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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

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

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

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

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

$$\begin{aligned} \sum_{ai} z_{ai} f_{ai} &= \sum_{ai} z_{ai} h_{ai} + \sum_{aij} z_{ai} \langle aj || ij \rangle \\ &= \sum_{\mu\nu ai} z_{ai} C_{\mu a}^* C_{\nu i} h_{\mu\nu}^{\text{AO}} + \sum_{aij} z_{ai} \langle aj || ij \rangle \end{aligned} \quad (19)$$

$$\begin{aligned} \sum_{ai} z_{ai}^* f_{ai}^* &= \sum_{ai} z_{ai}^* h_{ai}^* + \sum_{aij} z_{ai}^* \langle aj || ij \rangle^* \\ &= \sum_{ai} z_{ia} h_{ia} + \sum_{aij} z_{ia} \langle ij || aj \rangle \\ &= \sum_{\mu\nu ai} z_{ia} C_{\mu i}^* C_{\nu a} h_{\mu\nu}^{\text{AO}} + \sum_{aij} z_{ia} \langle ij || aj \rangle \end{aligned} \quad (20)$$

#### 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  $m_{K_\beta}$ :

$$\begin{aligned} \frac{d\mathcal{L}_{\text{MP2}}}{dm_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} &= \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &+ \sum_{ijab} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial T_{ij}^{ab}} \right) \left( \frac{\partial T_{ij}^{ab}}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{ijab} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial (T_{ij}^{ab})^*} \right) \left( \frac{\partial (T_{ij}^{ab})^*}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &+ \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}} \right) \left( \frac{\partial \kappa_{bj}}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial \kappa_{bj}^*} \right) \left( \frac{\partial \kappa_{bj}^*}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &+ \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}} \right) \left( \frac{\partial z_{bj}}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} + \sum_{bj} \left( \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}^*} \right) \left( \frac{\partial z_{bj}^*}{\partial m_{K_\beta}} \right) \Big|_{\mathbf{m}_K=\mathbf{0}} \\ &= \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=\mathbf{0}} \end{aligned} \quad (21)$$

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

$$\begin{aligned}
 & + \frac{1}{2} \sum_{\mu\nu ai} z_{ai} C_{\mu a}^* C_{\nu i} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=0} + \frac{1}{2} \sum_{\mu\nu ai} z_{ia} C_{\mu i}^* C_{\nu a} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=0} \\
 & = \sum_{\mu\nu} \frac{\partial h_{\mu\nu}^{\text{AO}}}{\partial m_{K_\beta}} \Big|_{\mathbf{m}_K=0} \left( D_{\mu\nu}^{\text{HF}} + D_{\mu\nu}^{\text{H}} + \frac{1}{2} \sum_{ai} z_{ai} C_{\mu a}^* C_{\nu i} + \frac{1}{2} \sum_{ai} z_{ia} C_{\mu i}^* C_{\nu a} \right)
 \end{aligned} \tag{22}$$

note that need to turn  $z_{ai}^*$  into  $z_{ia}$ ... what about  $z_{ia}$  block? what about  $(T_{ij}^{ab})^*$ ?

Trying to resolve  $z_{ia}$

$$\begin{aligned}
 & \sum_{\mu\nu ai} z_{ia} C_{\mu i}^* C_{\nu a} h_{\mu\nu}^{\text{AO}} \\
 & \stackrel{\mu \leftrightarrow \nu}{=} \sum_{\mu\nu ai} (z_{ai} C_{\mu a}^* C_{\nu i})^* h_{\nu\mu}^{\text{AO}}
 \end{aligned} \tag{23}$$

## 3.2 Stationary Constraints

### Brillouin Condition

$$\begin{aligned}
 0 &= \sum_{bj} \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}} \Big|_{\mathbf{m}_K=0} + \sum_{bj} \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial z_{bj}^*} \Big|_{\mathbf{m}_K=0} \\
 &= \frac{1}{2} \sum_{ai} \left( \frac{\partial z_{ai}}{\partial z_{bj}} f_{ai} \Big|_{\mathbf{m}_K=0} + \frac{\partial z_{ai}^*}{\partial z_{bj}^*} f_{ai}^* \Big|_{\mathbf{m}_K=0} \right) \\
 &= \frac{1}{2} \sum_{ai} (\delta_{ab} \delta_{ij} f_{ai} + \delta_{ab} \delta_{ij} f_{ai}^*) \\
 &= \frac{1}{2} (f_{bj} + f_{bj}^*)
 \end{aligned} \tag{24}$$

$$f_{bj} = h_{bj} + \sum_i \langle bi || ji \rangle \tag{25}$$

### MP2 Condition

$$\begin{aligned}
 0 &= \frac{\partial \mathcal{L}_{\text{MP2}}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=0} = \frac{\partial E_{\text{H}}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=0} \\
 &= \sum_{ij} h_{ij} \frac{\partial \gamma_{ij}^{\text{H}}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=0} + \sum_{ab} h_{ab} \frac{\partial \gamma_{ab}^{\text{H}}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=0} + \sum_{ijab} \langle ab || ij \rangle \frac{\partial (\Gamma^{\text{H}})_{ij}^{ab}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=0} \\
 &\quad + \sum_{ijkl} \langle ij || kl \rangle \frac{\partial (\Gamma^{\text{H}})_{kl}^{ij}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=0} + \sum_{ijab} \langle ai || bj \rangle \frac{\partial (\Gamma^{\text{H}})_{bj}^{ai}}{\partial T_{mn}^{ef}} \Big|_{\mathbf{m}_K=0}
 \end{aligned} \tag{26}$$

Density derivatives:

$$\frac{\partial \gamma_{ij}^{\text{H}}}{\partial T_{mn}^{ef}} = \frac{1}{2} \sum_{kab} \frac{\partial (T_{jk}^{ab})^*}{\partial T_{mn}^{ef}} T_{ki}^{ab} + \frac{1}{2} \sum_{kab} (T_{jk}^{ab})^* \frac{\partial T_{ki}^{ab}}{\partial T_{mn}^{ef}} \tag{27}$$

$$\frac{\partial \gamma_{ab}^{\text{H}}}{\partial T_{mn}^{ef}} = -\frac{1}{2} \sum_{ijc} \frac{\partial (T_{ij}^{ac})^*}{\partial T_{mn}^{ef}} T_{ij}^{cb} - \frac{1}{2} \sum_{ijc} (T_{ij}^{ac})^* \frac{\partial T_{ij}^{cb}}{\partial T_{mn}^{ef}} \tag{28}$$

$$\frac{\partial(\Gamma^H)_{ij}^{ab}}{\partial T_{mn}^{ef}} = \frac{1}{2} \frac{\partial(T_{ij}^{ab})^*}{\partial T_{mn}^{ef}} \quad (29)$$

$$\frac{\partial(\Gamma^H)_{kl}^{ij}}{\partial T_{mn}^{ef}} = \frac{1}{2} \sum_{m'ab} \frac{\partial(T_{km'}^{ab})^*}{\partial T_{mn}^{ef}} T_{m'i}^{ab} \delta_{jl} + \frac{1}{2} \sum_{m'ab} (T_{km'}^{ab})^* \frac{\partial T_{m'i}^{ab}}{\partial T_{mn}^{ef}} \delta_{jl} \quad (30)$$

$$\frac{\partial(\Gamma^H)_{bj}^{ai}}{\partial T_{mn}^{ef}} = -\frac{1}{2} \sum_{klc} \frac{\partial(T_{kl}^{ac})^*}{\partial T_{mn}^{ef}} T_{kl}^{cd} \delta_{ij} - \frac{1}{2} \sum_{klc} (T_{kl}^{ac})^* \frac{\partial T_{kl}^{cb}}{\partial T_{mn}^{ef}} \delta_{ij} \quad (31)$$

Contraction with electron integrals:

### Orbital Rotation Condition

$$0 = \frac{\partial \mathcal{L}_{MP2}}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=0} = \frac{\partial E_{HF}}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=0} + \frac{\partial E_H}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=0} + \frac{1}{2} \sum_{ai} z_{ai} \frac{\partial f_{ai}}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=0} + \frac{1}{2} \sum_{ai} z_{ai}^* \frac{\partial f_{ai}^*}{\partial \kappa_{bj}} \Big|_{\mathbf{m}_K=0} = \quad (32)$$