1 Derivative Evaluation

Here we explore the evaluation of the NMR shielding tensor σ^K of nucleus K as an example of calculating the second order response properties.
The expression for the shielding tensor is given by:

$$\sigma_{\alpha\beta}^K = \frac{\mathrm{d}^2 E}{\mathrm{d}B_\beta\, \mathrm{d}m_{K\alpha}}\Big|_{\mathbf{B},\boldsymbol{m}_K=\mathbf{0}} \tag{1}$$

The one-electron Hamiltonian in the magnetic field is (in Atomic Unit):

$$h(\mathbf{r},\mathbf{B},\mathbf{m}) = \frac{\boldsymbol{\pi}^2}{2} - \phi(\mathbf{r}) \tag{2}$$

in which:

$$\begin{aligned} \boldsymbol{\pi} =& \mathbf{p} + \mathbf{A}(\mathbf{r},\mathbf{B},\mathbf{m}) \\ =& -i\boldsymbol{\nabla} + \mathbf{A}(\mathbf{r},\mathbf{B},\mathbf{m}) \end{aligned} \tag{3}$$

$$\begin{aligned} \mathbf{A}(\mathbf{r},\mathbf{B},\mathbf{m}) =& \mathbf{A}_0 + \sum_K \mathbf{A}_K \\ =& \frac{1}{2}\mathbf{B}\times\mathbf{r}_0 + \alpha^2 \sum_K \frac{\mathbf{m}_K \times \mathbf{r}_K}{r_K^3} \end{aligned} \tag{4}$$

The one-electron Hamiltonian expands to be (details to be added later):

$$h(\mathbf{r},\mathbf{B},\mathbf{m}) = \frac{\mathbf{p}^2}{2} + \mathbf{A}\cdot\mathbf{p} + \mathbf{B}\cdot\mathbf{s} + \frac{\mathbf{A}^2}{2} - \phi(\mathbf{r}) \tag{5}$$

And the molecular Hamiltonian is given by:

$$H = \sum_i \frac{\mathbf{p}_i^2}{2} - \sum_{k,i} \frac{Z_K}{r_{iK}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_{K>L} \frac{Z_K Z_L}{R_{KL}} + \sum_i \mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i + \sum_i \mathbf{B}(\mathbf{r}_i)\cdot\mathbf{s}_i - \sum_i \phi(\mathbf{r}_i) + \sum_i \frac{\mathbf{A}^2(\mathbf{r}_i)}{2} \tag{6}$$

To evaluate the shielding tensor, we could write it into density matrix formalism. From previous chapter, we know that, for general one-body operator $\hat{O}$ and two-body operator $\hat{G}$:

$$\bar{O} = \frac{\langle\Psi|\hat{O}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \sum_{pq} o_{pq}\gamma_{qp} \tag{7}$$

$$\bar{G} = \frac{\langle\Psi|\hat{G}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{1}{4}\sum_{pqrs} \langle pq|\hat{g}|rs\rangle_{\mathrm{A}} \Gamma_{rspq} \tag{8}$$

TODO: derive the expression of shielding tensor in density matrix formalism

details to be added:

$$\frac{\partial h}{\partial B_i} = -\frac{i}{2}(\mathbf{r}\times\boldsymbol{\nabla})_i \tag{9}$$

$$\frac{\partial h}{\partial m_{Kj}} = -\frac{(\mathbf{r}_K\times\boldsymbol{\nabla})_j}{\mathbf{r}_K^3} \tag{10}$$

$$\frac{\partial^2 h}{\partial B_i \partial m_{Kj}} = \frac{1}{2}\frac{\mathbf{r}\cdot\mathbf{r}_K\delta_{ij} - r_j(\mathbf{r}_K)_i}{\mathbf{r}_K^3} \tag{11}$$

1.1 First Derivative

Taking first derivative w.r.t m_K or $\mathbf{B}$?
Could try both way.

$$\begin{aligned}
\frac{\mathrm{d}\mathcal{L}_{\mathrm{CC}}}{\mathrm{d}m_{K\alpha}} =& \frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial m_{K\alpha}} + \sum_{bj} \frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial \kappa_{bj}} \frac{\partial \kappa_{bj}}{\partial m_{K\alpha}} + \sum_{\mu} \frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial t_{\mu}} \frac{\partial t_{\mu}}{\partial m_{K\alpha}} \\
&+ \sum_{\nu} \frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial \lambda_{\nu}} \frac{\partial \lambda_{\nu}}{\partial m_{K\alpha}} + \sum_{z_{ai}} \frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial z_{ai}} \frac{\partial z_{ai}}{\partial m_{K\alpha}} + \sum_{pq} \frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial I_{pq}} \frac{\partial I_{pq}}{\partial m_{K\alpha}} \\
=& \frac{\partial \mathcal{L}_{\mathrm{CC}}}{\partial m_{K\alpha}} \qquad (12) \\
=& \text{density expression?} \qquad (13)
\end{aligned}$$

1.2 Second Derivative

The second derivative would involve density response terms. ($D_{\mu\nu}^{B_\beta}$ for example)