1 NMR Shielding

Shielding Tensor:

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

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:

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

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

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

$$E^{\text{SCF}} = \sum_i^N h_{ii} + \frac{1}{2}\sum_{ij}^N \langle ij||ij\rangle$$

$$= \sum_i \sum_{\mu\nu} C_{\mu i}^* h_{\mu\nu} C_{\nu i} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \tag{7}$$

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

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

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

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

Taking the first derivative against the nuclear magnetic moment gives:

$$\frac{\mathrm{d}E^{\text{SCF}}}{\mathrm{d}m_{K_\beta}} = \frac{\mathrm{d}}{\mathrm{d}m_{K_\beta}}\left(\sum_{i\mu\nu} C_{\mu i}^* h_{\mu\nu} C_{\nu i}\right)$$

$$= \sum_{i\mu\nu} C_{\mu i}^* C_{\nu i} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}}$$

$$= \sum_{\mu\nu} D_{\mu\nu}^{\text{SCF}} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}} \tag{11}$$

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:

$$\sigma_{\beta\alpha}^{\text{SCF},K} = \frac{\mathrm{d}^2 E^{\text{SCF}}}{\mathrm{d}B_\alpha\, \mathrm{d}m_{K_\beta}}$$

$$= \frac{\mathrm{d}}{\mathrm{d}B_\alpha}\left(\sum_{\mu\nu} D_{\mu\nu}^{\text{SCF}} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}}\right)$$

$$= \sum_{\mu\nu} D_{\mu\nu}^{\text{SCF}} \frac{\mathrm{d}^2 h_{\mu\nu}}{\mathrm{d}B_\alpha\, \mathrm{d}m_{K_\beta}} + \sum_{\mu\nu} \frac{\mathrm{d}D_{\mu\nu}^{\text{SCF}}}{\mathrm{d}B_\alpha} \frac{\mathrm{d}h_{\mu\nu}}{\mathrm{d}m_{K_\beta}} \tag{12}$$

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

$$\frac{\mathrm{d}D_{\mu\nu}^{\text{SCF}}}{\mathrm{d}B_\alpha} = \frac{\mathrm{d}}{\mathrm{d}B_\alpha}\left(\sum_i C_{\mu i}^*(\mathbf{B}) C_{\nu i}(\mathbf{B})\right)$$

$$= \frac{\mathrm{d}}{\mathrm{d}B_\alpha}\left(\sum_{ipq} C_{\mu p}^*(0) U_{pi}^*(\mathbf{B}) C_{\nu q}(0) U_{qi}(\mathbf{B})\right)$$

$$= \sum_{ip} C_{\mu p}^*(0) \frac{\mathrm{d}U_{pi}^*(\mathbf{B})}{\mathrm{d}B_\alpha} C_{\nu i}(\mathbf{B}) + \sum_{iq} C_{\mu i}^*(\mathbf{B}) \frac{\mathrm{d}U_{qi}(\mathbf{B})}{\mathrm{d}B_\alpha} C_{\nu q}(0) \tag{13}$$

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

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

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

3 MP2 Level

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

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

$$E_{\text{H}} = \sum_{ij}h_{ij}\gamma_{ij}^{\text{H}} + \sum_{ab}h_{ab}\gamma_{ab}^{\text{H}} + \sum_{pqrs}\langle pq||rs\rangle\Gamma_{rs}^{pq}$$

$$= \sum_{\mu\nu}D_{\mu\nu}^{\text{H}}h_{\mu\nu}^{\text{AO}} + \sum_{pqrs}\langle pq||rs\rangle\Gamma_{rs}^{pq} \tag{17}$$

$$D_{\mu\nu}^{\text{H}} = \sum_{ij}C_{\mu i}^*C_{\nu j}\gamma_{ij}^{\text{H}} + \sum_{ab}C_{\mu a}^*C_{\nu b}\gamma_{ab}^{\text{H}} \tag{18}$$

$$\sum_{ai}z_{ai}f_{ai} = \sum_{ai}z_{ai}h_{ai} + \sum_{aij}z_{ai}\langle aj||ij\rangle$$

$$= \sum_{\mu\nu ai}z_{ai}C_{\mu a}^*C_{\nu i}h_{\mu\nu}^{\text{AO}} + \sum_{aij}z_{ai}\langle aj||ij\rangle \tag{19}$$

$$\sum_{ai}z_{ai}^*f_{ai}^* = \sum_{ai}z_{ai}^*h_{ai}^* + \sum_{aij}z_{ai}^*\langle aj||ij\rangle^*$$

$$= \sum_{ai}z_{ia}h_{ia} + \sum_{aij}z_{ia}\langle ij||aj\rangle$$

$$= \sum_{\mu\nu ai}z_{ia}C_{\mu i}^*C_{\nu a}h_{\mu\nu}^{\text{AO}} + \sum_{aij}z_{ia}\langle ij||aj\rangle$$

$$\tag{20}$$

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}:

$$\frac{d\mathcal{L}_{\text{MP2}}}{dm_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} = \frac{\partial\mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{bj}\left(\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial\kappa_{bj}}\right)\left(\frac{\partial\kappa_{bj}}{\partial m_{K_\beta}}\right)\Big|_{\mathbf{m}_K=\mathbf{0}}$$

$$+ \sum_{ai}\left(\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial z_{ai}}\right)\left(\frac{\partial z_{ai}}{\partial m_{K_\beta}}\right)\Big|_{\mathbf{m}_K=\mathbf{0}}$$

$$= \frac{\partial\mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} \tag{21}$$

$$\frac{\partial\mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} = \sum_{\mu\nu}D_{\mu\nu}^{\text{HF}}\frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{\mu\nu}D_{\mu\nu}^{\text{H}}\frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}}$$

$$+ \frac{1}{2}\sum_{\mu\nu ai}z_{ai}C_{\mu a}^*C_{\nu i}\frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}} + \frac{1}{2}\sum_{\mu\nu ai}z_{ia}C_{\mu i}^*C_{\nu a}\frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}}\Big|_{\mathbf{m}_K=\mathbf{0}}$$

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

$$\tag{22}$$

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note that need to turn z_{ai}^* into z_{ia}... what about z_{ia} block?

Trying to resolve z_{ia}

$$\sum_{\mu\nu ai} z_{ia} C_{\mu i}^* C_{\nu a} h_{\mu\nu}^{\text{AO}}$$

$$\overset{\mu\leftrightarrow\nu}{=} \sum_{\mu\nu ai} \left(z_{ai} C_{\mu a}^* C_{\nu i} \right)^* h_{\nu\mu}^{\text{AO}} \tag{23}$$