

PNMRShift Program

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Chapter 1

Introduction

The PNMRSht program calculates the NMR shielding for a nucleus in a paramagnetic molecule using EPR spin Hamiltonian parameters for the shielding components specific to the electron paramagnetism. The default route of the code is based on an equation derived by Moon & Patchkovskii (Reference 1):

$$\sigma = \sigma^{\text{orb}} - \frac{\beta_e}{g_N \beta_N} \frac{S(S+1)}{3k_B T} \mathbf{g} \cdot \mathbf{A} \quad (1.1)$$

with \mathbf{A} in energy units. In SI units, $\mathbf{A}(\text{J}) = h \times 10^6 \times \mathbf{A}(\text{MHz})$. The result of this equation is unitless, but usually multiplied by 10^6 to convert it to the usual ppm units. The dot indicates here a matrix product. S is the effective spin, and other physical constants have usual notations. The spin Hamiltonian is assumed to have the following contributions: $\beta_e \mathbf{B} \mathbf{g} \mathbf{S}$ for the Zeeman interaction, and $\mathbf{S} \mathbf{A} \mathbf{I}$ for the hyperfine interaction. If the hyperfine interaction is based on the operator $\mathbf{I} \mathbf{A} \mathbf{S}$, for instance, then a matrix transpose for \mathbf{A} should be used in Equation 1.1.

In the simplest case, PNMRSht reads from an input file calculated tensors \mathbf{g} , \mathbf{A} and σ^{orb} (the latter is usually the corresponding shielding tensor of a closely related diamagnetic analog, or calculated for the paramagnetic system but excluding any contributions related to the electron paramagnetism), from the command line or a batch script used to call the program the values for S and T , a molecular structure from an xyz file, and assembles the shielding tensor as in Equation 1.1, or more sophisticated versions as explained below. For worked-out examples that we have used for an undergraduate computational chemistry laboratory course please see a related article in *J. Chem. Educ.*²

Equation 1.1 can be split up into several components in order to facilitate analysis. The \mathbf{g} -tensor is divided into three parts – the first is the nonrelativistic isotropic part due to g_e , and the remaining (relativistic) part, $\Delta \mathbf{g} = \mathbf{g} - g_e \mathbf{1}$, is further subdivided into its own isotropic part $\Delta g_{\text{iso}} \mathbf{1}$, and its anisotropic part $\Delta \tilde{\mathbf{g}}$.

$$\mathbf{g} = g_e \mathbf{1} + \Delta \mathbf{g} \quad (1.2)$$

$$\Delta \mathbf{g} = \mathbf{g} - g_e \mathbf{1} = \Delta g_{\text{iso}} \mathbf{1} + \Delta \tilde{\mathbf{g}} \quad (1.3)$$

Likewise, the hyperfine tensor is decomposed into five separate components - a nonrelativistic Fermi-Contact term \mathbf{A}_{nrfc} , nonrelativistic spin-dipole term \mathbf{A}_{nrsd} , relativistic corrections to the nonrelativistic terms (\mathbf{A}_{sofc} and \mathbf{A}_{sosd}), and a relativistic asymmetric part \mathbf{A}_{as} . The Fermi-Contact terms are often taken to be diagonal, isotropic tensors.

Table 1.1: All contributions to $\mathbf{g} \cdot \mathbf{A}$ Eq. 1.1

Term	Label	Order
Fermi-Contact Shift		
$g_e \mathbf{A}_{\text{nrfc}}$	GE. ANRFC	$\mathcal{O}(\alpha^2)$
$g_e \mathbf{A}_{\text{sofc}}$	GE. ASOFC	$\mathcal{O}(\alpha^4)$
$\Delta g_{\text{iso}} \mathbf{A}_{\text{nrfc}}$	dGiso. ANRFC	$\mathcal{O}(\alpha^4)$
$\Delta g_{\text{iso}} \mathbf{A}_{\text{sofc}}$	dGiso. ASOFC	$\mathcal{O}(\alpha^6)$
$\Delta \tilde{\mathbf{g}} \mathbf{A}_{\text{nrfc}}$	dGtilde. ANRFC	$\mathcal{O}(\alpha^4)$
$\Delta \tilde{\mathbf{g}} \mathbf{A}_{\text{nrsd}}$	dGtilde. ANRSD	$\mathcal{O}(\alpha^4)$
Pseudocontact Shift		
$g_e \mathbf{A}_{\text{nrsd}}$	GE. ANRSD	$\mathcal{O}(\alpha^2)$
$g_e \mathbf{A}_{\text{sosd}}$	GE. ASOSD	$\mathcal{O}(\alpha^4)$
$g_e \mathbf{A}_{\text{as}}$	GE. AS	$\mathcal{O}(\alpha^4)$
$\Delta g_{\text{iso}} \mathbf{A}_{\text{nrsd}}$	dGiso. ANRSD	$\mathcal{O}(\alpha^4)$
$\Delta g_{\text{iso}} \mathbf{A}_{\text{sosd}}$	dGiso. ASOSD	$\mathcal{O}(\alpha^6)$
$\Delta g_{\text{iso}} \mathbf{A}_{\text{as}}$	dGiso. AS	$\mathcal{O}(\alpha^6)$
$\Delta \tilde{\mathbf{g}} \mathbf{A}_{\text{sofc}}$	dGtilde. ASOFC	$\mathcal{O}(\alpha^6)$
$\Delta \tilde{\mathbf{g}} \mathbf{A}_{\text{sosd}}$	dGtilde. ASOSD	$\mathcal{O}(\alpha^6)$
$\Delta \tilde{\mathbf{g}} \mathbf{A}_{\text{as}}$	dGtilde. AS	$\mathcal{O}(\alpha^6)$

Therefore, $\mathbf{g} \cdot \mathbf{A}$ in Eq. 1.1 is a 15-term sum of these combinations.^{3,4} The 15 terms, along with the notation used in the output of PNMShift, are shown in Table 1.1.

Equation 1.1 is also split up into terms associated with the Fermi-Contact portions and the spin-dipole terms of the hyperfine tensor. These are commonly called the contact or Fermi-Contact (FC) shift and the pseudocontact (PC) shift, respectively.

$$\sigma = \sigma^{\text{orb}} - \underbrace{K \mathbf{g} \cdot \mathbf{A}^{\text{fc}}}_{\text{FC}} - \underbrace{K \mathbf{g} \cdot \mathbf{A}^{\text{sd}}}_{\text{PC}} \quad (1.4)$$

$$K = \frac{\beta_e}{g_N \beta_N} \frac{S(S+1)}{3k_B T} \quad (1.5)$$

Which of the 15 terms in the expansion belong to which contribution is also shown in Table 1.1. Under certain assumptions, these equations are equivalent to those given by McConnell & Robertson,⁵ Kurland & McGarvey,⁶ and Bertini et al.⁷

1.1 Including Zero-Field Splitting (ZFS)

1.1.1 Method of Soncini and Van den Heuvel

For molecules with spin $S > 1/2$ and calculations where the g - and hyperfine tensors are determined without spin-orbit interactions included in the ground state wavefunction or density matrix, zero-field

splitting should be included in the PNMR shielding equation. The equation analogous to Eq. 1.1 is^{8,9}

$$\sigma = \sigma^{\text{orb}} - \frac{\beta_e}{g_N \beta_N k_B T} \mathbf{g} \cdot \mathbf{Z} \cdot \mathbf{A} \quad (1.6)$$

The elements of the matrix \mathbf{Z} are given by

$$Z_{kl} = \frac{1}{Q} \sum_{\lambda} e^{-\frac{E_{\lambda}}{k_B T}} \left[\sum_{a,a'} \langle S\lambda a | \hat{S}_k | S\lambda a' \rangle \langle S\lambda a' | \hat{S}_l | S\lambda a \rangle \right. \\ \left. + 2k_B T \operatorname{Re} \sum_{\lambda' \neq \lambda} \sum_{a,a'} \frac{\langle S\lambda a | \hat{S}_k | S\lambda' a' \rangle \langle S\lambda' a' | \hat{S}_l | S\lambda a \rangle}{E_{\lambda'} - E_{\lambda}} \right] \quad (1.7)$$

The energies E_{λ} are obtained from diagonalizing the \mathbf{SDS} part of the EPR Hamiltonian where \mathbf{D} is the ZFS tensor. The labels λ and a refer to the $2S + 1$ ZFS eigenfunctions, the eigenvectors of the \mathbf{SDS} term, which are not necessarily degenerate as they are for a pure spin multiplet without ZFS. Q is the partition function for the split multiplet. For more information, see References 8, 9, and 10.

1.1.2 Method of Pennanen and Vaara

Previous versions of PNMRShift accounted for ZFS by calculating the PNMR shielding using the method of Vaara et al.,^{3,4} who used

$$Z_{kl} = \frac{1}{Q} \sum_{\lambda} e^{-\frac{E_{\lambda}}{k_B T}} \left[\sum_a \langle S\lambda a | \hat{S}_k \hat{S}_l | S\lambda a \rangle \right] \quad (1.8)$$

after diagonalizing the ZFS Hamiltonian in the basis of pseudo-spin- S eigenfunctions. This method is deprecated as it was shown by Soncini and Van den Heuvel to be incorrect.

1.2 Spin-orbit correction for the Hyperfine Tensor

If the hyperfine tensor is calculated without considering spin-orbit effects, there are certain approximations to the PNMR shift equations that are not entirely compatible with each other, as discussed in Reference 11. This is due to the use of g_e versus the full g -tensor in the equations. For organic radicals and perhaps first-row transition metals (generally, when the spin-orbit splitting is small compared to the gap between ground state and excited electronic states), these considerations should not matter much. For cases with stronger spin-orbit coupling, we proposed a correction to the hyperfine tensor that uses the calculated g -tensor elements.¹¹ The correction should be used with caution, however, as the full implications of applying it are not yet fully understood.

Chapter 2

Compilation and Usage

2.1 Compilation

2.1.1 Requirements

Compiling and using the PNMRSht program requires a Unix like system (Linux et al.) with a working set of compilers:

- A Fortran and C++ Compiler. Tested with:
 - GCC v4.4.6
 - GCC v4.7.2
 - Intel v12.1
- Boost (no compilation needed, just the Boost::format headers)
- CMake 2.6 or newer

The code is fairly standard C++ code, therefore other compilers should work just as well.

2.1.2 Compiling

Compilation is performed on the command line using CMake

```
mkdir build
cd build
cmake ../
make
```

And that is it. After building, the PNMRSht executable may be copied to anywhere you find convenient and where it is accessible. The executable is all that is needed.

2.1.3 Windows executables

See the file README.windows in the top level directory of the PNMRSht package for instructions how to cross-compile a Windows executable on a Linux system. For convenience, a pre-compiled Windows binary is provided. It needs to be executed from a command line window. We recommend using batch files (.bat) to run the code, as in the provided examples.

Table 2.1: Arguments to the PNMRShift program

Required	
-t <temperature>	Temperature in K
-s <spin>	Overall spin of the system. Doublet = 0.5, triplet = 1.0, etc.
-c <file>	XYZ file. This is a standard XYZ file with the first line being the number of atoms and the second line being the title (or a blank line). XYZ coordinates are in angstroms
-f <file>	Input file for the program containing the tensor information
Optional	
--geosd	Use a purely-dipolar hyperfine tensor that is generated solely from the geometry.
--keepfc	When combined with --geosd, keep the Fermi-Contact portions of the hyperfine tensor. Default is to erase them.
--correctA	Correct the hyperfine tensor with the g-tensor. See Section 1.2
--detail	Print the contributions to the overall shielding tensor of all 15 terms in Table 1.1. (Page 3)
-a <label>:<avg>	Averaging. See Section 2.2.4. Averaging can also be included in the input file.
--deltag	Input file contains delta-g (in ppt) rather than the full g-tensor.
--splitinp	Input file contains tensors split into components (g-tensor into dia- and paramagnetic, hyperfine into FCSD and PSOSO). Implies --deltag.
--pvzfs	Calculates the ZFS correction using the method of Pennanen and Vaara. Default is to use the method of Soncini and Van den Heuvel (See Section 1.1)

2.2 Usage

2.2.1 Basic Usage

If the program is invoked without options, a help screen is displayed. Table 2.1 shows the options for the program.

2.2.2 Selection Strings

In some places atoms can be specified with a string of numbers that includes ranges. For example, for all atoms 1 through 10, a string of 1-10 can be written. The following are all valid selection strings:

1,2,3,4,5

1-5

2,5,6-10,22

1-3,6,10-18,21,49-65

We hope that their use is self explanatory. Take note that duplicates will be removed and the list will be sorted. That is, 1-4,2,6,12 will include nuclei 1, 2, 3, 4, 6, and 12.

2.2.3 PNMShift Input File

PNMShift needs an input file containing the hyperfine tensors, g -tensors, and orbital shielding tensors, optionally ZFS tensors, as well as information on how to average certain quantities.

The file is constructed in a somewhat free form. All keywords are case insensitive, and numbers on the same line are separated with any number of spaces or tabs. (The geometry is read from a separate XYZ file.) The tensors are listed in any order. Each tensor is started with a header identifying which tensor it is, with the atom number corresponding to the atom ordering in the XYZ file) which is then followed by the tensor. The tensor itself is written in three or six lines containing three columns each. Six lines are used if the tensors are separated into contributions, which is needed for the detailed analysis according to Table 1.1.

A hyperfine tensor is written as a 3x3 matrix (three lines) in units of MHz. The header line is `atensor # X` where X is the element symbol and $\#$ is the number of the atom in the XYZ input ordering, with the first element being one. The file can contain multiple hyperfine tensor specifications.

```
atensor 2 H
-6.565   -2.565   -1.098
-2.565   -0.262    3.088
-1.098    3.088   -3.199
```

A similar input is used for the orbital shielding tensor, except the heading is now `orbtensor`. The input of the shielding tensor is in ppm.

```
orbtensor 2 C
75.872  17.920    5.629
17.920  31.850  -15.832
 5.629 -15.832 164.274
```

The g -tensor is input with the keyword `gtensor` with nothing else on the line.

```
gtensor
2.085      -0.000      0.000
0.000      2.085      0.000
0.000      0.000      2.003
```

Finally, the optional ZFS tensor is input under the heading `zfstensor`

```
zfstensor
 0.659659   -0.186353   -0.907466
-0.186353   -0.629593    0.128537
-0.907466    0.128537   -0.030066
```

After construction, this file is used as an input to `-A`, `-O`, `G`, and/or `-Z` arguments to the program.

2.2.4 Averaging

The PNMRSht program allows the user to average nuclei. This is particularly useful for symmetry-equivalent nuclei whose calculated shifts are not equal due to the calculation employing a broken-symmetry configuration, which is not uncommon with DFT calculations.

To specify an average, use the `-a` argument, followed by a label and selection string (Section 2.2.2). The label is an arbitrary name given (for example, "Methyl 1H"). The label and selection string are separated by a colon. Usually, the entire argument is surrounded in quotes to properly handle spaces in the label. For example, averaging three methyl groups, both carbon and proton shieldings, may look like

```
-a "Methyl 1H:8-10,19-21,23-25" -a "Methyl 13C:7,18,22"
```

Averaging information can also be included in the input file, under the heading 'averaging'. Each different average is placed on its own line. The section is processed until a blank line occurs.

```
averaging
ethyl 1H:8-10,19-21,23-25
ethyl 13C:11,22,26
```

In the output, the average will be printed in the main (isotropic) results table, as well as in separate detailed results tables.

2.3 Output

The output of PNMRSht is structured as follows (in order):

1. The user input (temperature, spin, and atomic coordinates in Å)
2. The g -tensor components, as well as its conversion from Δg to g
3. Hyperfine tensors as read in from the input file
4. Hyperfine tensors that are corrected or calculated using the geometry (`--correctA` and/or `--geosd`)
5. Orbital shieldings as read from the input file
6. ZFS Tensor. If there was no ZFS tensor input, this will be a 3×3 identity matrix
7. Calculated \mathbf{Z} matrix (see Eq. 1.7). If no ZFS tensor was input, this will be a 3×3 diagonal matrix with elements of $S(S+1)/3$
8. Main results table, showing the predicted isotropic values of the shielding, Fermi-Contact, and pseudocontact tensors)
9. If requested, a detailed breakdown of contributions with full tensors

If an atom was not input in some section (for example, if the input is missing the hyperfine tensor for an atom), that atom will show an 'xx' in the element column and the tensor may be zero.

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Bibliography

- [1] Moon, S.; Patchkovskii, S. First-principles calculations of paramagnetic NMR shifts. In *Calculation of NMR and EPR Parameters. Theory and Applications*; Kaupp, M.; Bühl, M.; Malkin, V. G., Eds.; Wiley-VCH: Weinheim, 2004 pages 325–338.
- [2] Pritchard, B.; Simpson, S.; Zurek, E.; Autschbach, J. *J. Chem. Educ.* **2014**, *91*, 1058-1063.
- [3] Pennanen, T. O.; Vaara, J. *Phys. Rev. Lett.* **2008**, *100*, 133002–4.
- [4] Liimatainen, H.; Pennanen, T. O.; Vaara, J. *Can. J. Chem.* **2009**, *87*, 954–964.
- [5] McConnell, H. M.; Robertson, R. E. *J. Chem. Phys.* **1958**, *29*, 1361–1365.
- [6] Kurland, R. J.; McGarvey, B. R. *J. Magn. Reson.* **1970**, *2*, 286–301.
- [7] Bertini, I.; Luchinat, C.; Parigi, G. *Prog. Nucl. Mag. Res. Sp.* **2002**, *40*, 249–273.
- [8] Soncini, A.; Van den Heuvel, W. *J. Chem. Phys.* **2013**, *138*, 021103.
- [9] Martin, B.; Autschbach, J. *J. Chem. Phys.* **2015**, *142*, 054108.
- [10] Van den Heuvel, W.; Soncini, A. *Phys. Rev. Lett.* **2012**, *109*, 073001.
- [11] Autschbach, J.; Patchkovskii, S.; Pritchard, B. *J. Chem. Theory Comput.* **2011**, *7*, 2175-2188.