

Non-Collinear Spin Density Functional: Ver. 1.0

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August 14, 2007

1 Non-collinear spin density functional

A two component spinor wave function is defined by

$$|\psi_\nu\rangle = |\varphi_\nu^\alpha\alpha\rangle + |\varphi_\nu^\beta\beta\rangle, \quad (1)$$

where $|\varphi_\nu^\alpha\alpha\rangle \equiv |\varphi_\nu^\alpha\rangle|\alpha\rangle$ with a spatial function $|\varphi_\nu^\alpha\rangle$ and a spin function $|\alpha\rangle$. In the notes we consider non-Bloch functions, but the generalization of the description to the Bloch function is straightforward. Then, a density operator is given by

$$\begin{aligned} \hat{n} &= \sum_\nu f_\nu |\psi_\nu\rangle\langle\psi_\nu|, \\ &= \sum_\nu f_\nu \left(|\varphi_\nu^\alpha\alpha\rangle + |\varphi_\nu^\beta\beta\rangle \right) \left(\langle\varphi_\nu^\alpha\alpha| + \langle\varphi_\nu^\beta\beta| \right), \end{aligned} \quad (2)$$

where f_ν should be a step function, but it is replaced by the Fermi function in the implementation of OpenMX. With the definition of density operator \hat{n} , a non-collinear electron density in real space is given by

$$\begin{aligned} n_{\sigma\sigma'} &= \langle\mathbf{r}\sigma|\hat{n}|\mathbf{r}\sigma'\rangle, \\ &= \sum_\nu f_\nu \varphi_\nu^\sigma \varphi_\nu^{\sigma'*}, \end{aligned} \quad (3)$$

where $\sigma, \sigma' = \alpha$ or β , and $|\mathbf{r}\rangle$ is a position eigenvector. The up- and down-spin densities $n'_\uparrow, n'_\downarrow$ at each point are defined by diagonalizing a matrix consisting of a non-collinear electron densities as follows:

$$\begin{aligned} \begin{pmatrix} n'_\uparrow & 0 \\ 0 & n'_\downarrow \end{pmatrix} &= U n U^\dagger, \\ &= U \begin{pmatrix} n_{\alpha\alpha} & n_{\alpha\beta} \\ n_{\beta\alpha} & n_{\beta\beta} \end{pmatrix} U^\dagger. \end{aligned} \quad (4)$$

Based on the spinor wave function Eq. (1), the non-collinear electron density Eq. (3), and the up- and down-spin densities, the total energy non-collinear functional [1, 2] could be written by

$$E_{\text{tot}} = \sum_{\sigma=\alpha,\beta} \sum_\nu f_\nu \langle\varphi_\nu^\sigma|\hat{T}|\varphi_\nu^\sigma\rangle + \sum_{\sigma\sigma'} \int w_{\sigma\sigma'} n_{\sigma'\sigma} + \frac{1}{2} \int \int \frac{n'(\mathbf{r})n'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} dv dv' + E_{\text{xc}}\{n_{\sigma\sigma'}\}, \quad (5)$$

where the first term is the kinetic energy, the second the electron-core Coulomb energy, the third term the electron-electron Coulomb energy, and the fourth term the exchange-correlation energy, respectively. Also the total electron density n' at each point is the sum of up- and down-spin densities

$n'_\uparrow, n'_\downarrow$. Alternatively, the total energy E_{tot} can be expressed in terms of the Kohn-Sham eigenenergies ϵ_ν as follows:

$$E_{\text{tot}} = E_{\text{band}} - \frac{1}{2} \int n' V_{\text{H}} dv - \int \text{Tr}(V_{\text{xc}} n) dv + E_{\text{xc}}, \quad (6)$$

where V_{xc} is a non-collinear exchange-correlation potential which will be discussed later on. Considering an orthogonality relation among spinor wave functions, let us introduce a functional F :

$$F = E_{\text{tot}} + \sum_{\nu\nu'} \epsilon_{\nu\nu'} (\delta_{\nu\nu'} - \langle \psi_\nu | \psi_{\nu'} \rangle). \quad (7)$$

The variation of F with respect to the spatial wave function φ is found as:

$$\frac{\delta F}{\delta \varphi_\mu^{\sigma,*}} = \hat{T} \varphi_\mu^\sigma + \sum_{\sigma'} w_{\sigma\sigma'} \varphi_\mu^{\sigma'} + V_{\text{H}} \varphi_\mu^\sigma + \sum_{\sigma'} V_{\text{xc}}^{\sigma\sigma'} \varphi_\mu^{\sigma'} - \sum_{\nu} \epsilon_{\mu\nu} \varphi_\nu^\sigma \quad (8)$$

with

$$V_{\text{H}} = \int \frac{d(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} dv, \quad (9)$$

$$V_{\text{xc}}^{\sigma\sigma'} = \frac{\delta E_{\text{xc}}}{\delta \mathbf{n}_{\sigma'\sigma}}. \quad (10)$$

By setting the variation of F with respect to the spatial wave function φ to zero, and considering a unitary transformation of φ_ν^σ so that $\epsilon_{\mu\nu}$ can be diagonalized, we can obtain the non-collinear Kohn-Sham equation as follows:

$$\left. \begin{array}{l} \frac{\delta F}{\delta \varphi_\mu^{\alpha,*}} = 0 \\ \frac{\delta F}{\delta \varphi_\mu^{\beta,*}} = 0 \end{array} \right\} \Rightarrow \begin{pmatrix} \hat{T} + w_{\alpha\alpha} + V_{\text{H}} + V_{\text{xc}}^{\alpha\alpha} & w_{\alpha\beta} + V_{\text{xc}}^{\alpha\beta} \\ w_{\beta\alpha} + V_{\text{xc}}^{\beta\alpha} & \hat{T} + w_{\beta\beta} + V_{\text{H}} + V_{\text{xc}}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \varphi_\mu^\alpha \\ \varphi_\mu^\beta \end{pmatrix} = \epsilon_\mu \begin{pmatrix} \varphi_\mu^\alpha \\ \varphi_\mu^\beta \end{pmatrix}. \quad (11)$$

We see that the off-diagonal potentials produce explicitly a direct interaction between α and β spin components in this α - β coupled equation. The off-diagonal potentials consist of the exchange-correlation potential V_{xc} and the other contributions w such as spin-orbit interactions.

The U -matrix in Eq. (4) which relates the non-collinear electron densities to the up- and down-spin densities is expressed by a rotation operator D [4]:

$$D \equiv \exp\left(\frac{-i\hat{\sigma} \cdot \mathbf{h}\phi}{2}\right) \quad (12)$$

with Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (13)$$

where \mathbf{h} is a unit vector along certain direction, and ϕ a rotational angle around \mathbf{h} . Then, consider the following two-step rotation of a unit vector (1,0) along the z-axis:

- First, rotate θ on the y-axis $\rightarrow \exp\left(-i\frac{\sigma_2\theta}{2}\right)$
- Second, rotate ϕ on the z-axis $\rightarrow \exp\left(-i\frac{\sigma_3\phi}{2}\right)$

The unit vector (1,0) along the z-axis is then transformed as follows:

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \Rightarrow \exp\left(-i\frac{\sigma_3\phi}{2}\right)\exp\left(-i\frac{\sigma_2\theta}{2}\right)\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (14)$$

where

$$\begin{aligned} \exp\left(-i\frac{\sigma_3\phi}{2}\right)\exp\left(-i\frac{\sigma_2\theta}{2}\right) &= \begin{pmatrix} \exp(-i\frac{\phi}{2}) & 0 \\ 0 & \exp(i\frac{\phi}{2}) \end{pmatrix} \begin{pmatrix} \cos(\frac{\theta}{2}) & -\sin(\frac{\theta}{2}) \\ \sin(\frac{\theta}{2}) & \cos(\frac{\theta}{2}) \end{pmatrix} \\ &= \begin{pmatrix} \exp(-i\frac{\phi}{2})\cos(\frac{\theta}{2}) & -\exp(-i\frac{\phi}{2})\sin(\frac{\theta}{2}) \\ \exp(i\frac{\phi}{2})\sin(\frac{\theta}{2}) & \exp(i\frac{\phi}{2})\cos(\frac{\theta}{2}) \end{pmatrix} \end{aligned} \quad (15)$$

Thus, if the direction of the spin is specified by the Euler angle (θ, ϕ) , the U -matrix in Eq. (4) is given by the conjugate transposed matrix of Eq. (15).

$$U = \begin{pmatrix} \exp(i\frac{\phi}{2})\cos(\frac{\theta}{2}) & \exp(-i\frac{\phi}{2})\sin(\frac{\theta}{2}) \\ -\exp(i\frac{\phi}{2})\sin(\frac{\theta}{2}) & \exp(-i\frac{\phi}{2})\cos(\frac{\theta}{2}) \end{pmatrix} \quad (16)$$

The meaning of Eq. (4) becomes more clear when it is written in a matrix form as follows:

$$UnU^\dagger = U \left\{ \sum_\nu f_\nu \begin{pmatrix} \varphi_\nu^\alpha \\ \varphi_\nu^\beta \end{pmatrix} \begin{pmatrix} \varphi_\nu^{\alpha,*} & \varphi_\nu^{\beta,*} \end{pmatrix} \right\} U^\dagger \quad (17)$$

We see that the U -matrix diagonalizes the total (average) non-collinear spin matrix rather than the non-collinear spin matrix of each state ν . Since the exchange-correlation term is approximated by the LDA or GGA, once the non-collinear spin matrix n is diagonalized, the diagonal up- and down-densities are used to evaluate the exchange-correlation potentials \bar{V}_{xc} within LDA or GGA:

$$\begin{aligned} \bar{V}_{xc} &= \begin{pmatrix} V_{xc}^\uparrow & 0 \\ 0 & V_{xc}^\downarrow \end{pmatrix}, \\ &= \frac{1}{2}(V_{xc}^\uparrow + V_{xc}^\downarrow)I + \frac{1}{2}(V_{xc}^\uparrow - V_{xc}^\downarrow)\sigma_3, \\ &= V_{xc}^0 I + \Delta V_{xc} \sigma_3. \end{aligned} \quad (18)$$

Then, the potential \bar{V}_{xc} is transformed to the non-collinear exchange-correlation potential V_{xc} as follows:

$$\begin{aligned} V_{xc} &= U^\dagger \bar{V}_{xc} U, \\ &= V_{xc}^0 I + \Delta V_{xc} U^\dagger \sigma_3 U, \\ &= V_{xc}^0 I + \Delta V_{xc} \bar{\sigma}_3, \\ &= \begin{pmatrix} V_{xc}^0 + \Delta V_{xc} \cos(\theta) & \Delta V_{xc} \exp(-i\phi) \sin(\theta) \\ \Delta V_{xc} \exp(i\phi) \sin(\theta) & V_{xc}^0 - \Delta V_{xc} \cos(\theta) \end{pmatrix}, \end{aligned} \quad (19)$$

where

$$\bar{\sigma}_3 = \begin{pmatrix} \cos(\theta) & \exp(-i\phi) \sin(\theta) \\ \exp(i\phi) \sin(\theta) & -\cos(\theta) \end{pmatrix}. \quad (20)$$

The Euler angle (θ, ϕ) and the up- and down-spin densities $(n'_\uparrow, n'_\downarrow)$ are determined from the non-collinear electron densities so that the following relation can be satisfied:

$$UnU^\dagger = \begin{pmatrix} n'_\uparrow & 0 \\ 0 & n'_\downarrow \end{pmatrix}. \quad (21)$$

After some algebra, they are given by

$$\phi = -\arctan\left(\frac{\text{Im } n_{\alpha\beta}}{\text{Re } n_{\alpha\beta}}\right) \quad (22)$$

$$\theta = \arctan\left(\frac{2(\text{Re } n_{\alpha\beta} \cos(\phi) - \text{Im } n_{\alpha\beta} \sin(\phi))}{n_{\alpha\alpha} - n_{\beta\beta}}\right) \quad (23)$$

$$n'_{\uparrow} = \frac{1}{2}(n_{\alpha\alpha} + n_{\beta\beta}) + \frac{1}{2}(n_{\alpha\alpha} - n_{\beta\beta}) \cos(\theta) + (\text{Re } n_{\alpha\beta} \cos(\phi) - \text{Im } n_{\alpha\beta} \sin(\phi)) \sin(\theta) \quad (24)$$

$$n'_{\downarrow} = \frac{1}{2}(n_{\alpha\alpha} + n_{\beta\beta}) - \frac{1}{2}(n_{\alpha\alpha} - n_{\beta\beta}) \cos(\theta) - (\text{Re } n_{\alpha\beta} \cos(\phi) - \text{Im } n_{\alpha\beta} \sin(\phi)) \sin(\theta) \quad (25)$$

Then, it is noted that the effective potential V_{eff} in Eq. (11) can be written in Pauli matrices as follows:

$$\begin{aligned} V_{\text{eff}} &= V_0 \sigma_0 + \Delta V_{\text{xc}} \bar{\sigma}_3 + W, \\ &= V_0 \sigma_0 + \mathbf{b} \cdot \hat{\sigma} + W, \end{aligned} \quad (26)$$

where

$$V_{\text{eff}}^0 = V_{\text{H}} + V_{\text{xc}}^0, \quad (27)$$

$$W = \begin{pmatrix} w_{\alpha\alpha} & w_{\alpha\beta} \\ w_{\beta\alpha} & w_{\beta\beta} \end{pmatrix}, \quad (28)$$

$$b_1 = \Delta V_{\text{xc}} \sin(\theta) \cos(\phi), \quad (29)$$

$$b_2 = \Delta V_{\text{xc}} \sin(\theta) \sin(\phi), \quad (30)$$

$$b_3 = \Delta V_{\text{xc}} \cos(\theta), \quad (31)$$

$$\hat{\sigma} = (\sigma_1, \sigma_2, \sigma_3). \quad (32)$$

As well, the non-collinear spin density can be also written in Pauli matrices as follows:

$$n(\mathbf{r}) = \frac{1}{2}(N(\mathbf{r})\sigma_0 + \mathbf{m}(\mathbf{r}) \cdot \sigma) \quad (33)$$

with

$$N(\mathbf{r}) = \sum_{\nu} f_{\nu} \psi_{\nu}^{\dagger}(\mathbf{r}) \psi_{\nu}(\mathbf{r}), \quad (34)$$

$$\mathbf{m}(\mathbf{r}) = \sum_{\nu} f_{\nu} \psi_{\nu}^{\dagger}(\mathbf{r}) \hat{\sigma} \psi_{\nu}(\mathbf{r}), \quad (35)$$

where σ_0 is a 2×2 unit matrix.

2 Spin-orbit coupling

In OpenMX, the spin-orbit coupling is incorporated through j -dependent pseudo potentials [3]. Under a spherical potential, a couple of Dirac equations for the radial part is given by

$$\frac{dG_{nlj}}{dr} + \frac{\kappa}{r}G_{nlj} - a \left[\frac{2}{a^2} + \varepsilon_{nlj} - V(r) \right] F_{nlj} = 0, \quad (36)$$

$$\frac{dF_{nlj}}{dr} - \frac{\kappa}{r}F_{nlj} + a [\varepsilon_{nlj} - V(r)] G_{nlj} = 0, \quad (37)$$

where G and L are the majority and minority components of the radial wave function. $a \equiv 1/c$ (1/137.036 in a.u.). $\kappa = l$ and $\kappa = -(l+1)$ for $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$, respectively. Combining both Eqs. and eliminating F , we have the following equation for G :

$$\left[\frac{1}{2M(r)} \left(\frac{d^2}{dr^2} + \frac{a^2}{2M(r)} \frac{dV}{dr} \frac{d}{dr} + \frac{a^2}{2M(r)} \frac{\kappa}{r} \frac{dV}{dr} - \frac{\kappa(\kappa+1)}{r^2} \right) + \varepsilon_{nlj} - V \right] G_{nlj} = 0 \quad (38)$$

with

$$M(r) = 1 + \frac{a^2(\varepsilon_{nlj} - V)}{2}. \quad (39)$$

By solving numerically Eq. (38) and generating j -dependent pseudo potential V_j^{ps} by the Troullier and Martine (TM) scheme, we can define a general pseudopotential by

$$V_{\text{ps}} = \sum_{lm} \left[|\Phi_J^M\rangle V_{\text{ps}}^{l+\frac{1}{2}} \langle \Phi_J^M| + |\Phi_{J'}^{M'}\rangle V_{\text{ps}}^{l-\frac{1}{2}} \langle \Phi_{J'}^{M'}| \right], \quad (40)$$

where for $J = l + \frac{1}{2}$ and $M = m + \frac{1}{2}$

$$|\Phi_J^M\rangle = \left(\frac{l+m+1}{2l+1} \right)^{\frac{1}{2}} |Y_l^m\rangle |\alpha\rangle + \left(\frac{l-m}{2l+1} \right)^{\frac{1}{2}} |Y_l^{m+1}\rangle |\beta\rangle, \quad (41)$$

and for $J' = l - \frac{1}{2}$ and $M' = m - \frac{1}{2}$

$$|\Phi_{J'}^{M'}\rangle = \left(\frac{l-m+1}{2l+1} \right)^{\frac{1}{2}} |Y_l^{m-1}\rangle |\alpha\rangle - \left(\frac{l+m}{2l+1} \right)^{\frac{1}{2}} |Y_l^m\rangle |\beta\rangle. \quad (42)$$

The Φ_J^M and $\Phi_{J'}^{M'}$ are constituents of the eigenfunction of Dirac equation. Since $-J \leq M \leq J$ and $-J' \leq M' \leq J'$, the degeneracies of J and J' are $2(l+1)$ and $2l$, respectively. In the use of the pseudopotential defined by Eq. (40), it is transformed to a separable form. By introducing a local potential V^{L} which approaches $-\frac{Z_{\text{eff}}}{r}$ as r increases, the j -dependent pseudo potential is divided into two contributions:

$$V_{\text{ps}}^{l+\frac{1}{2}} = V_{\text{NL}}^{l+\frac{1}{2}} + V_{\text{L}}, \quad (43)$$

$$V_{\text{ps}}^{l-\frac{1}{2}} = V_{\text{NL}}^{l-\frac{1}{2}} + V_{\text{L}}. \quad (44)$$

The non-local potentials $V_{\text{NL}}^{l+\frac{1}{2}}$ and $V_{\text{NL}}^{l-\frac{1}{2}}$ are non-zero within a certain radius. Then, the pseudopotential defined by Eq. (40) is written by

$$V_{\text{ps}} = V_{\text{L}} + \sum_{lm} \left[|\Phi_J^M\rangle V_{\text{NL}}^{l+\frac{1}{2}} \langle \Phi_J^M| + |\Phi_{J'}^{M'}\rangle V_{\text{NL}}^{l-\frac{1}{2}} \langle \Phi_{J'}^{M'}| \right], \quad (45)$$

$$= V_{\text{L}} + \hat{V}_{\text{NL}}^{l+\frac{1}{2}} + \hat{V}_{\text{NL}}^{l-\frac{1}{2}}. \quad (46)$$

The non-local part is transformed by the Blochl projector into a separable form:

$$\begin{aligned}
\hat{V}_{\text{NL}}^{l+\frac{1}{2}} &= \sum_{lm} |\Phi_J^M\rangle V_{\text{NL}}^{l+\frac{1}{2}} \langle \Phi_J^M|, \\
&= \sum_{lm} \sum_{\zeta} |V_{\text{NL}}^{l+\frac{1}{2}} \bar{R}_{J\zeta} \Phi_J^M\rangle \frac{1}{c_{J\zeta}} \langle \bar{R}_{J\zeta} \Phi_J^M V_{\text{NL}}^{l+\frac{1}{2}}|, \\
&= \sum_{l\zeta} \frac{1}{c_{J\zeta}} \left[\hat{P}_{\alpha\alpha}^{J\zeta} + \hat{P}_{\beta\beta}^{J\zeta} + \hat{P}_{\alpha\beta}^{J\zeta} + \hat{P}_{\beta\alpha}^{J\zeta} \right]
\end{aligned} \tag{47}$$

with

$$\hat{P}_{\alpha\alpha}^{J\zeta} = \sum_{m=-l-1}^l \left(\frac{l+m+1}{2l+1} \right) |C_{J\zeta} Y_l^m \alpha\rangle \langle C_{J\zeta} Y_l^m \alpha|, \tag{48}$$

$$\hat{P}_{\beta\beta}^{J\zeta} = \sum_{m=-l-1}^l \left(\frac{l-m}{2l+1} \right) |C_{J\zeta} Y_l^{m+1} \beta\rangle \langle C_{J\zeta} Y_l^{m+1} \beta|, \tag{49}$$

$$\hat{P}_{\alpha\beta}^{J\zeta} = \sum_{m=-l-1}^l \left(\frac{l+m+1}{2l+1} \right)^{\frac{1}{2}} \left(\frac{l-m}{2l+1} \right)^{\frac{1}{2}} |C_{J\zeta} Y_l^m \alpha\rangle \langle C_{J\zeta} Y_l^{m+1} \beta|, \tag{50}$$

$$\hat{P}_{\beta\alpha}^{J\zeta} = \sum_{m=-l-1}^l \left(\frac{l+m+1}{2l+1} \right)^{\frac{1}{2}} \left(\frac{l-m}{2l+1} \right)^{\frac{1}{2}} |C_{J\zeta} Y_l^{m+1} \beta\rangle \langle C_{J\zeta} Y_l^m \alpha|, \tag{51}$$

where $C_{J\zeta} \equiv \bar{R}_{J\zeta} V_{\text{NL}}^{l+\frac{1}{2}}$ and \bar{R} is an orthonormal set defined by a norm $\int r^2 dr R V_{\text{NL}}^{l+\frac{1}{2}} R'$, and is calculated by the following Gram-Schmidt orthogonalization:

$$\bar{R}_{J\zeta} = R_{J\zeta} - \sum_{\eta}^{\zeta-1} \bar{R}_{J\eta} \frac{1}{c_{J\zeta}} \int r^2 dr \bar{R}_{J\eta} V_{\text{NL}}^{l+\frac{1}{2}} R_{J\eta}, \tag{52}$$

$$c_{J\zeta} = \int r^2 dr \bar{R}_{J\zeta} V_{\text{NL}}^{l+\frac{1}{2}} \bar{R}_{J\zeta}, \tag{53}$$

Similarly,

$$\begin{aligned}
\hat{V}_{\text{NL}}^{l-\frac{1}{2}} &= \sum_{lm} |\Phi_{J'}^{M'}\rangle V_{\text{NL}}^{l-\frac{1}{2}} \langle \Phi_{J'}^{M'}|, \\
&= \sum_{\zeta} |V_{\text{NL}}^{l-\frac{1}{2}} \bar{R}_{J'\zeta} \Phi_{J'}^{M'}\rangle \frac{1}{c_{J'\zeta}} \langle \bar{R}_{J'\zeta} \Phi_{J'}^{M'} V_{\text{NL}}^{l-\frac{1}{2}}|, \\
&= \sum_{l\zeta} \frac{1}{c_{J'\zeta}} \left[\hat{P}_{\alpha\alpha}^{J'\zeta} + \hat{P}_{\beta\beta}^{J'\zeta} - \hat{P}_{\alpha\beta}^{J'\zeta} - \hat{P}_{\beta\alpha}^{J'\zeta} \right]
\end{aligned} \tag{54}$$

with

$$\hat{P}_{\alpha\alpha}^{J'\zeta} = \sum_{m=-l+1}^l \left(\frac{l-m+1}{2l+1} \right) |C_{J'\zeta} Y_l^{m-1} \alpha\rangle \langle C_{J'\zeta} Y_l^{m-1} \alpha|, \tag{55}$$

$$\hat{P}_{\beta\beta}^{J'\zeta} = \sum_{m=-l+1}^l \left(\frac{l+m}{2l+1} \right) |C_{J'\zeta} Y_l^m \beta\rangle \langle C_{J'\zeta} Y_l^m \beta|, \tag{56}$$

$$\hat{P}_{\alpha\beta}^{J'\zeta} = \sum_{m=-l+1}^l \left(\frac{l-m+1}{2l+1} \right)^{\frac{1}{2}} \left(\frac{l+m}{2l+1} \right)^{\frac{1}{2}} |C_{J'\zeta} Y_l^{m-1} \alpha\rangle \langle C_{J'\zeta} Y_l^m \beta|, \tag{57}$$

$$\hat{P}_{\beta\alpha}^{J'\zeta} = \sum_{m=-l+1}^l \left(\frac{l-m+1}{2l+1} \right)^{\frac{1}{2}} \left(\frac{l+m}{2l+1} \right)^{\frac{1}{2}} |C_{J'\zeta} Y_l^m \beta\rangle \langle C_{J'\zeta} Y_l^{m-1} \alpha|. \tag{58}$$

Moreover, by unitary transforming the complex spherical harmonics functions Y into the real spherical harmonics function \bar{Y} , we obtain the following expressions:

$$\hat{P}_{\alpha\alpha}^{J\zeta} = \sum_{mm'} |C_{J\zeta} \bar{Y}_l^m \alpha\rangle F_{l,mm'}^0 \langle C_{J\zeta} \bar{Y}_l^{m'} \alpha|, \quad (59)$$

$$\hat{P}_{\beta\beta}^{J\zeta} = \sum_{mm'} |C_{J\zeta} \bar{Y}_l^m \beta\rangle F_{l,mm'}^1 \langle C_{J\zeta} \bar{Y}_l^{m'} \beta|, \quad (60)$$

$$\hat{P}_{\alpha\beta}^{J\zeta} = \sum_{mm'} |C_{J\zeta} \bar{Y}_l^m \alpha\rangle F_{l,mm'}^2 \langle C_{J\zeta} \bar{Y}_l^{m'} \beta|, \quad (61)$$

$$\hat{P}_{\beta\alpha}^{J\zeta} = \sum_{mm'} |C_{J\zeta} \bar{Y}_l^m \beta\rangle F_{l,mm'}^3 \langle C_{J\zeta} \bar{Y}_l^{m'} \alpha|, \quad (62)$$

$$\hat{P}_{\alpha\alpha}^{J'\zeta} = \sum_{mm'} |C_{J'\zeta} \bar{Y}_l^m \alpha\rangle G_{l,mm'}^0 \langle C_{J'\zeta} \bar{Y}_l^{m'} \alpha|, \quad (63)$$

$$\hat{P}_{\beta\beta}^{J'\zeta} = \sum_{mm'} |C_{J'\zeta} \bar{Y}_l^m \beta\rangle G_{l,mm'}^1 \langle C_{J'\zeta} \bar{Y}_l^{m'} \beta|, \quad (64)$$

$$\hat{P}_{\alpha\beta}^{J'\zeta} = \sum_{mm'} |C_{J'\zeta} \bar{Y}_l^m \alpha\rangle G_{l,mm'}^2 \langle C_{J'\zeta} \bar{Y}_l^{m'} \beta|, \quad (65)$$

$$\hat{P}_{\beta\alpha}^{J'\zeta} = \sum_{mm'} |C_{J'\zeta} \bar{Y}_l^m \beta\rangle G_{l,mm'}^3 \langle C_{J'\zeta} \bar{Y}_l^{m'} \alpha| \quad (66)$$

with

$$F_0^0 = 1, \quad (67)$$

$$F_1^0 = \frac{2}{3}I + \frac{i}{3} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (68)$$

$$F_2^0 = \frac{3}{5}I + \frac{i}{5} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix}, \quad (69)$$

$$F_3^0 = \frac{4}{7}I + \frac{i}{7} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3 \\ 0 & 0 & 0 & 0 & 0 & 3 & 0 \end{pmatrix}, \quad (70)$$

$$F_0^1 = 1, \quad (71)$$

$$F_1^1 = (F_1^0)^*, \quad (72)$$

$$F_2^1 = (F_2^0)^*, \quad (73)$$

$$F_3^1 = (F_3^0)^*, \quad (74)$$

$$F_0^2 = 0, \quad (75)$$

$$F_1^2 = \frac{1}{3} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} + \frac{i}{3} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad (76)$$

$$F_2^2 = \frac{1}{5} \begin{pmatrix} 0 & 0 & 0 & -\sqrt{3} & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ \sqrt{3} & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \end{pmatrix} + \frac{i}{5} \begin{pmatrix} 0 & 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ -\sqrt{3} & -1 & 0 & 0 & 0 \end{pmatrix}, \quad (77)$$

$$F_3^2 = \frac{1}{7} \begin{pmatrix} 0 & -\sqrt{6} & 0 & 0 & 0 & 0 & 0 \\ \sqrt{6} & 0 & 0 & -\sqrt{\frac{5}{2}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sqrt{\frac{5}{2}} & 0 & 0 \\ 0 & \sqrt{\frac{5}{2}} & 0 & 0 & 0 & -\sqrt{\frac{3}{2}} & 0 \\ 0 & 0 & \sqrt{\frac{5}{2}} & 0 & 0 & 0 & -\sqrt{\frac{3}{2}} \\ 0 & 0 & 0 & \sqrt{\frac{3}{2}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{\frac{3}{2}} & 0 & 0 \end{pmatrix} + \frac{i}{7} \begin{pmatrix} 0 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{\frac{5}{2}} & 0 & 0 \\ -\sqrt{6} & 0 & 0 & -\sqrt{\frac{5}{2}} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{\frac{5}{2}} & 0 & 0 & 0 & \sqrt{\frac{3}{2}} \\ 0 & -\sqrt{\frac{5}{2}} & 0 & 0 & 0 & -\sqrt{\frac{3}{2}} & 0 \\ 0 & 0 & 0 & 0 & \sqrt{\frac{3}{2}} & 0 & 0 \\ 0 & 0 & 0 & -\sqrt{\frac{3}{2}} & 0 & 0 & 0 \end{pmatrix}, \quad (78)$$

$$F_0^3 = 0, \quad (79)$$

$$F_1^3 = (F_1^2)^\dagger, \quad (80)$$

$$F_2^3 = (F_2^2)^\dagger, \quad (81)$$

$$F_3^3 = (F_3^2)^\dagger, \quad (82)$$

$$G_0^0 = 0, \quad (83)$$

$$G_1^0 = \frac{1}{3}I - \frac{i}{3} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (84)$$

$$G_2^0 = \frac{2}{5}I - \frac{i}{5} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix}, \quad (85)$$

$$G_3^0 = \frac{3}{7}I - \frac{i}{7} \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3 \\ 0 & 0 & 0 & 0 & 0 & 3 & 0 \end{pmatrix}, \quad (86)$$

$$G_0^1 = 0, \quad (87)$$

$$G_1^1 = (G_1^0)^*, \quad (88)$$

$$G_2^1 = (G_2^0)^*, \quad (89)$$

$$G_3^1 = (G_3^0)^*, \quad (90)$$

$$G_0^2 = 0, \quad (91)$$

$$G_1^2 = F_1^2, \quad (92)$$

$$G_2^2 = F_2^2, \quad (93)$$

$$G_3^2 = F_3^2, \quad (94)$$

$$G_0^3 = 0, \quad (95)$$

$$G_1^3 = F_1^3, \quad (96)$$

$$G_2^3 = F_2^3, \quad (97)$$

$$G_3^3 = F_3^3, \quad (98)$$

where the real spherical harmonics functions \bar{Y} are denoted by (x, y, z) , $(3z^2 - r^2, x^2 - y^2, xy, xz, yz)$, and $(5z^2 - 3r^2, 5xz^2 - xr^2, 5yz^2 - yr^2, z^2 - zy^2, xyz, x^3 - 3xy^2, 3yx^2 - y^3)$ for p -, d -, and f -orbitals, respectively.

3 Non-collinear LDA+U

In conjunction with the on-site exchange term of the unrestricted Hartree-Fock theory, the total energy of a non-collinear LDA+U method could be defined by

$$E_{\text{LDA+U}} = E_{\text{LDA}} + E_{\text{U}} \quad (99)$$

with

$$\begin{aligned} E_{\text{U}} &= \frac{1}{2} \sum_i \sum_p \sum_l U_{ipl} [\text{Tr}(N_{ipl}) - \text{Tr}(N_{ipl}N_{ipl})], \\ &= \frac{1}{2} \sum_s U_s [\text{Tr}(N_s) - \text{Tr}(N_s N_s)], \end{aligned} \quad (100)$$

where i is a site index, l an angular momentum quantum number, p a multiplicity number of radial basis functions, and s an organized index of (ipl) . N is an diagonalized occupation matrix with the size of $2(2l+1) \times 2(2l+1)$. The U is the effective Coulomb electron-electron interaction energy. Also, E_{LDA} is given by Eq. (5). It should be noted that the occupation matrix is twice as size as the collinear case. In this definition it is assumed that the exchange interaction arises when an electron is occupied with a certain spin direction in each localized orbital. Considering the rotational invariance of total energy with respect to each sub-shell s , Eq. (100) can be transformed as follows:

$$\begin{aligned} E_{\text{U}} &= \frac{1}{2} \sum_s U_s [\text{Tr}(A_s N_s A_s^\dagger) - \text{Tr}(A_s N_s A_s^\dagger A_s N_s A_s^\dagger)], \\ &= \frac{1}{2} \sum_s U_s [\text{Tr}(n_s) - \text{Tr}(n_s n_s)], \\ &= \frac{1}{2} \sum_s U_s \left[\sum_{\sigma m} n_{s,mm}^{\sigma\sigma} - \sum_{\sigma m, \sigma' m'} n_{s,mm}^{\sigma\sigma'} n_{s,m'm}^{\sigma'\sigma} \right], \end{aligned} \quad (101)$$

where $\sigma, \sigma' = \alpha$ and β . In this Eq. (101), although off-diagonal occupation terms in each sub-shell s are taken into account, however, those between sub-shells are neglected. This treatment is consistent with their rotational invariant functional by Dudarev *et al.*[5], and is a simple extension of the rotational invariant functional for the case that a different U-value is given for each basis orbital indexed with $s \equiv (ipl)$. In addition, the functional is rotationally invariant in the spin-space. In this simple extension, we can not only include multiple d-orbitals as basis set, but also can easily derive the force on atoms in a simple form as discussed later on.

The total energy $E_{\text{LDA+U}}$ can be expressed in terms of the Kohn-Sham eigenenergies ε_ν as follows:

$$\begin{aligned} E_{\text{LDA+U}} &= E_{\text{LDA}} + E_{\text{U}}, \\ &= E_{\text{band}} + \left[E_{\text{ee}} + E_{\text{cc}} + E_{\text{xc}} - \sum_\nu \langle \psi_\nu | \hat{v}_{\text{LDA}} | \psi_\nu \rangle \right] + \left[E_{\text{U}} - \sum_\nu \langle \psi_\nu | \hat{v}_{\text{U}} | \psi_\nu \rangle \right], \\ &= E_{\text{band}} + \Delta E_{\text{LDA}} + \frac{1}{2} \sum_s U_s \sum_{\sigma m, \sigma' m'} n_{s,mm}^{\sigma\sigma'} n_{s,m'm}^{\sigma'\sigma}, \\ &= E_{\text{band}} + \Delta E_{\text{LDA}} + \Delta E_{\text{U}}, \end{aligned} \quad (102)$$

where ΔE_{LDA} and ΔE_{U} are the double counting corrections of LDA- and U-energies, respectively.

3.1 Occupation number

The occupation number n (which is written by an *italic* font, while the electron density, appears in Sec. 1, is denoted by a roman font) is defined by

$$n_{smm'}^{\sigma\sigma'} = \sum_{\nu} f_{\nu} \langle \psi_{\nu} | \hat{n}_{s,mm'}^{\sigma\sigma'} | \psi_{\nu} \rangle, \quad (103)$$

where, to count the occupation number n , we define three occupation number operators given by *on-site*

$$\hat{n}_{smm'}^{\sigma\sigma'} = |s\tilde{m}\sigma\rangle \langle s\tilde{m}'\sigma'|, \quad (104)$$

full

$$\hat{n}_{smm'}^{\sigma\sigma'} = |sm\sigma\rangle \langle sm'\sigma'|, \quad (105)$$

dual

$$\hat{n}_{smm'}^{\sigma\sigma'} = \frac{1}{2} \left(|s\tilde{m}\sigma\rangle \langle sm'\sigma'| + |sm\sigma\rangle \langle s\tilde{m}'\sigma'| \right), \quad (106)$$

where $|s\tilde{m}\sigma\rangle$ is the dual orbital of a original non-orthogonal basis orbital $|sm\sigma\rangle$, and is defined by

$$|s\tilde{m}\sigma\rangle = \sum_{s'm'} S_{sm,s'm'}^{-1} |s'm'\sigma\rangle \quad (107)$$

with the overlap matrix S between non-orthogonal basis orbitals. Then, the following bi-orthogonal relation is verified:

$$\langle s\tilde{m}\sigma | sm'\sigma' \rangle = \delta_{sm\sigma, s'm'\sigma'}. \quad (108)$$

The *on-site* and *full* occupation number operators have been proposed by Eschrig *et al.* [6] and Pickett *et al.* [7], respectively. It is noted that these definitions do not satisfy a sum rule that the trace of the occupation number matrix is equivalent to the total number of electrons, while only the *dual* occupation number operator fulfills the sum rule as follows:

$$\text{Tr}(n) = \frac{1}{2} \{ \text{Tr}(\rho S) + \text{Tr}(S\rho) \} = N_{\text{ele}}, \quad (109)$$

where ρ is the density matrix defined by

$$\begin{aligned} \rho_{sm,s'm'}^{\sigma\sigma'} &= \sum_{\nu} f_{\nu} \langle \psi_{\nu} | \hat{\rho}_{sm,s'm'}^{\sigma\sigma'} | \psi_{\nu} \rangle, \\ &= \sum_{\nu} f_{\nu} c_{\nu,sm}^{\sigma,*} c_{\nu,s'm'}^{\sigma'} \end{aligned} \quad (110)$$

with a density operator:

$$\hat{\rho}_{sm,s'm'}^{\sigma\sigma'} = |s\tilde{m}\sigma\rangle \langle s'\tilde{m}'\sigma'|. \quad (111)$$

For three definition of occupation number operators, *on-site*, *full*, and *dual*, the occupation numbers are given by

on-site

$$n_{smm'}^{\sigma\sigma'} = \rho_{sm,sm'}^{\sigma\sigma'}, \quad (112)$$

full

$$n_{smm'}^{\sigma\sigma'} = \sum_{tn,t'n'} \rho_{tn,t'n'}^{\sigma\sigma'} S_{tn,sm} S_{sm',t'n'}, \quad (113)$$

dual

$$n_{smm'}^{\sigma\sigma'} = \frac{1}{2} \sum_{tn} \left\{ \rho_{sm,tn}^{\sigma\sigma'} S_{tn,sm'} + S_{sm,tn} \rho_{tn,sm'}^{\sigma\sigma'} \right\}, \quad (114)$$

3.2 Effective potential

The derivative of the total energy Eq. (99) with respect to LCAO coefficient $c_{\nu,tn}^{\sigma}$ is given by

$$\begin{aligned} \frac{\partial E_{\text{LDA+U}}}{\partial c_{\nu,tn}^{\sigma,*}} &= \frac{\partial E_{\text{LDA}}}{\partial c_{\nu,tn}^{\sigma,*}} + \frac{\partial E_{\text{U}}}{\partial c_{\nu,tn}^{\sigma,*}}, \\ &= \frac{\partial E_{\text{LDA}}}{\partial c_{\nu,tn}^{\sigma,*}} + \sum_{\sigma'} \sum_{smm'} \frac{\partial E_{\text{U}}}{\partial n_{smm'}^{\sigma\sigma'}} \frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}}, \\ &= \frac{\partial E_{\text{LDA}}}{\partial c_{\nu,tn}^{\sigma,*}} + \sum_{\sigma'} \sum_{smm'} U_s \left(\frac{1}{2} \delta_{\sigma\sigma'} \delta_{mm'} - n_{sm'm}^{\sigma'\sigma} \right) \frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}}, \\ &= \frac{\partial E_{\text{LDA}}}{\partial c_{\nu,tn}^{\sigma,*}} + \sum_{\sigma'} \sum_{smm'} v_{\text{U},smm'}^{\sigma\sigma'} \frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}} \end{aligned} \quad (115)$$

with

on-site

$$\frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}} = \delta_{st} \delta_{mn} c_{\nu,sm'}^{\sigma'}, \quad (116)$$

full

$$\frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}} = \sum_{t'n'} S_{tn,sm} S_{sm',t'n'} c_{\nu,t'n'}^{\sigma'}, \quad (117)$$

dual

$$\frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}} = \frac{1}{2} \left\{ \delta_{st} \delta_{mn} \sum_{t'n'} c_{\nu,t'n'}^{\sigma'} S_{t'n',sm'} + S_{sm,tn} c_{\nu,sm'}^{\sigma'} \right\}. \quad (118)$$

Substituting Eqs. (116)-(118) for the second term of Eq. (115), we see

on-site

$$\sum_{smm'} v_{\text{U},smm'}^{\sigma\sigma'} \frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}} = \sum_{\sigma'''} \sum_{t'n'} \langle tn\sigma | \left[\sum_{\sigma'\sigma''} \sum_{smm'} |s\tilde{m}\sigma'\rangle v_{\text{U},smm'}^{\sigma'\sigma''} \langle s\tilde{m}'\sigma'' | \right] |t'n'\sigma'''\rangle c_{\nu,t'n'}^{\sigma'''} \quad (119)$$

full

$$\sum_{smm'} v_{\text{U},smm'}^{\sigma\sigma'} \frac{\partial n_{smm'}^{\sigma\sigma'}}{\partial c_{\nu,tn}^{\sigma,*}} = \sum_{\sigma'''} \sum_{t'n'} \langle tn\sigma | \left[\sum_{\sigma'\sigma''} \sum_{smm'} |sm\sigma'\rangle v_{\text{U},smm'}^{\sigma'\sigma''} \langle sm'\sigma'' | \right] |t'n'\sigma'''\rangle c_{\nu,t'n'}^{\sigma'''} \quad (120)$$

dual

$$\sum_{s\tilde{m}\sigma'} v_{\text{U},s\tilde{m}\sigma'}^{\sigma\sigma'} \frac{\partial n_{s\tilde{m}\sigma'}^{\sigma\sigma'}}{\partial c_{\nu,t\tilde{n}}^{\sigma,*}} = \sum_{\sigma'''} \sum_{t'n'} \langle tn\sigma | \frac{1}{2} \sum_{\sigma''} \sum_{s\tilde{m}\sigma'} [|s\tilde{m}\sigma'\rangle v_{\text{U},s\tilde{m}\sigma'}^{\sigma''\sigma''} \langle sm'\sigma'' | + |sm\sigma'\rangle v_{\text{U},s\tilde{m}\sigma'}^{\sigma''\sigma''} \langle sm'\sigma'' |] |t'n'\sigma'''\rangle c_{\nu,t'n'}^{\sigma'''} \rangle. \quad (121)$$

Therefore, the effective projector potentials \hat{v}_{U} can be expressed by

on-site

$$\hat{v}_{\text{U}} = \sum_{\sigma\sigma'} \sum_{s\tilde{m}\sigma'} |s\tilde{m}\sigma\rangle v_{\text{U},s\tilde{m}\sigma'}^{\sigma\sigma'} \langle s\tilde{m}'\sigma' |, \quad (122)$$

full

$$\hat{v}_{\text{U}} = \sum_{\sigma\sigma'} \sum_{s\tilde{m}\sigma'} |sm\sigma\rangle v_{\text{U},s\tilde{m}\sigma'}^{\sigma\sigma'} \langle sm'\sigma' |, \quad (123)$$

dual

$$\hat{v}_{\text{U}} = \frac{1}{2} \sum_{\sigma\sigma'} \sum_{s\tilde{m}\sigma'} [|s\tilde{m}\sigma\rangle v_{\text{U},s\tilde{m}\sigma'}^{\sigma\sigma'} \langle sm'\sigma' | + |sm\sigma\rangle v_{\text{U},s\tilde{m}\sigma'}^{\sigma\sigma'} \langle s\tilde{m}'\sigma' |]. \quad (124)$$

It is clear that the effective potentials of *on-site* and *full* are Hermitian. Also, it is verified that the effective potential of *dual* is Hermitian as follows:

$$\begin{aligned} \langle tn\sigma | \hat{v}_{\text{U}} | t'n'\sigma' \rangle &= \frac{1}{2} \sum_{m'} v_{\text{U},tnm'}^{\sigma\sigma'} S_{tm',t'n'} + \frac{1}{2} \sum_m S_{tn,t'm} v_{\text{U},t'mn'}^{\sigma\sigma'}, \\ &= ((t'n'\sigma' | \hat{v}_{\text{U}} | tn\sigma \rangle)^*. \end{aligned} \quad (125)$$

It should be noted that in the full and dual the v_{U}^{σ} of the site i can affect the different sites by the projector potentials Eqs. (123) and (124) because of the overlap.

3.3 Force on atom

The force on atom is evaluated by

$$\frac{\partial E_{\text{LDA+U}}}{\partial \mathbf{R}_k} = \frac{\partial E_{\text{LDA}}}{\partial \mathbf{R}_k} + \frac{\partial E_{\text{U}}}{\partial \mathbf{R}_k}, \quad (126)$$

The first term can be calculated in the same way as in the collinear case. The second term is evaluated as follows:

$$\begin{aligned} \frac{\partial E_{\text{U}}}{\partial \mathbf{R}_k} &= \sum_{\sigma\sigma'} \sum_{s\tilde{m}\sigma'} \frac{\partial E_{\text{U}}}{\partial n_{s\tilde{m}\sigma'}^{\sigma\sigma'}} \frac{\partial n_{s\tilde{m}\sigma'}^{\sigma\sigma'}}{\partial \mathbf{R}_k}, \\ &= \sum_{\sigma\sigma'} \sum_{s\tilde{m}\sigma'} v_{\text{U},s\tilde{m}\sigma'}^{\sigma\sigma'} \frac{\partial n_{s\tilde{m}\sigma'}^{\sigma\sigma'}}{\partial \mathbf{R}_k}, \\ &= \sum_{\nu} f_{\nu} \sum_{\sigma\sigma'} \sum_{tn,t'n'} \left\{ \frac{\partial c_{\nu,t\tilde{n}}^{\sigma,*}}{\partial \mathbf{R}_k} \langle tn\sigma | \hat{v}_{\text{U}} | t'n'\sigma' \rangle c_{\nu,t'n'}^{\sigma'} + c_{\nu,t\tilde{n}}^{\sigma,*} \langle tn\sigma | \hat{v}_{\text{U}} | t'n'\sigma' \rangle \frac{\partial c_{\nu,t'n'}^{\sigma'}}{\partial \mathbf{R}_k} \right. \\ &\quad \left. + c_{\nu,t\tilde{n}}^{\sigma,*} c_{\nu,t'n'}^{\sigma'} \frac{\partial \langle tn\sigma | \hat{v}_{\text{U}} | t'n'\sigma' \rangle}{\partial \mathbf{R}_k} \right\}. \end{aligned} \quad (127)$$

Considering $Hc_\nu = \varepsilon_\nu Sc_\nu$ and $C^\dagger SC = I$, the first and second terms in Eq. (127) can be transformed into derivatives of the overlap matrix. The third term in Eq. (127) means that only the differentiation for the overlap matrix is considered, And it is analytically differentiated, since it contains just two-center integrals.

3.4 Enhancement of orbital polarization

The LDA+U functional can possess multiple stationary points due to the degree of freedom in the configuration space of occupation ratio for degenerate orbitals. If electrons are occupied with a nearly same occupancy ratio in degenerate orbitals at the first stage of SCF steps, the final electronic state often converges a stationary minimum with non-orbital polarization after the SCF iteration. Also, it is often likely that electrons are disproportionately occupied in some of degenerate orbitals due to the exchange interaction, which is so-called 'orbital polarization'. As an example of the multiple minima, we can point out a cobalt oxide (CoO) bulk in which d-orbitals of the cobalt atom are split to t_{2g} and e_g states, and the five of seven d-electrons are occupied in t_{2g} and e_g states of the majority spin, and remaining two d-electrons are occupied in the t_{2g} state of the minority spin. Then, it depends on the initial occupancy ratios for the t_{2g} states of the minority spin how the remaining two d-electrons are occupied in three t_{2g} states. If the initial occupancy ratios are uniform, we may arrive at the non-orbital polarized state. In fact, unless any special treatment is considered for the initial occupancy ratios, we see the non-orbital polarized state of the CoO bulk. In order to explore the degree of freedom for the orbital occupation, therefore, it is needed to develop a general method which explicitly induces the orbital polarization. To induce the orbital polarization, a polarized redistribution scheme is proposed as follows:

$$\text{diagonalize} \quad d_s = V^\dagger n_s V \quad d_s : \text{ascending order} \quad (128)$$

$$\text{summation} \quad D = \sum_{m=1}^{2(2l+1)} d_{sm} \quad (129)$$

$$\begin{aligned} \text{redistribution} \quad & d'_{4l+2} = 1, \\ & d'_{4l+1} = 1, \\ & \dots, \\ & d'_m = D - (4l + 2 - m), \\ & d'_{m-1} = 0, \dots \end{aligned} \quad (130)$$

$$\text{where } D = \sum_m d'_m \quad (131)$$

$$\text{back transform} \quad n'_s = V d'_m V^\dagger \quad (132)$$

After diagonalizing each sub-shell matrix consisting of occupation numbers, we introduce a polarized redistribution scheme given by Eq. (130) while keeping Eq. (129). Then, by a back transformation Eq. (130), we can obtain a polarized occupation matrix for each sub-shell. This polarized redistribution scheme is applied during the first few SCF steps, and then no modification is made during subsequent SCF steps. This proposed scheme maybe applicable to a general case: any crystal field, any number of electrons in the sub-shell, and any orbitals: p,d,f,...

3.5 Density of states

Define

$$P_{i\kappa}^{\sigma\sigma'}(E) = \sum_{\mathbf{k}} \sum_{\nu} c_{\mathbf{k}\nu, i\kappa}^{\sigma,*} c_{\mathbf{k}\nu, i'\kappa'}^{\sigma'} S_{i'\kappa', i\kappa} \delta(E - \varepsilon_{\nu\mathbf{k}}). \quad (133)$$

Then, the density of states, D , is given by

$$D_{i\kappa}^{\uparrow}(E) = \frac{1}{2}(P_{i\kappa}^{\alpha\alpha} + P_{i\kappa}^{\beta\beta}) + \frac{1}{2}(P_{i\kappa}^{\alpha\alpha} - P_{i\kappa}^{\beta\beta}) \cos(\theta_i) + \left(\text{Re } P_{i\kappa}^{\alpha\beta} \cos(\phi_i) - \text{Im } P_{i\kappa}^{\alpha\beta} \sin(\phi_i) \right) \sin(\theta_i), \quad (134)$$

$$D_{i\kappa}^{\downarrow}(E) = \frac{1}{2}(P_{i\kappa}^{\alpha\alpha} + P_{i\kappa}^{\beta\beta}) - \frac{1}{2}(P_{i\kappa}^{\alpha\alpha} - P_{i\kappa}^{\beta\beta}) \cos(\theta_i) - \left(\text{Re } P_{i\kappa}^{\alpha\beta} \cos(\phi_i) - \text{Im } P_{i\kappa}^{\alpha\beta} \sin(\phi_i) \right) \sin(\theta_i). \quad (135)$$

Also, the Mulliken populations, Q , are given by

$$Q_i^{\sigma\sigma'} = \sum_{\kappa} \int dE f(E) P_{i\kappa}^{\sigma\sigma'}(E). \quad (136)$$

The local spin direction is determined by

$$\phi_i = -\arctan\left(\frac{\text{Im } Q_i^{\alpha\beta}}{\text{Re } Q_i^{\alpha\beta}}\right), \quad (137)$$

$$\theta_i = \arctan\left(\frac{2(\text{Re } Q_i^{\alpha\beta} \cos(\phi_i) - \text{Im } Q_i^{\alpha\beta} \sin(\phi_i))}{Q_i^{\alpha\alpha} - Q_i^{\beta\beta}}\right). \quad (138)$$

3.6 Zeeman term

The contribution to the total energy arising the Zeeman term is given by

$$E_z = E_{zs} + E_{zo}, \quad (139)$$

where

$$E_{zs} = \sum_i \mathbf{B}_i^s \cdot \mathbf{s}_i = \sum_i (B_{ix}^s s_{ix} + B_{iy}^s s_{iy} + B_{iz}^s s_{iz}), \quad (140)$$

$$E_{zo} = \frac{1}{2} \sum_i \mathbf{B}_i^o \cdot \mathbf{l}_i = \frac{1}{2} \sum_i (B_{ix}^o l_{ix} + B_{iy}^o l_{iy} + B_{iz}^o l_{iz}). \quad (141)$$

The vector components of the spin magnetic moment are given by

$$s_{ix} = \frac{1}{2}(N^{\uparrow} - N^{\downarrow}) \sin(\theta_i) \cos(\phi_i), \quad (142)$$

$$s_{iy} = \frac{1}{2}(N^{\uparrow} - N^{\downarrow}) \sin(\theta_i) \sin(\phi_i), \quad (143)$$

$$s_{iz} = \frac{1}{2}(N^{\uparrow} + N^{\downarrow}) \cos(\theta_i) \quad (144)$$

with

$$N_{i\uparrow}' = \frac{1}{2}(N_{i\alpha\alpha} + N_{i\beta\beta}) + \frac{1}{2}(N_{i\alpha\alpha} - N_{i\beta\beta}) \cos(\theta_i) + (\text{Re } N_{i\alpha\beta} \cos(\phi_i) - \text{Im } N_{i\alpha\beta} \sin(\phi_i)) \sin(\theta_i), \quad (145)$$

$$N'_{i\downarrow} = \frac{1}{2}(N_{i\alpha\alpha} + N_{i\beta\beta}) - \frac{1}{2}(N_{i\alpha\alpha} - N_{i\beta\beta}) \cos(\theta_i) - (\text{Re } N_{i\alpha\beta} \cos(\phi_i) - \text{Im } N_{i\alpha\beta} \sin(\phi_i)) \sin(\theta_i), \quad (146)$$

where $N_{i\sigma\sigma'}$ is given by

$$N_{i\sigma\sigma'} = \text{Tr}(n_i^{\sigma\sigma'}). \quad (147)$$

After some algebra we have

$$s_{ix} = \frac{1}{2}(N_{i\alpha\beta} + N_{i\beta\alpha}), \quad (148)$$

$$s_{iy} = \frac{i}{2}(N_{i\alpha\beta} - N_{i\beta\alpha}), \quad (149)$$

$$s_{iz} = \frac{1}{2}(N_{i\alpha\alpha} - N_{i\beta\beta}). \quad (150)$$

The vector components of the orbital magnetic moment are given by

$$\begin{aligned} l_{iv} &= \int dE \sum_{\mathbf{k}} \sum_{\nu} f(E) \langle \psi_{\mathbf{k}\nu} | \hat{l}_v | \psi_{\mathbf{k}\nu} \rangle \delta(E - \varepsilon_{\mathbf{k}\nu}), \\ &= \int dE \sum_{\mathbf{k}} \sum_{\nu} f(E) \left[\langle \varphi_{\mathbf{k}\nu}^{\alpha} | \hat{l}_v | \varphi_{\mathbf{k}\nu}^{\alpha} \rangle + \langle \varphi_{\mathbf{k}\nu}^{\beta} | \hat{l}_v | \varphi_{\mathbf{k}\nu}^{\beta} \rangle \right] \delta(E - \varepsilon_{\mathbf{k}\nu}), \\ &= \sum_{\mathbf{k}} \sum_{\nu} f(\varepsilon_{\mathbf{k}\nu}) \left[\sum_{\kappa, \kappa'} c_{\mathbf{k}\nu, i\kappa}^{\alpha, *} c_{\mathbf{k}\nu, i\kappa'}^{\alpha} \langle \phi_{i\kappa}^{\alpha} | \hat{l}_v | \phi_{i\kappa'}^{\alpha} \rangle + c_{\mathbf{k}\nu, i\kappa}^{\beta, *} c_{\mathbf{k}\nu, i\kappa'}^{\beta} \langle \phi_{i\kappa}^{\beta} | \hat{l}_v | \phi_{i\kappa'}^{\beta} \rangle \right], \\ &= \sum_{\kappa, \kappa'} \rho_{i\kappa, i\kappa'}^{\alpha\alpha} \langle \phi_{i\kappa}^{\alpha} | \hat{l}_v | \phi_{i\kappa'}^{\alpha} \rangle + \rho_{i\kappa, i\kappa'}^{\beta\beta} \langle \phi_{i\kappa}^{\beta} | \hat{l}_v | \phi_{i\kappa'}^{\beta} \rangle, \end{aligned} \quad (151)$$

where $v = x, y,$ or z . Noting that

$$\hat{l}_x = \frac{1}{2}(\hat{l}_+ + \hat{l}_-), \quad (152)$$

$$\hat{l}_y = \frac{1}{2i}(\hat{l}_+ - \hat{l}_-), \quad (153)$$

$$\hat{l}_z Y_l^m = m Y_l^m, \quad (154)$$

$$\hat{l}_+ Y_l^m = \sqrt{(l-m)(l+m+1)} Y_l^{m+1}, \quad (155)$$

$$\hat{l}_- Y_l^m = \sqrt{(l+m)(l-m+1)} Y_l^{m-1}, \quad (156)$$

and considering a unitary transformation of the spherical harmonic functions into a set of real harmonic functions defined by

$$Y_{px} = \frac{1}{\sqrt{2}}(-Y_1^{-1} + Y_1^1), \quad (157)$$

$$Y_{py} = \frac{1}{i\sqrt{2}}(Y_1^{-1} + Y_1^1), \quad (158)$$

$$Y_{pz} = -Y_1^0, \quad (159)$$

it can be shown that

$$\begin{pmatrix} \langle Y_{px} | \\ \langle Y_{py} | \\ \langle Y_{pz} | \end{pmatrix} \hat{l}_x (|Y_{px}\rangle, |Y_{py}\rangle, |Y_{pz}\rangle) = i \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad (160)$$

$$\begin{pmatrix} \langle Y_{px} | \\ \langle Y_{py} | \\ \langle Y_{pz} | \end{pmatrix} \hat{l}_y(|Y_{px}\rangle, |Y_{py}\rangle, |Y_{pz}\rangle) = i \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad (161)$$

$$\begin{pmatrix} \langle Y_{px} | \\ \langle Y_{py} | \\ \langle Y_{pz} | \end{pmatrix} \hat{l}_z(|Y_{px}\rangle, |Y_{py}\rangle, |Y_{pz}\rangle) = i \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (162)$$

It is noted that the expectation values of \hat{l}_v in terms of the real harmonic functions are purely imaginary numbers. The unitary transformation for the other L -components can be found in a subroutine 'Set_Comp2Real()' in 'SetPara_DFT.c'. Thus, one can obtain the matrix representation for \hat{l}_v in terms of the real harmonic functions.

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