Formulae of the Full Potential LMTO method: Second Edition (unfinished)

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I. INTRODUCTION

It is supposed that the crystalline space is divided into the atom centered spheres and the remaining interstitial region. The charge density and effective potential are expanded in spherical harmonics inside spheres:

$$\rho_\tau(\mathbf{r}_\tau) = \sum_{L}^{L_\tau^v} \rho_{L\tau}(r_\tau) i^l Y_L(\hat{r}) \tag{1}$$

$$V_\tau(\mathbf{r}_\tau) = \sum_{L}^{L_\tau^v} V_{L\tau}(r_\tau) i^l Y_L(\hat{r}) \tag{2}$$

The Schroedinger equation is solved in terms of the variational principle:

$$(-\nabla^2 + V - E_{\mathbf{k}\lambda})\psi_{\mathbf{k}\lambda} = 0 \tag{3}$$

$$\psi_{\mathbf{k}\lambda}(\mathbf{r}) = \sum_{L\kappa\tau}^{L_\tau^v} A_{L\kappa\tau}^{\mathbf{k}\lambda} \chi_{L\kappa\tau}^{\mathbf{k}}(\mathbf{r}) \tag{4}$$

and the eigenvalue problem is

$$\sum_{L\kappa\tau}^{L_\tau^b} \left(\langle \chi_{L'\kappa'\tau'}^{\mathbf{k}} | -\nabla^2 + V | \chi_{L\kappa\tau}^{\mathbf{k}} \rangle - E_{\mathbf{k}\lambda} \langle \chi_{L'\kappa'\tau'}^{\mathbf{k}} | \chi_{L\kappa\tau}^{\mathbf{k}} \rangle \right) A_{L\kappa\tau}^{\mathbf{k}\lambda} = 0 \tag{5}$$

II. BASIS FUNCTIONS

The space is partitioned into the non overlapping (or slightly overlapping) muffin–tin spheres s_R surrounding every atom and the remaining interstitial region Ω_{int}. Within the spheres, the basis functions are represented in terms of numerical solutions of the radial Schrödinger equation for the spherical part of the potential multiplied by spherical harmonics as well as their energy derivatives taken at some set of energies ϵ_ν at the centers of interest. In the interstitial region, where the potential is essentially flat, the basis functions are spherical waves taken as the solutions of Helmholtz's equation: $(-\nabla^2 - \epsilon) f(\mathbf{r}, \epsilon) = 0$ with some fixed value of the average kinetic energy $\epsilon = \kappa_\nu^2$. In particular, in the standard LMTO method using the atomic–sphere approximation (ASA), the approximation $\kappa_\nu^2 = 0$ is chosen. In the extensions of the LMTO method for a potential of arbitrary shape (full potential), a multiple–kappa basis set is normally used in order to increase the variational freedom of the basis functions while recent developments of a new LMTO technique promise to avoid this problem.

The general strategy for including the full–potential terms in the calculation is the use of the variational principle. A few different techniques have been developed for taking the non–spherical corrections into account in the framework of the LMTO method. They include Fourier transforms of the LMTOs in the interstitial region, one–center spherical–harmonics expansions within atomic cells, interpolations in terms of the Hankel functions as well as direct calculations of the charge density in the tight–binding representation. In two of these schemes the treatment of open structures such as, *e.g.* the diamond structure is complicated and interstitial spheres are usually placed between the atomic spheres. Therefore we will develop the linear–response LMTO technique using the plane–wave Fourier representation.

We introduce the following partial waves or muffin-tin orbitals defined in whole space:

$$\chi_{L\kappa\tau}(\mathbf{r}_\tau) = \left\{ \begin{array}{ll} \Phi_{L\kappa\tau}^H(\mathbf{r}_\tau) & r_\tau < S_\tau \\ H_{L\kappa\tau}(\mathbf{r}_\tau) & r_\tau > S_\tau \end{array} \right| \tag{6}$$

where $\Phi_{L\kappa\tau}^H(\mathbf{r}_\tau)$ is constructed from the linear combination of ϕ_ν and $\dot{\phi}_\nu$ with the condition of smooth augmentation at the sphere.

A. LMTOs within MT-Spheres

The LMTO-basis functions are obtained from the Bloch sum of these partial waves:

$$\chi^{\mathbf{k}}_{L\kappa\tau}(\mathbf{r}) = \sum_R e^{i\mathbf{kR}} \chi_{L\kappa\tau}(\mathbf{r}-\mathbf{R}-\tau) = \Phi^H_{L\kappa\tau}(\mathbf{r}_\tau)\delta_{\tau\tau'} - \sum_R{}' e^{i\mathbf{kR}} H_{L\kappa\tau}(\mathbf{r}-\mathbf{R}-\tau) \tag{7}$$

Using the addition theorem

$$\sum_{\mathbf{R}}{}' e^{i\mathbf{kR}} H_{L\kappa\tau}(\mathbf{r}-\mathbf{R}-\tau) = -\sum_{L'}^{L^t_\tau} J_{L'\kappa\tau'}(\mathbf{r}_{\tau'})\gamma_{l'\tau'} S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) \tag{8}$$

where $S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa)$ stand for the structure constants and where $\gamma_{l\tau} = \frac{1}{S_\tau(2l+1)}$, we obtain:

$$\chi^{\mathbf{k}}_{L\kappa\tau}(\mathbf{r}_{\tau'}) = \Phi^H_{L\kappa\tau}(\mathbf{r}_\tau)\delta_{\tau\tau'} - \sum_{L'}^{L^t_\tau} J_{L'\kappa\tau'}(\mathbf{r}_{\tau'})\gamma_{l'\tau'} S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) \tag{9}$$

Let us perform the augmentation inside MT-sphere

$$J_{L\kappa\tau}(\mathbf{r}_\tau) \to \Phi^J_{L\kappa\tau}(\mathbf{r}_\tau) \tag{10}$$

where $\Phi^J_{L\kappa\tau}(\mathbf{r}_\tau)$ is a linear combination of ϕ_ν and $\dot{\phi}_\nu$ with the condition of smooth augmentation at the sphere. Then, the basis functions in the MT-sphere are rewritten in the form (one-center expansion):

$$\chi^{\mathbf{k}}_{L\kappa\tau}(\mathbf{r}_{\tau'}) = \Phi^H_{L\kappa\tau}(\mathbf{r}_\tau)\delta_{\tau\tau'} - \sum_{L'}^{L^t_\tau} \Phi^J_{L'\kappa\tau'}(\mathbf{r}_{\tau'})\gamma_{l'\tau'} S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) \tag{11}$$

In the interstitial region our basis functions are defined as follows:

$$\chi^{\mathbf{k}}_{L\kappa\tau}(\mathbf{r}_{\tau'}) = H_{L\kappa\tau}(\mathbf{r}_\tau)\delta_{\tau\tau'} - \sum_{L'}^{L^t_\tau} J_{L'\kappa\tau'}(\mathbf{r}_{\tau'})\gamma_{l'\tau'} S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) \tag{12}$$

Formulas for numerical radial functions are:

$$\Phi^H_{L\kappa\tau}(r_\tau) = a^H_{l\kappa\tau}\phi_{L\kappa\tau}(r_\tau, E_\nu) + b^H_{l\kappa\tau}\dot{\phi}_{L\kappa\tau}(r_\tau, E_\nu) \tag{13}$$

$$\Phi^J_{L\kappa\tau}(r_\tau) = a^J_{l\kappa\tau}\phi_{L\kappa\tau}(r_\tau, E_\nu) + b^J_{l\kappa\tau}\dot{\phi}_{L\kappa\tau}(r_\tau, E_\nu) \tag{14}$$

where

$$a^H_{l\kappa\tau} = +W\{\dot{\phi}_{\nu l\kappa\tau} H_{l\kappa\tau}\} \tag{15}$$

$$b^H_{l\kappa\tau} = -W\{\phi_{\nu l\kappa\tau} H_{l\kappa\tau}\} \tag{16}$$

$$a^J_{l\kappa\tau} = +W\{\dot{\phi}_{\nu l\kappa\tau} J_{l\kappa\tau}\} \tag{17}$$

$$b^J_{l\kappa\tau} = -W\{\phi_{\nu l\kappa\tau} J_{l\kappa\tau}\} \tag{18}$$

and where we have used wronskian notations: $W_{f,g} = \dot{S}^2(fg' - fg') = S\ fg(D^g - D^f)$. Properties of orthonormalisation are:

$$\int_0^{S_\tau} \phi^2_{\nu l\kappa\tau}(r_\tau) r^2_\tau dr_\tau = W\{\dot{\phi}_{\nu l\kappa\tau}\phi_{\nu l\kappa\tau}\} = 1 \tag{19}$$

$$\int_0^{S_\tau} \phi_{\nu l\kappa\tau}(r_\tau)\dot{\phi}_{\nu l\kappa\tau}(r_\tau)r_\tau^2 dr_\tau = 0 \tag{20}$$

Comparing with the old definitions, we used the notations:

$$\Phi^{H,J}_{L\kappa\tau}(r_\tau) = \frac{(H,J)_{l\kappa\tau}}{\Phi_{l\kappa\tau}(D^H)}\Phi_{L\kappa\tau}(r_\tau, D^{H,J}) \tag{21}$$

and

$$\Phi_{L\kappa\tau}(r_\tau, D) = \phi_{L\kappa\tau}(r_\tau, E_\nu) + \omega_{l\kappa\tau}(D)\dot{\phi}_{L\kappa\tau}(r_\tau, E_\nu) \tag{22}$$

where

$$\omega_{l\kappa\tau}(D) = -\frac{\phi_{\nu l\kappa\tau}}{\dot{\phi}_{\nu l\kappa\tau}}\frac{D_{l\kappa\tau} - D_{\nu l\kappa\tau}}{D_{l\kappa\tau} - D_{\dot{\nu} l\kappa\tau}} \tag{23}$$

$$\Phi_{l\kappa\tau}(D) = \phi_{\nu l\kappa\tau}\frac{D_{\nu l\kappa\tau} - D_{\nu l\kappa\tau}}{D_{l\kappa\tau} - D_{\dot{\nu} l\kappa\tau}} \tag{24}$$

which satisfy to the following potential-parameter-combination:

$$S_\tau(D^1_{l\kappa\tau} - D^2_{l\kappa\tau})\Phi_{l\kappa\tau}(D^1)\Phi_{l\kappa\tau}(D^2) = \omega_{l\kappa\tau}(D^2) - \omega_{l\kappa\tau}(D^1) \tag{25}$$

B. Fourier transform of pseudoLMTOs.

Since this representation will be used for the description of the basis functions only within Ω_{int}, we can substitute the divergent part of the Hankel function by a smooth function for $r_R < s_R$. This regular function is is denoted as $\tilde{H}_{\kappa RL}$. We thus introduce a pseudoLMTO $|\tilde{\chi}^{\mathbf{k}}_{\kappa RL}\rangle$ defined in all space as follows:

$$\tilde{\chi}^{\mathbf{k}}_{L\kappa\tau}(\mathbf{r}) = \sum_R e^{i\mathbf{kR}}\tilde{H}_{L\kappa\tau}(\mathbf{r}_\tau - \mathbf{R}) = \sum_G \tilde{\chi}_{L\kappa\tau}(\mathbf{k}+\mathbf{G})e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \tag{26}$$

which is identical with the true sum in the interstitial region.

Consider a Hankel function $H_{\kappa L}(\mathbf{r}) = H_{\kappa l}(r)i^l Y_{lm}(\mathbf{r})$ of energy κ^2 which is singular at the origin. The three–dimensional Fourier transform of this function $H_{\kappa L}(\mathbf{k})$ is known to behave as k^{l-2} for large k. The task is to substitute the divergent part of $H_{\kappa l}(r)$ inside some sphere s by a smooth regular but otherwise arbitrary function. This function is chosen so that the Fourier transform is convergent fast. In the full–potential LMTO method of Weirich, the augmenting function is the linear combination of the Bessel function $J_{\kappa L}$ and its energy derivative $\dot{J}_{\kappa L}$ matched together with its first–order radial derivative with the Hankel function at the sphere boundary. The Fourier transform becomes convergent as k^{-4}. One can obviously include higher–order energy derivatives $\overset{(n)}{J}_{\kappa L}$ in order to have a smooth matching at the sphere up to the order n. This was done in connection with the problem of solving the Poisson equation by Weinert. The Fourier transform here converges as $k^{-(3+n)}$ but the prefactor increases as $(2l+2n+3)!!$ and this prohibits the use of large values of n. A similar procedure has been also used in the LMTO method of John Wills. In the present work we will use a different approach based on the Ewald method. The same idea was implemented by Methfessel and Mark Schilfgaarde. Instead of substituting the divergent part only for $r < s$ we consider the solution of the equation:

$$(-\nabla^2 - \kappa^2)\tilde{H}_{\kappa L}(\mathbf{r}) = a_l\left(\frac{r}{s}\right)^l e^{-r^2\eta^2+\kappa^2/\eta^2} i^l Y_{lm}(\mathbf{r}),$$

The function on the right-hand side of the Helmholtz equation is a decaying Gaussian. The parameter a_l is a normalization constant: $a_l = \sqrt{2/\pi}(2\eta^2)^{l+3/2}s^{2l+1}/(2l-1)!!$. The most important parameter is η. It is chosen such that the Gaussian is approximately zero when $r > s$ and η must depend on l as well as the sphere radius s. The solution $\tilde{K}_{\kappa L}(\mathbf{r})$ is thus the Hankel function for large r, it is a regular function for small r and it is smooth together with its radial derivatives at any r. The function $\tilde{H}_{\kappa l}(r)$ can be calculated in terms of the following error-function-like contour integral:

$$\tilde{H}_{\kappa l}(r) = \frac{(2s)^{l+1}}{\sqrt{\pi}(2l-1)!!} r^l \int_{0+}^{\eta} \xi^{2l} e^{-r^2\xi^2+\kappa^2/4\xi^2} d\xi.$$

When $\eta \to \infty$ this integral is known as the Hankel integral. The most important result is that the Fourier transform of $\tilde{H}_{\kappa l}(r)$ decays exponentially. It is given by:

$$\tilde{H}_{\kappa l}(r) = \frac{2}{\pi} \frac{s^{l+1}}{(2l-1)!!} \int_0^{\infty} k^2 dk j_l(kr) \frac{k^l e^{(\kappa^2-k^2)/4\eta^2}}{k^2-\kappa^2}.$$

Restoring the original notations, the pseudoLMTOs $\tilde{\chi}^{\mathbf{k}}_{\kappa RL}(\mathbf{r})$ are the Bloch waves of wave vector $\mathbf{k}$. The Fourier coefficients $\tilde{\chi}_{\kappa L\tau}(\mathbf{k}+\mathbf{G})$ are given by:

$$\tilde{\chi}_{L\kappa\tau}(\mathbf{k}+\mathbf{G}) = \frac{4\pi}{\Omega_c} \frac{s_\tau^{l+1}}{(2l-1)!!} \frac{|\mathbf{k}+\mathbf{G}|^l}{|\mathbf{k}+\mathbf{G}|^2-\kappa^2} e^{(\kappa^2-|\mathbf{k}+\mathbf{G}|^2)/4\eta_{l\tau}^2} Y_L(\mathbf{k}+\mathbf{G}) e^{-i(\mathbf{k}+\mathbf{G})\tau},$$

where Ω_c is the volume of the unit cell and where we have subscripted η with the indexes Rl and s with R.

In practical calculations the parameter $\eta_{l\tau}$ can be chosen from the ratio between the Hankel function at the sphere and the solution, i.e. $\tilde{H}_{\kappa l}(s_R)/\tilde{H}_{\kappa l}(s_R) = 1+\delta$. The error $|\delta|$ is usually taken not larger than 0.03 which leads to the number of plane waves per atom needed for the convergency varying from 150 to 250 when $l=2$. For the $s,p-$orbitals this number is smaller by a factor of $2-3$.

uxiliary densities. The exchange–correlation potential is found using the fast Fourier transform and the interstitial–potential matrix elements are explicitly evaluated.

III. HAMILTONIAN AND OVERLAP MATRIX (MT-PART)

The hamiltonian and overlap matrices are separated into the following contributions:

$$\begin{aligned} H^{\mathbf{k}}_{L'\kappa'\tau'L\kappa\tau} &= H^{\mathbf{k},MT}_{L'\kappa'\tau'L\kappa\tau} + H^{\mathbf{k},NMT}_{L'\kappa'\tau'L\kappa\tau} + \kappa^2 O^{\mathbf{k},INT}_{L'\kappa'\tau'L\kappa\tau} + V^{\mathbf{k},INT}_{L'\kappa'\tau'L\kappa\tau} \\ O^{\mathbf{k}}_{L'\kappa'\tau'L\kappa\tau} &= O^{\mathbf{k},MT}_{L'\kappa'\tau'L\kappa\tau} + O^{\mathbf{k},INT}_{L'\kappa'\tau'L\kappa\tau} \end{aligned}$$

where the first term in H-matrix represents the contribution of the MT-part of the one-electron hamiltonian and the second term is the non-muffin-tin correction within MT-space. The third term is the matrix element of kinetice energy in the interstitial region and the fourth term is the interstitial-potential matrix element. The O-matrix is also divided to the contributions from inside the spheres and from the interstitials. We first study the MT-part of these matrices.

A. EXPRESSIONS

The MT-part of the hamiltonian and overlap matrix is defined as follows:

$$H^{\mathbf{k},MT}_{L'\kappa'\tau'L\kappa\tau} =< \chi^{\mathbf{k}}_{L'\kappa'\tau'}| -\nabla^2 + V^{MT} |\chi^{\mathbf{k}}_{L\kappa\tau} >_{\Omega_{MT}} \tag{27}$$

$$O^{\mathbf{k},MT}_{L'\kappa'\tau'L\kappa\tau} =< \chi^{\mathbf{k}}_{L'\kappa'\tau'}|\chi^{\mathbf{k}}_{L\kappa\tau} >_{\Omega_{MT}} \tag{28}$$

where

$$H^{\mathbf{k},MT}_{L'\kappa'\tau'L\kappa\tau} = \delta_{\tau'\tau}\delta_{L'L} \left\{ H^{(1)MT,l\tau}_{\kappa'\kappa} + E_{\nu l\kappa\tau} O^{(1)MT,l\tau}_{\kappa'\kappa} \right\} - \tag{29}$$

$$\left\{ H^{(2,1)MT,l\tau}_{\kappa'\kappa} + E_{\nu l\kappa\tau} O^{(2.1)MT,l\tau}_{\kappa'\kappa} \right\} S^{\mathbf{k}*}_{L\tau L'\tau'}(\kappa') - \tag{30}$$

$$S^{\mathbf{k}}_{L'\tau'L\tau}(\kappa) \left\{ H^{(2.2)MT,l'\tau'}_{\kappa'\kappa} + E_{\nu l'\kappa\tau'} O^{(2.2)MT,l'\tau'}_{\kappa'\kappa} \right\} \tag{31}$$

$$+ \sum_{L''\tau''}^{L^t_{\tau''}} S^{\mathbf{k}*}_{L''\tau''L'\tau'}(\kappa') \left\{ H^{(3)MT,l''\tau''}_{\kappa'\kappa} + E_{\nu l''\kappa\tau''} O^{(3)MT,l''\tau''}_{\kappa'\kappa} \right\} S^{\mathbf{k}}_{L''\tau''L\tau}(\kappa) \tag{32}$$

and

$$O^{\mathbf{k},MT}_{L'\kappa'\tau' L\kappa\tau} = \delta_{\tau'\tau}\delta_{L'L}O^{(1)MT,l\tau}_{\kappa'\kappa} - O^{(2.1)MT,l\tau}_{\kappa'\kappa} S^{\mathbf{k}*}_{L\tau L'\tau'}(\kappa') - S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) O^{(2.2)MT,l'\tau'}_{\kappa'\kappa} + \sum_{L''\tau''}^{L^t_{\tau''}} S^{\mathbf{k}*}_{L''\tau'' L'\tau'}(\kappa') O^{(3)MT,l''\tau''}_{\kappa'\kappa} S^{\mathbf{k}}_{L''\tau'' L\tau}(\kappa)$$

The MT-potential parameters are

$$H^{(1)MT,l\tau}_{\kappa'\kappa} =< \Phi^H_{l\kappa'\tau}| - \nabla^2 + V^{MT}_\tau - E_{\nu l\kappa\tau}|\Phi^H_{l\kappa\tau} >_{S_\tau} \tag{33}$$

$$H^{(2.1)MT,l\tau}_{\kappa'\kappa} =< \Phi^J_{l\kappa'\tau}| - \nabla^2 + V^{MT}_\tau - E_{\nu l\kappa\tau}|\Phi^H_{l\kappa\tau} >_{S_\tau} \gamma_{l\tau} \tag{34}$$

$$H^{(2.2)MT,l\tau}_{\kappa'\kappa} =< \Phi^H_{l\kappa'\tau}| - \nabla^2 + V^{MT}_\tau - E_{\nu l\kappa\tau}|\Phi^J_{l\kappa\tau} >_{S_\tau} \gamma_{l\tau} \tag{35}$$

$$H^{(3)MT,\tau}_{\kappa'\kappa} =< \Phi^J_{l\kappa'\tau}| - \nabla^2 + V^{MT}_\tau - E_{\nu l\kappa\tau}|\Phi^J_{l\kappa\tau} >_{S_\tau} \gamma^2_{l\tau} \tag{36}$$

$$O^{(1)MT,l\tau}_{\kappa'\kappa} =< \Phi^H_{l\kappa'\tau}|\Phi^H_{l\kappa\tau} >_{S_\tau}= O^{(1)MT,l\tau*}_{\kappa\kappa'} \tag{37}$$

$$O^{(2.1)MT,l\tau}_{\kappa'\kappa} =< \Phi^J_{l\kappa'\tau}|\Phi^H_{l\kappa\tau} >_{S_\tau} \gamma_{l\tau} = O^{(2.1)MT,l\tau*}_{\kappa\kappa'} \tag{38}$$

$$O^{(2.2)MT,l\tau}_{\kappa'\kappa} =< \Phi^H_{l\kappa'\tau}|\Phi^J_{l\kappa\tau} >_{S_\tau} \gamma_{l\tau} = O^{(2.1)MT,l\tau*}_{\kappa\kappa'} \tag{39}$$

$$O^{(3)MT,l\tau}_{\kappa'\kappa} =< \Phi^J_{l\kappa'\tau}|\Phi^J_{l\kappa\tau} >_{S_\tau} \gamma^2_{l\tau} = O^{(3)MT,l\tau*}_{\kappa\kappa'}$$

B. MATRIX ELEMENTS

Expressions for the radial matrix elements are

$$< \Phi^f_{\kappa'}|\Phi^g_\kappa >= a^{f*}_{\kappa'} < \phi_{\nu\kappa'}|\phi_{\nu\kappa} > a^g_\kappa + b^{f*}_{\kappa'} < \dot\phi_{\nu\kappa'}|\dot\phi_{\nu\kappa} > b^g_\kappa + a^{f*}_{\kappa'} < \phi_{\nu\kappa'}|\dot\phi_{\nu\kappa} > b^g_\kappa + +b^{f*}_{\kappa'} < \dot\phi_{\nu\kappa'}|\phi_{\nu\kappa} > a^g_\kappa$$
$$< \Phi^f_{\kappa'}| - \nabla^2 + V^{MT} - E_{\nu\kappa}|\Phi^g_\kappa >= a^{f*}_{\kappa'} < \phi_{\nu\kappa'}|\phi_{\nu\kappa} > b^g_\kappa + b^{f*}_{\kappa'} < \dot\phi_{\nu\kappa'}|\phi_{\nu\kappa} > b^g_\kappa$$

where f, g stands for the combinations of H, J and where

$$< \phi_{\nu\kappa'}|\phi_{\nu\kappa} >= \frac{W\{\phi_{\nu\kappa'}\phi_{\nu\kappa}\}}{E_{\nu\kappa'} - E_{\nu\kappa}} \tag{40}$$

$$< \phi_{\nu\kappa'}|\dot\phi_{\nu\kappa} >= \frac{1}{E_{\nu\kappa'} - E_{\nu\kappa}} \left(W\{\phi_{\nu\kappa'}\dot\phi_{\nu\kappa}\}+ < \phi_{\nu\kappa'}|\phi_{\nu\kappa} >\right) \tag{41}$$

$$< \dot\phi_{\nu\kappa'}|\phi_{\nu\kappa} >= \frac{1}{E_{\nu\kappa'} - E_{\nu\kappa}} \left(W\{\dot\phi_{\nu\kappa'}\phi_{\nu\kappa}\}- < \phi_{\nu\kappa'}|\phi_{\nu\kappa} >\right) \tag{42}$$

$$< \dot\phi_{\nu\kappa'}|\dot\phi_{\nu\kappa} >= \frac{1}{E_{\nu\kappa'} - E_{\nu\kappa}} \left(W\{\dot\phi_{\nu\kappa'}\dot\phi_{\nu\kappa}\}+ < \dot\phi_{\nu\kappa'}|\phi_{\nu\kappa} > - < \phi_{\nu\kappa'}|\dot\phi_{\nu\kappa} >\right) \tag{43}$$

Wronskian is definded as follows:

$$W\{f\ g\} = S^2(fg' - f'g) = S\ fg(D^g - D^f) \tag{44}$$

and all the expressions are derived form the Green second identity

$$< f_L|\nabla^2|g_L > - < g_L|\nabla^2|f_L >= W\{f_l g_l\} \tag{45}$$

IV. HAMILTONIAN (NMT-PART WITHIN SPHERE)

A. EXPRESSIONS

The contribution to the hamiltonian going from the non-zero L-components of the potential within MT-spheres is

$$H^{\mathbf{k},NMT}_{L'\kappa'\tau'L\kappa\tau} =< \chi^{\mathbf{k}}_{L'\kappa'\tau'}|V^{NMT}|\chi^{\mathbf{k}}_{L\kappa\tau} >_{\Omega_{MT}} \tag{46}$$

where

$$H^{\mathbf{k},NMT}_{L'\kappa'\tau'L\kappa\tau} = \delta_{\tau'\tau}H^{(1)NMT,\tau}_{L'\kappa'L\kappa} - \sum_{L'}^{L^t_\tau} S^{\mathbf{k}*}_{L\tau L'\tau'}(\kappa')H^{(2.1)NMT,\tau}_{L'\kappa'L\kappa} - \sum_{L}^{L^t_\tau} H^{(2.2)NMT,\tau'}_{L'\kappa'L\kappa} S^{\mathbf{k}}_{L'\tau'L\tau}(\kappa) + \sum_{L''L'''\tau''}^{L^t} S^{k*}_{L\tau L''\tau''}(\kappa')H^{(3)NMT,\tau''}_{L''\kappa'L'''\kappa} S^{\mathbf{k}}_{L''',}$$

where NMT-potential parameters are

$$H^{(1)NMT,\tau}_{L'\kappa'L\kappa} =< \Phi^H_{L'\kappa'\tau}|V^{NMT}_\tau|\Phi^H_{L\kappa\tau} >_{S_\tau}= H^{(1)NMT,\tau*}_{L\kappa L'\kappa'} \tag{47}$$

$$H^{(2.1)NMT,\tau}_{L'\kappa'L\kappa} = \gamma_{L'\tau} < \Phi^J_{L'\kappa'\tau}|V^{NMT}_\tau|\Phi^H_{L\kappa\tau} >_{S_\tau}= H^{(2.2)NMT,\tau*}_{L\kappa L'\kappa'} \tag{48}$$

$$H^{(2.2)NMT,\tau}_{L'\kappa'L\kappa} =< \Phi^H_{L'\kappa'\tau}|V^{NMT}_\tau|\Phi^J_{L\kappa\tau} >_{S_\tau} \gamma_{L\tau} = H^{(2.1)NMT,\tau*}_{L\kappa L'\kappa'} \tag{49}$$

$$H^{(3)NMT,\tau}_{L'\kappa'L\kappa} = \gamma_{L'\tau} < \Phi^J_{L'\kappa'\tau}|V^{NMT}_\tau|\Phi^J_{L\kappa\tau} >_{S_\tau} \gamma_{L\tau} = H^{(3)NMT,\tau*}_{L\kappa L'\kappa'} \tag{50}$$

B. MATRIX ELEMENTS

The radial non-MT potential matrix elements are

$$< \Phi^f_{\kappa'}|V^{NMT}|\Phi^g_\kappa >= a^{f*}_{\kappa'} < \phi_{\nu\kappa'}|V^{NMT}|\phi_{\nu\kappa} > a^g_\kappa + b^{f*}_{\kappa'} < \dot\phi_{\nu\kappa'}|V^{NMT}|\dot\phi_{\nu\kappa} > b^g_\kappa + \tag{51}$$

$$a^{f*}_{\kappa'} < \phi_{\nu\kappa'}|V^{NMT}|\dot\phi_{\nu\kappa} > b^g_\kappa + b^{f*}_{\kappa'} < \dot\phi_{\nu\kappa'}|V^{NMT}|\phi_{\nu\kappa} > a^g_\kappa \tag{52}$$

where

$$< \phi_{L'}| \sum_{L''\neq 0}^{2L^w} V_{L''} i^{l''} Y_{L''}|\phi_L >= \sum_{L''\neq 0}^{L^v} C^{L''}_{LL'} i^{l-l'+l''} < \phi_{l'}|V_{L''}|\phi_l > \tag{53}$$

V. OVERLAP MATRIX (INTERSITITAL REGION)

A. EXPRESSIONS

The contribution from the interstitial region is given by the matrix:

$$O^{\mathbf{k},INT}_{L'\kappa'\tau'L\kappa\tau} =< \chi^{\mathbf{k}}_{L'\kappa'\tau'}|\chi^{\mathbf{k}}_{L\kappa\tau} >_{\Omega_{int}} \tag{54}$$

Via using multicenter expansions for our basis functions in the interstitial region we can arrive to the expressions for the overlap matrix:

$$O^{\mathbf{k},INT}_{L'\kappa'\tau'L\kappa\tau} = \delta_{\tau'\tau}\delta_{L'L}O^{(1)INT,l\tau}_{\kappa'\kappa} - O^{(2.1)INT,l\tau}_{\kappa'\kappa} S^{\mathbf{k}*}_{L\tau L'\tau'}(\kappa') - S^{\mathbf{k}}_{L'\tau'L\tau}(\kappa)O^{(2.2)INT,l'\tau'}_{\kappa'\kappa}$$

$$-\delta_{\epsilon'^*\epsilon}\dot S^{\mathbf{k}*}_{L\tau L'\tau'}(\kappa) + \sum_{L''\tau''}^{L^t_s} S^{k*}_{L''\tau''L'\tau'}(\kappa')O^{(3)INT,l''\tau''}_{\kappa'\kappa} S^k_{L''\tau''L\tau}(\kappa) \tag{55}$$

where the radial matrix elements in case $\kappa'^{2*} = \epsilon'^* \neq \kappa^2 = \epsilon$ are given by

$$O^{(1)INT,l\tau}_{\kappa'\kappa} = W\{H^*_{l\kappa'\tau} H_{l\kappa\tau}\}/(\epsilon - \epsilon'^*) = O^{(1)INT,l\tau *}_{\kappa\kappa'} \tag{56}$$

$$O^{(2.1)INT,l\tau}_{\kappa'\kappa} = W\{J^*_{l\kappa'\tau} H_{l\kappa\tau}\}/(\epsilon - \epsilon'^*)\gamma_{l\tau} = O^{(2.2)INT,l\tau *}_{\kappa\kappa'} \tag{57}$$

$$O^{(2.2),l\tau}_{\kappa'\kappa} = W\{H^*_{l\kappa'\tau} J_{l\kappa\tau}\}/(\epsilon - \epsilon'^*)\gamma_{l\tau} = O^{(2.1)INT,l\tau *}_{\kappa\kappa'} \tag{58}$$

$$O^{(3)INT,l\tau}_{\kappa'\kappa} = W\{J^*_{l\kappa'\tau} J_{l\kappa\tau}\}/(\epsilon - \epsilon'^*)\gamma^2_{l\tau} = O^{(3)INT,l\tau *}_{\kappa\kappa'} \tag{59}$$

For the diagonal case $\kappa'^{2*} = \epsilon'^* = \kappa^2 = \epsilon$ the expressions are:

$$O^{(1)INT,l\tau}_{\kappa\ \kappa} = W\{H^*_{l\kappa\tau} H_{l\kappa\tau}\} \tag{60}$$

$$O^{(2.1)INT,l\tau}_{\kappa\ \kappa} = W\{H_{l\kappa\tau} \dot{J}^*_{l\kappa\tau}\}\gamma_{l\tau} \tag{61}$$

$$O^{(2.2)INT,l\tau}_{\kappa\ \kappa} = W\{J_{l\kappa\tau} \dot{H}^*_{l\kappa\tau}\}\gamma_{l\tau} \tag{62}$$

$$O^{(3)INT,l\tau}_{\kappa\ \kappa} = W\{J_{l\kappa\tau} \dot{J}^*_{l\kappa\tau}\}\gamma^2_{l\tau} \tag{63}$$

B. DERIVATION

Consider $\epsilon'^* \neq \epsilon$ case in direct space:

$$\begin{aligned} O^{INT}_{L'\kappa'R'\tau'L\kappa R\tau} &= < H_{L'\kappa'\tau'}(r - R' - \tau')|H_{L\kappa\tau}(r - R - \tau) >_{V_{int}} = < H_{L'\kappa'R'\tau'}|H_{L\kappa R\tau} >_{V_{int}} = \\ &= \frac{1}{\epsilon'^* - \epsilon}\left(< H_{L'\kappa'R'\tau'}|\nabla^2|H_{L\kappa R\tau} >_{V_{int}} - < H_{L\kappa R\tau}|\nabla^2|H_{L'\kappa'R'\tau'} >_{V_{int}}\right) = \\ &\sum_{R''\tau''} \frac{S^2_{\tau''}}{\epsilon'^* - \epsilon_S} dS_{R''\tau''}\left(H^*_{L'\kappa'R'\tau'}\frac{\partial}{\partial n_{R''\tau''}}H_{L\kappa R\tau} - H_{L\kappa R\tau}\frac{\partial}{\partial n_{R''\tau''}}H^*_{L'\kappa'R'\tau'}\right) \end{aligned}$$

where the derivative is taken over internal normal for sphere $R''\tau''$. Going to the external normal we get:

$$O^{INT}_{L'\kappa'R'\tau'L\kappa R\tau} = \sum_{R''\tau''} \frac{S^2_{\tau''}}{\epsilon - \epsilon'^*} \oint_{S_{\tau''}} dS_{R''\tau''}\left(H^*_{L'\kappa'R'\tau'}\frac{\partial}{\partial r_{R''\tau''}}H_{L\kappa R\tau} - H_{L\kappa R\tau}\frac{\partial}{\partial r_{R''\tau''}}H^*_{L'\kappa'R'\tau'}\right)$$

Let us use the one-center expansion in sphere $R"\tau"$. There are a few cases:
1) $R = R' = R''$; $\tau = \tau' = \tau\prime$ – *one*-center integrals
2.a) $R' \neq R = R''$; $\tau' \neq \tau = \tau\prime$ – *two*-center integrals
2.*b*) $R = R' = R''$; $\tau \neq \tau' = \tau\prime$ – *two*-center integrals
3) $R \neq R' \neq R''$ — three-center integrals
Since

$$H_{L\kappa R\tau} = -\sum_{L'} J_{L'\kappa R'\tau'}\gamma_{L'\tau'} S_{L'R'\tau'LR\tau}(\kappa); \gamma_{l\tau} = \frac{1}{S_\tau(2l+1)} \tag{64}$$

we obtain for case 1:

$$O^{INT}_{L'\kappa'R\tau L\kappa R\tau} = \frac{1}{\epsilon - \epsilon'^*}\delta_{L'L} W\{H^*_{l\kappa'\tau} H_{l\kappa\tau}\} \tag{65}$$

we obtain for case 2.a

$$O^{INT}_{L'\kappa' R'\tau' L\kappa R\tau} = -\frac{1}{\epsilon - \epsilon'^{*}} \gamma_{l\tau} W\{J^{*}_{l\kappa'\tau} H_{l\kappa\tau}\} S^{*}_{LR\tau L'R\tau'}(\kappa') \tag{66}$$

we obtain for case 2.b

$$O^{INT}_{L'\kappa' R'\tau' L\kappa R\tau} = -\frac{1}{\epsilon - \epsilon'^{*}} S_{L'R'\tau' LR\tau}(\kappa) \gamma_{l'\tau'} W\{H^{*}_{l'\kappa'\tau'} J_{l'\kappa\tau'}\}$$

we obtain for case 3

$$O^{INT}_{L'\kappa' R'\tau' L\kappa R\tau} = \frac{1}{\epsilon - \epsilon'^{*}} \sum_{L''R''\tau''} S^{*}_{L''R''\tau'' L'R'\tau'}(\kappa') \gamma_{l''\tau''} W\{J^{*}_{l''\kappa'\tau''} J_{l''\kappa\tau''}\} \gamma_{l''\tau''} S_{L''R''\tau'' LR\tau}(\kappa)$$

Performing the summation over direct space:

$$O^{\mathbf{k},INT}_{L'\kappa'\tau' L\kappa\tau} = \sum_{R'} e^{i\mathbf{k}(\mathbf{R'}-\mathbf{R})} O^{INT}_{L'\kappa' R'\tau' L\kappa R\tau} \tag{67}$$

we get the expressions given above.

Consider $\epsilon'^{*} = \epsilon$ case:

$$O^{\mathbf{k},INT}_{L'\kappa'\tau' L\kappa\tau}(\epsilon - \epsilon'^{*}) \overset{\kappa' \Rightarrow \kappa}{=} \delta_{\tau'\tau}\delta_{L'L} W\{H^{*}_{l\kappa\tau} H_{l\kappa\tau}\} + (\epsilon'^{*} - \epsilon) W\{\dot{H}^{*}_{l\kappa\tau} H_{l\kappa\tau}\} + S^{k*}_{L\tau L'\tau'}(\kappa) +$$
$$(\epsilon'^{*} - \epsilon)\dot{S}^{k*}_{L\tau L'\tau'}(\kappa) - (\epsilon'^{*} - \epsilon)\gamma_{l\tau} W\{\dot{J}^{*}_{l\kappa\tau} H_{l\kappa\tau}\} S^{k*}_{L\tau L'\tau'}(\kappa) - S^{k}_{L'\tau' L\tau}(\kappa) - (\epsilon'^{*} - \epsilon) S^{k}_{L'\tau' L\tau}(\kappa)\gamma_{l'\tau'} W\{\dot{H}^{*}_{l'\kappa\tau'} J_{l'\kappa\tau'}\} +$$
$$(\epsilon'^{*} - \epsilon) \sum_{L''\tau''} S^{k*}_{L''\tau'' L'\tau'}(\kappa)\gamma_{l''\tau''} W\{J_{l''\kappa\tau''} \dot{J}^{*}_{l''\kappa\tau''} \gamma_{l''\tau''} S^{k}_{L''\tau'' L\tau}(\kappa)$$

It can be shown that

$$\delta_{\tau'\tau}\delta_{L'L} W\{H^{*}_{l\kappa\tau} H_{l\kappa\tau}\} + S^{k*}_{L\tau L'\tau'}(\kappa) - S^{k}_{L'\tau' L\tau}(\kappa) = 0 \tag{68}$$

It is obvious for $\kappa \leq 0$ (Hankel's functions are real ones and the structure constants are hermitian. When $\kappa > 0$ diagonal elements of the structure constants are complex (off-diagonal elements are hermitian) and their combination in the expression above gives zero.

VI. STRUCTURE CONSTANTS AND THEIR ENERGY DERIVATIVES

LMTO-structure constants are given by

$$S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) = (S_{\tau'} S_{\tau})^{1/2} \sum_{l''} g^{l''}_{L'L} (\kappa S_{WZ})^{l+l'-l''} \left(\frac{S_{\tau'}}{S_{WZ}}\right)^{l'+1/2} \left(\frac{S_{\tau}}{S_{WZ}}\right)^{l+1/2} \times \Sigma^{\mathbf{k}}_{l''m'-m,\tau'-\tau}(E)$$

where

$$g^{l''}_{L'L} = -\frac{8\pi}{\sqrt{4\pi}} \frac{(2l''-1)!!}{(2l'-1)!!(2l-1)!!} C^{L''}_{LL'} \tag{69}$$

and the lattice sum is given by:

$$\Sigma^{\mathbf{k}}_{L\delta}(\epsilon) = {\sum_{R}}' e^{i\mathbf{k}\mathbf{R}} H_{l\kappa WZ}(|R-\delta|)[\sqrt{4\pi} i^{l} Y_L(\hat{R}-\delta)]^{*} \tag{70}$$

Evald's transformation for the lattice sum is:

$$\Sigma^{\mathbf{k}}_{L\delta}(\epsilon) = \Sigma^{\mathbf{k}(1)}_{L\delta}(\epsilon) + \Sigma^{\mathbf{k}(2)}_{L\delta}(\epsilon) + \Sigma^{(3)}_{L\delta}(\epsilon) \tag{71}$$

where

$$\Sigma^{\mathbf{k}(1)}_{L\delta}(\epsilon) = \frac{8\pi\sqrt{\pi}}{(2l-1)!!} \frac{S^{l+1}_{WZ}}{\Omega_c} e^{\epsilon/4\eta^2} \sum_{\mathbf{G}} \frac{|\mathbf{k}+\mathbf{G}|^{l} e^{-|\mathbf{k}+\mathbf{G}|^2/4\eta^2}}{|\mathbf{k}+\mathbf{G}|^2 - \epsilon} e^{i(\mathbf{k}+\mathbf{G})\delta} Y^{*}_L(\widehat{\mathbf{k}+\mathbf{G}})$$

$$\Sigma_{L\delta}^{\mathbf{k}(2)}(\epsilon) = \frac{4(-2i)^{l+1}}{(2l-1)!!} S_{WZ}^{l+1} \sum_R e^{i\mathbf{kR}} |\mathbf{R}-\delta|^l Y_L^*(\mathbf{R}-\delta) \int_\eta^\infty d\xi \xi^{2l} e^{-|\mathbf{R}-\delta|^2\xi^2+\epsilon/4\xi^2}$$

(Nick commented that it should be)

$$\Sigma_{L\delta}^{\mathbf{k}(2)}(\epsilon) = \frac{4(-2i)^{l}}{(2l-1)!!} S_{WZ}^{l+1} \sum_R e^{i\mathbf{kR}} |\mathbf{R}-\delta|^l Y_L^*(\mathbf{R}\hat{-}\delta) \int_\eta^\infty d\xi \xi^{2l} e^{-|\mathbf{R}-\delta|^2\xi^2+\epsilon/4\xi^2}$$

$$\Sigma_{L\delta}^{(3)}(\epsilon) = \delta_{L0}\delta_{\delta 0} \frac{2\eta S_{WZ}}{\sqrt{\pi}} \sum_{n=0}^\infty \frac{(\epsilon/4\eta^2)^n}{n!(2n-1)} - \delta_{L0}\delta_{\delta 0} i S_{WZ}\sqrt{\epsilon}$$

and $\kappa^2 = \epsilon$ while ϵ can be considered in units $(1/a)^2$.
Energy derivatives of the LMTO-structure constants are given by

$$\dot{S}^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) = S_{WZ}^2 \frac{d}{d\epsilon} S^{\mathbf{k}}_{L'\tau' L\tau}(\kappa) = S_{WZ}^2 \left(\dot{S}^{\mathbf{k}(1)}_{L'\tau' L\tau}(\kappa) + \dot{S}^{\mathbf{k}(2)}_{L'\tau' L\tau}(\kappa) \right)$$

where we define:

$$\dot{S}^{\mathbf{k}(1)}_{L'\tau' L\tau}(\kappa) = \frac{1}{2}(S_{\tau'}S_\tau)^{1/2} \sum_{l''} g_{L'L}^{l''}(l+l'-l'')\frac{1}{2}(\kappa S_{WZ})^{l+l'-l''} \left(\frac{S_{\tau'}}{S_{WZ}}\right)^{l'+1/2} \left(\frac{S_{\tau}}{S_{WZ}}\right)^{l+1/2} \times$$

$$\Sigma^{\mathbf{k}}_{l''m'-m,\tau'-\tau}(\epsilon) \tag{72}$$

$$\dot{S}^{\mathbf{k}(2)}_{L'\tau' L\tau}(\kappa) = \sum_{l''} g_{L'L}^{l''}(\kappa S_{WZ})^{l+l'-l''} \left(\frac{S_{\tau'}}{S_{WZ}}\right)^{l'+1/2} \left(\frac{S_{\tau}}{S_{WZ}}\right)^{l+1/2} \times \dot{\Sigma}^{\mathbf{k}}_{l''m'-m,\tau'-\tau}(\epsilon)$$

and where the energy derivative of the lattice sum is:

$$\dot{\Sigma}^{\mathbf{k}}_{L\delta}(\epsilon) = \sum_R e^{i\mathbf{kR}} \dot{H}_{l\kappa WZ}(|\mathbf{R}-\delta|)[\sqrt{4\pi} i^l Y_L(\mathbf{R}-\delta)]^* \tag{73}$$

Evald's transformation for the lattice sum is:

$$\dot{\Sigma}^{\mathbf{k}}_{L\delta}(\epsilon) = \dot{\Sigma}^{\mathbf{k}(1)}_{L\delta}(\epsilon) + \dot{\Sigma}^{\mathbf{k}(2)}_{L\delta}(\epsilon) + \dot{\Sigma}^{(3)}_{L\delta}(\epsilon) \tag{74}$$

where

$$\dot{\Sigma}^{\mathbf{k}(1)}_{L\delta}(\epsilon) = \frac{8\pi\sqrt{\pi}S_{WZ}^{l-1}}{(2l-1)!!_{\Omega_c}} e^{\epsilon/4\eta^2} \sum_G \frac{|\mathbf{k}+\mathbf{G}|^l e^{-|\mathbf{k}+\mathbf{G}|^2/4\eta^2}}{|\mathbf{k}+\mathbf{G}|^2-\epsilon} e^{i(\mathbf{k}+\mathbf{G})\delta} Y_L^*(\mathbf{k}\hat{+}\mathbf{G}) \left(\frac{1}{4\eta^2} + \frac{1}{|\mathbf{k}+\mathbf{G}|^2-\epsilon}\right)$$

$$\dot{\Sigma}^{\mathbf{k}(2)}_{L\delta}(\epsilon) = \frac{4(-2i)^{l+1}}{(2l-1)!!} S_{WZ}^{l-1} \sum_R e^{i\mathbf{kR}} |\mathbf{R}-\delta|^l Y_L^*(\mathbf{R}-\delta) \frac{1}{4} \int_\eta^\infty d\xi \xi^{2l-2} e^{-|\mathbf{R}-\delta|^2\xi^2+\epsilon/4\xi^2}$$

$$\dot{\Sigma}^{(3)}_{L\delta}(\epsilon) = \delta_{L0}\delta_{\delta 0} \frac{1}{2\sqrt{\pi}\eta S_{W\ Z}} \sum_{n=0}^\infty \frac{(\epsilon/4\eta^2)^n}{n!(2n+1)} - \delta_{L0}\delta_{\delta 0} \frac{i}{2S_{WZ}\sqrt{\epsilon}}$$

Error function integrals are given by:

$$F_l(\eta, \Delta, \epsilon) = \int_\eta^\infty d\xi \xi^{2l} e^{-\Delta^2\xi^2+\epsilon/4\xi^2} \tag{75}$$

and satisfy to the following recurrent relationships:

$$2\Delta^2 F_{l+1}(\eta,\Delta,\epsilon) = e^{-\Delta^2\eta^2+\epsilon/4\eta^2}\eta^{2l+1} + (2l+1)F_l(\eta,\Delta,\epsilon) - \frac{\epsilon}{2}F_{l-1}(\eta,\Delta,\epsilon) \tag{76}$$

First integrals are:

$$F_0(\eta,\Delta,\epsilon)=\frac{e^{-\Delta^2\eta^2}}{2\Delta}\int_0^\infty\frac{dx}{(x+\Delta^2\eta^2)^{1/2}}e^{-x}\exp(\frac{\epsilon\Delta^2}{4(x+\Delta^2\eta^2)})\tag{77}$$

$$F_{-1}(\eta,\Delta,\epsilon)=\frac{\Delta}{2}e^{-\Delta^2\eta^2}\int_0^\infty\frac{dx}{(x+\Delta^2\eta^2)^{3/2}}e^{-x}\exp(\frac{\epsilon\Delta^2}{4(x+\Delta^2\eta^2)})\tag{78}$$

which have been reduced to Gauss-Laguerre quadrature integration.

Note that for $\epsilon=0$ the last contribution to $\dot{\Sigma}^{(3)}$ diverges. It must be dropped since it is cancelled out with the same divergency in wronskian $W\{H_\kappa\dot{H}_{\kappa'}\}$ when $\epsilon missmiss 0$. Note also that for $\epsilon>0$, S and $S-dot$ matrices are not hermitian since Hankel's functions are complex. This non-hermitianness goes from the last contribution to $\Sigma^{(3)}$ and, consequently, diagonal elements of S and $S-dot$ are complex numbers. This last contribution to $\Sigma^{(3)}$ is, indeed, equal to the lattice sum of Bessel's functions. By considering Neuman's functions for $E>0$ we can, in prinipле, obtain hermitian structure constants.

Usefull properties of Σ-constants in case real energies:

$$\Sigma^k_{lm,-\delta}(\epsilon)=(-1)^m\Sigma^{k*}_{l-m,\delta}(\epsilon)\tag{79}$$

$$\dot{\Sigma}^k_{lm,-\delta}(\epsilon)=(-1)^m\dot{\Sigma}^{k*}_{l-m,\delta}(\epsilon)\tag{80}$$

In case $k=0$, $\epsilon=0$ the divergent contribution with $G=0$ in $\Sigma^{(1)}_{l=0}$ must be dropped from *the electroneutrality condition*. Instead, $\Sigma^{(4)}_{l=0}$ contribution is appeared which is given by

$$\Sigma^{(4)}_{L\delta}(\epsilon=0)=\delta_{L0}\frac{-3}{4N_{atom}\eta^2S^2_{WZ}}\tag{81}$$

It can be shown that the singularities appeared in Σ-constants when $\epsilon{\to}0$ and $k{\to}0$ are also cancelled out if one assumes *the absence of dipol and quadrupole moments* of the whole crystal. This is valid if one first sets $\epsilon=0$ and then $k\to0$. If one sets $k=0$ and then considers the limit $\epsilon{\to}0$ one more term seems to appear:

$$S^{k=0}_{L'\tau'L\tau}(\epsilon=0)=???+\delta_{l'1}\delta_{l1}\delta_{m'm}\frac{8\pi\sqrt{\pi}}{\Omega_{cell}}S^2_{\tau'}S^2_\tau/\sqrt{4\pi}$$

In this case, only electroneutrality condition can be assumed to get this limit behavior.

More useful relations:

$$S^{-k}_{L'\tau'L\tau}(\epsilon)=(-)^{l'+m'+l+m}S^k_{L\tau L'\tau'}(\epsilon)\tag{82}$$

for any ϵ

$$S^{k*}_{L'\tau'L\tau}(\epsilon)=S^k_{L\tau L'\tau'}(\epsilon)\tag{83}$$

for real energies

$$S^{-k*}_{L'\tau'L\tau}(\epsilon)=(-)^{l'+m'+l+m}S^k_{L'\tau'L\tau}(\epsilon)\tag{84}$$

VII. FULL POTENTIAL

$$\begin{aligned}V^C(\mathbf{r})&=\sum_{R\tau}-\frac{Z_\tau e^2}{|\mathbf{r}-\mathbf{R}-\tau|}+e^2\int_V\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'=\\&=\sum_{R\tau}-\frac{Z_\tau e^2}{|\mathbf{r}-\mathbf{R}-\tau|}+e^2\int_{V_{MT}}\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+e^2\int_{V_{int}}\frac{\tilde{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'=\\&=\sum_{R\tau}-\frac{Z_\tau e^2}{|\mathbf{r}-\mathbf{R}-\tau|}+e^2\int_{V_{MT}}\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+e^2\int_V\frac{\tilde{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'-e^2\int_{V_{MT}}\frac{\tilde{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\end{aligned}$$

where

$$\tilde{\rho}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{\rho}(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}, \mathbf{r} \in \Omega_{int} \tag{85}$$

$$\rho(\mathbf{r}_\tau) = \sum_{L} \rho_L(r_\tau) i^l Y_{lm}(\hat{\mathbf{r}}_\tau), \mathbf{r} \in S_\tau$$

Multipole moments associated with the densities

$$M_{L\tau}^{tot} = -Z_\tau \delta_{L0} + M_{L\tau}^{\rho} = -Z_\tau \delta_{L0} + \sqrt{4\pi} \int_0^{S_\tau} \rho_{L\tau}(r_\tau) (\frac{r_\tau}{S_\tau})^l r_\tau^2 dr_\tau \tag{86}$$

$$\tilde{M}_{L\tau} = \int_{S_\tau} \tilde{\rho}(\mathbf{r}) (\frac{r_\tau}{S_\tau})^l [i^l Y_L(\mathbf{r}_\tau)]^* d\mathbf{r}_\tau = \sum_{\mathbf{G}} \frac{\sqrt{4\pi} S_\tau^2}{G} \tilde{\rho}(\mathbf{G}) e^{i\mathbf{G}\tau} Y_L^*(\hat{\mathbf{G}}) j_{l+1}(GS_\tau) \tag{87}$$

Also

$$\tilde{\rho}_1(\mathbf{r}_\tau) = \sum_L \tilde{Q}_{L\tau} a_{l\tau} \left(\frac{r_\tau}{s_\tau}\right)^l e^{-r_\tau^2 \beta_{l\tau}^2} i^l Y_{lm}(\hat{\mathbf{r}}_\tau)$$

$$a_{l\tau} = \sqrt{2/\pi} (2\beta_{l\tau}^2)^{l+3/2} s_\tau^{2l+1} / (2l-1)!!$$

$$\tilde{\rho}_1(\mathbf{G}) = \sum_{L\tau} \tilde{Q}_{L\tau} \frac{4\pi S_\tau^{l+1}}{\Omega_c (2l-1)!!} e^{-i\mathbf{G}\tau} G^l e^{-G^2/4\beta_{l\tau}^2} Y_L(\hat{\mathbf{G}})$$

is the auxiliary density which is only non–zero inside the spheres. It contains multipole charges $\tilde{Q}_{L\tau}$ which are given by

$$\tilde{Q}_{L\tau} = \frac{(M_{L\tau}^{tot} - \tilde{M}_{L\tau})}{G_{L\tau}}$$

$$G_{L\tau} = a_{l\tau} \int \left(\frac{r_\tau}{s_\tau}\right)^l e^{-r_\tau^2 \beta_{l\tau}^2} (\frac{r_\tau}{S_\tau})^l r_\tau^2 dr_\tau$$

They are choosen so that $\tilde{\rho}(\mathbf{r}_\tau) + \tilde{\rho}_1(\mathbf{r}_\tau)$ insde each sphere carries exactly the multipole charge $M_{L\tau}^{tot}$.

A. COULOMB PART WITHIN MT-SPHERE

Electrostatic potential inside MT-sphere is given by

$$\begin{aligned}
V_\tau^C(\mathbf{r}_\tau) = & \sum_{R\tau'} -\frac{Z_{\tau'} e^2}{|\mathbf{r}_\tau - \mathbf{R} - \tau'|} + e^2 \int_{S_\tau} \frac{\rho(\mathbf{r}')}{|\mathbf{r}_\tau - \mathbf{r}'|} d\mathbf{r}' + e^2 \int_{V_{MT}-S_\tau} \frac{\tilde{\rho}(\mathbf{r}') + \tilde{\rho}_1(\mathbf{r}')}{|\mathbf{r}_\tau - \mathbf{r}'|} d\mathbf{r}' + e^2 \int_V \frac{\tilde{\rho}(\mathbf{r}')}{|\mathbf{r}_\tau - \mathbf{r}'|} d\mathbf{r}' - e^2 \int_{V_{MT}} \frac{\tilde{\rho}(\mathbf{r}')}{|\mathbf{r}_\tau - \mathbf{r}'|} d\mathbf{r}' \\
= & \sum_{R\tau'} -\frac{Z_{\tau'} e}{|\mathbf{r}_\tau - \mathbf{R} - \tau'|} + e^2 \int_{S_\tau} \frac{\rho(\mathbf{r}')}{|\mathbf{r}_\tau - \mathbf{r}'|} d\mathbf{r}' + e^2 \int_{V-S_\tau} \frac{\tilde{\rho}(\mathbf{r}') + \tilde{\rho}_1(\mathbf{r}')}{|\mathbf{r}_\tau - \mathbf{r}'|} d\mathbf{r}' \\
& -\delta_{L0} \frac{Z_\tau e^2}{r_\tau} \sqrt{4\pi} Y_{00} + e^2 \sum_L \left(\frac{r_\tau}{S_\tau}\right)^l i^l Y_L(\hat{r}_\tau) \frac{4\pi}{2l+1} S_\tau^l \int_{r_\tau}^{S_\tau} \rho_{L\tau}(r'_\tau) r_\tau'^{-l-1} r_\tau'^2 dr'_\tau + \\
& + e^2 \sum_L \left(\frac{S_\tau}{r_\tau}\right)^{+l+1} i^l Y_L(\hat{r}_\tau) \frac{4\pi}{2l+1} S_\tau^{-l-1} \int_0^{r_\tau} \rho_{L\tau}(r'_\tau) r_\tau'^l r_\tau'^2 dr'_\tau + \\
& e^2 \sum_L \left(\frac{r_\tau}{S_\tau}\right)^l i^l Y_L(\hat{r}_\tau) \left[Q_{L\tau}^{(1)} + Q_{L\tau}^{(2)}\right]
\end{aligned}$$

$$Q_{L\tau}^{(1)} = \sum_{\mathbf{G}} \frac{16\pi^2 S_\tau}{(2l+1)G} \tilde{\rho}(\mathbf{G}) e^{-i\mathbf{G}\tau} Y_L^*(\hat{\mathbf{G}}) j_{l-1}(GS_\tau) \tag{88}$$

$$Q_{L\tau}^{(2)} = \sum_{\mathbf{G}} \frac{16\pi^2 S_\tau}{(2l+1)G} \tilde{\rho}_1(\mathbf{G}) e^{-i\mathbf{G}\tau} Y_L^*(\hat{\mathbf{G}}) j_{l-1}(GS_\tau) \tag{89}$$

B. COULOMB PART IN THE INTERSTITIAL REGION

$$V^C(\mathbf{r}) = \tilde{V}^C(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{V}^C(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}, \mathbf{r} \in \Omega_{int}$$

where

$$\tilde{V}^C(\mathbf{G}) = \frac{4\pi e^2}{G^2}[\tilde{\rho}(\mathbf{G}) + \tilde{\rho}_1(\mathbf{G})]$$

C. EXCHANGE-CORRELATION CONTRIBUTION

It is supposed that the non-spherical part of the charge density is small, i.e.

$$\rho_\tau(\mathbf{r}_\tau) = \rho_{L=0\tau}(r_\tau) Y_{00} + \sum_{L\neq 0} \rho_{L\tau}(r_\tau) i^l Y_L(\hat{r}_\tau) = \rho_\tau^{sph}(r_\tau) + \delta\rho_\tau(\mathbf{r}_\tau) \tag{90}$$

Then

$$V^{xc}[\rho_\tau(\mathbf{r}_\tau)] = V^{xc}[\rho_\tau^{sph}] + \frac{dV^{xc}}{d\rho}|_{\rho=\rho_\tau^{sph}} \delta\rho_\tau(r_\tau) + \frac{1}{2}\frac{d^2V^{xc}}{d^2\rho}|_{\rho=\rho_\tau^{sph}} [\delta\rho_\tau(r_\tau)]^2 \tag{91}$$

where

$$[\delta\rho_\tau(\mathbf{r}_\tau)]^2 \equiv \delta^2\rho_\tau(\mathbf{r}_\tau) = \sum_L \delta^2\rho_{L\tau}(r_\tau) i^l Y_L(\hat{r}_\tau) \tag{92}$$

and

$$\delta^2\rho_{L''\tau}(r_\tau) =_L \sum_{'L\neq 0} i^{l+l'-l''} \rho_{L\tau}(r_\tau) C_{LL''}^{L'} \rho_{L'\tau}(r_\tau) \tag{93}$$

Radial derivatives are given by

$$\delta^2\rho'_L(r_\tau) =_L \sum_{'L\neq 0} 2i^{l+l'-l"} \rho'_{L_\tau(r_\tau) C_{LLmiss}^{L'}} \rho_{L'\tau}(r_\tau) \tag{94}$$

$$\delta^2\rho'_{L'_{miss}}\tau(r_\tau) =_L \sum_{'L\neq 0} 2i^{l+l'-l"} \rho'_{L\tau}(r_\tau) C_{LL"}^{L'} \rho'_{L'\tau}(r_\tau) +_L \sum_{'L\neq 0} i^{l+l'-l"} \rho'_{L'\tau}(r_\tau) C_{LL"}^{L'} \rho_{L'\tau}(r_\tau)$$

and spherical part is given by

$$\delta^2\rho_{L"=0\tau}(r_\tau) = \frac{1}{\sqrt{4\pi}} \sum_{L\neq 0} (-1)^l \rho_{lm\tau}(r_\tau) \rho_{l-m\tau}(r_\tau) \tag{95}$$

With the above definitions the exchange-correlation part to the potential is

$$V_\tau^{xc}(r_\tau) = \sum_L V_{L\tau}^{xc}(r_\tau) i^l Y_L(\hat{r}_\tau) \tag{96}$$

$$V_{L\tau}^{xc}(r_\tau) = \sqrt{4\pi} V^{xc}[\rho_\tau^{sph}]\delta_{L0} + \mu^{xc}[\rho_\tau^{sph}]\rho_{L\tau}(1-\delta_{L0}) + \frac{1}{2}\eta^{xc}[\rho_\tau^{sph}]\delta^2\rho_{L"\tau}(r_\tau) \tag{97}$$

where the following notations have been used

$$\mu^{xc} = \frac{dV^{xc}}{d\rho}; \eta^{xc} = \frac{d^2V^{xc}}{d^2\rho}; \gamma^{xc} = \frac{d^3V^{xc}}{d^3\rho} \tag{98}$$

for different derivatives of local-density-approximation-formulas.

VIII. WAVE FUNCTIONS

A. DEFINITIONS

The wave function is given as the expansion over LMTOs:

$$\psi_{\mathbf{k}\lambda}(\mathbf{r}) = \sum_{L\kappa\tau}^{L_\tau^v} A^{\mathbf{k}\lambda}_{L\kappa\tau}\chi^{\mathbf{k}}_{L\kappa\tau}(\mathbf{r})$$

Inside MT-sphere it is represented as the one-center expansion:

$$\psi_{\mathbf{k}\lambda}(\mathbf{r}_\tau) = \sum_{L\kappa} A^{\mathbf{k}\lambda}_{L\kappa\tau}\Phi^H_{L\kappa\tau}(\mathbf{r}_\tau) - \sum_{L\kappa} S^{\mathbf{k}\lambda}_{L\kappa\tau}\gamma_{l\tau}\Phi^J_{L\kappa\tau}(\mathbf{r}_\tau)$$

and in the interstitial region the wave function has the same form:

$$\psi_{\mathbf{k}\lambda}(\mathbf{r}_\tau) = \sum_{L\kappa} A^{\mathbf{k}\lambda}_{L\kappa\tau}H_{L\kappa\tau}(\mathbf{r}_\tau) - \sum_{L\kappa} S^{\mathbf{k}\lambda}_{L\kappa\tau}\gamma_{l\tau}J_{L\kappa\tau}(\mathbf{r}_\tau)$$

where $A^{k\lambda}_{L\kappa\tau}$ are the variational coefficients of the LMTO-eigenvalue problem and $S^{k\lambda}_{L\kappa\tau}$ are their convolution with the structure constants, i.e

$$S^{\mathbf{k}\lambda}_{L\kappa\tau} = \sum_{L'\tau'} S^{\mathbf{k}}_{L\tau L'\tau'}(\kappa)A^{\mathbf{k}\lambda}_{L'\kappa\tau'}$$

B. SYMMETRY RELATIONS

Let us consider group operations transforming wave functions. If $\hat{g}$ is an operator of a space group it can be given by rotation $\hat{\gamma}$ and shift $\mathbf{a}$, i.e.

$$\hat{g} = \{\hat{\gamma}|a\}$$

$$\hat{g}^{-1} = \{\hat{\gamma}^{-1}| - \hat{\gamma}^{-1}a\}$$

$$\hat{g}\hat{p} = \{\hat{\gamma}|a\}\{\hat{\xi}|b\} = \{\hat{\gamma}\hat{\xi}|\hat{\gamma}b + a\}$$

such that

$$\hat{g}r = \hat{\gamma}r + a$$

$$\hat{g}^{-1}r = \hat{\gamma}^{-1}r - \hat{\gamma}^{-1}a$$

After applying a point group operation $\hat{\gamma}$ coefficients $A^{k\lambda}_{L\kappa\tau}$ are transformed in terms of Wigner's matrices:

$$A^{\hat{\gamma}\mathbf{k}}_{lm\kappa\tau} = \sum_{m'} U^l_{mm'}(\gamma)A^{\mathbf{k}\lambda}_{lm'\kappa g^{-1}\tau}e^{i\mathbf{k}\mathbf{R}_g}$$

$$\mathbf{R}_g = \hat{g}^{-1}\tau - [\hat{g}^{-1}\tau]_{inp}$$

where vector in brackets refers to an input basis vector. It can be readily proved that the coefficients S are transformed in the same manner if we account for the tranformation for LMTO-structure constants:

$$S^{\hat{\gamma}\mathbf{k}}_{l'm'\tau'lm\tau}(\kappa) = \sum_{m_1m_2} U^{l'}_{m'm_1}(\gamma)S^{\mathbf{k}}_{l'm_1g^{-1}\tau'lm_2g^{-1}\tau}(\kappa)U^{l*}_{mm_2}(\gamma)e^{i\mathbf{k}(\mathbf{R}'_g-\mathbf{R}_g)}$$

where

$$\mathbf{R}_g = \hat{g}^{-1}\tau - [\hat{g}^{-1}\tau]_{inp}$$

$$\mathbf{R}'_g = \hat{g}^{-1}\tau' - [\hat{g}^{-1}\tau']_{inp}$$

IX. FULL DENSITY

A. EXPRESSIONS

The full charge density inside MT-sphere is given by:

$$\rho_\tau(r_\tau) = \sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\psi^*_{\mathbf{k}\lambda}(\mathbf{r}_\tau)\psi_{\mathbf{k}\lambda}(\mathbf{r}_\tau) =$$
$$\sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} A^{\mathbf{k}\lambda*}_{L'\kappa'\tau}A^{\mathbf{k}\lambda}_{L\kappa\tau}\Phi^{H*}_{L'\kappa'\tau}(\mathbf{r}_\tau)\Phi^H_{L\kappa\tau}(\mathbf{r}_\tau) - \sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} A^{\mathbf{k}\lambda*}_{L'\kappa'\tau}S^{\mathbf{k}\lambda}_{L\kappa\tau}\Phi^{H*}_{L'\kappa'\tau}(\mathbf{r}_\tau)\Phi^J_{L\kappa\tau}(\mathbf{r}_\tau)\gamma_{l\tau} -$$
$$\sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} S^{\mathbf{k}\lambda*}_{L'\kappa'\tau}A^{\mathbf{k}\lambda}_{L\kappa\tau}\gamma_{l'\tau}\Phi^{J*}_{L'\kappa'\tau}(\mathbf{r}_\tau)\Phi^H_{L\kappa\tau}(\mathbf{r}_\tau) + \sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} S^{\mathbf{k}\lambda*}_{L'\kappa'\tau}S^{\mathbf{k}\lambda}_{L\kappa\tau}\gamma_{l'\tau}\Phi^{J*}_{L'\kappa'\tau}(\mathbf{r}_\tau)\Phi^J_{L\kappa\tau}(\mathbf{r}_\tau)\gamma_{l\tau}$$

or as an expansion in spherical harmonics

$$\rho_\tau(r_\tau) = \sum_{L''}^{L^v_\tau} \rho_{L''\tau}(r_\tau)i^{l''}Y_{L''}(\hat{r}_\tau)$$

where

$$\rho_{L''\tau}(r_\tau) = \sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}\Phi^{H*}_{L'\kappa'\tau}(r_\tau)\Phi^H_{L\kappa\tau}(r_\tau) - \sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}\Phi^{H*}_{L'\kappa'\tau}(r_\tau)\Phi^J_{L\kappa\tau}(r_\tau)\gamma_{l\tau} -$$
$$\sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}\gamma_{l'\tau}\Phi^{J*}_{L'\kappa'\tau}(r_\tau)\Phi^H_{L\kappa\tau}(r_\tau) + \sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}\gamma_{l'\tau}\Phi^{J*}_{L'\kappa'\tau}(r_\tau)\Phi^J_{L\kappa\tau}(r_\tau)\gamma_{l\tau}$$

The full charge density outside MT-sphere is given by

$$\rho_\tau(\mathbf{r}_\tau) = \sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\psi^*_{\mathbf{k}\lambda}(r_\tau)\psi_{\mathbf{k}\lambda}(\mathbf{r}_\tau) =$$
$$= \sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} A^{\mathbf{k}\lambda*}_{L'\kappa'\tau}A^{\mathbf{k}\lambda}_{L\kappa\tau}H^*_{L'\kappa'\tau}(\mathbf{r}_\tau)H_{L\kappa\tau}(\mathbf{r}_\tau) - \sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} A^{\mathbf{k}\lambda*}_{L'\kappa'\tau}S^{\mathbf{k}\lambda}_{L\kappa\tau}H^*_{L'\kappa'\tau}(r_\tau)J_{L\kappa\tau}(r_\tau)\gamma_{l\tau}$$
$$-\sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} S^{\mathbf{k}\lambda*}_{L'\kappa'\tau}A^{\mathbf{k}\lambda}_{L\kappa\tau}\gamma_{l'\tau}J^*_{L'\kappa'\tau}(\mathbf{r}_\tau)H_{L\kappa\tau}(\mathbf{r}_\tau) + \sum_{\mathbf{k}\lambda} 2f_{\mathbf{k}\lambda}\sum_{\substack{L'\kappa'\\ L\ \kappa}} S^{\mathbf{k}\lambda*}_{L'\kappa'\tau}S^{\mathbf{k}\lambda}_{L\kappa\tau}\gamma_{l'\tau}J^*_{L'\kappa'\tau}(\mathbf{r}_\tau)J_{L\kappa\tau}(\mathbf{r}_\tau)\gamma_{l\tau}$$

or as an expansion in spherical harmonics

$$\rho_\tau(r_\tau) = \sum_{L''}^{L^v_\tau} \rho_{L''\tau}(r_\tau)i^{l''}Y_{L''}(\hat{r}_\tau)$$

where

$$\rho_{L''\tau}(r_\tau) = \sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}H^*_{L'\kappa'\tau}(r_\tau)H_{L\kappa\tau}(r_\tau) + -\sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}H^*_{L'\kappa'\tau}(r_\tau)J_{L\kappa\tau}(r_\tau)\gamma_{l\tau}$$
$$-\sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}\gamma_{l'\tau}J^*_{L'\kappa'\tau}(r_\tau)H_{L\kappa\tau}(r_\tau) + \sum_{\substack{L'\kappa'\\ L\ \kappa}} C^{L''}_{L'L}i^{l-l'-l''}T^{\tau(1)}_{L'\kappa'L\kappa}\gamma_{l'\tau}J^*_{L'\kappa'\tau}(r_\tau)J_{L\kappa\tau}(r_\tau)\gamma_{l\tau}$$

B. NUMBERS OF STATES MATRIX

In order to find the charge density we have to calculate the following Brilloun zone integrals:

$$T^{\tau(1)}_{L'\kappa'L\kappa} = \sum_{\mathbf{k}\lambda}^{BZ} 2f_{\mathbf{k}\lambda}A^{\mathbf{k}\lambda*}_{L'\kappa'\tau}A^{\mathbf{k}\lambda}_{L\kappa\tau} = T^{\tau(1)*}_{L\kappa L'\kappa'}$$

$$T^{\tau(2)}_{L'\kappa' L\kappa} = \sum_{\mathbf{k}\lambda}^{BZ} 2f_{\mathbf{k}\lambda} A^{\mathbf{k}\lambda *}_{L'\kappa'\tau} S^{\mathbf{k}\lambda}_{L\kappa\tau} = T^{\tau(3)*}_{L\kappa L'\kappa'}$$

$$T^{\tau(3)}_{L'\kappa' L\kappa} = \sum_{\mathbf{k}\lambda}^{BZ} 2f_{\mathbf{k}\lambda} S^{\mathbf{k}\lambda *}_{L'\kappa'\tau} A^{\mathbf{k}\lambda}_{L\kappa\tau} = T^{\tau(2)*}_{L\kappa L'\kappa'}$$

$$T^{\tau(4)}_{L'\kappa' L\kappa} = \sum_{\mathbf{k}\lambda}^{BZ} 2f_{\mathbf{k}\lambda} S^{\mathbf{k}\lambda *}_{L'\kappa'\tau} S^{\mathbf{k}\lambda}_{L\kappa\tau} = T^{\tau(4)*}_{L\kappa L'\kappa'}$$

By using the tranformation properties of the variational coefficients these integrals are rediced to the irreducible Brilloun zone integrals, e.g.

$$\tilde{T}^{\tau(i)}_{L'\kappa' L\kappa} = \sum_{\mathbf{k}\lambda}^{IBZ} 2f_{\mathbf{k}\lambda} A^{\mathbf{k}\lambda *}_{L'\kappa'\tau} B^{\mathbf{k}\lambda}_{L\kappa\tau}$$

and, then, they are symmetrized over crystalline group as follows:

$$T^{\tau(i)}_{l'm'\kappa' lm\kappa} = \sum_{\gamma} \sum_{m_1 m_2} U^{l' *}_{m' m_1}(\gamma) \tilde{T}^{\hat{g}^{-1}\tau(i)}_{l' m_1 \kappa' l m_2 \kappa} U^{l}_{m m_2}(\gamma)$$

C. INTERSTITIAL REGION

$$\tilde{\rho}(\mathbf{r}) = \sum_{\mathbf{k}\lambda} f_{\mathbf{k}\lambda} \tilde{\psi}^*_{\mathbf{k}\lambda}(\mathbf{r}) \tilde{\psi}_{\mathbf{k}\lambda}(\mathbf{r}) = \sum_{\mathbf{k}\lambda} f_{\mathbf{k}\lambda} \sum_{\mathbf{G}\mathbf{G}'} \tilde{\psi}^*_{\mathbf{k}\lambda}(\mathbf{G}') \tilde{\psi}_{\mathbf{k}\lambda}(\mathbf{G}) e^{i(\mathbf{G}-\mathbf{G}')\mathbf{r}} =$$
$$= \sum_{\mathbf{G}''} e^{i\mathbf{G}''\mathbf{r}} \left[\sum_{\mathbf{k}\lambda} f_{\mathbf{k}\lambda} \sum_{\mathbf{G}} \tilde{\psi}^*_{\mathbf{k}\lambda}(\mathbf{G}-\mathbf{G}'') \tilde{\psi}_{\mathbf{k}\lambda}(\mathbf{G}) \right]$$

D. CORE DENSITY (MATTHEISS'S PROCEDURE)

According to Mattheiss the core density $\tilde{\rho}^c$ is a superposition of atomic densities ρ^c obtained from the solution of the Schrödinger (Dirac) equation for core levels. For given polyhedron (surrounded sphere) it can be written as a lattice *sum* :

$$\tilde{\rho}^c_{\tau_0}(r_{\tau_0}) = \sum_{R\ \tau} \rho^c_{\tau}(\mathbf{r}_{\tau_0} - \mathbf{R} - \tau + \tau_0) = \rho^c_{\tau_0}(r_{\tau_0}) + \sum_{R\ \tau}{}' \rho^c_{\tau}(\mathbf{r}_{\tau_0} - \boldsymbol{\Delta})$$

where $\Delta = R + \delta$ and $\delta = \tau - \tau_0$, and can be expanded in spherical harmonics:

$$\tilde{\rho}^c_{\tau_0}(\mathbf{r}_{\tau_0}) = \sum_{L} \tilde{\rho}^c_{L\tau_0}(r_{\tau_0}) i^l Y_L(\hat{r}_{\tau_0})$$

The expressions for L-components of the core density are:

$$i^l \tilde{\rho}^c_{L\tau_0}(r_{\tau_0}) = \delta_{L0} \rho^c_{\tau_0}(r_{\tau_0}) \sqrt{4\pi} + \sum_{\Delta}{}' f^{\Delta}_{L\tau_0}(r_{\tau_0}) \sum_{\Delta} Y^*_L(\hat{\Delta})$$

$$f^{\Delta}_{L\tau_0}(r_{\tau_0}) = \frac{2\pi}{r\Delta} \int_{-\Delta}^{+\Delta} x \rho^c_{\tau_0}(x) P_l\left(\frac{r^2 + \Delta^2 - x^2}{2r\Delta} \right) dx$$

where the summation over direct space is divided into summation over shells with $\Delta = const.$ as well as the angles $\hat{\Delta}$ and where P_l are the Legendere polynoms.

X. SPIN ORBIT COUPLING

Spin orbit coupling operator

$$H_{SO} = \alpha(r)\mathbf{ls} = \alpha(r)\sum_{\mu=-1,0,1} l^{\mu}s_{\mu}$$
$$\alpha(r) = \frac{1}{c^2}\frac{2}{r}\frac{dV}{dr}$$

Spin operators are expressed via Pauli matrices $\hat{\sigma}$ (do not confuse with index $\sigma =\uparrow,\downarrow$)

$$\hat{s}_{\mu} = \frac{1}{2}\hat{\sigma}_{\mu}$$
$$\hat{s}^{\mu} = \frac{1}{2}\hat{\sigma}^{\mu}$$
$$\hat{\sigma}_{\mu} = (-)^{\mu}\hat{\sigma}^{-\mu}$$
$$\hat{\sigma}^{+}_{\mu} = \hat{\sigma}^{\mu}$$
$$\hat{\sigma}_{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}, \hat{\sigma}_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \hat{\sigma}_{+1} = \frac{-1}{\sqrt{2}}\begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}$$
$$\hat{\sigma}^{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}, \hat{\sigma}^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \hat{\sigma}^{+1} = \frac{-1}{\sqrt{2}}\begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}$$
$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

A product of non-relativistic harmonic time the spin can be considered as a basis for spin orbtial hamiltonian

$$Y_{lm}(r)|\sigma\rangle$$

(This product however does not diagonalize spin orbital operator.) Spin states,$|\sigma\rangle$ are introduced, $\sigma =\uparrow,\downarrow\equiv 1,-1$

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$|\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Matrix elements of spin operators are

$$\langle\uparrow|\hat{s}_{-1}|\uparrow\rangle = -\langle\uparrow|\hat{s}^{+1}|\uparrow\rangle = 0$$
$$\langle\uparrow|\hat{s}_{-1}|\downarrow\rangle = -\langle\uparrow|\hat{s}^{+1}|\downarrow\rangle = 0$$
$$\langle\downarrow|\hat{s}_{-1}|\uparrow\rangle = -\langle\downarrow|\hat{s}^{+1}|\uparrow\rangle = +\frac{1}{\sqrt{2}}$$
$$\langle\downarrow|\hat{s}_{-1}|\downarrow\rangle = -\langle\downarrow|\hat{s}^{+1}|\downarrow\rangle = 0$$

$$\langle\uparrow|\hat{s}_{+1}|\uparrow\rangle = -\langle\uparrow|\hat{s}^{-1}|\uparrow\rangle = 0$$
$$\langle\uparrow|\hat{s}_{+1}|\downarrow\rangle = -\langle\uparrow|\hat{s}^{-1}|\downarrow\rangle = -\frac{1}{\sqrt{2}}$$
$$\langle\downarrow|\hat{s}_{+1}|\uparrow\rangle = -\langle\downarrow|\hat{s}^{-1}|\uparrow\rangle = 0$$
$$\langle\downarrow|\hat{s}_{+1}|\downarrow\rangle = -\langle\downarrow|\hat{s}^{-1}|\downarrow\rangle = 0$$

$$\langle\uparrow|\hat{s}_0|\uparrow\rangle = \langle\uparrow|\hat{s}^0|\uparrow\rangle = +\frac{1}{2}$$
$$\langle\uparrow|\hat{s}_0|\downarrow\rangle = \langle\uparrow|\hat{s}^0|\downarrow\rangle = 0$$
$$\langle\downarrow|\hat{s}_0|\uparrow\rangle = \langle\downarrow|\hat{s}^0|\uparrow\rangle = 0$$
$$\langle\downarrow|\hat{s}_0|\downarrow\rangle = \langle\downarrow|\hat{s}^0|\downarrow\rangle = -\frac{1}{2}$$

Orbital matrix elements are given by

$$\begin{aligned}\langle m'|\hat{l}_0|m\rangle &= \langle m'|\hat{l}^0|m\rangle = \delta_{m'm}m \\ \langle m'|\hat{l}_{-1}|m\rangle &= -\langle m'|\hat{l}^{+1}|m\rangle = \delta_{m'm-1}\frac{1}{\sqrt{2}}\sqrt{(l+m)(l-m+1)} \\ \langle m'|\hat{l}_{+1}|m\rangle &= -\langle m'|\hat{l}^{-1}|m\rangle = \delta_{m'm+1}\frac{-1}{\sqrt{2}}\sqrt{(l-m)(l+m+1)}\end{aligned}$$

Spin orbit coupling matrix elements are given by

$$\langle Y_{lm'}(r)\sigma'|\mathbf{ls}|Y_{lm}(r)\sigma\rangle = \delta_{m'm}m(\delta_{\sigma'\uparrow}\delta_{\sigma\uparrow}-\delta_{\sigma'\downarrow}\delta_{\sigma\downarrow})\frac{1}{2}+\delta_{m'm-1}\frac{1}{\sqrt{2}}\sqrt{(l+m)(l-m+1)}\delta_{\sigma'\uparrow}\delta_{\sigma\downarrow}\frac{1}{\sqrt{2}}+\delta_{m'm+1}\frac{1}{\sqrt{2}}\sqrt{(l-m)(l+m$$

As we see they do not diagonalize spin orbit coupling operator.
Let us perform a unitary transformation to spinor harmonics. For this, first introduce

$$\begin{aligned}\vec{Y}_{lm\uparrow}(\hat{r}) &= Y_{lm}(\hat{r})\begin{pmatrix}1\\0\end{pmatrix} \\ \vec{Y}_{lm\downarrow}(\hat{r}) &= Y_{lm}(\hat{r})\begin{pmatrix}0\\1\end{pmatrix}\end{aligned}$$

and second introduce a spinor harmonic $\vec{\Omega}^{(j=l\pm\frac{1}{2})}_{jm_j}(r)$, i.e.

$$\vec{\Omega}^{(j=l\pm\frac{1}{2})}_{jm_j}(\hat{r}) = \sum_{m\sigma}T^{(j=l\pm1/2)}_{jm_jm\sigma}Y_{lm}(\hat{r})|\vec{\sigma}\rangle = \sum_{m\sigma}T^{(j=l\pm1/2)}_{jm_jm\sigma}\vec{Y}_{lm\sigma}(\hat{r})$$

$$\begin{aligned}\vec{\Omega}^{(j=l-1/2)}_{jm_j}(\hat{r}) &= \begin{pmatrix}-\sqrt{\frac{j-m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j-\frac{1}{2}}(\hat{r}) \\ +\sqrt{\frac{j+m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j+\frac{1}{2}}(\hat{r})\end{pmatrix} \\ \vec{\Omega}^{(j=l+1/2)}_{jm_j}(\hat{r}) &= \begin{pmatrix}+\sqrt{\frac{j+m_j}{2j}}Y_{j-\frac{1}{2}m_j-\frac{1}{2}}(r) \\ +\sqrt{\frac{j-m_j}{2j}}Y_{j-\frac{1}{2}m_j+\frac{1}{2}}(r)\end{pmatrix}\end{aligned}$$

In general, transformation can be written in terms of the unitary transformation matrix $T^{(j=l\pm1/2)}_{jm_jm\sigma}$

$$\begin{aligned}\sum_{m\sigma}T^{(j=l\pm1/2)}_{jm_jm\sigma}T^{+(j'=l\pm\frac{1}{2})}_{m\sigma j'm'_{j'}} &= \delta_{jj'}\delta_{m_jm'_{j'}} \\ \sum_{m_j}T^{+(j=l-\frac{1}{2})}_{m\sigma jm_j}T^{(j=l-\frac{1}{2})}_{jm_jm'\sigma'}+\sum_{m_j}T^{+(j=l+\frac{1}{2})}_{m\sigma jm_j}T^{(j=l+\frac{1}{2})}_{jm_jm'\sigma'} &= \delta_{mm'}\delta_{\sigma\sigma'}\end{aligned}$$

and

$$\vec{\Omega}^{(j=l\pm1/2)}_{jm_j}(\hat{r}) = \sum_{m\sigma}T^{(j=l\pm1/2)}_{jm_jm\sigma}\vec{Y}_{lm\sigma}(\hat{r})$$

Consider spin orbit coupling in spinor harmonics

$$\langle\vec{\Omega}^{(j'=l\pm1/2)}_{j'm'_{j'}}|\mathbf{ls}|\vec{\Omega}^{(j=l\pm1/2)}_{jm_j}\rangle = \sum_{m'\sigma'}\sum_{m\sigma}T^{+(j=l\pm1/2)}_{j'm'_{j'}m'\sigma'}\langle\vec{Y}^{+}_{lm'\sigma'}(r)|\mathbf{ls}|\vec{Y}_{lm\sigma}\rangle T^{+(j=l\pm1/2)}_{jm_jm\sigma} = -\frac{1}{2}\delta_{j'j}\delta_{m'_{j'}m_j}(\kappa_j+1)$$

where

$$\begin{aligned}\kappa_{j=l-\frac{1}{2}} &= l \\ \kappa_{j=l+\frac{1}{2}} &= -l-1\end{aligned}$$

A. NON-COLLINEAR DEFINITIONS FOR DENSITY AND POTENTIAL

Density and magnetization calculation

$$
\begin{aligned}
\rho(\mathbf{r}) &= \sum_{\mathbf{k}j} f_{\mathbf{k}j} \langle \vec{\psi}_{\mathbf{k}j} | \hat{\imath} | \vec{\psi}_{\mathbf{k}j} \rangle_{spin} = \sum_{\mathbf{k}j\sigma} f_{\mathbf{k}j} |\psi^{(\sigma)}_{\mathbf{k}j}|^2 \\
m^0(\mathbf{r}) &= \mu_B \sum_{\mathbf{k}j} f_{\mathbf{k}j} \langle \vec{\psi}_{\mathbf{k}j} | \hat{s}^0 | \vec{\psi}_{\mathbf{k}j} \rangle_{spin} = \sum_{\mathbf{k}j} f_{\mathbf{k}j} |\psi^{(\uparrow)}_{\mathbf{k}j}|^2 - \sum_{\mathbf{k}j} f_{\mathbf{k}j} |\psi^{(\downarrow)}_{\mathbf{k}j}|^2 \\
m^{-1}(\mathbf{r}) &= \mu_B \sum_{\mathbf{k}j} f_{\mathbf{k}j} \langle \vec{\psi}_{\mathbf{k}j} | \hat{s}^{-1} | \vec{\psi}_{\mathbf{k}j} \rangle_{spin} = +\sqrt{2} \sum_{\mathbf{k}j} f_{\mathbf{k}j} \psi^{(\uparrow)*}_{\mathbf{k}j} \psi^{(\downarrow)}_{\mathbf{k}j} = +\sqrt{2}\rho_{\uparrow\downarrow} \\
m^{+1}(\mathbf{r}) &= \mu_B \sum_{\mathbf{k}j} f_{\mathbf{k}j} \langle \vec{\psi}_{\mathbf{k}j} | \hat{s}^{+1} | \vec{\psi}_{\mathbf{k}j} \rangle_{spin} = -\sqrt{2} \sum_{\mathbf{k}j} f_{\mathbf{k}j} \psi^{(\downarrow)*}_{\mathbf{k}j} \psi^{(\uparrow)}_{\mathbf{k}j} = -\sqrt{2}\rho_{\downarrow\uparrow}
\end{aligned}
$$

where we can define density matrix $\rho_{\sigma\sigma'}$

$$
\begin{aligned}
\rho_{\uparrow\uparrow}(\mathbf{r}) &= \sum_{\mathbf{k}j} f_{\mathbf{k}j} |\psi^{(\uparrow)}_{\mathbf{k}j}|^2 \\
\rho_{\downarrow\downarrow}(\mathbf{r}) &= \sum_{\mathbf{k}j} f_{\mathbf{k}j} |\psi^{(\downarrow)}_{\mathbf{k}j}|^2 \\
\rho_{\uparrow\downarrow}(\mathbf{r}) &= \sum_{\mathbf{k}j} f_{\mathbf{k}j} \psi^{(\uparrow)*}_{\mathbf{k}j} \psi^{(\downarrow)}_{\mathbf{k}j} = \rho^*_{\downarrow\uparrow} \\
\rho_{\downarrow\uparrow}(\mathbf{r}) &= \sum_{\mathbf{k}j} f_{\mathbf{k}j} \psi^{(\downarrow)*}_{\mathbf{k}j} \psi^{(\uparrow)}_{\mathbf{k}j} = \rho^*_{\uparrow\downarrow}
\end{aligned}
$$

and use the following transformations

$$
\begin{aligned}
\rho &= \rho_{\uparrow\uparrow} + \rho_{\downarrow\downarrow} \\
m^0 &= \rho_{\uparrow\uparrow} - \rho_{\downarrow\downarrow} = m_0 \\
m^{-1} &= +\sqrt{2}\rho_{\uparrow\downarrow} = -m_{+1} \\
m^{+1} &= -\sqrt{2}\rho_{\downarrow\uparrow} = -m_{-1}
\end{aligned}
$$

Inside the program spin density matrix array is defined as follows (checked **bnd_tospar.f** 01/25/2006)

$$((RHO(ISPIN, IORBS), ISPIN = 1, NSPIN), IORBS = 1, NORBS)$$

$$
\begin{aligned}
\rho^{11}(\mathbf{r}) &= \rho_{\uparrow\uparrow}(\mathbf{r}) = (\rho + m^0)/2 \\
\rho^{21}(\mathbf{r}) &= \rho_{\downarrow\downarrow}(\mathbf{r}) = (\rho - m^0)/2 \\
\rho^{12}(\mathbf{r}) &= +\sqrt{2}\rho_{\uparrow\downarrow}(\mathbf{r}) = m^{-1} \\
\rho^{22}(\mathbf{r}) &= -\sqrt{2}\rho_{\downarrow\uparrow}(\mathbf{r}) = m^{+1}
\end{aligned}
$$

Advantage:

No spin polarization, no spin–orbit coupling	$Nspin = 1, Norbs = 1$
Spin polarization, no spin–orbit coupling	$Nspin = 2, Norbs = 1$
No spin polarization, spin–orbit coupling	n/a
Spin polarization, spin–orbit coupling	$Nspin = 2, Norbs = 2$

The wave function is expanded into LMTO basis

$$\vec{\psi}_{\mathbf{k}j} = \sum_\alpha A^{\mathbf{k}j(\uparrow)}_\alpha \chi^{\mathbf{k}}_\alpha(r) |\uparrow\rangle + \sum_\alpha A^{\mathbf{k}j(\downarrow)}_\alpha \chi^{\mathbf{k}}_\alpha(r) |\downarrow\rangle$$

Inside the program, number of states matrix is defined as follows

$$T^{\uparrow\uparrow}_{\alpha\beta} = \sum_{\mathbf{k}j} f_{\mathbf{k}j} A^{\mathbf{k}j(\uparrow)*}_{\alpha} A^{\mathbf{k}j(\uparrow)}_{\beta}$$
$$T^{\downarrow\downarrow}_{\alpha\beta} = \sum_{\mathbf{k}j} f_{\mathbf{k}j} A^{\mathbf{k}j(\downarrow)*}_{\alpha} A^{\mathbf{k}j(\downarrow)}_{\beta}$$
$$T^{\uparrow\downarrow}_{\alpha\beta} = +\sqrt{2} \sum_{\mathbf{k}j} f_{\mathbf{k}j} A^{\mathbf{k}j(\uparrow)*}_{\alpha} A^{\mathbf{k}j(\downarrow)}_{\beta}$$
$$T^{\downarrow\uparrow}_{\alpha\beta} = -\sqrt{2} \sum_{\mathbf{k}j} f_{\mathbf{k}j} A^{\mathbf{k}j(\downarrow)*}_{\alpha} A^{\mathbf{k}j(\uparrow)}_{\beta}$$

Notice that in order to explore the rotational properties of the number of states matrix we need to deal with the integrals

$$\tilde{T}^{\sigma\sigma'}_{\alpha\beta} = \sum_{\mathbf{k}j} f_{\mathbf{k}j} A^{\mathbf{k}j(\sigma)*}_{\alpha} A^{\mathbf{k}j(\sigma')}_{\beta}$$

which do not have the $\pm\sqrt{2}$ prefactors in their off diagonal elements!
How to define similar maitrces $v_{\sigma\sigma'}$ $v(ij)$ for the potential - magnetic field

$$V, \mathbf{B} = \sum_{\mu} B^{\mu} \mathbf{e}_{\mu} = \sum_{\mu} B_{\mu} \mathbf{e}^{\mu}$$

First, typical contribution to the total energy related to the potential and density has the form

$$E = \int V\rho - \mathbf{Bm} = \int [V\rho^* - \mathbf{Bm}^*] = \int [V\rho - B^0 m_0 - B^{-1} m_{-1} - B^{+1} m_{+1} = V\rho - B^0[m^0]^* - B^{-1}[m^{-1}]^* - B^{+1}[m^{+1}]^*]$$

which we would like to write in the form similar to

$$E = \sum_{\sigma\sigma'} \int v_{\sigma\sigma'} \rho_{\sigma'\sigma}$$

The potential matrix is most naturally defined as the matrix elements of the operator

$$V\hat{\imath} - \mu_B \mathbf{B}\hat{\mathbf{s}} = V\hat{\imath} - 2\mathbf{B}\hat{\mathbf{s}} = V\hat{\imath} - \mathbf{B}\hat{\sigma} = V\hat{\imath} - B^0\hat{\sigma}_0 - B^{-1}\hat{\sigma}_{-1} - B^{+1}\hat{\sigma}_{+1}$$

which are computed as follows

$$\langle v_{\uparrow\uparrow}\rangle = \langle\uparrow|V\hat{\imath} - \mathbf{B}\hat{\sigma}|\uparrow\rangle = \langle\uparrow|V - B^0\hat{\sigma}_0|\uparrow\rangle = \langle V\rangle - \langle B^0\rangle$$
$$\langle v_{\downarrow\downarrow}\rangle = \langle\downarrow|V\hat{\imath} - \mathbf{B}\hat{\sigma}|\downarrow\rangle = \langle\downarrow|V - B^0\hat{\sigma}_0|\downarrow\rangle = \langle V\rangle + \langle B^0\rangle$$
$$\langle v_{\uparrow\downarrow}\rangle = \langle\uparrow|V\hat{\imath} - \mathbf{B}\hat{\sigma}|\downarrow\rangle = \langle\uparrow| - B^{+1}\hat{\sigma}_{+1}|\downarrow\rangle = -\langle B^{+1}\rangle(-\sqrt{2}) = +\langle B^{+1}\rangle\sqrt{2}$$
$$\langle v_{\downarrow\uparrow}\rangle = \langle\downarrow|V\hat{\imath} - \mathbf{B}\hat{\sigma}|\uparrow\rangle = \langle\downarrow| - B^{-1}\hat{\sigma}_{-1}|\uparrow\rangle = -\langle B^{-1}\rangle(+\sqrt{2}) = -\langle B^{-1}\rangle\sqrt{2}$$

We obtain the following definitions

$$\langle V\rangle = +\frac{1}{2}(\langle v_{\uparrow\uparrow}\rangle + v_{\downarrow\downarrow}\rangle)$$
$$\langle B^0\rangle = -\frac{1}{2}(\langle v_{\uparrow\uparrow}\rangle - v_{\downarrow\downarrow}\rangle)$$
$$\langle B^{-1}\rangle = -\langle v_{\downarrow\uparrow}\rangle/\sqrt{2}$$
$$\langle B^{+1}\rangle = +\langle v_{\uparrow\downarrow}\rangle/\sqrt{2}$$

Note that these definitions for $\langle v_{\sigma\sigma'}\rangle$ are different from the definitions for density matrix $\rho_{\sigma\sigma'}$ because potential matrix is interpreted as the spinor matrix elements with σ_μ (lower subscript) since we want to find the connections for upper subscripted B^μ.

Inside the program potential array is defined (similar to the density array) as follows (checked NMTPAR 01/25/2006)

$$((POT(ISPIN, IORBS), ISPIN = 1, NSPIN), IORBS = 1, NORBS)$$

$$\begin{aligned}
V^{11}(\mathbf{r}) &= v_{\uparrow\uparrow}(\mathbf{r}) = V - B^0 \\
V^{21}(\mathbf{r}) &= v_{\downarrow\downarrow}(\mathbf{r}) = V + B^0 \\
V^{12}(\mathbf{r}) &= +v_{\downarrow\uparrow}(\mathbf{r})/\sqrt{2} = -B^{-1} \\
V^{22}(\mathbf{r}) &= -v_{\uparrow\downarrow}(\mathbf{r})/\sqrt{2} = -B^{+1}
\end{aligned}$$

"–" in front of B_0 magnetic field accounts for the fact that if $m_z > 0$ points up, means that $n_\uparrow > n_\downarrow$ and consequently, $v_\uparrow < v_\downarrow$.

Matrix elements in the hamiltonian are therefore computed as follows

$$\begin{aligned}
\langle v_{\uparrow\uparrow}\rangle &= \langle V^{11}\rangle \\
\langle v_{\downarrow\downarrow}\rangle &= \langle V^{21}\rangle \\
\langle v_{\uparrow\downarrow}\rangle &= -\langle V^{22}\rangle\sqrt{2} \\
\langle v_{\downarrow\uparrow}\rangle &= +\langle V^{12}\rangle\sqrt{2}
\end{aligned}$$

Contribution to the total energy related to the potential and density has the form

$$\begin{aligned}
E &= V\rho - \mathbf{B}\mathbf{m} = V\rho^* - \mathbf{B}\mathbf{m}^* = V\rho - \sum_\mu B^\mu m_\mu = \\
&= \rho_{\uparrow\uparrow}v_{\uparrow\uparrow} + \rho_{\downarrow\downarrow}v_{\downarrow\downarrow} + v_{\downarrow\uparrow}\rho_{\downarrow\uparrow} + v_{\uparrow\downarrow}\rho_{\uparrow\downarrow} = \rho_{\uparrow\uparrow}v_{\uparrow\uparrow} + \rho_{\downarrow\downarrow}v_{\downarrow\downarrow} + v_{\downarrow\uparrow}\rho^*_{\uparrow\downarrow} + v_{\uparrow\downarrow}\rho^*_{\downarrow\uparrow} = \sum v_{\sigma\sigma'}\rho^*_{\sigma'\sigma} \\
&= \frac{1}{2}[v^{11} + v^{21}] \times [\rho^{11} + \rho^{21}] + \frac{1}{2}[v^{11} - v^{21}] \times [\rho^{11} - \rho^{21}] + v^{12}\rho^{12*} + v^{21}\rho^{21*} \\
&= v^{11}\rho^{11} + v^{21}\rho^{21} + v^{12}\rho^{12*} + v^{21}\rho^{21*} = \sum_{ij} v^{ij}\rho^{ij*}
\end{aligned}$$

$$\begin{aligned}
\frac{\delta E}{\delta \mathbf{m}} &= -\mathbf{B} \\
\frac{\delta E}{\delta m_\mu} &= -B^\mu \\
\frac{\delta E}{\delta \rho_{\sigma\sigma'}} &= v_{\sigma'\sigma}
\end{aligned}$$

$$\begin{aligned}
\rho_{\uparrow\uparrow}V_{\uparrow\uparrow} + \rho_{\downarrow\downarrow}V_{\downarrow\downarrow} &= \frac{1}{2}(\rho + m_z)(V - B_z) + \frac{1}{2}(\rho - m_z)(V + B_z) = \\
&= \rho V - m_z B_z
\end{aligned}$$

Note finally that the translation to cartesian coordinates has the form

$$\begin{aligned}
m_x &= \frac{1}{\sqrt{2}}(m^{-1} - m^{+1}) = \frac{1}{\sqrt{2}}(m_{-1} - m_{+1}) \\
m_y &= -\frac{i}{\sqrt{2}}(m^{-1} + m^{+1}) = +\frac{i}{\sqrt{2}}(m_{-1} + m_{+1}) \\
m_z &= m^0
\end{aligned}$$

$$\begin{aligned}
B_x &= \frac{1}{\sqrt{2}}(B^{-1} - B^{+1}) = \frac{1}{\sqrt{2}}(B_{-1} - B_{+1}) \\
B_y &= -\frac{i}{\sqrt{2}}(B^{-1} + B^{+1}) = +\frac{i}{\sqrt{2}}(B_{-1} + B_{+1}) \\
B_z &= B^0 = B_0
\end{aligned}$$

B. Exchange–Correlation Functionals in Non-Collinear Form

1. Local Density Approximation

We assume that in LDA exchange correlation energy is a functional of density $\rho = \rho_\uparrow + \rho_\downarrow$ and absolute value of magnetization$|\mathbf{m}| = m = \rho_\uparrow - \rho_\downarrow$.

$$E_{xc}^{LDA}[\rho, m] = E_{xc}^{LDA}[\rho_\uparrow, \rho_\downarrow]$$

Notice that $\rho_\uparrow, \rho_\downarrow$ densities here are NOT diagonal components of the density matrix $\rho_{\sigma\sigma'}$ but its eigenvales, and these have to be computed from the knowledge of total density and total absolute value of magnetization:

$$\begin{aligned}
\rho_\uparrow &= \frac{\rho + m}{2} \\
\rho_\downarrow &= \frac{\rho - m}{2} \\
\rho &= \rho_\uparrow + \rho_\downarrow \\
m &= \rho_\uparrow - \rho_\downarrow
\end{aligned}$$

The exchange–correlation potential is given by

$$\begin{aligned}
V_{xc}^{LDA}[\rho, m] &= \frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta \rho} \\
\mathbf{B}_{xc}^{LDA}[\rho, \mathbf{m}] &= -\frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta \mathbf{m}} = -\frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta m}\frac{\delta m}{\delta \mathbf{m}} = -\frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta m}\frac{\mathbf{m}}{m} = B_{xc}^{LDA}[\rho, m]\frac{\mathbf{m}}{m}
\end{aligned}$$

where the exchange correlation magnetic field is represented as the vector pointing in the direction of magnetization:

$$\begin{aligned}
\mathbf{B}_{xc}^{LDA}[\rho, \mathbf{m}] &= B_{xc}^{LDA}[\rho, m]\frac{\mathbf{m}}{m} \\
B_{xc}^{LDA}[\rho, m] &= -\frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta m}
\end{aligned}$$

Alternatively, we can introduce up and down potentials:

$$\begin{aligned}
V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] &= \frac{\delta E_{xc}^{LDA}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow} = V_{xc}^{LDA}[\rho, m] - B_{xc}^{LDA}[\rho, m] = \frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta \rho} - \frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta m} \\
V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] &= \frac{\delta E_{xc}^{LDA}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow} = V_{xc}^{LDA}[\rho, m] + B_{xc}^{LDA}[\rho, m] = \frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta \rho} + \frac{\delta E_{xc}^{LDA}[\rho, m]}{\delta m}
\end{aligned}$$

so that

$$\begin{aligned}
V_{xc}^{LDA}[\rho, m] &= +\frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] + V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow]\right) \\
B_{xc}^{LDA}[\rho, m] &= -\frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow]\right)
\end{aligned}$$

Program **pot_vexch.f** computes using LDA

$$\begin{aligned}
V_{xc}^{11} &= v_{xc\uparrow\uparrow} = V_{xc} - B_{xc}^{0} = V_{xc}^{LDA}[\rho, m] - B_{xc}^{LDA}[\rho, m]\frac{m^0}{m} = \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] + V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow]\right) + \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow,\right. \\
V_{xc}^{21} &= v_{xc\downarrow\downarrow} = V_{xc} + B_{xc}^{0} = V_{xc}^{LDA}[\rho, m] + B_{xc}^{LDA}[\rho, m]\frac{m^0}{m} = \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] + V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow]\right) - \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow,\right. \\
V_{xc}^{12} &= +v_{xc\downarrow\uparrow}/\sqrt{2} = -B_{xc}^{-1} = -B_{xc}^{LDA}[\rho, m]\frac{m^{-1}}{m} = \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow]\right)\frac{\rho^{12}}{m} \\
V_{xc}^{22} &= -v_{xc\uparrow\downarrow}/\sqrt{2} = -B_{xc}^{+1} = -B_{xc}^{LDA}[\rho, m]\frac{m^{+1}}{m} = \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow]\right)\frac{\rho^{22}}{m}
\end{aligned}$$

2. Generalized Gradient Approximation

In GGA the functional depends on density first and second gradients

$$E_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m] = E_{xc}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow]$$

The exchange–correlation potential and exchange correlation magnetic field are given by

$$\begin{aligned}
V_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m] &= \frac{\delta E_{xc}^{LDA}[[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta\rho} \\
\mathbf{B}_{xc}^{LDA}[\rho, \mathbf{m}, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m] &= -\frac{\delta E_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta\mathbf{m}} \\
&= -\frac{\delta E_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta m}\frac{\delta m}{\delta\mathbf{m}} \\
&= -\frac{\delta E_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta m}\frac{\mathbf{m}}{m} \\
&= B_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]\frac{\mathbf{m}}{m}
\end{aligned}$$

and program **pot_vexch.f** computes using GGA

$$\begin{aligned}
V_{xc}^{11} &= v_{xc\uparrow\uparrow} = V_{xc} - B_{xc}^0 = V_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m] - B_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]\frac{m^0}{m} \\
&= \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow] + V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow]\right) + \\
&\quad \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow]\right)\frac{m^0}{m} \\
V_{xc}^{21} &= v_{xc\downarrow\downarrow} = V_{xc} + B_{xc}^0 = V_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m] + B_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]\frac{m^0}{m} \\
&= \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow] + V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow]\right) - \\
&\quad \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow]\right)\frac{m^0}{m} \\
V_{xc}^{12} &= +v_{xc\downarrow\uparrow}/\sqrt{2} = -B_{xc}^{-1} = -B_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]\frac{m^{-1}}{m} \\
&= \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow]\right)\frac{\rho^{12}}{m} \\
V_{xc}^{22} &= -v_{xc\uparrow\downarrow}/\sqrt{2} = -B_{xc}^{+1} = -B_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]\frac{m^{+1}}{m} \\
&= \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow, \rho_\downarrow, \nabla_\alpha\rho_\uparrow, \nabla_\alpha\rho_\downarrow, \nabla_\alpha\nabla_\beta\rho_\uparrow, \nabla_\alpha\nabla_\beta\rho_\downarrow]\right)\frac{\rho^{22}}{m}
\end{aligned}$$

In principle there are contributions to the exchange correlation magnetic field given by the variations

$$\sum_\alpha \frac{\delta E_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_\alpha m)}\frac{\delta(\nabla_\alpha m)}{\delta\mathbf{m}} + \sum_{\alpha\beta}\frac{\delta E_{xc}^{LDA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_\alpha\nabla_\beta m)}\frac{\delta(\nabla_\alpha\nabla_\beta m)}{\delta\mathbf{m}}$$

where

$$\frac{\delta(\nabla_\alpha m)}{\delta\mathbf{m}} = \nabla_\alpha\left(\frac{\delta m}{\delta\mathbf{m}}\right) = \nabla_\alpha\left(\frac{\mathbf{m}}{m}\right)$$

and where

$$\frac{\delta(\nabla_\alpha\nabla_\beta m)}{\delta\mathbf{m}} = \nabla_\alpha\nabla_\beta\left(\frac{\delta m}{\delta\mathbf{m}}\right) = \nabla_\alpha\nabla_\beta\left(\frac{\mathbf{m}}{m}\right)$$

If unit vector $\mathbf{m}(\mathbf{r})/m(r)$ changes from one point to the other, as is the case of non–collinearity introduced by spin orbit coupling those terms are not equal to zero.

Denoting

$$G^{(1)}_{xc,\alpha}(\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m) = \frac{\delta E^{LDA}_{xc}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_\alpha m)}$$
$$G^{(2)}_{xc,\alpha\beta}(\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m) = \frac{\delta E^{LDA}_{xc}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_\alpha\nabla_\beta m)}$$

we have two additional contribitions to exchange–correlation magnetic field (not programmed in **pot_vexch.f)**

$$\sum_\alpha G^{(1)}_{xc,\alpha}(\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m)\nabla_\alpha\left(\frac{\mathbf{m}}{m}\right) + \sum_{\alpha\beta} G^{(2)}_{xc,\alpha\beta}(\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m)\nabla_\alpha\nabla_\beta\left(\frac{\mathbf{m}}{m}\right)$$

C. Non-Collinear Form of Exchange–Correlation in Linear Response Theory

1. *Local Density Approximation*

Let us furher evaluate the change of exchange correlation potential upon the appearance of induced density $\Delta\rho$ and magnetization $\mathbf{\Delta m}$. There are two limits which we can consider: $\Delta m \ll m$ which corresponds to magnetically ordered system and $\Delta m \gg m$ which corresponds to paramagnetic system ($m = 0$) or the case of very weak magnetization such as spin–orbit coupled calculation. For the case of magnetically ordered system, the change in absolute magnetization is given by

$$\Delta m = \frac{\delta m}{\delta\mathbf{m}}\mathbf{\Delta m} = \frac{\mathbf{m}\mathbf{\Delta m}}{m} = \sum_\beta \frac{m_\beta \Delta m_\beta}{m}$$

and the change in unit vector is given by

$$\Delta\left(\frac{m_\alpha}{m}\right) = \sum_\beta\left(\frac{\delta}{\delta m_\beta}\frac{m_\alpha}{m}\right)\Delta m_\beta = \sum_\beta \frac{1}{m}\left(\delta_{\alpha\beta} - \frac{m_\alpha m_\beta}{m^2}\right)\Delta m_\beta = \frac{\Delta m_\alpha}{m} - \frac{\Delta m}{m}\frac{m_\alpha}{m}$$

which is non zero only for a transverse perturbation relative to the original direction of $\mathbf{m}$. Changes in exchange correlation potential and magnetic fields are given by

$$\Delta V^{LDA}_{xc}[\rho, m] = \frac{\delta V^{LDA}_{xc}[\rho, m]}{\delta\rho}\Delta\rho + \frac{\delta V^{LDA}_{xc}[\rho, m]}{\delta m}\Delta m$$
$$\Delta B^{LDA}_{xc}[\rho, m] = \frac{\delta B^{LDA}_{xc}[\rho, m]}{\delta\rho}\Delta\rho + \frac{\delta B^{LDA}_{xc}[\rho, m]}{\delta m}\Delta m$$
$$\Delta B^{LDA}_{xc,\alpha}[\rho, \mathbf{m}] = \Delta\left(B^{LDA}_{xc}[\rho, m]\frac{m_\alpha}{m}\right) = \Delta B^{LDA}_{xc}[\rho, m]\frac{m_\alpha}{m} + B^{LDA}_{xc}[\rho, m]\Delta\left(\frac{m_\alpha}{m}\right)$$

or in the matrix form

$$\Delta V^{11}_{xc} = \Delta v_{xc\uparrow\uparrow} = \Delta V_{xc} - \Delta B^0_{xc} = \Delta V^{LDA}_{xc}[\rho, m] - \Delta B^{LDA}_{xc}[\rho, m]\frac{m^0}{m} - B^{LDA}_{xc}[\rho, m]\Delta\left(\frac{m^0}{m}\right)$$
$$\Delta V^{21}_{xc} = \Delta v_{xc\downarrow\downarrow} = \Delta V_{xc} + \Delta B^0_{xc} = \Delta V^{LDA}_{xc}[\rho, m] + \Delta B^{LDA}_{xc}[\rho, m]\frac{m^0}{m} + B^{LDA}_{xc}[\rho, m]\Delta\left(\frac{m^0}{m}\right)$$
$$\Delta V^{12}_{xc} = +\Delta v_{xc\downarrow\uparrow}/\sqrt{2} = -\Delta B^{-1}_{xc} = -\Delta B^{LDA}_{xc}[\rho, m]\frac{m^{-1}}{m} - B^{LDA}_{xc}[\rho, m]\Delta\left(\frac{m^{-1}}{m}\right)$$
$$\Delta V^{22}_{xc} = -\Delta v_{xc\uparrow\downarrow}/\sqrt{2} = -\Delta B^{+1}_{xc} = -\Delta B^{LDA}_{xc}[\rho, m]\frac{m^{+1}}{m} - B^{LDA}_{xc}[\rho, m]\Delta\left(\frac{m^{+1}}{m}\right)$$

We can introduce spin up and spin down induced densities in the form

$$
\begin{aligned}
\Delta\rho_\uparrow &= \frac{\Delta\rho + \Delta m}{2} \\
\Delta\rho_\downarrow &= \frac{\Delta\rho - \Delta m}{2} \\
\Delta\rho &= \Delta\rho_\uparrow + \Delta\rho_\downarrow \\
\Delta m &= \Delta\rho_\uparrow - \Delta\rho_\downarrow
\end{aligned}
$$

Note again that those are not the diagonal elements of the induced density matrix $\Delta\rho_{\sigma\sigma'}$ but its eigenvalues.

We can write

$$
\begin{aligned}
\Delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow] = \Delta V_{xc}^{LDA}[\rho,m] - \Delta B_{xc}^{LDA}[\rho,m] &= \frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\uparrow}\Delta\rho_\uparrow + \frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\downarrow}\Delta\rho_\downarrow \\
\Delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow] = \Delta V_{xc}^{LDA}[\rho,m] + \Delta B_{xc}^{LDA}[\rho,m] &= \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\uparrow}\Delta\rho_\uparrow + \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\downarrow}\Delta\rho_\downarrow
\end{aligned}
$$

$$
\begin{aligned}
\Delta V_{xc}^{LDA}[\rho,m] &= +\frac{1}{2}\left(\Delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow] + \Delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]\right) = \frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\uparrow} + \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\uparrow}\right)\Delta\rho_\uparrow + \left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\downarrow} + \ldots\right. \\
&= +\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} + \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma \\
\Delta B_{xc}^{LDA}[\rho,m] &= -\frac{1}{2}\left(\Delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow] - \Delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]\right) = -\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\uparrow} - \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\uparrow}\right)\Delta\rho_\uparrow - \left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\downarrow} - \ldots\right. \\
&= -\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} - \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma
\end{aligned}
$$

$$
\Delta V_{xc}^{11} = \sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} + \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma + \frac{m^0}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} - \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma + \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow \ldots\right.
$$

$$
\Delta V_{xc}^{21} = \sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} + \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma - \frac{m^0}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} - \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma - \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow \ldots\right.
$$

$$
\begin{aligned}
\Delta V_{xc}^{12} &= \frac{\rho^{12}}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} - \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma + \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]\right)\;\underbrace{\Delta\left(\frac{m^{-1}}{m}\right)}_{\frac{\Delta m^{-1}}{m} - \frac{\Delta m}{m}\frac{\rho^{12}}{m}} \\
\Delta V_{xc}^{22} &= \frac{\rho^{22}}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma} - \frac{\delta V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma + \frac{1}{2}\left(V_{xc\uparrow}^{LDA}[\rho_\uparrow,\rho_\downarrow] - V_{xc\downarrow}^{LDA}[\rho_\uparrow,\rho_\downarrow]\right)\;\underbrace{\Delta\left(\frac{m^{+1}}{m}\right)}_{\frac{\Delta m^{+1}}{m} - \frac{\Delta m}{m}\frac{\rho^{22}}{m}}
\end{aligned}
$$

We can combine last terms and obtain (if $\Delta m \neq 0$)

$$\begin{aligned}
\Delta V^{11}_{xc} &= \sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}+\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma+\frac{m^0}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma+\frac{1}{2}\Big(V^{LDA}_{xc\uparrow}[\rho_\uparrow \\
&= \sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}+\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma+\frac{m^0}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma-\frac{m^0}{m}\frac{1}{2}\Big(V^{LD}_{xc\uparrow} \\
&= \sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}+\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma+\frac{m^0}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\Bigg(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\Big(V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]-V}{m}
\end{aligned}$$

To summarize we obtain

$$\begin{aligned}
\Delta V^{11}_{xc} &= \sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}+\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma+\frac{m^0}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\Bigg(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\Big(V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]-V}{m} \\
\Delta V^{21}_{xc} &= \sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}+\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}\right)\Delta\rho_\sigma-\frac{m^0}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\Bigg(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\Big(V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]-V}{m} \\
\Delta V^{12}_{xc} &= \frac{\rho^{12}}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\left(V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]-V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]\right)}{m}(-1)^{\sigma+1}\right)\Delta\rho_\sigma+\frac{\Delta\rho^{12}}{\Delta m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\Bigg(\Big(V \\
\Delta V^{22}_{xc} &= \frac{\rho^{22}}{m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]}{\delta\rho_\sigma}-\frac{\left(V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]-V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]\right)}{m}(-1)^{\sigma+1}\right)\Delta\rho_\sigma+\frac{\Delta\rho^{22}}{\Delta m}\sum_{\sigma=\uparrow\downarrow}\frac{1}{2}\Bigg(\Big(V
\end{aligned}$$

2. Limt of vanishing magnetization in LDA

When $m \to 0$ we first notice that

$$\lim_{m\to 0}\frac{1}{2}\frac{\left(V^{LDA}_{xc\uparrow}[\rho_\uparrow,\rho_\downarrow]-V^{LDA}_{xc\downarrow}[\rho_\uparrow,\rho_\downarrow]\right)}{m} = -\lim_{m\to 0}\frac{B^{LDA}_{xc}[\rho,m]}{m} = \underbrace{-B^{LDA}_{xc}[\rho,m=0]}_{\equiv 0!}-\frac{\delta B^{LDA}_{xc}[\rho,m]}{\delta m}|_{m=0}$$

or using up/down potentials

$$
\begin{aligned}
&= \lim_{\rho_\uparrow \to \rho_\downarrow} \frac{1}{2} \frac{\left(V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow] - V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]\right)}{\rho_\uparrow - \rho_\downarrow} \\
&= \lim_{\rho_\uparrow \to \rho_\downarrow} \frac{1}{2} \frac{\left(V^{LDA}_{xc\uparrow}[\frac{\rho_\uparrow+\rho_\downarrow}{2} + \frac{\rho_\uparrow-\rho_\downarrow}{2}, \frac{\rho_\uparrow+\rho_\downarrow}{2} - \frac{\rho_\uparrow-\rho_\downarrow}{2}] - V^{LDA}_{xc\downarrow}[\frac{\rho_\uparrow+\rho_\downarrow}{2} + \frac{\rho_\uparrow-\rho_\downarrow}{2}, \frac{\rho_\uparrow+\rho_\downarrow}{2} - \frac{\rho_\uparrow-\rho_\downarrow}{2}]\right)}{\rho_\uparrow - \rho_\downarrow} \\
&= \frac{1}{4} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{1}{4} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{1}{4} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} + \frac{1}{4} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} \\
&= \frac{(\Delta\rho_\uparrow - \Delta\rho_\downarrow)}{4\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{(\Delta\rho_\uparrow - \Delta\rho_\downarrow)}{4\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{(\Delta\rho_\uparrow - \Delta\rho_\downarrow)}{4\Delta m} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} + \frac{(\Delta\rho_\uparrow - \Delta\rho}{4\Delta m} \\
&= \frac{\Delta\rho_\uparrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\Delta\rho_\uparrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} + \frac{\Delta\rho_\downarrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\Delta\rho_\downarrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} + \\
&\quad \underbrace{\frac{\Delta\rho_\uparrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\Delta\rho_\uparrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} + \frac{\Delta\rho_\downarrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\Delta\rho_\downarrow}{4\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow}}_{same} \\
&= \frac{\Delta\rho_\uparrow}{2\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\Delta\rho_\uparrow}{2\Delta m} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\uparrow}|_{\rho_\uparrow=\rho_\downarrow} + \frac{\Delta\rho_\downarrow}{2\Delta m} \frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\Delta\rho_\downarrow}{2\Delta m} \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\downarrow}|_{\rho_\uparrow=\rho_\downarrow} \\
&= \frac{1}{\Delta m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} \right) \Delta\rho_\sigma
\end{aligned}
$$

where the result should not depend on $\Delta m = \Delta\rho_\uparrow - \Delta\rho_\downarrow$.

Then the limits can be easily worked out

$$
\begin{aligned}
\lim_{m\to 0} \Delta V^{11}_{xc} &= \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} + \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} \right) \Delta\rho_\sigma + \frac{m^0}{m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta \\
&\quad - \frac{m^0}{m} \frac{1}{2} \frac{\left(V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow] - V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]\right)}{m} \Delta m + \frac{\Delta m^0}{\Delta m} \frac{1}{2} \frac{\left(V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow] - V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]\right)}{m} \Delta m \\
&= \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} + \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} \right) \Delta\rho_\sigma + \frac{m^0}{m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta \\
&\quad - \frac{m^0}{m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} \right) \Delta\rho_\sigma + \frac{\Delta m^0}{\Delta m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\delta V^{LL}_{xc\downarrow}}{} \right. \\
&= \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} + \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} \right) \Delta\rho_\sigma + \frac{\Delta m^0}{\Delta m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma}|_{\rho_\uparrow=\rho_\downarrow} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow,}{\delta \rho_\sigma} \right.
\end{aligned}
$$

and we obtain after cancellations

$$
\begin{aligned}
\Delta V^{11}_{xc} &= \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} + \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta\rho_\sigma + \frac{\Delta m^0}{\Delta m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta\rho_\sigma \\
\Delta V^{21}_{xc} &= \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} + \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta\rho_\sigma - \frac{\Delta m^0}{\Delta m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta\rho_\sigma \\
\Delta V^{12}_{xc} &= \frac{\Delta\rho^{12}}{\Delta m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta\rho_\sigma \\
\Delta V^{22}_{xc} &= \frac{\Delta\rho^{22}}{\Delta m} \sum_{\sigma=\uparrow\downarrow} \frac{1}{2} \left(\frac{\delta V^{LDA}_{xc\uparrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} - \frac{\delta V^{LDA}_{xc\downarrow}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma} \right) \Delta\rho_\sigma
\end{aligned}
$$

3. Purely Papamagnetic Case within LDA

In the case we have no magnetization in the unit cell, i.e., $m = 0$, the theory of exchange correlation is the Stoner theory where the induced magnetic field is given by

$$\Delta\mathbf{B}_{xc}^{LDA}[\rho, m] = I_{xc}[\rho]\Delta\mathbf{m}$$

with the Stoner enhancement factor

$$I_{xc}[\rho] = \frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta m}|_{m=0}$$

The direction of the exchange–correlation magnetic field is along the magnetization which is given by external field $\hat{b}_{ext}$ applied at first iteration. At the absence of spin orbit coupling this direction will remain in the self-consistent solution. The induced magnetic field due to $\Delta\mathbf{m}$ is thus given by

$$\Delta B_{xc,\alpha}^{LDA}[\rho, m] = I_{xc}[\rho]\Delta m_\alpha$$

For a general response due to $\Delta\rho$ and $\Delta\mathbf{m}$ the induced exchange–correlation potential and magnetic field in the paramagnetic case are described as follows

$$\begin{aligned}
\lim_{m\to 0} \Delta V_{xc}^{LDA}[\rho, m] &= \lim_{m\to 0} \frac{\delta V_{xc}^{LDA}[\rho, m]}{\delta\rho}\Delta\rho + \lim_{m\to 0} \frac{\delta V_{xc}^{LDA}[\rho, m]}{\delta m}\Delta m = \frac{\delta V_{xc}^{LDA}[\rho, m]}{\delta\rho}|_{m=0}\Delta\rho \\
\lim_{m\to 0} \Delta B_{xc}^{LDA}[\rho, m] &= \lim_{m\to 0} \frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta\rho}\Delta\rho + \lim_{m\to 0} \frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta m}\Delta m = \frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta m}|_{m=0}\Delta m = I_{xc}[\rho]\Delta m \\
\Delta\mathbf{B}_{xc}^{LDA}[\rho, m] &= I_{xc}[\rho]\Delta\mathbf{m} = I_{xc}[\rho]\Delta\mathbf{m}
\end{aligned}$$

or in the matrix form:

$$\begin{aligned}
\Delta V_{xc}^{11} &= \Delta v_{xc\uparrow\uparrow} = \Delta V_{xc} - \Delta B_{xc}^{0} = \frac{\delta V_{xc}^{LDA}[\rho, m]}{\delta\rho}|_{m=0}\Delta\rho - \frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta m}|_{m=0}\Delta m^0 \\
\Delta V_{xc}^{21} &= \Delta v_{xc\downarrow\downarrow} = \Delta V_{xc} + \Delta B_{xc}^{0} = \frac{\delta V_{xc}^{LDA}[\rho, m]}{\delta\rho}|_{m=0}\Delta\rho + \frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta m}|_{m=0}\Delta m^0 \\
\Delta V_{xc}^{12} &= +\Delta v_{xc\downarrow\uparrow}/\sqrt{2} = -\Delta B_{xc}^{-1} = -\frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta m}|_{m=0}\Delta m^{-1} \\
\Delta V_{xc}^{22} &= -\Delta v_{xc\uparrow\downarrow}/\sqrt{2} = -\Delta B_{xc}^{+1} = -\frac{\delta B_{xc}^{LDA}[\rho, m]}{\delta m}|_{m=0}\Delta m^{+1}
\end{aligned}$$

which is also derived previously by taking the limit $m \to 0$.

4. Generalized Gradient Approximation

In GGA, changes in exchange correlation potential and magnetic fields are given by

$$\begin{aligned}
\Delta V_{xc}^{GGA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m] = & \frac{\delta V_{xc}^{GGA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta\rho}\Delta\rho + \\
& \frac{\delta V_{xc}^{GGA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta m}\Delta m + \\
& \sum_{i=xyz} \frac{\delta V_{xc}^{GGA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i\rho)}\nabla_i(\Delta\rho) + \\
& \sum_{i=xyz} \frac{\delta V_{xc}^{GGA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i m)}\nabla_i(\Delta m) + \\
& \sum_{ij=xyz} \frac{\delta V_{xc}^{GGA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i\nabla_j\rho)}\nabla_i\nabla_j(\Delta\rho) + \\
& \sum_{ij=xyz} \frac{\delta V_{xc}^{GGA}[\rho, m, \nabla_\alpha\rho, \nabla_\alpha m, \nabla_\alpha\nabla_\beta\rho, \nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i\nabla_j m)}\nabla_i\nabla_j(\Delta m)
\end{aligned}$$

$$\Delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m] = \frac{\delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]}{\delta\rho}\Delta\rho +$$
$$\frac{\delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]}{\delta m}\Delta m +$$
$$\sum_{i=xyz}\frac{\delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i\rho)}\nabla_i(\Delta\rho) +$$
$$\sum_{i=xyz}\frac{\delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i m)}\nabla_i(\Delta m) +$$
$$\sum_{ij=xyz}\frac{\delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i\nabla_j\rho)}\nabla_i\nabla_j(\Delta\rho) +$$
$$\sum_{ij=xyz}\frac{\delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]}{\delta(\nabla_i\nabla_j m)}\nabla_i\nabla_j(\Delta m)$$

Similar terms exist when we vary the missing terms $G^{(1)}_{xc,\alpha}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]$ and $G^{(2)}_{xc,\alpha\beta}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha$
W obtain that the total change in magnetic field is given by

$$\Delta\mathbf{B}^{GGA}_{xc}[\rho,\mathbf{m},\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m] = \Delta\left(B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\frac{m_\alpha}{m}\right)$$
$$+\sum_\alpha\Delta\left(G^{(1)}_{xc,\alpha}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\nabla_\alpha\frac{\mathbf{m}}{m}\right)+\sum_{\alpha\beta}\Delta\left(G^{(2)}_{xc,\alpha\beta}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\nabla_\alpha\nabla_\beta\frac{\mathbf{m}}{m}\right)$$
$$=\Delta B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\frac{\mathbf{m}}{m}+B^{GGA}_{xc}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\Delta\left(\frac{\mathbf{m}}{m}\right)+$$
$$\sum_\alpha\Delta G^{(1)}_{xc,\alpha}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\left(\nabla_\alpha\frac{\mathbf{m}}{m}\right)+\sum_{\alpha\beta}\Delta G^{(2)}_{xc,\alpha\beta}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\left(\nabla_\alpha\nabla_\beta\frac{\mathbf{m}}{m}\right)+$$
$$\sum_\alpha G^{(1)}_{xc,\alpha}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\Delta\left(\nabla_\alpha\frac{\mathbf{m}}{m}\right)+\sum_{\alpha\beta}\Delta G^{(2)}_{xc,\alpha\beta}[\rho,m,\nabla_\alpha\rho,\nabla_\alpha m,\nabla_\alpha\nabla_\beta\rho,\nabla_\alpha\nabla_\beta m]\Delta\left(\nabla_\alpha\nabla_\beta\frac{\mathbf{m}}{m}\right)$$

5. *Limt of vanishing magnetization in GGA*

The $m \to 0$ limit is possible in GGA but we also need to consider the missing terms.

D. Green Function and Self-Energy in Non-Collinear Form

Green function is given by the density and magnetization parts

$$G(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{k}j}\frac{\psi^{R(\sigma)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\sigma)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}}$$
$$G^0_m(\mathbf{r},\mathbf{r}',\omega) = \mu_B\sum_{\mathbf{k}j}\frac{\langle\vec{\psi}^L_{\mathbf{k}j\omega}(\mathbf{r}')|\hat{s}^0|\vec{\psi}^R_{\mathbf{k}j\omega}(\mathbf{r})\rangle_{spin}}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}} = \sum_{\mathbf{k}j}\frac{\psi^{R(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}} - \sum_{\mathbf{k}j}\frac{\psi^{R(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}}$$
$$G^{-1}_m(\mathbf{r},\mathbf{r}',\omega) = \mu_B\sum_{\mathbf{k}j}\frac{\langle\vec{\psi}^L_{\mathbf{k}j\omega}(\mathbf{r}')|\hat{s}^{-1}|\vec{\psi}^R_{\mathbf{k}j\omega}(\mathbf{r})\rangle_{spin}}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}} = +\sqrt{2}\sum_{\mathbf{k}j}\frac{\psi^{R(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}} = -G_{m+1}(\mathbf{r},\mathbf{r}',\omega)$$
$$G^{+1}_m(\mathbf{r},\mathbf{r}',\omega) = \mu_B\sum_{\mathbf{k}j}\frac{\langle\vec{\psi}^L_{\mathbf{k}j\omega}(\mathbf{r}')|\hat{s}^{+1}|\vec{\psi}^R_{\mathbf{k}j\omega}(\mathbf{r})\rangle_{spin}}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}} = -\sqrt{2}\sum_{\mathbf{k}j}\frac{\psi^{R(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}} = -G_{m-1}(\mathbf{r},\mathbf{r}',\omega)$$

where we can define Green function matrix $G_{\sigma\sigma'}$

$$G_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{k}j} \frac{\psi^{R(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}}$$
$$G_{\downarrow\downarrow}(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{k}j} \frac{\psi^{R(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}}$$
$$G_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{k}j} \frac{\psi^{R(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}}$$
$$G_{\downarrow\uparrow}(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{k}j} \frac{\psi^{R(\downarrow)}_{\mathbf{k}j\omega}(\mathbf{r})\psi^{L(\uparrow)}_{\mathbf{k}j\omega}(\mathbf{r}')}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}}$$

and use the following transformations

$$\begin{aligned} G &= G_{\uparrow\uparrow} + G_{\downarrow\downarrow} \\ G^0_m &= G_{\uparrow\uparrow} - G_{\downarrow\downarrow} \\ G^{-1}_m &= +\sqrt{2}G_{\downarrow\uparrow} \\ G^{+1}_m &= -\sqrt{2}G_{\uparrow\downarrow} \end{aligned}$$

Note that the transverse components $G_{\downarrow\uparrow}$ and $G_{\uparrow\downarrow}$ are defined oppositely for density matrix elements $\rho_{\uparrow\downarrow}$ and $\rho_{\downarrow\uparrow}$. How to define similar maitrces $\Sigma_{\sigma\sigma'}$ for the self–energy

$$\Sigma, \mathbf{\Sigma_B} = \sum_\mu \Sigma^\mu_B \mathbf{e}_\mu$$

First, typical contribution to the total energy has the form

$$E = \sum_{i\omega} \int \Sigma(\mathbf{r},\mathbf{r}',i\omega)G(\mathbf{r}',\mathbf{r},i\omega)d\mathbf{r}d\mathbf{r}' - \sum_{i\omega} \int \mathbf{\Sigma}^\mu_B(\mathbf{r},\mathbf{r}',i\omega)G_{m\mu}(\mathbf{r}',\mathbf{r},i\omega)d\mathbf{r}d\mathbf{r}'$$

$$\begin{aligned} \frac{\delta E}{\delta \mathbf{G}_m(\mathbf{r}',\mathbf{r},\omega)} &= \mathbf{\Sigma}_m(\mathbf{r},\mathbf{r}',i\omega) \\ \frac{\delta E}{\delta G_{m\mu}(\mathbf{r}',\mathbf{r},\omega)} &= \Sigma^\mu_m(\mathbf{r},\mathbf{r}',i\omega) \end{aligned}$$

which we would like to write in the form similar to

$$E = \sum_{\sigma\sigma'} \int \Sigma_{\sigma\sigma'} G_{\sigma'\sigma}$$

The self–energy matrix is most naturally defined as the matrix elements of the operator

$$\Sigma\hat{\imath} - \mu_B \mathbf{\Sigma}_B \hat{\mathbf{s}} = \Sigma\hat{\imath} - 2\mathbf{\Sigma}_B\hat{\mathbf{s}} = \Sigma\hat{\imath} - \mathbf{\Sigma}_B\hat{\sigma} = \Sigma\hat{\imath} - \Sigma^0_B\hat{\sigma}_0 - \Sigma^{-1}_B\hat{\sigma}_{-1} - \Sigma^{+1}_B\hat{\sigma}_{+1}$$

which are computed as follows

$$\begin{aligned} \langle\Sigma_{\uparrow\uparrow}\rangle &= \langle\uparrow|\Sigma\hat{\imath} - \mathbf{\Sigma}_B\hat{\sigma}|\uparrow\rangle = \langle\uparrow|\Sigma - \Sigma^0_B\hat{\sigma}_0|\uparrow\rangle = \langle\Sigma\rangle - \langle\Sigma^0_B\rangle \\ \langle\Sigma_{\downarrow\downarrow}\rangle &= \langle\downarrow|\Sigma\hat{\imath} - \mathbf{\Sigma}_B\hat{\sigma}|\downarrow\rangle = \langle\downarrow|\Sigma - \Sigma^0_B\hat{\sigma}_0|\downarrow\rangle = \langle\Sigma\rangle + \langle\Sigma^0_B\rangle \\ \langle\Sigma_{\uparrow\downarrow}\rangle &= \langle\uparrow|\Sigma\hat{\imath} - \mathbf{\Sigma}_B\hat{\sigma}|\downarrow\rangle = \langle\uparrow| - \Sigma^{+1}_B\hat{\sigma}_{+1}|\downarrow\rangle = -\langle\Sigma^{+1}_B\rangle(-\sqrt{2}) = +\langle\Sigma^{+1}_B\rangle\sqrt{2} \\ \langle\Sigma_{\downarrow\uparrow}\rangle &= \langle\downarrow|\Sigma\hat{\imath} - \mathbf{\Sigma}_B\hat{\sigma}|\uparrow\rangle = \langle\downarrow| - \Sigma^{-1}_B\hat{\sigma}_{-1}|\uparrow\rangle = -\langle\Sigma^{-1}_B\rangle(+\sqrt{2}) = -\langle\Sigma^{-1}_B\rangle\sqrt{2} \end{aligned}$$

We obtain the following definitions

$$
\begin{aligned}
\langle\Sigma\rangle &= +\frac{1}{2}(\langle\Sigma_{\uparrow\uparrow}\rangle + \Sigma_{\downarrow\downarrow}\rangle)\\
\langle\Sigma_B^0\rangle &= -\frac{1}{2}(\langle\Sigma_{\uparrow\uparrow}\rangle - \Sigma_{\downarrow\downarrow}\rangle)\\
\langle\Sigma_B^{-1}\rangle &= -\langle\Sigma_{\downarrow\uparrow}\rangle/\sqrt{2}\\
\langle\Sigma_B^{+1}\rangle &= +\langle\Sigma_{\uparrow\downarrow}\rangle/\sqrt{2}
\end{aligned}
$$

Contribution to the total energy related to the potential and density has the form

$$
\begin{aligned}
E = \Sigma G - \mathbf{\Sigma}_B\mathbf{G}_m &= \sum_{i\omega}\int \Sigma(\mathbf{r},\mathbf{r}'\omega)G(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}' - \sum_{\mu}\sum_{i\omega}\int \Sigma_B^{\mu}(\mathbf{r},\mathbf{r}'\omega)G_{m\mu}(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}' =\\
&= \sum_{i\omega}\int \Sigma_{\uparrow\uparrow}(\mathbf{r},\mathbf{r}'\omega)G_{\uparrow\uparrow}(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}' + \sum_{i\omega}\int \Sigma_{\downarrow\downarrow}(\mathbf{r},\mathbf{r}'\omega)G_{\downarrow\downarrow}(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}' +\\
&\quad \sum_{i\omega}\int \Sigma_{\downarrow\uparrow}(\mathbf{r},\mathbf{r}'\omega)G_{\uparrow\downarrow}(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}' + \sum_{i\omega}\int \Sigma_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}'\omega)G_{\downarrow\uparrow}(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}'\\
&= \sum_{\sigma\sigma'}\sum_{i\omega}\int \Sigma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}'\omega)G_{\sigma'\sigma}(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}'
\end{aligned}
$$

If Green function is expanded into the basis set

$$
\begin{aligned}
G(\mathbf{r},\mathbf{r}',\omega) &= \sum_{\mathbf{k}}\sum_{\alpha\beta}\sum_{\sigma\sigma'} G_{\alpha\sigma\beta\sigma'}(\mathbf{k},\omega)\langle\vec{\chi}^{\mathbf{k}}_{\alpha\sigma}(\mathbf{r})|\hat{\imath}|\vec{\chi}^{\mathbf{k}+}_{\beta\sigma'}(\mathbf{r}')\rangle_{spin}\\
&= \sum_{\mathbf{k}}\sum_{\alpha\beta}[G_{\alpha\uparrow\beta\uparrow}(\mathbf{k},\omega) + G_{\alpha\downarrow\beta\downarrow}(\mathbf{k},\omega)]\chi^{\mathbf{k}}_{\alpha}(\mathbf{r})\chi^{\mathbf{k}*}_{\beta}(\mathbf{r}')\\
\mathbf{G}_m(\mathbf{r},\mathbf{r}',\omega) &= \sum_{\mathbf{k}}\sum_{\alpha\beta}\sum_{\sigma\sigma'} G_{\alpha\sigma\beta\sigma'}(\mathbf{k},\omega)\langle\vec{\chi}^{\mathbf{k}}_{\alpha\sigma}(\mathbf{r})|\mu_B\hat{\mathbf{s}}|\vec{\chi}^{\mathbf{k}+}_{\beta\sigma'}(\mathbf{r}')\rangle_{spin}\\
G^0_m(\mathbf{r},\mathbf{r}',\omega) &= \sum_{\mathbf{k}}\sum_{\alpha\beta}[G_{\alpha\uparrow\beta\uparrow}(\mathbf{k},\omega) - G_{\alpha\downarrow\beta\downarrow}(\mathbf{k},\omega)]\chi^{\mathbf{k}}_{\alpha}(\mathbf{r})\chi^{\mathbf{k}*}_{\beta}(\mathbf{r}')\\
G^{-1}_m(\mathbf{r},\mathbf{r}',\omega) &= +\sqrt{2}\sum_{\mathbf{k}}\sum_{\alpha\beta} G_{\alpha\downarrow\beta\uparrow}(\mathbf{k},\omega)\chi^{\mathbf{k}}_{\alpha}(\mathbf{r})\chi^{\mathbf{k}*}_{\beta}(\mathbf{r}')\\
G^{+1}_m(\mathbf{r},\mathbf{r}',\omega) &= -\sqrt{2}\sum_{\mathbf{k}}\sum_{\alpha\beta} G_{\alpha\uparrow\beta\downarrow}(\mathbf{k},\omega)\chi^{\mathbf{k}}_{\alpha}(\mathbf{r})\chi^{\mathbf{k}*}_{\beta}(\mathbf{r}')
\end{aligned}
$$

The matrix $G_{\alpha\sigma\beta\sigma'}(\mathbf{k},\omega)$ is given by

$$
\begin{aligned}
G^{-1}_{\alpha\sigma\beta\sigma'}(\mathbf{k},\omega) &= \langle\vec{\chi}^{\mathbf{k}}_{\alpha\sigma}| - \nabla^2\hat{\imath} + V\hat{\imath} - \mu_B\mathbf{B}\hat{\mathbf{s}} + \hat{\Sigma}(\omega)\hat{\imath} - \mu_B\hat{\mathbf{\Sigma}}_B(\omega)\hat{\mathbf{s}}|\vec{\chi}^{\mathbf{k}}_{\beta\sigma'}\rangle\\
&= (\omega+\mu)O_{\alpha\sigma\beta\sigma'}(\mathbf{k}) - H_{\alpha\sigma\beta\sigma'}(\mathbf{k}) - \Sigma_{\alpha\sigma\beta\sigma'}(\mathbf{k},\omega)\\
G_{\alpha\sigma\beta\sigma'}(\mathbf{k},\omega) &= [(\omega+\mu)\hat{O}(\mathbf{k}) - \hat{H}(\mathbf{k}) - \hat{\Sigma}(\mathbf{k},\omega)]^{-1}_{\alpha\sigma\beta\sigma'} = \sum_j \frac{A^{\mathbf{k}j\omega,R}_{\alpha\sigma}A^{\mathbf{k}j\omega,L}_{\beta\sigma'}}{\omega+\mu-\epsilon_{\mathbf{k}j\omega}}
\end{aligned}
$$

The contribution to the total energy is given by

$$
\begin{aligned}
E = \Sigma G - \mathbf{\Sigma}_B\mathbf{G}_m &= \sum_{\sigma\sigma'}\sum_{i\omega}\int \Sigma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}'\omega)G_{\sigma'\sigma}(\mathbf{r}',\mathbf{r},\omega)d\mathbf{r}d\mathbf{r}' = \sum_{\mathbf{k}}\sum_{i\omega}\sum_{\alpha\sigma\beta\sigma'}\int \chi^{\mathbf{k}*}_{\alpha}(\mathbf{r})\Sigma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}'\omega)\chi^{\mathbf{k}}_{\beta}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'G_{\beta\sigma'\alpha\sigma}(\mathbf{k},\omega) =\\
&= \sum_{\mathbf{k}}\sum_{i\omega}\sum_{\alpha\sigma\beta\sigma'} \Sigma_{\alpha\sigma\beta\sigma'}(\mathbf{k},i\omega)G_{\beta\sigma'\alpha\sigma}(\mathbf{k},i\omega)
\end{aligned}
$$

Inside the program the Green function matrix is defined as follows

$$((GRF(ISPIN, IORBS), ISPIN = 1, NSPIN), IORBS = 1, NORBS)$$

$$
\begin{aligned}
G^{11}_{\alpha\beta} &= G^{\uparrow\uparrow}_{\alpha\beta} = G - G^{0}_{m,\alpha\beta}\\
G^{21}_{\alpha\beta} &= G^{\downarrow\downarrow}_{\alpha\beta} = G + G^{0}_{\alpha\beta}\\
G^{12}_{\alpha\beta} &= G^{\uparrow\downarrow}_{\alpha\beta} = -G^{+1}_{m,\alpha\beta}/\sqrt{2}\\
G^{22}_{\alpha\beta} &= G^{\downarrow\uparrow}_{\alpha\beta} = +G^{-1}_{m,\alpha\beta}/\sqrt{2}
\end{aligned}
$$

Inside the program the self–energy matrix are defined as (See DMF_SGMPAR.F)

$$((SIG(ISPIN, IORBS), ISPIN = 1, NSPIN), IORBS = 1, NORBS)$$

$$
\begin{aligned}
\Sigma^{11}_{\alpha\beta} &= \Sigma^{\uparrow\uparrow}_{\alpha\beta} = \Sigma_{\alpha\beta} - \Sigma^{0}_{B,\alpha\beta}\\
\Sigma^{21}_{\alpha\beta} &= \Sigma^{\downarrow\downarrow}_{\alpha\beta} = \Sigma_{\alpha\beta} + \Sigma^{0}_{B,\alpha\beta}\\
\Sigma^{12}_{\alpha\beta} &= \Sigma^{\uparrow\downarrow}_{\alpha\beta} = +\Sigma^{+1}_{B,\alpha\beta}\sqrt{2}\\
\Sigma^{22}_{\alpha\beta} &= \Sigma^{\downarrow\uparrow}_{\alpha\beta} = -\Sigma^{-1}_{B,\alpha\beta}\sqrt{2}
\end{aligned}
$$

The contribution to the total energy is written as follows

$$
\begin{aligned}
E = \sum_{\mathbf{k}}\sum_{i\omega}\sum_{\alpha\sigma\beta\sigma'} &[\Sigma^{\uparrow\uparrow}_{\alpha\beta}(\mathbf{k},i\omega)G^{\uparrow\uparrow}_{\beta\alpha}(\mathbf{k},i\omega) + \Sigma^{\downarrow\downarrow}_{\alpha\beta}(\mathbf{k},i\omega)G^{\downarrow\downarrow}_{\beta\alpha}(\mathbf{k},i\omega) + \Sigma^{\uparrow\downarrow}_{\alpha\beta}(\mathbf{k},i\omega)G^{\downarrow\uparrow}_{\beta\alpha}(\mathbf{k},i\omega) + \Sigma^{\downarrow\uparrow}_{\alpha\beta}(\mathbf{k},i\omega)G^{\uparrow\downarrow}_{\beta\alpha}(\mathbf{k},i\omega)] =\\
= \sum_{\mathbf{k}}\sum_{i\omega}\sum_{\alpha\sigma\beta\sigma'} &[\Sigma^{11}_{\alpha\beta}(\mathbf{k},i\omega)G^{11}_{\beta\alpha}(\mathbf{k},i\omega) + \Sigma^{21}_{\alpha\beta}(\mathbf{k},i\omega)G^{21}_{\beta\alpha}(\mathbf{k},i\omega) + \Sigma^{12}_{\alpha\beta}(\mathbf{k},i\omega)G^{22}_{\beta\alpha}(\mathbf{k},i\omega) + \Sigma^{22}_{\alpha\beta}(\mathbf{k},i\omega)G^{12}_{\beta\alpha}(\mathbf{k},i\omega)]
\end{aligned}
$$

E. Non–collinear LDA+U functional

The density matrix is defined as follows

$$n_{\alpha\sigma\beta\sigma'} = \sum_{\mathbf{k}j}\sum_{i\omega} G_{\beta\sigma'\alpha\sigma}(\mathbf{k},i\omega) = \sum_{\mathbf{k}j}\sum_{i\omega}\frac{A^{\mathbf{k}j\omega,L}_{\alpha\sigma}A^{\mathbf{k}j\omega,R}_{\beta\sigma'}}{i\omega+\mu-\epsilon_{\mathbf{k}j\omega}}$$

Note that this definition is different from the definition of Green function matrix because of index swapping. However, the advantage of this formula is that density matrix as well as self-energy matrix are stored and therefore can be transformed in a similar way to spherical or cubic harmonics representations. Green function itself is not stored into the HUBFILE.

and use the following transformations

$$
\begin{aligned}
n_{\alpha\beta} &= n^{\uparrow\uparrow}_{\alpha\beta} + n^{\downarrow\downarrow}_{\alpha\beta} = \sum_{\sigma\sigma'}\delta_{\sigma\sigma'}n^{\sigma\sigma'}_{\alpha\beta}\\
m^{0}_{\alpha\beta} &= n^{\uparrow\uparrow}_{\alpha\beta} - n^{\downarrow\downarrow}_{\alpha\beta} = m_{0,\alpha\beta} = \sum_{\sigma\sigma'}\sigma^{0}_{\sigma\sigma'}n^{\sigma\sigma'}_{\alpha\beta}\\
m^{-1}_{\alpha\beta} &= +\sqrt{2}n^{\uparrow\downarrow}_{\alpha\beta} = -m_{+1,\alpha\beta} = \sum_{\sigma\sigma'}\sigma^{-1}_{\sigma\sigma'}n^{\sigma\sigma'}_{\alpha\beta}\\
m^{+1}_{\alpha\beta} &= -\sqrt{2}n^{\downarrow\uparrow}_{\alpha\beta} = -m_{-1,\alpha\beta} = \sum_{\sigma\sigma'}\sigma^{+1}_{\sigma\sigma'}n^{\sigma\sigma'}_{\alpha\beta}
\end{aligned}
$$

Inside the program spin density matrix array is defined as follows (HUB_RHOHUB.F, checked 01/25/2006)

$$((DHUB(ISPIN, IORBS), ISPIN = 1, NSPIN), IORBS = 1, NORBS)$$

$$
\begin{aligned}
n^{11}_{\alpha\beta} &= n^{\uparrow\uparrow}_{\alpha\beta} = (n_{\alpha\beta} + m^{0}_{\alpha\beta})/2 \\
n^{21}_{\alpha\beta} &= n^{\downarrow\downarrow}_{\alpha\beta} = (n_{\alpha\beta} - m^{0}_{\alpha\beta})/2 \\
n^{12}_{\alpha\beta} &= n^{\uparrow\downarrow}_{\alpha\beta} = +m^{-1}_{\alpha\beta}/\sqrt{2} \\
n^{22}_{\alpha\beta} &= n^{\downarrow\uparrow}_{\alpha\beta} = -m^{+1}_{\alpha\beta}/\sqrt{2}
\end{aligned}
$$

Expression for the energy correction within LDA+U is given by

$$
\begin{aligned}
E_{HF}[n^{\sigma\sigma'}_{\alpha\beta}] &= \frac{1}{2}\sum_{\alpha\beta\alpha'\beta'}\sum_{\sigma} U_{\alpha\beta\alpha'\beta'} n^{\sigma\sigma}_{\alpha\beta} n^{-\sigma-\sigma}_{\alpha'\beta'} + \frac{1}{2}\sum_{\alpha\beta\alpha'\beta'}\sum_{\sigma}(U_{\alpha\beta\alpha'\beta'} - J_{\alpha\beta\alpha'\beta'}) n^{\sigma\sigma}_{\alpha\beta} n^{\sigma\sigma}_{\alpha'\beta'} - \frac{1}{2}\sum_{\alpha\beta\alpha'\beta'}\sum_{\sigma} J_{\alpha\beta\alpha'\beta'} n^{\sigma-\sigma}_{\alpha\beta} n^{-\sigma\sigma}_{\alpha'\beta'} = \quad (99) \\
&= \frac{1}{2}\sum_{\alpha\beta\alpha'\beta'}\sum_{i} U_{\alpha\beta\alpha'\beta'} n^{ii}_{\alpha\beta} n^{(3-i)(3-i)}_{\alpha'\beta'} + \frac{1}{2}\sum_{\alpha\beta\alpha'\beta'}\sum_{i}(U_{\alpha\beta\alpha'\beta'} - J_{\alpha\beta\alpha'\beta'}) n^{ii}_{\alpha\beta} n^{ii}_{\alpha'\beta'} - \frac{1}{2}\sum_{\alpha\beta\alpha'\beta'}\sum_{i} J_{\alpha\beta\alpha'\beta'} n^{i(3-i)}_{\alpha\beta} n^{(3-i)}_{\alpha'\beta'} \quad (100)
\end{aligned}
$$

where the matrix elements of the Coulomb interaction are given by

$$
U_{\alpha\beta\alpha'\beta'} = \langle \alpha\alpha' | \frac{e^2}{r} | \beta\beta' \rangle = \int \chi^*_{\alpha}(\mathbf{r})\chi^*_{\alpha'}(\mathbf{r'}) v_C(\mathbf{r}-\mathbf{r'}) \chi_{\beta}(\mathbf{r})\chi_{\beta'}(\mathbf{r'}) d\mathbf{r} d\mathbf{r'} = U_{\alpha'\beta'\alpha\beta} \qquad (101)
$$

$$
J_{\alpha\beta\alpha'\beta'} = \langle \alpha\alpha' | \frac{e^2}{r} | \beta'\beta \rangle = \int \chi^*_{\alpha}(\mathbf{r})\chi^*_{\alpha'}(\mathbf{r'}) v_C(\mathbf{r}-\mathbf{r'}) \chi_{\beta'}(\mathbf{r})\chi_{\beta}(\mathbf{r'}) d\mathbf{r} d\mathbf{r'} = U_{\alpha\beta'\alpha'\beta} = U_{\alpha'\beta\alpha\beta'} = J_{\alpha'\beta'\alpha\beta} \qquad (102)
$$

Definition for the potential matrix

$$
\begin{aligned}
V^{\sigma\sigma}_{\alpha\beta} &= \sum_{\alpha'\beta'} U_{\alpha\beta\alpha'\beta'} n^{-\sigma-\sigma}_{\alpha'\beta'} + \sum_{m'k'} (U_{\alpha\beta\alpha'\beta'} - J_{\alpha\beta\alpha'\beta'}) n^{\sigma\sigma}_{\alpha'\beta'} \\
V^{\sigma-\sigma}_{\alpha\beta} &= -\sum_{\alpha'\beta'} J_{\alpha\beta\alpha'\beta'} n^{-\sigma\sigma}_{\alpha'\beta'}
\end{aligned}
$$

Contribution to the total energy is then given by

$$
E = \sum_{\alpha\beta}\sum_{\sigma\sigma'} n^{\sigma\sigma'}_{\alpha\beta} V^{\sigma\sigma'}_{\alpha\beta}
$$

Since denisty matrix has indexes swapped in comparison to the Green function matrix, this definition is now in agreement with the total energy expression for the self–energy Green function.

Inside the program, the potential matrix is packed as follows (See HUB_HUBPAR.F,HUB_HUBPOT.F,FTB_HUBINT.F)

$$
((VHUB(ISPIN, IORBS), ISPIN = 1, NSPIN), IORBS = 1, NORBS)
$$

$$
\begin{aligned}
V^{11}_{\alpha\beta} &= V^{\uparrow\uparrow}_{\alpha\beta} = V_{\alpha\beta} - B^{0}_{\alpha\beta} \\
V^{21}_{\alpha\beta} &= V^{\downarrow\downarrow}_{\alpha\beta} = V_{\alpha\beta} + B^{0}_{\alpha\beta} \\
V^{12}_{\alpha\beta} &= V^{\uparrow\downarrow}_{\alpha\beta} = +B^{+1}_{\alpha\beta}\sqrt{2} \\
V^{22}_{\alpha\beta} &= V^{\downarrow\uparrow}_{\alpha\beta} = -B^{-1}_{\alpha\beta}\sqrt{2}
\end{aligned}
$$

(Unfortunately with these definitions we don't have the property $B^{\mu}_{\alpha\beta} = \sum_{\sigma\sigma'} \sigma^{\mu}_{\sigma\sigma'} V^{\sigma\sigma'}_{\alpha\beta}$).

$$
\begin{aligned}
E &= \sum_{\alpha\beta}\sum_{\sigma\sigma'} n^{\sigma\sigma'}_{\alpha\beta} V^{\sigma\sigma'}_{\alpha\beta} = \sum_{\alpha\beta} [n^{11}_{\alpha\beta} V^{11}_{\alpha\beta} + n^{22}_{\alpha\beta} V^{22}_{\alpha\beta} + n^{12}_{\alpha\beta} V^{12}_{\alpha\beta} + n^{21}_{\alpha\beta} V^{21}_{\alpha\beta}] = \\
&= \sum_{\alpha\beta} (n^{\uparrow\uparrow}_{\alpha\beta} V^{\uparrow\uparrow}_{\alpha\beta} + n^{\downarrow\downarrow}_{\alpha\beta} V^{\downarrow\downarrow}_{\alpha\beta} + n^{\uparrow\downarrow}_{\alpha\beta} V^{\uparrow\downarrow}_{\alpha\beta} + n^{\downarrow\uparrow}_{\alpha\beta} V^{\downarrow\uparrow}_{\alpha\beta}) = \sum_{\alpha\beta} n_{\alpha\beta} V_{\alpha\beta} - \sum_{\alpha\beta} m^{0}_{\alpha\beta} B^{0}_{\alpha\beta} + \sum_{\alpha\beta} m^{-1}_{\alpha\beta} B^{+1}_{\alpha\beta} + \sum_{\alpha\beta} m^{+1}_{\alpha\beta} B^{-1}_{\alpha\beta} = \\
&= \sum_{\alpha\beta} n_{\alpha\beta} V_{\alpha\beta} - \sum_{\alpha\beta} m^{0}_{\alpha\beta} B_{0,\alpha\beta} - \sum_{\alpha\beta} m^{-1}_{\alpha\beta} B_{-1,\alpha\beta} - \sum_{\alpha\beta} m^{+1}_{\alpha\beta} B_{+1,\alpha\beta} = \sum_{\alpha\beta} n_{\alpha\beta} V_{\alpha\beta} - \sum_{\alpha\beta}\sum_{\mu} m^{\mu}_{\alpha\beta} B_{\mu,\alpha\beta}
\end{aligned}
$$

Let us now discuss the self–energy which can be expressed via the density matrix. When $\sigma \equiv \sigma'$ it is given by

$$V_{\alpha\beta}^{\sigma\sigma} = \frac{\delta E}{\delta n_{\alpha\beta}^{\sigma\sigma}} = \sum_{\alpha'\beta'} U_{\alpha\beta\alpha'\beta'} n_{\alpha'\beta'}^{-\sigma-\sigma} + \sum_{\alpha'\beta'} (U_{\alpha\beta\alpha'\beta'} - J_{\alpha\beta\alpha'\beta'}) n_{\alpha'\beta'}^{\sigma\sigma} \tag{103}$$

For off–diagonal elements it is given by (See HUB_HUBPOT.F)

$$V_{\alpha\beta}^{\sigma-\sigma} = \frac{\delta E_{HF}}{\delta n_{\alpha\beta}^{\sigma-\sigma}} = -\sum_{\alpha'\beta'} J_{\alpha\beta\alpha'\beta'} n_{\alpha'\beta'}^{-\sigma\sigma} \tag{104}$$

$$V_{\alpha\beta}^{i2} = -\sum_{\alpha'\beta'} J_{\alpha\beta\alpha'\beta'} n_{\alpha'\beta'}^{(3-i)2} \tag{105}$$

Correction to the hamiltonian matrix has the form

$$\Delta H_{\alpha\beta}^{\sigma\sigma} = \frac{\delta E}{\delta n_{\alpha\beta}^{\sigma\sigma}} = V_{\alpha\beta}^{\sigma\sigma}$$

$$\Delta H_{\alpha\beta}^{\uparrow\downarrow} = \frac{\delta E}{\delta n_{\alpha\beta}^{\uparrow\downarrow}} = V_{\alpha\beta}^{\uparrow\downarrow} = V_{\alpha\beta}^{12}$$

$$\Delta H_{\alpha\beta}^{\downarrow\uparrow} = \frac{\delta E}{\delta n_{\alpha\beta}^{\downarrow\uparrow}} = V_{\alpha\beta}^{\downarrow\uparrow} = V_{\alpha\beta}^{22}$$

Again this is consistent with the fact that the indexation of density matrix is swapped in comparison with the indexation of Green function matrix.

Double counting correction $E_{DC1}[n^\sigma]$ is given by (so called fully localized spin polarized limit)

$$\begin{aligned} E_{DC1}[n^\sigma] &= \frac{1}{2}\bar{U}\bar{n}(\bar{n}-1) - \frac{1}{2}\bar{J}\sum_\sigma[\bar{n}_\sigma(\bar{n}_\sigma - 1)] = \\ &= \frac{1}{2}\bar{U}\bar{n}\bar{n} - \frac{1}{2}\bar{J}\sum_\sigma \bar{n}_\sigma\bar{n}_\sigma - \frac{1}{2}\bar{U}\bar{n} + \frac{1}{2}\bar{J}\bar{n} = \\ &= \frac{1}{2}\bar{U}\sum_\sigma \bar{n}_\sigma\bar{n}_{-\sigma} + \frac{1}{2}(\bar{U}-\bar{J})\sum_\sigma \bar{n}_\sigma\bar{n}_\sigma - \frac{1}{2}\bar{U}\bar{n} + \frac{1}{2}\bar{J}\bar{n} \end{aligned}$$

which can be generalized to non–collinear case as follows:

$$\begin{aligned} E_{DC1}[n^{\sigma\sigma'}] &= \frac{1}{2}\bar{U}\bar{n}(\bar{n}-1) - \frac{1}{2}\bar{J}\sum_{\sigma\sigma'} \bar{n}_{\sigma\sigma'}(\bar{n}_{\sigma'\sigma} - \delta_{\sigma\sigma'}) \\ &= \frac{1}{2}\bar{U}\bar{n}\bar{n} - \frac{1}{2}\bar{J}\sum_\sigma \bar{n}_{\sigma\sigma}\bar{n}_{\sigma\sigma} - \frac{1}{2}\bar{U}\bar{n} + \frac{1}{2}\bar{J}\bar{n} - \frac{1}{2}\bar{J}\sum_\sigma \bar{n}_{\sigma-\sigma'}\bar{n}_{-\sigma\sigma} = \\ &= \frac{1}{2}\bar{U}\sum_\sigma \bar{n}_\sigma\bar{n}_{-\sigma} + \frac{1}{2}(\bar{U}-\bar{J})\sum_\sigma \bar{n}_\sigma\bar{n}_\sigma - \frac{1}{2}\bar{U}\bar{n} + \frac{1}{2}\bar{J}\bar{n} - \frac{1}{2}\bar{J}\sum_\sigma \bar{n}_{\sigma-\sigma}\bar{n}_{-\sigma\sigma} \end{aligned}$$

Double counting correction $E_{DC2}[n^\sigma]$ is given by (so called fully localized spin restriced limit)

$$\begin{aligned} E_{DC2}[\bar{n}] &= \frac{1}{2}\bar{U}\bar{n}(\bar{n}-1) - \frac{1}{2}\bar{J}[\frac{\bar{n}}{2}(\frac{\bar{n}}{2}-1) + \frac{\bar{n}}{2}(\frac{\bar{n}}{2}-1)] = \\ &= \frac{1}{2}\bar{U}\bar{n}\bar{n} - \frac{1}{2}\bar{J}[\frac{\bar{n}}{2}\frac{\bar{n}}{2} + \frac{\bar{n}}{2}\frac{\bar{n}}{2}] - \frac{1}{2}\bar{U}\bar{n} + \frac{1}{2}\bar{J}\bar{n} = \\ &= \frac{1}{2}\bar{U}(\frac{\bar{n}}{2}\frac{\bar{n}}{2} + \frac{\bar{n}}{2}\frac{\bar{n}}{2}) + \frac{1}{2}(\bar{U}-\bar{J})[\frac{\bar{n}}{2}\frac{\bar{n}}{2} + \frac{\bar{n}}{2}\frac{\bar{n}}{2}] - \frac{1}{2}\bar{U}\bar{n} + \frac{1}{2}\bar{J}\bar{n} \end{aligned}$$

Average density is defined as follows

$$\bar{n} = \sum_{\alpha\sigma} n_{\alpha\alpha}^{\sigma\sigma}$$

Average magnetic moment is defined as follows

$$\bar{m}^0 = \bar{m}_0 = \sum_\alpha n_{\alpha\alpha}^{\uparrow\uparrow} - \sum_\alpha n_{\alpha\alpha}^{\downarrow\downarrow}$$
$$\bar{m}^{-1} = -\bar{m}_{+1} = \sum_\alpha n_{\alpha\alpha}^{\uparrow\downarrow}$$
$$\bar{m}^{+1} = -\bar{m}_{-1} = \sum_\alpha n_{\alpha\alpha}^{\downarrow\uparrow}$$
$$|\bar{m}| = \sqrt{\sum_\mu \bar{m}^\mu \bar{m}_\mu} = \sqrt{[\bar{m}^0]^2 - [\bar{m}^{-1}]^2 - [\bar{m}^{+1}]^2}$$

The double counting correction in case 1 is given by

$$V_{\alpha\beta,DC1}^{\sigma\sigma'} = \frac{\delta E_{DC1}}{\delta n_{\alpha\beta}^{\sigma\sigma'}} = \delta_{\sigma\sigma'}\delta_{\alpha\beta}\bar{U}(\bar{n}-\frac{1}{2}) - \delta_{\alpha\beta}\bar{J}(\bar{n}_{\sigma\sigma'} - \frac{\delta_{\sigma\sigma'}}{2})] =$$
$$= \delta_{\sigma\sigma'}\delta_{\alpha\beta}[\bar{U}\bar{n}_{-\sigma-\sigma} + (\bar{U}-\bar{J})\bar{n}_{\sigma\sigma} - \frac{1}{2}(\bar{U}-\bar{J})] - \delta_{\alpha\beta}(1-\delta_{\sigma\sigma'})\bar{J}\bar{n}_{\sigma\sigma'}$$

The double counting correction is diagonal over spin and orbital indexes in case 2

$$V_{\alpha\beta,DC2}^{\sigma\sigma'} = \frac{\delta E_{DC2}}{\delta n_{\alpha\beta}^{\sigma\sigma'}} = \delta_{\sigma\sigma'}\delta_{\alpha\beta}[\bar{U}(\bar{n}-\frac{1}{2}) - \bar{J}(\frac{\bar{n}}{2}-\frac{1}{2})] =$$
$$= \delta_{\sigma\sigma'}\delta_{\alpha\beta}[\bar{U}\bar{n}/2 + (\bar{U}-\bar{J})\bar{n}/2 - \frac{1}{2}(\bar{U}-\bar{J})]$$

F. GREEN FUNCTION SYMMETRIZATION IN RELATIVISTIC CASE

Rotation of eigenvectors by Wigner matrices $U_{mm'}^l(\gamma)$ and $S_{\sigma\sigma'}^{j=1/2}(\gamma)$ after applying the symmetry operation $g = \{\gamma|a_\gamma\}$ made of rotation γ and possible shift a_γ for non-simmorphic crystal group.

$$A_{lm\sigma\tau}^{\gamma\mathbf{k}j} = \sum_{m'\sigma'} U_{mm'}^l(\gamma) S_{\sigma\sigma'}^{j=1/2}(\gamma) A_{lm'\sigma' g^{-1}\tau}^{\mathbf{k}j} e^{i\mathbf{k}\mathbf{R}_{g\tau}}$$

where

$$\mathbf{R}_{g\tau} = \hat{g}^{-1}\tau - [\hat{g}^{-1}\tau]_{inp}$$

Symmetrization for the Green function is done over entire crystal group $G = \{g\}$

$$G_{l_1m_1\sigma_1\tau_1l_2m_2\sigma_2\tau_2}(\omega) = \sum_\gamma \sum_{\mathbf{k}}^{IBZ} \frac{A_{l_1m_1\sigma_1\tau_1}^{\gamma\mathbf{k}j} A_{l_2m_2\sigma_2\tau_2}^{\gamma\mathbf{k}j*}}{\omega - E_{\mathbf{k}j}} = \sum_\gamma^G \sum_{m_1'\sigma_1'm_2'\sigma_2'} U_{m_1m_1'}^{l_1}(\gamma) S_{\sigma_1\sigma_1'}^{j=1/2}(\gamma) e^{i\mathbf{k}\mathbf{R}_{g\tau_1}} \Bigg[\sum_{\mathbf{k}}^{IBZ} \frac{A_{l_1m_1'\sigma_1'g^{-1}\tau_1}^{\mathbf{k}j} A_{l_2m_2\sigma_2 g^{-1}\tau}^{\mathbf{k}j*}}{\omega - E_{\mathbf{k}j}}$$

G. SUSCEPTIBILITY SYMMETRIZATION IN RELATIVISTIC CASE

Symmetrization for susceptibility is done over group $G_q = \{g_q\}$ of wavector $\mathbf{q}$: $\gamma\mathbf{q} = \mathbf{q}$ (because $\gamma\mathbf{k}+\mathbf{q} = \gamma(\mathbf{k}+\mathbf{q})$)

$$\chi_{l_1m_1\sigma_1\tau_1l_2m_2\sigma_2\tau_2l_3m_3\sigma_3\tau_3l_4m_4\sigma_4\tau_4}(\mathbf{q},\omega) = \sum_\gamma^{G_q} \sum_{\mathbf{k}}^{IBZ} \frac{f_{\mathbf{k}j} - f_{\mathbf{k}+\mathbf{q}j'}}{\omega - E_{\mathbf{k}j} + E_{\mathbf{k}+\mathbf{q}j'}} A_{l_1m_1\sigma_1\tau_1}^{\gamma\mathbf{k}j*} A_{l_2m_2\sigma_2\tau_2}^{\gamma\mathbf{k}+\mathbf{q}j'} A_{l_3m_3\sigma_3\tau_3}^{\gamma\mathbf{k}+\mathbf{q}j'*} A_{l_4m_4\sigma_4\tau_4}^{\gamma\mathbf{k}j} =$$
$$\sum_\gamma^{G_q} U_{m_1m_1'}^{l_1*}(\gamma) S_{\sigma_1\sigma_1'}^{j=1/2*}(\gamma) e^{-i\mathbf{k}\mathbf{R}_{g\tau_1}} U_{m_2m_2'}^{l_2}(\gamma) S_{\sigma_2\sigma_2'}^{j=1/2}(\gamma) e^{i(\mathbf{k}+\mathbf{q})\mathbf{R}_{g\tau_2}} \Bigg[\sum_{\mathbf{k}}^{IBZ} \frac{f_{\mathbf{k}j} - f_{\mathbf{k}+\mathbf{q}j'}}{\omega - E_{\mathbf{k}j} + E_{\mathbf{k}+\mathbf{q}j'}} A_{l_1m_1'\sigma_1'g^{-1}\tau_1}^{\mathbf{k}j*} A_{l_2m_2'\sigma_2'g^{-1}\tau_2}^{\mathbf{k}+\mathbf{q}j'} A_{l_3m_3'\sigma_3'g^{-1}\tau}^{\mathbf{k}+\mathbf{q}j'*}$$

XI. RADIAL SCHROEDINGER EQUATION

A. NON-RELATIVISTIC CASE

The radial Schrödinger equation is given by

$$-\frac{d^2\phi_l}{dr^2} - \frac{2}{r}\frac{d\phi_l}{dr} + \left(\frac{l(l+1)}{r^2} + V(r) - E\right)\phi_l(r) = 0$$

By substituting

$$P_l(r) = r\ \phi_l(r)$$

$$Q_l(r) = \frac{dP_l}{dr} - \frac{l+1}{r}P_l$$

we obtain the first order system of equations:

$$\begin{aligned}\frac{dP_l}{dr} &= Q_l(r) + \frac{l+1}{r}P_l(r)\\ \frac{dQ_l}{dr} &= [V(r) - E]P_l(r) - \frac{l+1}{r}Q_l(r)\end{aligned}$$

The assymptotic behavior of the radial functions is

$$P_l(r) = \alpha_l r^{l+1}\left(1 - \frac{Ze^2}{2(l+1)}r\right)$$

$$Q_l(r) = -\frac{Ze^2}{2(l+1)}\alpha_l r^{l+1}$$

Radial derivative

$$\frac{d\phi_l}{dr} = \frac{1}{r}(\frac{dP_l}{dr} - \frac{P_l}{r}) = \frac{Q_l}{r} + \frac{l}{r}P_l$$

Logarithmic derivative

$$D_l = \frac{r\phi_l'}{\phi_l} = r(\frac{Q_l}{P_l} + l)$$

Let us introduce the logarithmic mesh:

$$r(x) = b(e^x - 1)$$

$$b = S/(e^{\Delta N} - 1)$$

$$dr = be^x dx$$

where Δ is an increment and N is a total number of points. Then the system of equations is rewritten in the form

$$\begin{aligned}\frac{dP_l}{dx} &= be^x Q_l(x) + be^x\frac{l+1}{r(x)}P_l(x)\\ \frac{dQ_l}{dx} &= be^x[V(x) - E]P_l(x) - be^x\frac{l+1}{r(x)}Q_l(x)\end{aligned}$$

and can be solved numerically.

B. SCALAR-RELATIVISTIC CASE

The radial Schrödinger equation including Darwin and mass-velocity corrections is given by

$$-\frac{d^2\phi_l}{dr^2} - \frac{2}{r}\frac{d\phi_l}{dr} + \left(\frac{l(l+1)}{r^2} + V(r) - E \right) \phi_l(r) - \frac{(E-V(r))^2}{c^2}\phi_l(r) - \frac{dV}{dr}\frac{1}{c^2+E-V(r)}\frac{d\phi_l}{dr} = 0$$

By substituting

$$P_l(r) = r\ \phi_l(r)$$

$$Q_l(r) = \left(1 + \frac{1}{c^2}(E-V(r)\right)^{-1}\left(\frac{dP_l}{dr} - \frac{P_l}{r}\right)$$

we obtain the first order system of equations:

$$\frac{dP_l}{dr} = A(r)Q_l(r) + \frac{P_l(r)}{r}$$
$$\frac{dQ_l}{dr} = [V(r) - E + \frac{l(l+1)}{r^2A(r)}]P_l(r) - \frac{Q_l(r)}{r}$$

where

$$A(r) = 1 + \frac{1}{c^2}(E - V(r))$$

The assymptotic behavior of the radial functions is $P_l(r) = \alpha_l r^\gamma$ with $\gamma = \left(l(l+1)+1-\frac{4Z^2}{c^2}\right)^{1/2}$

$$Q_l(r) = \alpha_l r^\gamma \frac{(\gamma-1)}{2Z/c^2}$$

Radial derivative

$$\frac{d\phi_l}{dr} = \frac{1}{r}\frac{dP_l}{dr} - \frac{P_l}{r^2} = \frac{A(r)Q_l(r)}{r}$$

Logarithmic derivative

$$D_l = \frac{r\phi_l'}{\phi_l} = \frac{rA(r)Q_l(r)}{P_l(r)}$$

By introducing the logarithmic mesh defined above this system is rewritten in the form:

$$\frac{dP_l}{dx} = be^x A(x)Q_l(x) + \frac{P_l(x)}{r(x)}be^x$$
$$\frac{dQ_l}{dx} = be^x[V(x) - E] + \frac{l(l+1)}{r^2(x)A(x)}P_l(x) - be^x\frac{Q_l(x)}{r(x)}$$

and can be solved numerically.

C. FULLY RELATIVISTIC CASE

The first order system of equations is written for large and small component of the relativistic bispinor

$$g_l^{(j)}(r) = \frac{P_l^{(j)}(r)}{r}$$
$$f_l^{(j)}(r) = \frac{Q_l^{(j)}(r) + \frac{\kappa+1}{A(r)}\frac{P_l^{(j)}(r)}{r}}{rc}$$

Here index $\kappa = -l - 1 = -j - \frac{3}{2}$ when $j = l + \frac{1}{2}$ and $\kappa = l = j + \frac{1}{2}$ when $j = l - \frac{1}{2}$. (Do not confuse with the tail index!) We obtain

$$\frac{dP_l^{(j)}}{dr} = A(r)Q_l^{(j)}(r) + \frac{P_l^{(j)}(r)}{r}$$
$$\frac{dQ_l^{(j)}}{dr} = [V(r) - E + \frac{l(l+1)}{r^2 A(r)} - \frac{1}{r}\frac{dV}{dr}\frac{(\kappa+1)}{c^2 A^2(r)}]P_l^{(j)}(r) - \frac{Q_l^{(j)}(r)}{r}$$

where

$$A(r) = 1 + \frac{1}{c^2}(E - V(r))$$

The assymptotic behavior of the radial functions is $P_l(r) = \alpha_l r^\gamma$ with $\gamma = \left(l(l+1) + 1 - \frac{4Z^2}{c^2}\right)^{1/2}$

$$Q_l^{(j)}(r) = \alpha_l r^\gamma \frac{(\gamma - 1)}{2Z/c^2}$$

D. PAULI EQUATION

Consider Schroedinger equation with spin orbit term

$$(-\nabla^2 + V(r) - E + \alpha(r)\mathbf{ls})\vec{g}(\mathbf{r}, E) = 0$$

where

$$\alpha(r) = \frac{1}{c^2}\frac{2}{r}\frac{dV}{dr}$$

Let is represent

$$\vec{g}(\mathbf{r}, E) = \sum_l \sum_{jm_j} A_{jm_j} g_l^{(j=l\pm\frac{1}{2})}(r, E)\vec{\Omega}_{jm_j}^{(j=l\pm\frac{1}{2})}(\hat{r})$$

We obtain the equation for the radial part

$$(-\nabla_r^2 + \frac{l(l+1)}{r^2} + V(r) - E - \alpha(r)\frac{(\kappa_j+1)}{2})g_l^{(j)}(r, E) = 0$$
$$(-\nabla_r^2 + \frac{l(l+1)}{r^2} + V(r) - E - \frac{1}{c^2}\frac{(\kappa_j+1)}{r}\frac{dV}{dr})g_l^{(j)}(r, E) = 0$$

where

$$\kappa_{j=l-\frac{1}{2}} = l$$
$$\kappa_{j=l+\frac{1}{2}} = -l - 1$$

Let us rederive the radial equation from the Diraq equation

$$\frac{dP_l^{(j)}}{dr} = A(r)Q_l^{(j)}(r) + \frac{P_l^{(j)}(r)}{r}$$
$$\frac{dQ_l^{(j)}}{dr} = [V(r) - E + \frac{l(l+1)}{r^2 A(r)} - \frac{1}{r}\frac{dV}{dr}\frac{(\kappa_j+1)}{c^2 A^2(r)}]P_l^{(j)}(r) - \frac{Q_l^{(j)}(r)}{r}$$

$$\frac{dQ_l^{(j)}}{dr} = [V(r) - E + \frac{l(l+1)}{r^2 A(r)} - \frac{1}{r}\frac{dV}{dr}\frac{(\kappa_j+1)}{c^2A^2(r)}]P_l^{(j)}(r) - \frac{1}{rA(r)}[\frac{dP_l^{(j)}}{dr} - \frac{P_l^{(j)}(r)}{r}]$$

$$= [V(r) - E + \frac{l(l+1)}{r^2 A(r)} - \frac{1}{r}\frac{dV}{dr}\frac{(\kappa_j+1)}{c^2A^2(r)}]rg_l^{(j)}(r) - \frac{1}{A(r)}\frac{dg_l^{(j)}}{dr}$$

$$\frac{dQ_l^{(j)}}{dr} = \frac{d}{dr}\frac{r}{A(r)}\frac{dg_l^{(j)}}{dr} = \frac{r}{A(r)}\frac{d^2g_l^{(j)}}{dr^2} - \frac{r}{A^2(r)}\frac{dA}{dr}\frac{dg_l^{(j)}}{dr} + \frac{1}{A(r)}\frac{dg_l^{(j)}}{dr}$$

$$\frac{d^2g_l^{(j)}}{dr^2} - \frac{1}{A(r)}\frac{dA}{dr}\frac{dg_l^{(j)}}{dr} = [(V(r)-E)A(r) + \frac{l(l+1)}{r^2} - \frac{1}{r}\frac{dV}{dr}\frac{(\kappa_j+1)}{c^2A(r)}]g_l^{(j)}(r) - \frac{2}{r}\frac{dg_l^{(j)}}{dr}$$

We obtain

$$-\frac{d^2g_l^{(j)}}{dr^2} - \frac{2}{r}\frac{dg_l^{(j)}}{dr} + [(V(r)-E) + \frac{l(l+1)}{r^2} - \frac{1}{r}\frac{dV}{dr}\frac{(\kappa_j+1)}{c^2A(r)}]g_l^{(j)}(r,E) - \frac{(V(r)-E)^2}{c^2}g_l^{(j)}(r,E) - \frac{dV}{dr}\frac{1}{c^2A(r)}\frac{d}{dr}g_l^{(j)}(r,E) = 0$$

which is viewed almost like the equation above plus Darwin and mass velocity corrections. We solve it as follows

$$\frac{dP_l^{(j)}}{dr} = A(r)Q_l^{(j)}(r) + \frac{P_l^{(j)}(r)}{r}$$

$$\frac{dQ_l^{(j)}}{dr} = [V(r) - E + \frac{l(l+1)}{r^2A(r)} - \frac{1}{r}\frac{dV}{dr}\frac{(\kappa_j+1)}{c^2A^2(r)}]P_l^{(j)}(r) - \frac{Q_l^{(j)}(r)}{r}$$

$$g_l^{(j)}(r) = \frac{P_l^{(j)}(r)}{r}$$

$$\frac{dg_l^{(j)}(r)}{dr} = \frac{1}{r}\frac{dP_l^{(j)}(r)}{dr} - \frac{P_l^{(j)}(r)}{r^2} = \frac{1}{r}A(r)Q_l^{(j)}(r)$$

Thus, when neglecting the small component the solution of the relativistic equation can be viewed as a spinor

$$\vec{\phi}_{jm_j}^{(j=l\pm1/2)}(\mathbf{r},E) = g_l^{(j)}(r,E)\vec{\Omega}_{jm_j}^{(j=l\pm\frac{1}{2})}(\hat{r}) = g_l^{(j)}(r,E)\sum_{m\sigma}T_{jm_jm\sigma}^{(j=l\pm1/2)}Y_{lm}(\hat{r})|\vec{\sigma}\rangle = g_l^{(j)}(r,E)\sum_{m\sigma}T_{jm_jm\sigma}^{(j=l\pm1/2)}\vec{Y}_{lm\sigma}(\hat{r})$$

where $\vec{\Omega}_{jm_j}^{(j=l\pm\frac{1}{2})}(r)$ is a spinor harmonic, i.e.

$$\vec{\phi}_{jm_j}^{(j=l-1/2)}(\mathbf{r},E) = g_l^{(j)}(r,E)\begin{pmatrix} -\sqrt{\frac{j-m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j-\frac{1}{2}}(r) \\ +\sqrt{\frac{j+m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j+\frac{1}{2}}(r) \end{pmatrix}$$

$$\vec{\phi}_{jm_j}^{(j=l+1/2)}(\mathbf{r},E) = g_l^{(j)}(r,E)\begin{pmatrix} +\sqrt{\frac{j+m_j}{2j}}Y_{j-\frac{1}{2}m_j-\frac{1}{2}}(r) \\ +\sqrt{\frac{j-m_j}{2j}}Y_{j-\frac{1}{2}m_j+\frac{1}{2}}(r) \end{pmatrix}$$

and where

$$\vec{Y}_{lm\uparrow}(\hat{r}) = Y_{lm}(\hat{r})\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\vec{Y}_{lm\downarrow}(\hat{r}) = Y_{lm}(\hat{r})\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

In general transformation can be written in terms of the unitary transformation matrix $T_{jm_jm\sigma}^{(j=l\pm1/2)}$

$$\sum_{m\sigma}T_{jm_jm\sigma}^{(j=l\pm1/2)}T_{m\sigma j'm'_{j'}}^{+(j'=l\pm\frac{1}{2})} = \delta_{jj'}\delta_{m_jm'_{j'}}$$

$$\sum_{m_j}T_{m\sigma jm_j}^{+(j=l-\frac{1}{2})}T_{jm_jm'\sigma'}^{(j=l-\frac{1}{2})} + \sum_{m_j}T_{m\sigma jm_j}^{+(j=l+\frac{1}{2})}T_{jm_jm'\sigma'}^{(j=l+\frac{1}{2})} = \delta_{mm'}\delta_{\sigma\sigma'}$$

and

$$\vec{\phi}_{jm_j}^{(j=l\pm 1/2)}(\mathbf{r},E)=g_l^{(j=l\pm 1/2)}(r,E)\sum_{m\sigma}T_{jm_jm\sigma}^{(j=l\pm 1/2)}\vec{Y}_{lm\sigma}(\hat{r})$$

The reverse transformation can be written as follows

$$\vec{\phi}_{lm\sigma}(\mathbf{r},E)=g_l^{(j=l-1/2)}(r,E)\sum_{m_j}T_{m\sigma jm_j}^{+(j=l-\frac{1}{2})}\vec{\Omega}_{jm_j}^{(j=l-\frac{1}{2})}(\hat{r})+g_l^{(j=l+1/2)}(r,E)\sum_{m_j}T_{m\sigma jm_j}^{+(j=l+\frac{1}{2})}\vec{\Omega}_{jm_j}^{(j=l+\frac{1}{2})}(\hat{r})=\sum_{j=l\pm\frac{1}{2}}g_l^{(j)}(r,E)\sum_{m_j}T_{m\sigma}^{+}$$

Since the radial part depends on j, it cannot be reduced to spherical harmonics. However, if one neglects j dependence of the radial part, i.e. $g_l^{(j=l\pm 1/2)}(r,E)\sim\phi_l(r,E)$ we obtain

$$\vec{\phi}_{lm\sigma}(\mathbf{r},E)=\phi_l(r,E)\sum_{m_j}T_{m\sigma jm_j}^{+(j=l-\frac{1}{2})}\vec{\Omega}_{jm_j}^{(j=l-\frac{1}{2})}(\hat{r})+\phi_l(r,E)\sum_{m_j}T_{m\sigma jm_j}^{+(j=l+\frac{1}{2})}\vec{\Omega}_{jm_j}^{(j=l+\frac{1}{2})}(\hat{r})=\phi_l(r,E)Y_{lm}(\hat{r})|\vec{\sigma}\rangle=\phi_{lm}(\mathbf{r},E)|\vec{\sigma}\rangle$$

Let us introduce

$$\vec{Y}_{lm\sigma}^{(j=l-\frac{1}{2})}(r)=\sum_{m_j}T_{m\sigma jm_j}^{+(j=l-\frac{1}{2})}\vec{\Omega}_{jm_j}^{(j=l-\frac{1}{2})}(\hat{r})$$
$$\vec{Y}_{lm\sigma}^{(j=l+\frac{1}{2})}(r)=\sum_{m_j}T_{m\sigma jm_j}^{+(j=l+\frac{1}{2})}\vec{\Omega}_{jm_j}^{(j=l+\frac{1}{2})}(\hat{r})$$

We obtain

$$\vec{\phi}_{lm\sigma}(\mathbf{r},E)=g_l^{(j=l-1/2)}(r,E)\vec{Y}_{lm\sigma}^{(j=l-\frac{1}{2})}(\hat{r})+g_l^{(j=l+1/2)}(r,E)\vec{Y}_{lm\sigma}^{(j=l+\frac{1}{2})}(\hat{r})$$

Notice that

$$\vec{Y}_{lm\sigma}^{(j=l-\frac{1}{2})}(\hat{r})+\vec{Y}_{lm\sigma}^{(j=l+\frac{1}{2})}(\hat{r})=\vec{Y}_{lm\sigma}(\hat{r})$$

If we also intorduce the difference

$$\vec{Y}_{lm\sigma}^{(j=l-\frac{1}{2})}(\hat{r})-\vec{Y}_{lm\sigma}^{(j=l+\frac{1}{2})}(\hat{r})=\vec{Z}_{lm\sigma}(\hat{r})$$

we obtain

$$\vec{Y}_{lm\sigma}^{(j=l\mp\frac{1}{2})}(\hat{r})=\frac{1}{2}[\vec{Y}_{lm\sigma}(\hat{r})\pm\vec{Z}_{lm\sigma}(\hat{r})]$$

and

$$\vec{\phi}_{lm\sigma}(\mathbf{r},E)=\frac{1}{2}[g_l^{(j=l-1/2)}(r,E)+g_l^{(j=l+1/2)}(r,E)]\vec{Y}_{lm\sigma}(\hat{r})+\frac{1}{2}[g_l^{(j=l-1/2)}(r,E)-g_l^{(j=l+1/2)}(r,E)]\vec{Z}_{lm\sigma}(\hat{r})$$

Remarkably that the first term is a pure spin state and the second term is the relativistic correction.

Let us finally introduce

$$g_l^{(s)}(r,E)=\frac{1}{2}[g_l^{(j=l-1/2)}(r,E)+g_l^{(j=l+1/2)}(r,E)]$$
$$g_l^{(d)}(r,E)=\frac{1}{2}[g_l^{(j=l-1/2)}(r,E)-g_l^{(j=l+1/2)}(r,E)]$$

We obtain

$$\vec{\phi}_{lm\sigma}(\mathbf{r},E)=g_l^{(s)}(r,E)\vec{Y}_{lm\sigma}(\hat{r})+g_l^{(d)}(r,E)\vec{Z}_{lm\sigma}(\hat{r})$$

XII. HAMILTONIAN AND OVERLAP MATRIX IN SPIN ORBITAL CASE.

Assume that spin orbit splitting is large so that it is essential to construct LMTO by taking into account the fact that $\phi_l(r)$ is different for $j = l \pm \frac{1}{2}$. Therefore the spin orbital operator should not be treated in a variational manner but exactly. For this let us construct the LMTO $\chi^{\mathbf{k}}_{lm\kappa\tau}(\mathbf{r})$ which accounts for this. The original LMTO

$$\chi^{\mathbf{k}}_{lm\kappa\tau}(\mathbf{r}_{\tau'}) = \Phi^H_{lm\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'} \Phi^J_{l'm'\kappa\tau'}(\mathbf{r}) S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)$$

is first viewed as a spinor $\vec{\chi}^{\mathbf{k}}_{lm\sigma\kappa\tau\sigma}(\mathbf{r})$ with

$$\vec{\chi}^{\mathbf{k}}_{lm\kappa\tau\uparrow}(\mathbf{r}) = \chi^{\mathbf{k}}_{lm\kappa\tau}(\mathbf{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\vec{\chi}^{\mathbf{k}}_{lm\kappa\tau\downarrow}(\mathbf{r}) = \chi^{\mathbf{k}}_{lm\kappa\tau}(\mathbf{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\vec{\chi}^{\mathbf{k}}_{lm\sigma\kappa\tau}(\mathbf{r}_{\tau'}) = \vec{\Phi}^H_{lm\sigma\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'\sigma'} \vec{\Phi}^J_{l'm'\sigma'\kappa\tau'}(\mathbf{r}) S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)\delta_{\sigma'\sigma}$$

Then, we transform to spinor harmonics $\vec{\Omega}^{(j=l\pm\frac{1}{2})}_{jm_j}(r)$ representation

$$\vec{\chi}^{\mathbf{k}(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) = -\sqrt{\frac{j-m_j+1}{2(j+1)}}\vec{\chi}^{\mathbf{k}}_{j+\frac{1}{2}m_j-\frac{1}{2}\kappa\tau\uparrow}(\mathbf{r}) + \sqrt{\frac{j+m_j+1}{2(j+1)}}\vec{\chi}^{\mathbf{k}}_{j+\frac{1}{2}m_j+\frac{1}{2}\kappa\tau\downarrow}(\mathbf{r}) = \begin{pmatrix} -\sqrt{\frac{j-m_j+1}{2(j+1)}}\chi^{\mathbf{k}}_{j+\frac{1}{2}m_j-\frac{1}{2}\kappa\tau}(\mathbf{r}) \\ \sqrt{\frac{j+m_j+1}{2(j+1)}}\chi^{\mathbf{k}}_{j+\frac{1}{2}m_j+\frac{1}{2}\kappa\tau}(\mathbf{r}) \end{pmatrix}$$

$$\vec{\chi}^{\mathbf{k}(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) = +\sqrt{\frac{j+m_j}{2j}}\vec{\chi}^{\mathbf{k}}_{j-\frac{1}{2}m_j-\frac{1}{2}\kappa\tau\uparrow}(\mathbf{r}) + \sqrt{\frac{j-m_j}{2j}}\vec{\chi}^{\mathbf{k}}_{j-\frac{1}{2}m_j+\frac{1}{2}\kappa\tau\downarrow}(\mathbf{r}) = \begin{pmatrix} \sqrt{\frac{j+m_j}{2j}}\chi^{\mathbf{k}}_{j-\frac{1}{2}m_j-\frac{1}{2}\kappa\tau}(\mathbf{r}) \\ \sqrt{\frac{j-m_j}{2j}}\chi^{\mathbf{k}}_{j-\frac{1}{2}m_j+\frac{1}{2}\kappa\tau}(\mathbf{r}) \end{pmatrix}$$

or using the matrix notation

$$\begin{aligned}
\vec{\chi}^{\mathbf{k}(j=l\pm\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) &= \sum_{m\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma}\vec{\chi}^{\mathbf{k}}_{lm\sigma\kappa\tau}(\mathbf{r}) \\
&= \sum_{m\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma}\vec{\Phi}^H_{lm\sigma\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'\sigma'} \vec{\Phi}^J_{l'm'\sigma'\kappa\tau'}(\mathbf{r}) \sum_{m\sigma} S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)\delta_{\sigma'\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma} \\
&= \sum_{m\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma}\vec{\Phi}^H_{lm\sigma\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'}\sum_{m'\sigma'}\sum_{m''\sigma''}\sum_{m'_{j'}} \vec{\Phi}^J_{l'm''\sigma''\kappa\tau'}(\mathbf{r})[T^{(j'=l'-\frac{1}{2})}_{j'm'_{j'},m''\sigma''}T^{+(j'=l'-\frac{1}{2})}_{m'\sigma'j'm'_{j'}} + T^{(j'=l'+\frac{1}{2})}_{j'm'_{j'},m''\sigma''}T^{+(j'=l'+\frac{1}{2})}_{m'\sigma'j'm'_{j'}}] \\
&= \sum_{m\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma}\vec{\Phi}^H_{lm\sigma\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} \\
&\quad -\sum_{l'}\sum_{m''\sigma''}\sum_{m'_{j'}} \vec{\Phi}^J_{l'm''\sigma''\kappa\tau'}(\mathbf{r}) T^{(j'=l'-\frac{1}{2})}_{j'm'_{j'},m''\sigma''} \sum_{m'\sigma'}\sum_{m\sigma} T^{+(j'=l'-\frac{1}{2})}_{m'\sigma'j'm'_{j'}} S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)\delta_{\sigma'\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma} \\
&\quad -\sum_{l'}\sum_{m''\sigma''}\sum_{m'_{j'}} \vec{\Phi}^J_{l'm''\sigma''\kappa\tau'}(\mathbf{r}) T^{(j'=l'+\frac{1}{2})}_{j'm'_{j'},m''\sigma''} \sum_{m'\sigma'}\sum_{m\sigma} T^{+(j'=l'+\frac{1}{2})}_{m'\sigma'j'm'_{j'}} S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)\delta_{\sigma'\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma}
\end{aligned}$$

Let us now introduce structure constants in the relatvistic representation which are obtained by the following transformtation

$$\sum_{m'\sigma'm\sigma} T^{+(j'=l'\pm\frac{1}{2})}_{j'm'_{j'},m'\sigma'} S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)\delta_{\sigma'\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma} = S^{\mathbf{k}(j'=l'\pm\frac{1}{2})(j=l\pm\frac{1}{2})}_{j'm'_j\tau' jm_j\tau}(\kappa)$$

and

$$\vec{\Phi}^{H,J(j=l\pm\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) = \sum_{m\sigma} T^{(j=l\pm\frac{1}{2})}_{jm_jm\sigma}\vec{\Phi}^{H,J}_{lm\sigma\kappa\tau}(\mathbf{r})$$

We obtain

$$\vec{\chi}^{\mathbf{k}(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) = \begin{pmatrix} -\sqrt{\frac{j-m_j+1}{2(j+1)}}\chi^{\mathbf{k}(j=l-\frac{1}{2})}_{j+\frac{1}{2}m_j-\frac{1}{2}\kappa\tau}(\mathbf{r}) \\ \sqrt{\frac{j+m_j+1}{2(j+1)}}\chi^{\mathbf{k}(j=l-\frac{1}{2})}_{j+\frac{1}{2}m_j+\frac{1}{2}\kappa\tau}(\mathbf{r}) \end{pmatrix} = \vec{\Phi}^{H(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'_j}\vec{\Phi}^{J(j'=l'-\frac{1}{2})}_{j'm'_j\kappa\tau'}(\mathbf{r})S^{\mathbf{k}(j'=l'-\frac{1}{2})(j=l-\frac{1}{2})}_{j'm'_j\tau'jm_j\tau}(\kappa) - \sum_{l'm'_j}\vec{\Phi}^{J(j'=l'}_{j'm'_j\kappa}$$

$$\vec{\chi}^{\mathbf{k}(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) = \begin{pmatrix} \sqrt{\frac{j+m_j}{2j}}\chi^{\mathbf{k}(j=l+\frac{1}{2})}_{j-\frac{1}{2}m_j-\frac{1}{2}\kappa\tau}(\mathbf{r}) \\ \sqrt{\frac{j-m_j}{2j}}\chi^{\mathbf{k}(j=l+\frac{1}{2})}_{j-\frac{1}{2}m_j+\frac{1}{2}\kappa\tau}(\mathbf{r}) \end{pmatrix} = \vec{\Phi}^{H(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'_j}\vec{\Phi}^{J(j'=l'-\frac{1}{2})}_{j'm'_j\kappa\tau'}(\mathbf{r})S^{\mathbf{k}(j'=l'-\frac{1}{2})(j=l+\frac{1}{2})}_{j'm'_j\tau'jm_j\tau}(\kappa) - \sum_{l'm'_j}\vec{\Phi}^{J(j'=l'+\frac{1}{2})}_{j'm'_j\kappa\tau'}$$

This transformation involves a construction for two different $j = l \pm 1/2$, therefore can be done for two kinds of radial solutions $\phi^{(j)}_l(r,E) = g^{(j)}_l(r,E)$.

We can work with spinor LMTOs $\vec{\chi}^{\mathbf{k}(j=l\pm\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})$ since they have the same dimension $N_{at}N_\kappa([2j^{(-)}+1]+[2j^{(+)}+1])$.as the original non–relatvistic basis $N_{at}N_\kappa([2(2l+1)]$. $j^{(-)} = l-\frac{1}{2}, j^{(+)} = l+\frac{1}{2}, 2j^{(-)}+1+2j^{(+)}+1 = 2(2l+1)$

The overlap matrix becomes

$$O^{(j'=l'\pm\frac{1}{2})(j=l\pm\frac{1}{2})}_{j'm'_j\kappa'\tau'jm_j\kappa\tau}(\mathbf{k}) = \langle\vec{\chi}^{\mathbf{k}(j'=l'\pm\frac{1}{2})}_{j'm'_j\kappa'\tau'}|\vec{\chi}^{\mathbf{k}(j=l\pm\frac{1}{2})}_{jm_j\kappa\tau}\rangle$$

The MT part of the hamiltonian matrix becomes

$$H^{MT(j'=l'\pm\frac{1}{2})(j=l\pm\frac{1}{2})}_{j'm'_j\kappa'\tau'jm_j\kappa\tau}(\mathbf{k}) = \langle\vec{\chi}^{\mathbf{k}(j'=l'\pm\frac{1}{2})}_{j'm'_j\kappa'\tau'}| - \nabla^2 + V_{MT}(r) + \alpha\mathbf{ls}|\vec{\chi}^{\mathbf{k}(j=l\pm\frac{1}{2})}_{jm_j\kappa\tau}\rangle$$

We can also try to work in the original non relativistic representation. For this a properly constructed spinor LMTO $\vec{\chi}^{\mathbf{k}(j=l\pm\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})$ has to be converted back to original representation

$$\vec{\chi}^{\mathbf{k}}_{lm\kappa\tau\sigma}(\mathbf{r}) = \sum_{m_j}T^{+(j=l-\frac{1}{2})}_{lm\sigma jm_j}\vec{\chi}^{\mathbf{k}(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) + \sum_{m_j}T^{+(j=l+\frac{1}{2})}_{lm\sigma jm_j}\vec{\chi}^{\mathbf{k}(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})$$

We obtain

$$\begin{aligned}\vec{\chi}^{\mathbf{k}}_{lm\kappa\tau\sigma}(\mathbf{r}) = &\sum_{m_j}T^{+(j=l-\frac{1}{2})}_{m\sigma jm_j}\vec{\Phi}^{H(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'_{j'}}\vec{\Phi}^{J(j'=l'-\frac{1}{2})}_{j'm'_j\kappa\tau'}(\mathbf{r})\sum_{m_j}S^{\mathbf{k}(j'=l'-\frac{1}{2})(j=l-\frac{1}{2})}_{j'm'_j\tau'jm_j\tau}(\kappa)T^{+(j=l-\frac{1}{2})}_{lm\sigma jm_j} - \sum_{l'm'_{j'}}\vec{\Phi}^{J(j'=l'+\frac{1}{2})}_{j'm'_j\kappa\tau'}(\mathbf{r})\sum \\ &\sum_{m_j}T^{+(j=l+\frac{1}{2})}_{m\sigma jm_j}\vec{\Phi}^{H(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'_{j'}}\vec{\Phi}^{J(j'=l'-\frac{1}{2})}_{j'm'_j\kappa\tau'}(\mathbf{r})\sum_{m_j}S^{\mathbf{k}(j'=l'-\frac{1}{2})(j=l+\frac{1}{2})}_{j'm'_j\tau'jm_j\tau}(\kappa)T^{+(j=l+\frac{1}{2})}_{lm\sigma jm_j} - \sum_{lm'_{j'}}\vec{\Phi}^{J(j'=l'+\frac{1}{2})}_{j'm'_j\kappa\tau'}(\mathbf{r})\sum \\ = &\sum_{m_j}T^{+(j=l-\frac{1}{2})}_{m\sigma jm_j}\vec{\Phi}^{H(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} + \sum_{m_j}T^{+(j=l+\frac{1}{2})}_{m\sigma jm_j}\vec{\Phi}^{H(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'_{j'}}\vec{\Phi}^{J(j'=l'-\frac{1}{2})}_{j'm'_j\kappa\tau'}(\mathbf{r})S^{\mathbf{k}(j'=l'-\frac{1}{2})}_{j'm'_j\tau'lm\sigma\tau}(\kappa) - \sum_{l'm'_{j'}}\vec{\Phi}^{J(}_{j'}\end{aligned}$$

Using the unitary property of the transformtation matrix

$$\sum_{m_j}T^{(j=l-\frac{1}{2})}_{lm\sigma jm_j}T^{+(j=l-\frac{1}{2})}_{jm_jl'm'\sigma'} + \sum_{m_j}T^{(j=l+\frac{1}{2})}_{lm\sigma jm_j}T^{+(j=l+\frac{1}{2})}_{jm_jl'm'\sigma'} = \delta_{m\sigma m'\sigma'}$$

$$\sum_{lm\sigma}T^{+(j'=l\pm\frac{1}{2})}_{j'm'_{j'}lm\sigma}T^{(j=l\pm\frac{1}{2})}_{lm\sigma jm_j} = \delta_{j'm'_{j'}jm_j}$$

we obtain

$$\vec{\chi}^{\mathbf{k}}_{lm\kappa\tau\sigma}(\mathbf{r}) = \sum_{m_j}T^{+(j=l-\frac{1}{2})}_{m\sigma jm_j}\vec{\Phi}^{H(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} + \sum_{m_j}T^{+(j=l+\frac{1}{2})}_{m\sigma jm_j}\vec{\Phi}^{H(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'\sigma'}\left[\sum_{m'_{j'}}T^{+(j'=l'-\frac{1}{2})}_{m'\sigma'j'm'_{j'}}\vec{\Phi}^{J(j'=l'-\frac{1}{2})}_{j'm'_{j'}\kappa\tau'}(\mathbf{r}) + \sum_{m'_{j'}}T^{+}_{m'}\right.$$

Further simplification would be trivial if $\phi^{(j)}_l(r,E) = g^{(j)}_l(r,E)$ used to construct Φ^H and Φ^J does not depend on index (j). In this case the original non–relativistic LMTO will be obtained since

$$\vec{\Phi}^{H,J(j=l\pm\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) = \Phi^{H,J}_l(r)\vec{\Omega}^{(j=l\pm\frac{1}{2})}_{jm_j}(r)$$

In this case

$$\sum_{m_j} T^{+(j=l-\frac{1}{2})}_{m\sigma j m_j} \vec{\Phi}^{H,J(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) + \sum_{m_j} T^{+(j=l+\frac{1}{2})}_{m\sigma j m_j} \vec{\Phi}^{H,J(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) = \vec{\Phi}^{H,J}_{lm\sigma\kappa\tau}(\mathbf{r})$$

and

$$\vec{\chi}^{\mathbf{k}}_{lm\sigma\kappa\tau}(\mathbf{r}) = \vec{\Phi}^{H}_{lm\sigma\kappa\tau}(\mathbf{r})\delta_{\tau'\tau} - \sum_{l'm'\sigma'} \vec{\Phi}^{J}_{l'm'\sigma'\kappa\tau'}(\mathbf{r}) S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)\delta_{\sigma'\sigma}$$

In general case we can define $\vec{\Phi}^{H,J(rel)}_{lm\sigma\kappa\tau}(\mathbf{r})$

$$\begin{aligned}
\vec{\Phi}^{H,J(rel)}_{lm\sigma\kappa\tau}(\mathbf{r}) &= \sum_{m_j} T^{+(j=l-\frac{1}{2})}_{m\sigma j m_j} \vec{\Phi}^{H,J(j=l-\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) + \sum_{m_j} T^{+(j=l+\frac{1}{2})}_{m\sigma j m_j} \vec{\Phi}^{H,J(j=l+\frac{1}{2})}_{jm_j\kappa\tau}(\mathbf{r}) \\
&= \Phi^{H,J(j=l-\frac{1}{2})}_{l\kappa\tau}(r) \sum_{m_j} T^{+(j=l-\frac{1}{2})}_{m\sigma j m_j} \vec{\Omega}^{(j=l-\frac{1}{2})}_{jm_j}(\hat{r}) + \Phi^{H,J(j=l+\frac{1}{2})}_{l\kappa\tau}(r) \sum_{m_j} T^{+(j=l+\frac{1}{2})}_{m\sigma j m_j} \vec{\Omega}^{(j=l+\frac{1}{2})}_{jm_j}(\hat{r}) \\
&= \Phi^{H,J(j=l-\frac{1}{2})}_{l\kappa\tau}(r) \vec{Y}^{(j=l-\frac{1}{2})}_{lm\sigma}(r) + \Phi^{H,J(j=l+\frac{1}{2})}_{l\kappa\tau}(r) \vec{Y}^{(j=l+\frac{1}{2})}_{lm\sigma}(r) \\
&= \Phi^{H,J(s)}_{l\kappa\tau}(r) \vec{Y}_{lm\sigma}(\hat{r}) + \Phi^{H,J(d)}_{l\kappa\tau}(r) \vec{Z}_{lm\sigma}(\hat{r}) \\
&= \vec{\Phi}^{H,J(s)}_{lm\sigma\kappa\tau}(\mathbf{r}) + \vec{\Phi}^{H,J(d)}_{lm\sigma\kappa\tau}(\mathbf{r})
\end{aligned}$$

where $\Phi^{H,J(s)}_{l\kappa\tau}(r)$ is constructed from the sum of radial solutions $\frac{1}{2}[g_l^{(j=l-1/2)}(r, E_{\nu j=l-1/2}) + g_l^{(j=l+1/2)}(r, E_{\nu j=l+1/2})]$ as well as their energy derivatives while $\Phi^{H,J(d)}_{l\kappa\tau}(r)$ is constructed from the difference $\frac{1}{2}[g_l^{(j=l-1/2)}(r, E) - g_l^{(j=l+1/2)}(r, E)]$ as well as their energy derivatives. Note that since $\Phi^{H,J(j=l\pm\frac{1}{2})}_{l\kappa\tau}$ match smoothly to the Hankel/Bessel functions at the sphere boundary, so do $\Phi^{H,J(s)}_{l\kappa\tau}(r)$, while $\Phi^{H,J(d)}_{l\kappa\tau}(r)$ have zero and zero radial derivatives at the sphere boundary.

We finally obtain

$$\begin{aligned}
\vec{\chi}^{\mathbf{k}(rel)}_{lm\sigma\kappa\tau}(\mathbf{r}_{\tau'}) &= \vec{\Phi}^{H(rel)}_{lm\sigma\kappa\tau}(\mathbf{r}_\tau)\delta_{\tau'\tau} - \sum_{l'm'} \vec{\Phi}^{J(rel)}_{l'm'\sigma\kappa\tau'}(\mathbf{r}_{\tau'}) S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa) = \\
&= \vec{\Phi}^{H(s)}_{lm\sigma\kappa\tau}(\mathbf{r}_\tau)\delta_{\tau'\tau} - \sum_{l'm'} \vec{\Phi}^{J(s)}_{l'm'\sigma\kappa\tau'}(\mathbf{r}_{\tau'}) S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa) + \vec{\Phi}^{H(d)}_{lm\sigma\kappa\tau}(\mathbf{r}_\tau)\delta_{\tau'\tau} - \sum_{l'm'} \vec{\Phi}^{J(d)}_{l'm'\sigma\kappa\tau'}(\mathbf{r}_{\tau'}) S^{\mathbf{k}}_{l'm'\tau' lm\tau}(\kappa)
\end{aligned}$$

which represent a sum of non–relatvistic LMTO plus relativistic correction

$$\vec{\chi}^{\mathbf{k}(rel)}_{lm\sigma\kappa\tau}(\mathbf{r}) = \vec{\chi}^{\mathbf{k}(s)}_{lm\sigma\kappa\tau}(\mathbf{r}) + \vec{\chi}^{\mathbf{k}(d)}_{lm\sigma\kappa\tau}(\mathbf{r})$$

A. MATRIX ELEMENTS IN RELATIVISTIC CASE

Consider the average value of the spin orbital operator

$$\begin{aligned}
\langle \mathbf{ls} \rangle &= \frac{1}{2(2l+1)} \sum_{m_j} \langle \vec{\Omega}^{j=l-\frac{1}{2}}_{jm_j} | \mathbf{ls} | \vec{\Omega}^{j=l-\frac{1}{2}}_{jm_j} \rangle + \frac{1}{2(2l+1)} \sum_{m_j} \langle \vec{\Omega}^{j=l+\frac{1}{2}}_{jm_j} | \mathbf{ls} | \vec{\Omega}^{j=l+\frac{1}{2}}_{jm_j} \rangle \\
&= \frac{1}{2(2l+1)} \sum_{m_j} \frac{-(\kappa_{j=l-\frac{1}{2}}+1)}{2} + \frac{1}{2(2l+1)} \sum_{m_j} \frac{-(\kappa_{j=l+\frac{1}{2}}+1)}{2} = \\
&= \frac{1}{2(2l+1)} \sum_{m_j} \frac{-(l+1)}{2} + \frac{1}{2(2l+1)} \sum_{m_j} \frac{l}{2} = \\
&= \frac{2l}{2(2l+1)} \frac{-(l+1)}{2} + \frac{2l+2}{2(2l+1)} \frac{l}{2} = \frac{-l(l+1)}{2(2l+1)} + \frac{l(l+1)}{2(2l+1)} = 0
\end{aligned}$$

radial function

$$\vec{\phi}_{lm\sigma\nu}(\mathbf{r}) = \phi_l(r, E_{\nu l}) \vec{Y}_{lm\sigma}(\hat{r})$$

constructed from the solution of the equation:

$$(\hat{h}_l + \frac{2}{rc^2}\frac{dV}{dr}\langle \mathbf{ls}\rangle - E_\nu)\phi_l(r, E_{\nu l}) = 0$$

where $\hat{h}_l$ is a one–electron relatvistic hamiltonian without spin orbit term.

Our task is to evaluate the matrix elements

$$\langle \vec{\phi}_{lm'\sigma'\nu}|\hat{h}_l + \frac{2}{rc^2}\frac{dV}{dr}\mathbf{ls}|\vec{\phi}_{lm\sigma\nu}\rangle = \langle \phi_l|\hat{h}_l|\phi_l\rangle\delta_{m'm}\delta_{\sigma'\sigma} + \langle \phi_l|\frac{2}{rc^2}\frac{dV}{dr}|\phi_l\rangle\langle \vec{Y}_{lm'\sigma'}|\mathbf{ls}|\vec{Y}_{lm\sigma}\rangle$$

The first matrix element is given by

$$\begin{aligned}\langle \phi_l|\hat{h}_l|\phi_l\rangle &= \langle \phi_l|\hat{h}_l + \frac{2}{rc^2}\frac{dV}{dr}\langle \mathbf{ls}\rangle|\phi_l\rangle - \langle \phi_l|\frac{2}{rc^2}\frac{dV}{dr}\langle \mathbf{ls}\rangle|\phi_l\rangle = \\ &= E_\nu\langle \phi_l|\phi_l\rangle - \langle \phi_l|\frac{2}{rc^2}\frac{dV}{dr}\langle \mathbf{ls}\rangle|\phi_l\rangle = E_\nu\langle \phi_l|\phi_l\rangle\end{aligned}$$

since $\langle \mathbf{ls}\rangle = 0$.

XIII. OPTICAL PROPERTIES

Formula for $\varepsilon_{2\alpha\beta}^{inter}(\omega)$

$$\varepsilon_{2\alpha\beta}^{inter}(\omega)\tilde{} \sum_{\mathbf{k}jj'}\langle \mathbf{k}j| - i\nabla_\alpha|\mathbf{k}j'\rangle\langle \mathbf{k}j'| - i\nabla_\beta|\mathbf{k}j\rangle(f_{\mathbf{k}j} - f_{\mathbf{k}j'})\delta(E_{\mathbf{k}j} - E_{\mathbf{k}j'} + \omega)$$

In spherical coordinates

$$\varepsilon_{2\mu\nu}^{inter}(\omega)\tilde{} \sum_{\mathbf{k}jj'}\langle \mathbf{k}j| - i\nabla_\mu|\mathbf{k}j'\rangle\langle \mathbf{k}j'| - i\nabla_\nu|\mathbf{k}j\rangle(f_{\mathbf{k}j} - f_{\mathbf{k}j'})\delta(E_{\mathbf{k}j} - E_{\mathbf{k}j'} + \omega)$$

Note the properties of the matrix elements coming from the herimitaness of the momentum operator

$$\langle \mathbf{k}j'|(-i\nabla_\mu)|\mathbf{k}j\rangle = [\langle \mathbf{k}j|(-i\nabla_\mu)^*|\mathbf{k}j'\rangle]^* = -(-1)^\mu[\langle \mathbf{k}j|(-i\nabla_{-\mu})|\mathbf{k}j'\rangle]^*$$

Rotation of dielectric function

$$\begin{aligned}\varepsilon_{2\mu\nu}^{inter}(\omega) &= \sum_{\hat{\gamma}}\sum_{\mathbf{k}jj'}^{IBZ}\langle \hat{\gamma}\mathbf{k}j| - i\nabla_\mu|\hat{\gamma}\mathbf{k}j'\rangle\langle \hat{\gamma}\mathbf{k}j'| - i\nabla_\nu|\hat{\gamma}\mathbf{k}j\rangle(f_{\mathbf{k}j} - f_{\mathbf{k}j'})\delta(E_{\mathbf{k}j} - E_{\mathbf{k}j'} + \omega) = \\ &= \sum_{\hat{\gamma}}\sum_{\mu'\nu'}U_{\mu\mu'}^*(\hat{\gamma})U_{\nu\nu'}^*(\hat{\gamma})\sum_{\mathbf{k}jj'}^{IBZ}\langle \mathbf{k}j| - i\nabla_{\mu'}|\mathbf{k}j'\rangle\langle \mathbf{k}j'| - i\nabla_{\nu'}|\mathbf{k}j\rangle(f_{\mathbf{k}j} - f_{\mathbf{k}j'})\delta(E_{\mathbf{k}j} - E_{\mathbf{k}j'} + \omega) = \\ &\overset{\hat{\gamma}\to\hat{\gamma}^{-1}}{=} \sum_{\hat{\gamma}}\sum_{\mu'\nu'}U_{\mu'\mu}(\hat{\gamma})U_{\nu'\nu}(\hat{\gamma})\sum_{\mathbf{k}jj'}^{IBZ}\langle \mathbf{k}j| - i\nabla_{\mu'}|\mathbf{k}j'\rangle\langle \mathbf{k}j'| - i\nabla_{\nu'}|\mathbf{k}j\rangle(f_{\mathbf{k}j} - f_{\mathbf{k}j'})\delta(E_{\mathbf{k}j} - E_{\mathbf{k}j'} + \omega)\end{aligned}$$

Proof follows from the matrix element behaviour

$$\langle \hat{\gamma}\mathbf{k}j'|\nabla_\mu|\hat{\gamma}\mathbf{k}j\rangle = \int \psi_{\mathbf{k}j'}(\hat{g}^{-1}\mathbf{r})\frac{\partial}{\partial r^\mu}\psi_{\mathbf{k}j}(\hat{g}^{-1}\mathbf{r})dV = \int \psi_{\mathbf{k}j'}(\mathbf{r})\frac{\partial}{\partial(\hat{g}r)^\mu}\psi_{\mathbf{k}j}(\mathbf{r})dV = \sum_{\mu'}U_{\mu\mu'}^*(\hat{\gamma})\int \psi_{\mathbf{k}j'}(\mathbf{r})\frac{\partial}{\partial r^{\mu'}}\psi_{\mathbf{k}j}(\mathbf{r})dV$$

which is for example evident from plane wave case

$$\langle \hat{\gamma}\mathbf{k}|\nabla_\mu|\hat{\gamma}\mathbf{k}\rangle = i(\hat{\gamma}\mathbf{k})_\mu\tilde{}iY_{1\mu}(\hat{\gamma}\mathbf{k}) = i\sum_{\mu'}U_{\mu'\mu}(\hat{\gamma}^{-1})Y_{1\mu'}(\mathbf{k}) = i\sum_{\mu'}U_{\mu\mu'}^*(\hat{\gamma})Y_{1\mu'}(\mathbf{k})$$

Similar relationship can be proved considering the matrix element

$$\langle \hat{\gamma}\mathbf{k}j'|r_\mu|\hat{\gamma}\mathbf{k}j\rangle\tilde{} \int \psi_{\mathbf{k}j'}(\mathbf{r})rY_{1\mu}(\hat{\gamma}\mathbf{r})\psi_{\mathbf{k}j}(\mathbf{r})dV$$

Expression for the intraband contribution

$$\varepsilon_{2\alpha\beta}^{intra}(\omega)\tilde{}\sum_{\mathbf{k}j}\langle\mathbf{k}j|-i\nabla_\mu|\mathbf{k}j\rangle\langle\mathbf{k}j|-i\nabla_\nu|\mathbf{k}j\rangle\delta(E_{\mathbf{k}j}-E_F)$$

Matrix element can be related to the derivative

$$\langle\mathbf{k}j|-i\nabla_\mu|\mathbf{k}j\rangle=\frac{1}{2}\frac{dE_{\mathbf{k}j}}{dk^\mu}$$

For example, in free electron case

$$\langle\mathbf{k}|-i\nabla_\mu|\mathbf{k}\rangle=k_\mu$$

For tight-binding representation we compute matrix elements as derivatives of the Hamitonian

$$\nabla_\mu H_{\alpha\beta}^{\mathbf{k}}=\frac{dH_{\alpha\beta}^{\mathbf{k}}}{dk^\mu}=\sum_R iR_\mu e^{i\mathbf{k}\mathbf{R}}H_{\alpha\beta}(\mathbf{R})$$

XIV. APPENDIX: SPHERICAL FUNCTIONS

Spherical functions used here are defined as follows:

$$J_{l\kappa}(r)=\frac{(2l+1)!!}{(\kappa S)^l}j_l(\kappa r)=>\left(\frac{r}{S}\right)^l\left(1-\frac{(\kappa r)^2}{2(2l+3)}+...\right)$$

$$N_{l\kappa}(r)=-\frac{(\kappa S)^{l+1}}{(2l-1)!!}n_l(\kappa r)=>\left(\frac{r}{S}\right)^{-l-1}\left(1+\frac{(\kappa r)^2}{2(2l-1)}+...\right)$$

$$H_{l\kappa}(r)=-\frac{(\kappa S)^{l+1}}{(2l-1)!!}h_l(\kappa r)=>\left(\frac{r}{S}\right)^{-l-1}\left(1+\frac{(\kappa r)^2}{2(2l-1)}+...\right)$$

where j_l, n_l are the spherical Bessel and Neuman functions and $h_{ll}-i\ j_l$ are the Hankel functions.

Recurrent relations including radial derivatives:

$$\frac{dJ_{l\kappa}(r)}{dr}=-\frac{l+1}{r}J_{l\kappa}(r)+\frac{(2l+1)}{S}J_{l-1\kappa}(r)\ ;\ \forall E`$$

$$\frac{dJ_{l\kappa}(r)}{dr}=\frac{l}{r}J_{l\kappa}(r)+\ \frac{(|\kappa|S)^2}{S}\frac{1}{(2l+3)}J_{l+1\kappa}(r);E<0$$

$$\frac{dJ_{l\kappa}(r)}{dr}=\frac{l}{r}J_{l\kappa}(r)-\ \frac{(\kappa S)^2}{S}\frac{1}{(2l+3)}J_{l+1\kappa}(r);E>0$$

$$\frac{dH_{l\kappa}(r)}{dr}=-\frac{l+1}{r}H_{l\kappa}(r)-\frac{(|\kappa|S)^2}{S}\frac{1}{(2l-1)}H_{l-1\kappa}(r);E<0)$$

$$\frac{dH_{l\kappa}(r)}{dr}=-\frac{l+1}{r}H_{l\kappa}(r)+\frac{(\kappa S)^2}{S}\frac{1}{(2l-1)}H_{l-1\kappa}(r);E>0$$

$$\frac{dH_{l\kappa}(r)}{dr}=\frac{l}{r}H_{l\kappa}(r)-\ \frac{(2l+1)}{S}H_{l+1\kappa}(r);\forall E$$

Recurrent relations

$$J_{l+1\kappa}(r) = \frac{(2l+1)(2l+3)}{(|\kappa|S)^2}\left(J_{l-1\kappa}(r) - \frac{r}{S}J_{l\kappa}(r)\right); E<0$$

$$J_{l+1\kappa}(r) = \frac{(2l+1)(2l+3)}{(|\kappa|S)^2}\left(J_{l-1\kappa}(r) - \frac{r}{S}J_{l\kappa}(r)\right); E<0$$

$$J_{l+1\kappa}(r) = -\frac{(2l+1)(2l+3)}{(\kappa S)^2}\left(J_{l-1\kappa}(r) - \frac{r}{S}J_{l\kappa}(r)\right); E>0$$

Nick commented that it should be

$$J_{l+1\kappa}(r) = \frac{(2l+1)(2l+3)}{(|\kappa|S)^2}\left(J_{l-1\kappa}(r) - \frac{S}{r}J_{l\kappa}(r)\right); E<0$$

$$J_{l+1\kappa}(r) = \frac{(2l+1)(2l+3)}{(|\kappa|S)^2}\left(J_{l-1\kappa}(r) - \frac{S}{r}J_{l\kappa}(r)\right); E<0$$

$$J_{l+1\kappa}(r) = -\frac{(2l+1)(2l+3)}{(\kappa S)^2}\left(J_{l-1\kappa}(r) - \frac{S}{r}J_{l\kappa}(r)\right); E>0$$

$$H_{l+1\kappa}(r) = \frac{S}{r}H_{l\kappa}(r) + \frac{(|\kappa|S)^2}{(2l-1)(2l+1)}H_{l-1\kappa}(r); E<0$$

$$H_{l+1\kappa}(r) = \frac{S}{r}H_{l\kappa}(r) - \frac{(\kappa S)^2}{(2l-1)(2l+1)}H_{l-1\kappa}(r); E>0$$

Relations including second order derivatives

$$\frac{d^2J_{l\kappa}(r)}{d^2r} = \left(\frac{l(l+1)}{r^2} - E\right)J_{l\kappa}(r) - \frac{2}{r}\frac{dJ_{l\kappa}(r)}{dr}; \forall E$$

$$\frac{d^2H_{l\kappa}(r)}{d^2r} = \left(\frac{l(l+1)}{r^2} - E\right)H_{l\kappa}(r) - \frac{2}{r}\frac{dH_{l\kappa}(r)}{dr}; \forall E$$

Relations including energy derivatives

$$\frac{dJ_{l\kappa}(r)}{dE} = \dot{J}_{l\kappa}(r) = \frac{r}{2E}\left(\frac{dJ_{l\kappa}(r)}{dr} - \frac{l}{r}J_{l\kappa}(r)\right) = -\frac{rS}{2(2l+3)}J_{l+1\kappa}(r); \forall E (A.17)$$

$$\frac{dH_{l\kappa}(r)}{dE} = \dot{H}_{l\kappa}(r) = \frac{r}{2E}\left(\frac{dH_{l\kappa}(r)}{dr} + \frac{l+1}{r}J_{l\kappa}(r)\right) = \frac{rS}{2(2l-1)}H_{l-1\kappa}(r); \forall E (A.18)$$

$$\frac{d\dot{J}_{l\kappa}(r)}{dr} = \dot{J}'_{l\kappa}(r) = -\frac{S}{2(2l+3)}J_{l+1\kappa}(r) - \frac{rS}{2(2l+3)}J'_{l+1\kappa}(r); \forall E (A.19)$$

$$\frac{d\dot{H}_{l\kappa}(r)}{dr} = \dot{H}'_{l\kappa}(r) = \frac{S}{2(2l-1)}H_{l-1\kappa}(r) + \frac{rS}{2(2l-1)}H'_{l-1\kappa}(r); \forall E (A.20)$$

Special definitions:

$$H_{-1\kappa}(r) = -\frac{1}{|\kappa|S} H_{0\kappa}(r) \ ; \ E < 0$$

$$H_{-1\kappa}(r) = -\frac{i}{\kappa S} H_{0\kappa}(r) \ ; \ E > 0$$

Particular formulas for $E < 0$:

$$J_{0\kappa}(r) = -\frac{1}{2|\kappa|r}\left(e^{-|\kappa|r} - e^{|\kappa|r}\right)$$

$$J_{1\kappa}(r) = -\frac{3}{|\kappa|^2 rS} J_{0\kappa}(r) + \ \frac{3}{2|\kappa|^2 rS}\left(e^{-|\kappa|r} + e^{|\kappa|r}\right)$$

$$H_{0\kappa}(r) = \frac{S}{r} e^{-|\kappa|r}$$

$$H_{1\kappa}(r) = |\kappa|S\left(\frac{1}{|\kappa|r} + 1\right) H_{0\kappa}(r)$$

We set for convinience $H_{-1\kappa=0} = 1$ and $H'_{-1\kappa=0} = 0$ in order to obtain the smooth limit from finite κ to zero in the interstitial overlap matrix.

Gradients:

$$\nabla_\mu f(r) Y_{lm}(\hat{r}) = \sqrt{\frac{4\pi}{3}} C^{1\mu}_{lml+1m+\mu}\left(\frac{df}{dr} - \frac{l}{r} f\right) Y_{l+1m+\mu}(\hat{r}) + \sqrt{\frac{4\pi}{3}} C^{1\mu}_{lml-1m+\mu}\left(\frac{df}{dr} + \frac{l+1}{r} f\right) Y_{l-1m+\mu}(\hat{r})$$

$$\nabla_\mu J_{L\kappa}(\mathbf{r}) = \nabla_\mu J_{L\kappa}(r) i^l Y_{lm}(\hat{r}) = +i\sqrt{\frac{4\pi}{3}} C^{1\mu}_{lml+1m+\mu} \ \frac{\kappa^2 S}{2l+3} J_{l+1\kappa}(r) i^{l+1} Y_{l+1m+\mu}(\hat{r}) + \\ +i\sqrt{\frac{4\pi}{3}} C^{1\mu}_{lml-1m+\mu} \frac{2l+1}{S} J_{l-1\kappa}(r) i^{l-1} Y_{l-1m+\mu}(\hat{r})$$

$$\nabla_\mu H_{L\kappa}(\mathbf{r}) = \nabla_\mu H_{L\kappa}(r) i^l Y_{lm}(\hat{r}) = i\sqrt{\frac{4\pi}{3}} C^{1\mu}_{lml+1m+\mu} \ \frac{2l+1}{S} H_{l+1\kappa}(r) i^{l+1} Y_{l+1m+\mu}(\hat{r}) + \\ +i\sqrt{\frac{4\pi}{3}} C^{1\mu}_{lml-1m+\mu} \frac{\kappa^2 S}{2l-1} H_{l-1\kappa}(r) i^{l-1} Y_{l-1m+\mu}(\hat{r})$$

One–center expansions for standard spherical functions

$$h_L(\mathbf{r}-\mathbf{R}) = \sum_{L'} j_{L'}(\mathbf{r}-\mathbf{R}') \sum_{L''} 4\pi C^{L''}_{LL'} h^*_{L''}(\mathbf{R}-\mathbf{R}')$$

$$j_L(\mathbf{r}-\mathbf{R}) = \sum_{L'} j_{L'}(\mathbf{r}-\mathbf{R}') \sum_{L''} 4\pi C^{L''}_{LL'} j^*_{L''}(\mathbf{R}-\mathbf{R}')$$

$$h_L(\mathbf{r}-\mathbf{R}) = \sum_{L'} h_{L'}(\mathbf{r}-\mathbf{R}') \sum_{L''} 4\pi C^{L''}_{LL'} j^*_{L''}(\mathbf{R}-\mathbf{R}')$$

$$n_L(\mathbf{r}-\mathbf{R}) = \sum_{L'} j_{L'}(\mathbf{r}-\mathbf{R}') \sum_{L''} 4\pi C^{L''}_{LL'} h^*_{L''}(\mathbf{R}-\mathbf{R}')$$

where

$$h_L(\mathbf{r}) = h_l(\kappa r) i^l Y_L(\hat{r})$$
$$j_L(\mathbf{r}) = j_l(\kappa r) i^l Y_L(\hat{r})$$
$$n_L(\mathbf{r}) = n_l(\kappa r) i^l Y_L(\hat{r})$$

Defnitions inside the program

$$H_{L\tau}(\mathbf{r}-\mathbf{R}-\tau) = -\sum_{L'} J_{L'\tau'}(\mathbf{r}-\mathbf{R}'-\tau')\gamma_{l'\tau'} S^{(0)}_{L'R'\tau'LR\tau}$$
$$H_{L\tau}(\mathbf{r}-\mathbf{R}-\tau) = -\sum_{L'} H_{L'\tau'}(\mathbf{r}-\mathbf{R}'-\tau') S^{(1)}_{L'R'\tau'LR\tau}$$
$$\gamma_{l\tau} J_{L\tau}(\mathbf{r}-\mathbf{R}-\tau) = -\sum_{L'} J_{L'\tau'}(\mathbf{r}-\mathbf{R}'-\tau')\gamma_{l'\tau'} S^{(2)}_{L'R'\tau'LR\tau}$$

where

$$\gamma_{l\tau} = \frac{1}{S_\tau(2l+1)}$$

and

$$S^{(0)}_{L'R'\tau'LRT} = -4\pi \sum_{L''} C^{L''}_{LL'} \frac{(2l''-1)!!}{(2l'-1)!!(2l-1)!!} (\kappa S_{WZ})^{l+l'-l''} (\frac{S_{\tau'}}{S_{WZ}})^{l'} (\frac{S_\tau}{S_{WZ}})^{l} \frac{S_{\tau'} S_\tau}{S_{WZ}} H^*_{L''WZ}(\mathbf{R}+\tau-\mathbf{R}'-\tau')$$

$$S^{(1)}_{L'R'\tau'LRT} = -4\pi \sum_{L''} C^{L''}_{LL'} \frac{(2l'-1)!!}{(2l-1)!!(2l''+1)!!} (\kappa S_{WZ})^{l-l'+l''} (\frac{S_\tau}{S_{WZ}})^{l} (\frac{S_{\tau'}}{S_{WZ}})^{-l'} \frac{S_\tau}{S_{\tau'}} J^*_{L''WZ}(\mathbf{R}+\tau-\mathbf{R}'-\tau')$$

$$S^{(2)}_{L'R'\tau'LRT} = -4\pi \sum_{L''} C^{L''}_{LL'} \frac{(2l-1)!!}{(2l'-1)!!(2l''+1)!!} (\kappa S_{WZ})^{l'-l+l''} (\frac{S_\tau}{S_{WZ}})^{-l} (\frac{S_{\tau'}}{S_{WZ}})^{l'} \frac{S_{\tau'}}{S_\tau} J^*_{L''WZ}(\mathbf{R}+\tau-\mathbf{R}'-\tau')$$

$$S^{(0)}_{LR\tau L'R'T'} = S^{(0)*}_{L'R'\tau'LRT}$$
$$S^{(1)}_{LR\tau L'R'T'} = S^{(2)*}_{L'R'\tau'LRT}$$

XV. APPENDIX: SPHERICAL HARMONICS

Spherical harmonic Y is an eigenfunction of the angular part of the Laplace operator is defined as follows

$$Y_{lm}(\hat{r}) = (-1)^{\frac{m+|m|}{2}} \alpha_{l|m|} P_l^{|m|}(cos\theta) e^{im\varphi}$$

which is orthonormalized in a sphere S

$$\int_S Y^*_{l'm'}(\hat{r}) Y_{lm}(\hat{r}) d\hat{r} = \delta_{l'l}\delta_{m'm}$$

and P_l^m are the augemented Legandre polynoms while $\alpha_{l|m|}$ are the normalization coefficients:

$$\alpha_{l|m|} = \sqrt{\frac{2l+1}{4\pi}} \left(\frac{(l+|m|)!}{(l-|m|)!}\right)^{1/2}$$

The expansion of two spherical harmonics is given by:

$$Y^*_{L'}(\hat{r}) Y_L(\hat{r}) = \sum_{L''} C^{L''}_{L'L} Y_{L''}(\hat{r})$$

where

$$C_{L'L}^{L''} = \int_S Y_{L'}(\hat{r})Y_{L''}(\hat{r})Y_L^*(\hat{r})d\hat{r}$$

are the Gaunt coefficients. They are equal to zero unless mmiss = m - m' and $l'' = |l-l'|, |l-l'|+2, ..., l+l'$. The following relations are valid:

$$C_{l'm'lm}^{l''m-m'} = C_{l''m-m'lm}^{l'm'} = (-1)^{m-m'} C_{lml'm'}^{l''m'-m}$$

Also introduced are the g-coefficients which are given by

$$g_{L'L}^{l''} = -\frac{8\pi}{\sqrt{4\pi}} \frac{(2l''-1)!!}{(2l'-1)!!(2l-1)!!} C_{LL'}^{L''}$$

and

$$g_{L'L}^{l''} = (-1)^{m-m'} g_{LL'}^{l''}$$

Transformation of spherical harmonics after applying rotation γ is given by the Wigner matrices:

$$Y_{lm}(\hat{\gamma}^{-1}\hat{r}) = \sum_{m'} U_{m'm}^l(\gamma)Y_{lm'}(\hat{r})$$

$$Y_{lm}(\hat{\gamma}\hat{r}) = \sum_{m'} U_{m'm}^l(\gamma^{-1})Y_{lm'}(\hat{r})$$

$$Y_{lm}(\hat{\gamma}\hat{r}) = \sum_{m'} U_{m'm}^{l+}(\gamma)Y_{lm'}(\hat{r}) = \sum_{m'} U_{mm'}^{l*}(\gamma)Y_{lm'}(\hat{r})$$

The properties of Wigner's matrices are

$$U_{mm'}^l(\gamma^{-1}) = U_{mm'}^l(\gamma)^{-1}$$

$$U_{mm'}^l(\gamma)^{-1} = U_{mm'}^{l+}(\gamma) = U_{m'm}^{l*}(\gamma)$$

$$\sum_{m''} U_{mm''}^l(\gamma^{-1})U_{m''m'}^l(\gamma) = \delta_{m'm}$$

$$\sum_{m''} U_{mm''}^{l+}(\gamma)U_{m''m'}^l(\gamma) = \delta_{m'm}$$

$$C_{l'm'lm}^{l''m-m'} U_{m''m-m'}^{l''}(\gamma) = \sum_{m_1m_2} U_{m'm_1}^{l'+}(\gamma)C_{l'm_1lm_2}^{l''m''}U_{m_2m}^l(\gamma)$$

Particular cases:

$$U_{m0}^l(\gamma) = \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{lm}^*(\hat{\gamma}n)$$

where n is a vector lying along z-axes.

XVI. APPENDIX: CUBIC HARMONICS

A. S-wave

$$Y_{l=01}(r) = \frac{1}{\sqrt{4\pi}} = Y_{l=0m=0}(r)$$

B. P-wave

$$
\begin{aligned}
Y_{11}(r) = Y_x(r) &= \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r} = \frac{1}{\sqrt{2}}(Y_{1-1}(r) - Y_{1+1}(r)) \\
Y_{12}(r) = Y_y(r) &= \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r} = \frac{i}{\sqrt{2}}(Y_{1-1}(r) + Y_{1+1}(r)) \\
Y_{13}(r) = Y_z(r) &= \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r} = Y_{1+0}(r)
\end{aligned}
$$

$$
\begin{aligned}
Y_{1m=-1}(r) &= +\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{1}{\sqrt{2}}\frac{(x-iy)}{r} = \frac{+1}{\sqrt{2}}(Y_{11}(r) - iY_{12}(r)) \\
Y_{1m=+0}(r) &= \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r} = Y_{13}(r) \\
Y_{1m=+1}(r) &= -\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{1}{\sqrt{2}}\frac{(x+iy)}{r} = \frac{-1}{\sqrt{2}}(Y_{11}(r) + iY_{12}(r))
\end{aligned}
$$

C. D-wave

1. *Cubic t_{2g}*

$$
\begin{aligned}
Y_{21}(r) = Y_{yz}(r) &= 2\frac{yz}{r^2} = \frac{i}{\sqrt{2}}(Y_{2-1}(r) + Y_{2+1}(r)) \\
Y_{22}(r) = Y_{zx}(r) &= 2\frac{zx}{r^2} = \frac{1}{\sqrt{2}}(Y_{2-1}(r) - Y_{2+1}(r)) \\
Y_{23}(r) = Y_{xy}(r) &= 2\frac{xy}{r^2} = \frac{i}{\sqrt{2}}(Y_{2-2}(r) - Y_{2+2}(r))
\end{aligned}
$$

2. *Cubic e_g*

$$
\begin{aligned}
Y_{24}(r) = Y_{x^2-y^2}(r) &= \frac{x^2-y^2}{r^2} = \frac{1}{\sqrt{2}}(Y_{2-2}(r) + Y_{2+2}(r)) \\
Y_{25}(r) = Y_{3z^2-r^2}(r) &= \frac{1}{\sqrt{3}}\frac{3z^2-r^2}{r^2} = Y_{2+0}(r)
\end{aligned}
$$

3. *Spherical harmonics*

$$
\begin{aligned}
Y_{2-2}(r) &= +\frac{1}{\sqrt{2}}\frac{x^2-y^2-2ixy}{r^2}\\
Y_{2-1}(r) &= +\sqrt{2}\frac{zx-izy}{r^2}\\
Y_{2+0}(r) &= +\frac{1}{\sqrt{3}}\frac{3z^2-r^2}{r^2}\\
Y_{2+1}(r) &= -\sqrt{2}\frac{zx+izy}{r^2}\\
Y_{2+2}(r) &= +\frac{1}{\sqrt{2}}\frac{x^2-y^2+2ixy}{r^2}
\end{aligned}
$$

4. *Spin orbit coupling in t_{2g} block*

Spin orbit coupling matrix elments (assuming strength of it equal 1) are given by

$$\langle Y_{lm'}(r)\sigma'|\mathbf{ls}|Y_{lm}(r)\sigma\rangle = \delta_{m'm}m(\delta_{\sigma'\uparrow}\delta_{\sigma\uparrow}-\delta_{\sigma'\downarrow}\delta_{\sigma\downarrow})\frac{1}{2}+\delta_{m'm-1}\frac{1}{\sqrt{2}}\sqrt{(l+m)(l-m+1)}\delta_{\sigma'\uparrow}\delta_{\sigma\downarrow}\frac{1}{\sqrt{2}}+\delta_{m'm+1}\frac{1}{\sqrt{2}}\sqrt{(l-m)(l+m}$$

We write them as a matrix

$\mathbf{ls}$	$\|Y_{2-2}\uparrow\rangle$	$\|Y_{2-1}\uparrow\rangle$	$\|Y_{2+0}\uparrow\rangle$	$\|Y_{2+1}\uparrow\rangle$	$\|Y_{2+2}\uparrow\rangle$	$\|Y_{2-2}\downarrow\rangle$	$\|Y_{2-1}\downarrow\rangle$	$\|Y_{2+0}\downarrow\rangle$	$\|Y_{2+1}\downarrow\rangle$	$\|Y_{2+2}\downarrow\rangle$
$\langle Y_{2-2}\uparrow\|$	-1	0	0	0	0	0	1	0	0	0
$\langle Y_{2-1}\uparrow\|$	0	$-1/2$	0	0	0	0	0	$\sqrt{3/2}$	0	0
$\langle Y_{2+0}\uparrow\|$	0	0	0	0	0	0	0	0	$\sqrt{3/2}$	0
$\langle Y_{2+1}\uparrow\|$	0	0	0	$+1/2$	0	0	0	0	0	1
$\langle Y_{2+2}\uparrow\|$	0	0	0	0	$+1$	0	0	0	0	0
$\langle Y_{2-2}\downarrow\|$	0	0	0	0	0	$+1$	0	0	0	0
$\langle Y_{2-1}\downarrow\|$	1	0	0	0	0	0	$+1/2$	0	0	0
$\langle Y_{2+0}\downarrow\|$	0	$\sqrt{3/2}$	0	0	0	0	0	0	0	0
$\langle Y_{2+1}\downarrow\|$	0	0	$\sqrt{3/2}$	0	0	0	0	0	$-1/2$	0
$\langle Y_{2+2}\downarrow\|$	0	0	0	1	0	0	0	0	0	-1

Matrix elements for t_{2g} cubic harmonics are given by

$$\langle Y_{yz}(r)\sigma|\mathbf{ls}|Y_{yz}(r)\sigma\rangle = \langle\frac{i}{\sqrt{2}}(Y_{2-1}(r)+Y_{2+1}(r))\sigma|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-1}(r)+Y_{2+1}(r))\sigma\rangle = 0$$

$$\langle Y_{yz}(r)\uparrow|\mathbf{ls}|Y_{zx}(r)\uparrow\rangle = \langle\frac{i}{\sqrt{2}}(Y_{2-1}(r)+Y_{2+1}(r))\uparrow|\mathbf{ls}|\frac{1}{\sqrt{2}}(Y_{2-1}(r)-Y_{2+1}(r))\uparrow\rangle = \frac{-i}{2}(-\frac{1}{2}-\frac{1}{2}) = \frac{+i}{2}$$

$$\langle Y_{yz}(r)\downarrow|\mathbf{ls}|Y_{zx}(r)\downarrow\rangle = \frac{-i}{2}(+\frac{1}{2}+\frac{1}{2}) = \frac{-i}{2}$$

$$\langle Y_{yz}(r)\sigma|\mathbf{ls}|Y_{xy}(r)\sigma\rangle = \langle\frac{i}{\sqrt{2}}(Y_{2-1}(r)+Y_{2+1}(r))\sigma|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\sigma\rangle = 0$$

$$\langle Y_{zx}(r)\sigma|\mathbf{ls}|Y_{zx}(r)\sigma\rangle = \langle\frac{1}{\sqrt{2}}(Y_{2-1}(r)-Y_{2+1}(r))\sigma|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-1}(r)+Y_{2+1}(r))\sigma\rangle = 0$$

$$\langle Y_{zx}(r)\sigma|\mathbf{ls}|Y_{xy}(r)\sigma\rangle = \langle\frac{1}{\sqrt{2}}(Y_{2-1}(r)-Y_{2+1}(r))\sigma|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\sigma\rangle = 0$$

$$\langle Y_{xy}(r)\sigma|\mathbf{ls}|Y_{xy}(r)\sigma\rangle = \langle\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\sigma|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\sigma\rangle = 0$$

$$\langle Y_{yz}(r)\uparrow|\mathbf{ls}|Y_{xy}(r)\downarrow\rangle = \langle\frac{i}{\sqrt{2}}(Y_{2-1}(r)+Y_{2+1}(r))\uparrow|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\downarrow\rangle = \frac{1}{2}(-1)$$

$$\langle Y_{zx}(r)\uparrow|\mathbf{ls}|Y_{xy}(r)\downarrow\rangle = \langle\frac{1}{\sqrt{2}}(Y_{2-1}(r)-Y_{2+1}(r))\uparrow|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\downarrow\rangle = \frac{i}{2}(+1)$$

$$\langle Y_{xy}(r)\uparrow|\mathbf{ls}|Y_{yz}(r)\downarrow\rangle = \langle\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\uparrow|\mathbf{ls}|\frac{i}{\sqrt{2}}(Y_{2-1}(r)+Y_{2+1}(r))\downarrow\rangle = \frac{1}{2}(+1)$$

$$\langle Y_{xy}(r)\uparrow|\mathbf{ls}|Y_{zx}(r)\downarrow\rangle = \langle\frac{i}{\sqrt{2}}(Y_{2-2}(r)-Y_{2+2}(r))\uparrow|\mathbf{ls}|\frac{1}{\sqrt{2}}(Y_{2-1}(r)-Y_{2+1}(r))\downarrow\rangle = \frac{-i}{2}(+1)$$

The matrix elements between various t_{2g} states

ls	$\lvert Y_{yz}\uparrow\rangle$	$\lvert Y_{zx}\uparrow\rangle$	$\lvert Y_{xy}\uparrow\rangle$	$\lvert Y_{yz}\downarrow\rangle$	$\lvert Y_{zx}\downarrow\rangle$	$\lvert Y_{xy}\downarrow\rangle$
$\langle Y_{yz}\uparrow\rvert$	0	$+i/2$	0	0	0	$-1/2$
$\langle Y_{zx}\uparrow\rvert$	$-i/2$	0	0	0	0	$+i/2$
$\langle Y_{xy}\uparrow\rvert$	0	0	0	$+1/2$	$-i/2$	0
$\langle Y_{yz}\downarrow\rvert$	0	0	$+1/2$	0	$-i/2$	0
$\langle Y_{zx}\downarrow\rvert$	0	0	$+i/2$	$+i/2$	0	0
$\langle Y_{xy}\downarrow\rvert$	$-1/2$	$-i/2$	0	0	0	0

The answers should be (see arXiv:0907.2962) a j=1/2 doublet with the eigenvalue $\lambda = +1$ (as checked below)

$$|\frac{1}{2},+\frac{1}{2}\rangle = \frac{1}{\sqrt{3}}|Y_{yz}\downarrow\rangle + \frac{i}{\sqrt{3}}|Y_{zx}\downarrow\rangle + \frac{1}{\sqrt{3}}|Y_{xy}\uparrow\rangle$$

$$|\frac{1}{2},-\frac{1}{2}\rangle = \frac{1}{\sqrt{3}}|Y_{yz}\uparrow\rangle - \frac{i}{\sqrt{3}}|Y_{zx}\uparrow\rangle - \frac{1}{\sqrt{3}}|Y_{xy}\downarrow\rangle$$

and a J=3/2 quadruplet with the eigenvalue $\lambda = -\frac{1}{2}$ (as checked below)

$$|\frac{3}{2},+\frac{3}{2}\rangle = -\frac{1}{\sqrt{2}}|Y_{yz}\uparrow\rangle - \frac{i}{\sqrt{2}}|Y_{zx}\uparrow\rangle$$

$$|\frac{3}{2},+\frac{1}{2}\rangle = -\frac{1}{\sqrt{6}}|Y_{yz}\downarrow\rangle - \frac{i}{\sqrt{6}}|Y_{zx}\downarrow\rangle + \frac{2}{\sqrt{6}}|Y_{xy}\uparrow\rangle$$

$$|\frac{3}{2},-\frac{1}{2}\rangle = +\frac{1}{\sqrt{6}}|Y_{yz}\uparrow\rangle - \frac{i}{\sqrt{6}}|Y_{zx}\uparrow\rangle + \frac{2}{\sqrt{6}}|Y_{xy}\downarrow\rangle$$

$$|\frac{3}{2},-\frac{3}{2}\rangle = +\frac{1}{\sqrt{2}}|Y_{yz}\downarrow\rangle - \frac{i}{\sqrt{2}}|Y_{zx}\downarrow\rangle$$

Checking for doublet that $\langle Y_{\alpha'}(r)\sigma'|\mathbf{ls}|Y_\alpha(r)\sigma\rangle|\frac{1}{2},\pm\frac{1}{2}\rangle = 1\times|\frac{1}{2},+\frac{1}{2}\rangle$

$$\begin{pmatrix} 0 & +i/2 & 0 & 0 & 0 & -1/2 \\ -i/2 & 0 & 0 & 0 & 0 & +i/2 \\ 0 & 0 & 0 & +1/2 & -i/2 & 0 \\ 0 & 0 & +1/2 & 0 & -i/2 & 0 \\ 0 & 0 & +i/2 & +i/2 & 0 & 0 \\ -1/2 & -i/2 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ \frac{i}{\sqrt{3}} \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{\sqrt{3}}\frac{1}{2}+\frac{i}{\sqrt{3}}(\frac{-i}{2}) \\ \frac{1}{\sqrt{3}}\frac{1}{2}+\frac{i}{\sqrt{3}}(\frac{-i}{2}) \\ \frac{i}{\sqrt{3}} \\ 0 \end{pmatrix} = 1\begin{pmatrix} 0 \\ 0 \\ \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} \\ \frac{i}{\sqrt{3}} \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & +i/2 & 0 & 0 & 0 & -1/2 \\ -i/2 & 0 & 0 & 0 & 0 & +i/2 \\ 0 & 0 & 0 & +1/2 & -i/2 & 0 \\ 0 & 0 & +1/2 & 0 & -i/2 & 0 \\ 0 & 0 & +i/2 & +i/2 & 0 & 0 \\ -1/2 & -i/2 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \frac{1}{\sqrt{3}} \\ \frac{-i}{\sqrt{3}} \\ 0 \\ 0 \\ 0 \\ \frac{-1}{\sqrt{3}} \end{pmatrix} = \begin{pmatrix} \frac{-i}{\sqrt{3}}(\frac{i}{2})+(\frac{-1}{\sqrt{3}})(\frac{-1}{2}) \\ \frac{1}{\sqrt{3}}(\frac{-i}{2})+(\frac{-1}{\sqrt{3}})(\frac{i}{2}) \\ 0 \\ 0 \\ 0 \\ \frac{1}{\sqrt{3}}(\frac{-1}{2})+\frac{-i}{\sqrt{3}}(\frac{-i}{2}) \end{pmatrix} = 1\begin{pmatrix} \frac{1}{\sqrt{3}} \\ \frac{-i}{\sqrt{3}} \\ 0 \\ 0 \\ 0 \\ \frac{-1}{\sqrt{3}} \end{pmatrix}$$

Checking for quadruplet that $\langle Y_{\alpha'}(r)\sigma'|\mathbf{ls}|Y_\alpha(r)\sigma\rangle|\frac{3}{2},\pm\frac{3}{2}\rangle = -\frac{1}{2}\times|\frac{3}{2},\pm\frac{3}{2}\rangle$

$$\begin{pmatrix} 0 & +i/2 & 0 & 0 & 0 & -1/2 \\ -i/2 & 0 & 0 & 0 & 0 & +i/2 \\ 0 & 0 & 0 & +1/2 & -i/2 & 0 \\ 0 & 0 & +1/2 & 0 & -i/2 & 0 \\ 0 & 0 & +i/2 & +i/2 & 0 & 0 \\ -1/2 & -i/2 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} -\frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \frac{i}{2}\frac{-i}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}}\frac{-i}{2} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = -\frac{1}{2}\begin{pmatrix} -\frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & +i/2 & 0 & 0 & 0 & -1/2 \\ -i/2 & 0 & 0 & 0 & 0 & +i/2 \\ 0 & 0 & 0 & +1/2 & -i/2 & 0 \\ 0 & 0 & +1/2 & 0 & -i/2 & 0 \\ 0 & 0 & +i/2 & +i/2 & 0 & 0 \\ -1/2 & -i/2 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2}\frac{1}{\sqrt{2}}+\frac{-i}{2}\frac{-i}{\sqrt{2}} \\ \frac{-i}{2}\frac{-i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}}\frac{i}{2} \\ 0 \end{pmatrix} = -\frac{1}{2}\begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} \\ 0 \end{pmatrix}$$

Checking for quadruplet that $\langle Y_{\alpha'}(r)\sigma'|\mathbf{ls}|Y_\alpha(r)\sigma\rangle|\frac{3}{2},\pm\frac{1}{2}\rangle = -\frac{1}{2}\times|\frac{3}{2},\pm\frac{1}{2}\rangle$

$$\begin{pmatrix} 0 & +i/2 & 0 & 0 & 0 & -1/2 \\ -i/2 & 0 & 0 & 0 & 0 & +i/2 \\ 0 & 0 & 0 & +1/2 & -i/2 & 0 \\ 0 & 0 & +1/2 & 0 & -i/2 & 0 \\ 0 & 0 & +i/2 & +i/2 & 0 & 0 \\ -1/2 & -i/2 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ +\frac{2}{\sqrt{6}} \\ -\frac{1}{\sqrt{6}} \\ -\frac{i}{\sqrt{6}} \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{1}{2}\frac{-1}{\sqrt{6}}+\frac{-i}{2}\frac{-i}{\sqrt{6}} \\ \frac{1}{2}\frac{2}{\sqrt{6}}+\frac{-i}{2}\frac{-i}{\sqrt{6}} \\ \frac{i}{2}\frac{2}{\sqrt{6}}+\frac{i}{2}\frac{-1}{\sqrt{6}} \\ 0 \end{pmatrix} = -\frac{1}{2}\begin{pmatrix} 0 \\ 0 \\ \frac{2}{\sqrt{6}} \\ \frac{-1}{\sqrt{6}} \\ \frac{-i}{\sqrt{6}} \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & +i/2 & 0 & 0 & 0 & -1/2 \\ -i/2 & 0 & 0 & 0 & 0 & +i/2 \\ 0 & 0 & 0 & +1/2 & -i/2 & 0 \\ 0 & 0 & +1/2 & 0 & -i/2 & 0 \\ 0 & 0 & +i/2 & +i/2 & 0 & 0 \\ -1/2 & -i/2 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} +\frac{1}{\sqrt{6}} \\ -\frac{i}{\sqrt{6}} \\ 0 \\ 0 \\ 0 \\ +\frac{2}{\sqrt{6}} \end{pmatrix} = \begin{pmatrix} \frac{i}{2}\frac{-i}{\sqrt{6}}+\frac{-1}{2}\frac{2}{\sqrt{6}} \\ \frac{-i}{2}\frac{1}{\sqrt{6}}+\frac{i}{2}\frac{2}{\sqrt{6}} \\ 0 \\ 0 \\ 0 \\ \frac{-1}{2}\frac{1}{\sqrt{6}}+\frac{-i}{2}\frac{-i}{\sqrt{6}} \end{pmatrix} = -\frac{1}{2}\begin{pmatrix} \frac{1}{\sqrt{6}} \\ \frac{-i}{\sqrt{6}} \\ 0 \\ 0 \\ 0 \\ \frac{2}{\sqrt{6}} \end{pmatrix}$$

5. *Angular Momentum in t_{2g} block*

While e_g electrons have zero angluar momentum,

$$\begin{array}{ccc} \hat{l}_z & |Y_{x^2-y^2}\rangle & |Y_{z^2-1}\rangle \\ \langle Y_{x^2-y^2}| & 0 & 0 \\ \langle Y_{z^2-1}| & 0 & 0 \end{array}$$

t_{2g} electrons have non–zero effective angular momentum corresponding $l_{eff} = 1$. Consider $\hat{l}_z = \frac{\partial}{\partial\varphi}$ operator for t_{2g} cubic harmonics

$$\begin{array}{cccc} \hat{l}_z & |Y_{yz}\rangle & |Y_{zx}\rangle & |Y_{xy}\rangle \\ \langle Y_{yz}| & 0 & i & 0 \\ \langle Y_{zx}| & -i & 0 & 0 \\ \langle Y_{xy}| & 0 & 0 & 0 \end{array}$$

which after diagonalization produces the following linear combinations (see, e.g., PRL 102, 017205 (2009)):

$$\begin{aligned} |Y_{l_z=0}\rangle &= |Y_{xy}\rangle \\ |Y_{l_z=+1}\rangle &= \frac{-1}{\sqrt{2}}\left(i|Y_{zx}\rangle + |Y_{yz}\rangle\right) \\ |Y_{l_z=-1}\rangle &= \frac{-1}{\sqrt{2}}\left(i|Y_{zx}\rangle - |Y_{yz}\rangle\right) \end{aligned}$$

D. F-wave (still need to check)

$$\begin{aligned} Y_{31}(r) &= +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{1}{4}}\frac{5x^2-3r^2}{r^3} \\ Y_{32}(r) &= +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{1}{4}}\frac{5y^2-3r^2}{r^3} \\ Y_{33}(r) &= +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{1}{4}}\frac{5z^2-3r^2}{r^3} \\ Y_{34}(r) &= +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{4}}\frac{(x^2-z^2)y}{r^3} \\ Y_{35}(r) &= +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{4}}\frac{(x^2-y^2)z}{r^3} \\ Y_{36}(r) &= +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{4}}\frac{(y^2-z^2)x}{r^3} \\ Y_{37}(r) &= +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{1}}\frac{xyz}{r^3} \end{aligned}$$

$$Y_{3-3}(r) = +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{16}}\frac{(x-iy)^3}{r^3}$$
$$Y_{3-2}(r) = +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{8}}\frac{z(x-iy)^2}{r^3}$$
$$Y_{3-1}(r) = +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{16}}\frac{(5z^2-r^2)(x-iy)}{r^3}$$
$$Y_{3+0}(r) = +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{1}{4}}\frac{z(5z^2-3r^2)}{r^3}$$
$$Y_{3+1}(r) = -\sqrt{\frac{7}{4\pi}}\sqrt{\frac{3}{16}}\frac{(5z^2-r^2)(x+iy)}{r^3}$$
$$Y_{3+2}(r) = +\sqrt{\frac{7}{4\pi}}\sqrt{\frac{15}{8}}\frac{z(x+iy)^2}{r^3}$$
$$Y_{3+3}(r) = -\sqrt{\frac{7}{4\pi}}\sqrt{\frac{5}{16}}\frac{(x+iy)^3}{r^3}$$

XVII. APPENDIX: SPINOR HARMONICS

For a given l and $s = 1/2$, $j_1 = l - 1/2$, $j_2 = l + 1/2$,a set of relativistic hamonics Ω_{jm_j} can be defined as a linear combination

$$\vec{\Omega}^{(j=l-\frac{1}{2})}_{jm_j}(r) = \begin{pmatrix} -\sqrt{\frac{j-m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j-\frac{1}{2}}(r) \\ +\sqrt{\frac{j+m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j+\frac{1}{2}}(r) \end{pmatrix} = -\sqrt{\frac{j-m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j-\frac{1}{2}}(r)\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{j+m_j+1}{2(j+1)}}Y_{j+\frac{1}{2}m_j+\frac{1}{2}}(r)\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
$$\vec{\Omega}^{(j=l+\frac{1}{2})}_{jm_j}(r) = \begin{pmatrix} +\sqrt{\frac{j+m_j}{2j}}Y_{j-\frac{1}{2}m_j-\frac{1}{2}}(r) \\ +\sqrt{\frac{j-m_j}{2j}}Y_{j-\frac{1}{2}m_j+\frac{1}{2}}(r) \end{pmatrix} = \sqrt{\frac{j+m_j}{2j}}Y_{j-\frac{1}{2}m_j-\frac{1}{2}}(r)\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{j-m_j}{2j}}Y_{j-\frac{1}{2}m_j+\frac{1}{2}}(r)\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Let us introduce the transformation matrices

$$\vec{\Omega}^{(j=l-\frac{1}{2})}_{jm_j}(r) = \sum_{m=-l...+l}\sum_{\sigma=\uparrow,\downarrow} T^{(j=l-\frac{1}{2})}_{jm_jm\sigma}Y_{lm}(r)|\sigma\rangle$$
$$\vec{\Omega}^{(j=l+\frac{1}{2})}_{jm_j}(r) = \sum_{m=-l...+l}\sum_{\sigma=\uparrow\downarrow} T^{(j=l+\frac{1}{2})}_{jm_jm\sigma}Y_{lm}(r)|\sigma\rangle$$

which makes the spin–orbital operator diagonal, i.e.

$$\langle\vec{\Omega}^{(j'=l\mp\frac{1}{2})}_{j'm'_j}(r)|\mathbf{ls}|\vec{\Omega}^{(j=l\mp\frac{1}{2})}_{jm_j}(r)\rangle = -\frac{1}{2}\delta_{j'j}\delta_{m'_{j'},m_j}(\kappa_j+1)$$

where

$$\kappa_{j=l-\frac{1}{2}} = l$$
$$\kappa_{j=l+\frac{1}{2}} = -l-1$$

Lande g–factor

$$g_j = 1 + \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$$

Let us introduce

$$\vec{Y}^{(j=l-\frac{1}{2})}_{lm\sigma}(r) = \sum_{m_j} T^{+(j=l-\frac{1}{2})}_{m\sigma j m_j} \vec{\Omega}^{(j=l-\frac{1}{2})}_{jm_j}(\hat{r})$$
$$\vec{Y}^{(j=l+\frac{1}{2})}_{lm\sigma}(r) = \sum_{m_j} T^{+(j=l+\frac{1}{2})}_{m\sigma j m_j} \vec{\Omega}^{(j=l+\frac{1}{2})}_{jm_j}(\hat{r})$$

Notice that

$$\vec{Y}^{(j=l-\frac{1}{2})}_{lm\sigma}(\hat{r}) + \vec{Y}^{(j=l+\frac{1}{2})}_{lm\sigma}(\hat{r}) = \vec{Y}_{lm\sigma}(\hat{r})$$

If we also intorduce the difference

$$\vec{Y}^{(j=l-\frac{1}{2})}_{lm\sigma}(\hat{r}) - \vec{Y}^{(j=l+\frac{1}{2})}_{lm\sigma}(\hat{r}) = \vec{Z}_{lm\sigma}(\hat{r})$$

we obtain

$$\vec{Y}^{(j=l\mp\frac{1}{2})}_{lm\sigma}(\hat{r}) = \frac{1}{2}[\vec{Y}_{lm\sigma}(\hat{r}) \pm \vec{Z}_{lm\sigma}(\hat{r})]$$

Note that Y and Z harmonics should (most likely) be orthogonal

$$\langle \vec{Y}_{l'm'\sigma'} | \vec{Z}_{lm\sigma} \rangle = 0$$

A. S-wave,j=1/2

$l = 0, m = 0, \sigma =\uparrow\downarrow, j = \frac{1}{2}, m_j = \pm\frac{1}{2}$.

$$\vec{\Omega}^{(l=0)}_{j=\frac{1}{2} m_j=-\frac{1}{2}}(r) = Y_{00}(r) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
$$\vec{\Omega}^{(l=0)}_{j=\frac{1}{2} m_j=+\frac{1}{2}}(r) = Y_{00}(r) \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

	$\langle m_j\|\hat{l}_z\|m_j\rangle$	$\langle m_j\|2\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{j}_z\|m_j\rangle = \langle m_j\|\hat{l}_z + \hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{m}_z\|m_j\rangle = \langle m_j\|\hat{l}_z + 2\hat{s}_z\|m_j\rangle$	$g = \langle m_j\|\hat{m}_z\|m_j\rangle/\langle m_j\|\hat{j}$
$m_j = -\frac{1}{2}$	0	-1	$-1/2$	-1	2
$m_j = +\frac{1}{2}$	0	$+1$	$+1/2$	$+1$	2

$$g_{1/2} = 1 + \frac{0.5 * 1.5 + 0.5 * 1.5 - 0 * 1}{2 * 0.5 * 1.5} = 2$$

B. P-wave,j=1/2

$l = 1, m = -1, 0, 1, \sigma =\uparrow\downarrow, j = \frac{1}{2}, m_{j_1} = \pm\frac{1}{2}$

$$\vec{\Omega}^{(l=1)}_{j=\frac{1}{2} m_j=-\frac{1}{2}}(r) = -\sqrt{\frac{2}{3}} Y_{1-1}(r) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{1}{3}} Y_{10}(r) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$
$$\vec{\Omega}^{(l=1)}_{j=\frac{1}{2} m_j=+\frac{1}{2}}(r) = -\sqrt{\frac{1}{3}} Y_{10}(r) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sqrt{\frac{2}{3}} Y_{11}(r) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

	$\langle m_j\|\hat{l}_z\|m_j\rangle$	$\langle m_j\|2\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{j}_z\|m_j\rangle = \langle m_j\|\hat{l}_z + \hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{l}_z + 2\hat{s}_z\|m_j\rangle$	$g = \langle m_j\|\hat{m}_z\|m_j\rangle/\langle m_j\|\hat{j}_z\|m_j\rangle$
$m_j = -\frac{1}{2}$	-0.6666	$+0.33333$	$-1/2$	-0.33333	0.666666
$m_j = +\frac{1}{2}$	$+0.6666$	-0.33333	$+1/2$	$+0.33333$	0.666666

$$g_{1/2} = 1 + \frac{0.5 * 1.5 + 0.5 * 1.5 - 1 * 2}{2 * 0.5 * 1.5} = 0.6666666$$

C. P-wave,j=3/2

$l=1, m=-1,0,1, \sigma=\uparrow\downarrow, j=\frac{3}{2}, m_j=\pm\frac{1}{2},\pm\frac{3}{2}$

$$
\begin{aligned}
\vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=-\frac{3}{2}}(r) &= Y_{1-1}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=-\frac{1}{2}}(r) &= \sqrt{\frac{1}{3}}Y_{1-1}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{2}{3}}Y_{10}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=+\frac{1}{2}}(r) &= \sqrt{\frac{2}{3}}Y_{10}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{1}{3}}Y_{11}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=+\frac{3}{2}}(r) &= Y_{11}(r)\begin{pmatrix}1\\0\end{pmatrix}
\end{aligned}
$$

	$\langle m_j\|\hat{l}_z\|m_j\rangle$	$\langle m_j\|2\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{j}_z\|m_j\rangle=\langle m_j\|\hat{l}_z+\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{m}_z\|m_j\rangle=\langle m_j\|\hat{l}_z+2\hat{s}_z\|m_j\rangle$	$g=\langle m_j\|\hat{m}_z\|m_j\rangle/\langle m_j\|\hat{j}$
$m_j=-\frac{3}{2}$	-1	-1	-1.5	-2	1.333333
$m_j=-\frac{1}{2}$	-0.33333	-0.33333	-0.5	-0.66666	1.333333
$m_j=+\frac{1}{2}$	$+0.33333$	$+0.33333$	$+0.5$	$+0.66666$	1.333333
$m_j=+\frac{3}{2}$	$+1$	$+1$	$+1.5$	$+2$	1.333333

$$g_{3/2}=1+\frac{1.5*2.5+0.5*1.5-1*2}{2*1.5*2.5}=1.333333$$

D. D-wave,j=3/2

$l=2, m=-2,-1,0,1,2, \sigma=\uparrow\downarrow, j=\frac{3}{2}, m_j=\pm\frac{1}{2},\pm\frac{3}{2}$

$$
\begin{aligned}
\vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=-\frac{3}{2}}(r) &= -\sqrt{\frac{4}{5}}Y_{2-2}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{1}{5}}Y_{2-1}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=-\frac{1}{2}}(r) &= -\sqrt{\frac{3}{5}}Y_{2-1}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{2}{5}}Y_{20}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=+\frac{1}{2}}(r) &= -\sqrt{\frac{2}{5}}Y_{20}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{3}{5}}Y_{21}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=+\frac{3}{2}}(r) &= -\sqrt{\frac{1}{5}}Y_{21}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{4}{5}}Y_{22}(r)\begin{pmatrix}0\\1\end{pmatrix}
\end{aligned}
$$

	$\langle m_j\|\hat{l}_z\|m_j\rangle$	$\langle m_j\|2\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{j}_z\|m_j\rangle=\langle m_j\|\hat{l}_z+\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{m}_z\|m_j\rangle=\langle m_j\|\hat{l}_z+2\hat{s}_z\|m_j\rangle$	$g=\langle m_j\|\hat{m}_z\|m_j\rangle/\langle m_j\|\hat{j}$
$m_j=-\frac{3}{2}$	-1.8	$+0.6$	-1.5	-1.2	0.8
$m_j=-\frac{1}{2}$	-0.6	$+0.2$	-0.5	-0.4	0.8
$m_j=+\frac{1}{2}$	$+0.6$	-0.2	$+0.5$	$+0.4$	0.8
$m_j=+\frac{3}{2}$	$+1.8$	-0.6	$+1.5$	$+1.2$	0.8

$$g_{3/2}=1+\frac{1.5*2.5+0.5*1.5-2*3}{2*1.5*2.5}=0.8$$

E. D-wave,j=5/2

$l=2, m=-2,-1,0,1,2, \sigma=\uparrow\downarrow, j=\frac{5}{2}, m_j=\pm\frac{1}{2},\pm\frac{3}{2},\pm\frac{5}{2}$

$$
\begin{aligned}
\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{5}{2}}(r) &= Y_{2-2}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{3}{2}}(r) &= \sqrt{\frac{1}{5}}Y_{2-2}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{4}{5}}Y_{2-1}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{1}{2}}(r) &= \sqrt{\frac{2}{5}}Y_{2-1}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{3}{5}}Y_{20}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{1}{2}}(r) &= \sqrt{\frac{3}{5}}Y_{20}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{2}{5}}Y_{21}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{3}{2}}(r) &= \sqrt{\frac{4}{5}}Y_{21}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{1}{5}}Y_{22}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{5}{2}}(r) &= Y_{22}(r)\begin{pmatrix}1\\0\end{pmatrix}
\end{aligned}
$$

	$\langle m_j\|\hat{l}_z\|m_j\rangle$	$\langle m_j\|2\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{j}_z\|m_j\rangle=\langle m_j\|\hat{l}_z+\hat{s}_z\|m_j\rangle$	$\langle m_j\|\hat{m}_z\|m_j\rangle=\langle m_j\|\hat{l}_z+2\hat{s}_z\|m_j\rangle$	$g=\langle m_j\|\hat{m}_z\|m_j\rangle/\langle m_j\|\hat{j}$
$m_j=-\frac{5}{2}$	-2	-1	-2.5	-3	1.2
$m_j=-\frac{3}{2}$	-1.2	-0.6	-1.5	-1.8	1.2
$m_j=-\frac{1}{2}$	-0.4	-0.2	-0.5	-0.6	1.2
$m_j=+\frac{1}{2}$	$+0.4$	$+0.2$	$+0.5$	$+0.6$	1.2
$m_j=+\frac{3}{2}$	$+1.2$	$+0.6$	$+1.5$	$+1.8$	1.2
$m_j=+\frac{5}{2}$	$+2$	$+1$	$+2.5$	$+3$	1.2

$$g_{5/2}=1+\frac{2.5*3.5+0.5*1.5-2*3}{2*2.5*3.5}=1.2$$

F. F-wave,j=5/2

$l=3, m=-3,-2,-1,0,1,2,3, \sigma=\uparrow\downarrow, j=\frac{5}{2}, m_j=\pm\frac{1}{2},\pm\frac{3}{2},\pm\frac{5}{2}$

$$
\begin{aligned}
\vec{\Omega}^{(j=5/2)}_{j=5/2m_j=-5/2}(r) &= -\sqrt{\frac{6}{7}}Y_{3-3}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{1}{7}}Y_{3-2}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(j=5/2)}_{j=5/2m_j=-3/2}(r) &= -\sqrt{\frac{5}{7}}Y_{3-2}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{2}{7}}Y_{3-1}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(j=5/2)}_{j=5/2m_j=-1/2}(r) &= -\sqrt{\frac{4}{7}}Y_{3-1}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{3}{7}}Y_{30}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(j=5/2)}_{j=5/2m_j=+1/2}(r) &= -\sqrt{\frac{3}{7}}Y_{30}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{4}{7}}Y_{3+1}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(j=5/2)}_{j=5/2m_j=+3/2}(r) &= -\sqrt{\frac{2}{7}}Y_{3+1}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{5}{7}}Y_{3+2}(r)\begin{pmatrix}0\\1\end{pmatrix}\\
\vec{\Omega}^{(j=5/2)}_{j=5/2m_j=+5/2}(r) &= -\sqrt{\frac{1}{7}}Y_{3+2}(r)\begin{pmatrix}1\\0\end{pmatrix}+\sqrt{\frac{6}{7}}Y_{3+3}(r)\begin{pmatrix}0\\1\end{pmatrix}
\end{aligned}
$$

	$\langle m_j\vert\hat{l}_z\vert m_j\rangle$	$\langle m_j\vert 2\hat{s}_z\vert m_j\rangle$	$\langle m_j\vert\hat{j}_z\vert m_j\rangle = \langle m_j\vert\hat{l}_z+\hat{s}_z\vert m_j\rangle$	$\langle m_j\vert\hat{m}_z\vert m_j\rangle = \langle m_j\vert\hat{l}_z+2\hat{s}_z\vert m_j\rangle$	$g = \langle m_j\vert\hat{m}_z\vert m_j\rangle/\langle m_j\vert\hat{j}$
$m_j=-\frac{5}{2}$	-2.85714	0.714285	-2.5	-2.142854	0.85714285
$m_j=-\frac{3}{2}$	-1.71428	0.42856	-1.5	-1.28572	0.85714285
$m_j=-\frac{1}{2}$	-0.571428	0.142856	-0.5	-0.428572	0.85714285
$m_j=+\frac{1}{2}$	$+0.571428$	-0.142856	$+0.5$	$+0.428572$	0.85714285
$m_j=+\frac{3}{2}$	$+1.71428$	-0.42856	$+1.5$	$+1.28572$	0.85714285
$m_j=+\frac{5}{2}$	$+2.71428$	-0.42856	$+2.5$	$+2.142854$	0.85714285

$$g_{5/2} = 1 + \frac{2.5*3.5+0.5*1.5-3*4}{2*2.5*3.5} = 0.85714285$$

G. F-wave,j=7/2

$l=3, m=-3,-2,-1,0,1,2,3, \sigma=\uparrow\downarrow, j=\frac{7}{2}, m_j=\pm\frac{1}{2},\pm\frac{3}{2},\pm\frac{5}{2},\pm\frac{7}{2}$

$$\vec{\Omega}_{j=7/2m_j=-7/2}(r) = Y_{3-3}(r)\begin{pmatrix}0\\1\end{pmatrix}$$
$$\vec{\Omega}_{j=7/2m_j=-5/2}(r) = \sqrt{\frac{1}{7}}Y_{3-3}(r)\begin{pmatrix}1\\0\end{pmatrix} + \sqrt{\frac{6}{7}}Y_{3-2}(r)\begin{pmatrix}0\\1\end{pmatrix}$$
$$\vec{\Omega}_{j=7/2m_j=-3/2}(r) = \sqrt{\frac{2}{7}}Y_{3-2}(r)\begin{pmatrix}1\\0\end{pmatrix} + \sqrt{\frac{5}{7}}Y_{3-1}(r)\begin{pmatrix}0\\1\end{pmatrix}$$
$$\vec{\Omega}_{j=7/2m_j=-1/2}(r) = \sqrt{\frac{3}{7}}Y_{3-1}(r)\begin{pmatrix}1\\0\end{pmatrix} + \sqrt{\frac{4}{7}}Y_{3+0}(r)\begin{pmatrix}0\\1\end{pmatrix}$$
$$\vec{\Omega}_{j=7/2m_j=+1/2}(r) = \sqrt{\frac{4}{7}}Y_{3+0}(r)\begin{pmatrix}1\\0\end{pmatrix} + \sqrt{\frac{3}{7}}Y_{3+1}(r)\begin{pmatrix}0\\1\end{pmatrix}$$
$$\vec{\Omega}_{j=7/2m_j=+3/2}(r) = \sqrt{\frac{5}{7}}Y_{3+1}(r)\begin{pmatrix}1\\0\end{pmatrix} + \sqrt{\frac{2}{7}}Y_{3+2}(r)\begin{pmatrix}0\\1\end{pmatrix}$$
$$\vec{\Omega}_{j=7/2m_j=+5/2}(r) = \sqrt{\frac{6}{7}}Y_{3+2}(r)\begin{pmatrix}1\\0\end{pmatrix} + \sqrt{\frac{1}{7}}Y_{3+3}(r)\begin{pmatrix}0\\1\end{pmatrix}$$
$$\vec{\Omega}_{j=7/2m_j=+7/2}(r) = Y_{3+3}(r)\begin{pmatrix}1\\0\end{pmatrix}$$

	$\langle m_j\vert\hat{l}_z\vert m_j\rangle$	$\langle m_j\vert 2\hat{s}_z\vert m_j\rangle$	$\langle m_j\vert\hat{j}_z\vert m_j\rangle = \langle m_j\vert\hat{l}_z+\hat{s}_z\vert m_j\rangle$	$\langle m_j\vert\hat{m}_z\vert m_j\rangle = \langle m_j\vert\hat{l}_z+2\hat{s}_z\vert m_j\rangle$	$g = \langle m_j\vert\hat{m}_z\vert m_j\rangle/\langle m_j\vert\hat{j}$
$m_j=-\frac{7}{2}$	-3	-1	-3.5	-4	1.14285714
$m_j=-\frac{5}{2}$	-2.142857	-0.714286	-2.5	-2.857143	1.14285714
$m_j=-\frac{3}{2}$	-1.285714	-0.428572	-1.5	-1.714286	1.14285714
$m_j=-\frac{1}{2}$	-0.428571	-0.142858	-0.5	-0.571429	1.14285714
$m_j=+\frac{1}{2}$	$+0.428517$	$+0.142858$	$+0.5$	$+0.571429$	1.14285714
$m_j=+\frac{3}{2}$	$+1.285714$	$+0.428572$	$+1.5$	$+1.714286$	1.14285714
$m_j=+\frac{5}{2}$	$+2.142857$	$+0.714286$	$+2.5$	$+2.857143$	1.14285714
$m_j=+\frac{7}{2}$	$+3$	$+1$	$+3.5$	$+4$	1.14285714

$$g_{7/2} = 1 + \frac{3.5*4.5+0.5*1.5-3*4}{2*3.5*4.5} = 1.14285714$$

XVIII. APPENDIX: CUBIC RELATIVISTIC HARMONICS

See J. Phys. Soc. Japan, 21, 2400 (1966); Denote linear combinbations of spherical spinors $\vec{\Omega}^{(l)}_{j\alpha}(r)$

$$\vec{\Omega}^{(l)}_{j\alpha}(r) = \sum_{m_j} t^{(lj)}_{\alpha m_j}\vec{\Omega}^{(l)}_{jm_j}(r)$$

A. S-wave,j=1/2

S-wave $j = 1/2, \Gamma_6^+$ doublet

$$\vec{\Omega}^{(l=0,\Gamma_6^+)}_{j=\frac{1}{2}\alpha=1}(r) = \vec{\Omega}^{(l=0)}_{j=\frac{1}{2}m_j=-\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=0,\Gamma_6^+)}_{j=\frac{1}{2}\alpha=2}(r) = \vec{\Omega}^{(l=0)}_{j=\frac{1}{2}m_j=+\frac{1}{2}}(r)$$

Transformation matrix $t^{(l=0,j=1/2)}_{\alpha m_j}$

	$m_j = -1/2$	$m_j = +1/2$
$\alpha = 1(\Gamma_6^+)$	1	0
$\alpha = 2(\Gamma_6^+)$	0	1

	$\langle\alpha\|\hat{l}_z\|\alpha\rangle$	$\langle\alpha\|2\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{j}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + \hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{m}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + 2\hat{s}_z\|\alpha\rangle$	$g = \langle\alpha\|\hat{m}_z\|\alpha\rangle/\langle\alpha\|\hat{j}_z\|\alpha\rangle$
$\alpha = 1(\Gamma_6^+)$	0	-1	$-1/2$	-1	2
$\alpha = 2(\Gamma_6^+)$	0	$+1$	$+1/2$	$+1$	2

$$g_{1/2} = 1 + \frac{0.5 * 1.5 + 0.5 * 1.5 - 0 * 1}{2 * 0.5 * 1.5} = 2$$

B. P-wave, j=1/2

P–wave $j = 1/2$, Γ_6^- doublet

$$\vec{\Omega}^{(l=1,\Gamma_6^-)}_{j=\frac{1}{2}\alpha=1}(r) = \vec{\Omega}^{(l=1)}_{j=\frac{1}{2}m_j=-\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=1,\Gamma_6^-)}_{j=\frac{1}{2}\alpha=2}(r) = \vec{\Omega}^{(l=1)}_{j=\frac{1}{2}m_j=+\frac{1}{2}}(r)$$

Transformation matrix $t^{(l=1,j=1/2)}_{\alpha m_j}$

	$m_j = -1/2$	$m_j = +1/2$
$\alpha = 1(\Gamma_6^-)$	1	0
$\alpha = 2(\Gamma_6^-)$	0	1

	$\langle\alpha\|\hat{l}_z\|\alpha\rangle$	$\langle\alpha\|2\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{j}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + \hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{m}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + 2\hat{s}_z\|\alpha\rangle$	$g = \langle\alpha\|\hat{m}_z\|\alpha\rangle/\langle\alpha\|\hat{j}_z\|\alpha\rangle$
$\alpha = 1(\Gamma_6^-)$	-0.6666	$+0.33333$	$-1/2$	-0.33333	0.666666
$\alpha = 2(\Gamma_6^-)$	$+0.6666$	-0.33333	$+1/2$	$+0.33333$	0.666666

$$g_{1/2} = 1 + \frac{0.5 * 1.5 + 0.5 * 1.5 - 1 * 2}{2 * 0.5 * 1.5} = 0.6666666$$

C. P-wave, j=3/2

P-wave $j = 3/2$, Γ_8^- quadruplet

$$\vec{\Omega}^{(l=1,\Gamma_8^-)}_{j=\frac{3}{2}\alpha=1}(r) = \vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=-\frac{3}{2}}(r)$$
$$\vec{\Omega}^{(l=1,\Gamma_8^-)}_{j=\frac{3}{2}\alpha=2}(r) = \vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=-\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=1,\Gamma_8^-)}_{j=\frac{3}{2}\alpha=3}(r) = \vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=+\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=1,\Gamma_8^-)}_{j=\frac{3}{2}\alpha=4}(r) = \vec{\Omega}^{(l=1)}_{j=\frac{3}{2}m_j=+\frac{3}{2}}(r)$$

Transformation matrix $t^{(l=1,j=3/2)}_{\alpha m_j}$

	$m_j=-3/2$	$m_j=-1/2$	$m_j=+1/2$	$m_j=+3/2$
$\alpha=1(\Gamma_8^-)$	1	0	0	0
$\alpha=2(\Gamma_8^-)$	0	1	0	0
$\alpha=3(\Gamma_8^-)$	0	0	1	0
$\alpha=4(\Gamma_8^-)$	0	0	0	1

	$\langle\alpha\|\hat{l}_z\|\alpha\rangle$	$\langle\alpha\|2\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{j}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z+\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{m}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z+2\hat{s}_z\|\alpha\rangle$	$g = \langle\alpha\|\hat{m}_z\|\alpha\rangle/\langle\alpha\|\hat{j}_z\|\alpha\rangle$
$\alpha=1(\Gamma_8^-)$	-1	-1	-1.5	-2	1.333333
$\alpha=2(\Gamma_8^-)$	-0.33333	-0.33333	-0.5	-0.66666	1.333333
$\alpha=3(\Gamma_8^-)$	$+0.33333$	$+0.33333$	$+0.5$	$+0.66666$	1.333333
$\alpha=4(\Gamma_8^-)$	$+1$	$+1$	$+1.5$	$+2$	1.333333

$$g_{3/2} = 1 + \frac{1.5*2.5+0.5*1.5-1*2}{2*1.5*2.5} = 1.333333$$

D. D-wave, j=3/2

D-wave $j = 3/2$, Γ_8^+ quartet

$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{3}{2}\alpha=1}(r) = \vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=-\frac{3}{2}}(r)$$
$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{3}{2}\alpha=2}(r) = \vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=-\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{3}{2}\alpha=3}(r) = \vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=+\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{3}{2}\alpha=4}(r) = \vec{\Omega}^{(l=2)}_{j=\frac{3}{2}m_j=+\frac{3}{2}}(r)$$

Transformation matrix $t^{(l=2,j=3/2)}_{\alpha m_j}$

	$m_j=-3/2$	$m_j=-1/2$	$m_j=+1/2$	$m_j=+3/2$
$\alpha=1(\Gamma_8^+)$	1	0	0	0
$\alpha=2(\Gamma_8^+)$	0	1	0	0
$\alpha=3(\Gamma_8^+)$	0	0	1	0
$\alpha=4(\Gamma_8^+)$	0	0	0	1

Average z components

	$\langle\alpha\|\hat{l}_z\|\alpha\rangle$	$\langle\alpha\|2\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{j}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z+\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{m}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z+2\hat{s}_z\|\alpha\rangle$	$g = \langle\alpha\|\hat{m}_z\|\alpha\rangle/\langle\alpha\|\hat{j}_z\|\alpha\rangle$
$\alpha=1(\Gamma_8^+)$	-1.8	$+0.6$	-1.5	-1.2	0.8
$\alpha=2(\Gamma_8^+)$	-0.6	$+0.2$	-0.5	-0.4	0.8
$\alpha=3(\Gamma_8^+)$	$+0.6$	-0.2	$+0.5$	$+0.4$	0.8
$\alpha=4(\Gamma_8^+)$	$+1.8$	-0.6	$+1.5$	$+1.2$	0.8

$$g_{3/2} = 1 + \frac{1.5*2.5 + 0.5*1.5 - 2*3}{2*1.5*2.5} = 0.8$$

E. D-wave, j=5/2

D-wave $j = 5/2$, Γ_7^+ doublet

$$\vec{\Omega}^{(l=2,\Gamma_7^+)}_{j=\frac{5}{2}\alpha=1}(r) = +\sqrt{\frac{5}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{3}{2}}(r) - \sqrt{\frac{1}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{5}{2}}(r)$$
$$\vec{\Omega}^{(l=2,\Gamma_7^+)}_{j=\frac{5}{2}\alpha=2}(r) = -\sqrt{\frac{1}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{5}{2}}(r) + \sqrt{\frac{5}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{3}{2}}(r)$$

D-wave $j = 5/2$, Γ_8^+ quartet

$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{5}{2}\alpha=3}(r) = -\sqrt{\frac{5}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{5}{2}}(r) - \sqrt{\frac{1}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{3}{2}}(r)$$
$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{5}{2}\alpha=4}(r) = +\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{5}{2}\alpha=5}(r) = -\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=2,\Gamma_8^+)}_{j=\frac{5}{2}\alpha=6}(r) = +\sqrt{\frac{1}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=-\frac{3}{2}}(r) + \sqrt{\frac{5}{6}}\vec{\Omega}^{(l=2)}_{j=\frac{5}{2}m_j=+\frac{5}{2}}(r)$$

Transformation matrix $t^{(l=2,j=5/2)}_{\alpha m_j}$

	$m_j = -5/2$	$m_j = -3/2$	$m_j = -1/2$	$m_j = +1/2$	$m_j = +3/2$	$m_j = +5/2$
$\alpha = 1(\Gamma_7^+)$	0	$+\sqrt{\frac{5}{6}}$	0	0	0	$-\sqrt{\frac{1}{6}}$
$\alpha = 2(\Gamma_7^+)$	$-\sqrt{\frac{1}{6}}$	0	0	0	$+\sqrt{\frac{5}{6}}$	0
$\alpha = 3(\Gamma_8^+)$	$-\sqrt{\frac{5}{6}}$	0	0	0	$-\sqrt{\frac{1}{6}}$	0
$\alpha = 4(\Gamma_8^+)$	0	0	-1	0	0	0
$\alpha = 5(\Gamma_8^+)$	0	0	0	$+1$	0	0
$\alpha = 6(\Gamma_8^+)$	0	$+\sqrt{\frac{1}{6}}$	0	0	0	$+\sqrt{\frac{5}{6}}$

Average z components

	$\langle\alpha\|\hat{l}_z\|\alpha\rangle$	$\langle\alpha\|2\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{j}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + \hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{m}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + 2\hat{s}_z\|\alpha\rangle$	$g = \langle\alpha\|\hat{m}_z\|\alpha\rangle/\langle\alpha\|\hat{j}_z\|\alpha\rangle$
$\alpha = 1(\Gamma_7^+)$	-0.666	-0.333	-0.833	-1.000	1.2
$\alpha = 2(\Gamma_7^+)$	$+0.666$	$+0.333$	$+0.833$	$+1.000$	1.2
$\alpha = 3(\Gamma_8^+)$	-1.466	-0.733	-1.833	-2.200	1.2
$\alpha = 4(\Gamma_8^+)$	-0.4	-0.2	-0.5	-0.600	1.2
$\alpha = 5(\Gamma_8^+)$	$+0.4$	$+0.2$	$+0.5$	$+0.600$	1.2
$\alpha = 6(\Gamma_8^+)$	$+1.466$	$+0.733$	$+1.833$	$+2.200$	1.2

$$g_{5/2} = 1 + \frac{2.5*3.5 + 0.5*1.5 - 2*3}{2*2.5*3.5} = 1.2$$

F. F-wave, j=5/2

F-wave $j = 5/2$, Γ_7^- doublet

$$\vec{\Omega}^{(l=3,\Gamma_7^-)}_{j=\frac{5}{2}\alpha=1}(r) = +\sqrt{\frac{5}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=-\frac{3}{2}}(r) - \sqrt{\frac{1}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=+\frac{5}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_7^-)}_{j=\frac{5}{2}\alpha=2}(r) = -\sqrt{\frac{1}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=-\frac{5}{2}}(r) + \sqrt{\frac{5}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=+\frac{3}{2}}(r)$$

F-wave $j = 5/2$, Γ_8^- quartet

$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{5}{2}\alpha=3}(r) = -\sqrt{\frac{5}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=-\frac{5}{2}}(r) - \sqrt{\frac{1}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=+\frac{3}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{5}{2}\alpha=4}(r) = -\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=-\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{5}{2}\alpha=5}(r) = +\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=+\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{5}{2}\alpha=6}(r) = +\sqrt{\frac{1}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=-\frac{3}{2}}(r) + \sqrt{\frac{5}{6}}\vec{\Omega}^{(l=3)}_{j=\frac{5}{2}m_j=+\frac{5}{2}}(r)$$

Transformation Matrix $t^{(l=3,j=5/2)}_{\alpha m_j}$

	$m_j = -5/2$	$m_j = -3/2$	$m_j = -1/2$	$m_j = +1/2$	$m_j = +3/2$	$m_j = +5/2$
$\alpha = 1(\Gamma_7^-)$	0	$+\sqrt{\frac{5}{6}}$	0	0	0	$-\sqrt{\frac{1}{6}}$
$\alpha = 2(\Gamma_7^-)$	$-\sqrt{\frac{1}{6}}$	0	0	0	$+\sqrt{\frac{5}{6}}$	0
$\alpha = 3(\Gamma_8^-)$	$-\sqrt{\frac{5}{6}}$	0	0	0	$-\sqrt{\frac{1}{6}}$	0
$\alpha = 4(\Gamma_8^-)$	0	0	-1	0	0	0
$\alpha = 5(\Gamma_8^-)$	0	0	0	$+1$	0	0
$\alpha = 6(\Gamma_8^-)$	0	$+\sqrt{\frac{1}{6}}$	0	0	0	$+\sqrt{\frac{5}{6}}$

Average z components

	$\langle\alpha\vert\hat{l}_z\vert\alpha\rangle$	$\langle\alpha\vert 2\hat{s}_z\vert\alpha\rangle$	$\langle\alpha\vert\hat{j}_z\vert\alpha\rangle = \langle\alpha\vert\hat{l}_z + \hat{s}_z\vert\alpha\rangle$	$\langle\alpha\vert\hat{m}_z\vert\alpha\rangle = \langle\alpha\vert\hat{l}_z + 2\hat{s}_z\vert\alpha\rangle$	$g = \langle\alpha\vert\hat{m}_z\vert\alpha\rangle/\langle\alpha\vert\hat{j}_z\vert\alpha\rangle$
$\alpha = 1(\Gamma_7^-)$	-0.952	$+0.238$	-0.833	-0.714	0.85714285
$\alpha = 2(\Gamma_7^-)$	$+0.952$	-0.238	$+0.833$	$+0.714$	0.85714285
$\alpha = 3(\Gamma_8^-)$	-2.095	$+0.523$	-1.833	-1.572	0.85714285
$\alpha = 4(\Gamma_8^-)$	-0.571	$+0.142$	-0.500	-0.429	0.85714285
$\alpha = 5(\Gamma_8^-)$	$+0.571$	-0.142	$+0.500$	$+0.429$	0.85714285
$\alpha = 6(\Gamma_8^-)$	$+2.095$	-0.523	$+1.833$	$+1.572$	0.85714285

$$g_{5/2} = 1 + \frac{2.5 * 3.5 + 0.5 * 1.5 - 3 * 4}{2 * 2.5 * 3.5} = 0.85714285$$

G. F-wave, j=7/2

F-wave $j = 7/2$, Γ_6^- doublet

$$\vec{\Omega}^{(l=3,\Gamma_6^-)}_{j=\frac{7}{2}\alpha=1}(r) = +\sqrt{\frac{5}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{7}{2}}(r) + \sqrt{\frac{7}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_6^-)}_{j=\frac{7}{2}\alpha=2}(r) = -\sqrt{\frac{7}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{1}{2}}(r) - \sqrt{\frac{5}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{7}{2}}(r)$$

F-wave $j = 7/2$, Γ_7^- doublet

$$\vec{\Omega}^{(l=3,\Gamma_7^-)}_{j=\frac{7}{2}\alpha=3}(r) = +\sqrt{\frac{3}{4}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{5}{2}}(r) - \frac{1}{2}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{3}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_7^-)}_{j=\frac{7}{2}\alpha=4}(r) = +\frac{1}{2}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{3}{2}}(r) - \sqrt{\frac{3}{4}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{5}{2}}(r)$$

F-wave $j = 7/2$, Γ_8^- quartet

$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{7}{2}\alpha=5}(r) = +\sqrt{\frac{7}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{7}{2}}(r) - \sqrt{\frac{5}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{1}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{7}{2}\alpha=6}(r) = +\sqrt{\frac{3}{4}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{3}{2}}(r) + \frac{1}{2}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{5}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{7}{2}\alpha=7}(r) = +\frac{1}{2}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{5}{2}}(r) + \sqrt{\frac{3}{4}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{3}{2}}(r)$$
$$\vec{\Omega}^{(l=3,\Gamma_8^-)}_{j=\frac{7}{2}\alpha=8}(r) = -\sqrt{\frac{5}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=-\frac{1}{2}}(r) + \sqrt{\frac{7}{12}}\vec{\Omega}^{(l=3)}_{j=\frac{7}{2}m_j=+\frac{7}{2}}(r)$$

Transformation Matrix $t^{(l=3,j=7/2)}_{\alpha m_j}$

	$m_j = -7/2$	$m_j = -5/2$	$m_j = -3/2$	$m_j = -1/2$	$m_j = +1/2$	$m_j = +3/2$	$m_j = +5/2$	$m_j = +7/2$
$\alpha = 1(\Gamma_6^-)$	$+\sqrt{\frac{5}{12}}$	0	0	0	$+\sqrt{\frac{7}{12}}$	0	0	0
$\alpha = 2(\Gamma_6^-)$	0	0	0	$-\sqrt{\frac{7}{12}}$	0	0	0	$-\sqrt{\frac{5}{12}}$
$\alpha = 3(\Gamma_7^-)$	0	$+\sqrt{\frac{3}{4}}$	0	0	0	$-\frac{1}{2}$	0	0
$\alpha = 4(\Gamma_7^-)$	0	0	$+\frac{1}{2}$	0	0	0	$-\sqrt{\frac{3}{4}}$	0
$\alpha = 5(\Gamma_8^-)$	$+\sqrt{\frac{7}{12}}$	0	0	0	$-\sqrt{\frac{5}{12}}$	0	0	0
$\alpha = 6(\Gamma_8^-)$	0	0	$+\sqrt{\frac{3}{4}}$	0	0	0	$+\frac{1}{2}$	0
$\alpha = 7(\Gamma_8^-)$	0	$+\frac{1}{2}$	0	0	0	$+\sqrt{\frac{3}{4}}$	0	0
$\alpha = 8(\Gamma_8^-)$	0	0	0	$-\sqrt{\frac{5}{12}}$	0	0	0	$+\sqrt{\frac{7}{12}}$

Average z components

	$\langle\alpha\|\hat{l}_z\|\alpha\rangle$	$\langle\alpha\|2\hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{j}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + \hat{s}_z\|\alpha\rangle$	$\langle\alpha\|\hat{m}_z\|\alpha\rangle = \langle\alpha\|\hat{l}_z + 2\hat{s}_z\|\alpha\rangle$	$g = \langle\alpha\|\hat{m}_z\|\alpha\rangle/\langle\alpha\|\hat{j}_z\|\alpha\rangle$
$\alpha = 1(\Gamma_6^-)$	-1.000	-0.333	-1.166	-1.333	1.14285714
$\alpha = 2(\Gamma_6^-)$	$+1.000$	$+0.333$	$+1.166$	$+1.333$	1.14285714
$\alpha = 3(\Gamma_7^-)$	-1.285	-0.429	-1.5	-1.714	1.14285714
$\alpha = 4(\Gamma_7^-)$	$+1.285$	$+0.429$	$+1.5$	$+1.714$	1.14285714
$\alpha = 5(\Gamma_8^-)$	-1.572	-0.524	-1.834	-2.096	1.14285714
$\alpha = 6(\Gamma_8^-)$	-0.428	-0.143	-0.5	-0.571	1.14285714
$\alpha = 7(\Gamma_8^-)$	$+0.428$	$+0.143$	$+0.5$	0.571	1.14285714
$\alpha = 8(\Gamma_8^-)$	$+1.572$	$+0.523$	$+1.834$	$+2.096$	1.14285714

$$g_{7/2} = 1 + \frac{3.5 * 4.5 + 0.5 * 1.5 - 3 * 4}{2 * 3.5 * 4.5} = 1.14285714$$

XIX. APPENDIX: SPHERICAL COORDINATES

Cyclic coordinate system is obtained from the Cartesian coordinate system by the following transformation:

$$e_{+1} = -\frac{1}{\sqrt{2}}(e_x + ie_y)$$
$$e^{+1} = -\frac{1}{\sqrt{2}}(e_x - ie_y)$$

$$e_0 = e_z$$
$$e^0 = e_z$$

$$e_{-1} = +\frac{1}{\sqrt{2}}(e_x - ie_y)$$
$$e^{-1} = +\frac{1}{\sqrt{2}}(e_x + ie_y)$$

which have the following properties:

$$e^\mu = (-1)^\mu e_{-\mu} = e^*_\mu$$

$$e_\mu e^\nu = e_\mu e^*_\nu = \delta_{\mu\nu}$$

Back transformation is given by:

$$e_x = +\frac{1}{\sqrt{2}}(e_{-1} - e_{+1})$$
$$e_x = +\frac{1}{\sqrt{2}}(e^{-1} - e^{+1})$$

$$e_y = +\frac{i}{\sqrt{2}}(e_{-1} + e_{+1})$$
$$e_y = -\frac{i}{\sqrt{2}}(e^{-1} + e^{+1})$$

$$e_z = e_0$$
$$e_z = e^0$$

For any point

$$r = x\ e_x + y\ e_y + z\ e_z = \sum_i r_i e_i = \sum_\mu r_\mu e^\mu = \sum_\mu r^\mu e_\mu = \sum_\mu r^*_\mu e_\mu$$

the transition is:

$$r_{-1} = +\frac{1}{\sqrt{2}}(x - iy) = +\frac{1}{\sqrt{2}} r\ sin\theta\ e^{-i\varphi} \tilde{\ } Y_{1-1}$$
$$r^{-1} = +\frac{1}{\sqrt{2}}(x + iy) = +\frac{1}{\sqrt{2}} r\ sin\theta\ e^{i\varphi}$$

$$r_{+1} = -\frac{1}{\sqrt{2}}(x + iy) = -\frac{1}{\sqrt{2}} r\ sin\theta\ e^{i\varphi} \tilde{\ } Y_{1+1}$$
$$r^{+1} = -\frac{1}{\sqrt{2}}(x - iy) = -\frac{1}{\sqrt{2}} r\ sin\theta\ e^{-i\varphi}$$

$$r_0 = z = r\ cos\theta r^0 = z = r\ cos\theta\tilde{}Y_{10}$$

with the properties:

$$x^\mu = (-1)^\mu x_{-\mu} = x_\mu^*$$

Using

$$Y_{lm}(\hat{\gamma}\hat{r}) = \sum_{m'} U^{l+}_{m'm}(\gamma) Y_{lm'}(\hat{r}) = \sum_{m'} U^{l*}_{mm'}(\gamma) Y_{lm'}(\hat{r})$$

we obtain

$$\hat{\gamma} r_\mu {=} \sum_{\mu'} U^{l=1*}_{\mu\mu'}(\gamma) r_{\mu'}$$

Representation for gradient:

$$\nabla = \nabla_x e_x + \nabla_y e_y + \nabla_z e_z = \sum_i \nabla_i e_i = \sum_\mu \nabla_\mu e^\mu = \sum_\mu \nabla^\mu e_\mu = \sum_\mu \nabla^*_\mu e_\mu$$

where

$$\nabla_{+1} = \frac{\partial}{\partial x^{+1}} = -\frac{1}{\sqrt{2}}(\nabla_x + i\nabla_y)$$
$$\nabla^{+1} = \frac{\partial}{\partial x_{+1}} = -\frac{1}{\sqrt{2}}(\nabla_x - i\nabla_y)$$

$$\nabla_0 = \frac{\partial}{\partial x^0} = \nabla_z$$
$$\nabla^0 = \frac{\partial}{\partial x_0} = \nabla_z$$

$$\nabla_{-1} = \frac{\partial}{\partial x^{-1}} = +\frac{1}{\sqrt{2}}(\nabla_x - i\nabla_y)$$
$$\nabla^{-1} = \frac{\partial}{\partial x_{-1}} = +\frac{1}{\sqrt{2}}(\nabla_x - i\nabla_y)$$

with the properties

$$\nabla^\mu = (-1)^\mu \nabla_{-\mu} = \nabla_\mu^*$$

$$\nabla^\mu = \frac{\partial}{\partial x_\mu} = (-1)^\mu \left(\frac{\partial}{\partial x^{-\mu}}\right) = \left(\frac{\partial}{\partial x_\mu}\right)^*$$

$$\nabla_\mu = \frac{\partial}{\partial x^\mu} = (-1)^\mu \left(\frac{\partial}{\partial x_{-\mu}}\right) = \left(\frac{\partial}{\partial x_\mu}\right)^*$$

Define x as left-right axis, y as far-near axis and z as bottom-top axis. Then cross products are given by

$$e_z = [e_y e_x]$$
$$e_x = [e_z e_y]$$
$$e_y = [e_x e_z]$$

In spherical coordinates:

$$e_z = [e_y e_x] = [(-\frac{i}{\sqrt{2}}(e^{-1} + e^{+1}))(\frac{1}{\sqrt{2}}(e^{-1} - e^{+1}))] = i[e^{-1}e^{+1}]$$

$$\begin{aligned} e^{-1} - e^{+1} &= \sqrt{2}[e_z e_y] = -i[e^0 e^{-1}] - i[e^0 e^{+1}] \\ e^{-1} + e^{+1} &= i\sqrt{2}[e_x e_z] = -i[e^0 e^{-1}] + i[e^0 e^{+1}] \end{aligned}$$

$$\begin{aligned} e^0 &= i[e^{-1}e^{+1}] = -i[e_{+1}e^{+1}] = i[e^{+1}e_{+1}] = -i[e^{-1}e_{-1}] = i[e_{-1}e^{-1}] \\ e^{-1} &= -i[e^0 e^{-1}] = +i[e_0 e_{+1}] \\ e^{+1} &= +i[e^0 e^{+1}] = -i[e_0 e_{-1}] \end{aligned}$$

$$\begin{aligned} e_0 &= -i[e_{-1}e_{+1}] \\ e_{-1} &= +i[e_0 e_{-1}] = -i[e^0 e^{+1}] \\ e_{+1} &= -i[e_0 e_{+1}] = +i[e^0 e^{-1}] \end{aligned}$$

Cross products

$$\begin{aligned} [e_{-1}e^{-1}] &= -ie^0 = -ie_0 \\ [e_{-1}e^0] &= -ie^{+1} = ie_{-1} \\ [e_{-1}e^{+1}] &= 0 \end{aligned}$$

$$\begin{aligned} [e_0 e^{-1}] &= ie^{-1} = -ie_{+1} \\ [e_0 e^0] &= 0 \\ [e_0 e^{+1}] &= -ie^{+1} = +ie_{-1} \end{aligned}$$

$$\begin{aligned} [e_{+1}e^{-1}] &= 0 \\ [e_{+1}e^0] &= ie^{-1} = -ie_{+1} \\ [e_{+1}e^{+1}] &= ie^0 = ie_0 \end{aligned}$$

$$\begin{aligned} [e_{-1}e_{-1}] &= -[e_{-1}e^{+1}] = 0 \\ [e_{-1}e_0] &= -ie^{+1} = ie_{-1} \\ [e_{-1}e_{+1}] &= -[e_{-1}e^{-1}] = ie^0 = ie_0 \end{aligned}$$

$$\begin{aligned} [e_0 e_{-1}] &= -[e_0 e^{+1}] = ie^{+1} = -ie_{-1} \\ [e_0 e_0] &= 0 \\ [e_0 e_{+1}] &= -[e_0 e^{-1}] = -ie^{-1} = ie_{+1} \end{aligned}$$

$$\begin{aligned} [e_{+1}e_{-1}] &= -[e_{+1}e^{+1}] = -ie^0 = -ie_0 \\ [e_{+1}e_0] &= ie^{-1} = -ie_{+1} \\ [e_{+1}e_{+1}] &= 0 \end{aligned}$$

Conjugated cross products

$$\begin{aligned} [e^{-1}e_{-1}] &= +ie_0 = +ie^0 \\ [e^{-1}e_0] &= +ie_{+1} = -ie^{-1} \\ [e^{-1}e_{+1}] &= 0 \end{aligned}$$

$$
\begin{aligned}
[e^0 e_{-1}] &= -ie_{-1} = +ie^{+1} \\
[e^0 e_0] &= 0 \\
[e^0 e_{+1}] &= +ie_{+1} = -ie^{-1}
\end{aligned}
$$

$$
\begin{aligned}
[e^{+1} e_{-1}] &= 0 \\
[e^{+1} e_0] &= -ie_{-1} = +ie^{+1} \\
[e^{+1} e_{+1}] &= -ie_0 = -ie^0
\end{aligned}
$$

$$
\begin{aligned}
[e^{-1} e^{-1}] &= -[e^{-1} e_{+1}] = 0 \\
[e^{-1} e^0] &= +ie_{+1} = -ie^{-1} \\
[e^{-1} e^{+1}] &= -[e^{-1} e_{-1}] = -ie_0 = -ie^0
\end{aligned}
$$

$$
\begin{aligned}
[e^0 e^{-1}] &= -[e^0 e_{+1}] = -ie_{+1} = +ie^{-1} \\
[e^0 e^0] &= 0 \\
[e^0 e^{+1}] &= -[e^0 e_{-1}] = +ie_{-1} = -ie^{+1}
\end{aligned}
$$

$$
\begin{aligned}
[e^{+1} e^{-1}] &= -[e^{+1} e_{+1}] = +ie_0 = +ie^0 \\
[e^{+1} e^0] &= -ie_{-1} = +ie^{+1} \\
[e^{+1} e^{+1}] &= 0
\end{aligned}
$$

Cross product of two vectors in cartesian coordinates (refer to coordinate system mentioned above)

$$
[\mathbf{AB}] = \sum_{\alpha\beta} a_\alpha [\mathbf{e}_\alpha \mathbf{e}_\beta] b_\beta = (a_z b_y - a_y b_z)\mathbf{e}_x + (a_x b_z - a_z b_x)\mathbf{e}_y + (a_y b_x - b_y a_x)\mathbf{e}_z
$$

Cross product of two vectors in spherical coordinates

$$
\begin{aligned}
[\mathbf{AB}] = \sum_{\mu\nu} a^\mu [\mathbf{e}_\mu \mathbf{e}^\nu] b_\nu = \\
&+a^{-1}(-i\mathbf{e}^0)b_{-1} + a^{-1}(-i\mathbf{e}^{+1})b_0 \\
&+a^0(i\mathbf{e}^{-1})b_{-1} + a^0(-i\mathbf{e}^{+1})b_{+1} \\
&+a^{+1}(i\mathbf{e}^{-1})b_0 + a^{+1}(i\mathbf{e}^0)b_{+1} \\
= (a^{+1}b_0 + a^0 b_{-1})i\mathbf{e}^{-1} - (a^{-1}b_0 + a^0 b_{+1})i\mathbf{e}^{+1} + (a^{+1}b_{+1} - a^{-1}b_{-1})i\mathbf{e}^0
\end{aligned}
$$

A. Transformation between cubic and spherical harmonics

(**Program LIB_CUBHARM**) Transformation matrices between spherical, $Y_{lm}(\hat{r})$, and cubic, $Y_{l\alpha}(\hat{r})$, harmonics

$$
\begin{aligned}
Y_{lm}(\hat{r}) &= \sum_\alpha t^{c(l)}_{m\alpha} Y_{l\alpha}(\hat{r}) \\
Y_{l\alpha}(\hat{r}) &= \sum_m t^{s(l)}_{\alpha m} Y_{lm}(\hat{r})
\end{aligned}
$$

If matrix $A_{l'm'lm}\tilde{}\langle Y_{l'm'}|Y_{lm}\rangle$ is known in spherical harmonics , it can be transformed to cubic harmonics by matrix $t^{s(l)}_{m\alpha}$ as follows

$$
A_{l'\alpha l\beta} = \sum_{m'm} t^{s(l')*}_{\alpha m'} A_{l'm'lm} t^{s(l)}_{\beta m}
$$

If matrix $A_{l'\alpha l\beta}\tilde{}\langle Y_{l'\alpha}|Y_{l\beta}\rangle$ is known in cubic harmoncs, it can be transformed to spherical harmonics by matrix $t^{c(l)}_{\alpha m}$ as follows

$$
A_{l'm'lm} = \sum_{\alpha\beta} t^{c(l)*}_{m'\alpha} A_{l'\alpha l\beta} t^{c(l)}_{m\beta}
$$

Note that transformation matrices are unitary

$$\sum_\beta t^{c(l)}_{m'\beta} t^{s(l)}_{\beta m} = \delta_{m'm}$$

$$\sum_m t^{s(l)}_{\alpha m} t^{c(l)}_{m\beta} = \delta_{\alpha\beta}$$

$$t^{s(l)*}_{\alpha m} = t^{(c)(l)}_{m\alpha}$$

Therefore for hermitian matrices

$$A_{l\alpha l\beta} = \sum_{m'm} t^{s(l)*}_{\alpha m'} A_{lm'lm} t^{s(l)}_{\beta m} = \sum_{m'm} t^{c(l)}_{m'\alpha} A_{lm'lm} t^{c(l)*}_{m\beta} = \sum_{m'm} t^{c(l)*}_{m'\beta} A^*_{lm'lm} t^{c(l)}_{m\alpha}$$

Rotations of cubic harmonics

$$\begin{aligned} Y_{l\alpha}(\hat{\gamma}\hat{r}) &= \sum_\beta [\sum_{mm'} t^{c(l)}_{m'\beta} U^l_{m'm}(\gamma^{-1}) t^{s(l)}_{\alpha m}] Y_{l\beta}(\hat{r}) = \\ &= \sum_\beta [\sum_{mm'} t^{c(l)*}_{\beta m'} U^l_{m'm}(\gamma^{-1}) t^{s(l)}_{\alpha m}] Y_{l\beta}(\hat{r}) = \\ &= \sum_\beta U^l_{\alpha\beta}(\gamma^{-1}) Y_{l\beta}(\hat{r}) \end{aligned}$$

XX. APPENIDX: TWO-CENTER INTEGRALS FOR SPHERICAL FUNCTIONS

Consider the fintegrals between LMTO enevelopes defined as follows

$$\chi_{lm}(\mathbf{r}) = \left\{ \begin{array}{l} \phi^h_l(r) i^l Y_{lm}(r), r < S \\ H_l(r) i^l Y_{lm}(r), r > S \end{array} \right|$$

where $\phi^h_l(r)$ (and $\phi^j_l(r)$) are the radial solutions of Schroedinger's equation augmented to Hankel (and Bessel) functions. The two-center integrals we are interested in is given by

$$\langle \chi_{l'm'}(\mathbf{r})|H|\chi_{lm}(\mathbf{r}-\mathbf{R})\rangle = \int_V \phi^h_{l'}(r)(-i)^{l'} Y^*_{l'm'}(\hat{r}) H \chi_l(r-R) i^l Y_{lm}(r-R) d\mathbf{r}$$

The tails of the orbitals $\chi_{lm}(\mathbf{r}-\mathbf{R})$ obey one-center expansions like spherical functions

$$\chi_{lm}(\mathbf{r}-\mathbf{R}) = -\sum_{L'} \phi^j_{L'}(\mathbf{r}) \frac{1}{S(2l'+1)} \sum_{L''} 4\pi S C^{L''}_{LL'} \frac{(2l''-1)!!}{(2l'-1)!!(2l-1)!!} (\kappa S)^{l+l'-l''} H^*_{L''}(\mathbf{R})$$

therefore

$$\langle \chi_{l'm'}(\mathbf{r})|H|\chi_{lm}(\mathbf{r}-\mathbf{R})\rangle = -\sum_{L''} \frac{4\pi}{(2l'+1)} C^{L''}_{LL'} \frac{(2l''-1)!!}{(2l'-1)!!(2l-1)!!} (\kappa S)^{l+l'-l''} H^*_{L''}(\mathbf{R}) \int_0^\infty \phi^h_{l'}(r) H \phi^j_{l'}(r) r^2 dr$$

If we take a limit $\kappa \to 0$ the sum over l'' is reduced to the term l+l'

$$\langle \chi_{l'm'}(\mathbf{r})|H|\chi_{lm}(\mathbf{r}-\mathbf{R})\rangle = -\frac{4\pi}{(2l'+1)} C^{l+l'm'-m}_{lml'm'} \frac{(2l+2l'-1)!!}{(2l'-1)!!(2l-1)!!} \left(\frac{S}{R}\right)^{l+1} (-i)^{l+l'} Y_{l+l'm'-m}(\hat{R}) \int_0^\infty \phi^h_{l'}(r) H \phi^j_{l'}(r) r^2 dr$$

One can thus understand the sign structure of the obtained expression by computing the structural prefactor

$$S_{l'm'lm}(R) = \frac{\langle \chi_{l'm'}(\mathbf{r})|H|\chi_{lm}(\mathbf{r}-\mathbf{R})\rangle}{\int_0^\infty \phi^h_{l'}(r) H \phi^j_{l'}(r) r^2 dr} = -\frac{4\pi}{(2l'+1)} \frac{(2l+2l'-1)!!}{(2l'-1)!!(2l-1)!!} \left(\frac{S}{R}\right)^{l+1} C^{l+l'm'-m}_{lml'm'} (-i)^{l+l'} Y^*_{l+l'm'-m}(\hat{R})$$