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

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

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

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

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:

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

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:

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

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

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

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

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.