In density functioanl theory (DFT), the exchange-correlation (XC) energy, E^{xc} is expressed as a functional of the single particle reduced density matrix, $\boldsymbol{\gamma}$

$$E^{xc}[\boldsymbol{\gamma}] = \int_{\mathbb{R}^3} \mathrm{d}r\, f(V(r)), \quad V(r) \equiv V(\boldsymbol{\gamma}(r)), \tag{1}$$

where V is a set of fundamental density variables associated with $\boldsymbol{\gamma}$. The elements of V depend on a number of factors related both the spin structure of $\boldsymbol{\gamma}$ and the nature of the approximations assumed for E^{xc}, e.g. local density (LDA), generalized gradient (GGA) and meta-generalized gradient (MGGA) approximations. The spin structure of $\boldsymbol{\gamma}$ is revealed through its realization as an hermitian rank-2 complex tensor field on the spin manifold,

$$\boldsymbol{\gamma}(r) = \begin{bmatrix} \gamma^{\alpha\alpha}(r) & \gamma^{\alpha\beta}(r) \\ \gamma^{\beta\alpha}(r) & \gamma^{\beta\beta}(r) \end{bmatrix}. \tag{2}$$

Hermiticity dictates that $\gamma^{\alpha\alpha}, \gamma^{\beta\beta}$ are real valued while only restricting that $\gamma^{\alpha\beta} = \bar{\gamma}^{\beta\alpha}$. Therefore, it is often advantageous to express $\boldsymbol{\gamma}$ in the basis of Pauli matrices,

$$\boldsymbol{\gamma}(r) = \frac{1}{2}n(r)\mathbf{I}_2 + \frac{1}{2}m_z(r)\boldsymbol{\sigma}_z + \frac{1}{2}m_y(r)\boldsymbol{\sigma}_y + \frac{1}{2}m_x(r)\boldsymbol{\sigma}_x \tag{3}$$

where the Pauli matrices are defined as

$$\boldsymbol{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \boldsymbol{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \boldsymbol{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \tag{4}$$

and the transformed components are given by

$$n(r) = \gamma^{\alpha\alpha} + \gamma^{\beta\beta}, \tag{5}$$
$$m_z(r) = \gamma^{\alpha\alpha} - \gamma^{\beta\beta}, \tag{6}$$
$$m_y(r) = i(\gamma^{\alpha\beta} - \gamma^{\beta\alpha}) = -2\Im\gamma^{\alpha\beta}, \tag{7}$$
$$m_x(r) = \gamma^{\alpha\beta} + \gamma^{\beta\alpha} = 2\Re\gamma^{\alpha\beta}. \tag{8}$$

The functions n, m_x, m_y, m_z are all real valued and together completely describe $\boldsymbol{\gamma}$. By restricting certain elements of this set to be zero, we can impose various spin symmetries on our electronic wave function. In particular, we consider the following three spin classifications

$$\boldsymbol{\gamma}(r) \sim \begin{cases} n(r), m_z(r), m_y(r), m_x(r) & \text{(GKS)} \\ n(r), m_z(r) & \text{(UKS)} \\ n(r) & \text{(RKS)} \end{cases} \tag{9}$$

In the local density approximation (LDA), $V^{LDA}(\boldsymbol{\gamma})$ is taken to only include the non-zero density variables, e.g.

$$\begin{aligned} V^{LDA}_{GKS} &= \{n, m_z, m_y, m_x\} \\ V^{LDA}_{UKS} &= \{n, m_z\} \\ V^{LDA}_{RKS} &= \{n\} \end{aligned} \tag{10}$$

In the generalized-gradient approximation (GGA), $V^{GGA}(\boldsymbol{\gamma})$ is taken the include both the non-zero density variables and their gradients, e.g.

$$\begin{aligned} V^{GGA}_{GKS} &= V^{LDA}_{GKS} \cup \{\nabla n, \nabla m_z, \nabla m_y, \nabla m_x\} \\ V^{GGA}_{UKS} &= V^{LDA}_{UKS} \cup \{\nabla n, \nabla m_z\} \\ V^{GGA}_{RKS} &= V^{LDA}_{RKS} \cup \{\nabla n\} \end{aligned} \tag{11}$$

As scalars such as the energy are invariant with respect to Galilean transformations, the orientation dependence of the gradient variables required for e.g. GGA XC functional motivates the introduction of a set of varaiables which are invariant with respect to Galilean reference frame (i.e. invariate with respect to spatial rotations, etc). As such, we untroduce a set of auxilary variables, $U(\boldsymbol{\gamma})$ which take the following simple form for RKS

$$U^{LDA}_{RKS} = V^{LDA}_{RKS} \tag{12}$$
$$U^{GGA}_{RKS} = U^{LDA}_{RKS} \cup \{\eta\} \tag{13}$$

with $\eta = \|\nabla n\|^2$. The expressions for the auxilarary variables for UKS/GKS take on a slightly more complicated form.

$$U^{LDA}_{UKS/GKS} = \{\rho_+, \rho_-\} \tag{14}$$
$$U^{GGA}_{UKS/GKS} = U^{LDA}_{UKS/GKS} \cup \{\eta_{++}, \eta_{+-}, \eta_{--}\} \tag{15}$$

Due to the fact that spin and spatial degrees of freedom are decoupled in UKS, these variables take the following simple form

$$\rho^{UKS}_+ = \gamma^{\alpha\alpha}, \quad \rho^{UKS}_- = \gamma^{\beta\beta}, \tag{16}$$
$$\eta^{UKS}_{++} = \|\nabla\gamma^{\alpha\alpha}\|^2, \quad \eta^{UKS}_{+-} = \nabla\gamma^{\alpha\alpha}\cdot\nabla\gamma^{\beta\beta}, \quad \eta^{UKS}_{--} = \|\nabla\gamma^{\beta\beta}\|^2. \tag{17}$$

The coupling of spin and spatial degrees of freedom neccesitate the introduction of a more complidated set of auxillary variables

$$\rho^{GKS}_\pm = \frac{1}{2}n \pm \frac{1}{2}\sqrt{m_x^2 + m_y^2 + m_z^2}, \tag{18}$$

$$\eta^{GKS}_{\pm\pm} = \frac{1}{2}\|\nabla n\|^2 + \frac{1}{2}\left(\sum_{i=x,y,z}\|\nabla m_i\|^2\right) \pm \frac{\zeta_\nabla}{2}\sqrt{\sum_{i=x,y,z}\nabla n\cdot\nabla m_i}, \tag{19}$$

$$\eta^{GKS}_{+-} = \frac{1}{2}\|\nabla n\|^2 - \frac{1}{2}\left(\sum_{i=x,y,z}\|\nabla m_i\|^2\right) \tag{20}$$

$$\zeta_\nabla = \mathrm{sgn}\left(\sum_{i=x,y,z}(\nabla n\cdot\nabla m_i)m_i\right) \tag{21}$$

The introduction of the auxilarary variables neccesssitates the development of a kernel g defined as $g(U) = f(V)$, such that

$$E^{xc}[\boldsymbol{\gamma}] = \int_{\mathbb{R}^3} \mathrm{d}r\, g(U(r)), \quad U(r) \equiv U(V(\boldsymbol{\gamma}(r))), \tag{22}$$

1 Basis Set Expansions

It is typically the case that on expands $\boldsymbol{\gamma}$ in some basis $\{\chi_\mu(r)\}_{\mu=1}^{N_b}$. This is typically achieved through the introduction of a density matrix, $\mathbf{D} \in \mathbb{C}^{2N_b\times 2N_b}$ which adopts an identical spin structure to $\boldsymbol{\gamma}$,

$$\mathbf{D} = \begin{bmatrix}\mathbf{D}^{\alpha\alpha} & \mathbf{D}^{\alpha\beta}\\ \mathbf{D}^{\beta\alpha} & \mathbf{D}^{\beta\beta}\end{bmatrix}, \quad \mathbf{D}^{\sigma\sigma'} \in \mathbb{C}^{N_b\times N_b},\ \sigma,\sigma' \in \{\alpha,\beta\}, \tag{23}$$

such that

$$\gamma^{\sigma\sigma'}(r) = \sum_{\mu\nu} D^{\sigma\sigma'}_{\mu\nu}\chi_\mu(r)\chi_\nu(r). \tag{24}$$

In particular, it is also possible to define analogous Pauli basis components for the density matrix such that

$$\mathbf{D} = \frac{1}{2}\mathbf{N}\otimes\mathbf{I}_2 + \frac{1}{2}\mathbf{M}_z\otimes\boldsymbol{\sigma}_z + \frac{1}{2}\mathbf{M}_y\otimes\boldsymbol{\sigma}_y + \frac{1}{2}\mathbf{M}_x\otimes\boldsymbol{\sigma}_x, \tag{25}$$

where

$$\mathbf{N} = \mathbf{D}^{\alpha\alpha} + \mathbf{D}^{\beta\beta}, \tag{26}$$

$$\mathbf{M}_z = \mathbf{D}^{\alpha\alpha} - \mathbf{D}^{\beta\beta}, \tag{27}$$

$$\mathbf{M}_y = -2\Im\mathbf{D}^{\alpha\beta}, \tag{28}$$

$$\mathbf{M}_x = 2\Re\mathbf{D}^{\alpha\beta}. \tag{29}$$

such that

$$n(r) = \sum_{\mu\nu} N_{\mu\nu}\chi_\mu(r)\chi_\nu(r), \tag{30}$$

$$m_i(r) = \sum_{\mu\nu} (\mathbf{M}_i)_{\mu\nu}\chi_\mu(r)\chi_\nu(r), \quad i \in \{x, y, z\}. \tag{31}$$

2 Numerical Integration

The nonlinear character of the integration kernel f necessitates the evaluation of the XC energy (and associated quantities such as its derivatives) via numerical integration. For molecular integrations, i.e. those with non-trivial character in the vacinity of atomic nuclei, numerical integrations may be carried out via composite quadrature rule

$$E^{xc} \approx \sum_A \sum_{j\in\mathcal{Q}^A} w_j^A g(U(\boldsymbol{\gamma}(r_j^A))) \tag{32}$$

where $\mathcal{Q}^A$ is a spherical product quadrature centered at atomic center A. To avoid double-counting, the quadrature weights of $\mathcal{Q}^A$ are modified by a partition function

$$w_j^A = p_A(r_j^A)w_j, \quad j \in \mathcal{Q}^A, \tag{33}$$

where w_j is an unmodified quadrature weight associated with the base quadrature of $\mathcal{Q}^A$. The partition function p_A generally depends on the entire molecular geometry, though domain decomposition in often possible.

3 Gradients

This change of variables $V \mapsto U$ necessacarily complicates the derivation of functional gradients through the chain-rule. Given an arbitrary perturbation X, we may express the XC gradient as

$$\frac{\partial E^{xc}}{\partial X} = \sum_{IJ} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g(U)}{\partial U_I}\frac{\partial U_I}{\partial V_J}\frac{\partial V_J}{\partial X}, \tag{34}$$

$$\approx \sum_A \sum_{j\in\mathcal{Q}^A} \sum_{IJ} \frac{\partial w_j^A}{\partial X} g(U(r_j^A)) + w_j^A \frac{\partial g(U(r_j^A))}{\partial U_I}\frac{\partial U_I(r_j^A)}{\partial V_J}\frac{\partial V_J(r_j^A)}{\partial X} \tag{35}$$

The sums over I and J run over the auxillary (U) and density (V) variables, respectively. This decomposition breaks down the evaluation of the gradient into three contributions

1. Derivatives of the XC kernel with respect to the auxillary variables ($\frac{\partial g}{\partial U_I}$). These are independent of perturbation and spin classification, and are typically handled by external libraries (Libxc, ExchCXX, etc) for point-wise evaluations. As such, we do not consider them here.

2. The Jacobian for the variable transformation $V \mapsto U$ ($\mathcal{J}_{IJ} = \frac{\partial U_I}{\partial V_J}$). These are also independent of the perturbation but depend on the spin class being treated (RKS,UKS,GKS).

3. Two perturbation dependent pieces ($\frac{\partial w_j}{\partial X}$, $\frac{\partial V_J}{\partial X}$) which depend both on the perturbation and spin classification.

3.1 Auxillary Variable Jacobian

3.1.1 RKS

LDA - trivial.

GGA:

$$\frac{\partial \eta}{\partial(\nabla_i n)} = \frac{\partial}{\partial(\nabla_i n)} \nabla n \cdot \nabla n = 2\nabla_i n \tag{36}$$

3.1.2 UKS

LDA:

$$\frac{\partial \rho_\pm^{UKS}}{\partial n} = \frac{1}{2}\frac{\partial}{\partial n}(n \pm m_z) = \frac{1}{2} \tag{37}$$

$$\frac{\partial \rho_\pm^{UKS}}{\partial m_z} = \frac{1}{2}\frac{\partial}{\partial m_z}(n \pm m_z) = \pm\frac{1}{2} \tag{38}$$

GGA:

$$\begin{aligned}\frac{\partial \eta_{\pm\pm}}{\partial \nabla_i n} &= \frac{1}{4}\frac{\partial}{\partial \nabla_i n}\left((\nabla n \pm \nabla m_z)\cdot(\nabla n \pm \nabla m_z)\right) \\ &= \frac{1}{4}\frac{\partial}{\partial \nabla_i n}\left(\nabla n \cdot \nabla n \pm 2\nabla n \cdot \nabla m_z + \nabla m_z \cdot \nabla m_z\right) \\ &= \frac{1}{2}(\nabla_i n \pm \nabla_i m_z)\end{aligned} \tag{39}$$

$$\begin{aligned}\frac{\partial \eta_{\pm\pm}}{\partial \nabla_i m_z} &= \frac{1}{4}\frac{\partial}{\partial \nabla_i m_z}\left((\nabla n \pm \nabla m_z)\cdot(\nabla n \pm \nabla m_z)\right) \\ &= \frac{1}{4}\frac{\partial}{\partial \nabla_i m_z}\left(\nabla n \cdot \nabla n \pm 2\nabla n \cdot \nabla m_z + \nabla m_z \cdot \nabla m_z\right) \\ &= \frac{1}{2}(\nabla_i m_z \pm \nabla_i n)\end{aligned} \tag{40}$$

$$\begin{aligned}\frac{\partial \eta_{+-}}{\partial \nabla_i n} &= \frac{1}{4}\frac{\partial}{\partial \nabla_i n}\left((\nabla n + \nabla m_z)\cdot(\nabla n - \nabla m_z)\right) \\ &= \frac{1}{4}\frac{\partial}{\partial \nabla_i n}\left(\nabla n \cdot \nabla n - \nabla m_z \cdot \nabla m_z\right) \\ &= \frac{1}{2}\nabla_i n\end{aligned} \tag{41}$$

$$\begin{aligned}\frac{\partial \eta_{+-}}{\partial \nabla_i m_z} &= \frac{1}{4}\frac{\partial}{\partial \nabla_i m_z}\left((\nabla n + \nabla m_z)\cdot(\nabla n - \nabla m_z)\right) \\ &= \frac{1}{4}\frac{\partial}{\partial \nabla_i m_z}\left(\nabla n \cdot \nabla n - \nabla m_z \cdot \nabla m_z\right) \\ &= -\frac{1}{2}\nabla_i m_z\end{aligned} \tag{42}$$

3.1.3 GKS

TODO

3.2 Exchange-Correlation Potentials

Expressions for XC potentials may be derived as the gradient of the XC energy with respect to density matrix elements. Here we derive the primary perturbation dependent components and the final expressions

3.2.1 RKS XC Potential

Perturbation derivatives:

$$\frac{\partial n}{\partial N_{\lambda\kappa}} = \frac{\partial}{\partial N_{\lambda\kappa}} \sum_{\mu\nu} N_{\mu\nu}\chi_\mu\chi_\nu = \chi_\lambda\chi_\kappa \tag{43}$$

$$\frac{\partial \nabla n}{\partial N_{\lambda\kappa}} = \frac{\partial}{\partial N_{\lambda\kappa}} \sum_{\mu\nu} N_{\mu\nu}\nabla(\chi_\mu\chi_\nu) = \nabla(\chi_\lambda\chi_\kappa) \tag{44}$$

LDA:

$$\frac{\partial E^{xc}}{\partial N_{\mu\nu}} = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g(\mathbf{r})}{\partial n}\frac{\partial n}{\partial N_{\mu\nu}} = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g(\mathbf{r})}{\partial n}\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) \tag{45}$$

$$\frac{\partial E^{xc}}{\partial D^{\alpha\alpha}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}}\frac{\partial N_{\mu\nu}}{\partial D^{\alpha\alpha}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}} \tag{46}$$

GGA:

$$\begin{aligned}\frac{\partial E^{xc}}{\partial N_{\mu\nu}} &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g(\mathbf{r})}{\partial n}\frac{\partial n}{\partial N_{\mu\nu}} + \frac{\partial g(\mathbf{r})}{\partial \eta}\frac{\partial \eta}{\partial \nabla n}\cdot\frac{\partial \nabla n}{\partial N_{\mu\nu}} \\ &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g(\mathbf{r})}{\partial n}\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) + \frac{\partial g(\mathbf{r})}{\partial \eta}(2\nabla n)\cdot\nabla(\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})) \\ &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g(\mathbf{r})}{\partial n}\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) + 2\frac{\partial g(\mathbf{r})}{\partial \eta}\nabla n\cdot\nabla(\chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}))\end{aligned} \tag{47}$$

$$\frac{\partial E^{xc}}{\partial D^{\alpha\alpha}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}}\frac{\partial N_{\mu\nu}}{\partial D^{\alpha\alpha}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}} \tag{48}$$

3.2.2 UKS XC Potential

Perturbation derivatives:

$$\frac{\partial n}{\partial M^z_{\mu\nu}} = \frac{\partial \nabla n}{\partial M^z_{\mu\nu}} = \frac{\partial m_z}{\partial N_{\mu\nu}} = \frac{\partial \nabla m_z}{\partial N_{\mu\nu}} = 0 \tag{49}$$

$$\frac{\partial m_z}{\partial M^z_{\lambda\kappa}} = \frac{\partial}{\partial M^z_{\lambda\kappa}} \sum_{\mu\nu} M^z_{\mu\nu}\chi_\mu\chi_\nu = \chi_\lambda\chi_\kappa \tag{50}$$

$$\frac{\partial \nabla m_z}{\partial M^z_{\lambda\kappa}} = \frac{\partial}{\partial M^z_{\lambda\kappa}} \sum_{\mu\nu} M^z_{\mu\nu}\nabla(\chi_\mu\chi_\nu) = \nabla(\chi_\lambda\chi_\kappa) \tag{51}$$

LDA:

$$\begin{aligned}\frac{\partial E^{xc}}{\partial N_{\mu\nu}} &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial n}{\partial N_{\mu\nu}}\left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial n} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial n}\right) \\ &= \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left(\frac{\partial g}{\partial \rho_+} + \frac{\partial g}{\partial \rho_-}\right)\chi_\mu\chi_\nu\end{aligned} \tag{52}$$

$$\begin{aligned}\frac{\partial E^{xc}}{\partial M^z_{\mu\nu}} &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial m_z}{\partial M^z_{\mu\nu}}\left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial m_z} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial m_z}\right) \\ &= \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left(\frac{\partial g}{\partial \rho_+} - \frac{\partial g}{\partial \rho_-}\right)\chi_\mu\chi_\nu\end{aligned} \tag{53}$$

$$\begin{aligned}\frac{\partial E^{xc}}{\partial D^{\alpha\alpha}_{\mu\nu}} &= \frac{\partial E^{xc}}{\partial N_{\mu\nu}}\frac{\partial N_{\mu\nu}}{\partial D^{\alpha\alpha}_{\mu\nu}} + \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}}\frac{\partial M^z_{\mu\nu}}{\partial D^{\alpha\alpha}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}} + \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}} \\ &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g}{\partial \rho_+}\chi_\mu\chi_\nu\end{aligned} \tag{54}$$

$$\begin{aligned}\frac{\partial E^{xc}}{\partial D^{\beta\beta}_{\mu\nu}} &= \frac{\partial E^{xc}}{\partial N_{\mu\nu}}\frac{\partial N_{\mu\nu}}{\partial D^{\beta\beta}_{\mu\nu}} + \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}}\frac{\partial M^z_{\mu\nu}}{\partial D^{\beta\beta}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}} - \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}} \\ &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g}{\partial \rho_-}\chi_\mu\chi_\nu\end{aligned} \tag{55}$$

GGA:

$$\begin{aligned}
\frac{\partial E^{xc}}{\partial N_{\mu\nu}} &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial n}{\partial N_{\mu\nu}} \left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial n} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial n} \right) + \frac{\partial \nabla n}{\partial N_{\mu\nu}} \cdot \left(\frac{\partial g}{\partial \eta_{++}}\frac{\partial \eta_{++}}{\partial \nabla n} + \frac{\partial g}{\partial \eta_{+-}}\frac{\partial \eta_{+-}}{\partial \nabla n} + \frac{\partial g}{\partial \eta_{--}}\frac{\partial \eta_{--}}{\partial \nabla n} \right) \\
&= \frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left(\frac{\partial g}{\partial \rho_+} + \frac{\partial g}{\partial \rho_-} \right) \chi_\mu \chi_\nu + \left(\frac{\partial g}{\partial \eta_{++}}(\nabla n + \nabla m_z) + \frac{\partial g}{\partial \eta_{+-}}\nabla n + \frac{\partial g}{\partial \eta_{--}}(\nabla n - \nabla m_z) \right) \cdot \nabla(\chi_\mu \chi_\nu) \\
&= \frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left(\frac{\partial g}{\partial \rho_+} + \frac{\partial g}{\partial \rho_-} \right) \chi_\mu \chi_\nu + \left(\left[\frac{\partial g}{\partial \eta_{++}} + \frac{\partial g}{\partial \eta_{+-}} + \frac{\partial g}{\partial \eta_{--}} \right] \nabla n + \left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{--}} \right] \nabla m_z \right) \cdot \nabla(\chi_\mu \chi_\nu)
\end{aligned} \tag{56}$$

$$\begin{aligned}
\frac{\partial E^{xc}}{\partial M^z_{\mu\nu}} &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial m_z}{\partial M^z_{\mu\nu}} \left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial m_z} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial m_z} \right) + \frac{\partial \nabla n}{\partial M^z_{\mu\nu}} \cdot \left(\frac{\partial g}{\partial \eta_{++}}\frac{\partial \eta_{++}}{\partial \nabla m_z} + \frac{\partial g}{\partial \eta_{+-}}\frac{\partial \eta_{+-}}{\partial \nabla m_z} + \frac{\partial g}{\partial \eta_{--}}\frac{\partial \eta_{--}}{\partial \nabla m_z} \right) \\
&= \frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left(\frac{\partial g}{\partial \rho_+} - \frac{\partial g}{\partial \rho_-} \right) \chi_\mu \chi_\nu + \left(\frac{\partial g}{\partial \eta_{++}}(\nabla n + \nabla m_z) - \frac{\partial g}{\partial \eta_{+-}}\nabla m_z - \frac{\partial g}{\partial \eta_{--}}(\nabla n - \nabla m_z) \right) \cdot \nabla(\chi_\mu \chi_\nu) \\
&= \frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left(\frac{\partial g}{\partial \rho_+} - \frac{\partial g}{\partial \rho_-} \right) \chi_\mu \chi_\nu + \left(\left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{--}} \right] \nabla n + \left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{+-}} + \frac{\partial g}{\partial \eta_{--}} \right] \nabla m_z \right) \cdot \nabla(\chi_\mu \chi_\nu)
\end{aligned} \tag{57}$$

$$\frac{\partial E^{xc}}{\partial D^{\alpha\alpha}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}}\frac{\partial N_{\mu\nu}}{\partial D^{\alpha\alpha}_{\mu\nu}} + \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}}\frac{\partial M^z_{\mu\nu}}{\partial D^{\alpha\alpha}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}} + \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}}$$

$$= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g}{\partial \rho_+}\chi_\mu \chi_\nu + \left(\frac{\partial g}{\partial \eta_{++}}(\nabla n + \nabla m_z) + \frac{1}{2}\frac{\partial g}{\partial \eta_{+-}}(\nabla n - \nabla m_z) \right) \cdot \nabla(\chi_\mu \chi_\nu) \tag{58}$$

$$= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g}{\partial \rho_+}\chi_\mu \chi_\nu + \left(2\frac{\partial g}{\partial \eta_{++}}\nabla \rho_+ + \frac{\partial g}{\partial \eta_{+-}}\nabla \rho_- \right) \cdot \nabla(\chi_\mu \chi_\nu) \tag{59}$$

$$\frac{\partial E^{xc}}{\partial D^{\beta\beta}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}}\frac{\partial N_{\mu\nu}}{\partial D^{\beta\beta}_{\mu\nu}} + \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}}\frac{\partial M^z_{\mu\nu}}{\partial D^{\beta\beta}_{\mu\nu}} = \frac{\partial E^{xc}}{\partial N_{\mu\nu}} - \frac{\partial E^{xc}}{\partial M^z_{\mu\nu}}$$

$$= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g}{\partial \rho_-}\chi_\mu \chi_\nu + \left(\frac{\partial g}{\partial \eta_{--}}(\nabla n - \nabla m_z) + \frac{1}{2}\frac{\partial g}{\partial \eta_{+-}}(\nabla n + \nabla m_z) \right) \cdot \nabla(\chi_\mu \chi_\nu) \tag{60}$$

$$= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial g}{\partial \rho_-}\chi_\mu \chi_\nu + \left(2\frac{\partial g}{\partial \eta_{--}}\nabla \rho_- + \frac{\partial g}{\partial \eta_{+-}}\nabla \rho_+ \right) \cdot \nabla(\chi_\mu \chi_\nu) \tag{61}$$

3.3 Nuclear Gradients

3.3.1 RKS

Let

$$Z_\mu^N = \sum_\nu N_{\mu\nu}\chi_\nu \tag{62}$$

$$Z_\mu^{Nj} = \sum_\nu N_{\mu\nu}(\nabla_j \chi_\nu) \tag{63}$$

Perturbation derivatives:

$$\begin{aligned}\frac{\partial n}{\partial R_{A_i}} &= \sum_{\mu\nu} N_{\mu\nu}\frac{\partial}{\partial R_{A_i}}(\chi_\mu\chi_\nu) = 2\sum_{\mu\nu} N_{\mu\nu}\frac{\partial \chi_\mu}{\partial R_{A_i}}\chi_\nu = -2\sum_{\mu\in A}\sum_\nu N_{\mu\nu}(\nabla_i\chi_\mu)\chi_\nu \\ &= -2\sum_{\mu\in A}(\nabla_i\chi_\mu)Z_\mu^N\end{aligned} \tag{64}$$

$$\begin{aligned}\frac{\partial \nabla_j n}{\partial R_{A_i}} &= \sum_{\mu\nu} N_{\mu\nu}\frac{\partial}{\partial R_{A_i}}\nabla_j(\chi_\mu\chi_\nu) = \sum_{\mu\nu} N_{\mu\nu}\nabla_j\frac{\partial}{\partial R_{A_i}}(\chi_\mu\chi_\nu) = 2\sum_{\mu\nu} N_{\mu\nu}\nabla_j\left(\frac{\partial \chi_\mu}{\partial R_{A_i}}\chi_\nu\right) \\ &= -2\sum_{\mu\in A}\sum_\nu N_{\mu\nu}\nabla_j\left((\nabla_i\chi_\mu)\chi_\nu\right) \\ &= -2\sum_{\mu\in A}\sum_\nu N_{\mu\nu}\left((\nabla^{(2)}_{ij}\chi_\mu)\chi_\nu + (\nabla_i\chi_\mu)(\nabla_j\chi_\nu)\right) \\ &= -2\sum_{\mu\in A}\left((\nabla^{(2)}_{ij}\chi_\mu)Z_\mu^N + (\nabla_i\chi_\mu)Z_\mu^{Nj}\right)\end{aligned} \tag{65}$$

LDA:

$$\frac{\partial E^{xc}}{\partial R_{A_i}} = \int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,\frac{\partial g(\mathbf{r})}{\partial n}\frac{\partial n}{\partial R_{A_i}} = -2\sum_{\mu\in A}\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,\frac{\partial g(\mathbf{r})}{\partial n}(\nabla_i\chi_\mu)Z_\mu^N \tag{66}$$

GGA:

$$\begin{aligned}\frac{\partial E^{xc}}{\partial R_{A_i}} &= \int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,\frac{\partial g(\mathbf{r})}{\partial n}\frac{\partial n}{\partial R_{A_i}} + \frac{\partial g(\mathbf{r})}{\partial \eta}\frac{\partial \eta}{\partial \nabla n}\cdot\frac{\partial \nabla n}{\partial R_{A_i}} \\ &= -2\sum_{\mu\in A}\int_{\mathbb{R}^3}\mathrm{d}\mathbf{r}\,\frac{\partial g(\mathbf{r})}{\partial n}(\nabla_i\chi_\mu)Z_\mu^N + 2\frac{\partial g(\mathbf{r})}{\partial \eta}\sum_j \nabla_j n\left((\nabla^{(2)}_{ij}\chi_\mu)Z_\mu^N + (\nabla_i\chi_\mu)Z_\mu^{Nj}\right)\end{aligned} \tag{67}$$

3.3.2 UKS

Perturbation derivatives:

$$\frac{\partial m_z}{\partial R_{A_i}} = -2\sum_{\mu\in A}\sum_\nu M^z_{\mu\nu}(\nabla_i\chi_\mu)\chi_\nu \tag{68}$$

$$\frac{\partial \nabla_j m_z}{\partial R_{A_i}} = -2\sum_{\mu\in A}\sum_\nu M^z_{\mu\nu}\left((\nabla^{(2)}_{ij}\chi_\mu)\chi_\nu + (\nabla_i\chi_\mu)(\nabla_j\chi_\nu)\right) \tag{69}$$

LDA:

$$
\begin{aligned}
\frac{\partial E^{xc}}{\partial R_{A_i}} &= \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial n}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial n} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial n} \right) + \frac{\partial m_z}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial m_z} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial m_z} \right) \\
&= \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\partial n}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+} + \frac{\partial g}{\partial \rho_-} \right) + \frac{\partial m_z}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+} - \frac{\partial g}{\partial \rho_-} \right) \\
&= -\sum_{\mu \in A}\sum_{\nu} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left[N_{\mu\nu} \left(\frac{\partial g}{\partial \rho_+} + \frac{\partial g}{\partial \rho_-} \right) + M^z_{\mu\nu} \left(\frac{\partial g}{\partial \rho_+} - \frac{\partial g}{\partial \rho_-} \right) \right] (\nabla_i \chi_\mu)\chi_\nu \qquad (70) \\
&= -2\sum_{\mu \in A}\sum_{\nu} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \left[D^{\alpha\alpha}_{\mu\nu} \frac{\partial g}{\partial \rho_+} + D^{\beta\beta}_{\mu\nu} \frac{\partial g}{\partial \rho_-} \right] (\nabla_i \chi_\mu)\chi_\nu \qquad (71)
\end{aligned}
$$

GGA:

$$
\begin{aligned}
\frac{\partial E^{xc}}{\partial R_{A_i}} = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, & \frac{\partial n}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial n} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial n} \right) + \frac{\partial m_z}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+}\frac{\partial \rho_+}{\partial m_z} + \frac{\partial g}{\partial \rho_-}\frac{\partial \rho_-}{\partial m_z} \right) + \\
& \frac{\partial \nabla n}{\partial R_{A_i}} \cdot \left(\frac{\partial g}{\partial \eta_{++}}\frac{\partial \rho_+}{\partial \nabla n} + \frac{\partial g}{\partial \eta_{+-}}\frac{\partial \rho_-}{\partial \nabla n} + \frac{\partial g}{\partial \eta_{--}}\frac{\partial \rho_+}{\partial \nabla n} \right) + \\
& \frac{\partial \nabla m_z}{\partial R_{A_i}} \cdot \left(\frac{\partial g}{\partial \eta_{++}}\frac{\partial \rho_+}{\partial \nabla m_z} + \frac{\partial g}{\partial \eta_{+-}}\frac{\partial \rho_-}{\partial \nabla m_z} + \frac{\partial g}{\partial \eta_{--}}\frac{\partial \rho_+}{\partial \nabla m_z} \right) \\
= \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, & \frac{\partial n}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+} + \frac{\partial g}{\partial \rho_-} \right) + \frac{\partial m_z}{\partial R_{A_i}} \left(\frac{\partial g}{\partial \rho_+} - \frac{\partial g}{\partial \rho_-} \right) + \\
& \frac{\partial \nabla n}{\partial R_{A_i}} \cdot \left(\left[\frac{\partial g}{\partial \eta_{++}} + \frac{\partial g}{\partial \eta_{+-}} + \frac{\partial g}{\partial \eta_{--}} \right] \nabla n + \left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{--}} \right] \nabla m_z \right) + \\
& \frac{\partial \nabla m_z}{\partial R_{A_i}} \cdot \left(\left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{--}} \right] \nabla n + \left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{+-}} + \frac{\partial g}{\partial \eta_{--}} \right] \nabla m_z \right) \\
= -\sum_{\mu \in A}\sum_{\nu} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, & \left[N_{\mu\nu} \left(\frac{\partial g}{\partial \rho_+} + \frac{\partial g}{\partial \rho_-} \right) + M^z_{\mu\nu} \left(\frac{\partial g}{\partial \rho_+} - \frac{\partial g}{\partial \rho_-} \right) \right] (\nabla_i \chi_\mu)\chi_\nu + \\
& \sum_j \Bigg\{ N_{\mu\nu} \left(\left[\frac{\partial g}{\partial \eta_{++}} + \frac{\partial g}{\partial \eta_{+-}} + \frac{\partial g}{\partial \eta_{--}} \right] \nabla_j n + \left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{--}} \right] \nabla_j m_z \right) + \\
& M^z_{\mu\nu} \left(\left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{--}} \right] \nabla_j n + \left[\frac{\partial g}{\partial \eta_{++}} - \frac{\partial g}{\partial \eta_{+-}} + \frac{\partial g}{\partial \eta_{--}} \right] \nabla_j m_z \right) \Bigg\} \left((\nabla^{(2)}_{ij}\chi_\mu)\chi_\nu + (\nabla_i \chi_\mu)(\nabla_j \chi_\nu) \right)
\end{aligned}
\qquad (72)
$$

$$
\rho(r_A) = \sum_{BC}\sum_{\mu \in B, \nu \in C} P_{\mu\nu}\chi_\mu(R_B, r_A)\chi_\nu(R_C, r_A) \qquad (73)
$$

$$
\begin{aligned}
\frac{\partial \rho(r_A)}{\partial R_C} &= \sum_{BC}\sum_{\mu \in B, \nu \in C} P_{\mu\nu}\frac{\partial}{\partial R_D}(\chi_\mu(R_B, r_A)\chi_\nu(R_C, r_A)) \qquad (74) \\
&= \sum_{BC}\sum_{\mu \in B, \nu \in C} P_{\mu\nu}\frac{\partial \chi_\mu(R_B, r_A)}{\partial R_D}\chi_\nu(R_C, r_A) + \sum_{BC}\sum_{\mu \in B, \nu \in C} P_{\mu\nu}\chi_\mu(R_B, r_A)\frac{\partial \chi_\nu(R_C, r_A)}{\partial R_D} \qquad (75) \\
&= \sum_{BC}\sum_{\mu \in B, \nu \in C} P_{\mu\nu}\frac{\partial \chi_\mu(R_B, r_A)}{\partial R_D}\chi_\nu(R_C, r_A) + \sum_{BC}\sum_{\mu \in C, \nu \in B} P_{\mu\nu}\chi_\nu(R_B, r_A)\frac{\partial \chi_\mu(R_B, r_A)}{\partial R_D} \qquad (76) \\
& \qquad (77)
\end{aligned}
$$