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## 1 NMR Shielding

Shielding Tensor:

$$\sigma_{\beta\alpha}^K = \frac{d^2 E}{dB_\alpha dm_{K_\beta}} \Big|_{\mathbf{B}, \mathbf{m}_K=0} \quad (1)$$

How do I parameterize energy  $E$  with  $\mathbf{B}$  and  $\mathbf{m}_K$ ?

The one-electronic Hamiltonian in magnetic field:

$$h(\mathbf{r}, \mathbf{B}, \mathbf{m}) = \frac{1}{2}\boldsymbol{\pi}^2 - \phi(\mathbf{r}) \quad (2)$$

in which:

$$\boldsymbol{\pi} = -i\nabla + \mathbf{A} \quad (3)$$

is the kinetic momentum operator.

Vector potential:

$$\mathbf{A}_i = \mathbf{A}_0(\mathbf{r}_i) + \sum_K \mathbf{A}_K(\mathbf{r}_i) \quad (4)$$

with:

$$\mathbf{A}_0(\mathbf{r}_i) = \frac{1}{2}\mathbf{B} \times \mathbf{r}_0 \quad \mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r}) \quad (5)$$

$$\mathbf{A}_K(\mathbf{r}_i) = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3} \quad \mathbf{B}_K(\mathbf{r}) = \nabla \times \mathbf{A}_K(\mathbf{r}) \quad (6)$$

The first part is contribution from the external magnetic field, the second part from the nuclear magnetic moments.

Now parameterize with MO coefficients / densities?

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## 2 SCF Level

$$\begin{aligned} E^{\text{SCF}} &= \sum_i^N h_{ii} + \frac{1}{2} \sum_{ij}^N \langle ij || ij \rangle \\ &= \sum_i \sum_{\mu\nu} C_{\mu i}^* h_{\mu\nu} C_{\nu i} + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle \end{aligned} \quad (7)$$

$$D_{\mu\nu}^{\text{SCF}} = \sum_i C_{\mu i}^* C_{\nu i} \quad (8)$$

$$C_{\mu p}(\lambda) = \sum_q C_{\mu q}(0) U_{qp}(\lambda) \quad (9)$$

At SCF level, the NMR shielding tensor is given as:

$$\sigma_{\beta\alpha}^{\text{SCF},K} = \left. \frac{d^2 E^{\text{SCF}}}{dB_\alpha dm_{K_\beta}} \right|_{\mathbf{B}, \mathbf{m}_K=0} \quad (10)$$

Taking the first derivative against the nuclear magnetic moment gives:

$$\begin{aligned} \frac{dE^{\text{SCF}}}{dm_{K_\beta}} &= \frac{d}{dm_{K_\beta}} \left( \sum_{i\mu\nu} C_{\mu i}^* h_{\mu\nu} C_{\nu i} \right) \\ &= \sum_{i\mu\nu} C_{\mu i}^* C_{\nu i} \frac{dh_{\mu\nu}}{dm_{K_\beta}} \\ &= \sum_{\mu\nu} D_{\mu\nu}^{\text{SCF}} \frac{dh_{\mu\nu}}{dm_{K_\beta}} \end{aligned} \quad (11)$$

Note that the MO coefficients are variationally determined so  $\frac{d\mathbf{C}}{dm_{K_\beta}} = \mathbf{0}$ , and the basis function does not depend on the nuclear magnetic moment, i.e.  $\frac{d\phi_\mu}{dm_{K_\beta}} = 0$ .

Now taking the second derivative w.r.t. the external magnetic field:

$$\begin{aligned} \sigma_{\beta\alpha}^{\text{SCF},K} &= \frac{d^2 E^{\text{SCF}}}{dB_\alpha dm_{K_\beta}} \\ &= \frac{d}{dB_\alpha} \left( \sum_{\mu\nu} D_{\mu\nu}^{\text{SCF}} \frac{dh_{\mu\nu}}{dm_{K_\beta}} \right) \\ &= \sum_{\mu\nu} D_{\mu\nu}^{\text{SCF}} \frac{d^2 h_{\mu\nu}}{dB_\alpha dm_{K_\beta}} + \sum_{\mu\nu} \frac{dD_{\mu\nu}^{\text{SCF}}}{dB_\alpha} \frac{dh_{\mu\nu}}{dm_{K_\beta}} \end{aligned} \quad (12)$$

The response of SCF density to the magnetic field perturbation is:

$$\begin{aligned} \frac{dD_{\mu\nu}^{\text{SCF}}}{dB_\alpha} &= \frac{d}{dB_\alpha} \left( \sum_i C_{\mu i}^*(\mathbf{B}) C_{\nu i}(\mathbf{B}) \right) \\ &= \frac{d}{dB_\alpha} \left( \sum_{ipq} C_{\mu p}^*(0) U_{pi}^*(\mathbf{B}) C_{\nu q}(0) U_{qi}(\mathbf{B}) \right) \\ &= \sum_{ip} C_{\mu p}^*(0) \frac{dU_{pi}^*(\mathbf{B})}{dB_\alpha} C_{\nu i}(\mathbf{B}) + \sum_{iq} C_{\mu i}^*(\mathbf{B}) \frac{dU_{qi}(\mathbf{B})}{dB_\alpha} C_{\nu q}(0) \end{aligned} \quad (13)$$

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$$= \sum_{ip} C_{\mu p}^* (U_{pi}^{B_\alpha})^* C_{\nu i} + \sum_{ip} C_{\mu i}^* U_{pi}^{B_\alpha} C_{\nu p} \quad (14)$$

The virtual-occupied block of  $\mathbf{U}^B$  is obtained from the CPSCF equations, and the occupied-occupied block is chosen according to the orthonormality condition.

### 3 MP2 Level

Lagrangian:

$$\mathcal{L}_{\text{MP2}} = E_{\text{HF}} + E_{\text{H}} + \frac{1}{2} \sum_{ai} (z_{ai} f_{ai} + z_{ai}^* f_{ai}^*) \quad (15)$$

Energies:

$$E_{\text{HF}} = \sum_{\mu\nu} h_{\mu\nu} D_{\mu\nu}^{\text{HF}} + \frac{1}{2} \sum_{ij} \langle ij || ij \rangle \quad (16)$$

$$\begin{aligned} E_{\text{H}} &= \sum_{ij} h_{ij} \gamma_{ij}^{\text{H}} + \sum_{ab} h_{ab} \gamma_{ab}^{\text{H}} + \sum_{pqrs} \langle pq || rs \rangle \Gamma_{rs}^{pq} \\ &= \sum_{\mu\nu} D_{\mu\nu}^{\text{H}} h_{\mu\nu}^{\text{AO}} + \sum_{pqrs} \langle pq || rs \rangle \Gamma_{rs}^{pq} \end{aligned} \quad (17)$$

Unrelaxed densities:

$$D_{\mu\nu}^{\text{HF}} = \sum_i C_{\mu i}^* C_{\mu i} \quad (18)$$

$$D_{\mu\nu}^{\text{H}} = \sum_{ij} C_{\mu i}^* C_{\nu j} \gamma_{ij}^{\text{H}} + \sum_{ab} C_{\mu a}^* C_{\nu b} \gamma_{ab}^{\text{H}} \quad (19)$$

(20)

Brillouin conditions:

$$\begin{aligned} \sum_{ai} z_{ai} f_{ai} &= \sum_{ai} z_{ai} h_{ai} + \sum_{aij} z_{ai} \langle aj || ij \rangle \\ &= \sum_{\mu\nu ai} z_{ai} C_{\mu a}^* C_{\nu i} h_{\mu\nu}^{\text{AO}} + \sum_{aij} z_{ai} \langle aj || ij \rangle \end{aligned} \quad (21)$$

$$\begin{aligned} \sum_{ai} z_{ai}^* f_{ai}^* &= \sum_{ai} z_{ai}^* h_{ai}^* + \sum_{aij} z_{ai}^* \langle aj || ij \rangle^* \\ &= \sum_{ai} z_{ia} h_{ia} + \sum_{aij} z_{ia} \langle ij || aj \rangle \\ &= \sum_{\mu\nu ai} z_{ia} C_{\mu i}^* C_{\nu a} h_{\mu\nu}^{\text{AO}} + \sum_{aij} z_{ia} \langle ij || aj \rangle \end{aligned} \quad (22)$$

#### 3.1 First Derivative

We take the first derivative w.r.t. the nuclear magnetic moment  $m_{K_\beta}$  as only one-electron Hamiltonian  $h_{\mu\nu}$  depends on  $m_{K_\beta}$ :

$$\begin{aligned} \frac{d\mathcal{L}_{\text{MP2}}}{dm_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} &= \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &+ \sum_{ijab} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial T_{ij}^{ab}} \right) \left( \frac{\partial T_{ij}^{ab}}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{ijab} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial (T_{ij}^{ab})^*} \right) \left( \frac{\partial (T_{ij}^{ab})^*}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &+ \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}} \right) \left( \frac{\partial \kappa_{bj}}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}^*} \right) \left( \frac{\partial \kappa_{bj}^*}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &+ \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}} \right) \left( \frac{\partial z_{bj}}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}^*} \right) \left( \frac{\partial z_{bj}^*}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} \end{aligned}$$

$$= \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \quad (23)$$

$$\begin{aligned} \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} &= \sum_{\mu\nu} D_{\mu\nu}^{\text{HF}} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{\mu\nu} D_{\mu\nu}^{\text{H}} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &\quad + \frac{1}{2} \sum_{\mu\nu ai} z_{ai} C_{\mu a}^* C_{\nu i} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} + \frac{1}{2} \sum_{\mu\nu ai} z_{ia} C_{\mu i}^* C_{\nu a} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &= \sum_{\mu\nu} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \left( D_{\mu\nu}^{\text{HF}} + D_{\mu\nu}^{\text{H}} + \frac{1}{2} \sum_{ai} z_{ai} C_{\mu a}^* C_{\nu i} + \frac{1}{2} \sum_{ai} z_{ia} C_{\mu i}^* C_{\nu a} \right) \end{aligned} \quad (24)$$

Using the Hermitian property of the one-body Hamiltonian:

$$\begin{aligned} &\sum_{\mu\nu ai} z_{ia} C_{\mu i}^* C_{\nu a} h_{\mu\nu}^{\text{AO}} \\ &\stackrel{\mu \leftrightarrow \nu}{=} \sum_{\mu\nu ai} (z_{ai} C_{\mu a}^* C_{\nu i})^* h_{\nu\mu}^{\text{AO}} \\ &= \sum_{\mu\nu ai} (z_{ai} C_{\mu a}^* C_{\nu i})^* h_{\mu\nu}^{\text{AO}} \end{aligned} \quad (25)$$

Therefore:

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} = \sum_{\mu\nu} D_{\mu\nu}^{\text{R}} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \quad (26)$$

in which the orbital-relaxed density matrix is:

$$\begin{aligned} D_{\mu\nu}^{\text{R}} &= D_{\mu\nu}^{\text{HF}} + D_{\mu\nu}^{\text{H}} + \frac{1}{2} D_{\mu\nu}^z + \frac{1}{2} D_{\mu\nu}^{z*} \\ &= \sum_i C_{\mu i}^* C_{\nu i} + \sum_{ij} C_{\mu i}^* \gamma_{ij}^{\text{H}} C_{\nu j} + \sum_{ab} C_{\mu a}^* \gamma_{ab}^{\text{H}} C_{\nu b} \\ &\quad + \frac{1}{2} \sum_{ai} C_{\mu a}^* z_{ai} C_{\nu i} + \frac{1}{2} \sum_{ai} (C_{\mu a}^* z_{ai} C_{\nu i})^* \end{aligned} \quad (27)$$

In order to obtain the orbital-relaxed density matrices, we need:

- MO coefficients  $C_{\mu p}$  from HF equation (Brillouin condition)
- MP2 amplitudes  $T_{ij}^{ab}$  from MP2 stationary condition
- Z-Vector  $z_{ai}$  from Z-Vector equation

## 3.2 Stationary Constraints

### Brillouin Condition

$$\begin{aligned} 0 &= \sum_{bj} \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}} \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{bj} \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}^*} \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &= \frac{1}{2} \sum_{ai} \left( \frac{\partial z_{ai}}{\partial z_{bj}} f_{ai} \Big|_{\mathbf{m}_K=\mathbf{0}} + \frac{\partial z_{ai}^*}{\partial z_{bj}^*} f_{ai}^* \Big|_{\mathbf{m}_K=\mathbf{0}} \right) \end{aligned}$$

$$\begin{aligned}
 &= \frac{1}{2} \sum_{ai} \left( \delta_{ab} \delta_{ij} f_{ai} + \delta_{ab} \delta_{ij} f_{ai}^* \right) \\
 &= \frac{1}{2} (f_{bj} + f_{bj}^*)
 \end{aligned} \tag{28}$$

$$f_{bj} = h_{bj} + \sum_i \langle bi || ji \rangle \tag{29}$$

### MP2 Stationary Condition

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=\mathbf{0}} = \frac{\partial E_H}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=\mathbf{0}} = 0 \tag{30}$$

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial (T_{mn}^{ef})^*} \Big|_{\mathbf{m}_K=\mathbf{0}} = \frac{\partial E_H}{\partial (T_{mn}^{ef})^*} \Big|_{\mathbf{m}_K=\mathbf{0}} = 0 \tag{31}$$

Solving these equations we can obtain the expressions for MP2 amplitudes as:

$$T_{ij}^{ab} = \frac{\langle ab || ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{32}$$

$$(T_{ij}^{ab})^* = \frac{\langle ij || ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{33}$$

### Orbital Rotation Condition

$$0 = \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=\mathbf{0}} = \frac{\partial E_H}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=\mathbf{0}} + \frac{1}{2} \sum_{ai} z_{ai} \frac{\partial f_{ai}}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=\mathbf{0}} \tag{34}$$

$$0 = \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}^*} \Big|_{\mathbf{m}_K=\mathbf{0}} = \frac{\partial E_H}{\partial \kappa_{bj}^*} \Big|_{\mathbf{m}_K=\mathbf{0}} + \frac{1}{2} \sum_{ai} z_{ai}^* \frac{\partial f_{ai}^*}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=\mathbf{0}} \tag{35}$$

These produces the Z-Vector equations:

$$\frac{1}{2} (\varepsilon_b - \varepsilon_j) z_{bj} = -X_{bj} \tag{36}$$

$$\frac{1}{2} (\varepsilon_b - \varepsilon_j) z_{bj}^* = -X_{bj}^* \tag{37}$$

in which

$$X_{bj} = \frac{1}{2} \sum_{iac} \langle ac || bi \rangle (T_{ji}^{ac})^* - \frac{1}{2} \sum_{ika} \langle ja || ik \rangle (T_{ik}^{ba})^* + \sum_{ac} \langle aj || cb \rangle \gamma_{ac}^H + \sum_{kl} \langle jk || bl \rangle \gamma_{kl}^H \tag{38}$$

Now all parts of the orbital-relaxed density  $D_{\mu\nu}^R$  are ready, the first derivative could be computed.

### 3.3 Second Derivative

$$\begin{aligned}
 \frac{d^2 \mathcal{L}_{\text{MP2}}}{dm_{K_\beta} dB_\alpha} \Big|_{\mathbf{B}, \mathbf{m}_K=\mathbf{0}} &= \frac{\partial^2 \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta} \partial B_\alpha} \Big|_{\mathbf{B}, \mathbf{m}_K=\mathbf{0}} \\
 &= \sum_{\mu\nu} D_{\mu\nu}^R \frac{\partial^2 h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta} \partial B_\alpha} \Big|_{\mathbf{B}, \mathbf{m}_K=\mathbf{0}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}^R}{\partial B_\alpha} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{B}, \mathbf{m}_K=\mathbf{0}}
 \end{aligned} \tag{39}$$

Need to get the response of orbital-relaxed density under external magnetic field,  $\frac{\partial D_{\mu\nu}^R}{\partial \mathbf{B}} \Big|_{\mathbf{B}, \mathbf{m}_K=0}$  for the second derivative. We should denote this as  $D_{\mu\nu}^{R,\mathbf{B}}$  for convenience.

$$\begin{aligned} D_{\mu\nu}^R &= D_{\mu\nu}^{\text{HF}} + D_{\mu\nu}^H + \frac{1}{2}D_{\mu\nu}^z + \frac{1}{2}D_{\mu\nu}^{z*} \\ &= \sum_i C_{\mu i}^* C_{\nu i} + \sum_{ij} C_{\mu i}^* \gamma_{ij}^H C_{\nu j} + \sum_{ab} C_{\mu a}^* \gamma_{ab}^H C_{\nu b} \\ &\quad + \frac{1}{2} \sum_{ai} C_{\mu a}^* z_{ai} C_{\nu i} + \frac{1}{2} \sum_{ai} (C_{\mu a}^* z_{ai} C_{\nu i})^* \end{aligned} \quad (40)$$

$$D_{\mu\nu}^{R,\mathbf{B}} = D_{\mu\nu}^{\text{HF},\mathbf{B}} + D_{\mu\nu}^{H,\mathbf{B}} + \frac{1}{2}D_{\mu\nu}^{z,\mathbf{B}} + \frac{1}{2}D_{\mu\nu}^{z*,\mathbf{B}} \quad (41)$$

$$D_{\mu\nu}^{\text{HF},\mathbf{B}} = \sum_i C_{\mu i}^{*,\mathbf{B}} C_{\nu i} + \sum_i C_{\mu i}^* C_{\nu i}^{\mathbf{B}} \quad (42)$$

$$\begin{aligned} D_{\mu\nu}^{H,\mathbf{B}} &= \sum_{ij} C_{\mu i}^{*,\mathbf{B}} \gamma_{ij}^H C_{\nu j} + \sum_{ij} C_{\mu i}^* \gamma_{ij}^{H,\mathbf{B}} C_{\nu j} + \sum_{ij} C_{\mu i}^* \gamma_{ij}^H C_{\nu j}^{\mathbf{B}} \\ &\quad + \sum_{ab} C_{\mu a}^{*,\mathbf{B}} \gamma_{ab}^H C_{\nu b} + \sum_{ab} C_{\mu a}^* \gamma_{ab}^{H,\mathbf{B}} C_{\nu b} + \sum_{ab} C_{\mu a}^* \gamma_{ab}^H C_{\nu b}^{\mathbf{B}} \end{aligned} \quad (43)$$

$$D_{\mu\nu}^{z,\mathbf{B}} = \sum_{ai} C_{\mu a}^{*,\mathbf{B}} z_{ai} C_{\nu i} + \sum_{ai} C_{\mu a}^* z_{ai} C_{\nu i}^{\mathbf{B}} \quad (44)$$

The responses  $\kappa_{pq}^{\mathbf{B}}$ ,  $h_{\mu\nu}^{\text{AO},\mathbf{B}}$ ,  $S_{\mu\nu}^{\text{AO},\mathbf{B}}$  and  $\langle \mu\nu || \sigma\tau \rangle^{\mathbf{B}}$  are needed for these density responses. For the second derivative,  $h_{\mu\nu}^{\text{AO},\mathbf{m}_K}$  and  $h_{\mu\nu}^{\text{AO},\mathbf{m}_K,\mathbf{B}}$  are also required.

### HF Contribution

$S_{\mu\nu}^{\text{AO},\mathbf{B}}$  and  $\kappa_{pq}^{\mathbf{B}}$  are needed for HF contribution to the relaxed density response.

$$\begin{aligned} C_{\mu p}(\mathbf{B}) &= \sum_r C_{\mu r}(0) U_{rp}(\mathbf{B}) \\ &= \sum_{rt} C_{\mu r}(0) (S^{00})_{rt}^{-\frac{1}{2}}(\mathbf{B}) \exp[-\boldsymbol{\kappa}(\mathbf{B})]_{tp} \end{aligned} \quad (45)$$

$$C_{\mu p}^{\mathbf{B}} = \sum_{rt} C_{\mu r}(S^{00})_{rt}^{-\frac{1}{2},\mathbf{B}} \exp[-\boldsymbol{\kappa}]_{tp} + \sum_{rt} C_{\mu r}(S^{00})_{rt}^{-\frac{1}{2}} \exp[-\boldsymbol{\kappa}]_{tp}^{\mathbf{B}} \quad (46)$$

Since only first derivative of  $\mathbf{C}$  is needed and  $\boldsymbol{\kappa}(\mathbf{B}=0) = \mathbf{I}$ , we can expand the exponential up to first order:

$$\exp(-\boldsymbol{\kappa}) = \mathbf{I} - \boldsymbol{\kappa} \quad (47)$$

$$\begin{aligned} C_{\mu p}^{\mathbf{B}} &= \sum_{rt} C_{\mu r}(S^{00})_{rt}^{-\frac{1}{2},\mathbf{B}} \delta_{tp} + \sum_{rt} C_{\mu r}(S^{00})_{rt}^{-\frac{1}{2}} (\delta_{tp}^{\mathbf{B}} - \kappa_{tp}^{\mathbf{B}}) \\ &= \sum_r C_{\mu r}(S^{00})_{rp}^{-\frac{1}{2},\mathbf{B}} - \sum_{rt} C_{\mu r} \delta_{rt} \kappa_{tp}^{\mathbf{B}} \\ &= \sum_r C_{\mu r}(S^{00})_{rp}^{-\frac{1}{2},\mathbf{B}} - \sum_r C_{\mu r} \kappa_{rp}^{\mathbf{B}} \end{aligned} \quad (48)$$

$$S_{pq}^{00,\mathbf{B}} = \sum_{\mu\nu} C_{\mu p}^*(0) S_{\mu\nu}^{\text{AO},\mathbf{B}} C_{\nu q}(0) \quad (49)$$

and  $(\mathbf{S}^{00})^{-\frac{1}{2}, \mathbf{B}}$  could be obtained from differentiating the equation, noting that  $\mathbf{S}^{00,\dagger} = \mathbf{S}^{00}$  and  $\mathbf{S}^{00}(\mathbf{B} = \mathbf{0}) = \mathbf{I}$ :

$$(\mathbf{S}^{00})^{-\frac{1}{2}\dagger} \mathbf{S}^{00} (\mathbf{S}^{00})^{-\frac{1}{2}} = \mathbf{I} \quad (50)$$

$$\begin{aligned} \mathbf{0} &= (\mathbf{S}^{00})^{-\frac{1}{2}, \mathbf{B}} \mathbf{S}^{00} (\mathbf{S}^{00})^{-\frac{1}{2}} \Big|_{\mathbf{B}=\mathbf{0}} + (\mathbf{S}^{00})^{-\frac{1}{2}} \mathbf{S}^{00, \mathbf{B}} (\mathbf{S}^{00})^{-\frac{1}{2}} \Big|_{\mathbf{B}=\mathbf{0}} + (\mathbf{S}^{00})^{-\frac{1}{2}} \mathbf{S}^{00} (\mathbf{S}^{00})^{-\frac{1}{2}, \mathbf{B}} \Big|_{\mathbf{B}=\mathbf{0}} \\ &= (\mathbf{S}^{00})^{-\frac{1}{2}, \mathbf{B}} + \mathbf{S}^{00, \mathbf{B}} + (\mathbf{S}^{00})^{-\frac{1}{2}, \mathbf{B}} \\ &= 2(\mathbf{S}^{00})^{-\frac{1}{2}, \mathbf{B}} + \mathbf{S}^{00, \mathbf{B}} \end{aligned} \quad (51)$$

Therefore:

$$(\mathbf{S}^{00})^{-\frac{1}{2}, \mathbf{B}} = -\frac{1}{2} \mathbf{S}^{00, \mathbf{B}} \quad (52)$$

### Hylleraas Contribution

For Hylleraas contribution, we need  $S_{\mu\nu}^{\text{AO}, \mathbf{B}}$ ,  $\kappa_{pq}^{\mathbf{B}}$  and  $\langle \mu\nu || \sigma\tau \rangle^{\mathbf{B}}$ , as the MP2 amplitudes depend on the two-electron integrals.

$$\gamma_{ij}^{\text{H}} = \frac{1}{2} \sum_{kab} (T_{jk}^{ab})^* T_{ki}^{ab} \quad (53)$$

$$\gamma_{ab}^{\text{H}} = -\frac{1}{2} \sum_{ijc} (T_{ij}^{ac})^* T_{ij}^{cb} \quad (54)$$

$$\gamma_{ij}^{\text{H}, \mathbf{B}} = \frac{1}{2} \sum_{kab} (T_{jk}^{ab})^{*, \mathbf{B}} T_{ki}^{ab} + \frac{1}{2} \sum_{kab} (T_{jk}^{ab})^* (T_{ki}^{ab})^{\mathbf{B}} \quad (55)$$

$$\gamma_{ab}^{\text{H}, \mathbf{B}} = -\frac{1}{2} \sum_{ijc} (T_{ij}^{ac})^{*, \mathbf{B}} T_{ij}^{cb} - \frac{1}{2} \sum_{ijc} (T_{ij}^{ac})^* (T_{ij}^{cb})^{\mathbf{B}} \quad (56)$$

The MP2 amplitude response:

$$T_{ij}^{ab} = \frac{\langle ab || ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = \frac{1}{\Delta_{ab}^{ij}} \langle ab || ij \rangle \quad (57)$$

$$(T_{ij}^{ab})^* = \frac{\langle ij || ab \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} = \frac{1}{\Delta_{ab}^{ij}} \langle ij || ab \rangle \quad (58)$$

$$\begin{aligned} \langle pq || rs \rangle^{\mathbf{B}} &= \sum_{\mu\nu\sigma\tau} C_{\mu p}^* C_{\nu q}^* \langle \mu\nu || \sigma\tau \rangle^{\mathbf{B}} C_{\sigma r} C_{\tau s} \\ &+ \sum_{\mu\nu\sigma\tau} C_{\mu p}^{*, \mathbf{B}} C_{\nu q}^* \langle \mu\nu || \sigma\tau \rangle C_{\sigma r} C_{\tau s} + \sum_{\mu\nu\sigma\tau} C_{\mu p}^* C_{\nu q}^{*, \mathbf{B}} \langle \mu\nu || \sigma\tau \rangle C_{\sigma r} C_{\tau s} \\ &+ \sum_{\mu\nu\sigma\tau} C_{\mu p}^* C_{\nu q}^* \langle \mu\nu || \sigma\tau \rangle C_{\sigma r}^{\mathbf{B}} C_{\tau s} + \sum_{\mu\nu\sigma\tau} C_{\mu p}^* C_{\nu q}^* \langle \mu\nu || \sigma\tau \rangle C_{\sigma r} C_{\tau s}^{\mathbf{B}} \end{aligned} \quad (59)$$

$$(\Delta_{ab}^{ij})^{\mathbf{B}} = \varepsilon_i^{\mathbf{B}} + \varepsilon_j^{\mathbf{B}} - \varepsilon_a^{\mathbf{B}} - \varepsilon_b^{\mathbf{B}} \quad (60)$$

$$f_{pq}^{\mathbf{B}} = h_{pq}^{\mathbf{B}} + \sum_i \langle pi || q i \rangle^{\mathbf{B}} \quad (61)$$

$$h_{pq}^{\mathbf{B}} = \sum_{\mu\nu} C_{\mu p}^{*,\mathbf{B}} h_{\mu\nu}^{\text{AO}} C_{\nu q} + \sum_{\mu\nu} C_{\mu p}^* h_{\mu\nu}^{\text{AO},\mathbf{B}} C_{\nu q} + \sum_{\mu\nu} C_{\mu p}^* h_{\mu\nu}^{\text{AO}} C_{\nu q}^{\mathbf{B}} \quad (62)$$

$$\begin{aligned} (T_{ij}^{ab})^{\mathbf{B}} &= \frac{\langle ab||ij\rangle^{\mathbf{B}} \Delta_{ab}^{ij} - \langle ab||ij\rangle (\Delta_{ab}^{ij})^{\mathbf{B}}}{(\Delta_{ab}^{ij})^2} \\ &= \frac{\langle ab||ij\rangle^{\mathbf{B}}}{\Delta_{ab}^{ij}} - \frac{1}{\Delta_{ab}^{ij}} \left( \sum_m \frac{\langle ab||im\rangle}{\Delta_{ab}^{im}} f_{mj}^{\mathbf{B}} + \sum_m \frac{\langle ab||mj\rangle}{\Delta_{ab}^{mj}} f_{mi}^{\mathbf{B}} \right. \\ &\quad \left. - \sum_e \frac{\langle ae||ij\rangle}{\Delta_{ae}^{ij}} f_{eb}^{\mathbf{B}} - \sum_e \frac{\langle eb||ij\rangle}{\Delta_{eb}^{ij}} f_{ae}^{\mathbf{B}} \right) \\ &= \frac{1}{\Delta_{ab}^{ij}} \left( \langle ab||ij\rangle^{\mathbf{B}} - \sum_m T_{im}^{ab} f_{mj}^{\mathbf{B}} - \sum_m T_{mj}^{ab} f_{mi}^{\mathbf{B}} + \sum_e T_{ij}^{ae} f_{eb}^{\mathbf{B}} + \sum_e T_{ij}^{eb} f_{ae}^{\mathbf{B}} \right) \end{aligned} \quad (63)$$

$$(T_{ij}^{ab})^{*,\mathbf{B}} = \frac{1}{\Delta_{ab}^{ij}} \left( \langle ij||ab\rangle^{\mathbf{B}} - \sum_m (T_{im}^{ab})^* f_{mj}^{\mathbf{B}} - \sum_m (T_{mj}^{ab})^* f_{mi}^{\mathbf{B}} + \sum_e (T_{ij}^{ae})^* f_{eb}^{\mathbf{B}} + \sum_e (T_{ij}^{eb})^* f_{ae}^{\mathbf{B}} \right) \quad (64)$$

### Z-Vector Contribution

The perturbed Z-vectors are obtained by differentiating the zero-th order Z-vector equation and solving it iteratively:

$$\frac{1}{2} z_{bj} (\varepsilon_b - \varepsilon_j) + \frac{1}{2} \sum_{ai} (z_{ai} \langle aj||ib\rangle + z_{ai}^* \langle ij||ab\rangle) = -X_{bj} \quad (65)$$

$$X_{bj} = \frac{1}{2} \sum_{iac} \langle ac||bi\rangle (T_{ji}^{ac})^* - \frac{1}{2} \sum_{ika} \langle ja||ik\rangle (T_{ik}^{ba})^* + \sum_{ac} \langle aj||cb\rangle \gamma_{ac}^{\text{H}} + \sum_{kl} \langle jk||bl\rangle \gamma_{kl}^{\text{H}} \quad (66)$$

Differentiating the LHS:

$$\begin{aligned} &\frac{\partial}{\partial \mathbf{B}} \left( \frac{1}{2} z_{bj} (\varepsilon_b - \varepsilon_j) + \frac{1}{2} \sum_{ai} (z_{ai} \langle aj||ib\rangle + z_{ai}^* \langle ij||ab\rangle) \right) \\ &= \frac{1}{2} z_{bj}^{\mathbf{B}} (\varepsilon_b - \varepsilon_j) + \frac{1}{2} \sum_{ai} \left( z_{ai}^{\mathbf{B}} \langle aj||ib\rangle + z_{ai}^{*,\mathbf{B}} \langle ij||ab\rangle \right) \\ &\quad + \frac{1}{2} z_{bj} (\varepsilon_b^{\mathbf{B}} - \varepsilon_j^{\mathbf{B}}) + \frac{1}{2} \sum_{ai} (z_{ai} \langle aj||ib\rangle^{\mathbf{B}} + z_{ai}^* \langle ij||ab\rangle^{\mathbf{B}}) \end{aligned} \quad (67)$$

and the RHS:

$$\begin{aligned} \frac{\partial X_{bj}}{\partial \mathbf{B}} &= \frac{1}{2} \sum_{iac} \langle ac||bi\rangle^{\mathbf{B}} (T_{ji}^{ac})^* + \frac{1}{2} \sum_{iac} \langle ac||bi\rangle (T_{ji}^{ac})^{*,\mathbf{B}} - \frac{1}{2} \sum_{ika} \langle ja||ik\rangle^{\mathbf{B}} (T_{ik}^{ba})^* - \frac{1}{2} \sum_{ika} \langle ja||ik\rangle (T_{ik}^{ba})^{*,\mathbf{B}} \\ &\quad + \sum_{ac} \langle aj||cb\rangle^{\mathbf{B}} \gamma_{ac}^{\text{H}} + \sum_{ac} \langle aj||cb\rangle \gamma_{ac}^{\text{H},\mathbf{B}} + \sum_{kl} \langle jk||bl\rangle^{\mathbf{B}} \gamma_{kl}^{\text{H}} + \sum_{kl} \langle jk||bl\rangle \gamma_{kl}^{\text{H},\mathbf{B}} \end{aligned} \quad (68)$$

### 3.4 Implementation Plan

$$\frac{d^2 \mathcal{L}_{\text{MP2}}}{dm_{K_\beta} dB_\alpha} \Big|_{\mathbf{B}, \mathbf{m}_K = \mathbf{0}} = \sum_{\mu\nu} D_{\mu\nu}^{\text{R}} \frac{\partial^2 h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta} \partial B_\alpha} \Big|_{\mathbf{B}, \mathbf{m}_K = \mathbf{0}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}^{\text{R}}}{\partial B_\alpha} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{B}, \mathbf{m}_K = \mathbf{0}} \quad (69)$$

#### Orbital-Relaxed Density

Parts needed to compute relaxed density  $D_{\mu\nu}^{\text{R}}$ :

- MO coefficients for occupied orbitals  $C_{\mu i}$
- MO coefficients for virtual orbitals  $C_{\mu a}$
- 2 e integrals  $\langle pq || rs \rangle$
- 1 e integrals  $h_{pq}$

Main steps:

1. Compute MP2 amplitudes using  $\langle pq || rs \rangle$  and  $h_{pq}$  (or are orbital energies directly available?)
2. Compute the X-intermediates using  $\langle pq || rs \rangle$  and MP2 amplitudes
3. Compute Z-vectors with X-intermediates and orbital energies
4. Make contractions to compute  $D_{\mu\nu}^{\text{AO}}$

#### Density Response to Magnetic Field

Additional parts needed to compute  $D_{\mu\nu}^{\text{R,B}}$ :

- perturbed orbital rotation matrix  $\kappa_{pq}^{\mathbf{B}}$
- perturbed AO 1e integral  $h_{\mu\nu}^{\text{AO,B}}$
- perturbed AO overlap integral  $S_{\mu\nu}^{\text{AO,B}}$
- perturbed AO 2e integral  $\langle \mu\nu || \sigma\tau \rangle^{\mathbf{B}}$

Main steps:

1. Compute  $S_{pq}^{00,\mathbf{B}}$  with unperturbed MO coefficients  $C_{\mu p}$  and  $S_{\mu\nu}^{\text{AO,B}}$
2. Compute the perturbed MO coefficients  $C_{\mu p}^{\mathbf{B}}$  with  $\kappa_{pq}^{\mathbf{B}}$  and  $S_{pq}^{00,\mathbf{B}}$
3. Compute the perturbed MO 2e integrals  $\langle pq || rs \rangle^{\mathbf{B}}$  with  $\langle pq || rs \rangle$  and  $C_{\mu p}^{\mathbf{B}}$
4. Compute the perturbed fock matrix  $f_{pq}^{\mathbf{B}}$  using  $h_{\mu\nu}^{\text{AO,B}}$  and  $\langle pq || rs \rangle^{\mathbf{B}}$
5. Compute the perturbed MP2 amplitudes  $(T_{ij}^{ab})^{\mathbf{B}}$  with  $f_{pq}^{\mathbf{B}}$ ,  $\langle pq || rs \rangle^{\mathbf{B}}$  and  $T_{ij}^{ab}$
6. Compute the perturbed Hylleraas 1-RDMs  $\gamma_{ij}^{\text{H,B}}$  and  $\gamma_{ab}^{\text{H,B}}$  with  $(T_{ij}^{ab})^{\mathbf{B}}$  and  $T_{ij}^{ab}$
7. Compute the perturbed X-intermediates  $X_{bj}^{\mathbf{B}}$  using  $(T_{ij}^{ab})^{\mathbf{B}}$ ,  $T_{ij}^{ab}$ ,  $\langle pq || rs \rangle^{\mathbf{B}}$  and perturbed 1-RDMs
8. Compute the perturbed Z-vectors  $z_{bj}^{\mathbf{B}}$  with  $X_{bj}^{\mathbf{B}}$ ,  $f_{pq}^{\mathbf{B}}$  and  $z_{bj}$
9. Make contractions to compute  $D_{\mu\nu}^{\text{R,B}}$

### Second derivative

Additional parts needed to compute the second derivative:

- $h_{\mu\nu}^{\text{AO}, \mathbf{m}_K}$
- $h_{\mu\nu}^{\text{AO}, \mathbf{B}, \mathbf{m}_K}$