1 NMR Shielding

Shielding Tensor:

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

How do I parameterize energy E with $\mathbf{B}$ and $\mathbf{m}_K$?
The one-electronic Hamiltonian in magnetic field:

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

in which:

$$\boldsymbol{\pi} = -i\boldsymbol{\nabla} + \mathbf{A} \tag{3}$$

is the kinetic momentum operator.

Vector potential:

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

with:

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

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

The first part is contribution from the external magnetic field, the second part from the nuclear magnetic moments.
Now parameterize with MO coefficients / densities?

2 SCF Level

$$
\begin{aligned}
E^{\mathrm{SCF}} &= \sum_i^N h_{ii} + \frac{1}{2}\sum_{ij}^N \langle ij||ij\rangle \\
&= \sum_i \sum_{\mu\nu} C^*_{\mu i} h_{\mu\nu} C_{\nu i} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \qquad (7)\\
D^{\mathrm{SCF}}_{\mu\nu} &= \sum_i C^*_{\mu i} C_{\nu i} \qquad (8)\\
C_{\mu p}(\lambda) &= \sum_q C_{\mu q}(0) U_{qp}(\lambda) \qquad (9)
\end{aligned}
$$

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

$$
\sigma^{\mathrm{SCF},K}_{\beta\alpha} = \frac{\mathrm{d}^2 E^{\mathrm{SCF}}}{\mathrm{d}B_\alpha\,\mathrm{d}m_{K_\beta}}\Big|_{\mathbf{B},\mathbf{m}_K=0} \qquad (10)
$$

Taking the first derivative against the nuclear magnetic moment gives:

$$
\begin{aligned}
\frac{\mathrm{d}E^{\mathrm{SCF}}}{\mathrm{d}m_{K_\beta}} &= \frac{\mathrm{d}}{\mathrm{d}m_{K_\beta}}\left(\sum_{i\mu\nu} C^*_{\mu i} h_{\mu\nu} C_{\nu i}\right) \\
&= \sum_{i\mu\nu} C^*_{\mu i} C_{\nu i} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}} \\
&= \sum_{\mu\nu} D^{\mathrm{SCF}}_{\mu\nu} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}} \qquad (11)
\end{aligned}
$$

Note that the MO coefficients are variationally determined so $\frac{\mathrm{d}\mathbf{C}}{\mathrm{d}m_{K_\beta}} = \mathbf{0}$, and the basis function does not depend on the nuclear magnetic moment, i.e. $\frac{\mathrm{d}\phi_\mu}{\mathrm{d}m_{K_\beta}} = 0$.
Now taking the second derivative w.r.t. the external magnetic field:

$$
\begin{aligned}
\sigma^{\mathrm{SCF},K}_{\beta\alpha} &= \frac{\mathrm{d}^2 E^{\mathrm{SCF}}}{\mathrm{d}B_\alpha\,\mathrm{d}m_{K_\beta}} \\
&= \frac{\mathrm{d}}{\mathrm{d}B_\alpha}\left(\sum_{\mu\nu} D^{\mathrm{SCF}}_{\mu\nu} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}}\right) \\
&= \sum_{\mu\nu} D^{\mathrm{SCF}}_{\mu\nu} \frac{\mathrm{d}^2 h_{\mu\nu}}{\mathrm{d}B_\alpha\,\mathrm{d}m_{K_\beta}} + \sum_{\mu\nu} \frac{\mathrm{d}D^{\mathrm{SCF}}_{\mu\nu}}{\mathrm{d}B_\alpha}\frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}} \qquad (12)
\end{aligned}
$$

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

$$
\begin{aligned}
\frac{\mathrm{d}D^{\mathrm{SCF}}_{\mu\nu}}{\mathrm{d}B_\alpha} &= \frac{\mathrm{d}}{\mathrm{d}B_\alpha}\left(\sum_i C^*_{\mu i}(\mathbf{B}) C_{\nu i}(\mathbf{B})\right) \\
&= \frac{\mathrm{d}}{\mathrm{d}B_\alpha}\left(\sum_{ipq} C^*_{\mu p}(0) U^*_{pi}(\mathbf{B}) C_{\nu q}(0) U_{qi}(\mathbf{B})\right) \\
&= \sum_{ip} C^*_{\mu p}(0)\frac{\mathrm{d}U^*_{pi}(\mathbf{B})}{\mathrm{d}B_\alpha} C_{\nu i}(\mathbf{B}) + \sum_{iq} C^*_{\mu i}(\mathbf{B})\frac{\mathrm{d}U_{qi}(\mathbf{B})}{\mathrm{d}B_\alpha} C_{\nu q}(0) \qquad (13)
\end{aligned}
$$

$$= \sum_{ip} C^*_{\mu p} (U^{B_\alpha}_{pi})^* C_{\nu i} + \sum_{ip} C^*_{\mu i} U^{B_\alpha}_{pi} C_{\nu p} \tag{14}$$

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

3 MP2 Level

Lagrangian:

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

Energies:

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

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

Unrelaxed densities:

$$D_{\mu\nu}^{\text{HF}} = \sum_{i} C_{\mu i}^{*}C_{\mu i} \tag{18}$$

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

$$\tag{20}$$

Brillouin conditions:

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

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

3.1 First Derivative

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

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

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

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

Using the Hermitian property of the one-body Hamiltonian:

$$\begin{aligned}&\sum_{\mu\nu ai} z_{ia} C^*_{\mu i} C_{\nu a} h^{\text{AO}}_{\mu\nu} \\ &\overset{\mu\leftrightarrow\nu}{=} \sum_{\mu\nu ai}\left(z_{ai} C^*_{\mu a} C_{\nu i}\right)^* h^{\text{AO}}_{\nu\mu} \\ &= \sum_{\mu\nu ai}(z_{ai} C^*_{\mu a} C_{\nu i})^* h^{\text{AO}}_{\mu\nu}\end{aligned} \tag{25}$$

Therefore:

$$\frac{\partial \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} = \sum_{\mu\nu} D^{\text{R}}_{\mu\nu}\frac{\partial h^{\text{AO}}_{\mu\nu}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} \tag{26}$$

in which the orbital-relaxed density matrix is:

$$\begin{aligned}D^{\text{R}}_{\mu\nu} =& D^{\text{HF}}_{\mu\nu} + D^{\text{H}}_{\mu\nu} + \frac{1}{2}D^{z}_{\mu\nu} + \frac{1}{2}D^{z*}_{\mu\nu} \\ =& \sum_i C^*_{\mu i} C_{\nu i} + \sum_{ij} C^*_{\mu i}\gamma^{\text{H}}_{ij} C_{\nu j} + \sum_{ab} C^*_{\mu a}\gamma^{\text{H}}_{ab} C_{\nu b} \\ &+ \frac{1}{2}\sum_{ai} C^*_{\mu a} z_{ai} C_{\nu i} + \frac{1}{2}\sum_{ai}\left(C^*_{\mu a} z_{ai} C_{\nu i}\right)^*\end{aligned} \tag{27}$$

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

- MO coefficients $C_{\mu p}$ from HF equation (Brillouin condition)
- MP2 amplitudes T^{ab}_{ij} 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

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

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

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

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

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

Orbital Rotation Condition

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

$$
0=\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial\kappa^*_{bj}}\Big|_{\mathbf{m}_K=\mathbf{0}}=\frac{\partial E_{\text{H}}}{\partial\kappa^*_{bj}}\Big|_{\mathbf{m}_K=\mathbf{0}}+\frac{1}{2}\sum_{ai}z^*_{ai}\frac{\partial f^*_{ai}}{\partial\kappa_{bj}}\Big|_{\mathbf{m}_K=\mathbf{0}} \tag{35}
$$

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

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

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

3.3 Second Derivative

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

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

$$\begin{aligned}D^{\mathrm{R}}_{\mu\nu} =& D^{\mathrm{HF}}_{\mu\nu} + D^{\mathrm{H}}_{\mu\nu} + \frac{1}{2} D^{z}_{\mu\nu} + \frac{1}{2} D^{z*}_{\mu\nu} \\ =& \sum_i C^*_{\mu i} C_{\nu i} + \sum_{ij} C^*_{\mu i} \gamma^{\mathrm{H}}_{ij} C_{\nu j} + \sum_{ab} C^*_{\mu a} \gamma^{\mathrm{H}}_{ab} C_{\nu b} \\ &+ \frac{1}{2} \sum_{ai} C^*_{\mu a} z_{ai} C_{\nu i} + \frac{1}{2} \sum_{ai} \left(C^*_{\mu a} z_{ai} C_{\nu i} \right)^* \end{aligned} \tag{40}$$

$$D^{\mathrm{R},\mathbf{B}}_{\mu\nu} = D^{\mathrm{HF},\mathbf{B}}_{\mu\nu} + D^{\mathrm{H},\mathbf{B}}_{\mu\nu} + \frac{1}{2} D^{z,\mathbf{B}}_{\mu\nu} + \frac{1}{2} D^{z*,\mathbf{B}}_{\mu\nu} \tag{41}$$

$$D^{\mathrm{HF},\mathbf{B}}_{\mu\nu} = \sum_i C^{*,\mathbf{B}}_{\mu i} C_{\nu i} + \sum_i C^*_{\mu i} C^{\mathbf{B}}_{\nu i} \tag{42}$$

$$D^{\mathrm{H},\mathbf{B}}_{\mu\nu} = \sum_{ij} C^{*,\mathbf{B}}_{\mu i} \gamma^{\mathrm{H}}_{ij} C_{\nu j} + \sum_{ij} C^*_{\mu i} \gamma^{\mathrm{H},\mathbf{B}}_{ij} C_{\nu j} + \sum_{ij} C^*_{\mu j} \gamma^{\mathrm{H}}_{ij} C^{\mathbf{B}}_{\nu j} \tag{43}$$

$$D^{z,\mathbf{B}}_{\mu\nu} = \sum_{ai} C^{*,\mathbf{B}}_{\mu a} z_{ai} C_{\nu i} + \sum_{ai} C^*_{\mu a} z^{\mathbf{B}}_{ai} C_{\nu i} + \sum_{ai} C^*_{\mu a} z_{ai} C^{\mathbf{B}}_{\nu i} \tag{44}$$

The responses $C^{\mathbf{B}}_{\mu p}$, $h^{\mathrm{AO},\mathbf{B}}_{\mu\nu}$, $S^{\mathrm{AO},\mathbf{B}}_{\mu\nu}$ and $\langle \mu\nu || \sigma\tau \rangle^{\mathbf{B}}$ are needed.