= Q_1 Q_2 w(|\vec{R}_1-\vec{R}_2|) + \Big(\vec{D}_1 Q_2 - Q_1 \vec{D}_2 \Big) \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \frac{\vec{R}_1-\vec{R}_2}{|\vec{R}_1-\vec{R}_2|} \\
&\quad - \partial_r^2 w \Big|_{|\vec{R}_1-\vec{R}_2|} \frac{\vec{D}_1(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} \frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} - \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \left[\Big(\vec{D}_1 \vec{\nabla}_{R_1} \Big) \frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} \right] \\
&= Q_1 Q_2 w(|\vec{R}_1-\vec{R}_2|) + \Big(\vec{D}_1 Q_2 - Q_1 \vec{D}_2 \Big) \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \frac{\vec{R}_1-\vec{R}_2}{|\vec{R}_1-\vec{R}_2|} \\
&\quad - \partial_r^2 w \Big|_{|\vec{R}_1-\vec{R}_2|} \frac{\vec{D}_1(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} \frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} \\
&\quad - \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \left[\frac{\vec{D}_1 \vec{D}_2}{|\vec{R}_1-\vec{R}_2|} - \frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|^2} \frac{\vec{D}_1(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} \right] \\
&= Q_1 Q_2 w(|\vec{R}_1-\vec{R}_2|) + \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \left[\Big(\vec{D}_1 Q_2 - Q_1 \vec{D}_2 \Big) \frac{\vec{R}_1-\vec{R}_2}{|\vec{R}_1-\vec{R}_2|} - \frac{\vec{D}_1 \vec{D}_2}{|\vec{R}_1-\vec{R}_2|} \right] \\
&\quad + \left[-\partial_r^2 w \Big|_{|\vec{R}_1-\vec{R}_2|} + \frac{1}{|\vec{R}_1-\vec{R}_2|} \partial_r w \Big|_{|\vec{R}_1-\vec{R}_2|} \right] \frac{\vec{D}_1(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|} \frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|}
\end{aligned}
\tag{7.27}
$$

For the screened potential, we obtain:

$$
\begin{aligned}
E^{lr} &= \frac{e^2}{4\pi\epsilon_0}\mathrm{e}^{-\lambda|\vec{R}_1-\vec{R}_2|}\Bigg\{\frac{Q_1Q_2}{|\vec{R}_1-\vec{R}_2|}-\frac{1+\lambda|\vec{R}_1-\vec{R}_2|}{|\vec{R}_1-\vec{R}_2|^2}\left[\left(\vec{D}_1Q_2-Q_1\vec{D}_2\right)\frac{\vec{R}_1-\vec{R}_2}{|\vec{R}_1-\vec{R}_2|}-\frac{\vec{D}_1\vec{D}_2}{|\vec{R}_1-\vec{R}_2|}\right]\\
&\quad+\left[-2\frac{1+\lambda|\vec{R}_1-\vec{R}_2|+\frac{1}{2}\lambda^2|\vec{R}_1-\vec{R}_2|^2}{|\vec{R}_1-\vec{R}_2|^3}-\frac{1+\lambda|\vec{R}_1-\vec{R}_2|}{|\vec{R}_1-\vec{R}_2|^3}\right]\frac{\vec{D}_1(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|}\frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|}\Bigg\}\\
&= \frac{e^2}{4\pi\epsilon_0}\mathrm{e}^{-\lambda|\vec{R}_1-\vec{R}_2|}\Bigg\{\frac{Q_1Q_2}{|\vec{R}_1-\vec{R}_2|}-\frac{1+\lambda|\vec{R}_1-\vec{R}_2|}{|\vec{R}_1-\vec{R}_2|^2}\left[\left(\vec{D}_1Q_2-Q_1\vec{D}_2\right)\frac{\vec{R}_1-\vec{R}_2}{|\vec{R}_1-\vec{R}_2|}-\frac{\vec{D}_1\vec{D}_2}{|\vec{R}_1-\vec{R}_2|}\right]\\
&\quad-\frac{3\Big(1+\lambda|\vec{R}_1-\vec{R}_2|\Big)+\lambda^2|\vec{R}_1-\vec{R}_2|^2}{|\vec{R}_1-\vec{R}_2|^3}\frac{\vec{D}_1(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|}\frac{\vec{D}_2(\vec{R}_1-\vec{R}_2)}{|\vec{R}_1-\vec{R}_2|}\Bigg\}
\end{aligned}
\tag{7.28}
$$

With $\vec{R}_2=\vec{R}_1+\Delta\vec{e}_z$, we obtain

$$
\begin{aligned}
E^{lr} = \frac{e^2}{4\pi\epsilon_0}\mathrm{e}^{-\lambda\Delta}\Bigg\{&\frac{Q_1Q_2}{\Delta}+\frac{1+\lambda\Delta}{\Delta^2}\left[\left(\vec{e}_z\vec{D}_1Q_2-Q_1\vec{e}_z\vec{D}_2\right)+\frac{\vec{D}_1\vec{D}_2}{\Delta}\right]\\
&-\frac{3\Big(1+\lambda\Delta\Big)+\lambda^2\Delta^2}{\Delta^3}\Big(\vec{e}_z\vec{D}_1\Big)\Big(\vec{e}_z\vec{D}_2\Big)\Bigg\}
\end{aligned}
\tag{7.29}
$$

The potential of atom two and its gradient at $\vec{R}_1$ is obtained as

$$
\begin{aligned}
V(\vec{R}_1) &= \frac{\partial E^{lr}}{\partial Q_1}\\
\vec{\nabla}_{R_1}V(\vec{R}_1) &= \vec{\nabla}_{D_1}E^{lr}
\end{aligned}
\tag{7.30}
$$

7.4.3 Division of U-tensor into short- and long-ranged parts

In order to perform the integrations efficiently, we need to remove the long-ranged tails from the potential.

Let me make the following definitions.

$$
\begin{aligned}
n_{\alpha,\beta}(\vec{r}) &= \chi^*_\alpha(\vec{r})\chi_\beta(\vec{r})\\
n_{\gamma,\delta}(\vec{r}) &= \chi^*_\gamma(\vec{r})\chi_\delta(\vec{r})\\
v_{\alpha,\beta}(\vec{r}) &= \int d^3r'\; w(|\vec{r}-\vec{r'}|)n_{\alpha,\beta}(\vec{r'})\\
v_{\gamma,\delta}(\vec{r}) &= \int d^3r'\; w(|\vec{r}-\vec{r'}|)n_{\gamma,\delta}(\vec{r'})
\end{aligned}
\tag{7.31}
$$

Let me furthermore introduce the multipole representation of the density $n_{\alpha,\beta}(\vec{r})$ and $n_{\gamma,\delta}(\vec{r})$

$$
\begin{aligned}
p_{\alpha,\beta}(\vec{r}) &= Q_{\alpha,\beta}\delta(\vec{r}-\vec{R})-\vec{D}_{\alpha,\beta}\vec{\nabla}\delta(\vec{r}-\vec{R})\\
p_{\gamma,\delta}(\vec{r}) &= Q_{\gamma,\delta}\delta(\vec{r}-\vec{R}')-\vec{D}_{\gamma,\delta}\vec{\nabla}\delta(\vec{r}-\vec{R}')
\end{aligned}
\tag{7.32}
$$

The multipole representation has the same multipoles as the original density, but it is non-zero only at a point.

Then, the U-tensor matrix elements are

$$\begin{aligned}
U_{\alpha,\beta,\gamma,\delta} &= \int d^3r \int d^3r' \; n_{\alpha,\beta}(\vec{r}) w(|\vec{r}-\vec{r'}|) n_{\gamma,\delta}(\vec{r'}) \\
&= \int d^3r' \; v_{\alpha,\beta}(\vec{r'}) n_{\gamma,\delta}(\vec{r'}) \\
&= \int d^3r' \left[v_{\alpha,\beta}(\vec{r'}) - \int d^3r \; p_{\alpha,\beta}(\vec{r}) w(|\vec{r}-\vec{r'}|) \right] n_{\gamma,\delta}(\vec{r'}) \\
&\quad + \int d^3r \; p_{\alpha,\beta}(\vec{r}) v_{\gamma,\delta}(\vec{r}) \\
&= \int d^3r' \left[v_{\alpha,\beta}(\vec{r'}) - \int d^3r \; p_{\alpha,\beta}(\vec{r}) w(|\vec{r}-\vec{r'}|) \right] n_{\gamma,\delta}(\vec{r'}) \\
&\quad + \int d^3r \; p_{\alpha,\beta}(\vec{r}) \left[v_{\gamma,\delta}(\vec{r}) - \int d^3r' \; w(|\vec{r}-\vec{r'}|) p_{\gamma,\delta}(\vec{r'}) \right] \\
&\quad + \int d^3r \int d^3r' \; p_{\alpha,\beta}(\vec{r}) w(|\vec{r}-\vec{r'}|) p_{\gamma,\delta}(\vec{r'}) \\
&= \int d^3r' \; v^{sr}_{\alpha,\beta}(\vec{r'}) n_{\gamma,\delta}(\vec{r'}) + \int d^3r \; p_{\alpha,\beta}(\vec{r}) v^{sr}_{\gamma,\delta}(\vec{r}) + U^{lr}_{\alpha,\beta,\gamma,\delta}
\end{aligned} \tag{7.33}$$

OFFSITE NDDO U-TENSOR IN TERMS OF SHORT AND LONG-RANGED CONTRIBUTIONS

The following division is exact, even if the multipole expansion of the point representation $p(\vec{r})$ differs from that of the corresponding densitis $n(\vec{r})$. It is useful, whenm $n_{\alpha,\beta}$ and $n_{\gamma,\delta}$ have rapidly converging multipole expansions, which is well represented by the correasponding point representation.

$$U_{\alpha,\beta,\gamma,\delta} = \int d^3r' \; v^{sr}_{\alpha,\beta}(\vec{r'}) n_{\gamma,\delta}(\vec{r'}) + \int d^3r \; p_{\alpha,\beta}(\vec{r}) v^{sr}_{\gamma,\delta}(\vec{r}) + U^{lr}_{\alpha,\beta,\gamma,\delta} \tag{7.34}$$

with the short-ranged potentials

$$\begin{aligned}
v^{sr}_{\alpha,\beta}(\vec{r'}) &\stackrel{\text{def}}{=} v_{\alpha,\beta}(\vec{r'}) - \int d^3r \; w(|\vec{r'}-\vec{r}|) p_{\alpha,\beta}(\vec{r'}) \\
v^{sr}_{\gamma,\delta}(\vec{r}) &\stackrel{\text{def}}{=} v_{\gamma,\delta}(\vec{r}) - \int d^3r \; w(|\vec{r}-\vec{r'}|) p_{\gamma,\delta}(\vec{r})
\end{aligned} \tag{7.35}$$

and the long-ranged part of the U-tensor

$$U^{lr}_{\alpha,\beta,\gamma,\delta} \stackrel{\text{def}}{=} \int d^3r \int d^3r' \; p_{\alpha,\beta}(\vec{r}) w(\vec{r},\vec{r'}) p_{\gamma,\delta}(\vec{r'}) \tag{7.36}$$

7.5 Expansion of the density in angular momenta

In `simplelmto_onecenterqln`, we evaluate the quantities $q_{s,\alpha,\beta}$ and $q_{p,\alpha,\beta}$, which can be used to evaluate monopoles and dipoles. We divide an orbital into radial and angularpart, as

$$\chi_\alpha(\vec{r}) = f_\alpha(|\vec{r}-\vec{R}_\alpha|)Y_{L_\alpha}(\vec{r}-\vec{R}_\alpha) \tag{7.37}$$

Thus, we obtain the densities of two orbitals centered at the same site $\vec{R} = \vec{R}_\alpha = \vec{R}_\beta$

$$\begin{aligned} n_{\alpha,\beta}(\vec{r}) &= \chi^*_\alpha(\vec{r})\chi_\beta(\vec{r}) \\ &= f_\alpha(|\vec{r}-\vec{R}|)f_\beta(|\vec{r}-\vec{R}|)Y^*_{L_\alpha}(\vec{r}-\vec{R})Y_{L_\beta}(\vec{r}-\vec{R}) \\ &= \sum_L C_{L,L_\alpha,L_\beta} f_\alpha(|\vec{r}-\vec{R}|)f_\beta(|\vec{r}-\vec{R}|)Y_L(\vec{r}-\vec{R}) \end{aligned} \tag{7.38}$$

with the Gaunt coefficients $C_{L,L',L''} = \int d\Omega\, Y_L(\vec{r})Y_{L'}(\vec{r})Y_{L''}(\vec{r})$

$$\begin{aligned} Q_{\alpha,\beta} &= \int d^3r\, \chi^*_\alpha(\vec{r})\chi_\beta(\vec{r}) = \int d^3r\, \chi^*_\alpha(\vec{r})\chi_\beta(\vec{r}) \underbrace{\sqrt{4\pi}|\vec{r}-\vec{R}|^0 Y_s(\vec{r}-\vec{R})}_{=1} \\ &= C_{s,L_\alpha,L_\beta} \underbrace{\sqrt{4\pi}\int_0^\infty dr\, r^2 f_\alpha(r)f_\beta(r)}_{q_{s,\alpha,\beta}} \end{aligned} \tag{7.39}$$

$$\begin{aligned} D_{j,\alpha,\beta} &= \int d^3r\, \chi^*_\alpha(\vec{r})\chi_\beta(\vec{r}))(r_j - R_j) = \int d^3r\, \chi^*_\alpha(\vec{r})\chi_\beta(\vec{r})|\vec{r}-\vec{R}|^1 \underbrace{\sqrt{\frac{4\pi}{3}}Y_{p_j}(\vec{r}-\vec{R})}_{r_j} \\ &= C_{p_j,L_\alpha,L_\beta} \underbrace{\sqrt{\frac{4\pi}{3}}\int_0^\infty dr\, r^3 f_\alpha(r)f_\beta(r)}_{q_{p,\alpha,\beta}} \end{aligned} \tag{7.40}$$

The variables $q_{s,\alpha,\beta}$ and $q_{p,\alpha,\beta}$ are stored as `QLN(1,LN1,LN2)` and `QLN(2,LN1,LN2)`, respectively.

Short-ranged potentials

$$
\begin{aligned}
v^{sr}_{\gamma,\delta}(\vec{r}) &= \sum_L v^{sr}_{L,\gamma,\delta}(|\vec{r}-\vec{R}_2|)Y_L(\vec{r}-\vec{R}_2) \\
&= \sum_L C_{L_\gamma,L_\delta,L}\int d^3r'\; w(|\vec{r}-\vec{r'}|)f_\gamma(|\vec{r'}-\vec{R}_2|)f_\gamma(|\vec{r'}-\vec{R}_2|)Y_L(\vec{r'}-\vec{R}_2) \\
&\quad - \underbrace{C_{s,L_\gamma,L_\delta}q_{s,\gamma,\delta}}_{Q_{\gamma,\delta}}\sqrt{4\pi}w(|\vec{r}-\vec{R}_2|)Y_s(\vec{r}-\vec{R}_2) \\
&\quad - \sum_j \underbrace{C_{p_j,L_\gamma,L_\delta}q_{p,\gamma,\delta}}_{D_{j,\gamma,\delta}}\sqrt{\frac{4\pi}{3}}\Big(\partial_r w|_{|\vec{r}-\vec{R}_2|}\Big)Y_{p_j}(\vec{r}-\vec{R}_2) \\
&= \sum_L C_{L_\gamma,L_\delta,L}\Bigg\{\int d^3r'\; w_\ell(|\vec{r}-\vec{r'}|)f_\gamma(|\vec{r'}-\vec{R}_2|)f_\gamma(|\vec{r'}-\vec{R}_2|) \\
&\quad - \Bigg[\delta_{L,s}q_{s,\gamma,\delta}\sqrt{4\pi}w(|\vec{r}-\vec{R}_2|) + \sum_j \delta_{L,p_j}q_{p,\gamma,\delta}\sqrt{\frac{4\pi}{3}}\Big(\partial_r w|_{|\vec{r}-\vec{R}_2|}\Big)\Bigg]\Bigg\}Y_L(\vec{r'}-\vec{R}_2) \\
&= \sum_L C_{L_\gamma,L_\delta,L}\Bigg\{\int d^3r'\; w_\ell(|\vec{r}-\vec{r'}|)f_\gamma(|\vec{r'}-\vec{R}_2|)f_\gamma(|\vec{r'}-\vec{R}_2|) \\
&\quad - \Bigg[\delta_{\ell,0}q_{s,\gamma,\delta}\sqrt{4\pi}w(|\vec{r}-\vec{R}_2|) + \delta_{\ell,1}q_{p,\gamma,\delta}\sqrt{\frac{4\pi}{3}}\Big(\partial_r w|_{|\vec{r}-\vec{R}_2|}\Big)\Bigg]\Bigg\}Y_L(\vec{r'}-\vec{R}_2) \quad (7.41)
\end{aligned}
$$

This expression is used to construct the short-ranged potentials.

Correction

The middle term in Eq. 7.34, which I denote as X, is written as

$$
\begin{aligned}
X &\stackrel{\text{def}}{=} \int d^3r\; p_{\alpha,\beta}(\vec{r}) v^{sr}_{\gamma,\delta}(\vec{r}) \\
&= \int d^3r \left[Q_{\alpha,\beta}\delta(\vec{r}-\vec{R}_1) - \vec{D}_{\alpha,\beta}\vec{\nabla}\delta(\vec{r}-\vec{R}_1) \right] v^{sr}_{\gamma,\delta}(\vec{r}) \\
&= \int d^3r\; \delta(\vec{r}-\vec{R}_1) \left[Q_{\alpha,\beta} + \vec{D}_{\alpha,\beta}\vec{\nabla} \right] v^{sr}_{\gamma,\delta}(\vec{r}) \\
&= \left[Q_{\alpha,\beta} + \vec{D}_{\alpha,\beta}\vec{\nabla}_{R_1} \right] v^{sr}_{\gamma,\delta}(\vec{R}_1) \\
&= \underbrace{C_{L_\alpha,L_\beta,s} q_{s,\alpha,\beta}}_{Q_{\alpha,\beta}} + \sum_{j\in\{x,y,z\}} \underbrace{C_{L_\alpha,L_\beta,p_j} q_{p,\alpha,\beta}}_{D_{j,\alpha,\beta}} \frac{\partial}{\partial R_{1,j}} \Bigg] \\
&\quad \times \sum_L v^{sr}_{L,\gamma,\delta}(|\vec{R}_1-\vec{R}_2|) Y_L(\vec{R}_1-\vec{R}_2) \\
&= \sum_L C_{L_\alpha,L_\beta,s} q_{s,\alpha,\beta} v^{sr}_{L,\gamma,\delta}(|\vec{R}_1-\vec{R}_2|) Y_L(\vec{R}_1-\vec{R}_2) \\
&+ \sum_L \sum_{j\in\{x,y,z\}} C_{L_\alpha,L_\beta,p_j} q_{p,\alpha,\beta} \left(\partial_r v^{sr}_{L,\gamma,\delta}\big|_{|\vec{R}_1-\vec{R}_2|} \right) \frac{R_{1,j}-R_{2,j}}{|\vec{R}_1-\vec{R}_2|} Y_L(\vec{R}_1-\vec{R}_2) \\
&+ \sum_L \sum_{j\in\{x,y,z\}} C_{L_\alpha,L_\beta,p_j} q_{p,\alpha,\beta} v^{sr}_{L,\gamma,\delta}(|\vec{R}_1-\vec{R}_2|) \\
&\quad \times \underbrace{\sqrt{\frac{4\pi}{3}} \sum_{L'} C_{j,L,L'} \frac{1}{|\vec{R}_1-\vec{R}_2|} \left[-\ell + (2\ell+1)\delta_{\ell',\ell-1} \right] Y_{L'}(\vec{R}_1-\vec{R}_2)}_{\frac{\partial}{\partial R_{1,j}} Y_L(\vec{R}_1-\vec{R}_2)}
\end{aligned}
\tag{7.42}
$$

We used the expression for the gradient of spherical harmonics (Section 49.10 “Gradients of spherical harmonics” of Methods)

$$
\vec{\nabla}_j Y_L(\vec{r}) = \sqrt{\frac{4\pi}{3}} \sum_{L'} C_{j,L,L'} \frac{1}{|\vec{r}|} \left[-\ell + (2\ell+1)\delta_{\ell',\ell-1} \right] Y_{L'}(\vec{r}) \tag{7.43}
$$

In the following step I use $\vec{R}_1 - \vec{R}_2 = -\vec{e}_z|\vec{R}_1 - \vec{R}_2|$.

$$
\begin{aligned}
X = & \sum_L C_{L_\alpha,L_\beta,s} q_{s,\alpha,\beta} v^{sr}_{L,\gamma,\delta}(|\vec{R}_1 - \vec{R}_2|) Y_L(\vec{R}_1 - \vec{R}_2) \\
& + \sum_L \sum_{j\in\{x,y,z\}} C_{L_\alpha,L_\beta,p_j} q_{p,\alpha,\beta} \left(\partial_r v^{sr}_{L,\gamma,\delta}\Big|_{|\vec{R}_1-\vec{R}_2|} \right) \underbrace{\frac{R_{1,j} - R_{2,j}}{|\vec{R}_1 - \vec{R}_2|}}_{-\delta_{j,z}} \underbrace{Y_L(\vec{R}_1 - \vec{R}_2)}_{(-1)^\ell Y_L(+\vec{e}_z|\vec{R}_1-\vec{R}_2|)\delta_{m,0}} \\
& + \sum_L \sum_{j\in\{x,y,z\}} C_{L_\alpha,L_\beta,p_j} q_{p,\alpha,\beta} v^{sr}_{L,\gamma,\delta}(|\vec{R}_1 - \vec{R}_2|) \\
& \quad \times \sqrt{\frac{4\pi}{3}} \sum_{L'} C_{j,L,L'} \frac{1}{|\vec{R}_1 - \vec{R}_2|} \left[-\ell + (2\ell+1)\delta_{\ell',\ell-1}\right] \underbrace{Y_{L'}(\vec{R}_1 - \vec{R}_2)}_{\delta_{m',0}(-1)^{\ell'} Y_{L'}(+\vec{e}_z|\vec{R}_1-\vec{R}_2|)} \\
= & \sum_\ell C_{L_\alpha,L_\beta,s} q_{s,\alpha,\beta} (-1)^\ell Y_{\ell,0}(+e_z|\vec{R}_1 - \vec{R}_2|) v^{sr}_{(\ell,0),\gamma,\delta}(|\vec{R}_1 - \vec{R}_2|) \\
& + \sum_\ell C_{L_\alpha,L_\beta,p_z} q_{p,\alpha,\beta} \left(\partial_r v^{sr}_{(\ell,0),\gamma,\delta}\Big|_{|\vec{R}_1-\vec{R}_2|} \right) (-1)^{\ell+1} Y_{(\ell,0)}(+\vec{e}_z|\vec{R}_1 - \vec{R}_2|) \\
& + \sum_L \sum_{j\in\{x,y,z\}} C_{L_\alpha,L_\beta,p_j} q_{p,\alpha,\beta} \frac{v^{sr}_{L,\gamma,\delta}(|\vec{R}_1 - \vec{R}_2|)}{|\vec{R}_1 - \vec{R}_2|} \\
& \quad \times \sqrt{\frac{4\pi}{3}} \sum_{\ell'} C_{p_j,L,(\ell',0)} \left[-\ell + (2\ell+1)\delta_{\ell',\ell-1}\right] (-1)^{\ell'} Y_{(\ell',0)}(+\vec{e}_z|\vec{R}_1 - \vec{R}_2|)
\end{aligned}
\tag{7.44}
$$

Now we exploit that $C_{p_j,L,(\ell',0)}$ vanishes except when $m_{p_j} = m_L$ and $\ell_L - \ell' = \pm 1$.

$$
\begin{aligned}
X = & \sum_\ell C_{L_\alpha,L_\beta,s} q_{s,\alpha,\beta} v^{sr}_{(\ell,0),\gamma,\delta}(|\vec{R}_1 - \vec{R}_2|) (-1)^\ell Y_{\ell,0}(+e_z|\vec{R}_1 - \vec{R}_2|) \\
& + \sum_\ell C_{L_\alpha,L_\beta,p_z} q_{p,\alpha,\beta} \left(\partial_r v^{sr}_{(\ell,0),\gamma,\delta}\Big|_{|\vec{R}_1-\vec{R}_2|} \right) (-1)^{\ell+1} Y_{(\ell,0)}(+\vec{e}_z|\vec{R}_1 - \vec{R}_2|) \\
& + \sum_\ell \sum_{j\in\{x,y,z\}} C_{L_\alpha,L_\beta,p_j} q_{p,\alpha,\beta} \frac{v^{sr}_{(\ell,m_j),\gamma,\delta}(|\vec{R}_1 - \vec{R}_2|)}{|\vec{R}_1 - \vec{R}_2|} \sqrt{\frac{4\pi}{3}} \\
& \quad \times \Big\{ C_{p_j,(\ell,m_j),(\ell-1,0)} \left[\ell + 1\right] (-1)^{\ell-1} Y_{(\ell-1,0)}(+\vec{e}_z|\vec{R}_1 - \vec{R}_2|) \\
& \quad + C_{p_j,(\ell,m_j),(\ell+1,0)} \left[-\ell\right] (-1)^{\ell+1} Y_{(\ell+1,0)}(+\vec{e}_z|\vec{R}_1 - \vec{R}_2|) \Big\}
\end{aligned}
\tag{7.45}
$$

7.5.1 Tabulating data

$$
\begin{aligned}
U_{\alpha,\beta,\gamma,\delta} &= \int d^3r \int d^3r'\; n_{\alpha,\gamma}(\vec{r}) w(\vec{r}-\vec{r'}) n_{\beta,\delta}(\vec{r}) \\
&= \int d^3r\; n_{\alpha,\gamma}(\vec{r}) v(\vec{r}) \\
&= \sum_{L,L'} \sum_{L_\alpha,L_\gamma} \sum_{L_\beta,L_\delta} \delta_{m,m'} C_{L,L_\alpha,L_\gamma} C_{L',L_\beta,L_\delta} \int dr\; f_\alpha(\vec{r}-\vec{R}) f_\gamma(\vec{r}-\vec{R}) Y_L(\vec{r}-\vec{R}) \\
&\quad \times \underbrace{\int dr'\; w(\vec{r}-\vec{r'}) f_\beta(\vec{r'}-\vec{R'}) f_\delta(\vec{r'}-\vec{R'}) Y_{L'}(\vec{r'}-\vec{R'})}_{v_{\ell',\beta,\delta}(|\vec{r}-\vec{R'}|) Y_{L'}(\vec{r'}-\vec{R'})}
\end{aligned}
\tag{7.46}
$$

The integral is performed in `simplelmto_twocenter`.

$$
\begin{aligned}
I &= \int_{-\infty}^{\infty} dz \int_0^{2\pi} d\phi \int_0^{\infty} d\rho\; F(|\vec{r}|) Y_{\ell,m}(\vec{r}) G(|\vec{r}-d\vec{e}_z|) Y_{\ell',m'}(\vec{r}-d\vec{e}_z) \\
&= 2\pi\delta_{m,m'} \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} \sqrt{\frac{2\ell'+1}{4\pi}\frac{(\ell'-m)!}{(\ell'+m)!}} \\
&\quad \times \int_{-\infty}^{\infty} dz \int_0^{\infty} d\rho\; P_\ell^m\left(\frac{z}{\sqrt{\rho^2+z^2}}\right) P_{\ell'}^m\left(\frac{z-d}{\sqrt{\rho^2+(z-d)^2}}\right) F(|\vec{r}|) G(|\vec{r}-d\vec{e}_z|)
\end{aligned}
\tag{7.47}
$$

The z-axis is chosen along the interatomic distance vector. Thus the integral gives a non-zero result if the magnetic quantum numbers have the same value. ρ is the distance from the bond axis.

The Legendre polynomials are, with $m > 0$,

$$
\begin{aligned}
P_\ell^m(z) &= \frac{(-1)^m}{\ell! 2^\ell} (\sqrt{1-x^2})^m \left(\frac{d}{dx}\right)^{\ell+m} (1-x^2)^\ell \\
P_\ell^{-m}(z) &= (-1)^m \frac{(\ell-m)!}{\ell+m)!} P_\ell^m(x)
\end{aligned}
\tag{7.48}
$$

The method is taken from Genz and Malik[**?**], who use a variant of the method of van Dooren and de Ridder[**?**].

For comparison, see also the work of Romanowski and Jalbout. [**? ? ? ?**]

The radial functions of the local orbitals do not depend on the magnetic quantum number. Hence, the integral depends on $(\ell, \ell', m, \ell_\alpha, n_\alpha, \ell_\gamma, n_\gamma, \ell_\beta, n_\beta, \ell_\delta, n_\delta)$ with the same m. These integrals are calculated on a distance grid and then fitted by a set of interpolating exponentials.

The U-tensor is

$$
\begin{aligned}
U_{\alpha,\beta,\gamma,\delta} = \sum_{\ell,\ell'} \sum_m \sum_{\ell_\alpha,\ell_\gamma} \sum_{\ell_\beta,\ell_\delta} \Bigg(\sum_{m_\alpha,m_\gamma} \sum_{m_\beta,m_\delta} C_{\ell,m,L_\alpha,L_\gamma} C_{\ell',m,L_\beta,L_\delta} \Bigg) \\
\times I_{\ell,\ell',m,\ell_\alpha,n_\alpha,\ell_\gamma,n_\gamma,\ell_\beta,n_\beta,\ell_\delta,n_\delta} \Big([n_{\ell,\alpha,\gamma}], [v_{\ell',\beta,\delta}], d \Big)
\end{aligned}
\tag{7.49}
$$

7.5.2 Integrals with the point density

Let me consider the two-center integral Eq. 7.47, with the density $n_{\alpha,\beta}$ replaced by its point-density representation.

$$\begin{aligned} n_{\alpha,\beta}(\vec{R}+\vec{r}) &= \sum_L C_{L,L_\alpha,L_\beta} f_\alpha(|\vec{r}|) f_\beta(|\vec{r}|) Y_L(\vec{r}) \\ \rightarrow p_{\alpha,\beta}(\vec{R}+\vec{r}) &= C_{s,L_\alpha,L_\beta} q_{s,\alpha,\beta}\delta(\vec{r}) - \sum_j C_{p_j,L_\alpha,L_\beta} q_{p,\alpha,\beta}\partial_{r_j}\delta(\vec{r}) \end{aligned} \tag{7.50}$$

This implies that we need to replace

$$\begin{aligned} n_{\ell,\alpha,\beta}(\vec{R}+\vec{r}) &= f_\alpha(|\vec{r}|) f_\beta(|\vec{r}|) \\ \rightarrow p_{(\ell,m),\alpha,\beta}(\vec{R}+\vec{r}) &= \delta_{(\ell,m),s} q_{s,\alpha,\beta}\delta(\vec{r}) + \sum_j \delta_{(\ell,m),p_j} q_{p,\alpha,\beta}\delta(\vec{r})\partial_{r_j} \\ &= \delta(\vec{r})\left[\delta_{(\ell,m),s} q_{s,\alpha,\beta} + \sum_j \delta_{(\ell,m),p_j} q_{p,\alpha,\beta}\partial_{r_j}\right] \end{aligned} \tag{7.51}$$

The resulting integral is

$$
\begin{aligned}
& I_{\ell,\ell',m,\ell_\alpha,n_\alpha,\ell_\gamma,n_\gamma,\ell_\beta,n_\beta,\ell_\delta,n_\delta} \\
\overset{\text{Eq. 7.47}}{=} & \int d^3r \left(\delta_{(\ell,m),s} q_{s,\alpha,\beta} \delta(\vec{r}) - \sum_j \delta_{(\ell,m),p_j} q_{p,\alpha,\beta} \vec{\nabla} \delta(\vec{r}) \right) v_{(\ell',m),\gamma,\delta}(\vec{r} - (\vec{R}' - \vec{R})) Y_{\ell',m}(\vec{r} - (\vec{R}' - \vec{R})) \\
= & \; \delta_{(\ell,m),s} q_{s,\alpha,\beta} \Big(v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') \Big) Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \; \delta_{(\ell,m),p_z} q_{p,\alpha,\beta} \Big(\partial_r v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') \Big) Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \sum_{p_j \in p_x,p_y,p_z} \delta_{(\ell,m),p_j} q_{p,\alpha,\beta} \Big(v_{(\ell',m),\gamma,\delta}(\vec{R} - \vec{R}') \Big) \\
& \times \underbrace{\sqrt{\frac{4\pi}{3}} \frac{1}{|\vec{R} - \vec{R}'|} \sum_{L''} C_{p_j,(\ell',m),L''} \Big(-\ell' + (2\ell'+1)\delta_{l'',l'-1} \Big) Y_{L''}(\vec{R} - \vec{R}')}_{\vec{\nabla}_j Y_{\ell',m}(\vec{R} - \vec{R}'))\text{; seeEq. 7.53}} \\
= & \; \delta_{(\ell,m),s} \frac{q_{s,\alpha,\beta}}{\sqrt{4\pi}} v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \; \delta_{(\ell,m),p_z} q_{p,\alpha,\beta} \Big(\partial_r v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') \Big) Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \sum_{p_j \in p_x,p_y,p_z} \delta_{(\ell,m),p_j} \sqrt{\frac{4\pi}{3}} q_{p,\alpha,\beta} \frac{v_{(\ell',m),\gamma,\delta}(\vec{R} - \vec{R}')}{|\vec{R} - \vec{R}'|} \\
& \times \underbrace{\sum_{\ell''} C_{p_j,(\ell',m),(\ell'',0)} \Big(-\ell' + (2\ell'+1)\delta_{l'',l'-1} \Big) Y_{\ell'',0}(\vec{R} - \vec{R}')}_{-\ell' C_{p_j,(\ell',m),(\ell'+1,0)} Y_{\ell'+1,0}(\vec{R} - \vec{R}') + C_{p_j,(\ell',m),(\ell'-1,0)} (\ell'+1) Y_{\ell'-1,0}(\vec{R} - \vec{R}')} \\
= & \; \delta_{(\ell,m),s} \frac{q_{s,\alpha,\beta}}{\sqrt{4\pi}} v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \; \delta_{(\ell,m),p_z} q_{p,\alpha,\beta} \Big(\partial_r v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') \Big) Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \sum_{m'} \delta_{(\ell,m),(1,m')} \sqrt{\frac{4\pi}{3}} q_{p,\alpha,\beta} \frac{v_{(\ell',m),\gamma,\delta}(\vec{R} - \vec{R}')}{|\vec{R} - \vec{R}'|} \\
& \times \Big[-\ell' C_{(1,m'),(\ell',m),(\ell'+1,0)} Y_{\ell'+1,0}(\vec{R} - \vec{R}') + C_{(1,m'),(\ell',m),(\ell'-1,0)} (\ell'+1) Y_{\ell'-1,0}(\vec{R} - \vec{R}') \Big] \\
= & \; \delta_{(\ell,m),s} \frac{q_{s,\alpha,\beta}}{\sqrt{4\pi}} v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \; \delta_{(\ell,m),p_z} q_{p,\alpha,\beta} \Big(\partial_r v_{(\ell',0),\gamma,\delta}(\vec{R} - \vec{R}') \Big) Y_{\ell',0}(\vec{R} - \vec{R}') \\
+ & \; \delta_{\ell,1} \sqrt{\frac{4\pi}{3}} q_{p,\alpha,\beta} \frac{v_{(\ell',m),\gamma,\delta}(\vec{R} - \vec{R}')}{|\vec{R} - \vec{R}'|} \\
& \times \Big[-\ell' C_{(1,m),(\ell',m),(\ell'+1,0)} Y_{\ell'+1,0}(\vec{R} - \vec{R}') + C_{(1,m),(\ell',m),(\ell'-1,0)} (\ell'+1) Y_{\ell'-1,0}(\vec{R} - \vec{R}') \Big]
\end{aligned}
\tag{7.52}
$$

(Section 49.10 “Gradients of spherical harmonics” of Methods)

$$\vec{\nabla}_j Y_L(\vec{r}) = \sqrt{\frac{4\pi}{3}} \sum_{L'} C_{j,L,L'} \frac{1}{|\vec{r}|} \left[-\ell + (2\ell+1)\delta_{\ell',\ell-1}\right] Y_{L'}(\vec{r}) \tag{7.53}$$

7.5.3 Tests

- calculate U^{lr} as function of distance, once with the routine `MONOANDDIPOLE` and once with the code in `SIMPLELMTO_OFFSITEX22SETUP`, which is embedded in the routine.
- check that long range potentials and numercal potentials agree for long distances. Then, replace the potentials by the long range part.
- The term X (“correction”) gives the same result as U^{lr}.
- the two-center term agrees with U^{lr} in a certain distance range.

During the tests all contributions to the density and the potential with $\ell, \ell' > 0$ have been set to zero.

7.5.4 Complete long-range expansion

We use

$$\begin{aligned}
Q_{\alpha,\beta} &\overset{\text{Eq. 7.39}}{=} C_{s,L_\alpha,L_\beta} q_{s,\alpha,\beta} \\
D_{j,\alpha,\beta} &\overset{\text{Eq. 7.40}}{=} C_{p_j,L_\alpha,L_\beta} q_{p,\alpha,\beta} \\
n_{\alpha,\beta} &= \sum_L n_{L,\alpha,\beta}(|\vec{r}-\vec{R}|) Y_L(\vec{r}-\vec{R}) \\
n_{L,\alpha,\beta}(\vec{r}) &= f_\alpha(|\vec{r}-\vec{R}|) f_\beta(|\vec{r}-\vec{R}|) C_{L,L_\alpha,L_\beta} \\
n_{\gamma,\delta} &= \sum_L n_{L,\alpha,\beta}(|\vec{r}-\vec{R}|) Y_L(\vec{r}-\vec{R}) \\
n_{L,\alpha,\beta}(\vec{r}) &= f_\alpha(|\vec{r}-\vec{R}|) f_\beta(|\vec{r}-\vec{R}|) C_{L,L_\alpha,L_\beta}
\end{aligned} \tag{7.54}$$

$$\begin{aligned}
v^{sr}_{\gamma,\delta}(\vec{r}) &= \int d^3r'\; w(\vec{r}-\vec{r}') \left[\chi_\gamma(\vec{r}')\chi_\delta(\vec{r}') - Q_{\gamma,\delta}\delta(\vec{r}'-\vec{R}') + D_{\gamma,\delta}\vec{\nabla}'\delta(\vec{r}'-\vec{R}')\right] \\
&= \int d^3r'\; w(\vec{r}-\vec{r}') f_\gamma(|\vec{r}'-\vec{R}'|) f_\delta(|\vec{r}'-\vec{R}'|) \sum_L C_{L_\gamma,L_\delta,L} Y_L(\vec{r}'-\vec{R}') \\
&\quad - w(\vec{r}-\vec{R}') C_{s,L_\gamma,L_\delta} q_{s,\gamma,\delta} - \sum_{j=1}^{3} C_{p_j,L_\gamma,L_\delta,L} q_{p,\gamma,\delta} \vec{\nabla}_j w(\vec{r}-\vec{R}') \\
&= \sum_L C_{L_\gamma,L_\delta,L} Y_L(\vec{r}-\vec{R}') \Bigg[v_{L,\gamma,\delta}(|\vec{r}-\vec{R}'|) \\
&\quad - q_{s,\gamma,\delta}\sqrt{4\pi} w(|\vec{r}-\vec{R}'|)\delta_{L,s} - q_{p,\gamma,\delta}\sqrt{\frac{4\pi}{3}}\, \partial_r w|_{|\vec{r}-\vec{R}'|}\, \delta_{L,p_j} \Bigg]
\end{aligned} \tag{7.55}$$

$$\int d^3r'\ v^{sr}_{\alpha,\beta}(\vec{r'})n_{\gamma,\delta}(\vec{r'}) = \sum_{L,L'}\int d^3r'\ Y_L(\vec{r'}-\vec{R})Y_{L'}(\vec{r'}-\vec{R'})v^{sr}_{L,\alpha,\beta}(\vec{r'}-\vec{R}))n_{L',\gamma,\delta}(\vec{r'}-\vec{R'}))$$
$$= \sum_{L,L'} C_{L,L_\alpha,L_\beta}C_{L',L_\gamma,L_\delta}\int d^3r'\ Y_L(\vec{r'}-\vec{R})Y_{L'}(\vec{r'}-\vec{R'})v^{sr}_{L,\alpha,\beta}(\vec{r'}-\vec{R}))n_{L',\gamma,\delta}(\vec{r'}-\vec{R'})) \tag{7.56}$$

To complete the short-ranged part of the U-tensor matrix element, we need to evaluate

$$\begin{aligned}\left(Q_{\alpha,\beta}+\vec{D}_{\alpha,\beta}\vec{\nabla}_R\right)v^{sr}_{\gamma,\delta}(\vec{R}) &= \left(Q_{\alpha,\beta}+\vec{D}_{\alpha,\beta}\vec{\nabla}_R\right)\sum_L C_{L_\gamma,L_\delta,L}Y_L(\vec{R}-\vec{R'})v^{sr}_{L,\gamma,\delta}(\vec{R}-\vec{R'})\\
&= \sum_L C_{L_\gamma,L_\delta,L}\underbrace{Y_L(\vec{R}-\vec{R'})}_{\delta_{m,0}Y_{\ell,0}(-\vec{e}_z)}Q_{\alpha,\beta}v^{sr}_{L,\gamma,\delta}(\vec{R}-\vec{R'})\\
&+ \sum_L C_{L_\gamma,L_\delta,L}v^{sr}_{L,\gamma,\delta}(\vec{R}-\vec{R'})\vec{D}_{\alpha,\beta}\vec{\nabla}_R Y_L(\vec{R}-\vec{R'})\\
&+ \sum_L C_{L_\gamma,L_\delta,L}Y_L(\vec{R}-\vec{R'})\vec{D}_{\alpha,\beta}\vec{\nabla}_R v^{sr}_{L,\gamma,\delta}(\vec{R}-\vec{R'})\\
&= \sum_L C_{L_\gamma,L_\delta,L}\underbrace{Y_L(\vec{R}-\vec{R'})}_{\delta_{m,0}Y_{\ell,0}(-\vec{e}_z)}Q_{\alpha,\beta}v^{sr}_{L,\gamma,\delta}(\vec{R}-\vec{R'})\\
&+ \sum_L C_{L_\gamma,L_\delta,L}v^{sr}_{L,\gamma,\delta}(\vec{R}-\vec{R'})\vec{D}_{\alpha,\beta}\vec{\nabla}_R Y_L(\vec{R}-\vec{R'})\\
&+ \sum_L C_{L_\gamma,L_\delta,L}\underbrace{Y_L(\vec{R}-\vec{R'})}_{\delta_{m,0}Y_{\ell,0}(-\vec{e}_z)}D_{z,\alpha,\beta}\partial_r v^{sr}_{L,\gamma,\delta}(\vec{R}-\vec{R'})\end{aligned} \tag{7.57}$$

Chapter 8

Rotation of the density matrix

Consider the interatomic vector connecting two atoms

$$\vec{q} \stackrel{\text{def}}{=} \vec{R}_2 + \vec{t} - \vec{R}_1 \tag{8.1}$$

Our goal is to transform the density matrix into a coordinate system, in which the interatomic vector points along the new z-axis.

$$\vec{q}' = \vec{e}_z |\vec{q}| = \mathcal{R}\vec{q} \tag{8.2}$$

8.0.1 Active and passive rotation

Active rotation

Consider a rotation $\mathcal{R}$ which transforms the vector $\vec{q}$ into $\vec{q}'$ so that $\vec{q}' || \vec{e}_z$.

The coordinates q'_j of the new vector $\mathcal{R}\vec{q}$ are

$$q'_j = \vec{e}_j \vec{q}' = \vec{e}_j \mathcal{R}\vec{q} = \vec{e}_j \mathcal{R} \underbrace{\sum_k \vec{e}_k \otimes \vec{e}_k}_{\mathbf{1}} \vec{q} = \sum_k \underbrace{\vec{e}_j \mathcal{R} \vec{e}_k}_{\mathcal{R}_{j,k}} \underbrace{\vec{e}_k \vec{q}}_{q_k} = \sum_k R_{j,k} q_k \tag{8.3}$$

where

$$\mathcal{R}_{i\,j} \stackrel{\text{def}}{=} \vec{e}_i \mathcal{R} \vec{e}_j \tag{8.4}$$

Passive rotation

The problem at hand is a passive rotation, that is, we want to represent the same vector $\vec{q}$ in a new coordinate system. The new coordinate system shall be chosen such that the new coordinates have only a z-component.

Let me denote the new coordinate vectors by $\vec{E}_j$. I avoid the notation with primes, because this would imply a forward rotation of the unit vectors. The transformation of the coordinate axes shall satisfy

$$\vec{E}_j \vec{q} = \vec{e}_j \vec{q}' \tag{8.5}$$

where $\vec{q}'$ is the result of the active rotation, which turns the vector $\vec{q}$ into the z-direction.

$$\vec{E}_j\vec{q} = \vec{e}_j\vec{q}' = \vec{e}_j\mathcal{R}\vec{q} \Leftarrow \quad \vec{E}_j = \vec{e}_j\mathcal{R} = \mathcal{R}^\dagger\vec{e}_j \tag{8.6}$$

Thus the vector $\vec{q}$ can be represented as

$$\vec{q} = \sum_j \vec{e}_j q_j = \sum_j \vec{E}_j q'_j \quad \text{with } q'_j = \sum_k \mathcal{R}_{j,k} q_k \tag{8.7}$$

The rotation matrix can be represented in two ways, namely as

$$\vec{e}_i\vec{e'}_j = \vec{e}_i\left(\mathcal{R}\vec{e}_j\right) = \vec{e}_i\mathcal{R}\vec{e}_j = \mathcal{R}_{i,j} = \left(\mathcal{R}^\dagger\vec{e}_i\right)\vec{e}_j = \vec{E}_i\vec{e}_j \tag{8.8}$$

The rotation can be expressed as

$$\begin{aligned}\mathcal{R} &= \mathcal{R}\sum_j \vec{e}_j\otimes\vec{e}_j = \sum_j \vec{e'}_j\otimes\vec{e}_j \\ \mathcal{R} &= \mathcal{R}\sum_j \vec{E}_j\otimes\vec{E}_j \overset{\mathcal{R}\mathcal{R}^\dagger=\mathbf{1}}{=} \sum_j \vec{e}_j\otimes\vec{E}_j\end{aligned} \tag{8.9}$$

Using the same symbol for the rotated vector $\vec{e'}_j$ under active rotation and the new coordinate vectors $\vec{E}_j$ of the passive rotation, is a source of errors. On the level of the coordinates the active and the passive transformation do the same, so that I can use one matrix, namely $\mathcal{R}_{ij}$. However, the physical transformation of the vector $\vec{q}$ in the active transformation and that of the coordinate vectors $\vec{e}_j$ in the passive transformation are inverses of each other.

Transformation of the of the wave-function components

A wave function is expressed in local orbitals in terms of real spherical harmonics

$$\langle\vec{r}|\psi\rangle = \sum_L \langle\vec{r}|\chi_L\rangle c_L \tag{8.10}$$

The intention is to express the wave function in a new basis $|\bar{\chi}_L\rangle$, for which

$$\langle\vec{q}|\bar{\chi}_L\rangle = \langle|\vec{q}|\vec{e}_z|\chi\rangle\langle\mathcal{R}\vec{q}\chi\rangle \qquad \Leftarrow \qquad \langle\vec{r}|\bar{\chi}_L\rangle = \langle\mathcal{R}\vec{r}|\chi\rangle \tag{8.11}$$

$$\begin{aligned}|\psi\rangle &= \left(\sum_L |\bar{\chi}_L\rangle\langle\bar{\pi}_L|\right)\left(\sum_{L'} |\chi_{L'}\rangle\langle\pi_{L'}|\right)|\psi\rangle \\ &= \sum_L |\bar{\chi}_L\rangle \left(\underbrace{\sum_{L'} \overbrace{\langle\bar{\pi}_L|\chi_{L'}\rangle}^{\mathcal{R}_{L,L'}}\overbrace{\langle\pi_{L'}|\psi\rangle}^{\bar{c}_{L'}}}_{\bar{c}_L}\right)\end{aligned}$$

$$\mathcal{R}_{L,L'} = \langle\bar{\pi}_L|\chi_{L'}\rangle = \int d^3r\ \langle\bar{\pi}_L|\vec{r}\rangle\langle\vec{r}|\chi_{L'}\rangle = \int d^3r\ \langle\pi_L|\mathcal{R}\vec{r}\rangle\langle\vec{r}|\chi_{L'}\rangle \tag{8.12}$$

The transformation matrix $\mathcal{R}_{L,L'}$ is evaluated in `SPHERICAL$ROTATEYLMWDER(LMX,ROT,YLMROT)` or `SPHERICAL$ROTATEYLMWDER(LMX,N,ROT,DRO,YLMROT,DYLMROT)`. It takes as input the rotation matrix `ROT`, respectively its derivatives `DROT`, obtained from `SPHERICAL$AXISUROT(DR,ROT,DROT)`.

8.1 Rotation matrix

The rotation matrix for a vector $\vec{q}$ which satisfies

$$\vec{e}_z|\vec{q}| = \mathcal{R}\vec{q} \tag{8.13}$$

is determinned in `SPHERICAL$AXISUROT(DR,U,DU)`.

The rotation matrix is evaluated from the interatomic distance vector and another arbitrary vector $\vec{a}$. This vector should not be the coordinate vector $\vec{e}_j$ with the smallest projection on $\vec{Q}$, to avoid a divide-by-zero.

Then we construct

$$\begin{aligned}
\vec{y}_1 &= \vec{y}_2 \times \vec{y}_3 = (\vec{a} \times \vec{q}) \times \vec{q} = \vec{q} \times (\vec{q} \times \vec{a}) \\
&= \vec{q}(\vec{a}\vec{q}) - \vec{a}(\vec{q}^2) \\
\vec{y}_2 &= \vec{a} \times \vec{q} \\
\vec{y}_3 &= \vec{q}
\end{aligned} \tag{8.14}$$

The three vectors are mutually orthogonal, and can be used, after normalization, to set up the rotation matrix.

$$\mathcal{R} = \sum_j \frac{1}{\sqrt{\vec{y}_j^2}} \vec{e}_j \otimes \vec{y}_j \qquad \text{with } |\vec{a}| = 1 \tag{8.15}$$

This construction does not exclude an additional inversion.

$$\mathcal{R}_{\alpha,\beta} = \vec{e}_\alpha \mathcal{R} \vec{e}_\beta = \sum_j \frac{1}{\sqrt{\vec{y}_j^2}} (\vec{e}_\alpha \vec{e}_j)(\vec{y}_j \vec{e}_\beta) = \frac{(\vec{y}_\alpha \vec{e}_\beta)}{\sqrt{\vec{y}_\alpha^2}} = \frac{y_{\beta,\alpha}}{\sqrt{\vec{y}_\alpha^2}} \tag{8.16}$$

The inverse, respectively the transpose, matrix is

$$\mathcal{R}^\dagger = \sum_j \frac{1}{\sqrt{\vec{y}_j^2}} \vec{y}_j \otimes \vec{e}_j \tag{8.17}$$

8.2 Gradient of the rotation matrix

I work out the gradient of the rotation matrix $\mathcal{R}$ with resprect to the interatomic distance vector. What is actually required is

$$\frac{\partial \mathcal{R}}{\partial q_n} \mathcal{R}^\dagger \tag{8.18}$$

The rotation matrix was expressed in terms if the vectors $\vec{y}_j$ from Eq. 8.14. Let me calculate their derivatives. I will use the identity $\partial\vec{q}/\partial q_n = \vec{e}_n$.

$$\begin{aligned}
\frac{\partial \vec{y}_1}{\partial q_n} &= \frac{\partial}{\partial q_n}\left[\vec{q}(\vec{a}\vec{q}) - \vec{a}(\vec{q}^2)\right] = \vec{e}_n(\vec{a}\vec{q}) + \vec{q}(\vec{a}\vec{e}_n) - \vec{a}(2\vec{q}\vec{e}_n) \\
\frac{\partial \vec{y}_2}{\partial q_n} &= \frac{\partial}{\partial q_n}\vec{a} \times \vec{q} = \vec{a} \times \vec{e}_n \\
\frac{\partial \vec{y}_3}{\partial q_n} &= \frac{\partial}{\partial q_n}\vec{q} = \vec{e}_n
\end{aligned} \tag{8.19}$$

In the next step, I normalize the vectors $\vec{y}_j$

$$\vec{z}_j \stackrel{\text{def}}{=} \vec{y}_j \frac{1}{\sqrt{\vec{y}_j^2}} \tag{8.20}$$

with derivatives

$$\frac{\partial \vec{z}_j}{\partial q_n} = \frac{\partial \vec{y}_j}{dq_n} \frac{1}{\sqrt{\vec{y}_j^2}} + \vec{y}_j \left[-\frac{1}{2} (\vec{y}_j^2)^{-\frac{3}{2}} \left(2\vec{y}_j \frac{\partial \vec{y}_j}{dq_n} \right) \right] = \frac{1}{\sqrt{\vec{y}_j^2}} \left\{ \frac{\partial \vec{y}_j}{dq_n} - \vec{y}_j \frac{\vec{y}_j \frac{\partial \vec{y}_j}{dq_n}}{\vec{y}_j^2} \right\} \tag{8.21}$$

This is inserted into the equation obtained previously

$$\begin{aligned} \left(\frac{\partial \mathcal{R}}{\partial q_n} \mathcal{R}^\dagger \right)_{i,j} &= \sum_k \frac{\partial \mathcal{R}_{i,k}}{\partial q_n} \mathcal{R}^\dagger_{k,j} = \sum_k \frac{\partial \mathcal{R}_{i,k}}{\partial q_n} \mathcal{R}_{j,k} = \sum_k \frac{\partial z_{k,i}}{\partial q_n} z_{k,j} \\ &= \frac{\partial \vec{z}_i}{\partial q_n} \vec{z}_j \end{aligned} \tag{8.22}$$

8.3 .....

Appendix A

Exact Benchmark systems

Here I consider exact systems that can be described analytically. Usually these are one-electron systems, for which Hartree and exchange energies cancel exactly. They can nevertheless be used as benchmark.

A.1 Hydrogen atom

Let me first summarize the exact results for the energies related to the hydrogen atom

E_{tot}	E_{kin}	E_{pot}	ϵ_{1s}
$-\frac{1}{2}$ H -13.606 eV	$\frac{1}{2}$ H 13.606 eV	-1 H -27.211 eV	$-\frac{1}{2}$ H -13.606 eV
$\epsilon_{2s} - \epsilon_{1s}$	$E_{self} + Epot$	E_{self}	E_X
$\frac{3}{8}$ H 10.204 eV	-11/16 H=-0.6875 H -18.707 eV	5/16 H=+0.3125 H 8.503 eV	-5/16 H=-0.3125 H -8.503 eV

Here, E_{self} is the electrostatic self energy of the electron density. $E_{self} + E_{pot}$ is the Hartree energy including electron-electron and electron-proton interactions. The energies in eV are approximate.

The wave functions $\psi(\vec{r})$ of the hydrogen atom and its electron density $n(\vec{r})$ are[1]

$$\begin{aligned}\psi(\vec{r}) &= \frac{1}{\sqrt{\pi a_0^3}} \mathrm{e}^{-|\vec{r}|/a_0} \\ n(\vec{r}) &= \frac{1}{\pi a_0^3} \mathrm{e}^{-2|\vec{r}|/a_0}\end{aligned} \tag{A.3}$$

The Coulomb potential of the electronic charge density can be evaluated using the radial Green's function of the Poisson equation. (see ΦSX: Klassische Mechanik.)

$$\begin{aligned}v(\vec{r}) &= \frac{e^2}{4\pi\epsilon_0} 4\pi \left[\frac{1}{|\vec{r}|} \int_0^{|\vec{r}|} dr' \; (r')^2 n(r') + \int_{|\vec{r}|}^{\infty} dr' \; r' n(r') \right] \\ &= \frac{e^2}{4\pi\epsilon_0} 4\pi \frac{1}{\pi a_0^3} \left[\frac{1}{|\vec{r}|} \int_0^{|\vec{r}|} dr' \; (r')^2 \mathrm{e}^{-2r'/a_0} + \int_{|\vec{r}|}^{\infty} dr' \; r' \mathrm{e}^{-2r'/a_0} \right] \\ &= \frac{e^2}{4\pi\epsilon_0} 4\pi \frac{1}{\pi a_0^3} \left\{ \frac{1}{|\vec{r}|} \frac{a_0^3}{4} \left[1 - \left(2\left(\frac{r}{a_0}\right)^2 + 2\left(\frac{r}{a_0}\right) + 1 \right) \mathrm{e}^{-2r/a_0} \right] + \frac{a_0^3}{4} \frac{1}{a_0} \left(2\frac{r}{a_0} + 1 \right) \mathrm{e}^{-2r/a_0} \right\} \\ &= \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{1}{|\vec{r}|} \left[1 - \left(2\left(\frac{r}{a_0}\right)^2 + 2\left(\frac{r}{a_0}\right) + 1 \right) \mathrm{e}^{-2r/a_0} \right] + \frac{1}{r} \left(2\left(\frac{r}{a_0}\right)^2 + \left(\frac{r}{a_0}\right) \right) \mathrm{e}^{-2r/a_0} \right\} \\ &= \frac{e^2}{4\pi\epsilon_0 |\vec{r}|} \left\{ \left[1 - \left(\left(\frac{r}{a_0}\right) + 1 \right) \mathrm{e}^{-2r/a_0} \right] \right\}\end{aligned} \tag{A.4}$$

The potential at the origin can be used to evaluate the interaction energy between nucleus and electron density, i.e. the external-potential energy.

$$\begin{aligned}v(r=0) &= \frac{e^2}{4\pi\epsilon_0 a_0} \\ E_{e-nuc} &= -\frac{e^2}{4\pi\epsilon_0} \int d^3r \frac{n(r)}{r} = -\frac{e^2}{4\pi\epsilon_0 a_0}\end{aligned} \tag{A.5}$$

The self energy is the Coulomb interaction energy of the electron density with itself. This energy is cancelled by the exchange energy. Thus, the self energy can be used to obtain,

[1] The wave functions of the hydrogen atom are taken from ΦSX: Quantum Physics. The Coulomb potential of the charge density is obtained with the Help of Eq. 5.42 of PhiSX:Elektrodynamik. Furthermore, the following equations from Bronstein are used:

$$\int_0^x dx \; x\mathrm{e}^{ax} = \mathrm{e}^{ax}\left(\frac{x}{a} - \frac{1}{a^2}\right) \qquad \text{Bronstein p.61 Sec. 1.1.3.3 Eq.448}$$

$$\int_0^x dx \; x^2\mathrm{e}^{ax} = \mathrm{e}^{ax}\left(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right) \qquad \text{Bronstein p.61 Sec. 1.1.3.3 Eq.449} \tag{A.1}$$

$$\int_0^\infty dx x^n \mathrm{e}^{-ax} = \frac{n!}{a^{n+1}} \qquad \text{Bronstein p65 Sec. 1.1.3.4 Eq.1} \tag{A.2}$$

independently, the Hartree energy and the exchange energy.

$$\begin{aligned}
E_{self} &= \frac{1}{2}\int d^3r\; n(\vec{r})v(\vec{r}) \\
&= \frac{1}{2}\left(\frac{1}{\pi a_0^3}\right)\left(\frac{e^2}{4\pi\epsilon_0}\right)4\pi\int_0^\infty dr\; r^2 \mathrm{e}^{-2r/a_0}\frac{1}{r}\left[1-\left(\left(\frac{r}{a_0}\right)+1\right)\mathrm{e}^{-2r/a_0}\right] \\
&= \frac{1}{2}\left(\frac{1}{\pi a_0^3}\right)\left(\frac{e^2}{4\pi\epsilon_0}\right)4\pi a_0^2\int_0^\infty dx\; x\mathrm{e}^{-2x}\left[1-(x+1)\,\mathrm{e}^{-2x}\right] \\
&= \frac{1}{2}\frac{1}{\pi a_0^3}\frac{e^2}{4\pi\epsilon_0 a_0}4\pi a_0^3\int_0^\infty dx\;\left[x\mathrm{e}^{-2x}-x^2\mathrm{e}^{-4x}-x\mathrm{e}^{-4x}\right] \\
&= 2\underbrace{\frac{e^2}{4\pi\epsilon_0 a_0}}_{1H}\quad\underbrace{\left[\frac{1!}{2^2}-\frac{2!}{4^3}-\frac{1!}{4^2}\right]}_{1/4-1/32-1/16=(8-1-2)/32=5/32} \\
&= \frac{5}{16}\frac{e^2}{4\pi\epsilon_0 a_0} = 0.3125\; H \qquad \textit{(exact)}
\end{aligned} \tag{A.6}$$

The U-tensor is twice the self energy, Eq. A.6, i.e.

$$U = 2E_{self} = 2E_X = \frac{5}{8}\frac{e^2}{4\pi\epsilon_0 a_0} \tag{A.7}$$

The energy E_{e-nuc} is the complete electrostatic energy including Hartree energy $E_{pot}+E_{self}$ and exchange energy E_X. This tells us that $E_X = -E_{self}$ This result for the exchange energy $E_X = -0.3125$ is also given in [P.M.W. Gill and J.A. Pople, Phys Rev. A 47, 2383 (1993)][**?**].

A.2 Off-site matrix elements of dihydrogen

A.2.1 Two-center integral of spherical functions

The integrations of interest are of the form of a two-center integral of two spherical functions with centers that are separated by the distance d.

$$\begin{aligned}
\langle f|g\rangle &= \int d^3r\; f(|\vec{r}|)g(|\vec{e}_z d-\vec{r}|) \\
&= \int_0^\infty dr\; r^2\int_0^{2\pi} d\phi\int_0^\pi d\theta\sin(\theta)f(r)g(\sqrt{(d-r\cos(\theta))^2+(r\sin(\theta))^2}) \\
&= 2\pi\int_0^\infty dr\; r^2 f(r)\int_0^\pi d\theta\sin(\theta)g(\sqrt{d^2-2dr\cos(\theta))+r^2}) \\
&= 2\pi\int_0^\infty dr\; r^2 f(r)\frac{1}{dr}\int_{|d-r|}^{|d+r|} dy\; yg(y) \\
&= \frac{2\pi}{d}\int_0^\infty dr\; rf(r)\int_{|d-r|}^{|d+r|} dy\; yg(y) \\
&= \frac{2\pi}{d}\left[\int_0^d dr\; rf(r)\int_{d-r}^{r+d} dy\; yg(y)+\int_d^\infty dr\; rf(r)\int_{r-d}^{r+d} dy\; yg(y)\right]
\end{aligned} \tag{A.8}$$

We used

$$y(\theta) = \sqrt{d^2 - 2dr\cos(\theta) + r^2} \qquad \Rightarrow \qquad dy = \frac{1}{2y} 2dr\sin(\theta)d\theta$$
$$y(\theta = 0) = |d - r| \qquad \text{and} \qquad y(\theta = \pi) = d + r \tag{A.9}$$

A.2.2 Overlap

Let me evaluate the overlap of two hydrogen orbitals

$$\begin{aligned} S(d) &= \frac{1}{\pi a_0^3} \int d^3 r \mathrm{e}^{-|\vec{r}|/a_0} \mathrm{e}^{-|\vec{r} - \vec{e}_z d|/a_0} \\ &= \frac{1}{\pi} \int d^3 x \mathrm{e}^{-|\vec{x}|} \mathrm{e}^{-|\vec{x} - \vec{e}_z \frac{d}{a_0}|} \end{aligned} \tag{A.10}$$

With the undetermined integrals

$$\begin{aligned} \int dx\ \mathrm{e}^{-ax} &= -\frac{1}{a}\mathrm{e}^{-ax} \\ \int dx\ x\mathrm{e}^{-ax} &= -\frac{ax+1}{a^2}\mathrm{e}^{-ax} \\ \int dx\ x^2\mathrm{e}^{-ax} &= -\frac{(ax)^2 + 2ax + 2}{a^3}\mathrm{e}^{-ax} \\ \int dx\ x^n\mathrm{e}^{-ax} &= \frac{-n!}{a^{n+1}}\mathrm{e}^{-ax} \sum_{j=0}^{n} \frac{1}{j!}(ax)^j \end{aligned} \tag{A.11}$$

from Bronstein, I obtain, with $z \stackrel{\text{def}}{=} \frac{d}{a_0}$

$$\begin{aligned}
S(d = za_0) &= \frac{2}{z}\left[\int_0^z dx\, x\mathrm{e}^{-x}\int_{z-x}^{x+z} dy\, y\mathrm{e}^{-y} + \int_z^\infty dx\, x\mathrm{e}^{-x}\int_{x-z}^{x+z} dy\, y\mathrm{e}^{-y}\right] \\
&= \frac{2}{z}\left\{\int_0^z dx\, x\mathrm{e}^{-x}\Big[-(1+y)\mathrm{e}^{-y}\Big]_{z-x}^{x+z} + \int_z^\infty dx\, x\mathrm{e}^{-x}\Big[-(1+y)\mathrm{e}^{-y}\Big]_{x-z}^{x+z}\right\} \\
&= \frac{2}{z}\left\{\int_0^z dx\, x\mathrm{e}^{-x}\Big[-(1+x+z)\,\mathrm{e}^{-(x+z)} + (1+z-x)\,\mathrm{e}^{-(z-x)}\Big]\right. \\
&\quad \left. + \int_z^\infty dx\, x\mathrm{e}^{-x}\Big[-(1+x+z)\,\mathrm{e}^{-(x+z)} + (1+x-z)\,\mathrm{e}^{-(x-z)}\Big]\right\} \\
&= \frac{2}{z}\left\{\mathrm{e}^{-z}\int_0^z dx\,\Big[-(1+z)\,x\mathrm{e}^{-2x} - x^2\mathrm{e}^{-2x} + (1-z)\,x + x^2\Big]\right. \\
&\quad \left. + \int_z^\infty dx\,\Big[\Big(\mathrm{e}^{+z}(1-z) - \mathrm{e}^{-z}(1+z)\Big)x\mathrm{e}^{-2x} + \Big(\mathrm{e}^{+z} - \mathrm{e}^{-z}\Big)x^2\mathrm{e}^{-2x}\Big]\right\} \\
&= \frac{2}{z}\left\{\mathrm{e}^{-z}\left[-(1+z)\,\frac{-2x-1}{4}\mathrm{e}^{-2x} - \frac{(-2x)^2 - 2(-2x)+2}{-8}\mathrm{e}^{-2x} + \frac{1+z}{2}x^2 - \frac{1}{3}x^3\right]_0^z\right. \\
&\quad \left. + \left[\Big(\mathrm{e}^{+z}(1-z) - \mathrm{e}^{-z}(1+z)\Big)\frac{-2x-1}{4}\mathrm{e}^{-2x} + \Big(\mathrm{e}^{+z} - \mathrm{e}^{-z}\Big)\frac{(-2x)^2 - 2(-2x)+2}{-8}\mathrm{e}^{-2x}\right]_z^\infty\right\} \\
&= \frac{2}{z}\left\{\mathrm{e}^{-z}\left[(1+z)\,\frac{2z+1}{4}\mathrm{e}^{-2z} - \frac{2z^2+2z+1}{4}\mathrm{e}^{-2z} + \frac{1+z}{2}z^2 - \frac{1}{3}z^3 + (1+z)\,\frac{-1}{4} - \frac{1}{4}\right]\right. \\
&\quad \left. - \left[\Big(\mathrm{e}^{+z}(1-z) - \mathrm{e}^{-z}(1+z)\Big)\frac{-2z-1}{4}\mathrm{e}^{-2z} + \Big(\mathrm{e}^{+z} - \mathrm{e}^{-z}\Big)\frac{2z^2+2z+1}{-4}\mathrm{e}^{-2z}\right]\right\} \\
&= \Big(\frac{1}{3}z^2 + z + 1\Big)\mathrm{e}^{-z}
\end{aligned} \tag{A.12}$$

Thus, the overlap matrix element of two hydrogen 1s-orbitals is

OVERLAP OF TWO HYDROGEN 1S ORBITALS

$$S(d) = \left[\frac{1}{3}\left(\frac{d}{a_0}\right)^2 + \left(\frac{d}{a_0}\right) + 1\right]\mathrm{e}^{-\frac{d}{a_0}} \tag{A.13}$$

A.2.3 Electron-nucleus Coulomb matrix elements

The matrix elements from this subsection are copied from the internet and they are ot verified. http://www.pci.tu-bs.de/aggericke/PC4e/Kap_II/H2-Ion.htm

The **Coulomb integral** J is the Coulomb interaction of one atom with the nucleus of the other atom.

$$J = \frac{e^2}{4\pi\epsilon_0 d} - \int d^3r\, \psi_{1s}(\vec{r})\psi_{1s}(\vec{r})\frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{e}_z d|} = \left(1 + \frac{1}{d}\right)\mathrm{e}^{-2d/a_0} \tag{A.14}$$

The **resonance integral** K describes the overlap density of two orbils on different sites with

the nucleus of one site

$$K = \frac{e^2 S(d)}{4\pi\epsilon_0 d} - \int d^3r \, \frac{e^2 \psi_{1s}(\vec{r} - \vec{e}_z d)\psi_{1s}(\vec{r})}{4\pi\epsilon_0 |\vec{r} - \vec{e}_z d|} = \frac{e^2}{4\pi\epsilon_0}\left(\frac{a_0}{d} - \frac{2}{3}\frac{d}{a_0}\right) \mathrm{e}^{-d/a_0} \tag{A.15}$$

A.2.4 U-tensor

The 31 matrix elements are those with three orbitals on one site and one on the other. The 22 matrix elements are those with one denisty on one site and another density on the other.

$$\begin{aligned} 31 &= \int d^3r \int d^3r' \, \frac{e^2 \psi^2(\vec{r})\psi(\vec{r'})\psi(\vec{r'} - \vec{e}_z d)}{4\pi\epsilon_0 |\vec{r} - \vec{r'}|} = \int d^3r \, \Big(v_1(\vec{r})\psi(\vec{r})\Big)\psi(\vec{r} - \vec{e}_z d) \\ 22 &= \int d^3r \int d^3r' \, \frac{e^2 \psi^2(\vec{r})\psi^2(\vec{r'} - \vec{e}_z d)}{4\pi\epsilon_0 |\vec{r} - \vec{r'}|} = \int d^3r \, v_1(\vec{r})\psi^2(\vec{r'} - \vec{e}_z d) \end{aligned} \tag{A.16}$$

The Coulomb potential from the electrons of one hydrogen atom is Eq. A.4

$$v_1(\vec{r}) = \frac{e^2}{4\pi\epsilon_0 |\vec{r}|}\left[1 - \left(1 + \frac{r}{a_0}\right)\mathrm{e}^{-2r/a_0}\right] \tag{A.17}$$

Both integrations are of a similar form, namely $31 = I(3,1)$ and $22 = I(2,2)$ with

$$\begin{aligned} \frac{e^2}{4\pi\epsilon_0 a_0} I_{2+m,n}(d = z a_0) &\stackrel{\text{def}}{=} \int d^3r \, v_1(\vec{r})\psi_{1s}^n(\vec{r})\psi_{1s}^m(\vec{r} - \vec{e}_z d) \\ &= \frac{e^2}{4\pi\epsilon_0 a_0}\frac{1}{\pi a_0^3}\int d^3r \, \frac{a_0}{|\vec{r}|}\left[1 - \left(1 + \frac{|\vec{r}|}{a_0}\right)\mathrm{e}^{-2\frac{|\vec{r}|}{a_0}}\right]\mathrm{e}^{-m\frac{|\vec{r}|}{a_0}}\mathrm{e}^{-n\frac{|\vec{r} - \vec{e}_z d|}{a_0}} \\ &= \frac{e^2}{4\pi\epsilon_0 a_0}\frac{1}{\pi}\int d^3r \, \frac{1}{|\vec{x}|}\left[1 - (1 + |\vec{x}|)\,\mathrm{e}^{-2|\vec{x}|}\right]\mathrm{e}^{-m|\vec{r}|}\mathrm{e}^{-n|\vec{x} - \vec{e}_z z|} \end{aligned} \tag{A.18}$$

with $z = d/a_0$.

$$
\begin{aligned}
I_{4-n,n}(z) &= \frac{1}{\pi}\int d^3r\,\frac{1}{|\vec{x}|}\left[1-(1+|\vec{x}|)\,\mathrm{e}^{-2|\vec{x}|}\right]\mathrm{e}^{-(2-n)|\vec{r}|}\mathrm{e}^{-n|\vec{x}-\vec{e}_z z|}\\
&= \frac{1}{\pi}\frac{2\pi}{z}\left\{\int_0^z dx\; x\underbrace{\frac{1}{x}\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\mathrm{e}^{-(2-n)x}}_{f(x)}\int_{z-x}^{x+z} dy\; y\underbrace{\mathrm{e}^{-ny}}_{g(y)}\right.\\
&\quad\left.+\int_z^\infty dx\; x\underbrace{\frac{1}{x}\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\mathrm{e}^{-(2-n)x}}_{f(x)}\int_{x-z}^{x+z} dy\; y\underbrace{\mathrm{e}^{-ny}}_{g(y)}\right\}\\
&= \frac{2}{z}\left\{\int_0^z dx\;\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\mathrm{e}^{-(2-n)x}\left[\frac{-ny-1}{n^2}\mathrm{e}^{-ny}\right]_{z-x}^{x+z}\right.\\
&\quad\left.+\int_z^\infty dx\;\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\mathrm{e}^{-(2-n)x}\left[\frac{-ny-1}{n^2}\mathrm{e}^{-ny}\right]_{x-z}^{x+z}\right\}\\
&= \frac{-2}{n^2 z}\left\{\int_0^z dx\;\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\mathrm{e}^{-(2-n)x}\right.\\
&\qquad\qquad\left.\times\left[(1+n(z+x))\mathrm{e}^{-nz}\mathrm{e}^{-nx}-(1+nz-nx)\mathrm{e}^{-nz}\mathrm{e}^{+nx}\right]\right.\\
&\quad\left.+\int_z^\infty dx\;\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\mathrm{e}^{-(2-n)x}\right.\\
&\qquad\qquad\left.\times\left[(1+nz+nx)\mathrm{e}^{-nz}-(1-nz+nx)\mathrm{e}^{+nz}\right]\mathrm{e}^{-nx}\right\}\\
&= \frac{-2}{n^2 z}\left\{\int_0^z dx\;\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\right.\\
&\qquad\qquad\left.\times\mathrm{e}^{-nz}\left[(1+nz+nx)\mathrm{e}^{-2x}-(1+nz-nx)\mathrm{e}^{-(2-2n)x}\right]\right.\\
&\quad\left.+\int_z^\infty dx\;\left[1-(1+x)\,\mathrm{e}^{-2x}\right]\right.\\
&\qquad\qquad\left.\times\left[\Big((1+nz+nx)\mathrm{e}^{-nz}-(1-nz+nx)\mathrm{e}^{+nz}\Big)\right]\mathrm{e}^{-2x}\right\}
\end{aligned}
\tag{A.19}
$$

$$
\begin{aligned}
I_{22} = \frac{-2}{4z}\Bigg\{ & \int_0^z dx\ \left[1-(1+x)\,\mathrm{e}^{-2x}\right] \\
& \qquad \times \mathrm{e}^{-2z}\Big[(1+2z+2x)\mathrm{e}^{-2x}-(1+2z-2x)\mathrm{e}^{+2x}\Big] \\
& + \int_z^\infty dx\ \left[1-(1+x)\,\mathrm{e}^{-2x}\right] \\
& \qquad \times \Big[\Big((1+2z+2x)\mathrm{e}^{-2z}-(1-2z+2x)\mathrm{e}^{+2z}\Big)\Big]\mathrm{e}^{-2x}\Bigg\} \\
= \frac{-1}{2z}\Bigg\{ & \int_0^z dx\ \mathrm{e}^{-2z}\Big[(1+2z+2x)\mathrm{e}^{-2x}-(1+2z-2x)\mathrm{e}^{+2x}\Big] \\
& + \int_z^\infty dx\ \Big[\Big((1+2z+2x)\mathrm{e}^{-2z}-(1-2z+2x)\mathrm{e}^{+2z}\Big)\Big]\mathrm{e}^{-2x} \\
& - \int_0^z dx\ \mathrm{e}^{-2z}\Big[(1+2z+2x)\mathrm{e}^{-4x}-(1+2z-2x)\Big] \\
& - \int_z^\infty dx\ \Big[\Big((1+2z+2x)\mathrm{e}^{-2z}-(1-2z+2x)\mathrm{e}^{+2z}\Big)\Big]\mathrm{e}^{-4x} \\
& - \int_0^z dx\ \mathrm{e}^{-2z}\Big[(1+2z+2x)\mathrm{e}^{-4x}-(1+2z-2x)\Big]x \\
& - \int_z^\infty dx\ \Big[\Big((1+2z+2x)\mathrm{e}^{-2z}-(1-2z+2x)\mathrm{e}^{+2z}\Big)\Big]x\mathrm{e}^{-4x}\Bigg\} \\
= \frac{-1}{2z}\Bigg\{ & \left[\left(\frac{1+2z}{-2}-2\frac{1+2x}{4}\right)\mathrm{e}^{-2(x+z)}-\left(\frac{1+2z}{+2}+2\frac{1-2x}{4}\right)\mathrm{e}^{+2(x-z)}\right]_0^z \\
& + \left[\left(\frac{1+2z}{-2}-2\frac{2x+1}{4}\right)\mathrm{e}^{-2(x+z)}-\left(\frac{1-2z}{2}+2\frac{1-2x}{4}\right)\mathrm{e}^{+2(z-x)}\right)\Big]_z^\infty \\
& - \left[\left(\frac{1+2z}{-4}-2\frac{1+4x}{16}\right)\mathrm{e}^{-4x-2z}-\left(x+2xz-x^2\right)\mathrm{e}^{-2z}\right]_0^z \\
& - \left[\left(\frac{1+2z}{-4}-2\frac{1+4x}{16}\right)\mathrm{e}^{-2z-4x}-\left(\frac{1-2z}{-4}-2\frac{1+4x}{16}\right)\mathrm{e}^{+2z-4x}\right]_z^\infty \\
& - \left[\left(\frac{(1+2z)(1+4z)}{16}+2\frac{16x^2+8x+2}{(-4)^3}\right)\mathrm{e}^{-4x-2z}-\left(\frac{1+2z}{2}x^2-\frac{2}{3}x^3\right)\mathrm{e}^{-2z}\right]_0^z \\
& - \Bigg[\left(-\frac{(1+2z)(1+4x)}{16}+2\frac{16x^2+8x+2}{-4^3}\right)\mathrm{e}^{-2z-4x} \\
& \qquad -\left(-\frac{(1-2z)(1+4x)}{16}+2\frac{16x^2+8x+2}{-4^3}\right)\mathrm{e}^{+2z-4x}\Bigg]_z^\infty\Bigg\} \qquad \text{(A.20)}
\end{aligned}
$$

This calculation is not finished. I am continuing with the Result from Maple.

Maple:

$$\begin{aligned} I_{31}(z) &= \Big(z^2+\frac{1}{8}z+\frac{5}{16}\Big)\frac{1}{z}\mathrm{e}^{-z}-\Big(\frac{1}{8}z+\frac{5}{16}\Big)\frac{1}{z}\mathrm{e}^{-3z} \\ &= z\mathrm{e}^{-z}+\Big(\frac{1}{8}z+\frac{5}{16}\Big)\frac{1}{z}\left(\mathrm{e}^{-z}-\mathrm{e}^{-3z}\right) \\ I_{22} &= \frac{1}{z}-\Big(\frac{1}{6}z^3+\frac{3}{4}z^2+\frac{11}{8}z+1\Big)\frac{1}{z}\mathrm{e}^{-2z} \end{aligned} \tag{A.21}$$

OFFSITE U-TENSOR MATRIX ELEMENTS

The offsite U-tensor matrix elements $U_{31}=W_{1,1,1,2}$ and $U_{22}=W_{1,2,1,2}$ are

$$\begin{aligned} U_{31}(d=za_0) &= \frac{e^2}{4\pi\epsilon_0 a_0}I_{31}=\frac{e^2}{4\pi\epsilon_0 a_0}\left[z\mathrm{e}^{-z}+\Big(\frac{1}{8}z+\frac{5}{16}\Big)\frac{1}{z}\left(\mathrm{e}^{-z}-\mathrm{e}^{-3z}\right)\right] \\ U_{22}(d=za_0) &= \frac{e^2}{4\pi\epsilon_0 a_0}I_{22}=\frac{e^2}{4\pi\epsilon_0 a_0}\left[\frac{1}{z}-\Big(\frac{1}{6}z^3+\frac{3}{4}z^2+\frac{11}{8}z+1\Big)\frac{1}{z}\mathrm{e}^{-2z}\right] \end{aligned} \tag{A.22}$$

- Both terms approach at short distances

$$\begin{aligned} I_{33}(z) &= \frac{5}{8}+O(x^2) \\ I_{22}(z) &= \frac{5}{8}+O(x^2) \end{aligned} \tag{A.23}$$

  The limit $x\to 0$ is equal to the onsite U-tensor, becausem in this limit, all four orbitals are centered on a single site. The electrostatic self energy E_{self} of the hydrogen atom calculated above is 5/16, which is $\frac{1}{2}U$.

- at long distances the integrals approach

$$\begin{aligned} I_{22}(z) &\overset{z\to\infty}{\to} \frac{1}{z} \\ I_{33}(z) &\overset{z\to\infty}{\to} ze^{-z} \end{aligned} \tag{A.24}$$

In order to remove the long-ranged part, I subtracted the multipole expansion of the 22 term. This, however, introduces singularities of the remaining term at the origin. A better strategy would be to replace 1/r by

$$\begin{aligned} \frac{1}{z} &\to \frac{1}{z}-\left(1-\frac{1}{2}(\lambda z)^2\right)\frac{\mathrm{e}^{-\lambda z}}{z}\cdot \\ \frac{1}{z^2} &\to \frac{1}{z^2}-\left(1+(\lambda z)-\frac{1}{3}(\lambda z)^3\right)\frac{\mathrm{e}^{-\lambda z}}{z^2} \\ \frac{1}{z^3} &\to \frac{1}{z^3}-\left(1+(\lambda z)+\frac{1}{2}(\lambda z)^2-\frac{1}{8}(\lambda z)^4\right)\frac{\mathrm{e}^{-\lambda z}}{z^3} \\ \mathrm{e}^{-\lambda z} &\to (1+\lambda z)\mathrm{e}^{-\lambda z} \end{aligned} \tag{A.25}$$

For a finite screening we need to multiply the right hand sie with $(1+\gamma z)e^{-\gamma z}$, so that the slope at the origin remains zero.

$$\begin{aligned}
\frac{1}{z}e^{-\gamma z} &\to \left(\frac{1}{z} - \left(1 - \frac{1}{2}((\lambda+\gamma)z)^2\right)\frac{e^{-\lambda z}}{z}\cdot\right)e^{-\gamma z} \\
\frac{1}{z^2} &\to \frac{1}{z^2} - \left(1 + (\lambda z) - \frac{1}{3}\lambda^2\right)\frac{e^{-\lambda z}}{z^2} \\
\frac{1}{z^3} &\to \frac{1}{z^3} - \left(1 + (\lambda z) + \frac{1}{2}\lambda^2 - \frac{1}{8}(\lambda x)^4\right)\frac{e^{-\lambda z}}{z^3} \\
e^{-\lambda z} &\to (1+\lambda z)e^{-\lambda z}
\end{aligned} \tag{A.26}$$

A.3 Dihydrogen cation

The H_2^+ ion is another one-electron system. It will not be treated exactly, but rather in the basisset of the wave functions of atomic hydrogen. The goal of this is to benchmark the matrix elements for the off-site exchange.

With the knowledge of the matrix elements the individual contributions of the dihydrogen cation can be calculated in the basis of atomic orbitals.

Data are in `Testsimplelmto/Calc/H2cation`

The wave function is

$$|\psi\rangle = |\chi_1\rangle c_1 + |\chi_1\rangle c_2 = (|\chi_1\rangle + |\chi_1\rangle)\frac{1}{\sqrt{2+2S}} \tag{A.27}$$

where $S = \langle\chi_1|\chi_2\rangle$ is the offsite overlap matrix element.

Thus the density matrix elements all have the same value

$$\rho_{\alpha,\beta} = c_\alpha c_\beta = \frac{1}{2+2S} \tag{A.28}$$

The number of electrons on a single site $N_{on,i}$ and that N_{off} in the off-site terms is thus

$$\begin{aligned}
N_{on,i} &= c_\alpha^2 = \frac{1}{2+2S} \\
N_{off} &= c_1 S c_2 S + c_2 S c_1 = \frac{2S}{2+2S} \\
1 &= N_{on,1} + N_{on,1} + N_{off}
\end{aligned} \tag{A.29}$$

The onsite Hartree and the onsite exchange energy is

$$\begin{aligned}
E_{H,on,i} &= \frac{1}{2}U_{1111}\rho_{11}\rho_{11} \overset{\text{Eq. A.7}}{=} \frac{1}{2}\frac{5}{8}\frac{1}{(2+2S)^2} = \frac{5}{16}\frac{1}{(2+2S)^2} \\
E_{X,on,i} &= -E_{H,on,i}
\end{aligned} \tag{A.30}$$

The energy related to the offsite exchange terms are

$$\begin{aligned}
E_{X,22} &= -\frac{1}{2}\sum_{R\neq R'}\sum_{\alpha,\gamma\in R}\sum_{\beta,\delta\in R} W_{\alpha,\beta,\gamma,\delta}\rho_{\delta,\alpha}\rho_{\gamma,\beta} \\
&= -\frac{1}{2}\Big(W_{1,2,1,2}\rho_{2,1}\rho_{1,2} + W_{2,1,2,1}\rho_{2,1}\rho_{1,2}\Big) = -\frac{U_{22}}{(2+2S)^2} \\
E_{X,31} &= -\frac{1}{2}\sum_{R\neq R'} 4 \sum_{\alpha,\beta,\gamma\in R}\sum_{\delta\in R'} W_{\alpha,\beta,\gamma,\delta}\rho_{\delta,\alpha}\rho_{\gamma,\beta} \\
&= -\frac{1}{2}4\Big(W_{1,1,1,2}\rho_{2,1}\rho_{1,1} + W_{2,2,2,1}\rho_{1,2}\rho_{2,2}\Big) = -\frac{4U_{31}}{(2+2S)^2}
\end{aligned} \tag{A.31}$$

The following data have been calculated using the exact atomic orbitals for the hybrid correction. The lattice constant has been relaxed with the PBE functional for E_{PW}=30 Ry and $c_{dual} = 2$. The eneergies and matrix elements have been obtained for E_{PW}=50 Ry and $c_{dual} = 4$.

	PBE	PAW-HF	analytic HF
d_0	1.133 Å	=	=
E_{tot}	-0.6982656 H	-0.860456 H	
E_{kin}	0.599825 H	0.599825 H	
E_H	-0.966203 H	-0.966203 H	
E_{xc}	-0.331888 H	-0.331888 H	
ΔE_X	0	-0.162191 H	
$\Delta E_{kin\psi}$	0	0.014980 H	
$q_{on}/2$	?	0.31971	0.322838
q_{off}	?	0.35090	0.354322
$q_{on} + q_{off}$	?	0.99034	1.
ϵ_b	-18.488 eV	-28.138 eV	
ϵ_a	-8.476 eV	-5.727 eV	
$E_{X,on}/2$	–	-0.03194 H	-0.032570 H
$E_{DC,on}/2$		0.02962 H	
$E_{X,off}$	–	-0.15755 H	-0.160616 H
$E_{X,on+off}$	–	-0.22143 H	-0.225757 H
$E_{X,22}$	–		-0.042615 H
$E_{X,31}$	–		-0.118001 H
U_{on}			0.625000 H
U_{22}		+0.409187 H	0.408878 H
U_{31}		0.283071 H	0.283045 H
S		0.548777 H	0.548761 H

Appendix B

Definition of solid Hankel functions

The solid Hankel function has the form

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

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

- the function

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

  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

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

  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

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

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

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

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[**?**] in their Eq. 10.2.4.

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

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

B.1 Modified spherical Bessel functions

The modified spherical Bessel functions of the first kind obey (Abramowitz 10.2.1)

$$\begin{aligned} x^2\partial_x^2 + 2x\partial_x - \Big(x^2+\ell(\ell+1)\Big)w(x) = 0 \\ \Rightarrow \quad \Big(\frac{1}{x}\partial_x^2 x - \frac{\ell(\ell+1)}{x^2} - 1\Big)w(x) = 0 \end{aligned} \tag{B.7}$$

The regular solutions are modified bessel functions of the first kind. (abramowitz 10.2.2, abramowitz 10.2.13)

$$\begin{aligned} j_0(x) &= \sqrt{\frac{\pi|}{2x}}I_{\frac{1}{2}}(x) = \frac{\sinh(x)}{x} \\ j_1(x) &= \sqrt{\frac{\pi|}{2x}}I_{\frac{3}{2}}(x) = \frac{x\cosh(x)-\sinh(x)}{x^2} \\ j_2(x) &= \sqrt{\frac{\pi|}{2x}}I_{\frac{5}{2}}(x) = \frac{x^2\sinh(x)-3x\cosh(x)+3\sinh(x)}{x^3} \end{aligned} \tag{B.8}$$

They have the leading order (abramowitz 10.2.5)

$$j_\ell(x) = \frac{x^\ell}{(2\ell+1)!!} + O(x^{\ell+2}) \tag{B.9}$$

The irregular solutions are the **modified Bessel functions of the third kind** (abramowitz 10.2.4, abramowitz 10.2.17) $\frac{\pi}{2}h_\ell(x)$. We will name $h_\ell(x)$ Hankel function.

$$\begin{aligned} \frac{\pi}{2}h_0(x) &= \sqrt{\frac{\pi}{2x}}K_{\frac{1}{2}}(x) = \frac{\pi}{2}e^{-x}\frac{1}{x} \\ \frac{\pi}{2}h_1(x) &= \sqrt{\frac{\pi}{2x}}K_{\frac{3}{2}}(x) = \frac{\pi}{2}e^{-x}\frac{1+x}{x^2} \\ \frac{\pi}{2}h_2(x) &= \sqrt{\frac{\pi}{2x}}K_{\frac{5}{2}}(x) = \frac{\pi}{2}e^{-x}\frac{x^2+3x+3}{x^3} \end{aligned} \tag{B.10}$$

They have the leading order (abramowitz 10.2.6,abramowitz 10.2.4))

$$\frac{\pi}{2}h_\ell(x) = \frac{\pi}{2}\frac{(2\ell-1)!!}{x^{\ell+1}} + \dots \tag{B.11}$$

B.2 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[**?**]. He uses the theorem[**?**] that supposedy goes back to Kasterin (N. Kasterin, Proc. Acad. Sci Amsterdam 6, 460 (1897/98)); see Seegall[**?**], Eq. B4)

$$h_\ell^{(1)}(\kappa r)Y_{\ell,m}(\vec{r}) = i^{-\ell}\mathcal{Y}_{\ell,m}(\vec{\nabla}_r)h_0^{(1)}(\kappa r) \tag{B.12}$$

where $h_\ell^{(1)}(x)$ i the spherical Hankel function of the first kind (see Eq. B.18 below) and where (Eq. B5 of Segall[**?**])

$$\mathcal{Y}_{\ell,m}(\vec{\nabla}) = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\left(\frac{1}{ik}\right)^{|m|}\left(\partial_x \pm i\partial_y\right)\mathcal{P}_\ell^{|m|}\left(\frac{1}{ik}\partial_z\right) \tag{B.13}$$

where the positive sign applies for nonzero m and the negative sign for negative m. Furthermore (see Segall[**?**] 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[**?**] refers in his Eq. B7 to Morse and Feshbach[**?**] (part II, p. 1574) for

$$h_0^{(1)}(\kappa|\vec{r}-\vec{r'}|) = 4\pi\sum_L\left(h_\ell^{(1)}(\kappa|\vec{r'}|)Y_L(\vec{r'})\right)j_\ell(\kappa|\vec{r}|)Y_L^*(\vec{r}) \tag{B.14}$$

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

The two equations, Eq. B.12 and Eq. B.14, can be combined into

$$\begin{aligned}
h_\ell^{(1)}(\kappa|\vec{r}|)Y_{\ell,m}(\vec{r}) &\overset{\text{Eq. B.12}}{=} i^{-\ell}\mathcal{Y}_{\ell,m}(\vec{\nabla}_r)h_0^{(1)}(\kappa|\vec{r}|)\\
&= \quad i^{-\ell}\mathcal{Y}_{\ell,m}(\vec{\nabla}_r)h_0^{(1)}(\kappa|(\vec{r}-\vec{R})+\vec{R}|)\\
&\overset{\text{Eq. B.14}}{=} i^{-\ell}\mathcal{Y}_{\ell,m}(\vec{\nabla}_r)\left[4\pi\sum_{L'}\left(h_{\ell'}^{(1)}(\kappa|\vec{R}|)Y_{L'}(-\vec{R})\right)j_{\ell'}(\kappa|\vec{r}-\vec{R}|)Y_{L'}^*(\vec{r}-\vec{R})\right]\\
&\overset{\text{Eq. B.16}}{=} 4\pi\sum_{L'}\left(i^{-\ell}\mathcal{Y}_{\ell,m}(\vec{\nabla}_R)h_{\ell'}^{(1)}(\kappa|\vec{R}|)Y_{L'}(-\vec{R})\right)j_{\ell'}(\kappa|\vec{r}-\vec{R}|)Y_{L'}^*(\vec{r}-\vec{R})
\end{aligned}$$

Here we used that

$$\vec{\nabla}_r\left[f(\vec{R})g(\vec{r}-\vec{R})\right] = f(\vec{R})\vec{\nabla}_r g(\vec{r}-\vec{R}) = -f(\vec{R})\vec{\nabla}_R g(\vec{r}-\vec{R}) \tag{B.15}$$

$$= -\underbrace{\vec{\nabla}_R\overbrace{\left[f(\vec{R})g(\vec{r}-\vec{R})\right]}^{h(\vec{r})}}_{=0} + \left[\vec{\nabla}_R f(\vec{R})\right]g(\vec{r}-\vec{R})\Big] \tag{B.16}$$

We summarize the final result

CONDITION FOR STRUCTURE CONSTANTS (POSITIVE ENERGIES)

$$h_\ell^{(1)}(\kappa|\vec{r}|)Y_{\ell,m}(\vec{r}) = 4\pi \sum_{L'} \left(i^{-\ell} \mathcal{Y}_{\ell,m}(\vec{\nabla}_R) h_{\ell'}^{(1)}(\kappa|\vec{R}|) Y_{L'}(-\vec{R}) \right) j_{\ell'}(\kappa|\vec{r}-\vec{R}|) Y_{L'}^*(\vec{r}-\vec{R}) \tag{B.17}$$

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

$$h_\ell^{(1)}(x) \overset{AS10.1.1}{=} j_\ell(x) + i y_\ell(x) \overset{AS10.1.26}{=} x^\ell \left(-\frac{1}{x}\partial_x \right)^\ell \frac{\sin(x) - i\cos(x)}{x} \tag{B.18}$$

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.

$$S_{R',L',R,L} = -4\pi \sum_{L''} H_{L''}^B(\vec{R}' - \vec{R}) C_{L,L'',L} \left\{ \begin{array}{c} (-1)^{\ell'}(-ik)^{\ell+\ell'-\ell''} \\ (-1)^{\ell'}\delta_{\ell+\ell',\ell''} \\ (-1)^{\ell'}\kappa^{\ell+\ell'-\ell''} \end{array} \right\} \tag{B.19}$$

B.3 Consistency checks

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

$$K_{\vec{0},L}^\infty(\vec{r}) = (2\ell-1)!! \frac{1}{|\vec{r}|^{\ell+1}} Y_L(\vec{r}) \tag{B.20}$$

$$J_{\vec{0},L}(\vec{r}) = \frac{1}{(2\ell+1)!!} |\vec{r}|^\ell Y_L(\vec{r}) \tag{B.21}$$

The explicit form of the first few is

$$K_{\vec{0},s}^\infty(\vec{r}) = \frac{1}{\sqrt{4\pi}} \frac{1}{|\vec{r}|} \tag{B.22}$$

$$K_{\vec{0},p_x}^\infty(\vec{r}) = \sqrt{\frac{3}{4\pi}} \frac{x}{|\vec{r}|^3} \tag{B.23}$$

$$J_{\vec{0},s}(\vec{r}) = \frac{1}{\sqrt{4\pi}} \tag{B.24}$$

$$J_{\vec{0},p_x}(\vec{r}) = \frac{1}{3}\sqrt{\frac{3}{4\pi}} x \tag{B.25}$$

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

$$K^{\infty}_{\vec{0},s}(\vec{r}) = -S_{\vec{0},s;\vec{R},s} J_s(\vec{r}-\vec{R}) \\ -S_{\vec{0},s;\vec{R},p_x} J_{p_x}(\vec{r}-\vec{R}) - S_{\vec{0},s;\vec{R},p_y} J_{p_y}(\vec{r}-\vec{R}) - S_{\vec{0},s;\vec{R},p_z} J_{p_z}(\vec{r}-\vec{R}) \tag{B.26}$$

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

$$K^{\infty}_{\vec{0},s}(\vec{R}) = \frac{1}{\sqrt{4\pi}}\frac{1}{|\vec{R}|} = -\underbrace{\left(-\frac{1}{|\vec{R}|}\right)}_{S_{\vec{0},s,\vec{R},s}} \underbrace{\frac{1}{\sqrt{4\pi}}}_{J_{\vec{R},s}(\vec{R})} \tag{B.27}$$

$$\partial_x|_{\vec{R}}\, K^{\infty}_{\vec{0},s} = -\frac{1}{\sqrt{4\pi}}\frac{X}{|\vec{R}|^3} = -\underbrace{\sqrt{3}\frac{X}{|\vec{R}|^3}}_{S_{\vec{0},s;\vec{R},p_x}} \underbrace{\frac{1}{3}\sqrt{\frac{3}{4\pi}}}_{\partial_x J_{\vec{R},p_x}(\vec{R})} \tag{B.28}$$

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

$$\partial_x|_{\vec{R}}\, K^{\infty}_{\vec{0},p_x} = \sqrt{\frac{3}{4\pi}}\left(\frac{1}{|\vec{R}|^3} - 3\frac{X^2}{|\vec{R}|^5}\right) = -\underbrace{3\frac{3X^2-\vec{R}^2}{|\vec{R}|^2}}_{S_{\vec{0},p_x,\vec{R},p_x}} \underbrace{\frac{1}{3}\sqrt{\frac{3}{4\pi}}|\vec{R}|^{-3}}_{\partial_x|_{\vec{R}} J_{\vec{R},p_x}} \tag{B.29}$$

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

$$\boldsymbol{S}_{\vec{0},\vec{R}} = \begin{pmatrix} -|\vec{R}|^{-1} & \sqrt{3}X/|\vec{R}|^3 \\ -\sqrt{3}X/|\vec{R}|^3 & 3[3X^2/R^2-1] \end{pmatrix} \tag{B.30}$$

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

$$S_{RL,R'L'} = (-1)^{\ell'+1} 4\pi \sum_{L''} C_{L,L',L''} H_{L''}(\vec{R}'-\vec{R}) \delta^{\ell+\ell'-\ell''} \tag{B.31}$$

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

The structure constants obtained from this equation are

$$
\begin{aligned}
S_{\vec{0},s;\vec{R},s} &= (-1)4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{sss}} \cdot \underbrace{\frac{1}{\sqrt{4\pi}} \frac{1}{|\vec{R}|}}_{H_s(\vec{R})} = -\frac{1}{|\vec{R}|} \\
S_{\vec{0},s;\vec{R},p_x} &= 4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,p_x}} \underbrace{\sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3}}_{H_{p_x}(\vec{R})} = \sqrt{3} \frac{X}{|\vec{R}|^3} \\
S_{\vec{0},p_x;\vec{R},s} &= (-1)4\pi \underbrace{\frac{1}{\sqrt{4\pi}}}_{C_{p_x,s,s}} \sqrt{\frac{3}{4\pi}} \frac{X}{|\vec{R}|^3} = -\sqrt{3} \frac{X}{|\vec{R}|^3} \\
S_{\vec{0},p_x;\vec{R},p_x} &= 4\pi \underbrace{\frac{1}{\sqrt{5\pi}}}_{C_{p_x,p_x,d_{3x^2-r^2}}} \underbrace{\overbrace{\sqrt{\frac{5}{16\pi}} \frac{3X^2 - R^2}{|\vec{R}|^2}}^{Y_{3x^2-r^2}} \frac{3}{|\vec{R}|^3}}_{H_{3x^2-r^2}(\vec{R})} = 3 \frac{3X^2 - R^2}{|R^5|}
\end{aligned}
\tag{B.32}
$$

For Gaunt coefficients see footnote.[2]

[2]

$$
\begin{aligned}
Y_{p_x} Y_{p_x} = \frac{3}{4\pi} \frac{x^2}{r^2} = \frac{1}{4\pi} \frac{x^2}{r^2} + \frac{1}{4\pi} \frac{3x^2 - r^2}{r^2} = \frac{1}{\sqrt{4\pi}} Y_s + \frac{1}{4\pi} \sqrt{\frac{16\pi}{5}} Y_{3x^2-r^2} = \frac{1}{\sqrt{4\pi}} Y_s + \sqrt{\frac{1}{5\pi}} Y_{3x^2-r^2} \\
\Rightarrow C_{p_x,p_x,s} = \frac{1}{\sqrt{4\pi}} \qquad \text{and} \qquad C_{p_x,p_x,d_{3x^2-r^2}} = \frac{1}{\sqrt{5\pi}}
\end{aligned}
\tag{B.33}
$$

Appendix C

Bloch theorem revisited

The Bloch states are eigenstates of the discrete lattice translation

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

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

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

This eigenvalue equation can be recast into the form

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

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

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

with

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

Bloch theorem in a local orbital basis

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

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

Density matrix

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

Appendix D

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 E

Double counting

E.1 Other double-counting schemes

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

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)[**?**] and the other is called fully localized limit (FLL)[**?**].

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

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

with

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

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

Nekrasov, Pavlov Sadovskii scheme

Nekrasov et al.[**?**] 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

$$E^{DC} = E_{xc}[n_t - n_{corr}] - E_{xc}[n_t] \tag{E.3}$$

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

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

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

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

and an expression for the kinetic-energy correction

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

as well as the potential energy of exchange and correlation

$$U_{xc} = \frac{1}{2} \sum_{R,R'} \int d^3r \int d^3r' \left(\frac{n_R(\vec{r})}{n(\vec{r})}\right) \left(n(\vec{r}) \frac{e^2 \int_0^1 d\lambda\, h_{\lambda=1}(\vec{r},\vec{r'})}{4\pi\epsilon|\vec{r}-\vec{r'}|}\right) \left(\frac{n_{R'}(\vec{r'})}{n(\vec{r'})}\right) \tag{E.7}$$

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.

Only local terms

The equations above reproduce the full exchange correlation energy, respectively the kinetic energy correction as double sum over local terms.

If we employ the local approximation, only the diagonal terms in R, R' need to be considered. Thus, a double-counting correction for a set of correlated orbitals, which contribute n_R to the total density would be

$$E_{dc} = -\frac{1}{2}\sum_R \int d^3r \int d^3r' \left(\frac{n_R(\vec{r})}{n(\vec{r})}\right)\left(n(\vec{r})\frac{e^2\int_0^1 d\lambda\ h_\lambda(\vec{r},\vec{r'})}{4\pi\epsilon|\vec{r}-\vec{r'}|}\right)\left(\frac{n_R(\vec{r'})}{n(\vec{r'})}\right) \tag{E.8}$$

This integral can be approximated further as

$$E_{xc} = -\frac{1}{2}\sum_R \int d^3r\ n(\vec{r})\epsilon[n(\vec{r})]\left(\frac{n_R(\vec{r})}{n(\vec{r})}\right)^2 \tag{E.9}$$

E.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

$$\hat{W} = \frac{1}{2}\sum_{i,j,k,l} W_{i,j,l,k}\hat{c}_i^\dagger\hat{c}_j^\dagger\hat{c}_k\hat{c}_l \tag{E.10}$$

with

$$\begin{aligned} W_{i,j,k,l} &= \int d^4x \int d^4x' \ \frac{e^2\chi_i^*(\vec{x})\chi_j^*(\vec{x'})\chi_k(\vec{x})\chi_l(\vec{x})}{4\pi\epsilon_0|\vec{r}-\vec{r'}|} \\ &= \delta_{\sigma_i,\sigma_k}\delta_{\sigma_j,\sigma_l}\int d^3r \int d^3r' \ \frac{e^2\phi_i^*(\vec{r})\phi_j^*(\vec{r'})\phi_k(\vec{r})\phi_l(\vec{r})}{4\pi\epsilon_0|\vec{r}-\vec{r'}|} = \delta_{\sigma_i,\sigma_k}\delta_{\sigma_j,\sigma_l}U_{i,j,k,l} \end{aligned} \tag{E.11}$$

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

$$W_{i,j,k,l} = W_{j,i,l,k} = W^*_{k,l,i,j} = W^*_{l,k,j,i} \tag{E.12}$$

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

$$|\Phi_0\rangle = \prod_n \left(\hat{a}_n^\dagger\right)^{\sigma_n}|\mathcal{O}\rangle \tag{E.13}$$

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

$$\hat{a}_n^\dagger = \sum_j \hat{c}_j^\dagger\langle\pi_j|\psi_n\rangle \tag{E.14}$$

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

$$\sum_n \hat{a}_n^\dagger \langle \psi_n | \chi_i \rangle = \sum_j \hat{c}_j^\dagger \underbrace{\langle \pi_j | \underbrace{\sum_n |\psi_n\rangle\langle\psi_n|}_{=1} |\chi_i\rangle}_{\delta_{i,j}} = \hat{c}_i^\dagger \tag{E.15}$$

$$\begin{aligned}
\langle \Phi | \hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_o \hat{a}_p | \Phi \rangle &= \delta_{m,o}\delta_{n,p} \langle \Phi | \hat{a}_m^\dagger \underbrace{\hat{a}_n^\dagger \hat{a}_m}_{\delta_{m,n} - \hat{a}_m \hat{a}_n^\dagger} \hat{a}_n | \Phi \rangle + \delta_{m,p}\delta_{n,o} \langle \Phi | \hat{a}_m^\dagger \underbrace{\hat{a}_n^\dagger \hat{a}_n \hat{a}_m}_{-(\delta_{m,n} - \hat{a}_m \hat{a}_n^\dagger)\hat{a}_n} | \Phi \rangle \\
&\quad - \delta_{m,p}\delta_{n,o}\delta_{m,n} \langle \Phi | \hat{a}_m^\dagger \hat{a}_m^\dagger \underbrace{\hat{a}_m \hat{a}_m}_{=0} | \Phi \rangle \\
&= \delta_{m,o}\delta_{n,p} \Big[\delta_{m,n} \langle \Phi | \hat{a}_m^\dagger \hat{a}_n | \Phi \rangle - \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle \Big] \\
&\quad - \delta_{m,p}\delta_{n,o} \Big[\delta_{m,n} \langle \Phi | \hat{a}_m^\dagger \hat{a}_n | \Phi \rangle - \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle \Big] \\
&= -\delta_{m,o}\delta_{n,p} \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle + \delta_{m,p}\delta_{n,o} \langle \Phi | \hat{a}_m^\dagger \hat{a}_m | \Phi \rangle \langle \Phi | \hat{a}_n^\dagger \hat{a}_n | \Phi \rangle \\
&= f_m f_n \Big[\delta_{m,o}\delta_{n,p} - \delta_{m,p}\delta_{n,o} \Big]
\end{aligned} \tag{E.16}$$

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

Now we can evaluate the matrix elements for the interaction as

$$\begin{aligned}
\langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l | \Phi_0 \rangle &= \sum_{m,n,o,p} \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \langle \Phi_0 | \hat{a}_m^\dagger \hat{a}_n^\dagger \hat{a}_o \hat{a}_p | \Phi_0 \rangle \langle \chi_k | \psi_o \rangle \langle \chi_l | \psi_p \rangle \\
&= \sum_{m,n,o,p} \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \Big[f_m f_n \Big[\delta_{m,o}\delta_{n,p} - \delta_{m,p}\delta_{n,o} \Big] \Big] \langle \chi_k | \psi_o \rangle \langle \chi_l | \psi_p \rangle \\
&= \sum_{m,n} f_m f_n \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \langle \chi_k | \psi_m \rangle \langle \chi_l | \psi_n \rangle - \sum_{m,n} f_m f_n \langle \psi_m | \chi_i \rangle \langle \psi_n | \chi_j \rangle \langle \chi_k | \psi_n \rangle \langle \chi_l | \psi_m \rangle \\
&= \underbrace{\sum_m \langle \chi_k | \psi_m \rangle f_m \langle \psi_m | \chi_i \rangle}_{\rho_{k,i}} \underbrace{\sum_m \langle \chi_l | \psi_n \rangle f_n \langle \psi_n | \chi_j \rangle}_{\rho_{l,j}} - \underbrace{\sum_m \langle \chi_l | \psi_m \rangle f_m \langle \psi_m | \chi_i \rangle}_{\rho_{l,i}} \underbrace{\sum_n \langle \chi_k | \psi_n \rangle f_n \langle \psi_n | \chi_j \rangle}_{\rho_{k,j}} \\
&= \rho_{k,i}\rho_{l,j} - \rho_{l,i}\rho_{k,j} \\
&= \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_k | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_l | \Phi_0 \rangle - \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_l | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_k | \Phi_0 \rangle
\end{aligned} \tag{E.17}$$

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

$$\rho_{i,j} = \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_i | \Phi_0 \rangle = \sum_{m,n} \langle \psi_m | \chi_j \rangle \langle \chi_i | \psi_n \rangle \underbrace{\langle \Phi_0 | \hat{a}_m^\dagger \hat{c}_n | \Phi_0 \rangle}_{\delta_{m,n} f_n} = \sum_n \chi_i | \psi_n \rangle f_n \langle \psi_n | \chi_j \rangle \langle \tag{E.18}$$

$$\begin{aligned}
\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l &= \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l \\
&= \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_k | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_l | \Phi_0 \rangle - \langle \Phi_0 | \hat{c}_i^\dagger \hat{c}_l | \Phi_0 \rangle \langle \Phi_0 | \hat{c}_j^\dagger \hat{c}_k | \Phi_0 \rangle
\end{aligned} \tag{E.19}$$

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

$$\begin{aligned}\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l &= \delta_{j,k} \hat{c}_i^\dagger \hat{c}_l - \hat{c}_i^\dagger \hat{c}_k \hat{c}_j^\dagger \hat{c}_l \\ &= \delta_{j,l} \hat{c}_i^\dagger \hat{c}_k - \hat{c}_i^\dagger \hat{c}_l \hat{c}_j^\dagger \hat{c}_k \end{aligned} \tag{E.20}$$

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

$$\begin{aligned}\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_k \hat{c}_l = -\hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_l \hat{c}_k = -\hat{c}_j^\dagger \hat{c}_i^\dagger \hat{c}_k \hat{c}_l = \hat{c}_j^\dagger \hat{c}_i^\dagger \hat{c}_l \hat{c}_k \\ = \delta_{j,k} \hat{c}_i^\dagger \hat{c}_l - \hat{c}_i^\dagger \hat{c}_k \hat{c}_j^\dagger \hat{c}_l = \end{aligned} \tag{E.21}$$

$$\begin{aligned} &= \frac{1}{2} \sum_{i,j,k,l} W_{i,j,l,k} \frac{1}{2} \left[-\left(\hat{c}_i^\dagger \hat{c}_k \hat{c}_j^\dagger \hat{c}_l - \delta_{k,j} \hat{c}_i^\dagger \hat{c}_l \right) + \left(\hat{c}_i^\dagger \hat{c}_l \hat{c}_j^\dagger \hat{c}_k - \delta_{j,l} \hat{c}_i^\dagger \hat{c}_k \right) \right] \\ &\overset{i \leftrightarrow l}{=} \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left(\hat{n}_{i,k} \hat{n}_{j,l} - \delta_{k,j} \hat{n}_{i,l} \right) \end{aligned} \tag{E.22}$$

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

$$\begin{aligned} \hat{W}_{MF} &= \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left(\langle \hat{n}_{i,k} \rangle \langle \hat{n}_{j,l} \rangle - \delta_{k,j} \langle \hat{n}_{i,l} \rangle \right) \\ &+ \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left([\hat{n}_{i,k} - \langle \hat{n}_{i,k} \rangle] \langle \hat{n}_{j,l} \rangle + \langle \hat{n}_{i,k} \rangle [\hat{n}_{j,l} - \langle \hat{n}_{j,l} \rangle] - \delta_{k,j} [\hat{n}_{i,l} - \langle \hat{n}_{i,l} \rangle] \right) \\ &= \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left(\hat{n}_{i,k} \langle \hat{n}_{j,l} \rangle + \langle \hat{n}_{i,k} \rangle \hat{n}_{j,l} - \delta_{k,j} \hat{n}_{i,l} - \langle \hat{n}_{i,k} \rangle \langle \hat{n}_{j,l} \rangle \right) \end{aligned} \tag{E.23}$$

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[1] from the density-matrix functional with the density matrix $\rho_{i,j} = \langle \hat{c}_i^\dagger \hat{c}_j \rangle$

$$E_{AMF}^{DC} = \frac{1}{2} \sum_{i,j,k,l} \frac{W_{i,j,k,l} - W_{i,j,l,k}}{2} \left(\rho_{i,k} \rho_{j,l} - \delta_{k,j} \rho_{i,l} \right) \tag{E.24}$$

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

$$\begin{aligned} E_{AMF}^{DC} &\approx \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{i,j} \frac{W_{i,j,i,j} - W_{i,j,j,i}}{2} \rho_{i,i} \rho_{j,j} - \frac{1}{2} \sum_{i,j} \frac{W_{i,j,i,j} - W_{i,j,j,i}}{2} \rho_{i,i} \\ &= \frac{1}{2} \sum_{i \neq j} \frac{W_{i,j,j,i} - W_{i,j,i,j}}{2} \rho_{i,i} (\rho_{j,j} + 1) \end{aligned} \tag{E.25}$$

[1] 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.

$$\begin{aligned}
E^{DC}_{AMF} &\approx \frac{1}{2}\sum_{m,m'} \frac{U_{m,m',m,m'} - U_{m,m',m',m}\delta_{\sigma,\sigma'}}{2} n_{m,\sigma} n_{m',\sigma'} \\
&\quad - \frac{1}{2}\sum_{i}\left(\sum_{m',\sigma'} \frac{U_{m,m',m',m} - U_{m,m',m,m'}\delta_{\sigma,\sigma'}}{2}\right) n_{m,\sigma} \\
&= \frac{1}{2}\sum_{\sigma}\sum_{m} \frac{U_{m,m,m,m}}{2} n_{m,\sigma} n_{m,\bar{\sigma}} \\
&\quad + \frac{1}{2}\sum_{m\neq m'}\sum_{\sigma,\sigma'} \frac{U_{m,m',m,m'} - U_{m,m',m',m}\delta_{\sigma,\sigma'}}{2} n_{m,\sigma} n_{m',\sigma'} \\
&\quad - \frac{1}{2}\sum_{i}\left(\sum_{m'} \frac{2U_{m,m',m',m} - U_{m,m',m,m'}}{2}\right) n_{m,\sigma}
\end{aligned} \tag{E.26}$$

E.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[**?**] (see Eq. 5 of Shick et al.)

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

$$J := U - \frac{1}{2\ell(2\ell+1)}\sum_{m_1,m_2} (U_{m_1,m_2,m_1,m_2} - U_{m_1,m_2,m_2,m_1}) \tag{E.28}$$

where the Coulomb matrix elements are

$$U_{i,j,k,l} = \int d^3r \int d^3r' \; \frac{e^2 \chi_i^*(\vec{r})\chi_j^*(\vec{r'})\chi_k(\vec{r})\chi_l(\vec{r'})}{4\pi\epsilon_0|\vec{r}-\vec{r'}|} \tag{E.29}$$

The indices used here are spatial-orbital indices.

Appendix F

Numerical two-center integrals

Numerical two-center integrals

This section is a copy from my notes `methods` (In section "Mapping onto local orbitals").

The Gaussian fit was apparentluy not very accurate. Therefore, I am using a numerical method for two-dimensional integration. The method is the the adaptive algorithm of Genz and Malik[**?**], which rests on the work of van Dooren and de Riddler[**?**]. This method refines the integral obtained by Gauss quadrature over a rectangle by repeatedly bisecting the rectangles until the total estimated error falls below a given tolerance.

F.1 Variable transforms

The first step is to transform the volume integral into an integral over a two-dimensional area:

First we consider an interatomic distance vector which points into the positive z-direction and has length d. We consider the integral

$$I = \int d^3r \; f(|\vec{r}|)Y^*_{\ell,m}(\vec{r})g(|\vec{r} - d\vec{e}_z|)Y_{\ell',m'}(\vec{r} - d\vec{e}_z)$$

F.1.1 Cylindrical coordinates

The first step is a transformation into cylindrical coordinates.

$$\begin{aligned} x(\rho, \phi, z) &= \rho\cos(\phi) \\ y(\rho, \phi, z) &= \rho\sin(\phi) \\ z(\rho, \phi, z) &= z \end{aligned}$$

The Jacobian is

$$J = \det\left|\frac{d(x, y, z)}{d(\rho, \phi, z)}\right| = \det\begin{vmatrix} \cos(\phi) & -\rho\sin(\phi) & 0 \\ \sin(\phi) & \rho\cos(\phi) & 0 \\ 0 & 0 & 1 \end{vmatrix} = \rho$$

so that the integral turns into

$$
\begin{aligned}
I &= \int_{-\infty}^{\infty} dz \int_0^{2\pi} d\phi \int_0^{\infty} d\rho\ \rho\ f(|\vec{r}|) Y^*_{\ell,m}(\vec{r})\ g(|\vec{r} - d\vec{e}_z|) Y_{\ell',m'}(\vec{r} - d\vec{e}_z) \\
&= 2\pi\delta_{m,m'} \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} \sqrt{\frac{2\ell'+1}{4\pi}\frac{(\ell'-m)!}{(\ell'+m)!}} \\
&\quad \times \int_{-\infty}^{\infty} dz \int_0^{\infty} d\rho\ \rho\ P^m_\ell\left(\frac{z}{\sqrt{\rho^2+z^2}}\right) P^m_{\ell'}\left(\frac{z-d}{\sqrt{\rho^2+(z-d)^2}}\right) f(|\vec{r}|)\ g(|\vec{r} - d\vec{e}_z|)
\end{aligned}
$$

F.1.2 Distance from the two atoms

Next, we transform the two-dimensional coordinate system into one, where the two coordinates are the distances r_a, r_b from the two atoms.

$$
\begin{aligned}
z + z' &= d \\
z^2 + \rho^2 &= r_a^2 \\
z'^2 + \rho^2 &= r_b^2
\end{aligned}
$$

We obtain

$$
z^2 - z'^2 = r_a^2 - r_b^2 \qquad \Rightarrow \qquad \underbrace{(z - z')}_{2z_a - d}\underbrace{(z + z')}_{d} = r_a^2 - r_b^2 \qquad \Rightarrow \qquad 2dz - d^2 = r_a^2 - r_b^2
$$

$$
\begin{aligned}
\Rightarrow \qquad z &= \frac{1}{2d}(d^2 + r_a^2 - r_b^2) \\
\rho^2 &= r_a^2 - z^2 = r_a^2 - \frac{1}{4d^2}\left(d^2 + r_a^2 - r_b^2\right)^2 \\
\Rightarrow \qquad \rho &= \frac{1}{2d}\sqrt{4d^2 r_a^2 - \left(d^2 + r_a^2 - r_b^2\right)^2}
\end{aligned}
$$

Thus the transformation is

$$
\begin{aligned}
\rho(r_a, r_b) &= \frac{1}{2d}\sqrt{4d^2 r_a^2 - \left(d^2 + r_a^2 - r_b^2\right)^2} \\
z(r_a, r_b) &= \frac{1}{2d}(d^2 + r_a^2 - r_b^2)
\end{aligned}
$$

Let us work out the derivatives for the Jacobian

$$
\begin{aligned}
\frac{\partial\rho}{\partial r_a} &= \frac{1}{2d}\frac{1}{2\sqrt{\dots}}\left(4d^2 - 2(d^2 + r_a^2 - r_b^2)\right) 2r_a = \frac{1}{4d^2}\frac{r_a}{\rho}\left(4d^2 - 2(d^2 + r_a^2 - r_b^2)\right) \\
&= \frac{r_a}{2\rho}\left(1 - \frac{r_a^2 - r_b^2}{2d^2}\right) \\
\frac{\partial\rho}{\partial r_b} &= \frac{r_b}{2\rho}\left(1 + \frac{r_a^2 - r_b^2}{2d^2}\right) \\
\frac{\partial z}{\partial r_a} &= +\frac{r_a}{d} \\
\frac{\partial z}{\partial r_b} &= -\frac{r_b}{d}
\end{aligned}
$$

The Jacobian for the transformation is

$$\begin{aligned} J = \det\left|\frac{\partial(\rho,z)}{\partial(r_a,r_b)}\right| &= \left|\frac{\partial\rho}{\partial r_a}\frac{\partial z}{\partial r_b} - \frac{\partial\rho}{\partial r_b}\frac{\partial z}{\partial r_a}\right| \\ &= \left|\frac{r_a}{2\rho}\left(1-\frac{r_a^2-r_b^2}{2d^2}\right)\left(-\frac{r_b}{d}\right) - \frac{r_b}{2\rho}\left(1+\frac{r_a^2-r_b^2}{2d^2}\right)\frac{r_a}{d}\right| \\ &= \frac{r_a}{2\rho}\left(1-\frac{r_a^2-r_b^2}{2d^2}\right)\frac{r_b}{d} + \frac{r_b}{2\rho}\left(1+\frac{r_a^2-r_b^2}{2d^2}\right)\frac{r_a}{d} \\ &= \frac{r_a r_b}{\rho d} \end{aligned}$$

Thus our integral obtains the form

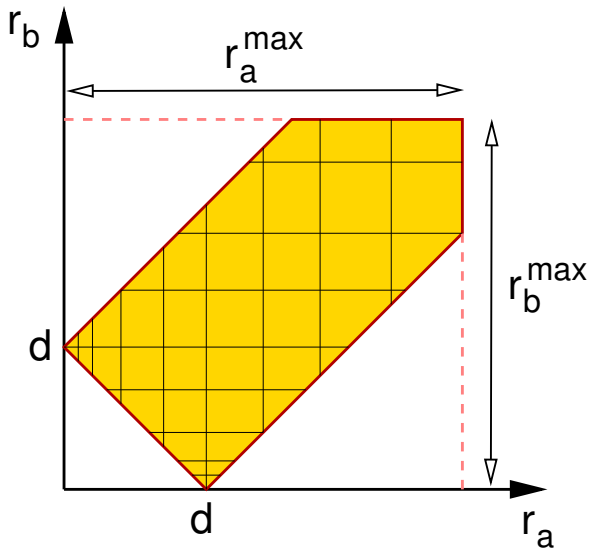
$$\begin{aligned} I &= 2\pi\delta_{m,m'}\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\sqrt{\frac{2\ell'+1}{4\pi}\frac{(\ell'-m)!}{(\ell'+m)!}} \\ &\quad\times\int_{-\infty}^{\infty}dz\int_0^{\infty}d\rho\;\rho\,P_\ell^m\!\left(\frac{z}{\sqrt{z^2+\rho^2}}\right)P_{\ell'}^m\!\left(\frac{z-d}{\sqrt{(z-d)^2+\rho^2}}\right)f(|\vec{r}|)g(|\vec{r}-d\vec{e}_z|) \\ &= 2\pi\delta_{m,m'}\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\sqrt{\frac{2\ell'+1}{4\pi}\frac{(\ell'-m)!}{(\ell'+m)!}} \\ &\quad\times\int_0^{\infty}dr_a\int_0^{\infty}dr_b\;\rho\cdot\frac{r_a r_b}{\rho d}\;P_\ell^m\!\left(\frac{z}{r_a}\right)P_{\ell'}^m\!\left(\frac{z-d}{r_b}\right)f(r_a)g(r_b) \\ &= 2\pi\delta_{m,m'}\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\sqrt{\frac{2\ell'+1}{4\pi}\frac{(\ell'-m)!}{(\ell'+m)!}} \\ &\quad\times\frac{1}{d}\int dr_a\int dr_b\;P_\ell^m\!\left(\frac{r_a^2-r_b^2+d^2}{2dr_a}\right)P_{\ell'}^m\!\left(\frac{r_a^2-r_b^2-d^2}{2dr_b}\right)\Big[r_a f(r_a)\Big]\Big[r_b g(r_b)\Big] \\ &\overset{r=xd}{=} 2\pi\delta_{m,m'}\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\sqrt{\frac{2\ell'+1}{4\pi}\frac{(\ell'-m)!}{(\ell'+m)!}} \\ &\quad\times\int_0^{\infty}dx_a\int_0^{\infty}dx_b\;P_\ell^m\!\left(\frac{x_a^2-x_b^2+1}{2x_a}\right)P_{\ell'}^m\!\left(\frac{x_a^2-x_b^2-1}{2x_b}\right)x_a x_b\cdot\Big[d^3 f(x_a d)g(x_b d)\Big] \end{aligned}$$

where we introduced the scaled coordinates

$$x_a = r_a/d \qquad \text{and} \qquad x_b = r_b/d$$

The integration area in (r_a, r_b)-coordinates is limited by the bounds

$$\begin{aligned} r_a + r_b &\geq d \\ |r_a - r_b| &\leq d \\ r_a &\leq r_a^{max} \\ r_b &\leq r_b^{max} \end{aligned}$$



This region is extended to a rectangle limited by

$$d \le r_a + r_b \le max\left(r_a^{\max}, r_b^{\max}\right) \qquad \text{and} \qquad -d \le r_a - r_b \le d$$

Often the **prolate spheroidal coordinate system** is introduced with the variables

$$\zeta(r_a, r_b) = \frac{1}{d}(r_a + r_b) = x_a + x_b$$
$$\eta(r_a, r_b) = \frac{1}{d}(r_a - r_b) = x_a - x_b$$

which essentially turns the integration area by 45°.

F.2 Integration using the adaptive algorithm

For the integration we use the adaptive algorithm of van Dooren and de Riddler[**?** **?**]

F.2.1 Gaussian quadrature on a square

One element of the method is the integration over an rectangle using Gaussian quadrature of 7th and 5th order, such, that the 5th-order algorithm uses the same positions as the 7th-order integration. The comparison of the two integrations provides an error estimate in addition to the integral.

This Gaussian-quadrature scheme containes 17 points for the square[**?**] $[-1,1] \otimes [-1,1]$

$(0,0)$	$(+\lambda_2,0)$ $(-\lambda_2,0)$ $(0,+\lambda_2)$ $(0,-\lambda_2)$	$(+\lambda_3,0)$ $(-\lambda_3,0)$ $(0,+\lambda_3)$ $(0,-\lambda_3)$	$(+\lambda_4,+\lambda_4)$ $(+\lambda_4,-\lambda_4)$ $(-\lambda_4,+\lambda_4)$ $(-\lambda_4,-\lambda_4)$	$(+\lambda_5,+\lambda_5)$ $(+\lambda_5,-\lambda_5)$ $(-\lambda_5,+\lambda_5)$ $(-\lambda_5,-\lambda_5)$
w_1	w_2	w_3	w_4	w_5
w_1'	w_2'	w_3'	w_4'	0

The weights sum up to four, the total area of the square. The weights w_i refer to the 7th order scheme, and the weights w_i' refer to the fifth-order scheme.

The values are

λ_1	λ_2	λ_3	λ_4	λ_5
	$\sqrt{9/70}$	$\sqrt{9/10}$	$\sqrt{9/10}$	$\sqrt{9/19}$
w_1	w_2	w_3	w_4	w_5
-15264/19683	11760/19683	4080/19683	800/19683	6859/19683
w_1'	w_2'	w_3'	w_4'	w_5'
-3884/729	1470/729	130/729	100/729	0

F.2.2 Refining the grid

Once the integral of a square is obtained, the error estimate tells us whether, we need to refine the grid by bisecting the square in use.

We need the information on which of the two ways of bisecting the square is more promising. For this purpose we use the result from the weighted sums according to the description.

points 1st direction	$(-\lambda_2, 0)$	$(-\lambda_3, 0)$	$(0,0)$	$(\lambda_3, 0)$	$(\lambda_2, 0)$
points 2nd direction	$(0, -\lambda_2)$	$(0, -\lambda_3)$	$(0,0)$	$(0, \lambda_3)$	$(0\lambda_2)$
weights	1	$-\left(\frac{\lambda_2}{\lambda_3}\right)^2$	$-2+2\left(\frac{\lambda_2}{\lambda_3}\right)^2$	$-\left(\frac{\lambda_1}{\lambda_3}\right)^2$	1

The direction with the larger absolute value is the next to be bisected.

The rectangles are kept on an ordered stack, where the rectangles are ordered according to the size of the predicted error. The top rectangle with the largest error is replaced by two rectangles covering the same area. The rectangle with the larger error is incorporated into the correct position starting from the top of the stack and proceeding until its error is larger than the next on the stack. Similarly, the rectangle with the smaller error is placed into the correct position starting from the bottom of the stack. For each bisected integral the stack grows by one segment.

The value of the integral and the estimated total error is updated by subtracting the contributions from the removed rectangle and by adding the the values and error estimates for the two new rectangles.

======

To obtain the value of the integrand for a point in the 2-dimensional square $[-1,1]\times[-1,1]$, we use the variable transform

$$\begin{pmatrix} r_a \\ r_b \end{pmatrix} = \begin{pmatrix} d \\ 0 \end{pmatrix} + \begin{pmatrix} r_x \\ r_x \end{pmatrix} \frac{1+p_1}{2} + \begin{pmatrix} -d \\ d \end{pmatrix} \frac{1+p_2}{2}$$

where $r_x = \max(r_a^{max}, r_b^{max})$

r_x is obtained by the condition that the rectangle shall cover the complete area of points with $r_a < r_a^{max}$ and $r_b < r_b^{max}$. Let us determine the values for (p_1, p_2) that correspond to (r_a, r_b).

We obtain

$$\begin{aligned} r_a^{max} &= d + r_x\frac{1+p_1}{2} - d\frac{1+p_2}{2} \qquad \text{and} \qquad r_b^{max} = r_x\frac{1+p_1}{2} + d\frac{1+p_2}{2} \\ \Rightarrow r_a^{max} + r_b^{max} - d &= r_x\underbrace{(1+p_1)}_{<2} \qquad \text{and} \qquad r_b^{max} - r_a^{max} + d = d(1+p_2) \\ \Rightarrow r_x &= \frac{r_a^{max} + r_b^{max} - d}{2} \qquad \text{and} \qquad p_2 = \frac{r_b^{max} - r_a^{max}}{d} \end{aligned}$$

By inspection we observe that there are situations where r_x can be chosen smaller. This is the case when the value of the resulting p_2 coordinate falls out of the allowed range, i.e. when $|r_b^{max} - r_a^{max}| > d$.

F.3 Long-range charge-charge term

Let us consider the Coulomb interaction of two non-overlapping charge distributions $\rho^{(A)}(\vec{r})$ and $\rho^{(B)}(\vec{r})$.

$$V(\vec{d}) = \int d^3r \int d^3r' \frac{e^2\rho^{(A)}(\vec{r})\rho^{(B)}(\vec{r'} - \vec{e}_z d)}{4\pi\epsilon_0|\vec{r} - \vec{r'}|}$$

Wir verwenden die Zerlegung der Poisson Gleichung in Kugelflaechenfunktionen, wa fuer den fernbereich das Potential

$$\begin{aligned} v(\vec{r}) &= \int d^3r' \frac{e^2\rho^{(A)}(\vec{r'})}{4\pi\epsilon_0|\vec{r} - \vec{r'}|} \\ &= \sum_L \frac{4\pi}{2\ell+1}\frac{e^2}{4\pi\epsilon_0}\underbrace{\left[\int d^3r\ \rho(\vec{r})r^\ell Y_L(\vec{r})\right]}_{Q_L^{(A)}}\frac{1}{|\vec{r}|^{\ell+1}}Y_L(\vec{r}) \end{aligned}$$

$$V(\vec{d}) = \frac{e^2}{4\pi\epsilon_0}\sum_L \frac{4\pi Q_L^{(A)}}{2\ell+1}\int d^3r \frac{1}{|\vec{r}|^{\ell+1}}Y_L(\vec{r})\rho^{(B)}(\vec{r'} - \vec{e}_z d)$$

$$\text{with} \qquad Q_L^{(A)} \stackrel{\text{def}}{=} \int d^3r\ \rho^{(A)}(\vec{r})r^\ell Y_L(\vec{r})$$

Next we use the decomposition of Hankel function into offsite-Besselfunctions for $\kappa = 0$.

$$\underbrace{(2\ell-1)!!\frac{1}{|\vec{r}|^{\ell+1}}Y_L(\vec{r})}_{H_L(\vec{r})} = -\sum_{L'}\underbrace{\left[\frac{1}{(2\ell'+1)!!}|\vec{r}-\vec{R}|^{\ell'}Y_{L'}(\vec{r}-\vec{R})\right]}_{J_{L'}(\vec{r}-\vec{R})} \times \underbrace{\left[-4\pi\sum_{L''}\frac{(2\ell''-1)!!}{|\vec{R}|^{\ell''+1}}Y_{L''}(\vec{R})C_{L,L',L''}(-1)^{\ell'}\delta_{\ell+\ell'-\ell''}\right]}_{S^{\dagger}_{R,L'0,L}}$$

$$\frac{1}{|\vec{r}|^{\ell+1}}Y_L(\vec{r}) = \sum_{L'}\left[|\vec{r}-\vec{R}|^{\ell'}Y_{L'}(\vec{r}-\vec{R})\right] \times\left[\sum_{L''}\delta_{\ell+\ell'-\ell''}C_{L,L',L''}\frac{(-1)^{\ell'}4\pi(2\ell''-1)!!}{(2\ell-1)!!(2\ell'+1)!!}\frac{1}{|\vec{R}|^{\ell''+1}}Y_{L''}(\vec{R})\right]$$

The double factorial is defined as

$$n!! = \begin{cases} 1 & \text{for } n = -1, 0 \\ 1\cdot 3\cdot 5\cdots n & \text{for } n > 0 \text{ odd} \\ 2\cdot 4\cdot 6\cdots n & \text{for } n > 0 \text{ even} \end{cases}$$

$$\begin{aligned} V(d) &= \frac{e^2}{4\pi\epsilon_0}\sum_L\frac{4\pi Q_L^{(A)}}{2\ell+1}\int d^3r\frac{1}{|\vec{r}|^{\ell+1}}Y_L(\vec{r})\rho^{(B)}(\vec{r'}-\vec{e}_z d) \\ &= \frac{e^2}{4\pi\epsilon_0}\sum_{L,L'}\frac{4\pi Q_L^{(A)}}{2\ell+1}\left[\sum_{L''}\delta_{\ell+\ell'-\ell''}C_{L,L',L''}\frac{(-1)^{\ell'}4\pi(2\ell''-1)!!}{(2\ell-1)!!(2\ell'+1)!!}\frac{1}{|\vec{d}|^{\ell''+1}}Y_{L''}(\vec{e}_z)\right] \\ &\quad\times\int d^3r\,|\vec{r}-\vec{e}_z d|^{\ell}Y_{L'}(\vec{r}-\vec{e}_z d)\rho^{(B)}(\vec{r'}-\vec{e}_z d) \\ &= \frac{e^2}{4\pi\epsilon_0}\sum_{L,L'}\frac{4\pi Q_L^{(A)}Q_{L'}^{(B)}}{2\ell+1}\left[\sum_{L''}\delta_{\ell+\ell'-\ell''}C_{L,L',L''}\frac{(-1)^{\ell'}4\pi(2\ell''-1)!!}{(2\ell-1)!!(2\ell'+1)!!}\frac{1}{|\vec{d}|^{\ell''+1}}Y_{L''}(\vec{e}_z)\right] \\ &= \frac{e^2}{4\pi\epsilon_0}\sum_{L,L'}\frac{4\pi Q_L^{(A)}Q_{L'}^{(B)}}{2\ell+1}\left[C_{L,L',\ell+\ell',m=0}\frac{(-1)^{\ell'}4\pi(2\ell+2\ell'-1)!!}{(2\ell-1)!!(2\ell'+1)!!}\frac{1}{|\vec{d}|^{\ell+\ell'+1}}Y_{\ell+\ell',m=0}(\vec{e}_z)\right] \\ &= \frac{e^2}{4\pi\epsilon_0}\sum_{L,L'}\frac{Q_L^{(A)}Q_{L'}^{(B)}}{|\vec{d}|^{\ell+\ell'+1}}\left[C_{L,L',\ell+\ell',m=0}\frac{(-1)^{\ell'}(4\pi)^2(2\ell+2\ell'-1)!!}{((2\ell+1)!!(2\ell'+1)!!}Y_{\ell+\ell',m=0}(\vec{e}_z)\right] \end{aligned}$$

If we conly consider monopoles and dipoles, we can use $\bar{Y}_1(\vec{e}_x) = \frac{1}{\sqrt{4\pi}}$, $\bar{Y}_3(\vec{e}_z) = \sqrt{\frac{3}{4\pi}}$ and $\bar{Y}_7(\vec{e}_z) = \sqrt{\frac{5}{4\pi}}$. The Gaunt coefficients needed for Monopole and dipole moments oriented along the z-direction are C_{sss}, $C_{sp_zp_z}$, $C_{p_xp_x,d_{3z^2-r^2}}$,$C_{p_yp_y,d_{3z^2-r^2}}$,$C_{p_zp_z,d_{3z^2-r^2}}$. With

$$\bar{Y}_s\bar{Y}_L = \frac{1}{\sqrt{4\pi}}\bar{Y}_L = C_{szz}\bar{Y}_L \qquad \Rightarrow C_{sss} = C_{sp_zp_z} = \frac{1}{\sqrt{4\pi}}$$

$$\bar{Y}_5 = \sqrt{\frac{15}{16\pi}}\frac{x^2-y^2}{\vec{r}^2} = \sqrt{\frac{15}{16\pi}}\frac{4\pi}{3}(Y^2_{p_x} - Y^2_{p_y})$$
$$\bar{Y}_7 = \sqrt{\frac{5}{16\pi}}\frac{3z^2-\vec{r}^2}{\vec{r}^2} = \sqrt{\frac{5}{16\pi}}\frac{4\pi}{3}(2Y^2_{p_z} - Y^2_{p_x} - Y^2_{p_y})$$
$$\bar{Y}_0 = \frac{1}{\sqrt{4\pi}}\frac{x^2+y^2+z^2}{\vec{r}^2} = \sqrt{\frac{4}{16\pi}}\frac{4\pi}{3}(Y^2_{p_x} + Y^2_{p_y} + Y^2_{p_z})$$
$$\bar{Y}^2_{p_z} = \frac{3}{4\pi}\frac{1}{3}\left(\sqrt{\frac{16\pi}{4}}\bar{Y}_0 + \sqrt{\frac{16\pi}{5}}\bar{Y}_7\right) = \sqrt{\frac{1}{4\pi}}\bar{Y}_0 + \sqrt{\frac{1}{5\pi}}\bar{Y}_7$$
$$\Rightarrow \bar{C}_{p_z p_z d_{3z^2-r^2}} = \frac{1}{\sqrt{5\pi}}$$
$$\bar{Y}^2_{p_x} = \frac{3}{4\pi}\frac{1}{6}\left(2\sqrt{\frac{16\pi}{4}}\bar{Y}_0 - \sqrt{\frac{16\pi}{5}}\bar{Y}_7 + 3\sqrt{\frac{16\pi}{15}}\bar{Y}_5\right) = \sqrt{\frac{1}{4\pi}}\bar{Y}_0 - \sqrt{\frac{1}{20\pi}}\bar{Y}_7 + \sqrt{\frac{3}{20\pi}}\bar{Y}_5$$
$$\Rightarrow \bar{C}_{p_x p_x d_{3z^2-r^2}} = \bar{C}_{p_y p_y d_{3z^2-r^2}} = -\frac{1}{\sqrt{20\pi}}$$

$$V(d) = \frac{e^2}{4\pi\epsilon_0}\sum_{L,L'}\frac{Q^{(A)}_L Q^{(B)}_{L'}}{|\vec{d}|^{\ell+\ell'+1}}\left[C_{L,L',\ell+\ell',m=0}\frac{(-1)^{\ell'}(4\pi)^2(2\ell+2\ell'-1)!!}{((2\ell+1)!!(2\ell'+1)!!}Y_{\ell+\ell',m=0}(\vec{e}_z)\right]$$
$$= \frac{e^2}{4\pi\epsilon_0}\left\{\frac{Q^{(A)}_s Q^{(B)}_s}{|\vec{d}|}\left[\frac{1}{\sqrt{4\pi}}(4\pi)^2\frac{1}{\sqrt{4\pi}}\right]\right.$$
$$+ \frac{Q^{(A)}_s Q^{(B)}_{p_z}}{|\vec{d}|^2}\left[\frac{1}{\sqrt{4\pi}}\frac{(-1)(4\pi)^2}{3}\sqrt{\frac{3}{4\pi}}\right] + \frac{Q^{(A)}_{p_z} Q^{(B)}_s}{|\vec{d}|^2}\left[\frac{1}{\sqrt{4\pi}}\frac{(4\pi)^2}{3}\sqrt{\frac{3}{4\pi}}\right]$$
$$+ \frac{Q^{(A)}_{p_z} Q^{(B)}_{p_z}}{|\vec{d}|^3}\left[\frac{1}{\sqrt{5\pi}}(4\pi)^2\frac{(-1)3}{3\cdot 3}\sqrt{\frac{5}{4\pi}}\right]$$
$$\left. + \frac{Q^{(A)}_{p_x} Q^{(B)}_{p_x} + Q^{(A)}_{p_y} Q^{(B)}_{p_y}}{|\vec{d}|^3}\left[-\frac{1}{\sqrt{20\pi}}(4\pi)^2\frac{(-1)3}{3\cdot 3}\sqrt{\frac{5}{4\pi}}\right]\right\}$$
$$= \frac{e^2}{4\pi\epsilon_0}\left\{\frac{Q^{(A)}_s Q^{(B)}_s}{|\vec{d}|}4\pi + \frac{Q^{(A)}_{p_z} Q^{(B)}_s - Q^{(A)}_s Q^{(B)}_{p_z}}{|\vec{d}|^2}\frac{4\pi}{\sqrt{3}}\right.$$
$$\left. + \frac{Q^{(A)}_{p_z} Q^{(B)}_{p_z}}{|\vec{d}|^3}\left(-4\pi\frac{2}{3}\right) + \frac{Q^{(A)}_{p_x} Q^{(B)}_{p_x} + Q^{(A)}_{p_y} Q^{(B)}_{p_y}}{|\vec{d}|^3}\left[\frac{1}{3}(4\pi)\right]\right\}$$
$$= 4\pi\cdot\frac{e^2}{4\pi\epsilon_0}\left\{\frac{Q^{(A)}_s Q^{(B)}_s}{|\vec{d}|} + \frac{1}{\sqrt{3}}\frac{Q^{(A)}_{p_z} Q^{(B)}_s}{d^2} - \frac{1}{\sqrt{3}}\frac{Q^{(A)}_s Q^{(B)}_{p_z}}{d^2}\right.$$
$$\left. -\frac{2}{3}\frac{Q^{(A)}_{p_z} Q^{(B)}_{p_z}}{|\vec{d}|^3} + \frac{1}{3}\frac{Q^{(A)}_{p_x} Q^{(B)}_{p_x}}{|\vec{d}|^3} + \frac{1}{3}\frac{Q^{(A)}_{p_y} Q^{(B)}_{p_y}}{|\vec{d}|^3}\right\}$$

This expression can also be divided into rotationally invariant repulsive terms and axial terms

that may be attractive or repulsive.

$$V(d) = 4\pi \cdot \frac{e^2}{4\pi\epsilon_0}\left\{ \frac{Q_s^{(A)}Q_s^{(B)}}{|\vec{d}|} + \frac{1}{3}\frac{Q_{p_x}^{(A)}Q_{p_x}^{(B)} + Q_{p_y}^{(A)}Q_{p_y}^{(B)} + Q_{p_z}^{(A)}Q_{p_z}^{(B)}}{|\vec{d}|^3} \right.$$
$$\left. -\frac{1}{\sqrt{3}}\frac{Q_s^{(A)}Q_{p_z}^{(B)} - Q_{p_z}^{(A)}Q_s^{(B)}}{d^2} - \frac{Q_{p_z}^{(A)}Q_{p_z}^{(B)}}{|\vec{d}|^3} \right\}$$

Now we introduce the definition for the dipole

$$q = \sqrt{4\pi}Q_s = \sqrt{4\pi}\int d^3r\ \rho(\vec{r})Y_s(\vec{r}) = \int d^3r\ \rho(\vec{r})$$

$$\vec{D} = \sqrt{\frac{4\pi}{3}}\begin{pmatrix} Q_{p_x} \\ Q_{p_y} \\ Q_{p_z} \end{pmatrix} = \sqrt{\frac{4\pi}{3}}\int d^3r\ \rho(\vec{r})|\vec{r}| \begin{pmatrix} Y_{p_x} \\ Y_{p_y} \\ Y_{p_z} \end{pmatrix} = \sqrt{\frac{4\pi}{3}}\int d^3r\ \rho(\vec{r})\sqrt{\frac{3}{4\pi}}\vec{r} = \int d^3r\ \rho(\vec{r})\vec{r}$$

so that

$$V(d) = \frac{e^2}{4\pi\epsilon_0}\left\{ \frac{q^{(A)}q^{(B)}}{|\vec{d}|} + \frac{\vec{D}^{(A)}\vec{D}^{(B)}}{|\vec{d}|^3} - \frac{q^{(A)}\vec{D}^{(B)}\vec{e}_z - \vec{D}^{(A)}\vec{e}_z q^{(B)}}{d^2} - \frac{3(\vec{e}_z\vec{D}^{(A)})(\vec{e}_z\vec{D}^{(B)})}{|\vec{d}|^3} \right\}$$

Appendix G

Screening length

In the random-phase approximation of the free electron gas the coulomb interaction in the exchange energy is replaced by a Yukawa potential.

$$v_{\text{Yukawa}}(\vec{r}) = \frac{e^2}{4\pi\epsilon_0|\vec{r}|}\mathrm{e}^{-\lambda|\vec{r}|} \tag{G.1}$$

In Fourier space the Yukawa potential

$$v_{\text{Yukawa}}(\vec{r}) = \int \frac{d^3G}{(2\pi)^3}\,\frac{e^2}{4\pi\epsilon_0}\frac{4\pi}{G^2+\lambda^2} \tag{G.2}$$

The potential can also be expressed in terms of a G-dependent dielectric constant.

$$\epsilon_r^{-1}(\vec{G}) = \frac{\vec{G}^2}{\vec{G}^2+\lambda^2} \tag{G.3}$$

This can be compared with the slide "An analogy between GW anmd hybrid functionals" in https://www.nersc.gov/assets/Uploads/VASP-lecture-RPA.pdf

I am using one data pair ($\epsilon_r^{-1} = 0.5$ for $G = 2^{-1}$) to arrive at $\lambda = 2a_0^{-1}$ or $r_{screen} = 0.5\ a_0$.

HSE06

The HSE06 functional is the prototypical range-separated hybrid density functional. A fortran implementation can be be found in the Thesis of Jochen Heyd, which can be found on the internet. (Caution: In the HSE03 functional different screening parameters have been used for the Fock term and the subtraction of the PBE exchange.)

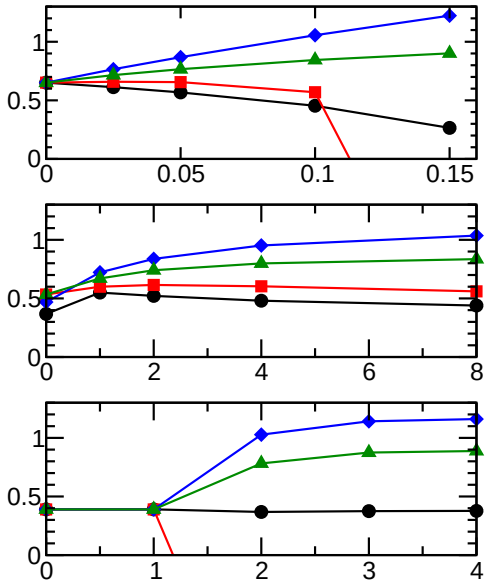
(See in Codes/Holefunction/src/hsfx.f90)

Krukau[**?**] finds that energies depend little on the range, if the range for the double counting and the screened Fock term are similar in the range 5 $a_B < r_{screen} < \infty$. This indicates that it is important to include the first nearest and next-nearest neighbor shells.

Krukau[**?**] shows in his table VIII that band gaps become better with increasing range, and that this improvement depends on the fock admixture, while it is fairly independent of the range in the double counting.

This suggests that we should use the same $\alpha_{Fock} = 0.25$ as HSE06 to get the correct band gaps. The screening length can be chosen smaller. Our double counting term is not consistent the off-site terms and differs from that of HSE06.

Test for Si



Band gap of silicon as function of (top) the Hartree Fock weight, (2) the screening length in Åand (bottom)the cutoff radius for the neighborlist. The standard values are 0.125 for the Hartree-Fock weight, 3 Åfor the screening length and 3 r_{cov}=3.33 Åfor the radius of the neighbor list. PBE0r (local terms only) black spheres, PBE0r+NDDO red squares, PBE0r+NDDO+31 (blue diamonds) and PBE0r+31 (green triangles).

- PBE0r: with increasing α_{fock}, the s-bands are shifted down in energy. The $ss\sigma$ hopping seems to be reduced (The band width of s-band is narrower). The conduction band has a lot of s-character. Thus the s-band shifts downward with increasing Fock-weight.
- 31: The $ss\sigma$ hopping is drastically increased.(band width of s-band is larger)
- NDDO for $\alpha_{fock} > 0.1$ develops ghost states

I changed $K2 = -1$ so that the tails of the local orbital have a kinetic energy of 1 Ry=0.5 H. The screening length has been set to 3 and the cutoff radius has been set to three times the sum of covalent radii, i.e. 6 Å.

Appendix H

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

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