Some notes on forces in LAPW

Kristjan Haule
Department of Physics, Rutgers University, Piscataway, NJ 08854, USA
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I. LAPW INTRO

First we refresh the basic LAPW equations. The LAPW basis in the interstitials is

$$\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} = \sum_{lm} \frac{4\pi i^l}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\mu} Y^*_{lm}(R_\mu(\hat{\mathbf{k}}+\hat{\mathbf{K}})) j_l(|\mathbf{k}+\mathbf{K}||\mathbf{r}-\mathbf{r}_\mu|) Y_{lm}(R_\mu(\mathbf{r}-\mathbf{r}_\alpha)) \tag{1}$$

and in the MT-spheres is

$$\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \sum_{lm,\mu} \frac{4\pi i^l S^2}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\mu} Y^*_{lm}(R_\mu(\mathbf{k}+\mathbf{K})) \left(\bar{a}_l^{\mathbf{k}+\mathbf{K}} u_l(|\mathbf{r}-\mathbf{r}_\mu|) + \bar{b}_l^{\mathbf{k}+\mathbf{K}} \dot{u}_l(|\mathbf{r}-\mathbf{r}_\mu|)\right) Y_{lm}(R_\mu(\mathbf{r}-\mathbf{r}_\mu)) \tag{2}$$

$$\chi_{\nu=(lm\mu)}(\mathbf{r}) = \sum_{m'\mu'} \frac{4\pi i^l S^2}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y^*_{lm'}(R_{\mu'}(\mathbf{k}+\mathbf{K}_\nu))(a_\nu^{lo} u_l(|\mathbf{r}-\mathbf{r}_{\mu'}|) + b_\nu^{lo}\dot{u}_l(|\mathbf{r}-\mathbf{r}_{\mu'}|) + c_\nu^{lo} u_l^{LO}(|\mathbf{r}-\mathbf{r}_{\mu'}|)) Y^*_{lm'}(R_{\mu'}\mathbf{r})$$

In the last term we take a combination of a^{lo}, b^{lo} and c^{lo} so that the combined orbital

$$u_\nu^{loc}(r) = a_\nu^{lo} u_l(r) + b_\nu^{lo}\dot{u}(r) + c_\nu^{lo} u_l^{LO} \tag{3}$$

vanishes at the MT-boundary. In LAPW method, we can also make derivative $du_\nu^{loc}(r = R_{MT})/dr$ vanish, while in APW+lo only the value $u_\nu^{loc}(r = R_{MT})$ vanishes. Note that the index for the local orbital ν comprises $(\mu, l, j_{lo}, \alpha, m)$ in this order, where (μ, l, j_{lo}, α, m) are (index of a sort, l, index enumerates local orbital, index of the equivalent atom, m).

Notice that the phase factor in the local orbital functions is taken to be the same as in augmented plane waves. Moreover, $\mathbf{K}_\nu$ is taken to be different for each local orbital component. Namely, each set of equivalent atoms and their m quantum numbers are assigmed a unique set of $\mathbf{K}$'s, usually just starting from the beginning of the list. For different atom types and different l's the reciprocal vectors repeat, so that for example each first atom of a new type and its first $m = -l$ will have $K_\nu = 0$ vector.

The matching conditions, which give continuous derivative of $\chi_{\mathbf{k}+\mathbf{K}}$ across S are

$$\begin{pmatrix} u_l(S) & \dot{u}_l(S) \\ \frac{d}{dr}u_l(S) & \frac{d}{dr}\dot{u}_l(S) \end{pmatrix} \begin{pmatrix} \bar{a}_l^{\mathbf{k}+\mathbf{K}} \\ \bar{b}_l^{\mathbf{k}+\mathbf{K}} \end{pmatrix} = \frac{1}{S^2} \begin{pmatrix} j_l(|\mathbf{k}+\mathbf{K}|S) \\ \frac{d}{dr}j_l(|\mathbf{k}+\mathbf{K}|S) \end{pmatrix} \tag{4}$$

with the solution

$$\begin{pmatrix} \bar{a}_l^{\mathbf{k}+\mathbf{K}} \\ \bar{b}_l^{\mathbf{k}+\mathbf{K}} \end{pmatrix} = \frac{1}{S^2} \begin{pmatrix} \frac{d}{dr}\dot{u}_l(S) & -\dot{u}_l(S) \\ -\frac{d}{dr}u_l(S) & u_l(S) \end{pmatrix} \frac{1}{u_l(S)\frac{d}{dr}\dot{u}_l(S) - \dot{u}_l(S)\frac{d}{dr}u_l(S)} \begin{pmatrix} j_l(|\mathbf{k}+\mathbf{K}|S) \\ \frac{d}{dr}j_l(|\mathbf{k}+\mathbf{K}|S) \end{pmatrix} \tag{5}$$

The two solutions satisfy the following equations

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{KS}(r) - E_\nu\right) r u_l(r) = 0 \tag{6}$$

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{KS}(r) - E_\nu\right) r \dot{u}_l(r) = r u_l(r) \tag{7}$$

We multiply the first equation by $r\dot{u}_l(r)$ and the second by $r u_l(r)$ to obtain

$$\int_0^S dr \left\{ r\dot{u}_l(r) \left(-\frac{d^2}{dr^2}\right) r u_l(r) - r u_l(r) \left(-\frac{d^2}{dr^2}\right) r\dot{u}_l(r) \right\} = -\int_0^S dr r^2 u_l(r) u_l(r) \tag{8}$$

Integration by parts gives

$$\left[-r\dot{u}_l(r)\frac{d}{dr}\left(ru_l(r)\right)+ru_l(r)\frac{d}{dr}\left(r\dot{u}_l(r)\right)\right]_0^S=-1 \tag{9}$$

which finally leads to

$$\dot{u}_l(S)\frac{d}{dr}u_l(S)-u_l(S)\frac{d}{dr}\dot{u}_l(S)=\frac{1}{S^2} \tag{10}$$

Hence, we can than simplify the solution for a_{lm} and b_{lm} to

$$\begin{pmatrix} \bar{a}_l^{\mathbf{k}+\mathbf{K}} \\ \bar{b}_l^{\mathbf{k}+\mathbf{K}} \end{pmatrix}=\begin{pmatrix} \dot{u}_l(S)\frac{d}{dr}j_l(|\mathbf{k}+\mathbf{K}|S)-\frac{d}{dr}\dot{u}_l(S)j_l(|\mathbf{k}+\mathbf{K}|S) \\ \frac{d}{dr}u_l(S)j_l(|\mathbf{k}+\mathbf{K}|S)-u_l(S)\frac{d}{dr}j_l(|\mathbf{k}+\mathbf{K}|S) \end{pmatrix} \tag{11}$$

This equation is implemented in Wien2k, and also in both dmft1 and dmft2 steps.

In the following we will many times use alternative shorter notation for these coefficients, namely,

$$\tilde{a}_{l\mathbf{K}}\equiv\bar{a}_l^{\mathbf{k}+\mathbf{K}} \tag{12}$$

$$\tilde{b}_{l\mathbf{K}}\equiv\bar{b}_l^{\mathbf{k}+\mathbf{K}} \tag{13}$$

To construct the basis functions u_l, the Hamiltonian in the muffin-thin sphere is solved in so-called spherical approximation to Kohn-Sham potential. The KS Hamiltonian has the form

$$H^{sph}=-\nabla^2+V_{KS}(\mathbf{r}) \tag{14}$$

where $V_{KS}(\mathbf{r})=V_{KS}^{sym}(r)+V_{KS}^{n-sym}(\mathbf{r})$ is split into spherically symmetryc and the rest. In the calculation we actually use an equivalent but more symmetric form of the kinetic energy operators, namely

$$T_{\mathbf{K}'\mathbf{K}}=\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle=\int_{\mathbf{r}}(\nabla\chi_{\mathbf{K}'}^*)\cdot(\nabla\chi_{\mathbf{K}})=\int_{\mathbf{r}}\nabla\cdot(\chi_{\mathbf{K}'}^*\nabla\chi_{\mathbf{K}})+\int\chi_{\mathbf{K}'}^*(-\nabla^2)\chi_{\mathbf{K}} \tag{15}$$

In the interstitials we use directly $\nabla\cdot\nabla$ operator, while in the MT-spheres, we need to add the surface term on the MT-sphere, i.e.,

$$\langle\chi_{\mathbf{K}'}|H^{sym}|\chi_{\mathbf{K}}\rangle_{MT}=\int_{MT}d\mathbf{r}\ \chi_{\mathbf{K}'}^*(-\nabla^2+V_{KS}^{sym})\chi_{\mathbf{K}}+\oint_{MT}d\vec{S}\chi_{\mathbf{K}'}^*\nabla_{\mathbf{r}}\chi_{\mathbf{K}} \tag{16}$$

(17)

To evaluate these terms in the MT-sphere, we first define

$$a_{lm\mathbf{K}}\equiv\bar{a}_l^{\mathbf{k}+\mathbf{K}}\ \frac{4\pi i^l S^2}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\mu}Y_{lm}^*(R_\mu(\mathbf{k}+\mathbf{K})) \tag{18}$$

$$b_{lm\mathbf{K}}\equiv\bar{b}_l^{\mathbf{k}+\mathbf{K}}\ \frac{4\pi i^l S^2}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\mu}Y_{lm}^*(R_\mu(\mathbf{k}+\mathbf{K})) \tag{19}$$

$$a_{\mathbf{K}_\nu,\nu,m,\mu}^{lo}\equiv a_\nu^{lo}\ \frac{4\pi i^l S^2}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K}_\nu)\mathbf{r}_\mu}Y_{lm}^*(R_\mu(\mathbf{k}+\mathbf{K}_\nu)) \tag{20}$$

$$b_{\mathbf{K}_\nu,\nu,m,\mu}^{lo}\equiv b_\nu^{lo}\ \frac{4\pi i^l S^2}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K}_\nu)\mathbf{r}_\mu}Y_{lm}^*(R_\mu(\mathbf{k}+\mathbf{K}_\nu)) \tag{21}$$

$$c_{\mathbf{K}_\nu,\nu,m,\mu}^{lo}\equiv c_\nu^{lo}\ \frac{4\pi i^l S^2}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K}_\nu)\mathbf{r}_\mu}Y_{lm}^*(R_\mu(\mathbf{k}+\mathbf{K}_\nu)) \tag{22}$$

(23)

We also define the following matrices of matrix elements

$$\mathcal{H}\equiv\left(\begin{array}{c|c|c} E_l-\varepsilon & \frac{1}{2} & \left(\frac{E_l+E_l'}{2}-\varepsilon\right)\langle u_l|u_l^{LO}\rangle \\ \hline \frac{1}{2} & (E_l-\varepsilon)\langle\dot{u}|\dot{u}\rangle & \left(\frac{E_l+E_l'}{2}-\varepsilon\right)\langle\dot{u}|u^{LO}\rangle+\frac{1}{2}\langle u_l|u_l^{LO}\rangle \\ \hline \left(\frac{E_l+E_l'}{2}-\varepsilon\right)\langle u_l|u_l^{LO}\rangle & \left(\frac{E_l+E_l'}{2}-\varepsilon\right)\langle\dot{u}_l|u_l^{LO}\rangle+\frac{1}{2}\langle u_l|u_l^{LO}\rangle & (E'_l-\varepsilon)\langle u_l^{LO}|u_l^{LO}\rangle \end{array}\right) \tag{24}$$

and for the surface term

$$\mathcal{H}^S = S^2 \left(\begin{array}{c|c|c} u_l \frac{du_l}{dr} & \frac{1}{2S^2} + u_l \frac{d\dot{u}_l}{dr} & \frac{1}{2}\left[u_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{du_l}{dr}\right] \\ \hline \frac{1}{2S^2} + u_l \frac{d\dot{u}_l}{dr} & \dot{u}_l \frac{d\dot{u}_l}{dr} & \frac{1}{2}\left[\dot{u}_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{d\dot{u}_l}{dr}\right] \\ \hline \frac{1}{2}\left[u_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{du_l}{dr}\right] & \frac{1}{2}\left[\dot{u}_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{d\dot{u}_l}{dr}\right] & u_l^{LO} \frac{du_l^{LO}}{dr} \end{array} \right)_{r=S} \tag{25}$$

The matrices correspond to $(\langle u_l^{\kappa'}|H_{sym} - \varepsilon|u_l^{\kappa}\rangle + \langle u_l^{\kappa}|H_{sym} - \varepsilon|u_l^{\kappa'}\rangle^*)/2$, where κ runs over $[u, \dot{u}, u^{LO}]$. The derivation of these matrix elements will become clear below. Note also that the $\mathcal{H}_{12}^S$ term looks different, but we could cast it into more symmetric form using Eq. 10, namely $\mathcal{H}_{12}^S = \frac{1}{2}[u_l \frac{d\dot{u}_l}{dr} + \dot{u}_l \frac{du_l}{dr}]$ so that the matrix is

$$\mathcal{H}^S = S^2 \left(\begin{array}{c|c|c} u_l \frac{du_l}{dr} & \frac{1}{2}[u_l \frac{d\dot{u}_l}{dr} + \dot{u}_l \frac{du_l}{dr}] & \frac{1}{2}\left[u_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{du_l}{dr}\right] \\ \hline \frac{1}{2}[u_l \frac{d\dot{u}_l}{dr} + \dot{u}_l \frac{du_l}{dr}] & \dot{u}_l \frac{d\dot{u}_l}{dr} & \frac{1}{2}\left[\dot{u}_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{d\dot{u}_l}{dr}\right] \\ \hline \frac{1}{2}\left[u_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{du_l}{dr}\right] & \frac{1}{2}\left[\dot{u}_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{d\dot{u}_l}{dr}\right] & u_l^{LO} \frac{du_l^{LO}}{dr} \end{array} \right)_{r=S} \tag{26}$$

Using Eq. 6 and 7 we can evaluate the Hamiltonian in the MT-sphere. First we calculate the terms without local orbitals:

$$\langle \chi_{\mathbf{K}'}|H^{sym} - \varepsilon|\chi_{\mathbf{K}}\rangle_{MT} = \int_{MT} d\mathbf{r}\; \chi_{\mathbf{K}'}^*(-\nabla^2 + V_{KS}^{sym} - \varepsilon)\chi_{\mathbf{K}} + \oint_{MT} d\vec{S}\chi_{\mathbf{K}'}^*\nabla_{\mathbf{r}}\chi_{\mathbf{K}} \tag{27}$$

$$= \sum_{lm} \int_{MT} d\mathbf{r}\; Y_{lm}^*(\mathbf{r})(a_{lm\mathbf{K}'}^* u_l + b_{lm\mathbf{K}'}^*\dot{u}_l)(-\nabla^2 + V_{KS}^{sym} - \varepsilon)(a_{lm\mathbf{K}}u_l + b_{lm\mathbf{K}}\dot{u}_l)Y_{lm}(\mathbf{r})$$

$$+S^2 \sum_{lm} \int_{MT} d\Omega(a_{lm\mathbf{K}'}^* u_l(S) + b_{lm\mathbf{K}'}^*\dot{u}_l(S))(a_{lm\mathbf{K}}\frac{du_l(S)}{dr} + b_{lm\mathbf{K}}\frac{d\dot{u}_l(S)}{dr})Y_{lm}^* Y_{lm}$$

$$= \sum_{lm} \int_{MT} dr(a_{lm\mathbf{K}'}^* u_l + b_{lm\mathbf{K}'}^*\dot{u}_l)\left[(E_l - \varepsilon)(a_{lm\mathbf{K}}u_l + b_{lm\mathbf{K}}\dot{u}_l) + b_{lm\mathbf{K}}u_l\right]$$

$$+S^2 \sum_{lm}(a_{lm\mathbf{K}'}^* u_l(S) + b_{lm\mathbf{K}'}^*\dot{u}_l(S))(a_{lm\mathbf{K}}\frac{du_l(S)}{dr} + b_{lm\mathbf{K}}\frac{d\dot{u}_l(S)}{dr})$$

$$= \sum_{lm}(E_l - \varepsilon)(a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}}\langle\dot{u}_l|\dot{u}_l\rangle) + a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} \tag{28}$$

$$+S^2 \sum_{lm}\left(a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}}u_l(S)\frac{du_l(S)}{dr} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}}\dot{u}_l(S)\frac{d\dot{u}_l(S)}{dr} + a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}}u_l(S)\frac{d\dot{u}_l(S)}{dr} + b_{lm\mathbf{K}'}^* a_{lm\mathbf{K}}\dot{u}_l(S)\frac{du_l(S)}{dr}\right)$$

Here we center the origin on studied atom, and assume that the axis was properly rotated to the local coordinate axis. We know that

$$\dot{u}(S)\frac{du(S)}{dr} - u(S)\frac{d\dot{u}(S)}{dr} = \frac{1}{S^2} \tag{29}$$

hence we can use this identity in the last term to obtain more symmetric result

$$\begin{aligned} \langle \chi_{\mathbf{K}'}|H^{sym} - \varepsilon|\chi_{\mathbf{K}}\rangle_{MT} &= (E_l - \varepsilon)(a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}}\langle\dot{u}_l|\dot{u}_l\rangle) + a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} \\ &+ S^2\left(a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}}u_l(S)\frac{du_l(S)}{dr} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}}\dot{u}_l(S)\frac{d\dot{u}_l(S)}{dr} + (a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* a_{lm\mathbf{K}})u_l(S)\frac{d\dot{u}_l(S)}{dr}\right) \end{aligned} \tag{30}$$

We can cast this equation into the following matrix form

$$\langle \chi_{\mathbf{K}'}|H^{sym} - \varepsilon|\chi_{\mathbf{K}}\rangle_{MT} = \begin{pmatrix} a_{lm\mathbf{K}'}^* & b_{lm\mathbf{K}'}^* & 0 \end{pmatrix}(\mathcal{H} + \mathcal{H}^S)\begin{pmatrix} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ 0 \end{pmatrix} \tag{31}$$

Next we calculate the local-orbital part. The mixed term of the Hamiltonian is symmetrize and takes the form

$$\widetilde{H}_{\mathbf{K}\nu} \equiv \frac{1}{2}\langle\chi_{\mathbf{K}}|H^{sym} - \varepsilon|\chi_\nu\rangle_{MT} + \frac{1}{2}\langle\chi_\nu|H^{sym} - \varepsilon|\chi_{\mathbf{K}}\rangle_{MT}^* = \tag{32}$$

$$\frac{1}{2}\int_{MT} d\mathbf{r}[\chi_{\mathbf{K}}^*(-\nabla^2 + V_{KS}^{sym} - \varepsilon)\chi_\nu + \chi_\nu(-\nabla^2 + V_{KS}^{sym} - \varepsilon)\chi_{\mathbf{K}}^*] + \frac{1}{2}\oint_{MT} d\vec{S}[\chi_{\mathbf{K}}^*\nabla_{\mathbf{r}}\chi_\nu + \chi_\nu\nabla_{\mathbf{r}}\chi_{\mathbf{K}}^*] \tag{33}$$

$$\widetilde{H}_{\mathbf{K}\nu} = \frac{(4\pi S^2)^2}{V} \sum_{m'\mu'} e^{i(\mathbf{K}_\nu - \mathbf{K})\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k})) Y^*_{lm'}(R_{\mu'}(\mathbf{K}_\nu + \mathbf{k})) \tag{34}$$

$$\times \left(\overline{\langle a^{lo}_\nu u_l + b^{lo}_\nu \dot{u}_l + c^{lo}_\nu u^{LO}_l | H - \varepsilon | \tilde{a}_{l\mathbf{K}} u_l + \tilde{b}_{l\mathbf{K}} \dot{u}_l \rangle} \right. \tag{35}$$

$$\left. + \frac{S^2}{2} \left((\tilde{a}_{l\mathbf{K}} u_l + \tilde{b}_{l\mathbf{K}} \dot{u}_l) \frac{du^{local}_l}{dr} + u^{local}_l \frac{d(\tilde{a}_{l\mathbf{K}} u_l + \tilde{b}_{l\mathbf{K}} \dot{u}_l)}{dr} \right) \Big|_{r=S} \right) \tag{36}$$

Here overline means symmetrize the matrix elements. Note that u^{loc}_ν is the orbital which vanishes at the MT-boundary

$$u^{loc}_\nu(r) = a^{lo}_\nu u_l(r) + b^{lo}_\nu \dot{u}(r) + c^{lo}_\nu u^{LO}_l \tag{37}$$

and hence we can drop the last term of Eq. 36. But in this derivation we will keep it, so that the result is more symmetric. We will again use the identity

$$\dot{u}_l(S) \frac{du_l(S)}{dr} = u_l(S) \frac{d\dot{u}_l(S)}{dr} + \frac{1}{S^2} \tag{38}$$

to obtain a symmetric form of the surface term

$$\frac{S^2}{2} (\tilde{a}_{l\mathbf{K}} u_l(S) + \tilde{b}_{l\mathbf{K}} \dot{u}_l(S)) \frac{du^{local}_l}{dr} + \frac{S^2}{2} u^{local}_l \frac{d(\tilde{a}_{l\mathbf{K}} u_l + \tilde{b}_{l\mathbf{K}} \dot{u}_l)}{dr} = \tag{39}$$

$$\tilde{a}_{l\mathbf{K}} a^{lo}_\nu S^2 u_l(S) \frac{du_l(S)}{dr} + \tilde{b}_{l\mathbf{K}} b^{lo}_\nu S^2 \dot{u}_l(S) \frac{d\dot{u}_l(S)}{dr} \tag{40}$$

$$+ (\tilde{a}_{l\mathbf{K}} b^{lo}_\nu + \tilde{b}_{l\mathbf{K}} a^{lo}_\nu)(\frac{1}{2} + S^2 u_l(S) \frac{d\dot{u}_l(S)}{dr}) \tag{41}$$

$$+ \tilde{a}_{l\mathbf{K}} c^{lo}_\nu \frac{S^2}{2} (u_l(S) \frac{du^{LO}_l(S)}{dr} + u^{LO}_l(S) \frac{u_l}{dr}) \tag{42}$$

$$+ \tilde{b}_{l\mathbf{K}} c^{lo}_\nu \frac{S^2}{2} (\dot{u}_l(S) \frac{du^{LO}(S)}{dr} + u^{LO}_l(S) \frac{\dot{u}_l}{dr}) \tag{43}$$

$$\tag{44}$$

Next we need the action of the Hamiltonian operator on the local orbital

$$(-\nabla^2 + V_{sym} - \varepsilon) u^{loc}_\nu(r) = a^{lo}_\nu u_l \; (E_l - \varepsilon) + b^{lo}_\nu (\dot{u}_l (E_l - \varepsilon) + u_l) + c^{lo}_\nu u^{LO}_l (E'_l - \varepsilon) = \tag{45}$$

$$(a^{lo}_\nu (E_l - \varepsilon) + b^{lo}_\nu) u_l + b^{lo}_\nu (E_l - \varepsilon) \dot{u}_l + c^{lo}_\nu (E'_l - \varepsilon) u^{LO}_l \tag{46}$$

and we also use the action of H on LAPW

$$(-\nabla^2 + V_{sym} - \varepsilon) u_l = (E_l - \varepsilon) u_l \tag{47}$$

$$(-\nabla^2 + V_{sym} - \varepsilon) \dot{u}_l = (E_l - \varepsilon) \dot{u}_l + u_l \tag{48}$$

We hence get the following expression (in the form used in lapw1)

$$\widetilde{H}_{\mathbf{K}\nu} = \frac{(4\pi S^2)^2}{V} \sum_{m'\mu'} e^{i(\mathbf{K}_\nu - \mathbf{K})\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k})) Y^*_{lm'}(R_{\mu'}(\mathbf{K}_\nu + \mathbf{k})) \times \tag{49}$$

$$\times \left[\tilde{a}_{l\mathbf{K}} (C^\nu_{11} + u_l(S) k_{inlo}) + \tilde{b}_{l\mathbf{K}} (C^\nu_{12} + \dot{u}_l(S) k_{inlo}) \right] \tag{50}$$

$$C^\nu_{11} = \frac{1}{2} (\langle u^{loc}_\nu | H_{sym} - \varepsilon | u_l \rangle + \langle u_l | H_{sym} - \varepsilon | u^{loc}_\nu \rangle) = a^{lo}_\nu (E_l - \varepsilon) + \frac{1}{2} b^{lo}_\nu + c^{lo}_\nu \langle u | u^{LO} \rangle \left(\frac{E_l + E'_l}{2} - \varepsilon \right) \tag{51}$$

$$C^\nu_{12} = \frac{1}{2} (\langle u^{loc}_\nu | H_{sym} - \varepsilon | \dot{u}_l \rangle + \langle \dot{u}_l | H_{sym} - \varepsilon | u^{loc}_\nu \rangle) =$$

$$= b^{lo}_\nu \langle \dot{u}_l | \dot{u}_l \rangle (E_l - \varepsilon) + c^{lo}_\nu \langle \dot{u}_l | u^{LO} \rangle \left(\frac{E_l + E'_l}{2} - \varepsilon \right) + \frac{1}{2} a^{lo}_\nu + \frac{1}{2} c^{lo}_\nu \langle u_l | u^{LO}_l \rangle \tag{52}$$

$$k_{inlo} = \frac{1}{2} S^2 \frac{du^{loc}_\nu(r)}{dr} |_{r=S} \tag{53}$$

Inserting the above quantities into the previous equation, we get an equivalent expression

$$\widetilde{H}_{\mathbf{K}\nu} = \sum_{m'\mu'} \begin{pmatrix} a^*_{lm'\mu'\mathbf{K}} & b^*_{lm'\mu'\mathbf{K}} & 0 \end{pmatrix} (\mathcal{H}+\mathcal{H}^S) \begin{pmatrix} a^{lo}_{\mathbf{K}_\nu,\nu,m',\mu'} \\ b^{lo}_{\mathbf{K}_\nu,\nu,m',\mu'} \\ c^{lo}_{\mathbf{K}_\nu,\nu,m',\mu'} \end{pmatrix} \tag{54}$$

Finally, we work our the local-orbital part of the form

$$\widetilde{H}_{\nu\nu'} \equiv \frac{1}{2}(\langle\chi_\nu|H^{sym}-\varepsilon|\chi_{\nu'}\rangle + \langle\chi_{\nu'}|H^{sym}-\varepsilon|\chi_\nu\rangle^*) \tag{55}$$

First we recognize

$$\langle\chi_\nu|H^{sym}-\varepsilon|\chi_{\nu'}\rangle = \frac{(4\pi S^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}_{\nu'}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y^*_{lm'}(R_{\mu'}(\mathbf{K}_{\nu'}+\mathbf{k}))Y_{lm'}(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k}))\times \tag{56}$$

$$(a^{lo}_\nu\langle u_l|H-\varepsilon|u^{loc}_{\nu'}\rangle + b^{lo}_\nu\langle\dot{u}_l|H-\varepsilon|u^{loc}_{\nu'}\rangle + c^{lo}_\nu\langle u^{LO}_l|H-\varepsilon|u^{loc}_{\nu'}\rangle) \tag{57}$$

and hence

$$\widetilde{H}_{\nu\nu'} = \frac{(4\pi S^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}_{\nu'}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y^*_{lm'}(R_{\mu'}(\mathbf{K}_{\nu'}+\mathbf{k}))Y_{lm'}(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k}))\times \begin{pmatrix} a^{lo}_\nu, & b^{lo}_\nu & c^{lo}_\nu \end{pmatrix} \mathcal{H} \begin{pmatrix} a^{lo}_{\nu'} \\ b^{lo}_{\nu'} \\ c^{lo}_{\nu'} \end{pmatrix} \tag{58}$$

In more compact form we can write

$$\widetilde{H}_{\nu\nu'} = \sum_{m''\mu''} \begin{pmatrix} a^{lo\,*}_{\mathbf{K}_\nu,\nu,m'',\mu''}, & b^{lo\,*}_{\mathbf{K}_\nu,\nu,m'',\mu''} & c^{lo\,*}_{\mathbf{K}_\nu,\nu,m''\mu''} \end{pmatrix} \mathcal{H} \begin{pmatrix} a^{lo}_{\mathbf{K}_{\nu'},\nu',m'',\mu''} \\ b^{lo}_{\mathbf{K}_{\nu'},\nu',m'',\mu''} \\ c^{lo}_{\mathbf{K}_{\nu'},\nu',m'',\mu''} \end{pmatrix} \tag{59}$$

The surface term vanishes here, as we are evaluating terms like $u^{loc}_{\nu'}(S)\frac{d}{dr}u^{loc}_\nu(S)$. We can therefore add to $\mathcal{H}$ the surface term $\mathcal{H}^S$ without changing the result. Namely, we could send $\mathcal{H}\to\mathcal{H}+\mathcal{H}^S$ in Eq. 59.

We will need quantities like

$$\sum_{\mathbf{K}'\mathbf{K}} A^\dagger_{i\mathbf{K}'}\widetilde{H}_{\mathbf{K}'\mathbf{K}}A_{\mathbf{K}j} \tag{60}$$

where $A_{\mathbf{K}i}$ are KS-eigenvectors and $\mathbf{K}$ runs over reciprocal vectors as well as local orbitals. Since $\mathcal{H}$ is equal in all terms, we can simplify

$$\begin{pmatrix} \sum_{\mathbf{K}'} A^\dagger_{i\mathbf{K}'}a^*_{lm\mu\mathbf{K}'} + \sum_{\mathbf{K}_\nu} A^\dagger_{i\mathbf{K}_\nu}a^{lo\,*}_{\mathbf{K}_\nu,\nu,m\mu} \\ \sum_{\mathbf{K}'} A^\dagger_{i\mathbf{K}'}b^*_{lm\mu\mathbf{K}'} + \sum_{\mathbf{K}_\nu} A^\dagger_{i\mathbf{K}_\nu}b^{lo\,*}_{\mathbf{K}_\nu,\nu,m\mu} \\ \sum_{\mathbf{K}_\nu} A^\dagger_{i\mathbf{K}_\nu}c^{lo\,*}_{\mathbf{K}_\nu,\nu,m\mu} \end{pmatrix} \mathcal{H} \begin{pmatrix} \sum_{\mathbf{K}} a_{lm\mu\mathbf{K}}A_{\mathbf{K}j} + \sum_{\mathbf{K}_\nu} a^{lo}_{\mathbf{K}_\nu,\nu,m\mu}A_{\mathbf{K}_\nu j} \\ \sum_{\mathbf{K}} b_{lm\mu\mathbf{K}}A_{\mathbf{K}j} + \sum_{\mathbf{K}_\nu} b^{lo}_{\mathbf{K}_\nu,\nu,m\mu}A_{\mathbf{K}_\nu j} \\ \sum_{\mathbf{K}_\nu} c^{lo}_{\mathbf{K}_\nu,\nu,m\mu}A_{\mathbf{K}_\nu j} \end{pmatrix} \tag{61}$$

and if we call

$$\begin{pmatrix} a_{i,lm\mu} \\ b_{i,lm\mu} \\ c_{i,lm\mu} \end{pmatrix} \equiv \begin{pmatrix} \sum_{\mathbf{K}} a_{lm\mu\mathbf{K}}A_{\mathbf{K}j} + \sum_{\mathbf{K}_\nu} a^{lo}_{\mathbf{K}_\nu,\nu,m\mu}A_{\mathbf{K}_\nu j} \\ \sum_{\mathbf{K}} b_{lm\mu\mathbf{K}}A_{\mathbf{K}j} + \sum_{\mathbf{K}_\nu} b^{lo}_{\mathbf{K}_\nu,\nu,m\mu}A_{\mathbf{K}_\nu j} \\ \sum_{\mathbf{K}_\nu} c^{lo}_{\mathbf{K}_\nu,\nu,m\mu}A_{\mathbf{K}_\nu j} \end{pmatrix} \tag{62}$$

we get

$$\begin{pmatrix} a^*_{i,lm\mu} \\ b^*_{i,lm\mu} \\ c^*_{i,lm\mu} \end{pmatrix} \mathcal{H} \begin{pmatrix} a_{j,lm\mu} \\ b_{j,lm\mu} \\ c_{j,lm\mu} \end{pmatrix} \tag{63}$$

——————— BELOW IS THE OLD TEXT, WHICH IS WRONG ———————

$$(H^{sph}-\varepsilon)\left|\chi_{\mathbf{K}}\right\rangle = Y_{lm}(\hat{\mathbf{r}})[a^{\mathbf{K}}_{lm}(E_l-\varepsilon)u_l(r)+b^{\mathbf{K}}_{lm}(E_l-\varepsilon)\dot{u}_l(r)+b^{\mathbf{K}}_{lm}u_l(r)] \tag{64}$$

Here we center the origin on studied atom, and assume that the axis was properly rotated to the local coordinate axis.

The Hamiltonian is then given by

$$\langle\chi_{\mathbf{K}'}|H^{sph}-\varepsilon|\chi_{\mathbf{K}}\rangle = \int dr[a^{\mathbf{K}'*}_{lm}u_l(r)+b^{\mathbf{K}'*}_{lm}\dot{u}_l(r)+c^{\mathbf{K}'*}_{lm}u_{LO}(r)][a^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)u_l(r)+b^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)\dot{u}_l(r)+b^{\mathbf{K}}_{lm}u_l(r)+c^{\mathbf{K}}_{lm}(E_\mu-\varepsilon)u_{LO}(r)] \tag{65}$$

which gives

$$\begin{aligned}\langle\chi_{\mathbf{K}'}|H^{sph}-\varepsilon|\chi_{\mathbf{K}}\rangle &= a^{\mathbf{K}'*}_{lm}[a^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)+b^{\mathbf{K}}_{lm}+c^{\mathbf{K}}_{lm}(E_\mu-\varepsilon)\left\langle u|u_{LO}\right\rangle]\\ &+ b^{\mathbf{K}'*}_{lm}[b^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)\left\langle\dot{u}_l|\dot{u}_l\right\rangle+c^{\mathbf{K}}_{lm}(E_\mu-\varepsilon)\left\langle\dot{u}_l|u_{LO}\right\rangle]\\ &+ c^{\mathbf{K}'*}_{lm}[a^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)\left\langle u_{LO}|u_l\right\rangle+b^{\mathbf{K}}_{lm}\left\langle u_{LO}|u_l\right\rangle+b^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)\left\langle u_{LO}|\dot{u}_l\right\rangle+c^{\mathbf{K}}_{lm}(E_\mu-\varepsilon)]\end{aligned} \tag{66}$$

Here we used the relation $\langle u_l|\dot{u}_l\rangle=0$. The Hamiltonian is Hermitian, but in its current form appears non-Hermitian, hence we will symmetrize it,

$$\begin{aligned}\langle\chi_{\mathbf{K}'}|H^{sph}-\varepsilon|\chi_{\mathbf{K}}\rangle &= a^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)+\frac{1}{2}[a^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}+b^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}]+\frac{1}{2}[a^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}+c^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}](E_\mu-\varepsilon)\left\langle u|u_{LO}\right\rangle+\\ &+ b^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)\left\langle\dot{u}_l|\dot{u}_l\right\rangle+\frac{1}{2}[b^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}+c^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}](E_\mu-\varepsilon)\left\langle\dot{u}_l|u_{LO}\right\rangle+\\ &+ \frac{1}{2}[c^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}+a^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}](E_\nu-\varepsilon)\left\langle u_{LO}|u_l\right\rangle+\frac{1}{2}[c^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}+b^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}][\left\langle u_{LO}|u_l\right\rangle+(E_\nu-\varepsilon)\left\langle u_{LO}|\dot{u}_l\right\rangle]+c^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}(E_\mu-\varepsilon)\end{aligned}$$

which is simlified to

$$\begin{aligned}\langle\chi_{\mathbf{K}'}|H^{sph}-\varepsilon|\chi_{\mathbf{K}}\rangle &= a^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)+b^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)\left\langle\dot{u}_l|\dot{u}_l\right\rangle+\frac{1}{2}[a^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}+b^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}]+\\ &+ c^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}(E_\mu-\varepsilon)+\frac{1}{2}[a^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}+c^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}](E_\mu+E_\nu-2\varepsilon)\left\langle u|u_{LO}\right\rangle+\\ &+ \frac{1}{2}[c^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}+b^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}][\left\langle u_{LO}|u_l\right\rangle+(E_\mu+E_\nu-2\varepsilon)\left\langle u_{LO}|\dot{u}_l\right\rangle]\end{aligned} \tag{67}$$

——————— END THE OLD TEXT ———————

1. *Extra term when using APW+lo*

For efficiency, wien2k uses APW+lo for many atoms (and for others LAPW), because less plane waves is needed in this case. The basis function in the MT part looks similar, except that $b_{lm}=0$, i.e.,

$$\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \left(a_{lm}u_l(|\mathbf{r}-\mathbf{r}_\alpha|)+c_{lm}u^{loc}(|\mathbf{r}-\mathbf{r}_\alpha|)\right)Y_{lm}(R(\hat{\mathbf{r}}-\hat{\mathbf{r}_\alpha})) \qquad MT-sphere \tag{68}$$

As u^{loc} vanishes at R_{MT} only the value of $\chi_{\mathbf{k}+\mathbf{K}}$ is matched to determine a_{lm}:

$$a_{lm} = \frac{4\pi i^l}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\alpha}Y^*_{lm}(R(\hat{\mathbf{k}}+\hat{\mathbf{K}}))j_l(|\mathbf{k}+\mathbf{K}|S)/u_l(S) \tag{69}$$

However, $u^{loc}(r)$ is constructed differently in APW+lo. In LAPW method, $u^{loc}(r)$ is constructed from u_l, $\dot{u}_l$ and u_l^2, where u_l^2 is linearized solution at some other energy E'_l, different from E_l. To costruct u^{loc}, however, we use just the combination of u_l and $\dot{u}_l$ only, i.e., $u^{loc}=\alpha u_l+\beta\dot{u}_l$. The combination of these two function suffices to achieve $u^{loc}(S)=0$ and $\int|u^{loc}|^2dr=1$. The dissadvatage of this basis is that the derivative of $\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$ across the MT-boundary is not continuous, hence additionsl term in the Hamiltonian and forces is present. But since the convergence with plane-wave cut-off is better, this is a small price to pay.

The form of the kinetic operator used in the interstitials is

$$T_{\mathbf{K}'\mathbf{K}} = \int d^3r(\nabla\chi^*_{\mathbf{K}'})(\nabla\chi_{\mathbf{K}}), \tag{70}$$

while in the MT-sphere, we use the alternative form $\langle\chi| - \nabla^2|\chi\rangle$. Using Stokes theorem, we can always change between the two forms

$$(\nabla\chi^*_{\mathbf{K}'})(\nabla\chi_{\mathbf{K}}) = \nabla\cdot(\chi^*_{\mathbf{K}'}\,\nabla\chi_{\mathbf{K}}) + \chi^*_{\mathbf{K}'}\,(-\nabla^2)\chi_{\mathbf{K}} \tag{71}$$

hence

$$\int d^3r(\nabla\chi^*_{\mathbf{K}'})(\nabla\chi_{\mathbf{K}}) = \int d^3r\chi^*_{\mathbf{K}'}\,(-\nabla^2)\chi_{\mathbf{K}} + \oint \vec{S}\,(\chi^*_{\mathbf{K}'}\,\nabla\chi_{\mathbf{K}}) \tag{72}$$

We use this for the MT-sphere part, and whenewer T needs to be evaluated, we add this extra surface term

$$\int_{MT} d^3r(\nabla\chi^*_{\mathbf{K}'})(\nabla\chi_{\mathbf{K}}) = \int_{MT} d^3r\chi^*_{\mathbf{K}'}\,(-\nabla^2)\chi_{\mathbf{K}} + \oint_{MT} d\vec{S}\,(\chi^*_{\mathbf{K}'}\,\nabla\chi_{\mathbf{K}}) \tag{73}$$

Discussion about this can be found in PRB **64**, 195134 (2001) in appendix.

II. FORCES

We start with DFT forces in LAPW. The DFT functional is

$$E = \mathrm{Tr}(-\nabla^2 G) + E_H[\rho] + E_{xc}[\rho] + \mathrm{Tr}[\rho V_{nucleous}] + E_{nucleous} \tag{74}$$

Here $E_{nucleous} = \frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}$ and $V_{nucleous}(\mathbf{r}) = -\sum_\alpha \frac{Z_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|}$

We can rearange the functional using the eigenvalues in the DFT solution

$$(-\nabla^2 + V_{KS} - \varepsilon_i)\,|\psi_{i\mathbf{k}}\rangle = 0 \tag{75}$$

and get

$$E = \mathrm{Tr}(\varepsilon_i G) - \mathrm{Tr}(V_{KS}\rho) + E_H[\rho] + E_{xc}[\rho] + \mathrm{Tr}[\rho V_{nucleous}] + E_{nucleous} = \tag{76}$$

$$\sum_i \varepsilon_i f_i - \mathrm{Tr}(V_{KS}\rho) + E_H[\rho] + E_{xc}[\rho] + \mathrm{Tr}[\rho V_{nucleous}] + E_{nucleous} \tag{77}$$

This is the equation being implemented, hence we have to look at small variation of this functional with respect to small movement of a nucleous $\delta\mathbf{R}_\alpha$.

We get Helman-Feynman forces $\mathbf{F}^{HF}$ by varying the following two terms

$$\frac{\delta E_{nucleous}}{\delta\mathbf{R}_\alpha} + \mathrm{Tr}(\rho\frac{\delta V_{nucleous}}{\delta\mathbf{R}_\alpha}) = -\mathbf{F}^{HF}_\alpha \tag{78}$$

The rest of the variations can contribute to Pulley forces

$$\delta E = \sum_i \delta\varepsilon_i f_i - \mathrm{Tr}(\rho\delta V_{KS}) - \mathrm{Tr}(V_{KS}\delta\rho) + \mathrm{Tr}(V_H\delta\rho) + \mathrm{Tr}(V_{xc}\delta\rho) + \mathrm{Tr}[V_{nucleous}\delta\rho] - \sum_\alpha \mathbf{F}^{HF}_\alpha\delta\mathbf{R}_\alpha \tag{79}$$

Notice that we did not varry f_i. This is because such term would contribute to entropy, which we neglected here anyway. Within DMFT, this has to be handled correctly. The terms 2-6 are all computed in real space with numeric integration, so we can safely cancel terms 3-6, since they are computed in exactly the same way. We get

$$\delta E = \sum_i \delta\varepsilon_i f_i - \mathrm{Tr}(\rho\delta V_{KS}) - \sum_\alpha \mathbf{F}^{HF}_\alpha\delta\mathbf{R}_\alpha \tag{80}$$

The first two terms do not cancel because of the discretization using LAPW basis set in computing eigenvalues.

To get variation of eigenvalues, we need to follow their computation, which is achieved through the following diagonalization

$$\sum_{\mathbf{K}\mathbf{K}'} A^*_{i,\mathbf{K}'}(H_{\mathbf{K}'\mathbf{K}} - \varepsilon_i O_{\mathbf{K}'\mathbf{K}})A_{i,\mathbf{K}} = 0 \tag{81}$$

Even when atoms move, this equation remains satisfied, hence variation of the equation has to vanish. The variation gives

$$0=\sum_{\mathbf{K}\mathbf{K}'}\delta A^*_{i,\mathbf{K}'}(H_{\mathbf{K}'\mathbf{K}}-\varepsilon_i O_{\mathbf{K}'\mathbf{K}})A_{i,\mathbf{K}}+A^*_{i,\mathbf{K}'}(H_{\mathbf{K}'\mathbf{K}}-\varepsilon_i O_{\mathbf{K}'\mathbf{K}})\delta A_{i,\mathbf{K}}+A^*_{i,\mathbf{K}'}(\delta H_{\mathbf{K}'\mathbf{K}}-\varepsilon_i \delta O_{\mathbf{K}'\mathbf{K}})A_{i,\mathbf{K}}-A^*_{i,\mathbf{K}'}O_{\mathbf{K}'\mathbf{K}}A_{i,\mathbf{K}}\delta\varepsilon_i$$

The first two terms vanish, the term $\sum_{\mathbf{K}\mathbf{K}'}A^*_{i,\mathbf{K}'}O_{\mathbf{K}'\mathbf{K}}A_{i,\mathbf{K}}=1$, hence

$$\delta\varepsilon_i=\sum_{\mathbf{K},\mathbf{K}'}A^*_{i,\mathbf{K}'}(\delta H_{\mathbf{K}'\mathbf{K}}-\varepsilon_i\delta O_{\mathbf{K}'\mathbf{K}})A_{i,\mathbf{K}} \tag{82}$$

Next we vary Hamiltonian and overlap

$$\delta\langle\chi_{\mathbf{K}'}|H|\chi_{\mathbf{K}}\rangle=\langle\delta\chi_{\mathbf{K}'}|H|\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|H|\delta\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|\delta H|\chi_{\mathbf{K}}\rangle \tag{83}$$

$$\delta\langle\chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle=\langle\delta\chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|\delta\chi_{\mathbf{K}}\rangle \tag{84}$$

to obtain

$$\delta\varepsilon_i=\sum_{\mathbf{K},\mathbf{K}'}A^*_{i,\mathbf{K}'}\left(\langle\delta\chi_{\mathbf{K}'}|H-\varepsilon_i|\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|H-\varepsilon_i|\delta\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|\delta H|\chi_{\mathbf{K}}\rangle\right)A_{i,\mathbf{K}} \tag{85}$$

Putting all terms together gives

$$\delta E=\sum_i f_i\sum_{\mathbf{K},\mathbf{K}'}A^*_{i,\mathbf{K}'}\left(\langle\delta\chi_{\mathbf{K}'}|H-\varepsilon_i|\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|H-\varepsilon_i|\delta\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|\delta H|\chi_{\mathbf{K}}\rangle\right)A_{i,\mathbf{K}}-\mathrm{Tr}(\rho\delta V_{KS})-\sum_\alpha\mathbf{F}^{HF}_\alpha\delta\mathbf{R}_\alpha \tag{86}$$

and hence Pulley forces are

$$\mathbf{F}^{Pulley}_\alpha=-\sum_i f_i\sum_{\mathbf{K},\mathbf{K}'}A^*_{i,\mathbf{K}'}\left(\langle\frac{\delta\chi_{\mathbf{K}'}}{\delta\mathbf{R}_\alpha}|H-\varepsilon_i|\chi_{\mathbf{K}}\rangle+\langle\chi_{\mathbf{K}'}|H-\varepsilon_i|\frac{\delta\chi_{\mathbf{K}}}{\delta\mathbf{R}_\alpha}\rangle+\langle\chi_{\mathbf{K}'}|\frac{\delta}{\delta\mathbf{R}_\alpha}H|\chi_{\mathbf{K}}\rangle\right)A_{i,\mathbf{K}}+\mathrm{Tr}(\rho\frac{\delta V_{KS}}{\delta\mathbf{R}_\alpha}) \tag{87}$$

which can also be written as

$$\mathbf{F}^{Pulley}_\alpha=-\sum_i f_i\left(\langle\frac{\partial\psi_{i\mathbf{k}}}{\partial\mathbf{R}_\alpha}|H-\varepsilon_i|\psi_{i\mathbf{k}}\rangle+\langle\psi_{i\mathbf{k}}|H-\varepsilon_i|\frac{\partial\psi_{i\mathbf{k}}}{\partial\mathbf{R}_\alpha}\rangle+\langle\psi_{i\mathbf{k}}|\frac{\delta}{\delta\mathbf{R}_\alpha}H|\psi_{i\mathbf{k}}\rangle\right)+\mathrm{Tr}(\rho\frac{\delta V_{KS}}{\delta\mathbf{R}_\alpha}) \tag{88}$$

Here

$$\langle\psi_{i\mathbf{k}}|\frac{\delta}{\delta\mathbf{R}_\alpha}H|\psi_{i\mathbf{k}}\rangle=\langle\psi_{i\mathbf{k}}|\frac{\delta V_{KS}}{\delta\mathbf{R}_\alpha}|\psi_{i\mathbf{k}}\rangle+\langle\psi_{i\mathbf{k}}|\frac{\delta T}{\delta\mathbf{R}_\alpha}|\psi_{i\mathbf{k}}\rangle \tag{89}$$

The first term $\sum_i f_i\langle\psi_{i\mathbf{k}}|\frac{\delta V_{KS}}{\delta\mathbf{R}_\alpha}|\psi_{i\mathbf{k}}\rangle=\mathrm{Tr}(\rho\frac{\delta V_{KS}}{\delta\mathbf{R}_\alpha})$ cancels with the last term above, when V_{KS} is treated exactly (not approximated by spherical symmetric part).

The kinetic part $\langle\psi_{i\mathbf{k}}|\frac{\delta T}{\delta\mathbf{R}_\alpha}|\psi_{i\mathbf{k}}\rangle$ is present when the $\langle\chi_{vK'}|\nabla^2|\chi_{\mathbf{K}}\rangle$ jumps across MT-boundary, as there is additional surface term.

A. Core

In core, the index is l,m instead of $\mathbf{K}$. The wave functions of core states have the following form $\chi^\alpha_{lm}(\mathbf{r}-\mathbf{R}_\alpha)$, hence they move with the atom, and their derivative is

$$\frac{\delta\chi^\alpha_{lm}(\mathbf{r}-\mathbf{R}_\alpha)}{\delta\mathbf{R}_\alpha}=-\nabla_{\mathbf{r}}\chi^\alpha_{lm} \tag{90}$$

hence we have

$$\mathbf{F}^{Pulley}_\alpha=\sum_{lm}\left(\langle\nabla\chi^\alpha_{lm}|H-\varepsilon_i|\chi^\alpha_{lm}\rangle+\langle\chi^\alpha_{lm}|H-\varepsilon_i|\nabla\chi^\alpha_{lm}\rangle-\langle\chi^\alpha_{lm}|\frac{\delta}{\delta\mathbf{R}_\alpha}H|\chi^\alpha_{lm}\rangle\right)+\mathrm{Tr}(\rho\frac{\delta V_{KS}}{\delta\mathbf{R}_\alpha}) \tag{91}$$

In core we approximate $V_{KS}(r)$ to be spherically symmetric. It is then easy to see that H is spherically symmetric too. In fact, all m's are degenerate, hence $\sum_m \nabla\chi^{\alpha}_{lm} \propto \mathrm{e}_{\mathbf{r}}$, and consequently all three terms on the left vanish, as they are odd in space. The only nonzero term is

$$\mathbf{F}^{Pulley}_{\alpha} = \mathrm{Tr}(\rho\frac{\delta V_{KS}}{\delta\mathbf{R}_{\alpha}}) = -\mathrm{Tr}(\rho\nabla_{\mathbf{r}}V^{\alpha}_{KS}) \tag{92}$$

Note that here spherical symmetric part ov $V_{KS}(r)$ does not contribute, as such term appears also in the thirt term above and we argued above that it is odd. Hence, only the non-spherical part of $V_{KS}(\mathbf{r})$ gives contribution to the integral

$$\mathbf{F}^{Pulley}_{\alpha} = -\mathrm{Tr}(\rho_{\alpha}\nabla_{\mathbf{r}}V^{non-sph,\alpha}_{KS}) \tag{93}$$

B. Valence states

1. *Basic Derivation*

In the interstitials, we use originless plane waves, hence

$$\frac{\delta\chi^{I}_{\mathbf{K}}}{\delta\mathbf{R}_{\alpha}} = 0. \tag{94}$$

In MT-part, we check definition of $\chi^{MT}_{\mathbf{K}}$ in Eqs. 2 and 11. The approximate formula is

$$\frac{\delta\chi^{MT}_{\mathbf{K}}}{\delta\mathbf{R}_{\alpha}} = i(\mathbf{K}+\mathbf{k})\chi^{MT}_{\mathbf{K}} - \nabla_{\mathbf{r}}\chi^{MT}_{\mathbf{K}} + \cdots \tag{95}$$

The first term comes from the phase factor of a_{lm}'s Eq. 11, while the second term is from differentiating $u_l(|\mathbf{r}-\mathbf{R}_{\alpha}|)Y_{lm}(\hat{\mathbf{r}}-\hat{\mathbf{R}}_{\alpha})$. There are additional terms when differentiating a_{lm}'s as $u_l(S)$ changes as well, but their contribution is here neglected.

We hence have

$$\mathbf{F}^{Pulley}_{\alpha} = -\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} i(\mathbf{K}-\mathbf{K}')\left\langle\chi_{\mathbf{K}'}|H-\varepsilon_i|\chi_{\mathbf{K}}\right\rangle_{MT} A_{i,\mathbf{K}} + \tag{96}$$

$$+\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'}\left(\left\langle\nabla_{\mathbf{r}}\chi_{\mathbf{K}'}|H-\varepsilon_i|\chi_{\mathbf{K}}\right\rangle_{MT} + \left\langle\chi_{\mathbf{K}'}|H-\varepsilon_i|\nabla_{\mathbf{r}}\chi_{\mathbf{K}}\right\rangle_{MT}\right) A_{i,\mathbf{K}} - \tag{97}$$

$$-\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'}\left(\left\langle\chi_{\mathbf{K}'}|\frac{\delta T}{\delta\mathbf{R}_{\alpha}}|\chi_{\mathbf{K}}\right\rangle + \left\langle\chi_{\mathbf{K}'}|\frac{\delta V_{KS}}{\delta\mathbf{R}_{\alpha}}|\chi_{\mathbf{K}}\right\rangle\right) A_{i,\mathbf{K}} + \mathrm{Tr}(\rho\frac{\delta V_{KS}}{\delta\mathbf{R}_{\alpha}}) \tag{98}$$

First we simplify Eq. 97. We split $H-\varepsilon = V_{KS}+T-\varepsilon$ and simplify

$$\int_{MT} d^3r\left((\nabla_{\mathbf{r}}\chi^*_{\mathbf{K}'+\mathbf{k}})(V_{KS}+T-\varepsilon_i)\chi_{\mathbf{K}+\mathbf{k}} + \chi^*_{\mathbf{K}'+\mathbf{k}}(V_{KS}+T-\varepsilon_i)\nabla_{\mathbf{r}}\chi_{\mathbf{K}+\mathbf{k}}\right) = \tag{99}$$

$$\int_{MT} d^3r V_{KS}\nabla_{\mathbf{r}}\left(\chi^*_{\mathbf{K}'+\mathbf{k}}\chi_{\mathbf{K}+\mathbf{k}}\right) + \int_{MT} d^3r\nabla_{\mathbf{r}}\left(\chi^*_{\mathbf{K}'+\mathbf{k}}(T-\varepsilon_i)\chi_{\mathbf{K}+\mathbf{k}}\right) \tag{100}$$

The last term is because ∇ comutes with ∇^2, i.e,

$$\int \nabla\chi^*(-\nabla^2\chi) + \chi^*(-\nabla^2)\nabla\chi = \int \nabla(\chi^*(-\nabla^2)\chi) \tag{101}$$

We thus have

$$\int_{MT} d^3r\left(\nabla_{\mathbf{r}}\chi^*_{\mathbf{K}'+\mathbf{k}}(H-\varepsilon_i)\chi_{\mathbf{K}+\mathbf{k}} + \chi^*_{\mathbf{K}'+\mathbf{k}}(H-\varepsilon_i)\nabla_{\mathbf{r}}\chi_{\mathbf{K}+\mathbf{k}}\right) = \tag{102}$$

$$\int_{MT} d^3r V_{KS}\nabla_{\mathbf{r}}\left(\chi^*_{\mathbf{K}'+\mathbf{k}}\chi_{\mathbf{K}+\mathbf{k}}\right) + \oint_{r=R^-_{MT}} d\vec{S}\chi^*_{\mathbf{K}'+\mathbf{k}}(T-\varepsilon_i)\chi_{\mathbf{K}+\mathbf{k}} \tag{103}$$

Inserting this simpliflaction into Eq. 97, we get

$$Eq.\ 97 = \int_{MT} d^3 V_{KS}(\mathbf{r}) \nabla_{\mathbf{r}} \rho^{val}(\mathbf{r}) + \sum_i f_i \sum_{\mathbf{K}\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} \oint_{r=R^-_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}} (T - \varepsilon_i) \chi_{\mathbf{K}+\mathbf{k}} \tag{104}$$

Next we simplify Eq. 98. The second and the third term cancel, as we compute density by $\rho(\mathbf{r}) = \sum_i f_i \sum_{\mathbf{K}\mathbf{K}'} A^*_{i,\mathbf{K}'} \chi^*_{\mathbf{K}'}(\mathbf{r}) A_{i,\mathbf{K}} \chi_{\mathbf{K}}(\mathbf{r})$, hence for any function $X(\mathbf{r})$ we have $\mathrm{Tr}(X(\mathbf{r})\rho(\mathbf{r})) = \sum_i f_i \sum_{\mathbf{K}\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} \int d^3 r \chi^*_{\mathbf{K}'}(\mathbf{r}) X(\mathbf{r}) \chi_{\mathbf{K}}(\mathbf{r})$. We are hence left with the first term in Eq. 98 only. When we integrate a function whith discontinuity at the MT-boundary, we need to take into account an extra term due to the jump. One can derive the following identity (see section IV C)

$$\langle \chi_\mu | \delta T | \chi_\nu \rangle = \delta \mathbf{R}_\alpha \oint_{RMT} d\vec{S} \left[(\chi^*_\mu T \chi_\nu)_{MT} - (\chi^*_\mu T \chi_\nu)_I \right] \tag{105}$$

This term is just because $\chi_\mu(\mathbf{r}) T \chi_\nu(\mathbf{r})$ is not continuous across the boundary, and hence the difference at the boundary adds an extra term to the ingeral. We thus conclude

$$Eq.\ 98 = -\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} \oint_{RMT} d\vec{S} \left[(\chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) T \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}))_{MT} - (\chi_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) T \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}))_I \right] \tag{106}$$

since $\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$ are continuous across MT-boundary, we can also write

$$Eq.\ 98 = -\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} \left[\oint_{r=R^-_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) (T - \varepsilon_i) \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) - \oint_{r=R^+_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) (T - \varepsilon_i) \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \right] \tag{107}$$

Finally, we notice that the second term in 104 and the MT-part of Eq. 107 cancel, hence we obtain

$$Eq.\ 97 + Eq.\ 98 = \int_{MT} d^3 V_{KS}(\mathbf{r}) \nabla_{\mathbf{r}} \rho^{val}(\mathbf{r}) + \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} \oint_{r=R^+_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) (T - \varepsilon_i) \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \tag{108}$$

Notice that the functions $\chi_{\mathbf{K}+\mathbf{k}}$, which appear in the integral, are evaluated in the interstitial, hence the symbol $r = R^+_{MT}$.

The final result for Pulley forces, which is the sum of Eqs. 96, 97 and 98 is

$$\mathbf{F}^{Pulley}_\alpha = -i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} (\mathbf{K} - \mathbf{K}') \langle \chi_{\mathbf{K}'} | H - \varepsilon_i | \chi_{\mathbf{K}} \rangle_{MT} A_{i,\mathbf{K}} + \tag{109}$$

$$+ \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} \oint_{r=R^+_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) (T - \varepsilon_i) \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) + \tag{110}$$

$$+ \int_{MT} d^3 V_{KS}(\mathbf{r}) \nabla_{\mathbf{r}} \rho^{val}(\mathbf{r}) \tag{111}$$

In the MT part, the kinetic part T does not have the form $(\nabla \cdot \nabla)$ proposed in Sec. I 1 (but $-\nabla^2$), hence we need to write

$$Eq.\ 109 = -i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} (\mathbf{K} - \mathbf{K}') \langle \chi_{\mathbf{K}'} | -\nabla^2 + V_{KS} - \varepsilon_i | \chi_{\mathbf{K}} \rangle_{MT} A_{i,\mathbf{K}} - \tag{112}$$

$$-i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} (\mathbf{K} - \mathbf{K}') \oint_{r=R^-_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) \nabla_{\mathbf{r}} \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \tag{113}$$

Moreover, the MT part is usually broaken into two parts, the spherically symmetric potential $V^{sym}_{KS}(r)$ and the non-symmetryc part $V^{n-sym}_{KS}(\mathbf{r})$, i.e.,

$$V_{KS}(\mathbf{r}) = V^{sym}_{KS}(r) + V^{n-sym}_{KS}(\mathbf{r})$$

hence we can write

$$Eq.\ 109 = -i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} (\mathbf{K} - \mathbf{K}') \langle \chi_{\mathbf{K}'} | -\nabla^2 + V^{sym}_{KS}(r) - \varepsilon_i | \chi_{\mathbf{K}} \rangle_{MT} A_{i,\mathbf{K}} - \tag{114}$$

$$-i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} (\mathbf{K} - \mathbf{K}') \langle \chi_{\mathbf{K}'} | V^{n-sym}_{KS}(\mathbf{r}) | \chi_{\mathbf{K}} \rangle_{MT} A_{i,\mathbf{K}} - \tag{115}$$

$$-i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} (\mathbf{K} - \mathbf{K}') \oint_{r=R^-_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) \nabla_{\mathbf{r}} \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \tag{116}$$

In the interstitails, T has the form $(\nabla\cdot\nabla)$ proposed in Sec. I 1, hence Eq. 110 takes the form

$$Eq.\ 110 = \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}}[(\mathbf{K}+\mathbf{k})(\mathbf{K}'+\mathbf{k})-\varepsilon_i] \oint_{r=R^+_{MT}} d\vec{S}\chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r})\chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) = \tag{117}$$

$$= \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}}[(\mathbf{K}+\mathbf{k})(\mathbf{K}'+\mathbf{k})-\varepsilon_i] R^2_{MT}\int d\Omega \frac{e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}}}{V_{cell}}\vec{e}_{\mathbf{r}} = \tag{118}$$

$$= \sum_i f_i \sum_{\mathbf{K},\mathbf{G}} A^*_{i,\mathbf{K}-\mathbf{G}} A_{i,\mathbf{K}}[(\mathbf{K}+\mathbf{k})(\mathbf{K}-\mathbf{G}+\mathbf{k})-\varepsilon_i] R^2_{MT}\int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}}\vec{e}_{\mathbf{r}} \tag{119}$$

where we used $\mathbf{K}'=\mathbf{K}-\mathbf{G}$.

Using the above derived identities Eqs.114,115,116,119, we transform $\mathbf{F}^{Pulley}$ to

$$\mathbf{F}^{Pulley}_\alpha = -i\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'}(\mathbf{K}-\mathbf{K}')\left<\chi_{\mathbf{K}'}\right| -\nabla^2 + V^{sym}_{KS}(r) - \varepsilon_i \left|\chi_{\mathbf{K}}\right>_{MT} A_{i,\mathbf{K}} - \tag{120}$$

$$-i\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'}(\mathbf{K}-\mathbf{K}')\left<\chi_{\mathbf{K}'}\right| V^{n-sym}_{KS}(\mathbf{r}) \left|\chi_{\mathbf{K}}\right>_{MT} A_{i,\mathbf{K}} - \tag{121}$$

$$-i\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'}A_{i,\mathbf{K}}(\mathbf{K}-\mathbf{K}') \oint_{r=R^-_{MT}} d\vec{S}\chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r})\nabla_{\mathbf{r}}\chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \tag{122}$$

$$+\sum_i f_i \sum_{\mathbf{K},\mathbf{G}} A^*_{i,\mathbf{K}-\mathbf{G}} A_{i,\mathbf{K}}[(\mathbf{K}+\mathbf{k})(\mathbf{K}-\mathbf{G}+\mathbf{k})-\varepsilon_i] R^2_{MT}\int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}}\vec{e}_{\mathbf{r}} \tag{123}$$

$$+\int_{MT} d^3 V_{KS}(\mathbf{r})\nabla_{\mathbf{r}}\rho^{val}(\mathbf{r}) \tag{124}$$

2. *Implementation of term 120*

The first contribution to $\mathbf{F}^{Pulley}$ we are considering is Eq. 120

$$\mathbf{F}(1)^{Pulley}_\alpha = -i\sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'}(\mathbf{K}-\mathbf{K}')\left<\chi_{\mathbf{K}'}\right| -\nabla^2 + V^{sym}_{KS}(r) - \varepsilon_i \left|\chi_{\mathbf{K}}\right>_{MT} A_{i,\mathbf{K}} \tag{125}$$

We first repeat Eq. 67, which gives spherically symetric part of Hamiltonian in the MT-part:

$$\begin{aligned}
\left<\chi_{\mathbf{K}'}\right| -\nabla^2 + V^{sym}_{KS}(r) - \varepsilon \left|\chi_{\mathbf{K}}\right> &= a^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}(E_\nu-\varepsilon) + b^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm}(E_\nu-\varepsilon)\left<\dot{u}_l|\dot{u}_l\right> + \frac{1}{2}[a^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm} + b^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}] + \\
&+ c^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}(E_\mu-\varepsilon) + \frac{1}{2}[a^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm} + c^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}](E_\mu+E_\nu-2\varepsilon)\left<u|u_{LO}\right> + \\
&+ \frac{1}{2}[c^{\mathbf{K}'*}_{lm}b^{\mathbf{K}}_{lm} + b^{\mathbf{K}'*}_{lm}c^{\mathbf{K}}_{lm}][\left<u_{LO}|u_l\right> + (E_\mu+E_\nu-2\varepsilon)\left<u_{LO}|\dot{u}_l\right>]
\end{aligned} \tag{126}$$

Clearly, we can split the sum over $\mathbf{K}$ and $\mathbf{K}'$ into two indepedent sums which take $O(N)$ time.[We want to avoid $O(N^2)$ scaling, since there are very many number of plane waves $\mathbf{K}$].

We first define (compute) the following quantities

$$a_{i,lm} = \sum_{\mathbf{K}} A_{i\mathbf{K}}\, a^{\mathbf{K}}_{lm} \tag{127}$$

$$\vec{\mathcal{A}}_{i,lm} = \sum_{\mathbf{K}} \mathbf{K}\, A_{i\mathbf{K}}\, a^{\mathbf{K}}_{lm} \tag{128}$$

which take $O(N)$ time to compute. Here $A_{i,\mathbf{K}}$ are eigenvectors corresponding to the Kohn-Sham energy ε_i. We assume corresponding expression for $b_{i,lm}$, $c_{i,lm}$, $\vec{\mathcal{B}}_{i,lm}$, $\vec{\mathcal{C}}_{i,lm}$.

The quadratic terms of the form $a^*_{lm}a_{lm}$ become

$$\sum_{\mathbf{K}\mathbf{K}'}(\mathbf{K}-\mathbf{K}')A^*_{i\mathbf{K}'}a^{\mathbf{K}'*}_{lm}a^{\mathbf{K}}_{lm}A_{i\mathbf{K}} = a^*_{i,lm}\vec{\mathcal{A}}_{i,lm} - \vec{\mathcal{A}}^*_{i,lm}a_{i,lm} = 2i\ \mathrm{Im}\{a^*_{i,lm}\vec{\mathcal{A}}_{i,lm}\} \tag{129}$$

while those of the form $a^*_{lm} b_{lm} + b^*_{lm} a_{lm}$ become

$$\sum_{\mathbf{K}\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \frac{1}{2} [a^{\mathbf{K}'*}_{lm} b^{\mathbf{K}}_{lm} + b^{\mathbf{K}'*}_{lm} a^{\mathbf{K}}_{lm}] A_{i\mathbf{K}} = \frac{1}{2} [a^*_{i,lm} \vec{\mathcal{B}}_{i,lm} - \vec{\mathcal{A}}^*_{i,lm} b_{i,lm} + b^*_{i,lm} \vec{\mathcal{A}}_{i,lm} - \vec{\mathcal{B}}^*_{i,lm} a_{i,lm}] =$$

$$= i\,\mathrm{Im}\{a^*_{i,lm} \vec{\mathcal{B}}_{i,lm} + b^*_{i,lm} \vec{\mathcal{A}}_{i,lm}\} \tag{130}$$

The entire term can be expressed in this way. We start from Eq. 126 and derive

$$\begin{aligned}
&\sum_{\mathbf{K}\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \left\langle \chi_{\mathbf{K}'} \right| -\nabla^2 + V^{sph}_{KS}(r) - \varepsilon_i \left| \chi_{\mathbf{K}} \right\rangle_{MT} A_{i\mathbf{K}} = \\
&i\mathrm{Im}\left\{ 2a^*_{i,lm} \vec{\mathcal{A}}_{i,lm} \left(E_\nu - \varepsilon_i\right) + 2b^*_{i,lm} \vec{\mathcal{B}}_{i,lm} \left(E_\nu - \varepsilon_i\right) \langle \dot{u}_l | \dot{u}_l \rangle + a^*_{i,lm} \vec{\mathcal{B}}_{i,lm} + b^*_{i,lm} \vec{\mathcal{A}}_{i,lm} \right\} + \\
+\;& i\mathrm{Im}\left\{ 2c^*_{i,lm} \vec{\mathcal{C}}_{i,lm} \left(E_\mu - \varepsilon_i\right) \langle u_{LO} | u_{LO} \rangle + [a^*_{i,lm} \vec{\mathcal{C}}_{i,lm} + c^*_{i,lm} \vec{\mathcal{A}}_{i,lm}](E_\mu + E_\nu - 2\varepsilon_i) \langle u | u_{LO} \rangle \right\} + \\
+\;& i\mathrm{Im}\left\{ [c^*_{i,lm} \vec{\mathcal{B}}_{i,lm} + b^*_{i,lm} \vec{\mathcal{C}}_{i,lm}][\langle u_{LO} | u_l \rangle + (E_\mu + E_\nu - 2\varepsilon_i) \langle u_{LO} | \dot{u}_l \rangle] \right\}
\end{aligned} \tag{131}$$

which finally gives

$$\mathbf{F}(1)^{Pulley}_\alpha = -i \sum_i f_i \sum_{\mathbf{K}\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \left\langle \chi_{\mathbf{K}'} \right| -\nabla^2 + V^{sym}_{KS} - \varepsilon_i \left| \chi_{\mathbf{K}} \right\rangle_{MT} A_{i\mathbf{K}} = \tag{132}$$

$$\begin{aligned}
&\sum_i f_i \,\mathrm{Im}\left\{ \left[2a^*_{i,lm} \left(E_\nu - \varepsilon_i\right) + b^*_{i,lm} + c^*_{i,lm} (E_\mu + E_\nu - 2\varepsilon_i) \langle u | u_{LO} \rangle \right] \vec{\mathcal{A}}_{i,lm} \right\} + \\
+\; &\sum_i f_i \,\mathrm{Im}\left\{ \left[a^*_{i,lm} + 2b^*_{i,lm} \left(E_\nu - \varepsilon_i\right) \langle \dot{u}_l | \dot{u}_l \rangle + c^*_{i,lm} [\langle u_{LO} | u_l \rangle + (E_\mu + E_\nu - 2\varepsilon_i) \langle u_{LO} | \dot{u}_l \rangle]\right] \vec{\mathcal{B}}_{i,lm} \right\} + \\
+\; &\sum_i f_i \,\mathrm{Im}\left\{ \left[b^*_{i,lm} \langle u_{LO} | u_l \rangle + [a^*_{i,lm} \langle u_{LO} | u_l \rangle + b^*_{i,lm} \langle u_{LO} | \dot{u}_l \rangle](E_\mu + E_\nu - 2\varepsilon_i) + 2c^*_{i,lm} \left(E_\mu - \varepsilon_i\right) \langle u_{LO} | u_{LO} \rangle \right] \vec{\mathcal{C}}_{i,lm} \right\}
\end{aligned}$$

This is implemented in function `fomai1`. Note that $\vec{\mathcal{A}}$,$\vec{\mathcal{B}}$ and $\vec{\mathcal{C}}$ are called *aalm*,*bblm*, and *cclm*. Also note that $\langle \dot{u} | \dot{u} \rangle = pei$, $\langle u_{LO} | u \rangle = pi12lo$, $\langle u_{LO} | \dot{u} \rangle = pe12lo$, $\langle u_{LO} | u_{LO} \rangle = pr12lo$.

This force is called `fsph` and is coded in `Force1`.

3. Implementation of term 121

The second term we are considering is Eq. 121

$$\mathbf{F}(2)^{Pulley}_\alpha = -i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} (\mathbf{K}-\mathbf{K}') \left\langle \chi_{\mathbf{K}'} \right| V^{n-sym}_{KS}(\mathbf{r}) \left| \chi_{\mathbf{K}} \right\rangle_{MT} A_{i,\mathbf{K}} - \tag{133}$$

In file case.nsh, we read non-spherical symmetric potential, which is given in the following form

$$V^{non-sph}_{\kappa_1 l_1 m_1 \kappa_2 l_2 m_2} = \int d^3 r Y^*_{l_1 m_1}(\hat{\mathbf{r}}) u^{\kappa_1} V^{n-sym}(\mathbf{r}) u^{\kappa_2} Y_{l_2 m_2}(\hat{\mathbf{r}}) \tag{134}$$

The data in case.nsh contains the following matrix elements

$$\langle u | V | u \rangle \to tuu \tag{135}$$
$$\langle u | V | \dot{u} \rangle \to tud \tag{136}$$
$$\langle \dot{u} | V | u \rangle \to tdu \tag{137}$$
$$\langle \dot{u} | V | \dot{u} \rangle \to tdd \tag{138}$$
$$\cdots \tag{139}$$

To evaluate the term, we substutute the definition for $\chi_{\mathbf{K}}$ to obtain

$$\sum_{\mathbf{K},\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \left\langle \chi_{\mathbf{K}'} \right| V^{n-sym} \left| \chi_{\mathbf{K}} \right\rangle_{MT} A_{i\mathbf{K}} = \tag{140}$$

$$\sum_{\mathbf{K},\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \langle Y_{l_1 m_1} \sum_{\kappa_1} a^{\kappa_1,\mathbf{K}'}_{l_1 m_1} u^{\kappa_1}_{l_1} | V^{n-sym} | Y_{l_2 m_2} \sum_{\kappa_2} a^{\kappa_2,\mathbf{K}}_{l_2 m_2} u^{\kappa_2}_{l_2} \rangle A_{i\mathbf{K}} \tag{141}$$

which simplifies to

$$\sum_{\mathbf{K},\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \langle \chi_{\mathbf{K}'} | V^{n-sym} | \chi_{\mathbf{K}} \rangle_{MT} A_{i\mathbf{K}} = \tag{142}$$

$$\sum_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} a^{*\kappa_1,i}_{l_1 m_1} \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2} V_{\kappa_1 l_1 m_1,\kappa_2 l_2 m_2} - \vec{\mathcal{A}}^{*\kappa_1,i}_{l_1 m_1} a^{\kappa_2,i}_{l_2 m_2} V_{\kappa_1 l_1 m_1,\kappa_2 l_2 m_2} = \tag{143}$$

$$2i\mathrm{Im}\left\{ \sum_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} a^{*\kappa_1,i}_{l_1 m_1} \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2} V_{\kappa_1 l_1 m_1,\kappa_2 l_2 m_2} \right\} \tag{144}$$

hence, we have

$$\mathbf{F}(2)^{Pulley}_{\alpha} = \sum_i f_i \sum_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} 2\mathrm{Im}\left\{ a^{*\kappa_1,i}_{l_1 m_1} V_{\kappa_1 l_1 m_1,\kappa_2 l_2 m_2} \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2} \right\} \tag{145}$$

This is implemented in `fomai1` and has name `fnsp`. Note that $\vec{\mathcal{A}}, \vec{\mathcal{B}}, \vec{\mathcal{C}}$ are called `aalm,bblm,cclm` and matrix elements of V are called tuu,tud,tdu,....

Implementation builds the following quantity

$$afac(\kappa_2, l_1 m_1, l_2 m_2) = \sum_{\kappa_1} a^{*\kappa_1,i}_{l_1 m_1} V_{\kappa_1 l_1 m_1,\kappa_2 l_2 m_2} \tag{146}$$

and evaluates

$$\mathbf{F}(2)^{Pulley}_{\alpha} = \sum_i f_i \sum_{l_1 m_1, l_2 m_2, \kappa_2} 2\mathrm{Im}[afac(\kappa_2, l_1 m_1, l_2 m_2) \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2}] \tag{147}$$

It is implemented in `Force2`.

4. Implementation of term 122

Next we consider Eq. 122, which is

$$\mathbf{F}(3)^{Pulley}_{\alpha} = -i \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} (\mathbf{K}-\mathbf{K}') \oint_{r=R^-_{MT}} d\vec{S} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) \nabla_{\mathbf{r}} \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \tag{148}$$

We know that the therm should be real, therefore we will symmetrize it to make it real

$$\mathbf{F}(3)^{Pulley}_{\alpha} = -\frac{i}{2} \sum_i f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} (\mathbf{K}-\mathbf{K}') \oint_{r=R^-_{MT}} d\vec{S} [\chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) \nabla_{\mathbf{r}} \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) + \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \nabla \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r})] \tag{149}$$

which is equal to

$$\mathbf{F}(3)^{Pulley}_{\alpha} = -\frac{i}{2} \sum_{\mathbf{k},i} f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i\mathbf{K}'} A_{i\mathbf{K}} \, (\mathbf{K}-\mathbf{K}') R^2_{MT} \oint_{r=R_{MT-}} d\Omega \, [\chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) \frac{\partial}{\partial r} \chi_{\mathbf{K}+\mathbf{k}} + \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \frac{\partial}{\partial r} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r})] \tag{150}$$

and inserting expression for χ we get

$$\mathbf{F}(3)^{Pulley}_{\alpha} = -\frac{i}{2} \sum_{\mathbf{k},i} f_i \sum_{\mathbf{K},\mathbf{K}'} A^*_{i\mathbf{K}'} A_{i\mathbf{K}} \, (\mathbf{K}-\mathbf{K}') R^2_{MT} \sum_{l,m,\kappa',\kappa} a^{\kappa'\,*}_{lm,\mathbf{K}'} u^{\kappa'}_l a^{\kappa}_{lm,\mathbf{K}} u'^{\kappa}_l + a^{\kappa'}_{lm,\mathbf{K}} u^{\kappa'}_l a^{\kappa\,*}_{lm,\mathbf{K}'} u'^{\kappa}_l \tag{151}$$

and summing over $\mathbf{K}$ and $\mathbf{K}'$ gives

$$\mathbf{F}(3)^{Pulley}_{\alpha} = -\frac{i}{2} \sum_{\mathbf{k},i} f_i R^2_{MT} \sum_{l,m,\kappa',\kappa} [a^{\kappa'\,*}_{i,lm} u^{\kappa'}_l \vec{\mathcal{A}}^{\kappa}_{i,lm} u'^{\kappa}_l + \vec{\mathcal{A}}^{\kappa'}_{i,lm} u^{\kappa'}_l a^{\kappa\,*}_{i,lm} u'^{\kappa}_l - \vec{\mathcal{A}}^{\kappa'\,*}_{i,lm} u^{\kappa'}_l a^{\kappa}_{i,lm} u'^{\kappa}_l - a^{\kappa'}_{i,lm} u^{\kappa'}_l \vec{\mathcal{A}}^{\kappa\,*}_{i,lm} u'^{\kappa}_l] \tag{152}$$

which can be simplified to

$$\mathbf{F}(3)^{Pulley}_{\alpha} = R^2_{MT} \sum_{\mathbf{k},i} f_i \sum_{l,m,\kappa',\kappa} \mathrm{Im}[a^{\kappa'\,*}_{i,lm} u^{\kappa'}_l \vec{\mathcal{A}}^{\kappa}_{i,lm} {u'}^{\kappa}_l - \vec{\mathcal{A}}^{\kappa'\,*}_{i,lm} u^{\kappa'}_l a^{\kappa}_{i,lm} {u'}^{\kappa}_l] \tag{153}$$

We can then define the following quantities

$$kinfac(1, ilm) = \sum_{\kappa} a^{\kappa}_{i,lm} u^{\kappa}_l(R_{MT}) \tag{154}$$

$$kinfac(2, ilm) = \sum_{\kappa} a^{\kappa}_{i,lm} {u'}^{\kappa}_l(R_{MT}) \tag{155}$$

$$kinfac(3, ilm) = \sum_{\kappa} \vec{\mathcal{A}}^{\kappa}_{i,lm} {u'}^{\kappa}_l(R_{MT}) \tag{156}$$

$$kinfac(4, ilm) = \sum_{\kappa} \vec{\mathcal{A}}^{\kappa}_{i,lm} u^{\kappa}_l(R_{MT}) \tag{157}$$

and write

$$\mathbf{F}(3)^{Pulley}_{\alpha} = R^2_{MT} \sum_{\mathbf{k},i} f_i \sum_{l,m} \mathrm{Im}[kinfac^*(1, ilm) kinfac(3, ilm) - kinfac^*(4, ilm) kinfac(2, ilm)] \tag{158}$$

This part of the force is named `fsph2` and is coded in `fomai1` within Wien2k, and in `Force3` in my code.

5. *Implementation of term 123*

Finally we discuss implementation of Eq. 123:

$$\mathbf{F}(4)^{Pulley}_{\alpha} = \sum_i f_i \sum_{\mathbf{K},\mathbf{G}} A^*_{i,\mathbf{K}-\mathbf{G}} A_{i,\mathbf{K}} [(\mathbf{K}+\mathbf{k})(\mathbf{K}-\mathbf{G}+\mathbf{k}) - \varepsilon_i] R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{159}$$

The convolution in $\mathbf{K}$ needs quadratic amount of time ($O(N^2)$). By using FFT and turning it into product in real space, it takes only $N\log(N)$ time, hence we will use FFT for the following quantities

$$\vec{X}_i(\mathbf{r}) = \sum_{\mathbf{K}} A_{i,\mathbf{K}} (\mathbf{K}+\mathbf{k}) e^{i\mathbf{K}\mathbf{r}} \tag{160}$$

$$Y_i(\mathbf{r}) = \sum_{\mathbf{K}} A_{i,\mathbf{K}} e^{i\mathbf{K}\mathbf{r}} \tag{161}$$

The inverse FFT should then be used to obtain aternative representation for convolution

$$\mathbf{F}(4)^{Pulley}_{\alpha} = \sum_i f_i \int d^3r e^{-i\mathbf{K}\mathbf{r}} [\vec{X}^*_i(\mathbf{r}) \vec{X}_i(\mathbf{r}) - \varepsilon_i Y^*_i(\mathbf{r}) Y_i(\mathbf{r})] R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{162}$$

Finally, one can check that

$$\int d\Omega e^{i\mathbf{G}\mathbf{r}} \vec{e}_{\mathbf{r}} = 4\pi \frac{\mathbf{G}}{|\mathbf{G}|} j_1(|\mathbf{G}| R_{MT}) i e^{i\mathbf{G}\mathbf{r}_{\alpha}} \tag{163}$$

This code appears in `Force_surface`.

6. *Implementation of term 124*

The last part in the Eq. 124 is

$$\mathbf{F}(5)^{Pulley}_{\alpha} = \int_{MT} d^3r V_{KS}(\mathbf{r}) \nabla\rho(\mathbf{r}) = \sum_{lml'm'} \int d^3r V_{l'm'}(r) Y^*_{l'm'}(\hat{\mathbf{r}}) \nabla(\rho_{lm}(r) Y_{lm}(\hat{\mathbf{r}})) \tag{164}$$

The operator ∇ is spheric harmonics is

$$\nabla f = \vec{e}_r \frac{\partial}{\partial r} + \frac{\sin\theta}{r} \begin{pmatrix} -\cos\theta\cos\phi \\ -\cos\theta\sin\phi \\ \sin\theta \end{pmatrix} \frac{\partial}{\partial(\cos\theta)} + \frac{1}{r\sin\theta} \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \frac{\partial}{\partial\phi} = \vec{e}_r \frac{\partial}{\partial r} + \frac{1}{r}\nabla_{\theta\phi} \tag{165}$$

The last form emphasizes that ∇ has the radial part and a angle part. Using this decomposition, we can write

$$\mathbf{F}(5)_\alpha^{Pulley} = \int d^3r V_{KS}(\mathbf{r})\nabla\rho(\mathbf{r}) = \sum_{lml'm'} \int_0^\infty drr^2 V_{l'm'}(r)\frac{d\rho_{lm}(r)}{dr} \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\vec{e}_r Y_{lm}(\hat{\mathbf{r}}) \tag{166}$$

$$+ \sum_{lml'm'} \int_0^\infty drr^2 \frac{V_{l'm'}(r)\rho_{lm}(r)}{r} \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\nabla_{\theta\phi} Y_{lm}(\hat{\mathbf{r}}) \tag{167}$$

In the following, we will need these integrals:

$$I^1_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\vec{e}_{\mathbf{r}} Y_{lm}(\hat{\mathbf{r}}) \tag{168}$$

$$I^2_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})(r\nabla Y_{lm}(\hat{\mathbf{r}})) \tag{169}$$

$$I^3_{l'm'lm} \equiv \int d\Omega (r\nabla Y^*_{l'm'}(\hat{\mathbf{r}}))\cdot(r\nabla Y_{lm}(\hat{\mathbf{r}}))\vec{e}_{\mathbf{r}} \tag{170}$$

$$\tag{171}$$

We first compute the following integral

$$I^1_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\vec{e}_r Y_{lm}(\hat{\mathbf{r}}) = \tag{172}$$

$$(-1)^{m+m'}\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m')!}{4\pi(l+m)!4\pi(l'+m')!}} \int_{-1}^1 dx P_{l'}^{m'}(x)P_l^m(x) \begin{pmatrix} \sqrt{1-x^2}\int_0^{2\pi} d\phi\; e^{i(m-m')\phi}\cos\phi \\ \sqrt{1-x^2}\int_0^{2\pi} d\phi\; e^{i(m-m')\phi}\sin\phi \\ x\int_0^{2\pi} d\phi\; e^{i(m-m')\phi} \end{pmatrix} \tag{173}$$

$$I^1_{l'm'lm} = (-1)^{m+m'}\pi\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m')!}{4\pi(l+m)!4\pi(l'+m')!}} \int_{-1}^1 dx P_{l'}^{m'}(x)P_l^m(x) \begin{pmatrix} \sqrt{1-x^2}\delta_{m'=m\pm1} \\ \mp i\sqrt{1-x^2}\delta_{m'=m\pm1} \\ 2x\delta_{mm'} \end{pmatrix} \tag{174}$$

which is equal to

$$I^1_{l'm'lm} = \pi\delta_{m'=m\pm1}\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m\mp1)!}{4\pi(l+m)!4\pi(l'+m\pm1)!}} \int_{-1}^1 dx P_{l'}^{m\pm1}(x)P_l^m(x)\sqrt{1-x^2} \begin{pmatrix} -1 \\ \pm i \\ 0 \end{pmatrix}$$

$$+2\pi\delta_{mm'}\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m)!}{4\pi(l+m)!4\pi(l'+m)!}} \int_{-1}^1 dx P_{l'}^m(x)P_l^m(x) x \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{175}$$

With the help of the following well known recursion relation

$$\sqrt{1-x^2}P_l^m = \frac{1}{2l+1}\left[P_{l-1}^{m+1} - P_{l+1}^{m+1}\right] \tag{176}$$

$$\sqrt{1-x^2}P_l^m = \frac{1}{2l+1}\left[(l-m+1)(l-m+2)P_{l+1}^{m-1} - (l+m-1)(l+m)P_{l-1}^{m-1}\right] \tag{177}$$

$$xP_l^m = \frac{1}{2l+1}\left[(l-m+1)P_{l+1}^m + (l+m)P_{l-1}^m\right] \tag{178}$$

we arrive at

$$I^1_{l'm'lm} = \begin{pmatrix} -1 \\ i \\ 0 \end{pmatrix} \frac{1}{2} \left[\delta_{l'=l-1} \sqrt{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}} - \delta_{l'=l+1} \sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}} \right] \delta_{m'=m+1} + \tag{179}$$

$$+ \begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix} \frac{1}{2} \left[\delta_{l'=l+1} \sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}} - \delta_{l'=l-1} \sqrt{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}} \right] \delta_{m'=m-1} + \tag{180}$$

$$+ \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \left[\delta_{l'=l+1} \sqrt{\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}} + \delta_{l'=l-1} \sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}} \right] \delta_{m'=m} \tag{181}$$

Let's define

$$a(l,m) = \sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}} \tag{182}$$

$$f(l,m) = \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} \tag{183}$$

$$\tag{184}$$

and rewrite

$$I^1_{l'm'lm} = \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \frac{1}{2} \left[a(l,m)\delta_{l'=l+1} - a(l',-m')\delta_{l'=l-1} \right] \delta_{m'=m+1} + \tag{185}$$

$$+ \begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix} \frac{1}{2} \left[a(l,-m)\delta_{l'=l+1} - a(l',m')\delta_{l'=l-1} \right] \delta_{m'=m-1} + \tag{186}$$

$$+ \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \left[f(l,m)\delta_{l'=l+1} + f(l',m')\delta_{l'=l-1} \right] \delta_{m'=m} \tag{187}$$

Next we compute the following integral

$$I^2_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}}) \nabla_{\theta\phi} Y_{lm}(\hat{\mathbf{r}}) = \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})(r\nabla) Y_{lm}(\hat{\mathbf{r}}) \tag{188}$$

From W2k paper, it follows that

$$r\frac{d}{dx} Y_{lm} = \frac{1}{2} \left[l\ a(l,m)\delta_{l'=l+1} + (l+1)\ a(l-1,-m-1)\delta_{l'=l-1} \right] \delta_{m'=m+1} Y_{l'm'} - \tag{189}$$

$$-\frac{1}{2} \left[l\ a(l,-m)\delta_{l'=l+1} + (l+1)\ a(l-1,m-1)\delta_{l'=l-1} \right] \delta_{m'=m-1} Y_{l'm'} \tag{190}$$

$$r\frac{d}{dy} Y_{lm} = \frac{1}{2i} \left[l\ a(l,m)\delta_{l'=l+1} + (l+1)\ a(l-1,-m-1)\delta_{l'=l-1} \right] \delta_{m'=m+1} Y_{l'm'} + \tag{191}$$

$$+\frac{1}{2i} \left[l\ a(l,-m)\delta_{l'=l+1} + (l+1)\ a(l-1,m-1)\delta_{l'=l-1} \right] \delta_{m'=m-1} Y_{l'm'} \tag{192}$$

$$r\frac{d}{dz} Y_{lm} = \left[-l\ f(l,m)\delta_{l'=l+1} + (l+1) f(l-1,m)\delta_{l'=l-1} \right] \delta_{m'=m} Y_{l'm'} \tag{193}$$

It is easy to prove the last term

$$r\frac{d}{dz}Y_{lm} = (-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}e^{im\phi}(1-x^2)\frac{d}{dx}P_l^m(x) = \tag{194}$$

$$= (-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}e^{im\phi}\frac{1}{2l+1}\left[(l+1)(l+m)P_{l-1}^m(x) - l(l-m+1)P_{l+1}^m\right] = \tag{195}$$

$$= (l+1)\sqrt{\frac{(l-m)(l+m)}{(2l+1)(2l-1)}}Y_{l-1,m} - l\sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}}Y_{l+1,m} \tag{196}$$

The x,y components are a bit more challenging. Due to Wigner-Eckart theorem, we know the dependence on m, m'. The dependence on l, l' can be either found numerically, or analytically using several recursion relations.

The result for I^2 is

$$I^2_{l'm'lm} = \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \frac{1}{2}\left[-l\; a(l,m)\delta_{l'=l+1} - (l+1)\; a(l',-m')\delta_{l'=l-1}\right]\delta_{m'=m+1} + \tag{197}$$

$$+ \begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix} \frac{1}{2}\left[-l\; a(l,-m)\delta_{l'=l+1} - (l+1)\; a(l',m')\delta_{l'=l-1}\right]\delta_{m'=m-1} + \tag{198}$$

$$+ \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \left[-l\; f(l,m)\delta_{l'=l+1} + (l+1)f(l',m')\delta_{l'=l-1}\right]\delta_{m'=m} \tag{199}$$

We can write both integrals in a common form, namely,

$$I^n_{l'm'lm} = c_{n,l}\left[a(l,m)\begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m+1} + a(l,-m)\begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m-1} + 2f(l,m)\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l+1} \tag{200}$$

$$-d_{n,l}\left[a(l',-m')\begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m+1} + a(l',m')\begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m-1} - 2f(l',m')\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l-1} \tag{201}$$

where

$$c_{1,l} = \tfrac{1}{2} \qquad d_{1,l} = \frac{1}{2} \tag{202}$$

$$c_{2,l} = -\tfrac{l}{2} \quad d_{2,l} = \frac{l+1}{2} \tag{203}$$

$$c_{3,l} = \tfrac{l(l+2)}{2} \quad d_{3,l} = \frac{(l-1)(l+1)}{2} \tag{204}$$

We also defined here I^3, which gives kinetic energy operatore integrated over the sphere of the MT-sphere.

In the code, we use real spheric harmonics $y_{lm\pm}$, which are related to complex spheric harmonics by

$$Y_{lm} \;\; = (-1)^m\sqrt{\frac{1+\delta_{m,0}}{2}}(y_{lm+} + iy_{lm-}) \tag{205}$$

$$Y_{l,-m} \;\; = \sqrt{\frac{1+\delta_{m,0}}{2}}(y_{lm+} - iy_{lm-}) \tag{206}$$

In Section. IV E we derive the connection between the matrix elements of the real harmonics and complex harmonics, and we also derive the matrix elements $\langle y_{l'm's'}|T|y_{lms}\rangle$. Here we just give the final result:

$$\langle y_{l'm'\pm}|T|y_{lm\pm}\rangle = c_{n,l}\ \delta_{l'=l+1}\begin{pmatrix} -a(l,m)\delta_{m'=m+1}\frac{(1\pm\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l,-m)\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}} \\ 0 \\ 2f(l,m)\delta_{m'=m}\frac{(1\pm\delta_{m=0})}{1+\delta_{m=0}} \end{pmatrix}$$
$$-d_{n,l}\ \delta_{l'=l-1}\begin{pmatrix} -a(l',-m')\delta_{m'=m+1}\frac{(1\pm\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l',m')\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}} \\ 0 \\ -2f(l',m')\delta_{m'=m}\frac{(1\pm\delta_{m=0})}{1+\delta_{m=0}} \end{pmatrix}\Bigg\} \tag{207}$$

and

$$\langle y_{l'm'\pm}|T|y_{lm\mp}\rangle = \pm\begin{pmatrix}0\\1\\0\end{pmatrix}\Bigg\{c_{n,l}\ \delta_{l'=l+1}\left(a(l,m)\delta_{m'=m+1}\frac{(1\mp\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l,-m)\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}}\right)$$
$$-d_{n,l}\ \delta_{l'=l-1}\left(a(l',-m')\delta_{m'=m+1}\frac{(1\mp\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l',m')\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}}\right)\Bigg\} \tag{208}$$

This term has name `fomai2` in Wien2k, and is coded in program `Force4_mine`. This part reads non-spherical potential $V_{KS}(\mathbf{r})$ and calls another subprogram `VdRho`, which performns the integration.

C. LDA+U Force term

For LDA+U calculation, the LDA+U potential is added to the Kohn-Sham potential, which takes the form

$$V(\mathbf{r},\mathbf{r}') = V^l_{m_1m_2}Y_{lm_1}(\hat{\mathbf{r}})\delta(r-r')Y^*_{lm_2}(\hat{\mathbf{r}}) \tag{209}$$

We are evaluating the following tem

$$\begin{aligned} F_U &= -i\sum_{i,\mathbf{k}} f_i \sum_{\mathbf{K},\mathbf{K}'}(\mathbf{K}-\mathbf{K}')A^*_{i\mathbf{K}'}\langle\chi_{\mathbf{K}'}|V|\chi_{\mathbf{K}}\rangle A_{i\mathbf{K}} = \\ &= -i\sum_{i,\mathbf{k}} f_i \sum_{\substack{\mathbf{K},\mathbf{K}',l\\ m_1,m_2,\kappa_1,\kappa_2}}(\mathbf{K}-\mathbf{K}')A^*_{i\mathbf{K}'}\langle a^{\kappa_1,\mathbf{K}'\,*}_{lm_1}u^{\kappa_1}_l Y^*_{lm_1}|V|Y_{lm_2}u^{\kappa_2}_l a^{\kappa_2,\mathbf{K}}_{lm}\rangle A_{i\mathbf{K}} \end{aligned} \tag{210}$$

which is

$$F_U = -i\sum_{i,\mathbf{k}} f_i \sum_{l,m_1,m_2,\kappa_1\kappa_2} V^l_{m_1m_2}\langle u^{\kappa_1}_l|u^{\kappa_2}_l\rangle \sum_{\mathbf{K},\mathbf{K}'}(\mathbf{K}-\mathbf{K}')A^*_{i\mathbf{K}'}A_{i\mathbf{K}}a^{\kappa_1,\mathbf{K}'\,*}_{lm_1}a^{\kappa_2,\mathbf{K}}_{lm} = \tag{211}$$

$$= \sum_i f_i \sum_{l,m_1,m_2,\kappa_1\kappa_2} 2\mathrm{Im}\left(a^{\kappa_1\,*}_{ilm_1}\vec{\mathcal{A}}^{\kappa_2}_{ilm_2}V^l_{m_1m_2}\langle u^{\kappa_1}_l|u^{\kappa_2}_l\rangle\right) \tag{212}$$

III. LDA+DMFT FORCES

The Luttinger-Ward functional is

$$\Gamma[G] = \mathrm{Tr}\log(G) - \mathrm{Tr}((G_0^{-1}-G^{-1})G) + \Phi[G] + E_{nucleous} + \mu N \tag{213}$$

where LDA+DFMT Φ functional is

$$\Phi[G] = E_H[\rho] + E_{xc}[\rho] + \Phi^{DMFT}[G_{loc}] - \Phi^{DC}[\rho_{loc}] \tag{214}$$

The stationarity gives

$$G^{-1} - G_0^{-1} + (V_H+V_{xc})\delta(\mathbf{r}-\mathbf{r}')\delta(\tau-\tau') + |\phi\rangle\,\Sigma\,\langle\phi| - |\phi\rangle\,V_{DC}\,\langle\phi| = 0 \tag{215}$$

Hence we have

$$G_0^{-1} - G^{-1} = (V_H + V_{xc})\delta(\mathbf{r}-\mathbf{r}') + |\phi\rangle (\Sigma - V_{DC}) \langle\phi| \tag{216}$$
$$G^{-1} = i\omega + \mu + \nabla^2 - (V_{nucl} + V_H + V_{xc})\delta(\mathbf{r}-\mathbf{r}') - |\phi\rangle (\Sigma - V_{DC}) \langle\phi| \tag{217}$$

We also solve the following KS-problem

$$(-\nabla^2 + V_{nucl} + V_H + V_{xc}) |\psi_{i\mathbf{k}}\rangle = \varepsilon_{i\mathbf{k}}^{LDA} |\psi_{i\mathbf{k}}\rangle \tag{218}$$

so thet we can write

$$G^{-1} = i\omega + \mu - |\psi_{i\mathbf{k}}\rangle \varepsilon_{i\mathbf{k}}^{LDA} \langle\psi_{i\mathbf{k}}| - |\phi\rangle (\Sigma - V_{DC}) \langle\phi| \tag{219}$$

In the extremum, Γ delivers free energy. Inserting $G_0^{-1} - G^{-1}$, and G^{-1} into the unctional Γ, we get

$$F = -\mathrm{Tr}\log\left(i\omega + \mu - |\psi_{i\mathbf{k}}\rangle \varepsilon_{i\mathbf{k}}^{LDA} \langle\psi_{i\mathbf{k}}| - |\phi\rangle (\Sigma - V_{dc}) \langle\phi|\right) - \mathrm{Tr}((V_H + V_{xc})\rho)$$
$$-\mathrm{Tr}(|\phi\rangle (\Sigma - V_{DC}) \langle\phi| G) + E_H[\rho] + E_{xc}[\rho] + \Phi^{DMFT}[G_{local}] - \Phi^{DC}[\rho_{local}] + E_{nucleous} + \mu N \tag{220}$$

A. LDA+U

First we consider static approximation for $\Phi^{DMFT} \to \Phi^U$ and we than call $\delta\Phi^U/\delta G \equiv V_U$, which is static.
We then incorporate V_U potential into KS-eigenvalue problem, i.e.,

$$\varepsilon_{i\mathbf{k}}^{LDA}\delta_{ij} + \langle\psi_{i\mathbf{k}}|\phi_m\rangle (V_U - V_{DC})_{mm'} \langle\phi_{m'}|\psi_{\mathbf{k}j}\rangle \equiv H_{ij}^{LDA+U} \tag{221}$$

and solve

$$H_{ij}^{LDA+U} B_{jp} = \varepsilon_{p\mathbf{k}} B_{ip} \tag{222}$$

hence

$$H_{ij}^{LDA+U} = (B\varepsilon_{\mathbf{k}} B^\dagger)_{ij} \tag{223}$$

so that

$$\langle\psi_{i\mathbf{k}}| \left(i\omega + \mu - |\psi_{i\mathbf{k}}\rangle \varepsilon_{i\mathbf{k}}^{LDA} \langle\psi_{i\mathbf{k}}| - |\phi\rangle (\Sigma - V_{dc}) \langle\phi|\right) |\psi_{j\mathbf{k}}\rangle = [B(i\omega + \mu - \varepsilon_{\mathbf{k}})B^\dagger]_{ij} \tag{224}$$

We then have

$$F = -\mathrm{Tr}\log(i\omega + \mu - \varepsilon_{i\mathbf{k}}) - \mathrm{Tr}((V_H + V_{xc})\rho) - \mathrm{Tr}(|\phi_m\rangle (V_U - V_{DC})_{mm'} \langle\phi_{m'}| G)$$
$$+E_H[\rho] + E_{xc}[\rho] + \phi^U[n_{local}] - \phi^{DC}[n_{local}] + E_{nucleous} \tag{225}$$

Small change of nucleous position $\delta\mathbf{R}_\alpha$ will give small change in F in the following way

$$\delta F = \mathrm{Tr}(G\delta\varepsilon_{\mathbf{k}}) - \mathrm{Tr}((\delta V_H + \delta V_{xc})\rho) - \delta\mathrm{Tr}(|\phi_m\rangle (V_U - V_{DC})_{mm'} \langle\phi_{m'}| G) + \mathrm{Tr}((V_U - V_{DC})\delta n) + \delta E_{nucleous} \tag{226}$$

We can arrange the trace in the third term in the following way

$$-\delta\mathrm{Tr}((V_U - V_{DC})_{mm'} \langle\phi_{m'}|G|\phi_m\rangle) = -\delta\mathrm{Tr}((V_U - V_{DC})_{mm'} n_{m'm}) = -\delta\mathrm{Tr}((V_U - V_{DC})n) \tag{227}$$
$$= -\mathrm{Tr}((\delta V_U - \delta V_{DC})n) - \mathrm{Tr}((V_U - V_{DC})\delta n) \tag{228}$$

hence we obtain

$$\delta F = \mathrm{Tr}(f_{\mathbf{k}}\delta\varepsilon_{\mathbf{k}}) - \mathrm{Tr}((\delta V_H + \delta V_{xc} + \delta V_{nuc})\rho) - \mathrm{Tr}((\delta V_U - \delta V_{DC})n) - \sum_\alpha \mathbf{F}_\alpha^{HF}\delta\mathbf{R}_\alpha \tag{229}$$

This equation is analogous to Eq. 80 in LDA method. We did not yet write definition for V_{KS} as there are two options, one could include V_U or not. We will exclude V_U and choose $V_{KS}^{LDA} = V_{nuc} + V_H + V_{xc}$.

When we vary $\delta\varepsilon_{\mathbf{k}}$, we have V_U potential included, hence using Eq. 85 we get

$$\delta\varepsilon_{\mathbf{k},i} = \sum_{\mathbf{K},\mathbf{K}'} A_{i,\mathbf{K}'}^* \left(\langle\delta\chi_{\mathbf{K}'}|H - \varepsilon_i|\chi_{\mathbf{K}}\rangle + \langle\chi_{\mathbf{K}'}|H - \varepsilon_i|\delta\chi_{\mathbf{K}}\rangle + \langle\chi_{\mathbf{K}'}|\delta T + \delta V_{KS}^{LDA} + \delta(|\phi_m\rangle (V_U - V_{DC})_{mm'} \langle\phi_{m'}|)\chi_{\mathbf{K}}\rangle\right) A_{i\mathbf{K}} \tag{230}$$

Inserting the last equation into δF, we get

$$\delta F = \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} \left(\langle \delta\chi_{\mathbf{K}'} | H - \varepsilon_i | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | H - \varepsilon_i | \delta\chi_{\mathbf{K}} \rangle \right) A_{i,\mathbf{K}} + \tag{231}$$

$$+ \sum_i f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | \delta T + \delta V_{KS}^{LDA} + \delta(|\phi_m\rangle (V_U - V_{DC})_{mm'} \langle \phi_{m'}|) | \psi_{i\mathbf{k}} \rangle$$

$$-\mathrm{Tr}((\delta V_H + \delta V_{xc} + \delta V_{nuc})\rho) - \mathrm{Tr}((\delta V_U - \delta V_{DC}) n) - \sum_\alpha \mathbf{F}_\alpha^{HF} \delta \mathbf{R}_\alpha$$

Note that the term $\mathrm{Tr}(\delta V_{KS}^{LDA}\rho)$ cancels, and we obtain

$$\delta F = \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} \left(\langle \delta\chi_{\mathbf{K}'} | H - \varepsilon_i | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | H - \varepsilon_i | \delta\chi_{\mathbf{K}} \rangle \right) A_{i,\mathbf{K}} \tag{232}$$

$$+ \sum_i f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | \delta(|\phi_m\rangle (V_U - V_{DC})_{mm'} \langle \phi_{m'}|) | \psi_{i\mathbf{k}} \rangle - \mathrm{Tr}((\delta V_U - \delta V_{DC}) n) \tag{233}$$

$$+ \sum_i f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | \delta T | \psi_{i\mathbf{k}} \rangle - \sum_\alpha \mathbf{F}_\alpha^{HF} \delta \mathbf{R}_\alpha \tag{234}$$

Note that the first two terms (Eq. 232) still include V_U term. It could be split into the following two terms

$$Eq.\ 232 = \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} \left(\langle \delta\chi_{\mathbf{K}'} | -\nabla^2 + V_{KS}^{LDA} - \varepsilon_i | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | -\nabla^2 + V_{KS}^{LDA} - \varepsilon_i | \delta\chi_{\mathbf{K}} \rangle \right) A_{i,\mathbf{K}} + \tag{235}$$

$$+ \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} \left(\langle \delta\chi_{\mathbf{K}'} | \phi_m \rangle (V_U - V_{DC})_{mm'} \langle \phi_{m'} | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | \phi_m \rangle (V_U - V_{DC})_{mm'} \langle \phi_{m'} | \delta\chi_{\mathbf{K}} \rangle \right) A_{i,\mathbf{K}} \tag{236}$$

Now we combinte 233 and 236, to obtain

$$Eq.\ 233 + Eq.\ 236 = \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} \delta \left(\langle \chi_{\mathbf{K}'} | \phi_m \rangle (V_U - V_{DC})_{mm'} \langle \phi_{m'} | \chi_{\mathbf{K}} \rangle \right) A_{i,\mathbf{K}} - \mathrm{Tr}(n(\delta V_U - \delta V_{DC})) \tag{237}$$

which can also be written as

$$Eq.\ 233 + Eq.\ 236 = \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} (V_U - V_{DC})_{mm'} \delta \left(\langle \chi_{\mathbf{K}'} | \phi_m \rangle \langle \phi_{m'} | \chi_{\mathbf{K}} \rangle \right) \tag{238}$$

Finally, we have

$$\delta F = \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} \left(\langle \delta\chi_{\mathbf{K}'} | -\nabla^2 + V_{KS}^{LDA} - \varepsilon_i | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | -\nabla^2 + V_{KS}^{LDA} - \varepsilon_i | \delta\chi_{\mathbf{K}} \rangle \right) A_{i,\mathbf{K}} + \tag{239}$$

$$+ \sum_i f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | \delta T | \psi_{i\mathbf{k}} \rangle - \sum_\alpha \mathbf{F}_\alpha^{HF} \delta \mathbf{R}_\alpha \tag{240}$$

$$+ \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} (V_U - V_{DC})_{mm'} \delta \left(\langle \chi_{\mathbf{K}'} | \phi_m \rangle \langle \phi_{m'} | \chi_{\mathbf{K}} \rangle \right) \tag{241}$$

which gives

$$\mathbf{F}_\alpha^{Pulley} = -\sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} \left(\langle \frac{\delta\chi_{\mathbf{K}'}}{\delta \mathbf{R}_\alpha} | -\nabla^2 + V_{KS}^{LDA} - \varepsilon_i | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | -\nabla^2 + V_{KS}^{LDA} - \varepsilon_i | \frac{\delta\chi_{\mathbf{K}}}{\delta \mathbf{R}_\alpha} \rangle \right) A_{i,\mathbf{K}} \tag{242}$$

$$- \sum_i f_{i\mathbf{k}} \langle \psi_{i\mathbf{k}} | \frac{\delta T}{\delta \mathbf{R}_\alpha} | \psi_{i\mathbf{k}} \rangle \tag{243}$$

$$- \sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A^*_{i,\mathbf{K}'} A_{i,\mathbf{K}} (V_U - V_{DC})_{m'm} \frac{\delta}{\delta \mathbf{R}_\alpha} \left(\langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle \right) \tag{244}$$

Eqs. 242 and 243 look just like the DFT part above. The extra forces due to the U terms are thus given by 244.

We thus need the following derivative of the projector

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle = \langle i(\mathbf{k}+\mathbf{K}')\chi_{\mathbf{K}'} - \nabla\chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | -\nabla\phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle \tag{245}$$

$$+ \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle -\nabla\phi_m | \chi_{\mathbf{K}} \rangle + \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | i(\mathbf{k}+\mathbf{K})\chi_{\mathbf{K}} - \nabla\chi_{\mathbf{K}} \rangle \tag{246}$$

$$= i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle \tag{247}$$

$$-(\langle \nabla\chi_{\mathbf{K}'} | \phi_{m'} \rangle + \langle \chi_{\mathbf{K}'} | \nabla\phi_{m'} \rangle) \langle \phi_m | \chi_{\mathbf{K}} \rangle - \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle (\langle \nabla\phi_m | \chi_{\mathbf{K}} \rangle + \langle \phi_m | \nabla\chi_{\mathbf{K}} \rangle) \tag{248}$$

We then recognize

$$\langle \nabla\phi_m | \chi_{\mathbf{K}} \rangle + \langle \phi_m | \nabla\chi_{\mathbf{K}} \rangle = \int d^3r \nabla(\phi_m^*(\mathbf{r})\chi_{\mathbf{K}}) = \oint_{R_{MT}^-} d\mathbf{S}\, \phi_m^*(\mathbf{r})\chi_{\mathbf{K}} \equiv \ll \phi_m | \chi_{\mathbf{K}} \gg \tag{249}$$

and use to rewrite the projector variation

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle - \ll \chi_{\mathbf{K}'} | \phi_{m'} \gg \langle \phi_m | \chi_{\mathbf{K}} \rangle - \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \ll \phi_m | \chi_{\mathbf{K}} \gg \tag{250}$$

Finally, we can write extra LDA+U Pulley forces as

$$\mathbf{F}_\alpha^{U+Pulley} = -\sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') A_{i,\mathbf{K}'}^* \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle (V_U - V_{DC})_{m'm} \langle \phi_m | \chi_{\mathbf{K}} \rangle A_{i,\mathbf{K}} \tag{251}$$

$$+\sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A_{i,\mathbf{K}'}^* \ll \chi_{\mathbf{K}'} | \phi_{m'} \gg (V_U - V_{DC})_{m'm} \langle \phi_m | \chi_{\mathbf{K}} \rangle A_{i,\mathbf{K}} \tag{252}$$

$$+\sum_i f_{i\mathbf{k}} \sum_{\mathbf{K},\mathbf{K}'} A_{i,\mathbf{K}'}^* \langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle (V_U - V_{DC})_{m'm} \ll \phi_m | \chi_{\mathbf{K}} \gg A_{i,\mathbf{K}} \tag{253}$$

Note that Wien2k implements the first term (Eq. 251), but neglects the other two (Eq. 252,253). It would be nice to check how much difference the last two terms make.

B. Proof that variation can be equivalently done in non-diagonal basis

In this section the LDA Hamiltonian will be H^0, i.e.,

$$H^0_{\mathbf{K}'\mathbf{K}} = \langle \chi_{\mathbf{K}'} | -\nabla^2 + V_{KS} | \chi_{\mathbf{K}} \rangle \tag{254}$$

which is diagonalized by the generalized eigenvalue problem Eq. 81

$$A^{0\dagger}_{j\mathbf{K}'} H^0_{\mathbf{K}'\mathbf{K}} A^0_{\mathbf{K}i} - A^{0\dagger}_{j\mathbf{K}'} O_{\mathbf{K}'\mathbf{K}} A^0_{\mathbf{K}i} \varepsilon^0_i = 0 \tag{255}$$

and the LDA+U Hamiltonian in KS basis:

$$H^U_{ij} = \varepsilon^0_i \delta_{ij} + \langle \psi^0_{i\mathbf{k}} | \phi_{m'} \rangle V_{m'm} \langle \phi_m | \psi^0_{j\mathbf{k}} \rangle \equiv (\varepsilon^0_{\mathbf{k}} + V)_{ij} \tag{256}$$

where $V = V_U - V_{DC}$.

Note that the generalized eigenvalue problem (such as Eq. 255) has the following properties (for both pairs H,A or H^0,A^0):

$$HA = OA\varepsilon \tag{257}$$

$$A^+ H = \varepsilon A^\dagger O \tag{258}$$

$$A^\dagger O A = 1 \tag{259}$$

$$A^\dagger H A = \varepsilon \tag{260}$$

We can also diagonalize the LDA+U Hamiltnonian with a unitary transformation B:

$$B^\dagger(\varepsilon^0_{\mathbf{k}} + V)B = \varepsilon_{\mathbf{k}}. \tag{261}$$

Using transformation B, we can then also express LDA+U eigenvectors A in terms of LDA eigenvectors A^0. We have

$$\langle\chi_{\mathbf{K}'}| -\nabla^2 + V_{KS} + |\phi_{m'}\rangle V_{m'm} \langle\phi_m| |\chi_{\mathbf{K}}\rangle A_{\mathbf{K}i} = O_{\mathbf{K}'\mathbf{K}} A_{\mathbf{K}i}\varepsilon_{\mathbf{k}i} \tag{262}$$

or

$$(H^0_{\mathbf{K}'\mathbf{K}} + \langle\chi_{\mathbf{K}'}|\psi^0_{i\mathbf{k}}\rangle \langle\psi^0_{i\mathbf{k}}|\phi_{m'}\rangle V_{m'm} \langle\phi_m|\psi^0_{j\mathbf{k}}\rangle \langle\psi^0_{j\mathbf{k}}|\chi_{\mathbf{K}}\rangle) A_{\mathbf{K}i} = O_{\mathbf{K}'\mathbf{K}} A_{\mathbf{K}i}\varepsilon_i \tag{263}$$

We notice $|\psi^0_{i\mathbf{k}}\rangle = \sum_{\mathbf{K}} A^0_{\mathbf{K}i} |\chi_{\mathbf{K}}\rangle$ hence $\langle\chi^0_{\mathbf{K}'}|\psi^0_{i\mathbf{k}}\rangle = O_{\mathbf{K}'\mathbf{K}} A^0_{\mathbf{K}i}$ and therefore

$$(H^0 + OA^0VA^{0\dagger}O)A = OA\varepsilon_{\mathbf{k}} \tag{264}$$

We also defined above that

$$\langle\psi^0_{i\mathbf{k}}| -\nabla^2 + V_{KS} + |\phi_{m'}\rangle V_{m'm} \langle\phi_m| |\psi^0_{j\mathbf{k}}\rangle = (\varepsilon^0_{\mathbf{k}} + V)_{ij} = (B\varepsilon_{\mathbf{k}}B^\dagger)_{ij} \tag{265}$$

which can be cast into the form

$$A^{0\dagger}_{i\mathbf{K}'} \langle\chi_{\mathbf{K}'}| -\nabla^2 + V_{KS} + |\phi_{m'}\rangle V_{m'm} \langle\phi_m| |\chi_{\mathbf{K}}\rangle A^0_{\mathbf{K}j} = B\varepsilon_{\mathbf{k}}B^\dagger \tag{266}$$

or

$$A^{0\dagger}HA^0 = B\varepsilon_{\mathbf{k}}B^\dagger \tag{267}$$

We multiply Eq. 267 with OA^0 from the left and B from the right to obtain

$$H(A^0B) = O(A^0B)\varepsilon_{\mathbf{k}} \tag{268}$$

Comparing Eq. 268 with Eq. 264 we recognize $A = A^0B$ and $H = H^0 + OA^0VA^{0\dagger}O$, hence

$$|\psi_{i\mathbf{k}}\rangle = \sum_{\mathbf{K}} |\chi_{\mathbf{K}}\rangle (A^0B)_{\mathbf{K}i} \tag{269}$$

when

$$|\psi^0_{i\mathbf{k}}\rangle = \sum_{\mathbf{K}} |\chi_{\mathbf{K}}\rangle A^0_{\mathbf{K}i} \tag{270}$$

Alternatively, we can derive the above identities from the fact that

$$B^\dagger(\varepsilon^0 + V)B = \varepsilon \tag{271}$$
$$A^{0\dagger}H^0A^0 = \varepsilon^0 \tag{272}$$

which immediately gives

$$B^\dagger(A^{0\dagger}H^0A^0 + V)B = \varepsilon \tag{273}$$
$$B^\dagger A^{0\dagger}(H^0 + A^{0\dagger^{-1}}VA^{0^{-1}})A^0B = \varepsilon \tag{274}$$
$$(A^0B)^\dagger(H^0 + OA^0VA^{0\dagger}O)A^0B = \varepsilon \tag{275}$$
$$(H^0 + OA^0VA^{0\dagger}O)A^0B = O(A^0B)\varepsilon \tag{276}$$

Now we check a small variation of the ε^0 by varying the secular equation

$$H^0A^0 = OA^0\varepsilon^0$$

Note that this equation is always satisifed, hence variation vanishes

$$(\delta H^0)A^0 + H^0(\delta A^0) - (\delta O)A^0\varepsilon^0 - O(\delta A^0)\varepsilon^0 - OA^0\delta\varepsilon^0 = 0 \tag{277}$$
$$A^{0\dagger}(\delta H^0)A^0 + A^{0\dagger}H^0(\delta A^0) - A^{0\dagger}(\delta O)A^0\varepsilon^0 - A^{0\dagger}O(\delta A^0)\varepsilon^0 - A^{0\dagger}OA^0\delta\varepsilon^0 = 0 \tag{278}$$

We note that $A^{0\dagger}OA^0 = 1$ and $A^{0\dagger}H^0 = \varepsilon^0A^{0\dagger}O$ hence

$$\delta\varepsilon^0 = A^{0\dagger}(\delta H^0)A^0 - A^{0\dagger}(\delta O)A^0\varepsilon^0 + \varepsilon^0A^{0\dagger}O(\delta A^0) - A^{0\dagger}O(\delta A^0)\varepsilon^0 \tag{279}$$

Note that although ε^0 is diagonal, its variation is not. However, if only the diagonal components are needed, i.e., $(\delta\varepsilon^0)_{ii}$ then the last two terms cancel, and we get

$$(\delta\varepsilon^0)_{ii} = (A^{0\dagger}(\delta H^0)A^0 - A^{0\dagger}(\delta O)A^0\varepsilon^0)_{ii} \tag{280}$$

This equation is identical to Eq. 82, however, now we also have generalized variation of $\delta\varepsilon^0_{ij}$ in matrix form.

We are now ready to take the variation of LDA+U functional Eq. 220

$$\begin{aligned} F = -\mathrm{Tr}\log\left((i\omega+\mu-\varepsilon^0_{\mathbf{k}})1 - \langle\psi^0_{i\mathbf{k}}|\phi_{m'}\rangle (V_U - V_{DC})_{m'm} \langle\phi_m|\psi^0_{j\mathbf{k}}\rangle\right) - \mathrm{Tr}((V_H + V_{xc})\rho) \\ -\mathrm{Tr}(|\phi\rangle (V_U - V_{DC}) \langle\phi|\,\rho) + E_H[\rho] + E_{xc}[\rho] + \phi^U[n] - \phi^{DC}[n] + E_{nucleous} \end{aligned} \tag{281}$$

We get

$$\begin{aligned} \delta F = \mathrm{Tr}\left(G\delta(\varepsilon^0_{\mathbf{k}} + (\langle\psi^0_{i\mathbf{k}}|\phi_{m'}\rangle (V_U - V_{DC})_{m'm} \langle\phi_m|\psi^0_{j\mathbf{k}}\rangle))\right) - \mathrm{Tr}((\delta V_H + \delta V_{xc} + \delta V_{nucl})\rho) \\ -\delta\mathrm{Tr}((\delta V_U - \delta V_{DC})\langle\phi|\rho|\phi\rangle) - \sum_\alpha F^{HF}_\alpha \delta R_\alpha \end{aligned} \tag{282}$$

First we are going to concentrate on the first term, which comes from derivative of logarithm

$$\delta F^0 = \mathrm{Tr}(G\delta H).$$

In matrix form, we have

$$\delta F^0 = \mathrm{Tr}(\rho\delta(\varepsilon^0 + V)) \tag{283}$$

We also know that $\varepsilon^0 + V = B\varepsilon B^\dagger$ and hence $\rho = B\rho^d B^\dagger$, where ρ^d is density matrix in diagonal basis. The latter is important for some permutations of terms we want to do. We get

$$\delta F^0 = \mathrm{Tr}(B\rho^d B^\dagger \delta(\varepsilon^0 + V)) \tag{284}$$

We are first going to repeat the derivation from the previous section, which transforms H into diagonal form:

$$\delta F^0 = \mathrm{Tr}(B\rho^d B^\dagger \delta(B\varepsilon B^\dagger)) \tag{285}$$

which gives

$$\delta F^0 = \mathrm{Tr}(\rho^d\delta\varepsilon) + \mathrm{Tr}(\rho^d B^\dagger \delta B\varepsilon + B\rho^d\varepsilon\delta B^\dagger) \tag{286}$$

Notice that both ρ^d and ε are diagional matrices, hence they comute, hence we can write the last two terms in the form $\mathrm{Tr}(\rho^d(B^\dagger\delta B + \delta B^\dagger B)\varepsilon) = 0$ because $B^\dagger B = 1$ is always unitary and its variation has to vanish. Hence we have

$$\delta F^0 = \mathrm{Tr}(\rho^d\delta\varepsilon) \tag{287}$$

We could of course derive this equation directly from variation of Green's function in diagonal form $\delta F^0 = -\delta\ln(i\omega + \mu - \varepsilon)$, but we wanted to check that the two derivations give identical results.

We next use Eq. 280 to get

$$\delta F^0 = \mathrm{Tr}(\rho^d(A^\dagger(\delta H)A - A^\dagger(\delta O)A\varepsilon)) \tag{288}$$

notice that because ρ^d is diagonal and we have Tr, only the diagonal components of Eq. 279 are needed. We also know from Eq. 264 that $H = H^0 + OA^0VA^{0\dagger}O$, hence

$$\delta F^0 = \mathrm{Tr}(\rho^d(A^\dagger(\delta H^0)A - A^\dagger(\delta O)A\varepsilon)) + \mathrm{Tr}(\rho^d A^\dagger\delta(OA^0VA^{0\dagger}O)A) \tag{289}$$

Next we notice that $OA^0VA^{0\dagger}O$ is $\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle V_{m'm}\langle\phi_m|\chi_{\mathbf{K}}\rangle$ (see Eq. 263), and when combined with $-\mathrm{Tr}(n_{mm'}\delta V_{m'm})$ from Eq. 282, we get

$$\begin{aligned} \delta F^0 - \mathrm{Tr}(n_{mm'}\delta V_{m'm}) &= \mathrm{Tr}(\rho^d(A^\dagger(\delta H^0)A - A^\dagger(\delta O)A\varepsilon)) && (290)\\ &+ \mathrm{Tr}(\rho^d_{ii}A^\dagger_{i\mathbf{K}'}\delta(\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle V_{m'm}\langle\phi_m|\chi_{\mathbf{K}}\rangle)A_{\mathbf{K}i}) - \mathrm{Tr}(n_{mm'}\delta V_{m'm}) && (291)\\ &= \mathrm{Tr}(\rho^d(A^\dagger(\delta H^0)A - A^\dagger(\delta O)A\varepsilon)) + \mathrm{Tr}(\rho^d_{ii}A^\dagger_{i\mathbf{K}'}V_{m'm}A_{\mathbf{K}i}\delta(\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\langle\phi_m|\chi_{\mathbf{K}}\rangle)) && (292) \end{aligned}$$

The last term is exactly the additional LDA+U force that we derived in previous chapter Eq. 244.

This was just equivalent derivation (using matrix notation) of the derivation from the previous chapter. But now we want to see that variation in basis, which is not an eigenbasis of H^0+V, also leads to the same result. This is important in DMFT since H^0+V basis is frequency dependent, while H^0 basis is not, and we want to do most of the calculation in frequency independent basis.

Notice that in DMFT transformation B is frequency dependent B_ω, hence the expression in diagonal basis would be

$$\begin{aligned}\delta F^0 - \mathrm{Tr}(G_{mm'}\delta\Sigma_{m'm}) &= \mathrm{Tr}([B_\omega G^d_\omega B^\dagger_\omega](A^{0\dagger}(\delta H^0)A^0)) - \mathrm{Tr}([B_\omega\varepsilon_\omega G^d_\omega B^\dagger_\omega]A^{0\dagger}(\delta O)A^0)\\ &+ \mathrm{Tr}([(B_\omega G^d_\omega B^\dagger_\omega)_{ij}\Sigma^\omega_{m'm}]A^{0\dagger}_{j\mathbf{K}'}\delta(\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\langle\phi_m|\chi_{\mathbf{K}}\rangle)A^0_{\mathbf{K}i})\end{aligned}$$

In particular, the last term would require

$$(w\Sigma)_{ijm'm} = \frac{1}{\beta}\sum_{i\omega}(B_\omega G^d_\omega B^\dagger_\omega)_{ij}\Sigma^\omega_{m'm} \tag{293}$$

We are hoping to find better expression in non-diagonal case.

The challenge now is to show that variation of δF^0 leads to Eq. 289 even when we do not transform to eigenbasis. We return to Eq. 284, and write

$$\delta F^0 = \mathrm{Tr}(B\rho^d B^\dagger\delta(\varepsilon^0+V)) = \mathrm{Tr}(B\rho^d B^\dagger\left(A^{0\dagger}(\delta H^0)A^0 - A^{0\dagger}(\delta O)A^0\varepsilon^0 + \varepsilon^0 A^{0\dagger}O(\delta A^0) - A^{0\dagger}O(\delta A^0)\varepsilon^0\right)) + \mathrm{Tr}(B\rho^d B^\dagger\delta V))$$

Notice that we had to use the non-diagonal form of $\delta\varepsilon^0$ (Eq. 279) and that diagonal form Eq. 280 would not be sufficient here.

We next notice that $A^0B = A$ and $B^\dagger A^{0\dagger} = A^\dagger$ hence

$$\delta F^0 = \mathrm{Tr}(\rho^d\left(A^\dagger(\delta H^0)A - A^\dagger(\delta O)AB^\dagger\varepsilon^0B + B^\dagger\varepsilon^0BA^\dagger O(\delta A^0)B - A^\dagger O(\delta A^0)BB^\dagger\varepsilon^0B\right)) + \mathrm{Tr}(B\rho^dB^\dagger\delta V)) \tag{294}$$

Next we replace $B^\dagger\varepsilon^0B = \varepsilon - B^\dagger VB$ therefore

$$\delta F^0 = \mathrm{Tr}(\rho^d\left(A^\dagger(\delta H^0)A - A^\dagger(\delta O)A(\varepsilon - B^\dagger VB) + (\varepsilon - B^\dagger VB)A^\dagger O(\delta A^0)B - A^\dagger O(\delta A^0)B(\varepsilon - B^\dagger VB)\right)) + \mathrm{Tr}(B\rho^dB^\dagger\delta V))$$

and now we notice that both ε and ρ^d are diagonal matrices, hence the third and fourth terms have parts that cancel, i.e., $\mathrm{Tr}(\rho^d(\varepsilon A^\dagger O(\delta A^0)B - A^\dagger O(\delta A^0)B\varepsilon) = 0$, hence

$$\begin{aligned}\delta F^0 &= \mathrm{Tr}(\rho^d\left(A^\dagger(\delta H^0)A - A^\dagger(\delta O)A\varepsilon\right)) &(295)\\ &+ \mathrm{Tr}(\rho^d\left(A^\dagger(\delta O)AB^\dagger VB - (B^\dagger VB)A^\dagger O(\delta A^0)B + A^\dagger O(\delta A^0)BB^\dagger VB\right)) + \mathrm{Tr}(B\rho^dB^\dagger\delta V)) &(296)\end{aligned}$$

Eq. 295 is already in the required form of Eq. 289. The second part Eq. 296 needs some further manipulation. We write

$$Eq.\ 296 = \mathrm{Tr}(A\rho^dA^\dagger\left((\delta O)AB^\dagger VBA^{-1} - {A^\dagger}^{-1}B^\dagger VBA^\dagger O(\delta A^0)BA^{-1} + O(\delta A^0)VBA^{-1}\right)) + \mathrm{Tr}(B\rho^dB^\dagger\delta V)) \tag{297}$$

and we use $A^\dagger OA = 1$ and $AB^\dagger = A^0$ and $BA^\dagger = A^{0\dagger}$

$$Eq.\ 296 = \mathrm{Tr}(A\rho^dA^\dagger\left((\delta O)A^0VA^{0\dagger}O - OA^0VA^{0\dagger}O(\delta A^0)A^{0\dagger}O + O(\delta A^0)VA^{0\dagger}O\right)) + \mathrm{Tr}(B\rho^dB^\dagger\delta V) \tag{298}$$

Next we vary $A^\dagger OA = 1$ to obtain

$$A^{0\dagger}O(\delta A^0) = -(\delta A^{0\dagger})OA^0 - A^{0\dagger}(\delta O)A^0$$

hence

$$Eq.\ 296 = \mathrm{Tr}(A\rho^dA^\dagger\left((\delta O)A^0VA^{0\dagger}O + OA^0V((\delta A^{0\dagger})O + A^{0\dagger}(\delta O))A^0A^{0\dagger}O + O(\delta A^0)VA^{0\dagger}O\right)) + \mathrm{Tr}(B\rho^dB^\dagger\delta V) \tag{299}$$

we next use $A^0A^{0\dagger}O = 1$ (which is a consequence of $A^{0\dagger}OA^0 = 1$) to obtain

$$Eq.\ 296 = \mathrm{Tr}(A\rho^dA^\dagger\left((\delta O)A^0VA^{0\dagger}O + OA^0V(\delta A^{0\dagger})O + OA^0VA^{0\dagger}(\delta O) + O(\delta A^0)VA^{0\dagger}O\right)) + \mathrm{Tr}(B\rho^dB^\dagger\delta V) \tag{300}$$

We also notice that $\mathrm{Tr}(B\rho^d B^\dagger \delta V) = \mathrm{Tr}(A^0 B\rho^d B^\dagger A^{0\dagger} O A^0 \delta V A^{0\dagger} O) = \mathrm{Tr}(A\rho^d A^\dagger O A^0 \delta V A^{0\dagger} O)$ which gives

$$\begin{aligned} Eq.\ 296 &= \mathrm{Tr}(A\rho^d A^\dagger \left((\delta O) A^0 V A^{0\dagger} O + O A^0 V (\delta A^{0\dagger}) O + O A^0 V A^{0\dagger} (\delta O) + O(\delta A^0) V A^{0\dagger} O + O A^0 \delta V A^{0\dagger} O\right)) \\ &= \mathrm{Tr}(A\rho^d A^\dagger \delta \left(O A^0 V A^{0\dagger} O\right)) \end{aligned} \tag{301}$$

hence we conclude

$$\delta F^0 = \mathrm{Tr}(\rho^d \left(A^\dagger (\delta H^0) A - A^\dagger (\delta O) A\varepsilon\right)) + \mathrm{Tr}(A\rho^d A^\dagger \delta \left(O A^0 V A^{0\dagger} O\right)) \tag{302}$$

This is equal to Eq. 289, hence we proved that variation in the basis of diagonal H or diagonal H^0 leads to the same result.

C. LDA+DMFT

We first diagonalize the LDA+DMFT Green's function. We write self-energy in static Kohn-Sham basis $|\psi_i^0\rangle$, in which the LDA+DMFT eigenproblem is

$$\varepsilon_i^0 \delta_{ij} + \langle\psi_i^0|\Sigma(\omega) - V_{DC}|\psi_j^0\rangle = (B_\omega^R \varepsilon_\omega B_\omega^L)_{ij} \tag{303}$$

This defines the frequency dependent transformation B_ω between the DMFT and DFT eigenbasis, which is not unitary (because $H^0 + \Sigma$ is not Hermitian). The Green's function in the diagonal basis is then simply given by

$$G^d(i\omega) = \frac{1}{i\omega + \mu - \varepsilon_\omega} \tag{304}$$

For convenience, we also define the following matrix

$$(V_\omega)_{ij} \equiv \langle\psi_i^0|\Sigma(\omega) - V_{DC}|\psi_j^0\rangle \tag{305}$$

We will also need explicit formula for embedding self-energy into Kohn-Sham basis

$$(V_\omega)_{ij} = \langle\psi_i^0|\Sigma(\omega) - V_{DC}|\psi_j^0\rangle = \langle\psi_i^0|\phi_m\rangle\, \tilde{\Sigma}_{mm'}\, \langle\phi_{m'}|\psi_j^0\rangle \tag{306}$$

where $\tilde{\Sigma}_{mm'} = \Sigma_{mm'}(\omega) - V_{DC,mm'}$.

For DFT Hamiltonian H^0 we have eigenvalue proble

$$\varepsilon^0 = A^{0\dagger} H^0 A^0 \tag{307}$$

which together with Eq. 303 leads to the following LDA+DMFT eigenproblem

$$(H^0 + O A^0 V_\omega A^{0\dagger} O) A_\omega^R = O A_\omega^R \varepsilon_\omega \tag{308}$$

where $A_\omega^R = A^0 B_\omega^R$. Similarly, $A_\omega^L = B_\omega^L A^{0\dagger}$.

We vary eigenproblem Eq. 308 to get

$$(\delta H^0) A_\omega^R + \delta(O A^0 V_\omega A^{0\dagger} O) A_\omega^R - (\delta O) A_\omega^R \varepsilon_\omega - O A_\omega^R \delta\varepsilon_\omega + (H^0 + O A^0 V_\omega A^{0\dagger} O)(\delta A_\omega^R) - O(\delta A_\omega^R)\varepsilon_\omega = 0 \tag{309}$$

and multiplying by A_ω^L from left leads to

$$A_\omega^L (\delta H^0) A_\omega^R + A_\omega^L \delta(O A^0 V_\omega A^{0\dagger} O) A_\omega^R - A_\omega^L (\delta O) A_\omega^R \varepsilon_\omega - \delta\varepsilon_\omega + \varepsilon_\omega A_\omega^L O(\delta A_\omega^R) - A_\omega^L O(\delta A_\omega^R)\varepsilon_\omega = 0 \tag{310}$$

which finally gives

$$\delta\varepsilon_\omega = A_\omega^L (\delta H^0) A_\omega^R + A_\omega^L \delta(O A^0 V_\omega A^{0\dagger} O) A_\omega^R - A_\omega^L (\delta O) A_\omega^R \varepsilon_\omega + \varepsilon_\omega A_\omega^L O(\delta A_\omega^R) - A_\omega^L O(\delta A_\omega^R)\varepsilon_\omega \tag{311}$$

Notice that when only the diagonal components of the variation are needed, the last two terms cancel as ε_ω is diagonal matrix

$$(\delta\varepsilon_\omega)_{ii} = (A_\omega^L (\delta H^0) A_\omega^R + A_\omega^L \delta(O A^0 V_\omega A^{0\dagger} O) A_\omega^R - A_\omega^L (\delta O) A_\omega^R \varepsilon_\omega)_{ii} \tag{312}$$

To derive a small variation of DMFT free energy, we start from the expression Eq. 220.

$$F = -\mathrm{Tr}\log\left(i\omega+\mu-|\psi_{i\mathbf{k}}\rangle\,\varepsilon^{LDA}_{i\mathbf{k}}\,\langle\psi_{i\mathbf{k}}| - |\phi\rangle\,(\Sigma-V_{dc})\,\langle\phi|\right) - \mathrm{Tr}((V_H+V_{xc})\rho)$$
$$-\mathrm{Tr}(|\phi\rangle\,(\Sigma-V_{DC})\,\langle\phi|\,G) + E_H[\rho]+E_{xc}[\rho]+\phi^{DMFT}[G_{local}]-\phi^{DC}[\rho_{local}]+E_{nucleous}+\mu N \tag{313}$$

which can now be rewritten as

$$F = -\mathrm{Tr}\log\left(i\omega+\mu-\varepsilon_\omega\right) - \mathrm{Tr}((V_H+V_{xc})\rho) - \mathrm{Tr}(\tilde{\Sigma}\,\langle\phi|G|\phi\rangle) + E_H[\rho]+E_{xc}[\rho]$$
$$+\phi^{DMFT}[G_{local}]-\phi^{DC}[\rho_{local}]+E_{nucleous}+\mu N \tag{314}$$

The variation then gives

$$\delta F = \mathrm{Tr}(G^d\delta\varepsilon_\omega) - \mathrm{Tr}(G_{local}\delta\tilde{\Sigma}) - \mathrm{Tr}((\delta V_H+\delta V_{xc}+\delta V_{nucl})\rho) - \sum_\alpha F^{HF}_\alpha\delta R_\alpha + \mu\delta N \tag{315}$$

The charge neutrality is always enforced, hence δN vanishes. G^d is the Green's function in diagonal basis, i.e., $G^d = 1/(i\omega+\mu-\varepsilon_\omega)$. We then insert the diagonal components of variation $(\delta\varepsilon_\omega)_{ii}$, determined in Eq. 312, to obtain

$$\delta F = \mathrm{Tr}\left(G^d(A^L_\omega(\delta H^0)A^R_\omega + A^L_\omega\delta(OA^0V_\omega A^{0\dagger}O)A^R_\omega - A^L_\omega(\delta O)A^R_\omega\varepsilon_\omega)\right) - \mathrm{Tr}(G_{local}\delta\tilde{\Sigma}) - \mathrm{Tr}(\delta V_{KS}\rho) - \sum_\alpha F^{HF}_\alpha\delta R_\alpha$$

We then split the eigenvectors into frequency dependent and independnt parts $A^L_\omega = B^L_\omega A^{0\dagger}$ and $A^R_\omega = A^0 B^R_\omega$ and obtain

$$\delta F = \mathrm{Tr}\left(B^R_\omega G^d B^L_\omega A^{0\dagger}(\delta H^0)A^0\right) + \mathrm{Tr}\left(B^R_\omega G^d B^L_\omega A^{0\dagger}\delta(OA^0V_\omega A^{0\dagger}O)A^0\right) - \mathrm{Tr}\left(B^R_\omega\varepsilon_\omega G^d B^L_\omega A^{0\dagger}(\delta O)A^0\right) \tag{316}$$
$$-\mathrm{Tr}(G_{local}\delta\tilde{\Sigma}) - \mathrm{Tr}(\delta V_{KS}\rho) - \sum_\alpha F^{HF}_\alpha\delta R_\alpha$$

which can also be cast into the form

$$\delta F = \mathrm{Tr}\left(B^R_\omega G^d B^L_\omega A^{0\dagger}(\delta H^0)A^0\right) - \mathrm{Tr}\left(B^R_\omega\varepsilon_\omega G^d B^L_\omega A^{0\dagger}(\delta O)A^0\right) - \mathrm{Tr}(\delta V_{KS}\rho) - \sum_\alpha F^{HF}_\alpha\delta R_\alpha \tag{317}$$
$$+\mathrm{Tr}\left((B^R_\omega G^d B^L_\omega)_{ij}A^{0\dagger}_{j\mathbf{K}'}\delta(\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\,\tilde{\Sigma}_{m'm}\,\langle\phi_m|\chi_{\mathbf{K}}\rangle)A^0_{\mathbf{K}i}\right) \tag{318}$$
$$-\mathrm{Tr}\left((B^R_\omega G^d B^L_\omega)_{ij}A^{0\dagger}_{j\mathbf{K}'}\,\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\,\delta(\tilde{\Sigma}_{m'm})\,\langle\phi_m|\chi_{\mathbf{K}}\rangle\,A^0_{\mathbf{K}i}\right) \tag{319}$$

where we used

$$G_{local\;mm'} = \langle\phi_m|G|\phi_{m'}\rangle = \langle\phi_m|\chi_{\mathbf{K}}\rangle\,(A^R_\omega G^d A^L_\omega)_{\mathbf{K}\mathbf{K}'}\,\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle = \langle\phi_m|\chi_{\mathbf{K}}\rangle\,(A^0B^R_\omega G^d B^L_\omega A^{0\dagger})_{\mathbf{K}\mathbf{K}'}\,\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle \tag{320}$$

We thus obtain

$$\delta F = \mathrm{Tr}\left(B^R_\omega G^d B^L_\omega A^{0\dagger}(\delta H^0)A^0\right) - \mathrm{Tr}\left(B^R_\omega\varepsilon_\omega G^d B^L_\omega A^{0\dagger}(\delta O)A^0\right) - \mathrm{Tr}(\delta V_{KS}\rho) - \sum_\alpha F^{HF}_\alpha\delta R_\alpha \tag{321}$$
$$+\mathrm{Tr}\left((B^R_\omega G^d B^L_\omega)_{ij}A^{0\dagger}_{j\mathbf{K}'}A^0_{\mathbf{K}i}\tilde{\Sigma}_{m'm}\delta(\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\,\langle\phi_m|\chi_{\mathbf{K}}\rangle)\right) \tag{322}$$

We next define the following quantities

$$\rho^{DMFT} \equiv \frac{1}{\beta}\sum_{i\omega}B^R_\omega\frac{1}{i\omega+\mu-\varepsilon_\omega}B^L_\omega = \mathcal{B}\;w\;\mathcal{B}^\dagger \tag{323}$$
$$(\rho\varepsilon)^{DMFT} \equiv \frac{1}{\beta}\sum_{i\omega}B^R_\omega\varepsilon_\omega\frac{1}{i\omega+\mu-\varepsilon_\omega}B^L_\omega = \mathcal{B}\;(\widetilde{w\varepsilon})\;\mathcal{B}^\dagger = \widetilde{\mathcal{B}}\;w_\varepsilon\;\widetilde{\mathcal{B}}^\dagger \tag{324}$$
$$G(i\omega)_{ij} \equiv \left(B^R_\omega\frac{1}{i\omega+\mu-\varepsilon_\omega}B^L_\omega\right)_{ij} \tag{325}$$

The first line decomposes the DMFT density ρ^{DMFT} by unitary transformation $\mathcal{B}$ to produce diagonal matrix of weights w, which is possible because ρ^{DMFT} is a Hermitian positive definite matrix. The second equation determines an auxiliary off-diagonal matrix of energy $\widetilde{w\varepsilon}$, which is also Hermitian, since $(\rho\varepsilon)^{DMFT}$ is hermitian. Finally, the last equation in Eq. 324 determines another unitary transformation $\widetilde{\mathcal{B}}$ which diagonalizes Hermitian matrix $(\rho\varepsilon)^{DMFT}$.

Using the above defined quantities, we get for the variaton of the free energy:

$$\delta F = \mathrm{Tr}\left(\rho^{DMFT} A^{0\dagger}(\delta H^0)A^0\right) - \mathrm{Tr}\left((\rho\varepsilon)^{DMFT} A^{0\dagger}(\delta O)A^0\right) - \mathrm{Tr}(\delta V_{KS}\rho) - \sum_\alpha F_\alpha^{HF}\delta R_\alpha$$
$$+\mathrm{Tr}\left(A^0_{\mathbf{K}i} G(i\omega)_{ij} A^{0\dagger}_{j\mathbf{K}'}\,\tilde{\Sigma}_{m'm}(\omega)\delta(\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\langle\phi_m|\chi_{\mathbf{K}}\rangle)\right) \tag{326}$$

We then derive the variation of LDA Hamiltonian and overlap matrix elements using either Krakauer's formalism (Eqs. 525, 526), or Soler/Williams formalism (527, 528, 529). In both cases we get

$$\frac{\delta O}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle_{MT} - \oint d\vec{S}\;\tilde{\chi}^*_{\mathbf{K}'}\tilde{\chi}_{\mathbf{K}} \tag{327}$$
$$\frac{\delta\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle_{MT} - \oint d\vec{S}\;\tilde{\chi}^*_{\mathbf{K}'}T\tilde{\chi}_{\mathbf{K}} \tag{328}$$
$$\frac{\delta\langle\chi_{\mathbf{K}'}|V_{KS}|\chi_{\mathbf{K}}\rangle}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|V_{KS}|\chi_{\mathbf{K}}\rangle_{MT} - \oint d\vec{S}\;\tilde{\chi}^*_{\mathbf{K}'}V_{KS}\tilde{\chi}_{\mathbf{K}} + \langle\chi_{\mathbf{K}'}|\frac{\delta V_{KS}}{\mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle + \langle\chi_{\mathbf{K}'}|\nabla V_{KS}|\chi_{\mathbf{K}}\rangle_{MT} \tag{329}$$

Notice that in Soler/Williams formalism we would use Gauss theorem to write an equivalent form

$$\frac{\delta O}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\left[\langle\chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle_{MT} - \langle\tilde{\chi}_{\mathbf{K}'}|\tilde{\chi}_{\mathbf{K}}\rangle_{MT}\right] \tag{330}$$
$$\frac{\delta\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\left[\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle_{MT} - \langle\tilde{\chi}_{\mathbf{K}'}|T|\tilde{\chi}_{\mathbf{K}}\rangle_{MT}\right] \tag{331}$$
$$\frac{\delta\langle\chi_{\mathbf{K}'}|V_{KS}|\chi_{\mathbf{K}}\rangle}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\left[\langle\chi_{\mathbf{K}'}|V_{KS}|\chi_{\mathbf{K}}\rangle_{MT} - \langle\tilde{\chi}_{\mathbf{K}'}|V_{KS}|\tilde{\chi}_{\mathbf{K}}\rangle_{MT}\right] + \langle\chi_{\mathbf{K}'}|\frac{\delta V_{KS}}{\mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle$$
$$+\langle\chi_{\mathbf{K}'}|\nabla V_{KS}|\chi_{\mathbf{K}}\rangle_{MT} - \langle\tilde{\chi}_{\mathbf{K}'}|\nabla V_{KS}|\tilde{\chi}_{\mathbf{K}}\rangle_{MT} \tag{332}$$

Using Krakauer form, we obtain

$$\frac{\delta H^0}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|H^0|\chi_{\mathbf{K}}\rangle_{MT} - \oint_{MT} d\vec{S}\;\tilde{\chi}^*_{\mathbf{K}'}H^0\tilde{\chi}_{\mathbf{K}} + \langle\chi_{\mathbf{K}'}|\frac{\delta V^{LDA}_{KS}}{\mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle$$
$$-\int_{MT} d^3r V^{LDA}_{KS}\nabla(\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}}) + \oint_{MT} d\vec{S}\chi^*_{\mathbf{K}'}V^{LDA}_{KS}\chi_{\mathbf{K}} \tag{333}$$

For the last two terms we used integration by parts to turn $\int\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}}\nabla V_{KS}$ into $-\int V_{KS}\nabla(\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}})$ plus the surface term.

Slight reshuffling of terms then gives

$$\frac{\delta H^0}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|H^0|\chi_{\mathbf{K}}\rangle_{MT} + \langle\chi_{\mathbf{K}'}|\frac{\delta V_{KS}}{\mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle - \int_{MT} d^3r V_{KS}\nabla_{\mathbf{r}}(\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}})$$
$$-\oint_{MT} d\vec{S}\;\tilde{\chi}^*_{\mathbf{K}'}T\tilde{\chi}_{\mathbf{K}} + \oint_{MT} d\vec{S}\left[\chi^*_{\mathbf{K}'}V_{KS}\chi_{\mathbf{K}} - \tilde{\chi}^*_{\mathbf{K}'}V_{KS}\tilde{\chi}_{\mathbf{K}}\right] \tag{334}$$

The last term can be neglected if expansion in the MT-sphere goes to large enough cutoff-l_{max}, as $\chi_{\mathbf{K}}$ becomes continuous across the MT-sphere. This term is neglected in Wien2K.

As explained in previous sections, in the interstitials we use the symmetric form of the kinetic energy operator, i.e., $\nabla\psi_{\mathbf{k}}\cdot\nabla\psi_{\mathbf{k}}$. In the MT-part, however, we use more common form of $\psi_{\mathbf{k}}(-\nabla^2)\psi_{\mathbf{k}}$. Consequently, there is an extra term generated on the surface of the MT sphere, which takes the form

$$\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle_{MT} = \langle\chi_{\mathbf{K}'}| -\nabla^2|\chi_{\mathbf{K}}\rangle_{MT} + \oint_{MT} d\vec{S}\chi^*_{\mathbf{K}'}\nabla_{\mathbf{r}}\chi_{\mathbf{K}} \tag{335}$$

This finally gives

$$\frac{\delta H^0}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'}| -\nabla^2 + V_{KS}|\chi_{\mathbf{K}}\rangle_{MT} + i(\mathbf{K}-\mathbf{K}') \oint_{MT} d\vec{S}\chi^*_{\mathbf{K}'}\nabla_{\mathbf{r}}\chi_{\mathbf{K}} + \langle \chi_{\mathbf{K}'}|\frac{\delta V^{LDA}_{KS}}{\delta \mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle \tag{336}$$

$$- \int_{MT} d^3r V_{KS}\nabla_{\mathbf{r}}\left(\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}}\right) - (\mathbf{k}+\mathbf{K}')(\mathbf{k}+\mathbf{K}) \oint_{MT} d\vec{S}\; \tilde{\chi}^*_{\mathbf{K}'+\mathbf{k}}\tilde{\chi}_{\mathbf{K}+\mathbf{k}} + \oint_{MT} d\vec{S}\left[\chi^*_{\mathbf{K}'}V_{KS}\chi_{\mathbf{K}} - \tilde{\chi}^*_{\mathbf{K}'}V_{KS}\tilde{\chi}_{\mathbf{K}}\right]$$

$$\frac{\delta O}{\delta \mathbf{R}_\alpha} = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle_{MT} - \oint_{MT} d\vec{S}\; \tilde{\chi}^*_{\mathbf{K}'}\tilde{\chi}_{\mathbf{K}} \tag{337}$$

Notice that

$$\rho(\mathbf{r}) = \langle \mathbf{r}|\psi^0_{\mathbf{k}i}\rangle\, \rho^{DMFT}_{ij}\, \langle \psi^0_{\mathbf{k}j}|\mathbf{r}\rangle = \langle \mathbf{r}|\chi_{\mathbf{K}}\rangle\, A^0_{\mathbf{K}i}\rho^{DMFT}_{ij} A^{0\dagger}_{j\mathbf{K}'}\, \langle \chi_{\mathbf{K}'}|\mathbf{r}\rangle \tag{338}$$

hence

$$\mathrm{Tr}\left(\rho^{DMFT}_{ij} A^{0\dagger}_{j\mathbf{K}'}\, \langle \chi_{\mathbf{K}'}|\frac{\delta V^{LDA}_{KS}}{\delta \mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle\, A^0_{\mathbf{K}i}\right) = \mathrm{Tr}(\rho\frac{\delta V^{LDA}_{KS}}{\delta \mathbf{R}_\alpha}) \tag{339}$$

$$\mathrm{Tr}\left(\rho^{DMFT}_{ij} A^{0\dagger}_{j\mathbf{K}'} \int_{MT} d^3r V_{KS}\nabla_{\mathbf{r}}\left(\chi^*_{\mathbf{K}'+\mathbf{k}}\chi_{\mathbf{K}+\mathbf{k}}\right) A^0_{\mathbf{K}i}\right) = \int_{MT} d^3r V_{KS}(\mathbf{r})\nabla\rho^{DMFT}(\mathbf{r}) \tag{340}$$

For convenience, we define the following quantities

$$R^{(1)}_{\mathbf{K}'\mathbf{K}} \equiv i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'}| -\nabla^2 + V_{KS}|\chi_{\mathbf{K}}\rangle_{MT} \tag{341}$$

$$R^{(2)}_{\mathbf{K}'\mathbf{K}} \equiv (\mathbf{k}+\mathbf{K}')(\mathbf{k}+\mathbf{K}) \oint_{MT} d\vec{S}\tilde{\chi}^*_{\mathbf{K}'}(\mathbf{r})\tilde{\chi}_{\mathbf{K}}(\mathbf{r}) \tag{342}$$

$$R^{(3)}_{\mathbf{K}'\mathbf{K}} \equiv i(\mathbf{K}-\mathbf{K}') \oint_{MT} d\vec{S}\chi^*_{\mathbf{K}'}\nabla_{\mathbf{r}}\chi_{\mathbf{K}} \tag{343}$$

$$R^{(4)}_{\mathbf{K}'\mathbf{K}} \equiv \oint_{MT} d\vec{S}\left[\chi^*_{\mathbf{K}'}V_{KS}\chi_{\mathbf{K}} - \tilde{\chi}^*_{\mathbf{K}'}V_{KS}\tilde{\chi}_{\mathbf{K}}\right] \tag{344}$$

$$Q^{(1)}_{\mathbf{K}'\mathbf{K}} \equiv i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle_{MT} \tag{345}$$

$$Q^{(2)}_{\mathbf{K}'\mathbf{K}} \equiv \oint_{r=R_{MT}} d\vec{S}\tilde{\chi}^*_{\mathbf{K}'}(\mathbf{r})\tilde{\chi}_{\mathbf{K}}(\mathbf{r}) \tag{346}$$

$$\tag{347}$$

so that

$$\frac{\delta H^0}{\delta \mathbf{R}_\alpha} = R^{(1)} - R^{(2)} + R^{(3)} + R^{(4)} - \int_{MT} d^3r V_{KS}\nabla_{\mathbf{r}}\left(\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}}\right) + \langle \chi_{\mathbf{K}'}|\frac{\delta V^{LDA}_{KS}}{\delta \mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle \tag{348}$$

$$\frac{\delta O}{\delta \mathbf{R}_\alpha} = Q^{(1)} - Q^{(2)} \tag{349}$$

Notice that in Soler/Williams formalism, we would get a term like $i(\mathbf{K}-\mathbf{K}')\langle\tilde{\chi}_{\mathbf{K}'}|T|\tilde{\chi}_{\mathbf{K}}\rangle_{MT}$ which can be shown to be equivalent to $R^{(2)}$. Also the term $i(\mathbf{K}-\mathbf{K}')\langle\tilde{\chi}_{\mathbf{K}'}|\tilde{\chi}_{\mathbf{K}}\rangle_{MT}$ is equivalent to $Q^{(2)}$.

We can then evaluate term by term of δF. The first term is

$$\mathrm{Tr}\left(\rho^{DMFT}A^{0\dagger}\frac{\delta H^0}{\delta \mathbf{R}_\alpha}A^0\right) = \mathrm{Tr}(\rho^{DMFT}A^{0\dagger}(R^{(1)} - R^{(2)} + R^{(3)} + R^{(4)})A^0) + \tag{350}$$

$$+\ \mathrm{Tr}(\rho^{DMFT}\frac{\delta V^{LDA}_{KS}}{\delta \mathbf{R}_\alpha}) - \int_{MT} d^3r V^{LDA}_{KS}(\mathbf{r})\nabla\rho^{DMFT}(\mathbf{r})$$

The second term is

$$\mathrm{Tr}\left((\rho\varepsilon)^{DMFT}A^{0\dagger}\frac{\delta O}{\delta \mathbf{R}_\alpha}A^0\right) = \mathrm{Tr}((\rho\varepsilon)^{DMFT}A^{0\dagger}(Q^{(1)} - Q^{(2)})A^0) \tag{351}$$

The variation of the DMFT projector

$$\frac{\delta}{\delta \mathbf{R}_\alpha}\langle \chi_{\mathbf{K}'}|\phi_{m'}\rangle\langle\phi_m|\chi_{\mathbf{K}}\rangle$$

is a bit subtle. First, the DMFT projector is zero outside MT-sphere, hence $\delta\tilde{V}/\delta\mathbf{R}_\alpha = 0$ and $\tilde{V} = 0$ outside MT-sphere. We move the projector rigidly with the MT-sphere, hence inside MT-sphere we only have $\delta V/\delta\mathbf{R}_\alpha = -\nabla V$. We then use formulas derived in Eq. 525, which in this case takes the form

$$\frac{\delta}{\delta\mathbf{R}_\alpha}\langle\chi_{\mathbf{K}'}|V|\chi_{\mathbf{K}}\rangle = \langle\frac{\delta\chi_{\mathbf{K}'}}{\delta\mathbf{R}_\alpha}|V|\chi_{\mathbf{K}}\rangle_{MT} + \langle\chi_{\mathbf{K}'}|V|\frac{\delta\chi_{\mathbf{K}}}{\delta\mathbf{R}_\alpha}\rangle_{MT} - \langle\chi_{\mathbf{K}'}|\nabla V|\chi_{\mathbf{K}}\rangle_{MT} + \oint_{MT} d\vec{S}\chi^*_{\mathbf{K}'}V\chi_{\mathbf{K}} \tag{352}$$

$$= i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|V|\chi_{\mathbf{K}}\rangle_{MT} \tag{353}$$

We just derived that

$$\frac{\delta}{\delta\mathbf{R}_\alpha}\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\langle\phi_m|\chi_{\mathbf{K}}\rangle = i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\langle\phi_m|\chi_{\mathbf{K}}\rangle. \tag{354}$$

We now insert all these terms in Eq. 326, and obtain the Pulley forces

$$\mathbf{F}_\alpha^{Pulley} = -\mathrm{Tr}(\rho^{DMFT}A^{0\dagger}(R^{(1)} - R^{(2)} + R^{(3)} + R^{(4)})A^0) + \mathrm{Tr}((\rho\varepsilon)^{DMFT}A^{0\dagger}(Q^{(1)} - Q^{(2)})A^0) \tag{355}$$

$$+\int_{MT} d^3r V_{KS}(\mathbf{r})\nabla\rho^{DMFT}(\mathbf{r}) - \mathrm{Tr}\left(A^0_{\mathbf{K}i}G(i\omega)_{ij}A^{0\dagger}_{j\mathbf{K}'}i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\widetilde{\Sigma}_{m'm}(i\omega)\langle\phi_m|\chi_{\mathbf{K}}\rangle\right) \tag{356}$$

We then use Eqs. 323 and 324 and introduce the “DMFT” coefficients

$$A \equiv A^0\mathcal{B} \tag{357}$$

to obtain Pulley forces in the form

$$\mathbf{F}_\alpha^{Pulley} = -\mathrm{Tr}(wA^\dagger(R^{(1)} - R^{(2)} + R^{(3)} + R^{(4)})A) + \mathrm{Tr}((\widetilde{w\varepsilon})A^\dagger(Q^{(1)} - Q^{(2)})A) \tag{358}$$

$$+\int_{MT} d^3r V_{KS}(\mathbf{r})\nabla\rho^{DMFT}(\mathbf{r}) - \mathrm{Tr}\left(A^0_{\mathbf{K}i}G(i\omega)_{ij}A^{0\dagger}_{j\mathbf{K}'}i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\widetilde{\Sigma}_{m'm}(i\omega)\langle\phi_m|\chi_{\mathbf{K}}\rangle\right) \tag{359}$$

This can also be cast into the form

$$\mathbf{F}_\alpha^{Pulley} = -\sum_{i,j,\mathbf{K}\mathbf{K}'} A^\dagger_{j\mathbf{K}'}i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|(-\nabla^2 + V_{KS})w_i^{DMFT}\delta_{ij} - (\widetilde{w\varepsilon})_{ij}|\chi_{\mathbf{K}}\rangle_{MT} A_{\mathbf{K}i} \tag{360}$$

$$+\sum_{i,j\mathbf{K}\mathbf{K}'} A^\dagger_{j\mathbf{K}'}[(\mathbf{k}+\mathbf{K}')(\mathbf{k}+\mathbf{K})w_i^{DMFT}\delta_{ij} - (\widetilde{w\varepsilon})_{ij}]A_{\mathbf{K}i}\oint_{R_{MT}} d\vec{S}\tilde{\chi}^*_{\mathbf{k}+\mathbf{K}'}(\mathbf{r})\tilde{\chi}_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \tag{361}$$

$$-\sum_i w_i^{DMFT}\sum_{\mathbf{K}\mathbf{K}'} A^\dagger_{i\mathbf{K}'}i(\mathbf{K}-\mathbf{K}')A_{\mathbf{K}i}\oint_{R^-_{MT}} d\vec{S}\chi^*_{\mathbf{k}+\mathbf{K}'}(\mathbf{r})\nabla_{\mathbf{r}}\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \tag{362}$$

$$+\int_{MT} d^3r V_{KS}(\mathbf{r})\nabla\rho^{DMFT}(\mathbf{r}) \tag{363}$$

$$-\frac{1}{\beta}\sum_{i\omega,ij,\mathbf{K}\mathbf{K}'} A^0_{\mathbf{K}i}G_{ij}(i\omega)A^{0\dagger}_{j\mathbf{K}'}i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle\widetilde{\Sigma}_{m'm}(i\omega)\langle\phi_m|\chi_{\mathbf{K}}\rangle \tag{364}$$

$$-\sum_i w_i^{DMFT}\sum_{\mathbf{K},\mathbf{K}'} A^\dagger_{i\mathbf{K}'}A_{\mathbf{K}i}\oint_{MT} d\vec{S}\,[\chi^*_{\mathbf{K}'}V_{KS}\chi_{\mathbf{K}} - \tilde{\chi}^*_{\mathbf{K}'}V_{KS}\tilde{\chi}_{\mathbf{K}}] \tag{365}$$

Notice that the last term is neglected as it should be small when l_{max} is sufficiently large.

D. Implementation of Eq. 360, symmetric part

This is implemented in `Force1_DMFT`.
Let’s start with the part containing spherical symmetric Hamiltonian

$$-i\sum_{i,\mathbf{K}\mathbf{K}'} w_i^{DMFT}(\mathbf{K}-\mathbf{K}')A^*_{\mathbf{K}'i}\langle\chi_{\mathbf{K}'}|(-\nabla^2 + V_{KS})|\chi_{\mathbf{K}}\rangle_{MT} A_{\mathbf{K}i} \tag{366}$$

We first repeat Eq. 67, which gives spherically symetric part of Hamiltonian in the MT-part:

$$\begin{aligned}\langle\chi_{\mathbf{K}'}|-\nabla^2+V_{KS}^{sym}(r)|\chi_{\mathbf{K}}\rangle_{MT} &= a_{lm}^{\mathbf{K}'*}a_{lm}^{\mathbf{K}}E_\nu+b_{lm}^{\mathbf{K}'*}b_{lm}^{\mathbf{K}}E_\nu\langle\dot{u}_l|\dot{u}_l\rangle+\frac{1}{2}[a_{lm}^{\mathbf{K}'*}b_{lm}^{\mathbf{K}}+b_{lm}^{\mathbf{K}'*}a_{lm}^{\mathbf{K}}]+\\ &+ c_{lm}^{\mathbf{K}'*}c_{lm}^{\mathbf{K}}E_\mu\langle u_{LO}|u_{LO}\rangle+\frac{1}{2}[a_{lm}^{\mathbf{K}'*}c_{lm}^{\mathbf{K}}+c_{lm}^{\mathbf{K}'*}a_{lm}^{\mathbf{K}}](E_\mu+E_\nu)\langle u|u_{LO}\rangle+\\ &+ \frac{1}{2}[c_{lm}^{\mathbf{K}'*}b_{lm}^{\mathbf{K}}+b_{lm}^{\mathbf{K}'*}c_{lm}^{\mathbf{K}}][\langle u_{LO}|u_l\rangle+(E_\mu+E_\nu)\langle u_{LO}|\dot{u}_l\rangle]\end{aligned}\tag{367}$$

Clearly, we can split the sum over $\mathbf{K}$ and $\mathbf{K}'$ into two indepedent sums which take $O(N)$ time.[We want to avoid $O(N^2)$ scaling, since there are very many number of plane waves $\mathbf{K}$].

We first define (compute) the following quantities

$$a_{i,lm}=\sum_{\mathbf{K}}A_{\mathbf{K}i}\,a_{lm}^{\mathbf{K}}\tag{368}$$

$$\vec{\mathcal{A}}_{i,lm}=\sum_{\mathbf{K}}\mathbf{K}\,A_{\mathbf{K}i}\,a_{lm}^{\mathbf{K}}\tag{369}$$

which take $O(N)$ time to compute. Here $A_{\mathbf{K},i}$ are eigenvectors corresponding to the Kohn-Sham energy ε_i. We assume corresponding expression for $b_{i,lm}$, $c_{i,lm}$, $\vec{\mathcal{B}}_{i,lm}$, $\vec{\mathcal{C}}_{i,lm}$.

The quadratic terms of the form $a_{lm}^*a_{lm}$ become

$$\sum_{\mathbf{K}\mathbf{K}'}(\mathbf{K}-\mathbf{K}')A_{\mathbf{K}'i}^*a_{lm}^{\mathbf{K}'*}a_{lm}^{\mathbf{K}}A_{i\mathbf{K}}=a_{i,lm}^*\vec{\mathcal{A}}_{i,lm}-\vec{\mathcal{A}}_{i,lm}^*a_{i,lm}=2i\,\mathrm{Im}\{a_{i,lm}^*\vec{\mathcal{A}}_{i,lm}\}\tag{370}$$

while those of the form $a_{lm}^*b_{lm}+b_{lm}^*a_{lm}$ become

$$\begin{aligned}\sum_{\mathbf{K}\mathbf{K}'}(\mathbf{K}-\mathbf{K}')A_{\mathbf{K}'i}^*\frac{1}{2}[a_{lm}^{\mathbf{K}'*}b_{lm}^{\mathbf{K}}+b_{lm}^{\mathbf{K}'*}a_{lm}^{\mathbf{K}}]A_{\mathbf{K}i}&=\frac{1}{2}[a_{i,lm}^*\vec{\mathcal{B}}_{i,lm}-\vec{\mathcal{A}}_{i,lm}^*b_{i,lm}+b_{i,lm}^*\vec{\mathcal{A}}_{i,lm}-\vec{\mathcal{B}}_{i,lm}^*a_{i,lm}]=\\ &=i\,\mathrm{Im}\{a_{i,lm}^*\vec{\mathcal{B}}_{i,lm}+b_{i,lm}^*\vec{\mathcal{A}}_{i,lm}\}\end{aligned}\tag{371}$$

The term with H^0 can then be expressed by

$$\begin{aligned}&\sum_{\mathbf{K}\mathbf{K}'}(\mathbf{K}-\mathbf{K}')A_{\mathbf{K}'i}^*\langle\chi_{\mathbf{K}'}|-\nabla^2+V_{KS}^{sph}(r)|\chi_{\mathbf{K}}\rangle_{MT}A_{\mathbf{K}i}=\\ &i\mathrm{Im}\left\{\left(2a_{i,lm}^*E_\nu+b_{i,lm}^*+c_{i,lm}^*(E_\mu+E_\nu)\langle u|u_{LO}\rangle\right)\vec{\mathcal{A}}_{i,lm}\right\}+\\ +\;&i\mathrm{Im}\left\{\left(a_{i,lm}^*+2b_{i,lm}^*E_\nu\langle\dot{u}_l|\dot{u}_l\rangle+c_{i,lm}^*[\langle u_{LO}|u_l\rangle+(E_\mu+E_\nu)\langle u_{LO}|\dot{u}_l\rangle]\right)\vec{\mathcal{B}}_{i,lm}\right\}+\\ +\;&i\mathrm{Im}\left\{\left(a_{i,lm}^*(E_\mu+E_\nu)\langle u|u_{LO}\rangle+b_{i,lm}^*[\langle u_{LO}|u_l\rangle+(E_\mu+E_\nu)\langle u_{LO}|\dot{u}_l\rangle]+2E_\mu\,c_{i,lm}^*\langle u_{LO}|u_{LO}\rangle\right)\vec{\mathcal{C}}_{i,lm}\right\}\end{aligned}\tag{372}$$

The overlap term is

$$i\sum_{i,j,\mathbf{K}\mathbf{K}'}(\widetilde{w\varepsilon})_{ij}(\mathbf{K}-\mathbf{K}')A_{\mathbf{K}'j}^*\langle\chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle_{MT}A_{\mathbf{K}i}\tag{373}$$

and the overlap of augmented PW functions is

$$\begin{aligned}\langle\chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle_{MT} &= a_{lm}^{\mathbf{K}'*}a_{lm}^{\mathbf{K}}+b_{lm}^{\mathbf{K}'*}b_{lm}^{\mathbf{K}}\langle\dot{u}_l|\dot{u}_l\rangle+\\ &+ c_{lm}^{\mathbf{K}'*}c_{lm}^{\mathbf{K}}\langle u_{LO}|u_{LO}\rangle+[a_{lm}^{\mathbf{K}'*}c_{lm}^{\mathbf{K}}+c_{lm}^{\mathbf{K}'*}a_{lm}^{\mathbf{K}}]\langle u|u_{LO}\rangle+\\ &+ [c_{lm}^{\mathbf{K}'*}b_{lm}^{\mathbf{K}}+b_{lm}^{\mathbf{K}'*}c_{lm}^{\mathbf{K}}]\langle u_{LO}|\dot{u}_l\rangle\end{aligned}\tag{374}$$

hence we obtain

$$
\begin{aligned}
&\sum_{ij}(\widetilde{w\varepsilon})_{ij}\sum_{\mathbf{KK'}}(\mathbf{K}-\mathbf{K'})A^*_{\mathbf{K'}j}\left\langle\chi_{\mathbf{K'}}|\chi_{\mathbf{K}}\right\rangle_{MT}A_{\mathbf{K}i} = \\
&2i\mathrm{Im}\left\{\sum_{ij}(\widetilde{w\varepsilon})_{ij}\left(a^*_{j,lm}+c^*_{j,lm}\left\langle u_{LO}|u\right\rangle\right)\vec{\mathcal{A}}_{i,lm}\right\}+ \\
+\;&2i\mathrm{Im}\left\{\sum_{ij}(\widetilde{w\varepsilon})_{ij}\left(b^*_{j,lm}\left\langle\dot{u}_l|\dot{u}_l\right\rangle+c^*_{j,lm}\left\langle u_{LO}|\dot{u}_l\right\rangle\right)\vec{\mathcal{B}}_{i,lm}\right\}+ \\
+\;&2i\mathrm{Im}\left\{\sum_{ij}(\widetilde{w\varepsilon})_{ij}\left(a^*_{j,lm}\left\langle u|u_{LO}\right\rangle+b^*_{j,lm}\left\langle\dot{u}_l|u_{LO}\right\rangle+c^*_{j,lm}\left\langle u_{LO}|u_{LO}\right\rangle\right)\vec{\mathcal{C}}_{i,lm}\right\}
\end{aligned}
$$

and the final result becomes

$$
\begin{aligned}
&\mathbf{F}(1)^{Pulley}_{\alpha} = -\sum_{i,j,\mathbf{KK'}}A^{\dagger}_{j\mathbf{K'}}i(\mathbf{K}-\mathbf{K'})\left\langle\chi_{\mathbf{K'}}|(-\nabla^2+V_{KS})w_i^{DMFT}\delta_{ij}-(\widetilde{w\varepsilon})_{ij}|\chi_{\mathbf{K}}\right\rangle A_{\mathbf{K}i} = \\
&\sum_{i,lm}\mathrm{Im}\left\{\left(w_i\left[2a^*_{i,lm}E_\nu+b^*_{i,lm}+c^*_{i,lm}(E_\mu+E_\nu)\left\langle u|u_{LO}\right\rangle\right]-2\sum_j(\widetilde{w\varepsilon})_{ij}\left[a^*_{j,lm}+c^*_{j,lm}\left\langle u|u_{LO}\right\rangle\right]\right)\vec{\mathcal{A}}_{i,lm}\right\}+ \\
&+\sum_{i,lm}\mathrm{Im}\left\{\left(w_i\left[a^*_{i,lm}+2b^*_{i,lm}E_\nu\left\langle\dot{u}_l|\dot{u}_l\right\rangle+c^*_{i,lm}[\left\langle u_{LO}|u_l\right\rangle+(E_\mu+E_\nu)\left\langle u_{LO}|\dot{u}_l\right\rangle]\right]-2\sum_j(\widetilde{w\varepsilon})_{ij}\left[b^*_{j,lm}\left\langle\dot{u}_l|\dot{u}_l\right\rangle+c^*_{j,lm}\left\langle u_{LO}|\dot{u}_l\right\rangle\right]\right)\vec{\mathcal{B}}_{i,lm}\right\}+ \\
&+\sum_{i,lm}\mathrm{Im}\Big\{\Big(w_i\left[a^*_{i,lm}(E_\mu+E_\nu)\left\langle u|u_{LO}\right\rangle+b^*_{i,lm}[\left\langle u_{LO}|u_l\right\rangle+(E_\mu+E_\nu)\left\langle u_{LO}|\dot{u}_l\right\rangle]+2E_\mu\,c^*_{i,lm}\left\langle u_{LO}|u_{LO}\right\rangle\right]- \\
&\qquad -2\sum_j(\widetilde{w\varepsilon})_{ij}\left[a^*_{j,lm}\left\langle u|u_{LO}\right\rangle+b^*_{j,lm}\left\langle\dot{u}_l|u_{LO}\right\rangle+c^*_{j,lm}\left\langle u_{LO}|u_{LO}\right\rangle\right]\Big)\vec{\mathcal{C}}_{i,lm}\Big\}
\end{aligned}
\tag{375}
$$

This force is called `fsph`.
Note that $\vec{\mathcal{A}}$, $\vec{\mathcal{B}}$ and $\vec{\mathcal{C}}$ are called *aalm*, *bblm*, and *cclm*.
In Wien2k, this is implemented in function `fomai1`. Also note that $\langle\dot{u}|\dot{u}\rangle = pei$, $\langle u_{LO}|u\rangle = pi12lo$, $\langle u_{LO}|\dot{u}\rangle = pe12lo$, $\langle u_{LO}|u_{LO}\rangle = pr12lo$.

E. Implementation of Eq. 360, non-symmetric part

This is implemented in `Force2`.
The non-sperically symmetric part of Eq. 360 takes the form

$$\mathbf{F}(2)^{Pulley}_{\alpha} = -i\sum_i w_i\sum_{\mathbf{K},\mathbf{K'}}A^*_{i,\mathbf{K'}}(\mathbf{K}-\mathbf{K'})A_{i,\mathbf{K}}\left\langle\chi_{\mathbf{K'}}|V^{n-sym}_{KS}(\mathbf{r})|\chi_{\mathbf{K}}\right\rangle_{MT} \tag{376}$$

In file case.nsh, we read non-spherical symmetric potential, which is given in the following form

$$V^{non-sph}_{\kappa_1 l_1 m_1 \kappa_2 l_2 m_2} = \int d^3r Y^*_{l_1m_1}(\hat{\mathbf{r}})u^{\kappa_1}V^{n-sym}(\mathbf{r})u^{\kappa_2}Y_{l_2m_2}(\hat{\mathbf{r}}) \tag{377}$$

The data in case.nsh contains the following matrix elements

$$\langle u|V|u\rangle \to tuu \tag{378}$$
$$\langle u|V|\dot{u}\rangle \to tud \tag{379}$$
$$\langle \dot{u}|V|u\rangle \to tdu \tag{380}$$
$$\langle \dot{u}|V|\dot{u}\rangle \to tdd \tag{381}$$
$$\cdots \tag{382}$$

To evaluate the term, we substutute the definition for $\chi_{\mathbf{K}}$ to obtain

$$\sum_{\mathbf{K},\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \left\langle \chi_{\mathbf{K}'} | V^{n-sym} | \chi_{\mathbf{K}} \right\rangle_{MT} A_{i\mathbf{K}} = \tag{383}$$

$$\sum_{\mathbf{K},\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \langle Y_{l_1 m_1} \sum_{\kappa_1} a^{\kappa_1,\mathbf{K}'}_{l_1 m_1} u^{\kappa_1}_{l_1} | V^{n-sym} | Y_{l_2 m_2} \sum_{\kappa_2} a^{\kappa_2,\mathbf{K}}_{l_2 m_2} u^{\kappa_2}_{l_2} \rangle \, A_{i\mathbf{K}} \tag{384}$$

which simplifies to

$$\sum_{\mathbf{K},\mathbf{K}'} (\mathbf{K}-\mathbf{K}') A^*_{i\mathbf{K}'} \left\langle \chi_{\mathbf{K}'} | V^{n-sym} | \chi_{\mathbf{K}} \right\rangle_{MT} A_{i\mathbf{K}} = \tag{385}$$

$$\sum_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} a^{*\kappa_1,i}_{l_1 m_1} \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2} V_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} - \vec{\mathcal{A}}^{*\kappa_1,i}_{l_1 m_1} a^{\kappa_2,i}_{l_2 m_2} V_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} = \tag{386}$$

$$2i\mathrm{Im}\left\{ \sum_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} a^{*\kappa_1,i}_{l_1 m_1} \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2} V_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} \right\} \tag{387}$$

hence, we have

$$\mathbf{F}(2)^{Pulley}_{\alpha} = \sum_i w_i \sum_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} 2\mathrm{Im}\left\{ a^{*\kappa_1,i}_{l_1 m_1} V_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2} \right\} \tag{388}$$

Implementation builds the following quantity

$$afac(\kappa_2, l_1 m_1, l_2 m_2) = \sum_{\kappa_1} a^{*\kappa_1,i}_{l_1 m_1} V_{\kappa_1 l_1 m_1, \kappa_2 l_2 m_2} \tag{389}$$

and evaluates

$$\mathbf{F}(2)^{Pulley}_{\alpha} = \sum_i f_i \sum_{l_1 m_1, l_2 m_2, \kappa_2} 2\mathrm{Im}[afac(\kappa_2, l_1 m_1, l_2 m_2) \vec{\mathcal{A}}^{\kappa_2,i}_{l_2 m_2}] \tag{390}$$

Note that this force has name `fnsp`. Also note that $\vec{\mathcal{A}}, \vec{\mathcal{B}}, \vec{\mathcal{C}}$ are called `aalm,bblm,cclm` and matrix elements of V are called tuu,tud,tdu,....

Within Wien2k this is implemented in `fomai1`.

F. Implementation of term 361

Next we discuss implementation of Eq. 361:

$$\mathbf{F}(4)^{Pulley}_{\alpha} = \sum_{i,\mathbf{K},\mathbf{G}} w^{DMFT}_i (A^0\mathcal{B})^*_{\mathbf{K}-\mathbf{G},i} (\mathbf{k}+\mathbf{K}-\mathbf{G}) (A^0\mathcal{B})_{\mathbf{K},i} (\mathbf{k}+\mathbf{K}) R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{391}$$

$$- \sum_{ij,\mathbf{K},\mathbf{G}} (A^0\mathcal{B})_{\mathbf{K},i} (\widetilde{w\varepsilon})_{ij} (A^0\mathcal{B})^*_{\mathbf{K}-\mathbf{G},j} R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{392}$$

or

$$\mathbf{F}(4)^{Pulley}_{\alpha} = \sum_{i,\mathbf{K},\mathbf{G}} w^{DMFT}_i (A^0\mathcal{B})^*_{\mathbf{K}-\mathbf{G},i} (\mathbf{K}+\mathbf{k}-\mathbf{G}) (A^0\mathcal{B})_{\mathbf{K},i} (\mathbf{K}+\mathbf{k}) R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{393}$$

$$- \sum_{ij,\mathbf{K},\mathbf{G}} A^0_{\mathbf{K}i} (\mathcal{B}(\widetilde{w\varepsilon})\mathcal{B}^\dagger)_{ij} A^{0*}_{\mathbf{K}-\mathbf{G},j} R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{394}$$

or

$$\mathbf{F}(4)^{Pulley}_{\alpha} = \sum_{i,\mathbf{K},\mathbf{G}} w^{DMFT}_i (A^0\mathcal{B})^*_{\mathbf{K}-\mathbf{G},i} (\mathbf{K}+\mathbf{k}-\mathbf{G}) (A^0\mathcal{B})_{\mathbf{K},i} (\mathbf{K}+\mathbf{k}) R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{395}$$

$$- \sum_{ij,\mathbf{K},\mathbf{G}} A^0_{\mathbf{K}i} (\rho\varepsilon)^{DMFT}_{ij} A^{0*}_{\mathbf{K}-\mathbf{G},j} R^2_{MT} \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_{\mathbf{r}} \tag{396}$$

We next diagonalize the density matrix

$$(\rho\varepsilon)^{DMFT} = \widetilde{\mathcal{B}} w_\varepsilon \widetilde{\mathcal{B}}^\dagger \tag{397}$$

and simplify

$$\mathbf{F}(4)_\alpha^{Pulley} = \sum_{i,\mathbf{K},\mathbf{G}} w_i^{DMFT} (A^0\mathcal{B})^*_{\mathbf{K}-\mathbf{G},i}(\mathbf{K}+\mathbf{k}-\mathbf{G})(A^0\mathcal{B})_{\mathbf{K},i}(\mathbf{K}+\mathbf{k}) R_{MT}^2 \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_\mathbf{r} \tag{398}$$

$$- \sum_{ij,\mathbf{K},\mathbf{G}} (A^0\widetilde{\mathcal{B}})_{\mathbf{K}i} w_{\varepsilon,i} (A^0\widetilde{\mathcal{B}})^*_{\mathbf{K}-\mathbf{G},i} R_{MT}^2 \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_\mathbf{r} \tag{399}$$

The convolution in $\mathbf{K}$ needs quadratic amount of time ($O(N^2)$). By using FFT and turning it into product in real space, it takes only $N\log(N)$ time, hence we will use FFT for the following quantities

$$\vec{X}_i(\mathbf{r}) = \sum_\mathbf{K} (A^0\mathcal{B})_{\mathbf{K},i}(\mathbf{K}+\mathbf{k}) e^{i\mathbf{K}\mathbf{r}} \tag{400}$$

$$Y_i(\mathbf{r}) = \sum_\mathbf{K} (A^0\widetilde{\mathcal{B}})_{\mathbf{K},i} e^{i\mathbf{K}\mathbf{r}} \tag{401}$$

The inverse FFT should then be used to obtain aternative representation for convolution

$$\mathbf{F}(4)_\alpha^{Pulley} = \int \frac{d^3r}{V} \sum_i e^{-i\mathbf{G}\mathbf{r}} [\vec{X}_i^*(\mathbf{r}) w_i \vec{X}_i(\mathbf{r}) - Y_i^*(\mathbf{r}) w_{\varepsilon,i} Y_i(\mathbf{r})] R_{MT}^2 \int d\Omega \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} \vec{e}_\mathbf{r} \tag{402}$$

Finally, one can check that

$$\int d\Omega e^{i\mathbf{G}\mathbf{r}} \vec{e}_\mathbf{r} = 4\pi \frac{\mathbf{G}}{|\mathbf{G}|}\; j_1(|\mathbf{G}|R_{MT}) i e^{i\mathbf{G}\mathbf{r}_\alpha} \tag{403}$$

In the code we compute

$$ekink = \int \frac{d^3r}{V} \sum_i e^{-i\mathbf{G}\mathbf{r}} [\vec{X}_i^*(\mathbf{r}) w_i \vec{X}_i(\mathbf{r}) - Y_i^*(\mathbf{r}) w_{\varepsilon,i} Y_i(\mathbf{r})] \tag{404}$$

which is computed in `l2main`.

The final part of this force is implemented in `Force_surface`.

G. Implementation of Eq. 362

Next we consider Eq. 362, which is

$$\mathbf{F}(3)_\alpha^{Pulley} = -\sum_i w_i^{DMFT} \sum_{\mathbf{K}\mathbf{K}'} A^\dagger_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') A_{\mathbf{K}i} \oint_{R_{MT}^-} d\vec{S} \chi^*_{\mathbf{k}+\mathbf{K}'}(\mathbf{r}) \nabla_\mathbf{r} \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \tag{405}$$

We know that the therm should be real, therefore we will symmetrize it to show this explicitely

$$\mathbf{F}(3)_\alpha^{Pulley} = -\frac{1}{2}\sum_i w_i \sum_{\mathbf{K},\mathbf{K}'} A^\dagger_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') A_{\mathbf{K}i} \oint_{r=R_{MT}^-} d\vec{S} [\chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) \nabla_\mathbf{r} \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) + \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \nabla \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r})] \tag{406}$$

which is equal to

$$\mathbf{F}(3)_\alpha^{Pulley} = -\frac{1}{2}\sum_{\mathbf{k},i} w_i \sum_{\mathbf{K},\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') A^*_{\mathbf{K}'i} A_{\mathbf{K}i}\; R_{MT}^2 \oint_{r=R_{MT-}} d\Omega\; [\chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r}) \frac{\partial}{\partial r} \chi_{\mathbf{K}+\mathbf{k}} + \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) \frac{\partial}{\partial r} \chi^*_{\mathbf{K}'+\mathbf{k}}(\mathbf{r})] \tag{407}$$

and inserting expression for χ we get

$$\mathbf{F}(3)_\alpha^{Pulley} = -\frac{1}{2}\sum_{\mathbf{k},i} w_i \sum_{\mathbf{K},\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') A^*_{\mathbf{K}'i} A_{\mathbf{K}i}\; R_{MT}^2 \sum_{l,m,\kappa',\kappa} a^{\kappa'\,*}_{lm,\mathbf{K}'} u^{\kappa'}_l a^{\kappa}_{lm,\mathbf{K}} u'^{\kappa}_l + a^{\kappa'}_{lm,\mathbf{K}} u^{\kappa'}_l a^{\kappa\,*}_{lm,\mathbf{K}'} u'^{\kappa}_l \tag{408}$$

and summing over $\mathbf{K}$ and $\mathbf{K'}$ gives

$$\mathbf{F}(3)^{Pulley}_\alpha = -\frac{i}{2}\sum_{\mathbf{k},i} w_i R_{MT}^2 \sum_{l,m,\kappa',\kappa} [a^{\kappa'\,*}_{i,lm} u^{\kappa'}_l \vec{\mathcal{A}}^{\kappa}_{i,lm} u'^{\kappa}_l + \vec{\mathcal{A}}^{\kappa'}_{i,lm} u^{\kappa'}_l a^{\kappa\,*}_{i,lm} u'^{\kappa}_l - \vec{\mathcal{A}}^{\kappa'\,*}_{i,lm} u^{\kappa'}_l a^{\kappa}_{i,lm} u'^{\kappa}_l - a^{\kappa'}_{i,lm} u^{\kappa'}_l \vec{\mathcal{A}}^{\kappa\,*}_{i,lm} u'^{\kappa}_l] \tag{409}$$

which can be simplified to

$$\mathbf{F}(3)^{Pulley}_\alpha = R_{MT}^2 \sum_{\mathbf{k},i} w_i \sum_{l,m,\kappa',\kappa} \mathrm{Im}[a^{\kappa'\,*}_{i,lm} u^{\kappa'}_l \vec{\mathcal{A}}^{\kappa}_{i,lm} u'^{\kappa}_l + \vec{\mathcal{A}}^{\kappa'}_{i,lm} u^{\kappa'}_l a^{\kappa\,*}_{i,lm} u'^{\kappa}_l] \tag{410}$$

We can then define the following quantities

$$kinfac(1,ilm) = \sum_\kappa a^{\kappa}_{i,lm} u^{\kappa}_l(R_{MT}) \tag{411}$$

$$kinfac(2,ilm) = \sum_\kappa a^{\kappa}_{i,lm} u'^{\kappa}_l(R_{MT}) \tag{412}$$

$$kinfac(3,ilm) = \sum_\kappa \vec{\mathcal{A}}^{\kappa}_{i,lm} u'^{\kappa}_l(R_{MT}) \tag{413}$$

$$kinfac(4,ilm) = \sum_\kappa \vec{\mathcal{A}}^{\kappa}_{i,lm} u^{\kappa}_l(R_{MT}) \tag{414}$$

and write

$$\mathbf{F}(3)^{Pulley}_\alpha = R_{MT}^2 \sum_{\mathbf{k},i} w_i \sum_{l,m} \mathrm{Im}[(kinfac(1,ilm))^* kinfac(3,ilm) + kinfac(4,ilm)(kinfac(2,ilm))^*] \tag{415}$$

This part of the force is named `fsph2` and is coded in `fomai1` within Wien2k, and in `Force3` in my code.

1. *Alternative implementation using plane waves*

We are free to choose any form of the kinetic energy, either $\nabla\cdot\nabla$ or $-\nabla^2$. We could choose the form to be $-\nabla^2$ and then we would get the same term computed with the interstitial basis functions. The problem is that these functions are not continuous and hence the left derivative is different that the right derivative. The best way out is than to use the average of the left and right derivative, hence we will compute the same term with interstitial charge, and then average over both terms.

The Eq. 362 using plane wave functions is

$$\mathbf{F}(3)^{Pulley}_\alpha = -\frac{1}{2}\sum_i w_i \sum_{\mathbf{K},\mathbf{K'}} A^\dagger_{i\mathbf{K'}} i(\mathbf{K}-\mathbf{K'}) A_{\mathbf{K}i} \oint_{r=R_{MT}} d\vec{S}[\tilde{\chi}^*_{\mathbf{K'}+\mathbf{k}}(\mathbf{r})\nabla_{\mathbf{r}}\tilde{\chi}_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) + \tilde{\chi}_{\mathbf{K}+\mathbf{k}}(\mathbf{r})\nabla\tilde{\chi}^*_{\mathbf{K'}+\mathbf{k}}(\mathbf{r})] = \tag{416}$$

$$= -\frac{1}{2}\sum_i w_i \sum_{\mathbf{K},\mathbf{K'}} A^\dagger_{i\mathbf{K'}} i(\mathbf{K}-\mathbf{K'}) A_{\mathbf{K}i} \oint_{r=R_{MT}} d\vec{S}\nabla_{\mathbf{r}}(\tilde{\chi}^*_{\mathbf{K'}+\mathbf{k}}(\mathbf{r})\tilde{\chi}_{\mathbf{K}+\mathbf{k}}(\mathbf{r})) \tag{417}$$

If we go one step back and check derivation of kinetic energy part, Eq. 328, we see that replacing ∇^2 in the interstitials with $\nabla\cdot\nabla$ would generate a term

$$\oint_{MT} d\vec{S}\tilde{\chi}^*_{\mathbf{K'}}(-\nabla^2)\tilde{\chi}_{\mathbf{K}} = \oint_{MT} d\vec{S}\nabla\tilde{\chi}^*_{\mathbf{K'}}\cdot\nabla\tilde{\chi}_{\mathbf{K}} - \oint_{MT} d\vec{S}\nabla\cdot(\tilde{\chi}^*_{\mathbf{K'}}\nabla\tilde{\chi}_{\mathbf{K}}) \tag{418}$$

which, when inserted into Pulley force, leads to a term

$$\mathbf{F} = -\sum_i w_i \sum_{\mathbf{KK}} A^\dagger_{i\mathbf{K'}} A_{\mathbf{K}i} \oint_{MT} d\vec{S}\nabla\cdot(\tilde{\chi}^*_{\mathbf{K'}}\nabla\tilde{\chi}_{\mathbf{K}}) \to -\frac{1}{2}\sum_i w_i \sum_{\mathbf{KK}} A^\dagger_{i\mathbf{K'}} A_{\mathbf{K}i} \oint_{MT} d\vec{S}\nabla\cdot(\tilde{\chi}^*_{\mathbf{K'}}\nabla\tilde{\chi}_{\mathbf{K}} + \tilde{\chi}_{\mathbf{K}}\nabla\tilde{\chi}^*_{\mathbf{K'}}) \tag{419}$$

The last simplification is obtained by symmetrizing the term, as force should be real. We can notice that this expression is equivalent to the above derived Eq. 416, however, now we can rewrite the integral into even a simpler form

$$\mathbf{F} = -\frac{1}{2}\sum_i w_i \sum_{\mathbf{KK}} A^\dagger_{i\mathbf{K'}} A_{\mathbf{K}i} \oint_{MT} d\vec{S}\nabla^2(\tilde{\chi}^*_{\mathbf{K'}}\tilde{\chi}_{\mathbf{K}}) = -\frac{1}{2}\oint_{MT} d\vec{S}\nabla^2\tilde{\rho}(\mathbf{r}). \tag{420}$$

We will show below that both forms Eq. 417 and Eq. 420 lead to the same expression for the force.

Starting from Eq. 417 we get

$$\mathbf{F}(3)_\alpha^{Pulley} = \frac{1}{2}\sum_i w_i \sum_{\mathbf{K},\mathbf{K}'} A^\dagger_{i\mathbf{K}'}(\mathbf{K}-\mathbf{K}')A_{\mathbf{K}i}\, e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha} \oint_{r=R_{MT}} d\vec{S}\cdot(\mathbf{K}-\mathbf{K}')\frac{1}{V_{cell}} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}} \tag{421}$$

or

$$\mathbf{F}(3)_\alpha^{Pulley} = \frac{1}{2}\sum_{i,\mathbf{K},\mathbf{G}} A^*_{\mathbf{K}-\mathbf{G},i} w_i A_{\mathbf{K}i}\, \mathbf{G}\, e^{i\mathbf{G}\mathbf{R}_\alpha} \oint_{r=R_{MT}} d\vec{S}\cdot\mathbf{G}\frac{1}{V_{cell}} e^{i\mathbf{G}\mathbf{r}} \tag{422}$$

We then recognize the density in the interstitials, which was previously computed by FFT

$$\tilde{\rho}_\mathbf{G} = \frac{1}{V_{cell}}\sum_{i,\mathbf{K},\mathbf{k}} A^*_{\mathbf{K}-\mathbf{G},i} w_i A_{\mathbf{K}i} \tag{423}$$

Our force then becomes

$$\mathbf{F}(3)_\alpha^{Pulley} = \frac{1}{2}\sum_\mathbf{G} \tilde{\rho}_\mathbf{G}\mathbf{G}\, e^{i\mathbf{G}\mathbf{R}_\alpha} \oint_{r=R_{MT}} d\vec{S}\cdot\mathbf{G} e^{i\mathbf{G}\mathbf{r}} \tag{424}$$

It is straighorward to show

$$\int d\Omega(\vec{e}_\mathbf{r}\cdot\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} = 4\pi i j_1(|G|R_{MT})|G| \tag{425}$$

hence the force is

$$\mathbf{F}(3)_\alpha^{Pulley} = \frac{R_{MT}^2}{2}\sum_\mathbf{G} \tilde{\rho}_\mathbf{G} 4\pi j_1(|\mathbf{G}|R_{MT}) i e^{i\mathbf{G}\mathbf{R}_\alpha}|\mathbf{G}|\mathbf{G} \tag{426}$$

For alternative derivation we start from Eq. 420 and write

$$\mathbf{F} = -\frac{1}{2}\oint_{MT} d\vec{S}\nabla^2\tilde{\rho}(\mathbf{r}) = \frac{1}{2}\oint_{MT} d\vec{S}\sum_\mathbf{G} G^2\tilde{\rho}_\mathbf{G} e^{i\mathbf{G}\mathbf{R}_\alpha} e^{i\mathbf{G}\mathbf{r}} = \frac{R_{MT}^2}{2}\sum_\mathbf{G} G^2\tilde{\rho}_\mathbf{G} e^{i\mathbf{G}\mathbf{R}_\alpha}\int d\Omega e^{i\mathbf{G}\mathbf{r}}\vec{e}_\mathbf{r} \tag{427}$$

It is easy to show that

$$\int d\Omega\vec{e}_\mathbf{r} e^{i\mathbf{G}\mathbf{r}} = 4\pi i j_1(GR_{MT})\frac{\mathbf{G}}{|\mathbf{G}|} \tag{428}$$

hence we obtain the same expression

$$\mathbf{F} = \frac{R_{MT}^2}{2}\sum_\mathbf{G} \tilde{\rho}_\mathbf{G} e^{i\mathbf{G}\mathbf{R}_\alpha} 4\pi i j_1(GR_{MT})|\mathbf{G}|\mathbf{G} \tag{429}$$

[It turns out that this formula does not give the same value as its implementation with augmented plane waves (inside MT sphere) Eq 410. I do not understand why. Misterious!].

H. Implementation of Eq. 363

$$\mathbf{F}(5)_\alpha^{Pulley} = \int_{MT} d^3r V_{KS}(\mathbf{r})\nabla\rho(\mathbf{r}) = \sum_{lmsl'm's'}\int d^3r V_{l'm's'}(r) y_{l'm's'}(\hat{\mathbf{r}})\nabla(\rho_{lms}(r) y_{lms}(\hat{\mathbf{r}})) \tag{430}$$

Here we use the real spheric harmonics, introduced in Kurki-Suonio, which are defined by

$$y_{lm+} = \frac{1}{\sqrt{2(1+\delta_{m,0})}}(Y_{l,-m} + (-1)^m Y_{l,m}) = \sqrt{\frac{2}{1+\delta_{m,0}}}(-1)^m \mathrm{Re}Y_{lm} \tag{431}$$

$$y_{lm-} = \frac{1}{\sqrt{2(1+\delta_{m,0})}}(Y_{l,-m} - (-1)^m Y_{l,m}) = \sqrt{\frac{2}{1+\delta_{m,0}}}(-1)^m \mathrm{Im}Y_{lm} \tag{432}$$

Notice that in Wien2k Y_{lm}'s are not defined in a standard way as in most QM textbooks, but are defined as in classical mechanics with an extra $(-1)^m$. Hence, in Wien2k, one needs to add $(-1)^m$ to the above definitions.

The operator ∇ in spheric harmonics is

$$\nabla f = \vec{e}_r \frac{\partial}{\partial r} + \frac{\sin\theta}{r} \begin{pmatrix} -\cos\theta\cos\phi \\ -\cos\theta\sin\phi \\ \sin\theta \end{pmatrix} \frac{\partial}{\partial(\cos\theta)} + \frac{1}{r\sin\theta} \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \frac{\partial}{\partial\phi} = \vec{e}_r \frac{\partial}{\partial r} + \frac{1}{r}\nabla_{\theta\phi} \tag{433}$$

The last form emphasizes that ∇ has the radial part and a angle part. Using this decomposition, we can write

$$\mathbf{F}(5)^{Pulley}_{\alpha} = \int d^3r V_{KS}(\mathbf{r})\nabla\rho(\mathbf{r}) \;=\; \sum_{lmsl'm's'} \int_0^\infty drr^2 V_{l'm's'}(r)\frac{d\rho_{lms}(r)}{dr} \int d\Omega y_{l'm's'}(\hat{\mathbf{r}})\vec{e}_r y_{lms}(\hat{\mathbf{r}}) \tag{434}$$

$$+ \sum_{lmsl'm's'} \int_0^\infty drr^2 \frac{V_{l'm's'}(r)\rho_{lms}(r)}{r} \int d\Omega y_{l'm's'}(\hat{\mathbf{r}})\nabla_{\theta\phi} Y_{lms}(\hat{\mathbf{r}}) \tag{435}$$

We then define the following integrals

$$I^1_{l'm's'lms} \equiv \int d\Omega y_{l'm's'}(\hat{\mathbf{r}})\vec{e}_{\mathbf{r}} y_{lms}(\hat{\mathbf{r}}) \tag{436}$$

$$I^2_{l'm's'lms} \equiv \int d\Omega y_{l'm's'}(\hat{\mathbf{r}})(r\nabla) y_{lms}(\hat{\mathbf{r}}) \tag{437}$$

$$I^3_{l'm's'lms} \equiv \int d\Omega (r\nabla y_{l'm's'}(\hat{\mathbf{r}}))\cdot(r\nabla y_{lms}(\hat{\mathbf{r}}))\vec{e}_{\mathbf{r}} \tag{438}$$

and rewrite

$$\mathbf{F}(5)^{Pulley}_{\alpha} = \sum_{lmsl'm's'} \int_0^\infty drr^2 V_{l'm's'}(r)\frac{d\rho_{lms}(r)}{dr} I^1_{l'm's'lms} + \sum_{lmsl'm's'} \int_0^\infty drr^2 \frac{V_{l'm's'}(r)\rho_{lms}(r)}{r} I^2_{l'm's'lms} \tag{439}$$

In the following, we will need these integrals:

$$I^1_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\vec{e}_{\mathbf{r}} Y_{lm}(\hat{\mathbf{r}}) \tag{440}$$

$$I^2_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})(r\nabla Y_{lm}(\hat{\mathbf{r}})) \tag{441}$$

$$I^3_{l'm'lm} \equiv \int d\Omega (r\nabla Y^*_{l'm'}(\hat{\mathbf{r}}))\cdot(r\nabla Y_{lm}(\hat{\mathbf{r}}))\vec{e}_{\mathbf{r}} \tag{442}$$

$$\tag{443}$$

We first compute the following integral

$$I^1_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\vec{e}_r Y_{lm}(\hat{\mathbf{r}}) = \tag{444}$$

$$(-1)^{m+m'}\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m')!}{4\pi(l+m)!4\pi(l'+m')!}} \int_{-1}^1 dx P_{l'}^{m'}(x)P_l^m(x) \begin{pmatrix} \sqrt{1-x^2}\int_0^{2\pi} d\phi\; e^{i(m-m')\phi}\cos\phi \\ \sqrt{1-x^2}\int_0^{2\pi} d\phi\; e^{i(m-m')\phi}\sin\phi \\ x\int_0^{2\pi} d\phi\; e^{i(m-m')\phi} \end{pmatrix} \tag{445}$$

$$I^1_{l'm'lm} = (-1)^{m+m'}\pi\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m')!}{4\pi(l+m)!4\pi(l'+m')!}} \int_{-1}^1 dx P_{l'}^{m'}(x)P_l^m(x) \begin{pmatrix} \sqrt{1-x^2}\delta_{m'=m\pm1} \\ \mp i\sqrt{1-x^2}\delta_{m'=m\pm1} \\ 2x\delta_{mm'} \end{pmatrix} \tag{446}$$

which is equal to

$$I^1_{l'm'lm} = \pi\delta_{m'=m\pm1}\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m\mp1)!}{4\pi(l+m)!4\pi(l'+m\pm1)!}} \int_{-1}^1 dx P_{l'}^{m\pm1}(x)P_l^m(x)\sqrt{1-x^2} \begin{pmatrix} -1 \\ \pm i \\ 0 \end{pmatrix}$$

$$+2\pi\delta_{mm'}\sqrt{\frac{(2l+1)(l-m)!(2l'+1)(l'-m)!}{4\pi(l+m)!4\pi(l'+m)!}} \int_{-1}^1 dx P_{l'}^{m}(x)P_l^m(x)x \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{447}$$

With the help of the following well known recursion relation

$$\sqrt{1-x^2}P_l^m = \frac{1}{2l+1}\left[P_{l-1}^{m+1} - P_{l+1}^{m+1}\right] \tag{448}$$

$$\sqrt{1-x^2}P_l^m = \frac{1}{2l+1}\left[(l-m+1)(l-m+2)P_{l+1}^{m-1} - (l+m-1)(l+m)P_{l-1}^{m-1}\right] \tag{449}$$

$$xP_l^m = \frac{1}{2l+1}\left[(l-m+1)P_{l+1}^m + (l+m)P_{l-1}^m\right] \tag{450}$$

we arrive at

$$I^1_{l'm'lm} = \begin{pmatrix}-1\\ i\\ 0\end{pmatrix}\frac{1}{2}\left[\delta_{l'=l-1}\sqrt{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}} - \delta_{l'=l+1}\sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}}\right]\delta_{m'=m+1} + \tag{451}$$

$$+\begin{pmatrix}-1\\ -i\\ 0\end{pmatrix}\frac{1}{2}\left[\delta_{l'=l+1}\sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}} - \delta_{l'=l-1}\sqrt{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}}\right]\delta_{m'=m-1} + \tag{452}$$

$$+\begin{pmatrix}0\\ 0\\ 1\end{pmatrix}\left[\delta_{l'=l+1}\sqrt{\frac{(l-m+1)(l+m+1)}{(2l+1)(2l+3)}} + \delta_{l'=l-1}\sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}}\right]\delta_{m'=m} \tag{453}$$

Let's define

$$a(l,m) = \sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}} \tag{454}$$

$$f(l,m) = \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} \tag{455}$$

$$\tag{456}$$

and rewrite

$$I^1_{l'm'lm} = \begin{pmatrix}1\\ -i\\ 0\end{pmatrix}\frac{1}{2}\left[a(l,m)\delta_{l'=l+1} - a(l',-m')\delta_{l'=l-1}\right]\delta_{m'=m+1} + \tag{457}$$

$$+\begin{pmatrix}-1\\ -i\\ 0\end{pmatrix}\frac{1}{2}\left[a(l,-m)\delta_{l'=l+1} - a(l',m')\delta_{l'=l-1}\right]\delta_{m'=m-1} + \tag{458}$$

$$+\begin{pmatrix}0\\ 0\\ 1\end{pmatrix}\left[f(l,m)\delta_{l'=l+1} + f(l',m')\delta_{l'=l-1}\right]\delta_{m'=m} \tag{459}$$

Next we compute the following integral

$$I^2_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\nabla_{\theta\phi}Y_{lm}(\hat{\mathbf{r}}) = \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})(r\nabla)Y_{lm}(\hat{\mathbf{r}}) \tag{460}$$

Due to Wigner-Eckart theorem, we know the dependence on m, m' is equal to $I^1_{l'm'lm}$. The dependence on l, l' can be either found numerically, or analytically using several recursion relations.

The result for I^2 is

$$I^2_{l'm'lm} = \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix} \frac{1}{2} \left[-l\; a(l,m)\delta_{l'=l+1} - (l+1)\; a(l',-m')\delta_{l'=l-1}\right]\delta_{m'=m+1} + \tag{461}$$

$$+ \begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix} \frac{1}{2} \left[-l\; a(l,-m)\delta_{l'=l+1} - (l+1)\; a(l',m')\delta_{l'=l-1}\right]\delta_{m'=m-1} + \tag{462}$$

$$+ \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \left[-l\; f(l,m)\delta_{l'=l+1} + (l+1) f(l',m')\delta_{l'=l-1}\right]\delta_{m'=m} \tag{463}$$

We can write both integrals in a common form, namely,

$$I^n_{l'm'lm} = c_{n,l}\left[a(l,m)\begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m+1} + a(l,-m)\begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m-1} + 2f(l,m)\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l+1} \tag{464}$$

$$-d_{n,l}\left[a(l',-m')\begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m+1} + a(l',m')\begin{pmatrix} -1 \\ -i \\ 0 \end{pmatrix}\delta_{m'=m-1} - 2f(l',m')\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l-1} \tag{465}$$

where

$$c_{1,l} = \tfrac{1}{2} \qquad d_{1,l} = \frac{1}{2} \tag{466}$$

$$c_{2,l} = -\tfrac{l}{2} \qquad d_{2,l} = \frac{l+1}{2} \tag{467}$$

$$c_{3,l} = \tfrac{l(l+2)}{2} \quad d_{3,l} = \frac{(l-1)(l+1)}{2} \tag{468}$$

We also gave coefficients for I^3, which gives kinetic energy operator integrated over the sphere of the MT-sphere.

In the code, we use real spheric harmonics $y_{lm\pm}$, which are related to complex spheric harmonics by

$$Y_{lm} \quad = (-1)^m\sqrt{\frac{1+\delta_{m,0}}{2}}(y_{lm+} + i y_{lm-}) \tag{469}$$

$$Y_{l,-m} \quad = \sqrt{\frac{1+\delta_{m,0}}{2}}(y_{lm+} - i y_{lm-}) \tag{470}$$

In Section. IV E we derive the connection between the matrix elements of the real harmonics and complex harmonics, and we also derive the matrix elements $\langle y_{l'm's'}|T|y_{lms}\rangle$. Here we just give the final result:

$$\langle y_{l'm'\pm}|T|y_{lm\pm}\rangle = c_{n,l}\;\delta_{l'=l+1}\begin{pmatrix} -a(l,m)\delta_{m'=m+1}\frac{(1\pm\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l,-m)\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}} \\ 0 \\ 2f(l,m)\delta_{m'=m}\frac{(1\pm\delta_{m=0})}{1+\delta_{m=0}} \end{pmatrix}$$
$$-d_{n,l}\;\delta_{l'=l-1}\left.\begin{pmatrix} -a(l',-m')\delta_{m'=m+1}\frac{(1\pm\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l',m')\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}} \\ 0 \\ -2f(l',m')\delta_{m'=m}\frac{(1\pm\delta_{m=0})}{1+\delta_{m=0}} \end{pmatrix}\right\} \tag{471}$$

and

$$\langle y_{l'm'\pm}|T|y_{lm\mp}\rangle = \pm\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}\left\{c_{n,l}\;\delta_{l'=l+1}\left(a(l,m)\delta_{m'=m+1}\frac{(1\mp\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l,-m)\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}}\right)\right.$$
$$\left.-d_{n,l}\;\delta_{l'=l-1}\left(a(l',-m')\delta_{m'=m+1}\frac{(1\mp\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l',m')\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}}\right)\right\} \tag{472}$$

This term has name `fomai2` in Wien2k, and is coded in program `Force4_mine`. This part reads non-spherical potential $V_{KS}(\mathbf{r})$ and calls another subprogram `VdRho`, which performns the integration.

I. Implementation of Eq. 364

This is implemented in `cmpLogGdloc`.

We will first rearange terms from Eq. 364 in the following way

$$Eq.\ 364 = -\frac{1}{\beta}\sum_{i\omega} G_{ij}(i\omega)\left\{\langle\psi_j^0|\phi_{m'}\rangle\,\Sigma_{m'm}(i\omega)\,\langle\phi_m|\psi_{i'}^0\rangle\,\langle\psi_{i'}^0|\chi_{\mathbf{K}}\rangle\, i\mathbf{K}A^0_{\mathbf{K}i} - A^{0\dagger}_{j\mathbf{K}'}i\mathbf{K}'\,\langle\chi_{\mathbf{K}'}|\psi_{i'}^0\rangle\,\langle\psi_{i'}^0|\phi_{m'}\rangle\,\Sigma_{m'm}(i\omega)\,\langle\phi_m|\psi_i^0\rangle\right\}$$

Now we recognize that $\langle\chi^0_{\mathbf{K}'}|\psi_i^0\rangle = O_{\mathbf{K}'\mathbf{K}}A^0_{\mathbf{K}i}$ and $U_{im} = \langle\psi_i^0|\phi_m\rangle$ hence

$$Eq.\ 364 = -\frac{1}{\beta}\sum_{i\omega} G_{ij}(i\omega)\left\{U_{jm'}\Sigma_{m'm}(i\omega)U^\dagger_{mi'}(A^{0\dagger}O)_{i'\mathbf{K}}i\mathbf{K}A^0_{\mathbf{K}i} - A^{0\dagger}_{j\mathbf{K}'}i\mathbf{K}'(OA^0)_{\mathbf{K}'i'}U_{i'm'}\Sigma_{m'm}(i\omega)U^\dagger_{mi}\right\}$$

We next define the following quantites

$$\vec{\mathcal{R}}_{ij} = \sum_{\mathbf{K}} A^{0\dagger}_{i\mathbf{K}}\mathbf{K}(OA^0)_{\mathbf{K}j} \tag{473}$$

$$\vec{U}_{im} = \sum_j \vec{\mathcal{R}}_{ij}U_{jm} \tag{474}$$

In practice, we can directly compute $\vec{U}$ from the following

$$\vec{U}_{im} = \sum_{\mathbf{k}} A^{0*}_{\mathbf{K}i}\mathbf{K}\,\langle\chi_{\mathbf{K}}|\phi_m\rangle \tag{475}$$

We then simplify

$$Eq.\ 364 = -\frac{1}{\beta}\sum_{i\omega} i\left\{\vec{U}^\dagger G(i\omega)U - U^\dagger G(i\omega)\vec{U}\right\}_{mm'}\Sigma_{m'm}(i\omega)$$

The first term has the form $\mathrm{Tr}\left(\vec{U}^\dagger G(i\omega)U\Sigma(i\omega)\right)$ and if we just replace $i\omega \to -i\omega$, we get an equivalent form $\mathrm{Tr}\left(\vec{U}^\dagger G(-i\omega)U\Sigma(-i\omega)\right)$, which can also be written as $\mathrm{Tr}\left(\vec{U}^\dagger G^\dagger(i\omega)U\Sigma^\dagger(i\omega)\right) = \mathrm{Conjugate}\left(\mathrm{Tr}\left(\Sigma(i\omega)U^\dagger G(i\omega)\vec{U}\right)\right) = \mathrm{Conjugate}\left(\mathrm{Tr}\left(U^\dagger G(i\omega)\vec{U}\Sigma(i\omega)\right)\right)$. The last form is equal to the second term, but conjugated, hence, the result is real. We can hence also write

$$Eq.\ 364 = 2\mathrm{Im}\left\{\frac{1}{\beta}\sum_{i\omega,mm'}\left[\vec{U}^\dagger G(i\omega)U\right]_{mm'}\Sigma_{m'm}(i\omega)\right\} \tag{476}$$

We hence need to compute vector projector $\vec{U}$ in addition to U and project the DMFT Green's function to this vector form. We define the following generalized projector

$$\vec{\tau}^{mm'}_{ij} = i(\vec{U}^*_{im}U_{jm'} - U^*_{im}\vec{U}_{jm'}) \tag{477}$$

which is called "lgtrans" in the code. We then have

$$Eq.\ 364 = -\frac{1}{\beta}\sum_{i\omega,mm'}\Sigma_{m'm}(i\omega)\sum_{ij}\vec{\tau}^{mm'}_{ij}G_{ij}(i\omega)$$

We call $\vec{G}^{mm'}_{d\ local} = \sum_{ij}\vec{\tau}^{mm'}_{ij}G_{ij}(i\omega)$ and compute it in "cmp_dmft_weights".

J. Implementation of Eq. 365

We start with the plane-wave part of Eq. 365, which takes the form

$$\mathbf{F}^{Pulley} = \sum_i w_i^{DMFT} \sum_{\mathbf{K},\mathbf{K}'} A^\dagger_{i\mathbf{K}'} A_{\mathbf{K}i} \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} V_{KS} \tilde{\chi}_{\mathbf{K}} \tag{478}$$

$$= \sum_{\mathbf{G}} e^{i\mathbf{G}\mathbf{R}_\alpha} \sum_{i,\mathbf{K}} A^*_{\mathbf{K}-\mathbf{G}i} w_i^{DMFT} A_{\mathbf{K}i} \oint_{R_{MT}} d\vec{S} \frac{e^{i\mathbf{G}\mathbf{r}}}{V_{cell}} V_{KS}(\hat{\mathbf{r}}) \tag{479}$$

We use FFT to compute the convolution (charge in the interstitials):

$$\widetilde{\rho}_{\mathbf{G}} = \frac{1}{V_{cell}} \sum_{\mathbf{k},i,\mathbf{K}} A^{\mathbf{k}*}_{\mathbf{K}-\mathbf{G}i} w^{DMFT}_{\mathbf{k},i} A^{\mathbf{k}}_{\mathbf{K}i} \tag{480}$$

and the expansion of the KS-potential in terms of real spheric harmonics

$$V_{KS}(\mathbf{r}) = \sum_{lms} V^{KS}_{lms}(r)\, y_{lms}(\mathbf{r}) \tag{481}$$

to obtain

$$\mathbf{F}^{Pulley} = \sum_{\mathbf{G}} e^{i\mathbf{G}\mathbf{R}_\alpha}\, \widetilde{\rho}_{\mathbf{G}}\, R^2_{MT} \sum_{lms} V^{KS}_{lms}(R_{MT}) \int d\Omega\, y_{lms}(\hat{\mathbf{r}}) e^{i\mathbf{G}\mathbf{r}} \vec{e}_{\mathbf{r}} \tag{482}$$

Notice here that V_{KS} is written in the local coordinate system, hence y_{lms}'s also need to be specified in the local coordinate system attached to an atom. On the other hand, $e^{i\mathbf{G}\mathbf{R}_\alpha}$ can be computed in the global coordinate systsem.

Next we use the well known expansion of plane wave in spherical waves

$$e^{i\mathbf{G}\mathbf{r}} = \sum_{l,m} 4\pi i^l j_l(Gr) Y^*_{lm}(\hat{\mathbf{G}}) Y_{lm}(\hat{\mathbf{r}}) = \sum_l 4\pi i^l j_l(Gr) \sum_{m\ge 0, s=\pm} y_{lms}(\hat{\mathbf{G}}) y_{lms}(\hat{\mathbf{r}}) \tag{483}$$

The second form is for real harmonics used for potential and charge within Wien2k. We hence obtain

$$\mathbf{F}^{Pulley} = \sum_{\mathbf{G}} e^{i\mathbf{G}\mathbf{R}_\alpha}\, \widetilde{\rho}_{\mathbf{G}}\, R^2_{MT} \sum_{lms} V^{KS}_{lms}(R_{MT}) \sum_{l'm's'} 4\pi i^{l'} j_{l'}(Gr) y_{l'm's'}(\hat{\mathbf{G}}) \int d\Omega\, y_{lms}(\hat{\mathbf{r}}) \vec{e}_{\mathbf{r}} y_{l'm's'}(\hat{\mathbf{r}}) \tag{484}$$

We then recognize the interstitial charge density on the MT-sphere, i.e.,

$$\rho_{lms}(R_{MT}) = \sum_{\mathbf{G}} \widetilde{\rho}_{\mathbf{G}}\, e^{i\mathbf{G}\mathbf{R}_\alpha} 4\pi i^l j_l(GR_{MT}) y_{lms}(\hat{\mathbf{G}}) \tag{485}$$

and the matrix elements previously computed

$$\vec{I}^1_{l'm's'lms} \equiv \langle y_{l'm's'} | \vec{e}_{\mathbf{r}} | y_{lms} \rangle \tag{486}$$

to simplify

$$\mathbf{F}^{Pulley} = R^2_{MT} \sum_{lms} \rho_{lms}(R_{MT}) \sum_{l'm's'} V^{KS}_{l'm's'} I^1_{lmsl'm's'} \tag{487}$$

For each atom, we precompute the quantity

$$\vec{V}_{lms}(R_\alpha) = \sum_{l'm's'} V^{KS}_{l'm's'}(R_{MT}) \vec{I}^1_{l'm's'lms} \tag{488}$$

which gives simple expression for the force

$$\mathbf{F}^{Pulley} = R^2_{MT} \sum_{lms} \rho_{lms}(R_{MT}) \vec{V}_{lms}(R_\alpha) \tag{489}$$

The most time consuming is calculation of the interstitial charge on the MT-sphere. It can be computed in the following way

$$\rho_{lms}(R_{MT}) = 4\pi \sum_{\mathbf{G}_0} \widetilde{\rho}_{\mathbf{G}}\, i^l j_l(GR_{MT}) \sum_{\mathbf{G}\in\mathbf{G}_0-star} e^{i\mathbf{G}\mathbf{R}_\alpha} y_{lms}(\hat{\mathbf{G}}) \tag{490}$$

The MT-part can also be computed with Eq. 489, except that ρ_{lms} is in this case already computed and stored, hence the calculation is trivial.

Alternatively, we can check the MT-part by using previously computed voulme integrlas $\mathrm{Tr}(V_{KS}\nabla\rho)$. We start from

$$\mathbf{F}^{Pulley} = -\sum_i w_i^{DMFT} \sum_{\mathbf{K},\mathbf{K}'} A^\dagger_{i\mathbf{K}'} A_{\mathbf{K}i} \oint_{MT} d\vec{S} \chi^*_{\mathbf{K}'} V_{KS} \chi_{\mathbf{K}} \tag{491}$$

and use Gauss theorem to derive

$$\oint_{MT} d\vec{S} \chi^*_{\mathbf{K}'} V_{KS} \chi_{\mathbf{K}} = \int_{MT} d^3r\, (\nabla(\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}}) V_{KS} + \chi^*_{\mathbf{K}'}\chi_{\mathbf{K}} \nabla V_{KS}) \tag{492}$$

hence

$$F^{Pulley} = -\sum_i w_i^{DMFT} \sum_{\mathbf{K},\mathbf{K}'} A^\dagger_{i\mathbf{K}'} A_{\mathbf{K}i} \int_{MT} d^3r\, (V_{KS}\nabla(\chi^*_{\mathbf{K}'}\chi_{\mathbf{K}}) + \chi^*_{\mathbf{K}'}\chi_{\mathbf{K}} \nabla V_{KS}) = -\mathrm{Tr}(V_{KS}\nabla\rho) - \mathrm{Tr}(\rho\nabla V_{KS}) \tag{493}$$

Above we computed $\mathrm{Tr}(V_{KS}\nabla\rho)$. In the same way we can also compute $\mathrm{Tr}(\rho\nabla V_{KS})$.

K. Check equivalence with LDA+U formula

To check previous equation on LDA+U, we notice that in Wien2k implementation, the projector is $Y^*_{lm'}(\hat{\mathbf{r}})\delta(r - r')Y_{lm}(\hat{\mathbf{r}}')$. We then have $U_{im'}\Sigma_{m'm}U^\dagger_{mj} = \langle\psi^0_i|\phi_{m'}\rangle \Sigma_{m'm} \langle\phi_m|\psi^0_j\rangle = A^{0\dagger}_{i\mathbf{K}'} \langle\chi_{\mathbf{K}'}|\phi_{m'}\rangle \Sigma_{m'm} \langle\phi_m|\chi_{\mathbf{K}}\rangle A^0_{\mathbf{K}j}$ and $\vec{\mathcal{R}}^\dagger = A^{0\dagger} O\mathbf{K} A^0$ hence

$$U_{im'}\Sigma_{m'm}U^\dagger_{mj'}\vec{\mathcal{R}}^\dagger_{j'j} = A^{0\dagger}_{i\mathbf{K}'} a^{\mathbf{K}'\kappa'\,*}_{lm'} \Sigma^l_{m'm} a^{\mathbf{K}\kappa}_{lm} \langle u^{\kappa'}_l|u^\kappa_l\rangle (A^0 A^{0\dagger} O\mathbf{K} A^0)_{\mathbf{K}j} \tag{494}$$

$$= A^{0\dagger}_{i\mathbf{K}'} a^{\mathbf{K}'\kappa'\,*}_{lm'} \Sigma^l_{m'm} a^{\mathbf{K}\kappa}_{lm} \langle u^{\kappa'}_l|u^\kappa_l\rangle \mathbf{K} A^0_{\mathbf{K}j} = a^{\kappa'\,*}_{ilm'} \Sigma^l_{m'm} \langle u^{\kappa'}_l|u^\kappa_l\rangle \vec{\mathcal{A}}^\kappa_{jlm} \tag{495}$$

In LDA+U the self-energy Σ is static, hence summation over $i\omega$ of $G(i\omega)$ gives $\delta_{ij} f_{\mathbf{k}i}$ and then Eq. 364 is equivalent to

$$2\mathrm{Im}\left\{\sum_i f_{\mathbf{k}i} a^{\kappa'\,*}_{ilm'} \Sigma^l_{m'm} \langle u^{\kappa'}_l|u^\kappa_l\rangle \vec{\mathcal{A}}^\kappa_{ilm}\right\}$$

which is exactly the LDA+U force implemented in Eq. 212

IV. APPENDICES

A. Equivalence between Krakauer and Soler derivation

In Krakauer/Singh method, one uses an expansion of the basis function to calculate matrix elements of overlap and kinetic energy. The change of the basis functions due to a shift is

$$\frac{\delta\chi_{\mathbf{K}}(\mathbf{r}-\mathbf{R}_\alpha)}{\delta\mathbf{R}_\alpha} \approx i(\mathbf{k}+\mathbf{K})\chi_{\mathbf{K}}(\mathbf{r}-\mathbf{R}_\alpha) - \nabla_{\mathbf{r}}\chi_{\mathbf{K}}(\mathbf{r}-\mathbf{R}_\alpha) + \cdots \tag{496}$$

and according to Singh, one should calculate the change of the matrix elements in the following way

$$\delta\left\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle = \left\langle\delta\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle + \left\langle\chi_{\mathbf{K}'}|T|\delta\chi_{\mathbf{K}}\right\rangle + \left\langle\chi_{\mathbf{K}'}|\delta T|\chi_{\mathbf{K}}\right\rangle \tag{497}$$

$$= \left\langle i(\mathbf{k}+\mathbf{K}')\chi_{\mathbf{K}'} - \nabla\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle + \left\langle\chi_{\mathbf{K}'}|T|i(\mathbf{k}+\mathbf{K})\chi_{\mathbf{K}} - \nabla\chi_{\mathbf{K}}\right\rangle \tag{498}$$

$$+ \oint_{r=R_{MT}^-} d\vec{S}\chi^*_{\mathbf{K}'}T\chi_{\mathbf{K}} - \oint_{r=R_{MT}^+} d\vec{S}\widetilde{\chi}^*_{\mathbf{K}'}T\widetilde{\chi}_{\mathbf{K}} \tag{499}$$

The last line stands for the discontinuity term, which appears when the matrix elements $\chi_{\mathbf{K}'}T\chi_{\mathbf{K}}$ are not continuous across the MT boundary. For $r = R_{MT}^+$ we used different symbol for χ to emphasize its form as plane wave in the interstitials [This convention is used in Soler/Williams work].

It was shown by Soler/Williams in PRB 47, 6784 (1993) that this expression is equivalent to their formulation of the force. For us, it is important to get equivalent expression, which I can rationalize (see below).

Let's simplify the above expression

$$\delta\left\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle = i(\mathbf{K}-\mathbf{K}')\left\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle_{MT} - \int_{r<R_{MT}} d^3r[(\nabla\chi^*_{\mathbf{K}'})T\chi_{\mathbf{K}} + \chi^*_{\mathbf{K}'}T\nabla\chi_{\mathbf{K}}] \tag{500}$$

$$+ \oint_{r=R_{MT}^-} d\vec{S}\chi^*_{\mathbf{K}'}T\chi_{\mathbf{K}} - \oint_{r=R_{MT}^+} d\vec{S}\widetilde{\chi}^*_{\mathbf{K}'}T\widetilde{\chi}_{\mathbf{K}} \tag{501}$$

Using Stokes theorem, we can convert

$$\int_{r<R_{MT}} d^3r[(\nabla\chi^*_{\mathbf{K}'})T\chi_{\mathbf{K}} + \chi^*_{\mathbf{K}'}T\nabla\chi_{\mathbf{K}} = \int_{r<R_{MT}} d^3r\nabla(\chi^*_{\mathbf{K}'}T\chi_{\mathbf{K}}) = \oint_{r=R_{MT}^-} d\vec{S}\chi^*_{\mathbf{K}'}T\chi_{\mathbf{K}} \tag{502}$$

which cancels a term in Eq. 501 and gives

$$\delta\left\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle = i(\mathbf{K}-\mathbf{K}')\left\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle_{MT} - \oint_{r=R_{MT}^+} d\vec{S}\widetilde{\chi}^*_{\mathbf{K}'}T\widetilde{\chi}_{\mathbf{K}} \tag{503}$$

We can use Stokes theorem one more time to obtain

$$\oint_{r=R_{MT}^+} d\vec{S}\widetilde{\chi}^*_{\mathbf{K}'}T\widetilde{\chi}_{\mathbf{K}} = \int_{r<R_{MT}} d^3r\nabla(\widetilde{\chi}^*_{\mathbf{K}'}T\widetilde{\chi}_{\mathbf{K}}) = \left\langle\nabla\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\right\rangle_{MT} + \left\langle\widetilde{\chi}_{\mathbf{K}'}|T|\nabla\widetilde{\chi}_{\mathbf{K}}\right\rangle_{MT} \tag{504}$$

and since $\widetilde{\chi}_{\mathbf{K}}$ are plane waves, we get

$$\oint_{r=R_{MT}^+} d\vec{S}\widetilde{\chi}^*_{\mathbf{K}'}T\widetilde{\chi}_{\mathbf{K}} = i(\mathbf{K}-\mathbf{K}')\left\langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\right\rangle_{MT} \tag{505}$$

Inserting this expression back into Eq. 503, gives

$$\delta\left\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle = i(\mathbf{K}-\mathbf{K}')\left[\left\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\right\rangle_{MT} - \left\langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\right\rangle_{MT}\right] \tag{506}$$

This latter expression Eq. 506 was used in Soler/Williams, and can be derived explicitely from the form of the basis functions $\chi_{\mathbf{K}}$. For simplicity, we will work with APW basis functions, but the result is general and works also for LAPW functions. The explicit form of $\chi_{\mathbf{K}}$ inside the MT-sphere at $\mathbf{R}_\alpha$ is

$$\chi_{\mathbf{K}}(\mathbf{r}) = u_l(|\mathbf{r}-\mathbf{R}_\alpha|)Y_{lm}(R(\hat{\mathbf{r}}-\hat{\mathbf{R}}_\alpha))\frac{4\pi i^l}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K})\mathbf{R}_\alpha}Y^*_{lm}(R(\mathbf{k}+\mathbf{K}))\frac{j_l(|\mathbf{k}+\mathbf{K}|S)}{u_l(S)} \tag{507}$$

The form in the interstitial is as always the plane wave

$$\widetilde{\chi}_{\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \tag{508}$$

When we move the atom α, we do not change the interstitial part $\widetilde{\chi}_{\mathbf{K}}$ or any other atom, except atom at $\mathbf{R}_\alpha$. (We imagine moving α atom at the fixed interstitial wave function.) The reason that χ changes is because of the matching condition at the MT sphere changes. We have explicitely

$$\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle = \langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\rangle_I + \sum_\beta \langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle_{MT-\beta} = \langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\rangle + \sum_\beta \langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle_{MT-\beta} - \langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\rangle_{MT-\beta} \tag{509}$$

The first term is now extended to the entire space, and is constant as we move the atom. The second term is changed, but only $MT-\alpha$ term, when atom at $\mathbf{R}_\alpha$ is moved. We can also explicitely write the second term

$$\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle = \langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\rangle + \sum_\alpha e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha} Y_{l'm'}(R(\mathbf{k}+\mathbf{K}'))Y^*_{lm}(R(\mathbf{k}+\mathbf{K}))\frac{(4\pi)^2 j_l(|\mathbf{k}+\mathbf{K}|S)j_{l'}(|\mathbf{k}+\mathbf{K}'|S)}{V u_l(S)u_{l'}(S)}$$

$$\times \int_{MT-\alpha} d^3r\, u_{l'}(|\mathbf{r}-\mathbf{R}_\alpha|)Y^*_{l'm'}(R(\hat{\mathbf{r}}-\hat{\mathbf{R}}_\alpha))\hat{T}u_l(|\mathbf{r}-\mathbf{R}_\alpha|)Y_{lm}(R(\hat{\mathbf{r}}-\hat{\mathbf{R}}_\alpha)) \tag{510}$$

$$-e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha}\int_{MT-\alpha} d^3r\, e^{-i(\mathbf{k}+\mathbf{K}')(\mathbf{r}-\mathbf{R}_\alpha)}\hat{T}e^{i(\mathbf{k}+\mathbf{K})(\mathbf{r}-\mathbf{R}_\alpha)} \tag{511}$$

We work at fixed u_l functions, hence the form of $u_l(r)$ does not change as we move the atom. Their position however changes. In the last two parts of the above equation we can change the integration variable from $\mathbf{r}-\mathbf{R}_\alpha$ to $\mathbf{r}$ and we see

$$\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle = \langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\rangle + \sum_\alpha e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha} Y_{l'm'}(R(\mathbf{k}+\mathbf{K}'))Y^*_{lm}(R(\mathbf{k}+\mathbf{K}))\frac{(4\pi)^2 j_l(|\mathbf{k}+\mathbf{K}|S)j_{l'}(|\mathbf{k}+\mathbf{K}'|S)}{V u_l(S)u_{l'}(S)}$$

$$\times \int_{r<S} d^3r\, u_{l'}(r)Y^*_{l'm'}(R\hat{\mathbf{r}})\hat{T}u_l(r)Y_{lm}(R\hat{\mathbf{r}}) \tag{512}$$

$$-e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha}\int_{r<S} d^3r\, e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}}\hat{T}e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \tag{513}$$

The only place where $\mathbf{R}_\alpha$ appears is in the phase factor $e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha}$, while the real space integral is not affected at all by moving atom α. As the first term $\langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\rangle$ is not affected by moving the atom, we conclude

$$\frac{\delta}{\delta\mathbf{R}_\alpha}\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle = i(\mathbf{K}-\mathbf{K}')e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha}\left\{Y_{l'm'}(R(\mathbf{k}+\mathbf{K}'))Y^*_{lm}(R(\mathbf{k}+\mathbf{K}))\frac{(4\pi)^2 j_l(|\mathbf{k}+\mathbf{K}|S)j_{l'}(|\mathbf{k}+\mathbf{K}'|S)}{V u_l(S)u_{l'}(S)}\right.$$

$$\left.\times \int_{r<S} d^3r\, u_{l'}(r)Y^*_{l'm'}(R\hat{\mathbf{r}})\hat{T}u_l(r)Y_{lm}(R\hat{\mathbf{r}}) - \int_{r<S} d^3r\, e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}}\hat{T}e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}}\right\} \tag{514}$$

We can summarize our result by more concise equation

$$\frac{\delta}{\delta\mathbf{R}_\alpha}\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle = i(\mathbf{K}-\mathbf{K}')\left[\langle\chi_{\mathbf{K}'}|T|\chi_{\mathbf{K}}\rangle_{MT-\alpha} - \langle\widetilde{\chi}_{\mathbf{K}'}|T|\widetilde{\chi}_{\mathbf{K}}\rangle_{MT-\alpha}\right] \tag{515}$$

B. General form of small variation within both methods Krakauer and Soler

To show the connection between the Krakauer/Singh and Soler/Williams more clearly, we write a case of 1D functions. Imagine we have a 1D functions $f(x) = e^{ika}f_0(x-a)$, $g(x) = e^{iqa}g_0(x-a)$, defined in the interval $[a-S, a+S]$. Outside this interval $f(x)$ and $g(x)$ are different functions [such as plane waves] denoted by $\tilde{f}(x)$ and $\tilde{g}(x)$. The functions outside the interval $[a-S, a+S]$ $\tilde{f}$ and $\tilde{g}$ do not change with the shift.

We will discuss two types of operators, which we call "rigid" and "non-rigid". If $\frac{\delta V}{\delta a} = 0$, we call the operator "rigid". An example is kinetic energy operator $T = \nabla\cdot\nabla$, which does not change as we shift the atom.

A "non-rigid" operator, such as Kohn-Sham potential, can be writen within muffin-thin sphere as $V(a, x-a)$, to emphasize that an operator shifts with the atom, but it also changes its shape within the sphere (the shape changes even if we look at it in the coordinate system attached to the shifting atom). The derivative of such an operator is then

$$\frac{\delta}{\delta a}V(a,x-a) = \left(\frac{\partial V}{\partial a}\right)_{x-a} - \left(\frac{\partial V}{\partial x}\right)_{a} \tag{516}$$

In the rest of the system (interstitals) and other MT-spheres – in which the basis does not change – we replace all functions with their smoothened equivalents, i.e., $V \to \tilde{V}(a,x)$. We allowed V to depend on the shift of a, as the charge distribution changes, hence the Hartree potential will change as well (is a solution of Poisson equation). Hence, the Hartree potential does depend on a also in the interstitials. The local exchange-correlation potential however does not change outside the MT-sphere as the charge outside MT-sphere does not change, hence for xc-potential $\delta\tilde{V}_{xc}/\delta a = 0$.

The matrix element of such an operator can then be computed by

$$\langle f|V|g\rangle = \int_{-\infty}^{a-S}\tilde{f}(x)\tilde{V}\tilde{g}(x) + \int_{a+S}^{\infty}\tilde{f}(x)\tilde{V}\tilde{g}(x) + \int_{a-S}^{a+S} f(x)V(a,x-a)g(x) \tag{517}$$

which can also be simplified to

$$\begin{aligned}\langle f|V|g\rangle &= \int_{-\infty}^{a-S}\tilde{f}(x)\tilde{V}\tilde{g}(x) + \int_{a+S}^{\infty}\tilde{f}(x)\tilde{V}\tilde{g}(x) + \int_{a-S}^{a+S} e^{i(q-k)a} f_0(x-a)V(a,x-a)g_0(x-a)\\ &= \int_{-\infty}^{a-S}\tilde{f}(x)\tilde{V}\tilde{g}(x) + \int_{a+S}^{\infty}\tilde{f}(x)\tilde{V}\tilde{g}(x) + e^{i(q-k)a}\int_{-S}^{S} f_0(x)V(a,x)g_0(x)\end{aligned} \tag{518}$$

If we move the interval for a bit $a \to a+\delta a$ we can take the derivative of either Eq. 517 or Eq. 518 to get two equivalent expressions for the same quantity.

Let's first take the derivative of Eq. 517

$$\frac{\delta}{\delta a}\langle f|V|g\rangle = (\tilde{f}V\tilde{g})(x=a-S) - (\tilde{f}V\tilde{g})(x=a+S) + (fVg)(x=a+S) - (fVg)(x=a-S) \tag{519}$$

$$+\int_{a-S}^{a+S}(\frac{\delta f}{\delta a})Vgdx + \int_{a-S}^{a+S} fV(\frac{\delta g}{\delta a})dx + \int_{a-S}^{a+S} f(\frac{\delta V}{\delta a})gdx + \int_{-\infty}^{a-S}\tilde{f}(x)\frac{\delta\tilde{V}}{\delta a}\tilde{g}(x) + \int_{a+S}^{\infty}\tilde{f}(x)\frac{\delta\tilde{V}}{\delta a}\tilde{g}(x) \tag{520}$$

Here $(\frac{\delta V}{\delta a})$ contains both terms for the rigid and non-rigid part from Eq. 516. We can siplify this expression to obtain

$$\frac{\delta}{\delta a}\langle f|V|g\rangle = \langle\frac{\delta f}{\delta a}|V|g\rangle_{MT} + \langle f|V|\frac{\delta g}{\delta a}\rangle_{MT} + (fVg - \tilde{f}V\tilde{g})(x=a+S) - (fVg - \tilde{f}V\tilde{g})(x=a-S) + \langle f|\frac{\delta V}{\delta a}|g\rangle \tag{521}$$

At the boundary $x = a \pm S$ the two forms of the potential are equal $V(a,S) = \tilde{V}(a,a+S)$, hence we droped tilde sign. Notice also that one term ($\langle f|\frac{\delta V}{\delta a}|g\rangle$) extends over the entire space, while all others are integrated only within MT-sphere. This form of the differential is the Krakauer's way of differentiating matrix elements.

The alternative way is to differentiate Eq. 518, to obtain

$$\begin{aligned}\frac{\delta}{\delta a}\langle f|V|g\rangle = (\tilde{f}V\tilde{g})(x=a-S) - (\tilde{f}V\tilde{g})(x=a+S) + i(q-k)e^{i(q-k)a}\int_{-S}^{S} f_0(x)Vg_0(x)\\ +e^{i(q-k)a}\int_{-S}^{S} f_0(x)\left(\frac{\partial V}{\partial a}\right)_{x-a} g_0(x) + \int_{-\infty}^{a-S}\tilde{f}(x)\frac{\delta\tilde{V}}{\delta a}\tilde{g}(x) + \int_{a+S}^{\infty}\tilde{f}(x)\frac{\delta\tilde{V}}{\delta a}\tilde{g}(x)\end{aligned} \tag{522}$$

which can also be written as

$$\frac{\delta}{\delta a}\langle f|V|g\rangle = (\tilde{f}V\tilde{g})(x=a-S) - (\tilde{f}V\tilde{g})(x=a+S) + i(q-k)\langle f|V|g\rangle_{MT} + \langle f|\frac{\delta V}{\delta a}|g\rangle + \langle f|\left(\frac{\partial V}{\partial x}\right)|g\rangle_{MT} \tag{523}$$

or equivalently

$$\frac{\delta}{\delta a}\langle f|V|g\rangle = i(q-k)\langle f|V|g\rangle_{MT} + \langle f|\frac{\delta V}{\delta a}|g\rangle + \langle f|\left(\frac{\partial V}{\partial x}\right)|g\rangle_{MT} - \int_{a-S}^{a+S}(\frac{d\tilde{f}}{dx}V\tilde{g} + \tilde{f}\frac{dV}{dx}\tilde{g} + \tilde{f}V\frac{d\tilde{g}}{dx}) \tag{524}$$

In 3D we can similarly derive two forms of differentiating the matrix elements. The Krakauer's form is

$$\frac{\delta}{\delta\mathbf{R}_\alpha}\langle\chi_{\mathbf{K}'}|V|\chi_{\mathbf{K}}\rangle = \langle\frac{\delta\chi_{\mathbf{K}'}}{\delta\mathbf{R}_\alpha}|V|\chi_{\mathbf{K}}\rangle_{MT} + \langle\chi_{\mathbf{K}'}|V|\frac{\delta\chi_{\mathbf{K}}}{\delta\mathbf{R}_\alpha}\rangle_{MT} + \langle\chi_{\mathbf{K}'}|\frac{\delta V}{\delta\mathbf{R}_\alpha}|\chi_{\mathbf{K}}\rangle + \oint_{MT} d\vec{S}(\chi^*_{\mathbf{K}'}V\chi_{\mathbf{K}} - \tilde{\chi}^*_{\mathbf{K}'}V\tilde{\chi}_{\mathbf{K}}) \tag{525}$$

where $\frac{\delta V}{\delta \mathbf{R}_\alpha}$ contains both "rigid" and "non-rigid" part of the derivative, and $\tilde{\chi}_\mathbf{K}$ ($\chi_\mathbf{K}$) are plane wave functions (augmented basis functions), which are used in the interstitials $r > S$ (in MT spheres $r < S$). Notice that the kinetic energy part does not have terms like $\frac{\delta V}{\delta \mathbf{R}_\alpha}$ because such derivative is absent. We thus have

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'}|T|\chi_\mathbf{K}\rangle = \langle \frac{\delta \chi_{\mathbf{K}'}}{\delta \mathbf{R}_\alpha}|T|\chi_\mathbf{K}\rangle_{MT} + \langle \chi_{\mathbf{K}'}|T|\frac{\delta \chi_\mathbf{K}}{\delta \mathbf{R}_\alpha}\rangle_{MT} + \oint_{MT} d\vec{S}(\chi^*_{\mathbf{K}'} T \chi_\mathbf{K} - \tilde{\chi}^*_{\mathbf{K}'} T \tilde{\chi}_\mathbf{K}) \tag{526}$$

The alternative form, which is used in Soler/Williams, is

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'}|V|\chi_\mathbf{K}\rangle = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'}|V|\chi_\mathbf{K}\rangle_{MT} + \langle \chi_{\mathbf{K}'}|\frac{\delta V}{\delta \mathbf{R}_\alpha}|\chi_\mathbf{K}\rangle + \langle \chi_{\mathbf{K}'}|\nabla V|\chi_\mathbf{K}\rangle_{MT} - \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} V \tilde{\chi}_\mathbf{K} \tag{527}$$

This can also be simplified to get

$$\begin{aligned}\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'}|V|\chi_\mathbf{K}\rangle = i(\mathbf{K}-\mathbf{K}') \left[\langle \chi_{\mathbf{K}'}|V|\chi_\mathbf{K}\rangle_{MT} - \langle \tilde{\chi}_{\mathbf{K}'}|V|\tilde{\chi}_\mathbf{K}\rangle_{MT}\right] + \langle \chi_{\mathbf{K}'}|\frac{\delta V}{\delta \mathbf{R}_\alpha}|\chi_\mathbf{K}\rangle \\ + \langle \chi_{\mathbf{K}'}|\nabla V|\chi_\mathbf{K}\rangle_{MT} - \langle \tilde{\chi}_{\mathbf{K}'}|\nabla V|\tilde{\chi}_\mathbf{K}\rangle_{MT}\end{aligned} \tag{528}$$

For the kinetic energy there is no change of operator associated with the shift, hence $\frac{\delta T}{\delta \mathbf{R}_\alpha} = 0$ and $\nabla T = 0$. We thus have

$$\begin{aligned}\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'}|T|\chi_\mathbf{K}\rangle &= i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'}|T|\chi_\mathbf{K}\rangle_{MT} - \oint_{\mathbf{r}=R^-_{MT}} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} T \tilde{\chi}_\mathbf{K} \\ &= i(\mathbf{K}-\mathbf{K}') \left[\langle \chi_{\mathbf{K}'}|T|\chi_\mathbf{K}\rangle_{MT} - \langle \tilde{\chi}_{\mathbf{K}'}|T|\tilde{\chi}_\mathbf{K}\rangle_{MT}\right]\end{aligned} \tag{529}$$

C. Discontinuous functions

Let's start with discontinuity in 1D. If $H(x)$ is continuous function in the interval $[-\infty, \infty]$, and we move the entire function for a small amount a, we expect no change in the following integral

$$0 = \int dx[H(x-a) - H(x)] = -a \int \frac{dH}{dx} dx = -a[H(\infty) - H(-\infty)] \tag{530}$$

If the function is continuous and goes to zero at large distances, this clearly works. But lets now take a function $H(x)$, which has a single jump at x_0 so that $H(x_0^-) \neq H(x_0^+)$. We then need to add the following term

$$\int dx[H(x-a) - H(x)] = -a \int \frac{dH}{dx} dx + a(H[x_0^-] - H[x_0^+]) \tag{531}$$

and by rearranging we have

$$\int dx H(x-a) = \int dx H(x) - a \int \frac{dH}{dx} dx + a(H[x_0^-] - H[x_0^+]) \tag{532}$$

In higher D we have similar equation. Let's move a sphere for a small amount $\vec{a}$. We get

$$\int d^3r H(\vec{r} - \vec{a}) = \int d^3r H(\vec{r}) - \vec{a} \int d^3r \nabla_\mathbf{r} H(\mathbf{r}) + \vec{a} \oint d\vec{S}(H[r_0^-] - H[r_0^+]) \tag{533}$$

In summary, if we have a function $H(\mathbf{r})$ and we move the sphere for vector $\vec{a}$, its change is $\delta H/\delta \vec{a} = -\nabla_\mathbf{r} H(\mathbf{r})$. If there is discountinuity, we have

$$\frac{\delta}{\delta \vec{a}} \int d^3r H(\vec{r}) = \vec{a} \int d^3r \frac{\delta H}{\delta \vec{a}} + \vec{a} \oint d\vec{S}(H[r_0^-] - H[r_0^+]) \tag{534}$$

D. Another formula

$$\oint_{R_{MT}^-} d\vec{S}\nabla\chi^*_{\mathbf{K}'}(\mathbf{r})\cdot\nabla\chi_{\mathbf{K}}(\mathbf{r}) = a^{\mathbf{K}',\kappa'\,*}_{l'm'} a^{\mathbf{K},\kappa}_{lm}\int d\Omega\vec{e}_r\,(r\nabla)\left(\frac{u^{\kappa'}_{l'}}{r}Y^*_{l'm'}\right)\cdot(r\nabla)\left(\frac{u^{\kappa}_{l}}{r}Y_{lm}\right) \tag{535}$$

We know that

$$(r\nabla)\left(\frac{u}{r}Y_{lm}\right) = \vec{e}_r r\frac{d}{dr}\left(\frac{u}{r}\right) + \frac{u}{r}(r\nabla)Y_{lm}$$

hence

$$Eq.\ 535 = a^{\mathbf{K}',\kappa'\,*}_{l'm'} a^{\mathbf{K},\kappa}_{lm}\left[r^2\frac{d}{dr}\left(\frac{u^{\kappa'}_{l'}}{r}\right)\frac{d}{dr}\left(\frac{u^{\kappa}_{l}}{r}\right)\oint Y^*_{l'm'}\vec{e}_r Y_{lm}d\Omega + \left(\frac{u^{\kappa'}_{l'}}{r}\right)\left(\frac{u^{\kappa}_{l}}{r}\right)\int(r\nabla)Y^*_{l'm'}(\hat{\mathbf{r}})\cdot(r\nabla)Y_{lm}(\hat{\mathbf{r}})\,\vec{e}_r d\Omega\right]$$

We know that

$$\int(r\nabla)Y^*_{l'm'}(\hat{\mathbf{r}})\,(r\nabla)Y_{lm}(\hat{\mathbf{r}})\,d\Omega = l(l+1)\delta_{ll'}\delta_{mm'}.$$

To derive

$$I^3_{l'm'lm} = \int((r\nabla)Y^*_{l'm'}(\hat{\mathbf{r}}))\cdot((r\nabla)Y_{lm}(\hat{\mathbf{r}}))\vec{e}_r\,d\Omega \tag{536}$$

we use the standard procedure discussed above to obtain

$$\begin{aligned} I^3_{l'm'lm} = &\frac{l(l+2)}{2}\left[a(l,m)\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l,-m)\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} + 2f(l,m)\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l+1}\\ &-\frac{(l-1)(l+1)}{2}\left[a(l',-m')\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l',m')\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} - 2f(l',m')\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l-1} \end{aligned} \tag{537}$$

which can also be written as

$$\begin{aligned} I^3_{l'm'lm} = &\frac{l(l+2)}{2}\,\delta_{l'=l+1}\begin{pmatrix}a(l,m)\delta_{m'=m+1} - a(l,-m)\delta_{m'=m-1}\\ -i[a(l,m)\delta_{m'=m+1} + a(l,-m)\delta_{m'=m-1}]\\ 2f(l,m)\delta_{m'=m}\end{pmatrix}\\ &-\frac{(l-1)(l+1)}{2}\delta_{l'=l-1}\begin{pmatrix}a(l',-m')\delta_{m'=m+1} - a(l',m')\delta_{m'=m-1}\\ -i[a(l',-m')\delta_{m'=m+1} + a(l',m')\delta_{m'=m-1}]\\ -2f(l',m')\delta_{m'=m}\end{pmatrix} \end{aligned} \tag{538}$$

E. Matrix elements of the Spheric harmonics

We are interested in the following integrals:

$$I^1_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})\vec{e}_{\mathbf{r}}Y_{lm}(\hat{\mathbf{r}}) \tag{539}$$

$$I^2_{l'm'lm} \equiv \int d\Omega Y^*_{l'm'}(\hat{\mathbf{r}})(r\nabla Y_{lm}(\hat{\mathbf{r}})) \tag{540}$$

$$I^3_{l'm'lm} \equiv \int d\Omega(r\nabla Y^*_{l'm'}(\hat{\mathbf{r}}))\cdot(r\nabla Y_{lm}(\hat{\mathbf{r}}))\vec{e}_{\mathbf{r}} \tag{541}$$

$$\tag{542}$$

These integrals, computed above, take the form

$$I^1_{l'm'lm} = \frac{1}{2}\left[a(l,m)\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l,-m)\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} + 2f(l,m)\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l+1}$$
$$-\frac{1}{2}\left[a(l',-m')\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l',m')\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} - 2f(l',m')\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l-1} \quad (543)$$

$$I^2_{l'm'lm} = -\frac{l}{2}\left[a(l,m)\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l,-m)\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} + 2f(l,m)\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l+1}$$
$$-\frac{l+1}{2}\left[a(l',-m')\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l',m')\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} - 2f(l',m')\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l-1} \quad (544)$$

$$I^3_{l'm'lm} = \frac{l(l+2)}{2}\left[a(l,m)\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l,-m)\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} + 2f(l,m)\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l+1}$$
$$-\frac{(l-1)(l+1)}{2}\left[a(l',-m')\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l',m')\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} - 2f(l',m')\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l-1} \quad (545)$$

We can write all three integrals in a common form, namely,

$$I^n_{l'm'lm} = c_{n,l}\left[a(l,m)\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l,-m)\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} + 2f(l,m)\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l+1}$$
$$-d_{n,l}\left[a(l',-m')\begin{pmatrix}1\\-i\\0\end{pmatrix}\delta_{m'=m+1} + a(l',m')\begin{pmatrix}-1\\-i\\0\end{pmatrix}\delta_{m'=m-1} - 2f(l',m')\begin{pmatrix}0\\0\\1\end{pmatrix}\delta_{m'=m}\right]\delta_{l'=l-1} \quad (546)$$

where

$$c_{1,l} = \tfrac{1}{2} \quad d_{1,l} = \frac{1}{2} \quad (547)$$
$$c_{2,l} = -\tfrac{l}{2} \quad d_{2,l} = \frac{l+1}{2} \quad (548)$$
$$c_{3,l} = \tfrac{l(l+2)}{2} \quad d_{3,l} = \frac{(l-1)(l+1)}{2} \quad (549)$$

Next we want to derive the integrals in real spheric harmonics $y_{lm\pm}$ which are related to complex spheric harmonics by

$$Y_{lm} = (-1)^m\sqrt{\frac{1+\delta_{m,0}}{2}}(y_{lm+} + iy_{lm-}) \quad (550)$$
$$Y_{l,-m} = \sqrt{\frac{1+\delta_{m,0}}{2}}(y_{lm+} - iy_{lm-}) \quad (551)$$

Here we want to find the connection between $\langle Y^*_{l'm'}|T|Y_{lm}\rangle$ and $\langle y_{l'm's'}|T|y_{lms}\rangle$. We will derive the connection for the case of T being a real operator. We have

$$\langle y_{l'm'+}|T|y_{lm+}\rangle + \langle y_{l'm'-}|T|y_{lm-}\rangle = \mathrm{Re}\left(\langle y_{l'm'+} - iy_{l'm'-}|T|y_{lm+} + iy_{lm-}\rangle\right) = \frac{(-1)^{m+m'}}{\sqrt{\mathcal{D}}} 2\mathrm{Re}\left(\langle Y^*_{l'm'}|T|Y_{lm}\rangle\right)$$

$$\langle y_{l'm'+}|T|y_{lm+}\rangle - \langle y_{l'm'-}|T|y_{lm-}\rangle = \mathrm{Re}\left(\langle y_{l'm'+} + iy_{l'm'-}|T|y_{lm+} + iy_{lm-}\rangle\right) = \frac{(-1)^{m}}{\sqrt{\mathcal{D}}} 2\mathrm{Re}\left(\langle Y^*_{l'-m'}|T|Y_{lm}\rangle\right)$$

$$\langle y_{l'm'+}|T|y_{lm-}\rangle - \langle y_{l'm'-}|T|y_{lm+}\rangle = \mathrm{Im}\left(\langle y_{l'm'+} - iy_{l'm'-}|T|y_{lm+} + iy_{lm-}\rangle\right) = \frac{(-1)^{m+m'}}{\sqrt{\mathcal{D}}} 2\mathrm{Im}\left(\langle Y^*_{l'm'}|T|Y_{lm}\rangle\right)$$

$$\langle y_{l'm'+}|T|y_{lm-}\rangle + \langle y_{l'm'-}|T|y_{lm+}\rangle = \mathrm{Im}\left(\langle y_{l'm'+} + iy_{l'm'-}|T|y_{lm+} + iy_{lm-}\rangle\right) = \frac{(-1)^{m}}{\sqrt{\mathcal{D}}} 2\mathrm{Im}\left(\langle Y^*_{l'-m'}|T|Y_{lm}\rangle\right)$$

where $\mathcal{D} = (1+\delta_{m=0})(1+\delta_{m'=0})$. We then have

$$\langle y_{l'm'+}|T|y_{lm+}\rangle = \frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m,0})(1+\delta_{m',0})}}\mathrm{Re}\left(\langle Y^*_{l'm'}|T|Y_{lm}\rangle + (-1)^{m'}\langle Y^*_{l'-m'}|T|Y_{lm}\rangle\right) \tag{552}$$

$$\langle y_{l'm'-}|T|y_{lm-}\rangle = \frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m,0})(1+\delta_{m',0})}}\mathrm{Re}\left(\langle Y^*_{l'm'}|T|Y_{lm}\rangle - (-1)^{m'}\langle Y^*_{l'-m'}|T|Y_{lm}\rangle\right) \tag{553}$$

$$\langle y_{l'm'+}|T|y_{lm-}\rangle = \frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m,0})(1+\delta_{m',0})}}\mathrm{Im}\left(\langle Y^*_{l'm'}|T|Y_{lm}\rangle + (-1)^{m'}\langle Y^*_{l'-m'}|T|Y_{lm}\rangle\right) \tag{554}$$

$$-\langle y_{l'm'-}|T|y_{lm+}\rangle = \frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m,0})(1+\delta_{m',0})}}\mathrm{Im}\left(\langle Y^*_{l'm'}|T|Y_{lm}\rangle - (-1)^{m'}\langle Y^*_{l'-m'}|T|Y_{lm}\rangle\right) \tag{555}$$

To proceed, we first turn the above complex harmonics integrals into slightly different form:

$$\begin{aligned}\langle Y_{l'm'}|T|Y_{lm}\rangle = c_{n,l}\;\delta_{l'=l+1}&\begin{pmatrix} a(l,m)\delta_{m'=m+1} - a(l,-m)\delta_{m'=m-1} \\ -i[a(l,m)\delta_{m'=m+1} + a(l,-m)\delta_{m'=m-1}] \\ 2f(l,m)\delta_{m'=m}\end{pmatrix} \\ -d_{n,l}\;\delta_{l'=l-1}&\begin{pmatrix} a(l',-m')\delta_{m'=m+1} - a(l',m')\delta_{m'=m-1} \\ -i[a(l',-m')\delta_{m'=m+1} + a(l',m')\delta_{m'=m-1}] \\ -2f(l',m')\delta_{m'=m}\end{pmatrix}\end{aligned} \tag{556}$$

For real spheric harmonics, we also need $\langle Y_{l'-m'}|T|Y_{lm}\rangle$. But we are interested only in the case when both $m >= 0$ and $m' >= 0$:

$$\begin{aligned}\langle Y_{l'-m'}|T|Y_{lm}\rangle = c_{n,l}\;\delta_{l'=l+1}&\begin{pmatrix} -a(l,-m)\delta_{m'=-m+1}(\delta_{m=0}+\delta_{m=1}) \\ -ia(l,-m)\delta_{m'=-m+1}(\delta_{m=0}+\delta_{m=1}) \\ 2f(l,m)\delta_{m'=-m}\delta_{m=0}\end{pmatrix} \\ -d_{n,l}\;\delta_{l'=l-1}&\begin{pmatrix} -a(l',-m')\delta_{m'=-m+1}(\delta_{m=0}+\delta_{m=1})) \\ -ia(l',-m')\delta_{m'=-m+1}(\delta_{m=0}+\delta_{m=1}) \\ -2f(l',-m')\delta_{m'=-m}\delta_{m=0}\end{pmatrix}\end{aligned} \tag{557}$$

If the two equations are put together, we obtain (for $m >= 0$ and $m' >= 0$):

$$\begin{aligned}\langle Y_{l'm'}|T|Y_{lm}\rangle \pm (-1)^{m'}\langle Y_{l'-m'}|T|Y_{lm}\rangle = c_{n,l}\;\delta_{l'=l+1}&\begin{pmatrix} a(l,m)\delta_{m'=m+1}(1\pm\delta_{m=0}) - a(l,-m)\delta_{m'=m-1}(1\pm\delta_{m=1}) \\ -i[a(l,m)\delta_{m'=m+1}(1\mp\delta_{m=0}) + a(l,-m)\delta_{m'=m-1}(1\pm\delta_{m=1})] \\ 2f(l,m)\delta_{m'=m}(1\pm\delta_{m=0})\end{pmatrix} \\ -d_{n,l}\;\delta_{l'=l-1}&\begin{pmatrix} a(l',-m')\delta_{m'=m+1}(1\pm\delta_{m=0}) - a(l',m')\delta_{m'=m-1}(1\pm\delta_{m=1}) \\ -i[a(l',-m')\delta_{m'=m+1}(1\mp\delta_{m=0}) + a(l',m')\delta_{m'=m-1}(1\pm\delta_{m=1})] \\ -2f(l',m')\delta_{m'=m}(1\pm\delta_{m=0})\end{pmatrix}\end{aligned}$$

hence we have

$$\langle y_{l'm'\pm}|T|y_{lm\pm}\rangle = \frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m=0})(1+\delta_{m'=0})}}\mathrm{Re}\left(\langle Y_{l'm'}|T|Y_{lm}\rangle \pm (-1)^{m'}\langle Y_{l'-m'}|T|Y_{lm}\rangle\right) =$$
$$\frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m=0})(1+\delta_{m'=0})}}\left\{c_{n,l}\;\delta_{l'=l+1}\begin{pmatrix} a(l,m)\delta_{m'=m+1}(1\pm\delta_{m=0}) - a(l,-m)\delta_{m'=m-1}(1\pm\delta_{m=1}) \\ 0 \\ 2f(l,m)\delta_{m'=m}(1\pm\delta_{m=0}) \end{pmatrix}\right.$$
$$\left. -d_{n,l}\;\delta_{l'=l-1}\begin{pmatrix} a(l',-m')\delta_{m'=m+1}(1\pm\delta_{m=0}) - a(l',m')\delta_{m'=m-1}(1\pm\delta_{m=1}) \\ 0 \\ -2f(l',m')\delta_{m'=m}(1\pm\delta_{m=0}) \end{pmatrix}\right\} \quad (558)$$

and

$$\langle y_{l'm'\pm}|T|y_{lm\mp}\rangle = \pm\frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m=0})(1+\delta_{m'=0})}}\mathrm{Im}\left(\langle Y_{l'm'}|T|Y_{lm}\rangle \pm (-1)^{m'}\langle Y_{l'-m'}|T|Y_{lm}\rangle\right) =$$
$$\pm\frac{(-1)^{m+m'}}{\sqrt{(1+\delta_{m=0})(1+\delta_{m'=0})}}\left\{c_{n,l}\;\delta_{l'=l+1}\begin{pmatrix} 0 \\ -[a(l,m)\delta_{m'=m+1}(1\mp\delta_{m=0}) + a(l,-m)\delta_{m'=m-1}(1\pm\delta_{m=1})] \\ 0 \end{pmatrix}\right.$$
$$\left. -d_{n,l}\delta_{l'=l-1}\begin{pmatrix} 0 \\ -[a(l',-m')\delta_{m'=m+1}(1\mp\delta_{m=0}) + a(l',m')\delta_{m'=m-1}(1\pm\delta_{m=1})] \\ 0 \end{pmatrix}\right\} \quad (559)$$

These equations can be simplified, which gives the final result:

$$\langle y_{l'm'\pm}|T|y_{lm\pm}\rangle = c_{n,l}\;\delta_{l'=l+1}\begin{pmatrix} -a(l,m)\delta_{m'=m+1}\frac{(1\pm\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l,-m)\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}} \\ 0 \\ 2f(l,m)\delta_{m'=m}\frac{(1\pm\delta_{m=0})}{1+\delta_{m=0}} \end{pmatrix}$$
$$\left. -d_{n,l}\;\delta_{l'=l-1}\begin{pmatrix} -a(l',-m')\delta_{m'=m+1}\frac{(1\pm\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l',m')\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}} \\ 0 \\ -2f(l',m')\delta_{m'=m}\frac{(1\pm\delta_{m=0})}{1+\delta_{m=0}} \end{pmatrix}\right\} \quad (560)$$

and

$$\langle y_{l'm'\pm}|T|y_{lm\mp}\rangle = \pm\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}\left\{c_{n,l}\;\delta_{l'=l+1}\left(a(l,m)\delta_{m'=m+1}\frac{(1\mp\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l,-m)\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}}\right)\right.$$
$$\left. -d_{n,l}\;\delta_{l'=l-1}\left(a(l',-m')\delta_{m'=m+1}\frac{(1\mp\delta_{m=0})}{\sqrt{1+\delta_{m=0}}} + a(l',m')\delta_{m'=m-1}\frac{(1\pm\delta_{m'=0})}{\sqrt{1+\delta_{m'=0}}}\right)\right\} \quad (561)$$

F. Debugging

We can compute exact force in a very particular situation, in which we rigidly move Kohn-Sham potential with the sphere of the moving atom. In this case the change of matrix elements of the potential are really simple The alternative form, which is used in Soler/Williams, is

$$\frac{\delta}{\delta\mathbf{R}_\alpha}\langle\chi_{\mathbf{K}'}|V|\chi_{\mathbf{K}}\rangle = i(\mathbf{K}-\mathbf{K}')\langle\chi_{\mathbf{K}'}|V|\chi_{\mathbf{K}}\rangle_{MT} - \oint_{MT} d\vec{S}\tilde{\chi}^*_{\mathbf{K}'}V\tilde{\chi}_{\mathbf{K}} \quad (562)$$

This is because the MT-part is not changing except for the phase factor in front $e^{i(\mathbf{k}+\mathbf{K})\mathbf{R}_\alpha}$, while the interstitial part has a surface term because there is slightly more interstitial volume behind the sphere and less infront.

The equation can also be memorized as a special case in which

$$\frac{\delta V}{\delta \mathbf{R}_\alpha} = -\nabla V.$$

Note that in Wien2K the convolution of $V^{KS}_{\mathbf{G}}$ and the plane wave with the MT-hole's is computed in lapw0 step. Hence, when the potential is kept constant, we actually fix also $\langle \tilde{\chi}_{\mathbf{K}} | \tilde{V}^{KS} | \tilde{\chi}_{\mathbf{K}'} \rangle_{interstitials}$ (the Kohn-Sham potential in interestitials), hence the last term of above equation is absent.

For the kinetic part, similar equation holds

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'} | T | \chi_{\mathbf{K}} \rangle = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | T | \chi_{\mathbf{K}} \rangle_{MT} - \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} T \tilde{\chi}_{\mathbf{K}} \tag{563}$$

hence we have

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'} | H^0 | \chi_{\mathbf{K}} \rangle = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | H^0 | \chi_{\mathbf{K}} \rangle_{MT} - \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} H^0 \tilde{\chi}_{\mathbf{K}} \tag{564}$$

But if we fix potential in lapw0, we actually just need

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'} | H^0 | \chi_{\mathbf{K}} \rangle = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | H^0 | \chi_{\mathbf{K}} \rangle_{MT} - \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} T \tilde{\chi}_{\mathbf{K}} \tag{565}$$

For the overlap, the equation

$$\frac{\delta}{\delta \mathbf{R}_\alpha} \langle \chi_{\mathbf{K}'} | \chi_{\mathbf{K}} \rangle = i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | \chi_{\mathbf{K}} \rangle_{MT} - \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} \tilde{\chi}_{\mathbf{K}} \tag{566}$$

is exact.

We want to simulate the following equations

$$(A^{0\dagger} \frac{\delta O}{\delta \mathbf{R}_\alpha} A^0)_{ij} = \sum_{\mathbf{K}\mathbf{K}'} A^{0\dagger}_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | \chi_{\mathbf{K}} \rangle_{MT} A^0_{\mathbf{K}j} - A^{0\dagger}_{i\mathbf{K}'} \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} \tilde{\chi}_{\mathbf{K}} A^0_{\mathbf{K}j} \tag{567}$$

$$(A^{0\dagger} \frac{\delta H^0}{\delta \mathbf{R}_\alpha} A^0)_{ij} = \sum_{vK\mathbf{K}'} A^{0\dagger}_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | H^0 | \chi_{\mathbf{K}} \rangle_{MT} A^0_{\mathbf{K}j} - A^{0\dagger}_{i\mathbf{K}'} \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} T \tilde{\chi}_{\mathbf{K}} A^0_{\mathbf{K}j} \tag{568}$$

and check it with simulating a finite difference. The latter is obtained by computing H^0 and O for unperturbed system, we then move an atom and recompute H^0 and O, and then take numerically finite difference and compare with analytically obtained derivative.

For the overlap, we need the following two terms: The first term is

$$(A^{0\dagger} O_{MT} A^0)_{ij} \equiv \sum_{\mathbf{K}\mathbf{K}'} A^{\dagger}_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'} | \chi_{\mathbf{K}} \rangle_{MT} A_{\mathbf{K}j} = \tag{569}$$

$$= \sum_{\mathbf{K}\mathbf{K}'} A^{\dagger}_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') \begin{pmatrix} a^*_{lm\mathbf{K}'}, & b^*_{lm\mathbf{K}'} & c^*_{lm\mathbf{K}'} \end{pmatrix} \begin{pmatrix} \langle u_l|u_l\rangle & \langle u_l|\dot{u}_l\rangle & \langle u_l|u_l^{LO}\rangle \\ \langle \dot{u}_l|u_l\rangle & \langle \dot{u}_l|\dot{u}_l\rangle & \langle \dot{u}_l|u_l^{LO}\rangle \\ \langle u_l^{LO}|u_l\rangle & \langle u_l^{LO}|\dot{u}_l\rangle & \langle u_l^{LO}|u_l^{LO}\rangle \end{pmatrix} \begin{pmatrix} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ c_{lm\mathbf{K}} \end{pmatrix} A_{\mathbf{K}j}$$

$$= i \begin{pmatrix} a^*_{i,lm}, & b^*_{i,lm} & c^*_{i,lm} \end{pmatrix} \begin{pmatrix} 1 & 0 & \langle u_l|u_l^{LO}\rangle \\ 0 & \langle \dot{u}_l|\dot{u}_l\rangle & \langle \dot{u}_l|u_l^{LO}\rangle \\ \langle u_l|u_l^{LO}\rangle & \langle \dot{u}_l|u_l^{LO}\rangle & 1 \end{pmatrix} \begin{pmatrix} \vec{\mathcal{A}}_{j,lm} \\ \vec{\mathcal{B}}_{j,lm} \\ \vec{\mathcal{C}}_{j,lm} \end{pmatrix} \tag{570}$$

$$-i \begin{pmatrix} \vec{\mathcal{A}}^*_{i,lm}, & \vec{\mathcal{B}}^*_{i,lm} & \vec{\mathcal{C}}^*_{i,lm} \end{pmatrix} \begin{pmatrix} 1 & 0 & \langle u_l|u_l^{LO}\rangle \\ 0 & \langle \dot{u}_l|\dot{u}_l\rangle & \langle \dot{u}_l|u_l^{LO}\rangle \\ \langle u_l|u_l^{LO}\rangle & \langle \dot{u}_l|u_l^{LO}\rangle & 1 \end{pmatrix} \begin{pmatrix} a_{j,lm} \\ b_{j,lm} \\ c_{j,lm} \end{pmatrix}$$

which is equal to

$$(A^{0\dagger} O_{MT} A^0) = i(\mathcal{O} - \mathcal{O}^\dagger) \tag{571}$$

where

$$\mathcal{O}_{ij} \equiv \left(a^*_{i,lm},\ \ b^*_{i,lm}\ \ c^*_{i,lm} \right) \begin{pmatrix} 1 & 0 & \langle u_l|u_l^{LO}\rangle \\ 0 & \langle \dot{u}_l|\dot{u}_l\rangle & \langle \dot{u}_l|u_l^{LO}\rangle \\ \langle u_l|u_l^{LO}\rangle & \langle \dot{u}_l|u_l^{LO}\rangle & 1 \end{pmatrix} \begin{pmatrix} \vec{\mathcal{A}}_{j,lm} \\ \vec{\mathcal{B}}_{j,lm} \\ \vec{\mathcal{C}}_{j,lm} \end{pmatrix} \tag{572}$$

The second term is

$$(A^{0\dagger} O_S A^0)_{ii} \equiv \sum_{\mathbf{K}\mathbf{K}'} A^{0\dagger}_{i\mathbf{K}'} \oint_{MT} d\vec{S} \tilde{\chi}^*_{\mathbf{K}'} \tilde{\chi}_{\mathbf{K}} A^0_{\mathbf{K}i} = \sum_{\mathbf{K}\mathbf{K}'} A^{0*}_{\mathbf{K}'i} A^0_{\mathbf{K}i} \oint d\vec{S} \frac{e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}}}{V} = \sum_{\mathbf{K}\mathbf{G}} A^{0*}_{\mathbf{K}-\mathbf{G},i} A^0_{\mathbf{K}i} \frac{R^2_{MT}}{V} e^{i\mathbf{G}\mathbf{R}_\alpha} \int d\Omega \vec{e}_{\mathbf{r}} e^{i\mathbf{G}\mathbf{r}}$$

The final result is clearly

$$(A^{0\dagger} \frac{\delta O}{\delta \mathbf{R}_\alpha} A^0)_{ii} = (A^{0\dagger} O_{MT} A^0)_{ii} - (A^{0\dagger} O_S A^0)_{ii} \tag{573}$$

We need the following quantity

$$D_{\mathbf{G}} \equiv \sum_{\mathbf{K}} A^{0*}_{\mathbf{K}-\mathbf{G},i} A^0_{\mathbf{K}i} \tag{574}$$

which is computed by FFT. We first compute

$$Y_i(\mathbf{r}_l) = \sum_{\mathbf{K}} A^0_{\mathbf{K}i} e^{-i\mathbf{K}\mathbf{r}_l} \tag{575}$$

and then obtain

$$D_{\mathbf{G}} = \frac{1}{N_l} \sum_{\mathbf{r}_l} Y_i^*(\mathbf{r}_l) Y_i(\mathbf{r}_l) e^{i\mathbf{K}\mathbf{r}_l} \tag{576}$$

We hence have

$$(A^{0\dagger} O_S A^0)_{ii} = \sum_{\mathbf{G}} D_{\mathbf{G}} \frac{R^2_{MT}}{V} e^{i\mathbf{G}\mathbf{R}_\alpha} \int d\Omega \vec{e}_{\mathbf{r}} e^{i\mathbf{G}\mathbf{r}} \tag{577}$$

and because

$$\int d\Omega e^{i\mathbf{G}\mathbf{r}} \vec{e}_{\mathbf{r}} = 4\pi i \frac{\mathbf{G}}{|\mathbf{G}|}\, j_1(|\mathbf{G}| R_{MT}) \tag{578}$$

we obtain

$$(A^{0\dagger} O_S A^0)_{ii} = \frac{4\pi R^2_{MT}}{V} \sum_{\mathbf{G}} D_{\mathbf{G}}\ i e^{i\mathbf{G}\mathbf{R}_\alpha} \frac{\mathbf{G}}{|\mathbf{G}|}\, j_1(|\mathbf{G}| R_{MT}) \tag{579}$$

For the Hamiltonian, we need many more terms. We write

$$(A^{0\dagger} \frac{\delta H^0}{\delta \mathbf{R}_\alpha} A^0)_{ij} = (A^{0\dagger} H^{sym}_{MT} A^0)_{ij} + (A^{0\dagger} H^{nsym}_{MT} A^0)_{ij} + (A^{0\dagger} dT_{MT} A^0)_{ij} - (A^{0\dagger} T_S A^0)_{ij} - (A^{0\dagger} V_S A^0)_{ij} \tag{580}$$

Note that the last term is absent when potential is held fixed in lapw0.

We start with the spherically-symmetric part in the MT-sphere:

$$\begin{aligned}
(A^{0\dagger} H^{sym}_{MT} A^0)_{ij} \;\equiv\; & \sum_{\mathbf{K}\mathbf{K}'} A^\dagger_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') \langle \chi_{\mathbf{K}'}| -\nabla^2 + V^{sph}_{KS}(r) |\chi_{\mathbf{K}}\rangle_{MT} A_{\mathbf{K}j} = \\
& \sum_{\mathbf{K}\mathbf{K}'} A^\dagger_{i\mathbf{K}'} i(\mathbf{K}-\mathbf{K}') \left(a^*_{lm\mathbf{K}'},\ \ b^*_{lm\mathbf{K}'}\ \ c^*_{lm\mathbf{K}'} \right) \mathcal{H} \begin{pmatrix} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ c_{lm\mathbf{K}} \end{pmatrix} A_{\mathbf{K}j} \\
& = i \left(a^*_{i,lm},\ \ b^*_{i,lm}\ \ c^*_{i,lm} \right) \mathcal{H} \begin{pmatrix} \vec{\mathcal{A}}_{j,lm} \\ \vec{\mathcal{B}}_{j,lm} \\ \vec{\mathcal{C}}_{j,lm} \end{pmatrix} - i \left(\vec{\mathcal{A}}^*_{i,lm},\ \ \vec{\mathcal{B}}^*_{i,lm}\ \ \vec{\mathcal{C}}^*_{i,lm} \right) \mathcal{H} \begin{pmatrix} a_{j,lm} \\ b_{j,lm} \\ c_{j,lm} \end{pmatrix}
\end{aligned} \tag{581}$$

where

$$\mathcal{H} = \begin{pmatrix} \overline{\langle u_l|H|u_l\rangle} & \overline{\langle u_l|H|\dot{u}_l\rangle} & \overline{\langle u_l|H|u_l^{LO}\rangle} \\ \overline{\langle \dot{u}_l|H|u_l\rangle} & \overline{\langle \dot{u}_l|H|\dot{u}_l\rangle} & \overline{\langle \dot{u}_l|H|u_l^{LO}\rangle} \\ \overline{\langle u_l^{LO}|H|u_l\rangle} & \overline{\langle u_l^{LO}|H|\dot{u}_l\rangle} & \overline{\langle u_l^{LO}|H|u_l^{LO}\rangle} \end{pmatrix} \tag{582}$$

and $\overline{\langle u_l^{LO}|H|u_l\rangle} = \frac{1}{2}(\langle u_l^{LO}|H|u_l\rangle + \langle u_l|H|u_l^{LO}\rangle)$. When $H = -\nabla^2 + V^{sph}$, we get for the MT part 3×3 matrix

$$\mathcal{H} \equiv \begin{pmatrix} E_l & \frac{1}{2} & \frac{1}{2}(E_l + E_l^{LO})\langle u|u^{LO}\rangle \\ \frac{1}{2} & E_l\langle \dot{u}|\dot{u}\rangle & \frac{1}{2}(E_l + E_l^{LO})\langle \dot{u}|u^{LO}\rangle + \frac{1}{2}\langle u_l|u_l^{LO}\rangle \\ \frac{1}{2}(E_l + E_l^{LO})\langle u_l|u_l^{LO}\rangle & \frac{1}{2}(E_l + E_l^{LO})\langle \dot{u}_l|u_l^{LO}\rangle + \frac{1}{2}\langle u_l|u_l^{LO}\rangle & E_l^{LO} \end{pmatrix} \tag{583}$$

The result is

$$(A^{0\dagger} H_{MT}^{sym} A^0) = i(\mathcal{R} - \mathcal{R}^\dagger) \tag{584}$$

with

$$\mathcal{R} = \begin{pmatrix} a^*_{i,lm}, & b^*_{i,lm} & c^*_{i,lm} \end{pmatrix} \mathcal{H} \begin{pmatrix} \vec{\mathcal{A}}_{j,lm} \\ \vec{\mathcal{B}}_{j,lm} \\ \vec{\mathcal{C}}_{j,lm} \end{pmatrix} \tag{585}$$

Next we add non-spherically symmetric part

$$(A^{0\dagger} H_{MT}^{nsym} A^0)_{ij} \equiv \sum_{\mathbf{K}\mathbf{K}'} A^\dagger_{i\mathbf{K}'} i(\mathbf{K} - \mathbf{K}') \langle \chi_{\mathbf{K}'}|V_{KS}^{nsph}(r)|\chi_{\mathbf{K}}\rangle_{MT} A_{\mathbf{K}j} = \tag{586}$$

$$\sum_{\mathbf{K}\mathbf{K}' l'm'\kappa', lm\kappa} A^\dagger_{i\mathbf{K}'} i(\mathbf{K} - \mathbf{K}') a^{\kappa'\,*}_{l'm',\mathbf{K}'} a^{\kappa}_{lm\mathbf{K}} A_{\mathbf{K}j} \int d\mathbf{r} u^{\kappa'}_{l'}(r) Y^*_{l'm'}(\mathbf{r}) V^{non-sph}(\mathbf{r}) Y_{lm}(\mathbf{r}) u^{\kappa}_l(r) \tag{587}$$

The non-spherical symmetric potential is read from case.nsh, and takes the form

$$V^{non-sph}_{\kappa_1 l_1 m_1 \kappa_2 l_2 m_2} = \int d^3r Y^*_{l_1 m_1}(\hat{\mathbf{r}}) u^{\kappa_1} V^{n-sym}(\mathbf{r}) u^{\kappa_2} Y_{l_2 m_2}(\hat{\mathbf{r}}) \tag{588}$$

The result then is

$$(A^{0\dagger} H_{MT}^{nsym} A^0)_{ij} = i \sum_{l'm'\kappa', lm\kappa} a^{\kappa'\,*}_{i,l'm'} V^{non-sph}_{\kappa' l'm'\kappa lm} \vec{\mathcal{A}}^{\kappa}_{j,lm} - (\vec{\mathcal{A}}^{\kappa'}_{i,l'm'} V^{non-sph\,*}_{\kappa' l'm'\kappa lm} a^{\kappa\,*}_{j,lm})^* \tag{589}$$

We next use the fact that

$$V^{non-sph\,*}_{\kappa' l'm'\kappa lm} = V^{non-sph}_{\kappa lm\kappa' l'm'}$$

to obtain

$$(A^{0\dagger} H_{MT}^{nsym} A^0)_{ij} = i \sum_{l'm'\kappa', lm\kappa} a^{\kappa'\,*}_{i,l'm'} V^{non-sph}_{\kappa' l'm'\kappa lm} \vec{\mathcal{A}}^{\kappa}_{j,lm} - (a^{\kappa'\,*}_{j,l'm'} V^{non-sph}_{\kappa' l'm'\kappa lm} \vec{\mathcal{A}}^{\kappa}_{i,lm})^* = i(\mathcal{R} - \mathcal{R}^\dagger)_{ij} \tag{590}$$

where

$$\mathcal{R}_{ij} = \sum_{l'm'\kappa', lm\kappa} a^{\kappa'\,*}_{i,l'm'} V^{non-sph}_{\kappa' l'm'\kappa lm} \vec{\mathcal{A}}^{\kappa}_{j,lm} \tag{591}$$

We also need to add the surface term because we use $\nabla\cdot\nabla$ in the interstitial and $-\nabla^2$ in the MT-sphere. This term is

$$(A^{0\dagger} dT_{MT} A^0)_{ij} \equiv \sum_{\mathbf{K}\mathbf{K}'} A^\dagger_{i\mathbf{K}'} i(\mathbf{K} - \mathbf{K}') A_{\mathbf{K}j} \overline{\oint_{R^-_{MT}} d\vec{S} \chi^*_{\mathbf{k}+\mathbf{K}'}(\mathbf{r}) \nabla_{\mathbf{r}} \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})} = \tag{592}$$

$$R^2_{MT} \sum_{\mathbf{K}\mathbf{K}'} A^\dagger_{i\mathbf{K}'} i(\mathbf{K} - \mathbf{K}') \begin{pmatrix} a^*_{lm\mathbf{K}'}, & b^*_{lm\mathbf{K}'} & c^*_{lm\mathbf{K}'} \end{pmatrix} \mathcal{R} \begin{pmatrix} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ c_{lm\mathbf{K}} \end{pmatrix} A_{\mathbf{K}j} = \tag{593}$$

$$i\, R^2_{MT} \left[\begin{pmatrix} a^*_{i,lm}, & b^*_{i,lm} & c^*_{i,lm} \end{pmatrix} \mathcal{R} \begin{pmatrix} \vec{\mathcal{A}}_{j,lm} \\ \vec{\mathcal{B}}_{j,lm} \\ \vec{\mathcal{C}}_{j,lm} \end{pmatrix} - \begin{pmatrix} \vec{\mathcal{A}}^*_{i,lm}, & \vec{\mathcal{B}}^*_{i,lm} & \vec{\mathcal{C}}^*_{i,lm} \end{pmatrix} \mathcal{R} \begin{pmatrix} a_{j,lm} \\ b_{j,lm} \\ c_{j,lm} \end{pmatrix} \right] \tag{594}$$

where

$$\mathcal{R} = \begin{pmatrix} u_l \frac{du_l}{dr} & u_l \frac{d\dot{u}_l}{dr} + \frac{1}{2R^2} & \frac{1}{2}(u_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{du_l}{dr}) \\ u_l \frac{d\dot{u}_l}{dr} + \frac{1}{2R^2} & \dot{u}_l \frac{d\dot{u}_l}{dr} & \frac{1}{2}(\dot{u}_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{d\dot{u}_l}{dr}) \\ \frac{1}{2}(u_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{du_l}{dr}) & \frac{1}{2}(\dot{u}_l \frac{du_l^{LO}}{dr} + u_l^{LO} \frac{d\dot{u}_l}{dr}) & u_l^{LO} \frac{du_l^{LO}}{dr} \end{pmatrix} \tag{595}$$

so that

$$(A^{0\dagger} dT_{MT} A^0)_{ij} = i(\mathcal{O} - \mathcal{O}^\dagger) \tag{596}$$

with

$$\mathcal{O} = R_{MT}^2 \begin{pmatrix} a_{i,lm}^*, & b_{i,lm}^* & c_{i,lm}^* \end{pmatrix} \mathcal{R} \begin{pmatrix} \vec{\mathcal{A}}_{j,lm} \\ \vec{\mathcal{B}}_{j,lm} \\ \vec{\mathcal{C}}_{j,lm} \end{pmatrix} \tag{597}$$

$$(A^{0\dagger} T_S A^0)_{ii} \equiv \sum_{\mathbf{K}\mathbf{K}'} A_{i\mathbf{K}'}^{0\dagger} \oint_{MT} d\vec{S} \tilde{\chi}_{\mathbf{K}'}^* T \tilde{\chi}_{\mathbf{K}} A_{\mathbf{K}i}^0 = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'i}^{0*} A_{\mathbf{K}i}^0 (\mathbf{K}' + \mathbf{k}) \cdot (\mathbf{K} + \mathbf{k}) \oint d\vec{S} \frac{e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}}}{V} = \tag{598}$$

$$\sum_{\mathbf{K}\mathbf{G}} A_{\mathbf{K}-\mathbf{G},i}^{0*} (\mathbf{K} - \mathbf{G} + \mathbf{k}) \cdot (\mathbf{K} + \mathbf{k}) A_{\mathbf{K}i}^0 \frac{R_{MT}^2}{V} e^{i\mathbf{G}\mathbf{R}_\alpha} \int d\Omega \vec{e}_{\mathbf{r}} e^{i\mathbf{G}\mathbf{r}} \tag{599}$$

We then define

$$C_{\mathbf{G}} \equiv \sum_{\mathbf{K}} A_{\mathbf{K}-\mathbf{G},i}^{0*} (\mathbf{K} - \mathbf{G} + \mathbf{k}) \cdot (\mathbf{K} + \mathbf{k}) A_{\mathbf{K}i}^0 \tag{600}$$

which is obtained by FFT of

$$\vec{X}_i(\mathbf{r}_l) = \sum_{\mathbf{K}} A_{\mathbf{K}i}^0 (\mathbf{K} + \mathbf{k}) e^{-i\mathbf{K}\mathbf{r}_l} \tag{601}$$

and

$$C_{\mathbf{G}} = \frac{1}{N_l} \sum_{\mathbf{r}_l} \vec{X}_i^* \cdot \vec{X}_i e^{i\mathbf{K}\mathbf{r}_l} \tag{602}$$

We finally have

$$(A^{0\dagger} T_S A^0)_{ii} = \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}\mathbf{R}_\alpha} \frac{R_{MT}^2}{V} \int d\Omega \vec{e}_{\mathbf{r}} e^{i\mathbf{G}\mathbf{r}} = \frac{4\pi R_{MT}^2}{V} \sum_{\mathbf{G}} C_{\mathbf{G}}\; i e^{i\mathbf{G}\mathbf{R}_\alpha} \frac{\mathbf{G}}{|\mathbf{G}|}\; j_1(|\mathbf{G}| R_{MT}) \tag{603}$$

We conclude with the potential part

$$(A^{0\dagger} V_S A^0)_{ii} = \sum_{\mathbf{K}'\mathbf{K}} A_{\mathbf{K}'i}^{0*} A_{\mathbf{K}i}^0 \oint_{MT} d\vec{S} \frac{e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}}}{V} V_{KS}(\mathbf{r}) \tag{604}$$

The expansion of the potential exists

$$V_{KS}(\mathbf{r}) = \sum_{\mathbf{G}_0} e^{-i\mathbf{G}_0\mathbf{r}} V_{\mathbf{G}_0}, \tag{605}$$

which gives

$$(A^{0\dagger} V_S A^0)_{ii} = \sum_{\mathbf{K}'\mathbf{K}\mathbf{G}_0} A_{\mathbf{K}'i}^{0*} A_{\mathbf{K}i}^0 V_{\mathbf{G}_0} \oint_{MT} d\vec{S} \frac{e^{i(\mathbf{K}-\mathbf{K}'-\mathbf{G}_0)\mathbf{r}}}{V} = \sum_{\mathbf{K}\mathbf{G}\mathbf{G}_0} A_{\mathbf{K}-\mathbf{G}_0-\mathbf{G},i}^{0*} A_{\mathbf{K},i}^0 V_{\mathbf{G}_0} \oint_{MT} d\vec{S} \frac{e^{i\mathbf{G}\mathbf{r}}}{V} \tag{606}$$

We then perform FFT on A^0 and V to obtain

$$Y_i(\mathbf{r}_l) = \sum_{\mathbf{K}} e^{-i\mathbf{K}\mathbf{r}_l} A_{\mathbf{K},i} \tag{607}$$

$$V(\mathbf{r}_l) = \sum_{\mathbf{G}_0} e^{i\mathbf{G}_0\mathbf{r}_l} V_{\mathbf{G}_0} \tag{608}$$

We can then show that

$$E_{\mathbf{G}} \equiv \sum_{\mathbf{K}\mathbf{G}_0} A^{0*}_{\mathbf{K}-\mathbf{G}_0-\mathbf{G},i} A^0_{\mathbf{K},i} V_{\mathbf{G}_0} = \frac{1}{N_l}\sum_{\mathbf{r}_l} Y_i^*(\mathbf{r}_l)V(\mathbf{r}_l)Y_i(\mathbf{r}_l)e^{i\mathbf{G}\mathbf{r}_l} \tag{609}$$

hence

$$(A^{0\dagger}V_S A^0)_{ii} = \sum_{\mathbf{G}} E_{\mathbf{G}} e^{i\mathbf{G}\mathbf{R}_\alpha}\frac{R_{MT}^2}{V}\int d\Omega \vec{e}_{\mathbf{r}} e^{i\mathbf{G}\mathbf{r}} = \frac{4\pi R_{MT}^2}{V}\sum_{\mathbf{G}} E_{\mathbf{G}}\; i e^{i\mathbf{G}\mathbf{R}_\alpha}\frac{\mathbf{G}}{|\mathbf{G}|}\; j_1(|\mathbf{G}|R_{MT}) \tag{610}$$

If we want to compute the potential on the MT-sphere using interstitial potential, we write

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}} = e^{-i\mathbf{G}\mathbf{R}_\alpha} V_{\mathbf{G}} 4\pi \sum_{lm} (-i)^l j_l(|G|R_{MT}) y_{lms}(\hat{\mathbf{G}}) y_{lms}(\hat{\mathbf{r}}) \tag{611}$$

and compute

$$V_{lms}(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}} = \sum_{\mathbf{G}} e^{-i\mathbf{G}\mathbf{R}_\alpha} y_{lms}(\hat{\mathbf{G}}) V_{\mathbf{G}} 4\pi (-i)^l j_l(|G|R_{MT}) \tag{612}$$

G. Calculation of H in lapw1

1. *Interstitails*

Note that in lapw1, the plane wave basis function (valid in the interstitial) is defined by

$$\tilde{\chi}_{\mathbf{k}+\mathbf{K}} = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \tag{613}$$

In the interstitials, the overlap is

$$\tilde{O}_{\mathbf{K}\mathbf{K}'} = \langle \tilde{\chi}_{\mathbf{K}'}|\tilde{\chi}_{\mathbf{K}}\rangle = \int_{interstitial} d^3 \tilde{\chi}^*_{\mathbf{K}'}\tilde{\chi}_{\mathbf{K}} = \delta_{\mathbf{K}\mathbf{K}'} - \sum_{\mathbf{R}_\alpha} e^{i\mathbf{R}_\alpha(\mathbf{K}-\mathbf{K}')}\int_{MT} d^3r \frac{e^{i\mathbf{r}(\mathbf{K}-\mathbf{K}')}}{V} \tag{614}$$

$$= \delta_{\mathbf{K}\mathbf{K}'} - 4\pi R_{MT}^2 \frac{j_1(|\mathbf{K}-\mathbf{K}'|R_{MT})}{V_{cell}|\mathbf{K}-\mathbf{K}'|}\sum_{\mathbf{R}_\alpha} e^{i\mathbf{R}_\alpha(\mathbf{K}-\mathbf{K}')} \tag{615}$$

$$= \delta_{\mathbf{K}\mathbf{K}'} - 3\frac{V_{MT}}{V_{cell}}\frac{j_1(|\mathbf{K}-\mathbf{K}'|R_{MT})}{|\mathbf{K}-\mathbf{K}'|R_{MT}}\sum_{\mathbf{R}_\alpha} e^{i\mathbf{R}_\alpha(\mathbf{K}-\mathbf{K}')} \tag{616}$$

and the kinetic part is

$$\tilde{T}_{\mathbf{K}\mathbf{K}'} = \langle \tilde{\chi}_{\mathbf{K}'}|T|\tilde{\chi}_{\mathbf{K}}\rangle = \int_{interstitial} d^3 \tilde{\chi}^*_{\mathbf{K}'} T\tilde{\chi}_{\mathbf{K}} = (\mathbf{K}'+\mathbf{k})(\mathbf{K}+\mathbf{k})\int_{interstitial} d^3\tilde{\chi}^*_{\mathbf{K}'}\tilde{\chi}_{\mathbf{K}} = (\mathbf{K}'+\mathbf{k})(\mathbf{K}+\mathbf{k})\tilde{O}_{\mathbf{K}'\mathbf{K}} \tag{617}$$

The potential part is

$$\tilde{V}_{\mathbf{K}\mathbf{K}'} = \langle \tilde{\chi}_{\mathbf{K}'}|\tilde{V}|\tilde{\chi}_{\mathbf{K}}\rangle = \int_{interstitial} d^3\tilde{\chi}^*_{\mathbf{K}'}\sum_{\mathbf{G}} V_{\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}}\tilde{\chi}_{\mathbf{K}} = \sum_{\mathbf{G}} V_{\mathbf{G}}\int_{interstitial} e^{i(\mathbf{K}-\mathbf{K}'-\mathbf{G})\mathbf{r}} = \tag{618}$$

$$\sum_{\mathbf{G}} V_{\mathbf{G}}\left(\delta_{\mathbf{K}-\mathbf{K}'-\mathbf{G}} - \sum_{\alpha} e^{i(\mathbf{K}-\mathbf{K}'-\mathbf{G})\mathbf{R}_\alpha} 4\pi R_{MT}^2 \frac{j_1(|\mathbf{K}-\mathbf{K}'-\mathbf{G}|R_{MT})}{|\mathbf{K}-\mathbf{K}'-\mathbf{G}|}\right) \tag{619}$$

We compute this by computing convolution of $V_{\mathbf{G}}$ and the following quantity

$$\mathcal{R}_{\mathbf{K}} = \delta_{\mathbf{K}} - \sum_{\alpha} e^{i\mathbf{K}\mathbf{R}_\alpha} 4\pi R_{MT}^2 \frac{j_1(|\mathbf{K}|R_{MT})}{|\mathbf{K}|} \tag{620}$$

Let's define

$$U_{\mathbf{K}} \equiv \sum_{\mathbf{G}} V_{\mathbf{G}} \mathcal{R}_{\mathbf{K}-\mathbf{G}} \tag{621}$$

We then see that the result is

$$\tilde{V}_{\mathbf{K}\mathbf{K}'} = U_{\mathbf{K}-\mathbf{K}'} \tag{622}$$

Note that $U_{\mathbf{K}}$ is named *warp* or *warpin*, and is stored in *case.vns*.

2. Muffin-thin, non-local orbitals

The basis inside MT-part is

$$\chi_{\mathbf{K}}(\mathbf{r}) = \sum_{lm\mu'} \frac{4\pi i^l R_{MT}^2}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_{\mu'}} Y_{lm}(R_{\mu'}(\mathbf{k}+\mathbf{K}))(\tilde{a}_{l\mathbf{K}} u_l(r) + \tilde{b}_{l\mathbf{K}} \dot{u}_l(r)) Y_{lm}^*(R_{\mu'}^{-1}\mathbf{r}) \tag{623}$$

We first perform the calculation in the absence of local orbitals. For overlap, we have

$$\langle \chi_{\mathbf{K}'} | \chi_{\mathbf{K}} \rangle_{MT} = \int_{MT} dr (a_{lm\mathbf{K}'}^* u_l + b_{lm\mathbf{K}'}^* \dot{u}_l)(a_{lm\mathbf{K}} u_l + b_{lm\mathbf{K}} \dot{u}_l) = a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} \langle \dot{u} | \dot{u} \rangle \tag{624}$$

For Hamiltonian, we have two parts, i.e,

$$\langle \chi_{\mathbf{K}'} | H^{sym} | \chi_{\mathbf{K}} \rangle_{MT} = \int_{MT} \chi_{\mathbf{K}'}^* (-\nabla^2 + V_{KS}^{sym}) \chi_{\mathbf{K}} + \oint_{MT} d\vec{S} \chi_{\mathbf{K}'}^* \nabla_{\mathbf{r}} \chi_{\mathbf{K}} \tag{625}$$

$$= \int_{MT} d^3 r Y_{lm}^*(\mathbf{r}) (a_{lm\mathbf{K}'}^* u_l + b_{lm\mathbf{K}'}^* \dot{u}_l)(-\nabla^2 + V_{KS}^{sym})(a_{lm\mathbf{K}} u_l + b_{lm\mathbf{K}} \dot{u}_l) Y_{lm}(\mathbf{r})$$

$$+ R_{MT}^2 \int_{MT} d\Omega (a_{lm\mathbf{K}'}^* u_l(R) + b_{lm\mathbf{K}'}^* \dot{u}_l(R))(a_{lm\mathbf{K}} \frac{du_l(R)}{dr} + b_{lm\mathbf{K}} \frac{d\dot{u}_l(R)}{dr}) Y_{lm}^* Y_{lm}$$

$$= \int_{MT} dr (a_{lm\mathbf{K}'}^* u_l + b_{lm\mathbf{K}'}^* \dot{u}_l) \left[\varepsilon_l (a_{lm\mathbf{K}} u_l + b_{lm\mathbf{K}} \dot{u}_l) + b_{lm\mathbf{K}} u_l\right]$$

$$+ R_{MT}^2 (a_{lm\mathbf{K}'}^* u_l(R) + b_{lm\mathbf{K}'}^* \dot{u}_l(R))(a_{lm\mathbf{K}} \frac{du_l(R)}{dr} + b_{lm\mathbf{K}} \frac{d\dot{u}_l(R)}{dr})$$

$$= \varepsilon_l (a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} \langle \dot{u}_l | \dot{u}_l \rangle) + a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} \tag{626}$$

$$+ R_{MT}^2 \left(a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} u_l(R) \frac{du_l(R)}{dr} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} \dot{u}_l(R) \frac{d\dot{u}_l(R)}{dr} + a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} u_l(R) \frac{d\dot{u}_l(R)}{dr} + b_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} \dot{u}_l(R) \frac{du_l(R)}{dr} \right)$$

We know that

$$\dot{u}(R) \frac{du(R)}{dr} - u(R) \frac{d\dot{u}(R)}{dr} = \frac{1}{R^2} \tag{627}$$

hence we can use this identity in the last term to obtain more symmetric result

$$\begin{aligned} \langle \chi_{\mathbf{K}'} | H^{sym} | \chi_{\mathbf{K}} \rangle_{MT} &= \varepsilon_l (a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} \langle \dot{u}_l | \dot{u}_l \rangle) + a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} \\ &+ R_{MT}^2 \left(a_{lm\mathbf{K}'}^* a_{lm\mathbf{K}} u_l(R) \frac{du_l(R)}{dr} + b_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} \dot{u}_l(R) \frac{d\dot{u}_l(R)}{dr} + (a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} + b_{lm\mathbf{K}'}^* a_{lm\mathbf{K}}) u_l(R) \frac{d\dot{u}_l(R)}{dr} \right) \end{aligned} \tag{628}$$

In all cases, we have terms like $a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}}$, which can be further simplified

$$\sum_m a_{lm\mathbf{K}'}^* b_{lm\mathbf{K}} = \frac{(4\pi R_{MT}^2)^2}{V} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha} \tilde{a}_{l\mathbf{K}'} \tilde{b}_{l\mathbf{K}} \sum_m Y_{lm}(R_\alpha(\mathbf{K}'+\mathbf{k})) Y_{lm}^*(R_\alpha(\mathbf{K}+\mathbf{k})) \tag{629}$$

$$= \frac{(4\pi R_{MT}^2)^2}{V} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha} \tilde{a}_{l\mathbf{K}'} \tilde{b}_{l\mathbf{K}} \frac{2l+1}{4\pi} P_l((\mathbf{K}'+\mathbf{k})(\mathbf{K}+\mathbf{k})) \tag{630}$$

$$= \frac{4\pi R_{MT}^4}{V} (2l+1) P_l((\mathbf{K}'+\mathbf{k})(\mathbf{K}+\mathbf{k})) e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha} \tilde{a}_{l\mathbf{K}'} \tilde{b}_{l\mathbf{K}} \tag{631}$$

where

$$\begin{pmatrix} \tilde{a}_{l\mathbf{K}} \\ \tilde{b}_{l\mathbf{K}} \end{pmatrix} = \begin{pmatrix} \dot{u}_l(S)\frac{d}{dr}j_l(|\mathbf{k}+\mathbf{K}|S) - \frac{d}{dr}\dot{u}_l(S)j_l(|\mathbf{k}+\mathbf{K}|S) \\ \frac{d}{dr}u_l(S)j_l(|\mathbf{k}+\mathbf{K}|S) - u_l(S)\frac{d}{dr}j_l(|\mathbf{k}+\mathbf{K}|S) \end{pmatrix} \tag{632}$$

We first define

$$C_l(\mathbf{K}',\mathbf{K}) = \left(\sum_{\alpha\in equivalent} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{R}_\alpha}\right)\frac{4\pi R_{MT}^4}{V}(2l+1)P_l((\mathbf{K}'+\mathbf{k})(\mathbf{K}+\mathbf{k})) \tag{633}$$

For the overlap we can get

$$O_{\mathbf{K}\mathbf{K}'} \equiv \langle\chi_{\mathbf{K}'}|\chi_{\mathbf{K}}\rangle_{MT} = C_l(\mathbf{K}',\mathbf{K})\left(\tilde{a}_{l\mathbf{K}'}\tilde{a}_{l\mathbf{K}} + \tilde{b}_{l\mathbf{K}'}\tilde{b}_{l\mathbf{K}}\langle\dot{u}|\dot{u}\rangle\right) \tag{634}$$

And for the Hamiltonian, we get

$$\begin{aligned} H_{\mathbf{K}\mathbf{K}'} \equiv \langle\chi_{\mathbf{K}'}|H^{sym}|\chi_{\mathbf{K}}\rangle_{MT} = C_l(\mathbf{K}',\mathbf{K})\{&\varepsilon_l(\tilde{a}_{l\mathbf{K}'}\tilde{a}_{l\mathbf{K}} + \tilde{b}_{l\mathbf{K}'}\tilde{b}_{l\mathbf{K}}\langle\dot{u}_l|\dot{u}_l\rangle) + \tilde{a}_{l\mathbf{K}'}\tilde{b}_{l\mathbf{K}} + \tilde{b}_{l\mathbf{K}'}\tilde{a}_{l\mathbf{K}} \\ &+R_{MT}^2\left[\tilde{a}_{l\mathbf{K}'}u_l(R)\frac{du_l(R)}{dr} + \tilde{b}_{l\mathbf{K}'}u_l(R)\frac{d\dot{u}_l(R)}{dr}\right]\tilde{a}_{l\mathbf{K}} \\ &+R_{MT}^2\left[\tilde{b}_{l\mathbf{K}'}\dot{u}_l(R)\frac{d\dot{u}_l(R)}{dr} + \tilde{a}_{l\mathbf{K}'}u_l(R)\frac{d\dot{u}_l(R)}{dr}\right]\tilde{b}_{l\mathbf{K}}\} \end{aligned} \tag{635}$$

3. Muffin-thin, local orbitals

The basis inside the MT-part, in which Hamiltonian is diagonalized, is

$$\chi_{\mathbf{K}}(\mathbf{r}) = \sum_{lm\mu'}\frac{4\pi i^l R_{MT}^2}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_{\mu'}}Y_{lm}(R_{\mu'}(\mathbf{k}+\mathbf{K}))(\tilde{a}_{l\mathbf{K}}u_l(r) + \tilde{b}_{l\mathbf{K}}\dot{u}_l(r))Y_{lm}^*(R_{\mu'}^{-1}\mathbf{r}) \tag{636}$$

$$\chi_\nu(\mathbf{r}) = \sum_{m'\mu'}\frac{4\pi i^l R_{MT}^2}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{K}_\nu)\mathbf{r}_{\mu'}}Y_{lm'}(R_{\mu'}(\mathbf{k}+\mathbf{K}_\nu))(a_\nu^{lo}u_l(r) + b_\nu^{lo}\dot{u}_l(r) + c_\nu^{lo}u_l^{LO}(r))Y_{lm'}^*(R_{\mu'}^{-1}\mathbf{r}) \tag{637}$$

In the last term we compute a^{lo}, b^{lo} and c^{lo} so that $\chi_\nu(r = R_{MT}) = 0$. In LAPW method, we can also make derivative $d\chi_\nu(r = R_{MT})/dr$ vanish, while in APW+lo only the value $\chi_\nu(r = R_{MT})$ vanishes. Note that the index for the local orbital ν comprises $(i, l, j_{lo}, \alpha, m)$ in this order, where (i, l, j_{lo}, α, m) are (index of a sort, l, index enumerates local orbital, index of the equivalent atom, m).

Notice that the phase factor in the local orbital functions is taken to be the same as in augmented plane waves. Moreover, $\mathbf{K}_\nu$ is taken to be different for each local orbital component. Namely, each set of equivalent atoms and their m quantum numbers are assigmed a unique set of $\mathbf{K}$'s, usually just starting from the beginning of the list. For different atom types and different l's the reciprocal vectors repeat, so that for example each first atom of a new type and its first $m = -l$ will have $K_\nu = 0$ vector. I do not know why is such extra phase factor necessary.... but this is how it is implemented in Wien2k.

The orbital, which vanishes at the MT-boundary, has the following form:

$$u_\nu^{loc}(r) = a_\nu^{lo}u_l(r) + b_\nu^{lo}\dot{u}(r) + c_\nu^{lo}u_l^{LO} \tag{638}$$

$$(-\nabla^2 + V_{sym})u_\nu^{loc}(r) = a_\nu^{lo}u_l\,E_\mu^l + b_\nu^{lo}(\dot{u}_lE_\mu^l + u_l) + c_\nu^{lo}u_l^{LO}E_{\mu'}^l = (a_\nu^{lo}E_\mu^l + b_\nu^{lo})u_l + b_\nu^{lo}E_\mu^l\dot{u}_l + c_\nu^{lo}E_{\mu'}^l u_l^{LO} \tag{639}$$

In the code we define

$$C_1^\nu = \langle u_\nu^{loc}|u_l\rangle = a_\nu^{lo} + c_\nu^{lo}\langle u_l|u_l^{LO}\rangle \tag{640}$$

$$C_2^\nu = \langle u^{loc}|\dot{u}_l\rangle = b_\nu^{lo}\langle \dot{u}_l|\dot{u}_l\rangle + c_\nu^{lo}\langle \dot{u}_l|u_l^{LO}\rangle \tag{641}$$

$$C_3^\nu = \langle u^{loc}|u_l^{LO}\rangle = c_\nu^{lo} + b_\nu^{lo}\langle \dot{u}_l|u_l^{LO}\rangle + a_\nu^{lo}\langle u_l|u_l^{LO}\rangle \tag{642}$$

$$C_{11}^\nu = \frac{1}{2}(\langle u_\nu^{loc}|H_{sym}|u_l\rangle + \langle u_l|H_{sym}|u_\nu^{loc}\rangle) = a_\nu^{lo}E_\mu^l + \frac{1}{2}b_\nu^{lo} + \frac{1}{2}c_\nu^{lo}\langle u|u^{LO}\rangle(E_\mu^l + E_{\mu'}^l) \tag{643}$$

$$C_{12}^\nu = \frac{1}{2}(\langle u_\nu^{loc}|H_{sym}|\dot{u}_l\rangle + \langle \dot{u}_l|H_{sym}|u_\nu^{loc}\rangle) = b_\nu^{lo}\langle \dot{u}_l|\dot{u}_l\rangle E_\mu^l + \frac{1}{2}a_\nu^{lo} + \frac{1}{2}c_\nu^{lo}\langle u_l|u_l^{LO}\rangle + c_\nu^{lo}\langle \dot{u}_l|u^{LO}\rangle\frac{1}{2}(E_\mu^l + E_{\mu'}^l) \tag{644}$$

$$C_{13}^\nu = \frac{1}{2}(\langle u_\nu^{loc}|H_{sym}|u_l^{LO}\rangle + \langle u_l^{LO}|H_{sym}|u_\nu^{loc}\rangle) = c_\nu^{lo}E_{\mu'} + \frac{1}{2}b_\nu^{lo}\langle u_l|u_l^{LO}\rangle + \left(a_\mu^{lo}\langle u_l|u_l^{LO}\rangle + b_\nu^{lo}\langle \dot{u}_l|u_l^{LO}\rangle\right)\frac{1}{2}(E_\mu + E_{\mu'})$$

$$ak_{inlo} = \frac{1}{2}R_{MT}^2\frac{du_\nu^{loc}(r)}{dr}|_{r=R_{MT}} \tag{645}$$

We need to calculate the overlap terms, such as

$$O_{\mathbf{K},\nu} = \langle\chi_\nu|\chi_\mathbf{K}\rangle = \frac{(4\pi R_{MT}^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k}))Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k})) \tag{646}$$

$$\times\langle a_\nu^{lo}u_l + b_\nu^{lo}\dot{u}_l + c_\nu^{lo}u_l^{LO}|\tilde{a}_{l\mathbf{K}}u_l + \tilde{b}_{l\mathbf{K}}\dot{u}_l\rangle = \tag{647}$$

$$= \frac{(4\pi R_{MT}^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k}))Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k}))\times(\tilde{a}_{l\mathbf{K}}C_1^\nu + \tilde{b}_{l\mathbf{K}}C_2^\nu) \tag{648}$$

Hamiltonian, which takes the form

$$\langle\chi_\mathbf{K}|H^{sym}|\chi_\nu\rangle_{MT} = \int\chi_\mathbf{K}^*(-\nabla^2 + V_{KS}^{sym})\chi_\nu + \oint_{MT} d\vec{S}\chi_\mathbf{K}^*\nabla_\mathbf{r}\chi_\nu \tag{649}$$

is then given by

$$H_{\mathbf{K}\nu} \equiv \frac{1}{2}(\langle\chi_\nu|H^{sym}|\chi_\mathbf{K}\rangle_{MT} + \langle\chi_\mathbf{K}|H^{sym}|\chi_\nu\rangle_{MT}^*)$$

$$H_{\mathbf{K}\nu} = \frac{(4\pi R_{MT}^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k}))Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k})) \tag{650}$$

$$\times\left(\overline{\langle a_\nu^{lo}u_l + b_\nu^{lo}\dot{u}_l + c_\nu^{lo}u_l^{LO}|H|\tilde{a}_{l\mathbf{K}}u_l + \tilde{b}_{l\mathbf{K}}\dot{u}_l\rangle}\right. \tag{651}$$

$$\left. + \frac{R_{MT}^2}{2}\left(\frac{du_l^{local}}{dr}(\tilde{a}_{l\mathbf{K}}u_l + \tilde{b}_{l\mathbf{K}}\dot{u}_l) + u_l^{local}\frac{d(\tilde{a}_{l\mathbf{K}}u_l + \tilde{b}_{l\mathbf{K}}\dot{u}_l)}{dr}\right)\Bigg|_{r=R_{MT}}\right) \tag{652}$$

Here overline means symmetrize the matrix elements. Note that $u_l^{local} = 0$, hence we can drop the last term. The code computes this quantity:

$$H_{\mathbf{K}\nu} = \frac{(4\pi R_{MT}^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k}))Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k}))\times(\tilde{a}_{l\mathbf{K}}C_{11}^\nu + \tilde{b}_{l\mathbf{K}}C_{12}^\nu) + \tag{653}$$

$$+\frac{(4\pi R_{MT}^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k}))Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k}))(\tilde{a}_{l\mathbf{K}}u_l(R_{MT}) + \tilde{b}_{l\mathbf{K}}\dot{u}_l(R_{MT}))ak_{inlo} \tag{654}$$

Hence the original surface term

$$\frac{(4\pi R_{MT}^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k}))Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k}))\frac{R_{MT}^2}{2}\left[(\tilde{a}_{l\mathbf{K}}u_l + \tilde{b}_{l\mathbf{K}}\dot{u}_l)\frac{du_\nu^{loc}}{dr} + u_\nu^{loc}\frac{\tilde{a}_{l\mathbf{K}}u_l + \tilde{b}_{l\mathbf{K}}\dot{u}_l}{dr}\right]\Bigg|_{r=R_{MT}}$$

was simplified to

$$\frac{(4\pi R_{MT}^2)^2}{V}\sum_{m'\mu'} e^{i(\mathbf{K}-\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}+\mathbf{k}))Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu+\mathbf{k}))\frac{R_{MT}^2}{2}\left[(\tilde{a}_{l\mathbf{K}}u_l + \tilde{b}_{l\mathbf{K}}\dot{u}_l)\frac{du_\nu^{loc}}{dr}\right]\Bigg|_{r=R_{MT}}$$

because $u_l^{local} = 0$.

Finally, for the last term we have

$$O_{\nu'\nu} = \langle \chi_\nu | \chi_{\nu'} \rangle = \frac{(4\pi R_{MT}^2)^2}{V} \sum_{m'\mu'} e^{i(\mathbf{K}_{\nu'} - \mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}_{\nu'} + \mathbf{k})) Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu + \mathbf{k}))(a_{\nu'}^{lo} C_1^\nu + b_{\nu'}^{lo} C_2^\nu + c_{\nu'}^{lo} C_3^\nu) \tag{655}$$

and

$$\langle \chi_\nu | H^{sym} | \chi_{\nu'} \rangle = \frac{(4\pi R_{MT}^2)^2}{V} \sum_{m'\mu'} e^{i(\mathbf{K}_{\nu'} - \mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}_{\nu'} + \mathbf{k})) Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu + \mathbf{k})) \times \tag{656}$$

$$(a_{\nu'}^{lo} \langle u_l | u_\nu^{loc} \rangle + b_{\nu'}^{lo} \langle \dot{u}_l | u_\nu^{loc} \rangle + c_{\nu'}^{lo} \langle u_l^{LO} | u_\nu^{loc} \rangle) \tag{657}$$

so that

$$H_{\nu'\nu} \equiv \frac{1}{2}(\langle \chi_\nu | H^{sym} | \chi_{\nu'} \rangle + \langle \chi_{\nu'} | H^{sym} | \chi_\nu \rangle^*) \tag{658}$$

is

$$H_{\nu'\nu} = \frac{(4\pi R_{MT}^2)^2}{V} \sum_{m'\mu'} e^{i(\mathbf{K}_{\nu'} - \mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}_{\nu'} + \mathbf{k})) Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu + \mathbf{k})) \times (a_{\nu'}^{lo} C_{11}^\nu + b_{\nu'}^{lo} C_{12}^\nu + c_{\nu'}^{lo} C_{13}^\nu) \tag{659}$$

Note that this can also be written as

$$H_{\nu'\nu} = \frac{(4\pi R_{MT}^2)^2}{V} \sum_{m'\mu'} e^{i(\mathbf{K}_{\nu'} - \mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y_{lm'}(R_{\mu'}(\mathbf{K}_{\nu'} + \mathbf{k})) Y_{lm'}^*(R_{\mu'}(\mathbf{K}_\nu + \mathbf{k})) \times \begin{pmatrix} a_\nu^{lo}, & b_\nu^{lo} & c_\nu^{lo} \end{pmatrix} \mathcal{H} \begin{pmatrix} a_{\nu'}^{lo} \\ b_{\nu'}^{lo} \\ c_{\nu'}^{lo} \end{pmatrix} \tag{660}$$

4. Non-spherical part

We first construct $a_{lm\mathbf{K}}$, $b_{lm\mathbf{K}}$, $c_{lm\mathbf{K}}$ coefficients, which take the form

$$\begin{pmatrix} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ c_{lm\mathbf{K}} \end{pmatrix} = \begin{pmatrix} \tilde{a}_{l\mathbf{K}} \\ \tilde{b}_{l\mathbf{K}} \\ 0 \end{pmatrix} \frac{4\pi R_{MT}^2}{\sqrt{V}} i^l e^{i(\mathbf{K}+\mathbf{k})\mathbf{R}_\alpha} Y_{lm}^*(\mathbf{k} + \mathbf{K}) \tag{661}$$

for first $N_\mathbf{K}$ reciprocal vectors. For $\mathbf{K}$ index above $N_\mathbf{K}$, we populate $a_{lm\mathbf{K}}$ with local orbitals, where the same coefficients take the form

$$\begin{pmatrix} a_{lm\mathbf{K}_\nu} \\ b_{lm\mathbf{K}_\nu} \\ c_{lm\mathbf{K}_\nu} \end{pmatrix} = \begin{pmatrix} a_\nu^{lo} \\ b_\nu^{lo} \\ c_\nu^{lo} \end{pmatrix} \frac{4\pi R_{MT}^2}{\sqrt{V}} i^l e^{i(\mathbf{K}_\nu+\mathbf{k})\mathbf{R}_\alpha} Y_{lm}^*(\mathbf{k} + \mathbf{K}_\nu) \tag{662}$$

We then calculate

$$H_{\mathbf{K},\mathbf{K}'}^{non-sym} \equiv \langle \chi_{\mathbf{K}'} | V^{non-sym} | \chi_\mathbf{K} \rangle = \tag{663}$$

$$\int_\mathbf{r} (a_{l'm'\mathbf{K}'}^* u_{l'}(r) + b_{l'm'\mathbf{K}'}^* \dot{u}_{l'}(r) + c_{l'm'\mathbf{K}'}^* u_{l'}^{LO}(r)) Y_{l'm'}^*(\mathbf{r}) V(\mathbf{r}) Y_{lm}(\mathbf{r}) (a_{lm\mathbf{K}} u_l(r) + b_{lm\mathbf{K}} \dot{u}_l(r) + c_{lm\mathbf{K}} u^{LO}(r))$$

We can define the following matrix

$$V^{l'm',lm} = \int_\mathbf{r} \begin{pmatrix} u_{l'}(r) \\ \dot{u}_{l'}(r) \\ u_{l'}^{LO}(r) \end{pmatrix} Y_{l'm'}^*(\mathbf{r}) V(\mathbf{r}) Y_{lm}(\mathbf{r}) \begin{pmatrix} u_{l'}(r), & \dot{u}_{l'}(r), & u_{l'}^{LO}(r) \end{pmatrix} \tag{664}$$

and use it to evaluate the sum

$$H_{\mathbf{K},\mathbf{K}'}^{non-sym} = \begin{pmatrix} a_{l'm'\mathbf{K}'}^*, & b_{l'm'\mathbf{K}'}^*, & c_{l'm'\mathbf{K}'}^* \end{pmatrix} V^{l'm',lm} \begin{pmatrix} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ c_{lm\mathbf{K}} \end{pmatrix}$$

H. Alternative derivation

When calculating Hamiltonian or forces, we want to calculate the following matrix elements

$$\frac{1}{2}(\langle\chi_{\mathbf{K}'}|H|\chi_{\mathbf{K}}\rangle + \langle\chi_{\mathbf{K}}|H|\chi_{\mathbf{K}'}\rangle^* = \tag{665}$$

$$= \frac{1}{2}\left(\begin{array}{ccc} a^*_{lm\mathbf{K}'}, & b^*_{lm\mathbf{K}'} & c^*_{lm\mathbf{K}'}\end{array}\right)\left(\begin{array}{ccc} \langle u_l|H|u_l\rangle & \langle u_l|H|\dot{u}_l\rangle & \langle u_l|H|u_l^{LO}\rangle \\ \langle \dot{u}_l|H|u_l\rangle & \langle \dot{u}_l|H|\dot{u}_l\rangle & \langle \dot{u}_l|H|u_l^{LO}\rangle \\ \langle u_l^{LO}|H|u_l\rangle & \langle u_l^{LO}|H|\dot{u}_l\rangle & \langle u_l^{LO}|H|u_l^{LO}\rangle \end{array}\right)\left(\begin{array}{c} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ c_{lm\mathbf{K}}\end{array}\right) \tag{666}$$

$$+\frac{1}{2}\left(\begin{array}{ccc} a_{lm\mathbf{K}}, & b_{lm\mathbf{K}} & c_{lm\mathbf{K}}\end{array}\right)\left(\begin{array}{ccc} \langle u_l|H|u_l\rangle & \langle u_l|H|\dot{u}_l\rangle & \langle u_l|H|u_l^{LO}\rangle \\ \langle \dot{u}_l|H|u_l\rangle & \langle \dot{u}_l|H|\dot{u}_l\rangle & \langle \dot{u}_l|H|u_l^{LO}\rangle \\ \langle u_l^{LO}|H|u_l\rangle & \langle u_l^{LO}|H|\dot{u}_l\rangle & \langle u_l^{LO}|H|u_l^{LO}\rangle \end{array}\right)^*\left(\begin{array}{c} a^*_{lm\mathbf{K}'} \\ b^*_{lm\mathbf{K}'} \\ c^*_{lm\mathbf{K}'}\end{array}\right) \tag{667}$$

The product $\vec{a}_{\mathbf{K}'}H\vec{a}_{\mathbf{K}} + \vec{a}_{\mathbf{K}}H^*\vec{a}_{\mathbf{K}'}$ can be rearranged as $\vec{a}_{\mathbf{K}'}(H+H^\dagger)\vec{a}_{\mathbf{K}}$, hence we have

$$\frac{1}{2}(\langle\chi_{\mathbf{K}'}|H|\chi_{\mathbf{K}}\rangle + \langle\chi_{\mathbf{K}}|H|\chi_{\mathbf{K}'}\rangle^* = \tag{668}$$

$$= \left(\begin{array}{ccc} a^*_{lm\mathbf{K}'}, & b^*_{lm\mathbf{K}'} & c^*_{lm\mathbf{K}'}\end{array}\right)\left(\begin{array}{ccc} \overline{\langle u_l|H|u_l\rangle} & \overline{\langle u_l|H|\dot{u}_l\rangle} & \overline{\langle u_l|H|u_l^{LO}\rangle} \\ \overline{\langle \dot{u}_l|H|u_l\rangle} & \overline{\langle \dot{u}_l|H|\dot{u}_l\rangle} & \overline{\langle \dot{u}_l|H|u_l^{LO}\rangle} \\ \overline{\langle u_l^{LO}|H|u_l\rangle} & \overline{\langle u_l^{LO}|H|\dot{u}_l\rangle} & \overline{\langle u_l^{LO}|H|u_l^{LO}\rangle} \end{array}\right)\left(\begin{array}{c} a_{lm\mathbf{K}} \\ b_{lm\mathbf{K}} \\ c_{lm\mathbf{K}}\end{array}\right) \tag{669}$$

where $\overline{\langle u_l^{LO}|H|u_l\rangle} = \frac{1}{2}(\langle u_l^{LO}|H|u_l\rangle + \langle u_l|H|u_l^{LO}\rangle)$

For example, for $H = -\nabla^2 + V^{sim}$ and MT-part, we get for the 3×3 matrix

$$\mathcal{H} \equiv \left(\begin{array}{ccc} E_l & \frac{1}{2} & \frac{1}{2}(E_l+E_l^{LO})\,\langle u|u^{LO}\rangle \\ \frac{1}{2} & E_l\,\langle\dot{u}|\dot{u}\rangle & \frac{1}{2}(E_l+E_l^{LO})\,\langle\dot{u}|u^{LO}\rangle + \frac{1}{2}\,\langle u_l|u_l^{LO}\rangle \\ \frac{1}{2}(E_l+E_l^{LO})\,\langle u_l|u_l^{LO}\rangle & \frac{1}{2}(E_l+E_l^{LO})\,\langle\dot{u}_l|u_l^{LO}\rangle + \frac{1}{2}\,\langle u_l|u_l^{LO}\rangle & E_l^{LO} \end{array}\right) \tag{670}$$

To get the component of the force, which takes the form

$$\delta H_{ij} = \sum_{\mathbf{K}\mathbf{K}'} {A^0}^\dagger_{i,\mathbf{K}'}\; i(\mathbf{K}-\mathbf{K}')\overline{\langle\chi_{\mathbf{K}'}|H|\chi_{\mathbf{K}}\rangle}{A^0}_{\mathbf{K},j} \tag{671}$$

we immediately get

$$\delta H_{ij} = i\left(\begin{array}{ccc} a^*_{lm,i}, & b^*_{lm,i} & c^*_{lm,i}\end{array}\right)\mathcal{H}\left(\begin{array}{c}\mathcal{A}_{lm,j}\\ \mathcal{B}_{lm,j}\\ \mathcal{C}_{lm,j}\end{array}\right) - i\left(\begin{array}{ccc} \mathcal{A}^*_{lm,i}, & \mathcal{B}^*_{lm,i} & \mathcal{C}^*_{lm,i}\end{array}\right)\mathcal{H}\left(\begin{array}{c} a_{lm,j}\\ b_{lm,j}\\ c_{lm,j}\end{array}\right) \tag{672}$$

or

$$\delta H_{ij} = i\left(\begin{array}{ccc} a^*_{lm,i}, & b^*_{lm,i} & c^*_{lm,i}\end{array}\right)\mathcal{H}\left(\begin{array}{c}\mathcal{A}_{lm,j}\\ \mathcal{B}_{lm,j}\\ \mathcal{C}_{lm,j}\end{array}\right) - i\left[\left(\begin{array}{ccc} \mathcal{A}_{lm,i}, & \mathcal{B}_{lm,i} & \mathcal{C}_{lm,i}\end{array}\right)\mathcal{H}\left(\begin{array}{c} a^*_{lm,j}\\ b^*_{lm,j}\\ c^*_{lm,j}\end{array}\right)\right]^* \tag{673}$$

or

$$\delta H_{ij} = i\left(\begin{array}{ccc} a^*_{lm,i}, & b^*_{lm,i} & c^*_{lm,i}\end{array}\right)\mathcal{H}\left(\begin{array}{c}\mathcal{A}_{lm,j}\\ \mathcal{B}_{lm,j}\\ \mathcal{C}_{lm,j}\end{array}\right) - i\left[\left(\begin{array}{ccc} a^*_{lm,j}, & b^*_{lm,j} & c^*_{lm,j}\end{array}\right)\mathcal{H}\left(\begin{array}{c}\mathcal{A}_{lm,i}\\ \mathcal{B}_{lm,i}\\ \mathcal{C}_{lm,i}\end{array}\right)\right]^* \tag{674}$$

and finally

$$\delta H_{ij} = i(\mathcal{H} - \mathcal{H}^\dagger)_{ij} \tag{675}$$

where

$$\mathcal{H} \equiv \left(\begin{array}{ccc} E_l & \frac{1}{2} & \frac{1}{2}(E_l+E_l^{LO})\,\langle u|u^{LO}\rangle \\ \frac{1}{2} & E_l\,\langle\dot{u}|\dot{u}\rangle & \frac{1}{2}(E_l+E_l^{LO})\,\langle\dot{u}|u^{LO}\rangle + \frac{1}{2}\,\langle u_l|u_l^{LO}\rangle \\ \frac{1}{2}(E_l+E_l^{LO})\,\langle u_l|u_l^{LO}\rangle & \frac{1}{2}(E_l+E_l^{LO})\,\langle\dot{u}_l|u_l^{LO}\rangle + \frac{1}{2}\,\langle u_l|u_l^{LO}\rangle & E_l^{LO} \end{array}\right) \tag{676}$$

I. How to get $a_{i,lm}$

In dmft2, we need to compute coefficients $a_{i,lm}$ (i is band index) from $a_{lm\mathbf{K}}$ and a_ν. First, lets refresh the form of the orbitals

$$\chi_{\mathbf{K}}(\mathbf{r}) = \sum_{lm\mu'} \frac{4\pi i^l R_{MT}^2}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_{\mu'}} Y^*_{lm}(R_{\mu'}(\mathbf{k}+\mathbf{K}))(\tilde{a}_{l\mathbf{K}} u_l(r) + \tilde{b}_{l\mathbf{K}} \dot{u}_l(r)) Y_{lm}(R^{-1}_{\mu'}\mathbf{r}) \tag{677}$$

$$\chi_{\nu}(\mathbf{r}) = \sum_{m'\mu'} \frac{4\pi i^l R_{MT}^2}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}_\nu)\mathbf{r}_{\mu'}} Y^*_{lm'}(R_{\mu'}(\mathbf{k}+\mathbf{K}_\nu))(a^{lo}_\nu u_l(r) + b^{lo}_\nu \dot{u}_l(r) + c^{lo}_\nu u^{LO}_l(r)) Y_{lm'}(R^{-1}_{\mu'}\mathbf{r}) \tag{678}$$

The eigenvectors are large vectors of the form: $(A_{\mathbf{K},i}, A_{\nu,i})$. We want to write the KS-orbitals in the MT-spheres as

$$\psi_i(\mathbf{r}) = \sum_{\mu,lm} (a^\mu_{i,lm} u_l(r) + b^\mu_{i,lm} \dot{u}_l(r) + \sum_{j_{lo}} c^\mu_{i,lm,j_{lo}} u_l^{LO,j_{lo}}(r)) Y_{lm}(R^{-1}_\mu \mathbf{r}) \tag{679}$$

Here $\nu = (i^\nu_{atom}, l^\nu, j^\nu_{lo}, \mu^\nu, m^\nu)$

We clearly have

$$\begin{pmatrix} a^\mu_{i,lm} \\ b^\mu_{i,lm} \\ c^\mu_{i,lm,j_{lo}} \end{pmatrix} = \sum_{\mathbf{K}} A_{i,\mathbf{K}} \frac{4\pi i^l R_{MT}^2}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}_\mu} Y^*_{lm}(R_\mu(\mathbf{k}+\mathbf{K})) \begin{pmatrix} \tilde{a}_{l\mathbf{K}} \\ \tilde{b}_{l\mathbf{K}} \\ 0 \end{pmatrix}$$

$$+ \sum_{\nu\to\mu^\nu, m^\nu} A_{i,\nu} \frac{4\pi i^l R_{MT}^2}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}_\nu)\mathbf{r}_\mu} Y^*_{lm}(R_\mu(\mathbf{k}+\mathbf{K})) \begin{pmatrix} a^{lo}_\nu \\ b^{lo}_\nu \\ c^{lo,j_{lo}}_\nu \end{pmatrix} \delta(l^\nu - l)\delta(i^\nu_{atom} - i_{atom})\delta(j^\nu_{lo} - j_{lo}) \tag{680}$$