pNMR Shift Theory and Relaxation Simulations

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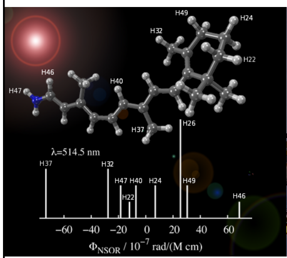
pNMR

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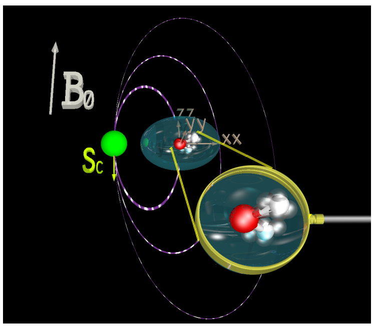
Outline

Juha Vaara: The 2008 shift theory in practice

Jiří Mareš: Extensions of the 2008 theory and simulation of Curie relaxation

Jyrki Rantaharju: Spin dynamics simulation of electron spin relaxation in Ni^{2+}(*aq*)



The 2008 shift theory in practice

PRL 100, 133002 (2008) PHYSICAL REVIEW LETTERS week ending 4 APRIL 2008

Nuclear Magnetic Resonance Chemical Shift in an Arbitrary Electronic Spin State

Teemu O. Pennanen and Juha Vaara*
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(Received 14 December 2007; published 2 April 2008)

We present a general and systematic electronic structure theory of the nuclear magnetic resonance shielding tensor and the associated chemical shift for paramagnetic atoms, molecules, and nonmetallic solids. The approach is for the first time rigorous for an arbitrary spin state as well as arbitrary spatial symmetry and is formulated without reference to spin susceptibility. The leading-order magnetic-field dependence of shielding is derived. The theory is demonstrated by first principles calculations of organometallic molecules.

DOI: 10.1103/PhysRevLett.100.133002 PACS numbers: 33.25.+k, 31.15.ap, 76.60.Cq, 82.56.−b

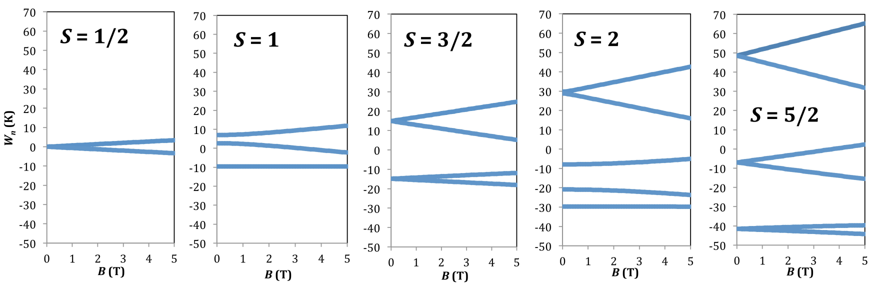
Goals:

- Systematic first-principles electronic structure treatment of the pNMR shielding tensor
- Generalisation of the contact and dipolar shielding terms of McConnell and Chesnut (1958)
- Pseudocontact shifts without using the empirical spin magnetisability tensor χ
- Zero-field splitting effects included *a priori*, from first principles

Sketch of the theory

$$\gamma \sum_{\epsilon\tau} B_{0,\epsilon}\sigma_{\epsilon\tau}(\boldsymbol{B}_0) I_\tau = \frac{\sum_n E_n(\boldsymbol{B}_0,\boldsymbol{I}) \exp[-W_n(\boldsymbol{B}_0,\boldsymbol{I})/kT]}{\sum_n \exp[-W_n(\boldsymbol{B}_0,\boldsymbol{I})/kT]}$$

ZFS and Zeeman dominate: $W_n(\boldsymbol{B}_0,\boldsymbol{I}) \approx W_n(\boldsymbol{B}_0,0)$



[Note: shielding is **NOT** a second derivative of energy…!]

$$E_n(\boldsymbol{B}_0,\boldsymbol{I}) = E_n^{(0,0)} + \sum_\mu E_n^{(\mu,0)} B_{0,\mu} + \sum_\tau E_n^{(0,\tau)} I_\tau + \sum_{\mu\tau} E_n^{(\mu,\tau)} B_{0,\mu} I_\tau + \frac{1}{2}\sum_{\mu\nu} E_n^{(\mu\nu,0)} B_{0,\mu}B_{0,\nu} + \frac{1}{2}\sum_{\mu\nu\tau} E_n^{(\mu\nu,\tau)} B_{0,\mu}B_{0,\nu} I_\tau + \ldots$$

$$W_n(\boldsymbol{B}_0,0) = W_n^{(0,0)} + \sum_\mu W_n^{(\mu,0)} B_{0,\mu} + \frac{1}{2}\sum_{\mu\nu} W_n^{(\mu\nu,0)} B_{0,\mu}B_{0,\nu} + \ldots$$

$$\exp[-W_n(\boldsymbol{B}_0,0)/kT] \approx e^{-W_n^{(0,0)}/kT}\left\{1 - \frac{1}{kT}\left[\sum_\mu W_n^{(\mu,0)} B_{0,\mu} + \ldots\right] + \ldots\right\}$$

$$\sigma_{\epsilon\tau}(\boldsymbol{B}_0) = \sigma_{\epsilon\tau}^{(0)} + \frac{1}{3!}\sum_{\mu\nu} \sigma_{\epsilon\tau\mu\nu}^{(2)} B_{0,\mu}B_{0,\nu} + \ldots$$

$$\gamma \sum_{\epsilon\tau} B_{0,\epsilon}\sigma_{\epsilon\tau}(\boldsymbol{B}_0) I_\tau \sum_n \exp[-W_n(\boldsymbol{B}_0,0)/kT] = \sum_n E_n(\boldsymbol{B}_0,\boldsymbol{I}) \exp[-W_n(\boldsymbol{B}_0,0)/kT]$$

$\mathcal{O}(B_0^1) \Rightarrow$

$$\sigma_{\epsilon\tau}^{(0)} = \frac{1}{\gamma}\langle E^{(\epsilon,\tau)}\rangle_0 - \frac{1}{\gamma kT}\langle W^{(\epsilon,0)} E^{(0,\tau)}\rangle_0$$

$$\langle A\rangle_0 = \frac{\sum_n \langle n|A|n\rangle \exp[-W_n(0,0)/kT]}{\sum_n \exp[-W_n(0,0)/kT]}$$

$\mathcal{O}(B_0^3) \Rightarrow$

$$\begin{aligned}\sigma_{\epsilon\mu\nu\tau}^{(2)} = \frac{1}{\gamma}\frac{1}{3!}P_{\epsilon\mu\nu}\Big\{&\langle E^{(\epsilon\mu\nu,\tau)}\rangle_0 \\ &- \frac{1}{kT}\Big[\langle W^{(\epsilon\mu\nu,0)}E^{(0,\tau)}\rangle_0 + 3\langle W^{(\epsilon\mu,0)}E^{(\nu,\tau)}\rangle_0 + 3\langle W^{(\epsilon,0)}E^{(\mu\nu,\tau)}\rangle_0 \\ &\qquad + \frac{1}{2}\gamma\sigma_{\epsilon\tau}^{(0)}\langle W^{(\mu\nu,0)}\rangle_0\Big] \\ &+ \frac{1}{(kT)^2}\Big[3\langle W^{(\epsilon,0)}W^{(\mu\nu,0)}E^{(0,\tau)}\rangle_0 + 3\langle W^{(\epsilon,0)}W^{(\mu,0)}E^{(\nu,\tau)}\rangle_0 \\ &\qquad + \frac{1}{2}\gamma\sigma_{\epsilon\tau}^{(0)}\langle W^{(\mu,0)}W^{(\nu,0)}\rangle_0\Big] \\ &- \frac{1}{(kT)^3}\langle W^{(\epsilon,0)}W^{(\mu,0)}W^{(\nu,0)}E^{(0,\tau)}\rangle_0\Big\}\end{aligned}$$

A so far exact expression, further progress requires approximations:

- Assume 1:1 relationship of pseudospin and real spin
- Assume weak spin-orbit coupling
- Limit states *n* to the ground-state manifold
- Use the following spin Hamiltonian:

$$H_{\mathrm{ESR}} = -\gamma \boldsymbol{B}_0 \cdot (\boldsymbol{1} - \boldsymbol{\sigma}_{\mathrm{orb}}) \cdot \boldsymbol{I} + \mu_{\mathrm{B}} \boldsymbol{B}_0 \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{A} \cdot \boldsymbol{I} + \boldsymbol{S} \cdot \boldsymbol{D} \cdot \boldsymbol{S}$$

$$\Rightarrow \boxed{\begin{aligned} \sigma^{(0)}_{\epsilon\tau} &= \frac{1}{\gamma}\langle E^{(\epsilon,\tau)}\rangle_0 - \frac{1}{\gamma kT}\langle E^{(\epsilon,0)} E^{(0,\tau)}\rangle_0 \\ &= \sigma^{\mathrm{orb}}_{\epsilon\tau} - \frac{\mu_{\mathrm{B}}}{\gamma kT}\sum_{ab} g_{\epsilon a}\langle S_a S_b\rangle_0 A_{b\tau} \end{aligned}}$$

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$$\sigma^{(0)}_{\epsilon\tau} = \sigma^{\mathrm{orb}}_{\epsilon\tau} - \frac{\mu_{\mathrm{B}}}{\gamma kT}\sum_{ab} g_{\epsilon a}\langle S_a S_b\rangle_0 A_{b\tau}$$

$$\langle A\rangle_0 = \frac{\sum_n \langle n|A|n\rangle \exp[-W_n(0,0)/kT]}{\sum_n \exp[-W_n(0,0)/kT]}$$

$\langle S_a S_b\rangle_0$ is a symmetric 3 x 3 matrix with Tr$\langle \boldsymbol{S}\boldsymbol{S}\rangle_0 = S\,(S+1)$

→ in the doublet case: $\langle S_a S_b\rangle_0 = \frac{1}{3}\delta_{ab} S\,(S+1) \rightarrow \boldsymbol{g}\cdot\boldsymbol{A}$

→ in the general case: solve for the eigenstates $|n\rangle$ and eigenvalues $W_n(0,0)$ of $\boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S}$

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Analysis in terms of the contributions to g and A.

$$\boldsymbol{g} = (\overbrace{g_e}^{\alpha^0} + \overbrace{\Delta g_{\mathrm{iso}}}^{\alpha^2})\mathbf{1} + \overbrace{\Delta\tilde{\boldsymbol{g}}}^{\alpha^2}$$

$$\boldsymbol{A} = (\underbrace{A_{\mathrm{con}}}_{\alpha^2} + \underbrace{A_{\mathrm{PC}}}_{\alpha^4})\mathbf{1} + \underbrace{\boldsymbol{A}_{\mathrm{dip}}}_{\alpha^2} + \underbrace{\boldsymbol{A}_{\mathrm{dip},2}}_{\alpha^4} + \underbrace{\boldsymbol{A}_{\mathrm{as}}}_{\alpha^4}$$

Term in hyperfine $\sigma_{\epsilon\tau}$	Symbol	Number	Order	Tensorial rank $S=\frac{1}{2}$	Tensorial rank $S>\frac{1}{2}$
$\sum_{ab} \Delta\tilde{g}_{\epsilon a} A_{b\tau}^{\mathrm{dip}} \langle S_a S_b \rangle_0$	δ_{pc}	9	$\mathcal{O}(\alpha^4)$	**0**, 2, 1	**0**, 2, 1
$A_{\mathrm{con}} \sum_a \Delta\tilde{g}_{\epsilon a} \langle S_a S_\tau \rangle_0$	$\delta_{\mathrm{c,aniso}}$	8	$\mathcal{O}(\alpha^4)$	2, 1	**0**, 2, 1
$\Delta g_{\mathrm{iso}} \sum_b A_{b\tau}^{\mathrm{dip}} \langle S_\epsilon S_b \rangle_0$	$\delta_{\mathrm{dip,3}}$	7	$\mathcal{O}(\alpha^4)$	2	**0**, 2, 1
$\Delta g_{\mathrm{iso}} A_{\mathrm{con}} \langle S_\epsilon S_\tau \rangle_0$	$\delta_{\mathrm{con,3}}$	6	$\mathcal{O}(\alpha^4)$	**0**	**0**, 2
$g_e \sum_b A_{b\tau}^{\mathrm{as}} \langle S_\epsilon S_b \rangle_0$	δ_{as}	5	$\mathcal{O}(\alpha^4)$	1	2, 1
$g_e \sum_b A_{b\tau}^{\mathrm{dip,2}} \langle S_\epsilon S_b \rangle_0$	$\delta_{\mathrm{dip,2}}$	4	$\mathcal{O}(\alpha^4)$	2	**0**, 2, 1
$g_e A_{\mathrm{PC}} \langle S_\epsilon S_\tau \rangle_0$	$\delta_{\mathrm{con,2}}$	3	$\mathcal{O}(\alpha^4)$	**0**	**0**, 2
$g_e \sum_b A_{b\tau}^{\mathrm{dip}} \langle S_\epsilon S_b \rangle_0$	δ_{dip}	2	$\mathcal{O}(\alpha^2)$	2	**0**, 2, 1
$g_e A_{\mathrm{con}} \langle S_\epsilon S_\tau \rangle_0$	δ_{con}	1	$\mathcal{O}(\alpha^2)$	**0**	**0**, 2

Contact: ranks 0, 2

Dipolar: ranks 0, 2, 1

Pseudocontact: ranks 0, 2, 1

Anis. contact: ranks 0, 2, 1

Antisymmetric: ranks 2, 1

Theory references:

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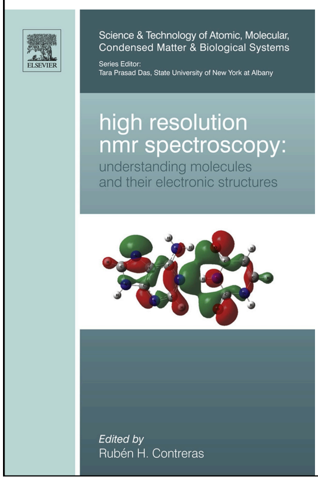

Chapter 3

Chemical Shift in Paramagnetic Systems

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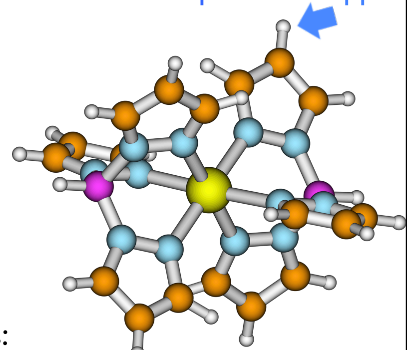
Chapter Outline

Example case

Exp: δ = 43.2 ppm



Appl. Magn. Reson. (2008) 35, 271–283
DOI 10.1007/s00723-008-0161-1
Printed in The Netherlands

Applied Magnetic Resonance

Analysis of NMR Shifts of High-Spin Cobalt(II) Pyrazolylborate Complexes

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[2] Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan, USA
[3] Institute of Nuclear Chemistry and Technology, Warsaw, Poland

Isotropic ^{1}H shifts in Co^{II} (S=3/2) systems:

- $\boldsymbol{g}$ and $\boldsymbol{D}$ from CASSCF(7,5)/NEVPT2 calculations (Def2-SVP basis)
- $\boldsymbol{A}$ and σ^{orb} from DFT/PBE calculations
- Computations carried out on ORCA 3.0.1 ($\boldsymbol{g}$, $\boldsymbol{D}$, $\boldsymbol{A}$), G09 (σ^{orb})

```
g-matrix:
   1.512038     0.097941    -0.055956
   0.158371     2.798102    -0.669070
  -0.101945    -0.665906     2.036543

 Raw matrix (cm-1):
  81.501204   -11.304102     7.389614
 -11.304102   -18.759580    42.045843
   7.389614    42.045843    29.838265
```

```
Raw HFC matrix (all values in MHz):
-------------------------------
 1.1757              0.5522              -0.3216
 0.5334             -0.0123              -0.1325
-0.3070             -0.1317              -0.1694

  29  H    Isotropic =   26.5858  Anisotropy =    3.2349
XX=    28.2750  YX=   -2.4886  ZX=   -0.1174
XY=     0.1491  YY=   25.8127  ZY=   -0.1814
XZ=     0.1546  YZ=    0.0945  ZZ=   25.6698
Eigenvalues:   25.3422   25.6729   28.7424
```


S. A. Rouf, J. Mareš, JV *(to be published)*

Construct $\boldsymbol{G} = \boldsymbol{g}^T\boldsymbol{g}$, diagonalise it, take the square root of eigenvalues, and convert back to the original coordinate frame → effective $\boldsymbol{g}$:

```
g = gdprime; MatrixForm[g]
```

$$\begin{pmatrix} 1.51488 & 0.139603 & -0.0859188 \\ 0.139603 & 2.79614 & -0.666696 \\ -0.0859188 & -0.666696 & 2.03628 \end{pmatrix}$$

The $\Delta\boldsymbol{g}$ tensor:

```
dg = g - ge * one33; MatrixForm[dg]
```

$$\begin{pmatrix} -0.487439 & 0.139603 & -0.0859188 \\ 0.139603 & 0.793825 & -0.666696 \\ -0.0859188 & -0.666696 & 0.0339585 \end{pmatrix}$$

Traceless $\boldsymbol{D}$ tensor:

```
MatrixForm[dmat]
```

$$\begin{pmatrix} 50.6412 & -11.3041 & 7.38961 \\ -11.3041 & -49.6195 & 42.0458 \\ 7.38961 & 42.0458 & -1.0217 \end{pmatrix}$$

Matrix of $H_{ZFS} = \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S}$ in the basis $|S,M_S>$ (in a.u., eigenfunctions of S^2 and S_z):

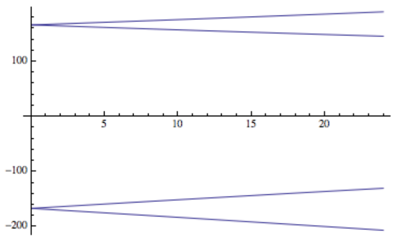
```
MatrixForm[hesr[3 / 2, 0, 0, 0]]
```

$$\begin{pmatrix} -6.9828\times10^{-6} & -0.0000583174 - 0.000331818\,i & 0.000395619 - 0.0000892098\,i & 0. \\ -0.0000583174 + 0.000331818\,i & 6.9828\times10^{-6} & 0. + 0.\,i & 0.000395619 - 0.0000892098\,i \\ 0.000395619 + 0.0000892098\,i & 0. + 0.\,i & 6.9828\times10^{-6} & 0.0000583174 + 0.000331818\,i \\ 0. & 0.000395619 + 0.0000892098\,i & 0.0000583174 - 0.000331818\,i & -6.9828\times10^{-6} \end{pmatrix}$$

S. A. Rouf, J. Mareš, JV *(to be published)*

Energy (in K) vs. magn. field $\boldsymbol{B}_0$:

```
Plot[au2k*Eigenvalues[hesr[3/2, 0, 0, bz]], {bz, 0, 24}]
```



$$\langle S_a S_b \rangle_0 = \frac{\sum_n \boxed{\langle n | S_a S_b | n \rangle} \exp[-W_n(0,0)/kT]}{\boxed{\sum_n \exp[-W_n(0,0)/kT]}}$$

Boltzmann weights of the states at 298 K:

```
wei[3/2, 0, 0, 0, 298]
{0.123242, 0.376758, 0.123242, 0.376758}
```

Examples of the components of the dyadic in the $|n\rangle$ basis:

```
Chop[MatrixForm[ksx2[3/2, 0, 0, 0]]]
```

$$\langle m | S_x S_x | n \rangle \begin{pmatrix} 1.9064 & -0.49135 + 0.146534\,i & 0 & -0.284646 + 0.474571\,i \\ -0.49135 - 0.146534\,i & 0.593599 & -0.277521 + 0.478773\,i & 0 \\ 0 & -0.277521 - 0.478773\,i & 1.9064 & 0.489105 + 0.153861\,i \\ -0.284646 - 0.474571\,i & 0 & 0.489105 - 0.153861\,i & 0.593599 \end{pmatrix}$$

```
Chop[MatrixForm[ksxsy[3/2, 0, 0, 0]]]
```

$$\langle m | S_x S_y | n \rangle \begin{pmatrix} -0.146521 + 0.346811\,i & -0.00194055 + 1.04772\,i & 0.0913463 + 0.0846056\,i & 0.563458 + 0.369476\,i \\ -0.00194055 - 0.251951\,i & 0.146521 + 0.35735\,i & 0.388628 + 0.194028\,i & -0.0877172 - 0.0837144\,i \\ -0.0913463 + 0.0846056\,i & 0.568917 - 0.361013\,i & -0.146521 - 0.346811\,i & -0.0137189 + 1.04763\,i \\ 0.385685 - 0.199815\,i & 0.0877172 - 0.0837144\,i & -0.00182533 - 0.251952\,i & 0.146521 - 0.35735\,i \end{pmatrix}$$

etc.

S. A. Rouf, J. Mareš, JV (*to be published*)

Thermally averaged *SS* -dyadic:

$$\langle S_a S_b \rangle_0 = \frac{\sum_n \langle n | S_a S_b | n \rangle \exp[-W_n(0,0)/kT]}{\sum_n \exp[-W_n(0,0)/kT]}$$

```
kssm[t_] := kss[3/2, 0, 0, 0, t]; Chop[MatrixForm[kssm[298]]]
```

$$\begin{pmatrix} 0.917183 & 0.0742913 & -0.048565 \\ 0.0742913 & 1.5761 & -0.276328 \\ -0.048565 & -0.276328 & 1.25671 \end{pmatrix}$$

$$\left[\mathrm{Tr}\,\langle S_a S_b \rangle_0 = S(S+1) = \frac{15}{4} \right]$$

Had we (erroneously) neglected ZFS:

```
MatrixForm[N[kssnozfs[3/2]]]
```

$$\begin{pmatrix} 1.25 & 0. & 0. \\ 0. & 1.25 & 0. \\ 0. & 0. & 1.25 \end{pmatrix}$$

$$\left[\mathrm{Tr}\,\langle S_a S_b \rangle_0 = S(S+1) = \frac{15}{4} \right]$$

The trace is invariant and, therefore, the dominating isotropic shielding terms are not affected!

S. A. Rouf, J. Mareš, JV (*to be published*)

Nonrelativistic hyperfine coupling $\boldsymbol{A}_{\text{con+dip}}$:

```
anr = a - aso; anr = (anr + Transpose[anr]) / 2;
MatrixForm[anr]
```

$$\begin{pmatrix} 1.1522 & 0.5229 & -0.302 \\ 0.5229 & -0.001 & -0.1279 \\ -0.302 & -0.1279 & -0.1557 \end{pmatrix}$$

Contact and dipolar parts, A_{con} and $\boldsymbol{A}_{\text{dip}}$:

```
acon = (anr[[1, 1]] + anr[[2, 2]] + anr[[3, 3]]) / 3
```

0.331833

```
adip = anr - acon * one33; MatrixForm[adip]
```

$$\begin{pmatrix} 0.820367 & 0.5229 & -0.302 \\ 0.5229 & -0.332833 & -0.1279 \\ -0.302 & -0.1279 & -0.487533 \end{pmatrix}$$

SO corrections to hyperfine coupling $\boldsymbol{A}_{\text{SO}}$:

```
MatrixForm[aso]
```

$$\begin{pmatrix} 0.0235 & 0.0293 & -0.0196 \\ 0.0105 & -0.0113 & -0.0046 \\ -0.005 & -0.0038 & -0.0137 \end{pmatrix}$$

Isotropic, symmetric anisotropic, and antisymmetric anisotropic contributions, A_{PC}, $\boldsymbol{A}_{\text{dip,2}}$, $\boldsymbol{A}_{\text{as}}$:

```
apc = (aso[[1, 1]] + aso[[2, 2]] + aso[[3, 3]]) / 3
```

-0.0005

```
adip2 = (aso + Transpose[aso]) / 2 - apc * one33; MatrixForm[adip2]
```

$$\begin{pmatrix} 0.024 & 0.0199 & -0.0123 \\ 0.0199 & -0.0108 & -0.0042 \\ -0.0123 & -0.0042 & -0.0132 \end{pmatrix}$$

```
aas = aso - apc * one33 - adip2; MatrixForm[aas]
```

$$\begin{pmatrix} 0. & 0.0094 & -0.0073 \\ -0.0094 & 0. & -0.0004 \\ 0.0073 & 0.0004 & 0. \end{pmatrix}$$

Total shielding tensor:

$$\sigma^{(0)}_{\epsilon\tau} = \sigma^{\text{orb}}_{\epsilon\tau} - \frac{\mu_{\text{B}}}{\gamma kT}\sum_{ab} g_{\epsilon a}\langle S_a S_b\rangle_0 A_{b\tau}$$

```
MatrixForm[totalshi]
```

$$\begin{pmatrix} -73.2743 & -40.8086 & 23.483 \\ -187.459 & 7.06868 & 23.6575 \\ 108.156 & 24.4522 & 35.3219 \end{pmatrix}$$

```
shiconstant =
  (totalshi[[1, 1]] + totalshi[[2, 2]] + totalshi[[3, 3]]) / 3
```

-10.2946

Contact shielding terms:

Term in hyperfine $\sigma_{\epsilon\tau}$	Symbol	Number	Order	Tensorial rank $S=\frac{1}{2}$	Tensorial rank $S>\frac{1}{2}$
$g_e A_{\text{con}}\langle S_\epsilon S_\tau\rangle_0$	δ_{con}	1	$\mathcal{O}(\alpha^2)$	**0**	**0**, 2
$g_e A_{\text{PC}}\langle S_\epsilon S_\tau\rangle_0$	$\delta_{\text{con,2}}$	3	$\mathcal{O}(\alpha^4)$	**0**	**0**, 2
$\Delta g_{\text{iso}} A_{\text{con}}\langle S_\epsilon S_\tau\rangle_0$	$\delta_{\text{con,3}}$	6	$\mathcal{O}(\alpha^4)$	**0**	**0**, 2

```
MatrixForm[contact]
```

$$\begin{pmatrix} -32.2623 & -2.61322 & 1.70829 \\ -2.61322 & -55.44 & 9.71994 \\ 1.70829 & 9.71994 & -44.2054 \end{pmatrix}$$

```
MatrixForm[conpc]
```

$$\begin{pmatrix} 0.0486121 & 0.00393755 & -0.00257402 \\ 0.00393755 & 0.0835359 & -0.0146458 \\ -0.00257402 & -0.0146458 & 0.0666079 \end{pmatrix}$$

```
MatrixForm[gisocon]
```

$$\begin{pmatrix} -1.82793 & -0.148061 & 0.0967892 \\ -0.148061 & -3.14114 & 0.550716 \\ 0.0967892 & 0.550716 & -2.50461 \end{pmatrix}$$

Dipolar shielding terms:

Term in hyperfine $\sigma_{\epsilon\tau}$	Symbol	Number	Order	Tensorial rank $S=\frac{1}{2}$	Tensorial rank $S>\frac{1}{2}$	
$g_e \sum_b A_{b\tau}^{\mathrm{dip}} \langle S_\epsilon S_b \rangle_0$	δ_{dip}	2	$\mathcal{O}(\alpha^2)$	2	$\mathbf{0}$, 2, 1	MatrixForm[dipolar] $\begin{pmatrix} -85.4322 & -48.8759 & 27.8591 \\ -102.668 & 47.7428 & 9.46613 \\ 59.771 & 9.98098 & 59.646 \end{pmatrix}$
$g_e \sum_b A_{b\tau}^{\mathrm{dip},2} \langle S_\epsilon S_b \rangle_0$	$\delta_{\mathrm{dip},2}$	4	$\mathcal{O}(\alpha^4)$	2	$\mathbf{0}$, 2, 1	MatrixForm[dipolar2] $\begin{pmatrix} -2.55342 & -1.87133 & 1.16098 \\ -3.87402 & 1.52464 & 0.411916 \\ 2.34501 & 0.345603 & 1.5721 \end{pmatrix}$
$\Delta g_{\mathrm{iso}} \sum_b A_{b\tau}^{\mathrm{dip}} \langle S_\epsilon S_b \rangle_0$	$\delta_{\mathrm{dip},3}$	7	$\mathcal{O}(\alpha^4)$	2	$\mathbf{0}$, 2, 1	MatrixForm[gisodip] $\begin{pmatrix} -4.84045 & -2.76923 & 1.57845 \\ -5.81703 & 2.70503 & 0.536336 \\ 3.38653 & 0.565506 & 3.37945 \end{pmatrix}$

S. A. Rouf, J. Mareš, JV *(to be published)*

Antisymmetric, anisotropic contact, and pseudocontact terms:

Term in hyperfine $\sigma_{\epsilon\tau}$	Symbol	Number	Order	Tensorial rank $S=\frac{1}{2}$	Tensorial rank $S>\frac{1}{2}$	
$g_e \sum_b A_{b\tau}^{\mathrm{as}} \langle S_\epsilon S_b \rangle_0$	δ_{as}	5	$\mathcal{O}(\alpha^4)$	1	2, 1	MatrixForm[antisymm] $\begin{pmatrix} 0.111607 & -0.911849 & 0.712887 \\ 1.7843 & -0.0623094 & 0.124317 \\ -1.24782 & -0.00489468 & -0.0492974 \end{pmatrix}$
$A_{\mathrm{con}} \sum_a \Delta\tilde{g}_{\epsilon a} \langle S_a S_\tau \rangle_0$	$\delta_{\mathrm{c,aniso}}$	8	$\mathcal{O}(\alpha^4)$	2, 1	$\mathbf{0}$, 2, 1	MatrixForm[anisocon] $\begin{pmatrix} 9.42627 & -3.49818 & 2.06187 \\ -3.7061 & -22.2568 & 18.1406 \\ 2.18665 & 18.1857 & -1.55477 \end{pmatrix}$
$\sum_{ab} \Delta\tilde{g}_{\epsilon a} A_{b\tau}^{\mathrm{dip}} \langle S_a S_b \rangle_0$	δ_{pc}	9	$\mathcal{O}(\alpha^4)$	$\mathbf{0}$, 2, 1	$\mathbf{0}$, 2, 1	MatrixForm[pseudocon] $\begin{pmatrix} 15.9149 & 17.5678 & -10.2598 \\ -60.7441 & 9.49179 & -14.701 \\ 35.4777 & -14.1955 & -6.71517 \end{pmatrix}$

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Isotropic shielding contributions:

Term in hyperfine $\sigma_{\epsilon\tau}$	Symbol	Number	Order	Tensorial rank $S=\frac{1}{2}$	Tensorial rank $S>\frac{1}{2}$	
$\sum_{ab}\Delta\tilde{g}_{\epsilon a}A_{b\tau}^{\text{dip}}\langle S_a S_b\rangle_0$	δ_{pc}	9	$\mathcal{O}(\alpha^4)$	**0**, 2, 1	**0**, 2, 1	6.23
$A_{\text{con}}\sum_a \Delta\tilde{g}_{\epsilon a}\langle S_a S_\tau\rangle_0$	$\delta_{\text{c,aniso}}$	8	$\mathcal{O}(\alpha^4)$	2, 1	**0**, 2, 1	-4.80
$\Delta g_{\text{iso}}\sum_b A_{b\tau}^{\text{dip}}\langle S_\epsilon S_b\rangle_0$	$\delta_{\text{dip,3}}$	7	$\mathcal{O}(\alpha^4)$	2	**0**, 2, 1	0.41
$\Delta g_{\text{iso}}A_{\text{con}}\langle S_\epsilon S_\tau\rangle_0$	$\delta_{\text{con,3}}$	6	$\mathcal{O}(\alpha^4)$	**0**	**0**, 2	-2.49
$g_e\sum_b A_{b\tau}^{\text{as}}\langle S_\epsilon S_b\rangle_0$	δ_{as}	5	$\mathcal{O}(\alpha^4)$	1	2, 1	0.00
$g_e\sum_b A_{b\tau}^{\text{dip,2}}\langle S_\epsilon S_b\rangle_0$	$\delta_{\text{dip,2}}$	4	$\mathcal{O}(\alpha^4)$	2	**0**, 2, 1	0.18
$g_e A_{\text{PC}}\langle S_\epsilon S_\tau\rangle_0$	$\delta_{\text{con,2}}$	3	$\mathcal{O}(\alpha^4)$	**0**	**0**, 2	0.07
$g_e\sum_b A_{b\tau}^{\text{dip}}\langle S_\epsilon S_b\rangle_0$	δ_{dip}	2	$\mathcal{O}(\alpha^2)$	2	**0**, 2, 1	7.32
$g_e A_{\text{con}}\langle S_\epsilon S_\tau\rangle_0$	δ_{con}	1	$\mathcal{O}(\alpha^2)$	**0**	**0**, 2	-43.97

Orbital part: 26.59

Total: -10.29

Chemical shift wrt. TMS:

$$\delta = \sigma_{\text{ref}} - \sigma = 31.50 - (-10.29) = 41.79 \text{ ppm}$$

Experiment: 43.2 ppm