EPR and Paramagnetic NMR NWChem Tutorial

This tutorial involves tensor/matrix operations, which can be readily done with Octave, a GNU license MATLAB-like program, freely available in any Linux or Cygwin (Windows) distribution. Octave will be used to demonstrate tensor manipulation and calculation of g-tensor, A-tensor, and paramagnetic NMR parameters obtained from an example NWChem output.

Example input:

```
echo

start ch3radical_rot
title ch3radical_rot

geometry noautoz units angstrom nocenter
symmetry c1
c +0.00000000   +0.00000000   +0.00000000
h -0.21385373   +0.98738914   +0.39826283
h -0.78597592   -0.69448290   +0.28059107
h +0.09050298   +0.04455726   -1.08102723
end

BASIS "ao basis" PRINT
 * library 6-311G
END

relativistic
 zora on
 zora:cutoff_NMR 1d-8
 zora:cutoff 1d-30
end

dft
 odft
 mult 2
 xc b3lyp
end
task dft

property
 gshift
 hyperfine
 shielding
end
task dft property
```

First, the following constants and values are needed:

```
>ge = 2.002319304; Be = 9.27400915e-24; k = 1.3806504e-23; u0 = 4*pi*(10^7);
h = 6.62606896e-34; BN = 5.05078317e-27; gnC = 1.4044;
```

gnC is the nuclear g-factor for a ^{13}C nucleus; it is calculated from the measured gyromagnetic ratio (in 10^6 rad s^{-1} T^{-1}) for ^{13}C:

```
>gammaC = 67.262;
>gnC = gammaC*(h/(2*pi))/BN*(10^6);
```

Note that the example system CH_3 ground state is a doublet.

```
>S = 0.5;
```

Since paramagnetic NMR is temperature-dependent, specify a temperature in Kelvin:

```
>T = 305.15;
```

Reconciling the g-tensor from NWChem calculation:
Note that the tensor from a g-shift (Δg) calculation from NWChem is in ppt (parts-per-thousand).
Enter the total Δg (g-shift) tensor into Octave:

```
>GShiftTens = [0.1740 0.2216 -0.2640; 0.2216 0.6888 0.0981; -0.2640
0.0981 0.6542];
```

Transform Δg tensor to g tensor:

```
>GTens = 0.001*GShiftTens + (ge*eye(3))
   2.0025e+00   2.2160e-04  -2.6400e-04
   2.2160e-04   2.0030e+00   9.8100e-05
  -2.6400e-04   9.8100e-05   2.0030e+00
```

Note that `'eye(3)'` stands for the 3x3 identity matrix (diagonal 1's and off-diagonal 0's).
To obtain gxx, gyy, and gzz from the g tensor matrix, find the eigenvalues of gg^T and take the square root of the eigenvalues:

```
>sqrt(eig(GTens*transpose(GTens)))
ans =

   2.0023
   2.0031
   2.0031
```

To obtain g_{iso}, take the trace of g and divide by 3:

```
>trace(GTens)/3
2.0028
```

Reconciling the A-tensor from NWChem calculation:
Enter the total A tensor (for convenience use the tensor that is in MHz) for the first carbon atom listed:

```
>ATensC = [428.6293 -58.2145 69.3689;-58.2145 293.3841 -25.7459; 69.3689 -
25.7459 302.4571];
```

Correct this matrix by rotating it into the reference frame of the g-tensor (obtained in the last section):

```
>ATensC_Corr = (ATensC/ge)*GTens
   428.651   -58.184    69.332
   -58.184   293.477   -25.732
    69.332   -25.732   302.546
```

To find Axx, Ayy, Azz, find the eigenvalues of AA^T and take the square root of the eigenvalues:

```
> sqrt(eig(ATensC_Corr*transpose(ATensC_Corr)))
ans =

   271.88
   271.88
   480.91
```

To calculate A_{iso}, take the trace of the corrected A tensor and divide by 3:

```
>trace(ATensC_Corr)/3
341.56
```

Reconciling the pNMR parameters from NWChem calculation:
Calculate the dipolar form of the corrected A tensor for the carbon atom:

```
>ATensC_Corr_Dip = ATensC_Corr – (trace(ATensC_Corr)/3)*eye(3)
   87.093  -58.184   69.332
  -58.184  -48.081  -25.732
   69.332  -25.732  -39.012
```

For convenience, convert the hyperfine tensors units from MHz to J:

```
>ATensC_Energy = (10^6)*h*ATensC
   2.8401e-25  -3.8573e-26   4.5964e-26
  -3.8573e-26   1.9440e-25  -1.7059e-26
   4.5964e-26  -1.7059e-26   2.0041e-25
>ATensC_Corr_Energy = (10^6)*h*ATensC_Corr
   2.8403e-25  -3.8553e-26   4.5940e-26
  -3.8553e-26   1.9446e-25  -1.7050e-26
   4.5940e-26  -1.7050e-26   2.0047e-25
>ATensC_Corr_Dip_Energy =(10^6)*h*ATensC_Corr_Dip
   5.7708e-26  -3.8553e-26   4.5940e-26
  -3.8553e-26  -3.1859e-26  -1.7050e-26
   4.5940e-26  -1.7050e-26  -2.5850e-26
```

To calculate the Fermi contact shift:

```
>FCShiftC =
(10^6)*trace(GTens)/3*Be/(gnC*BN)*(S*(S+1))/(3*k*T)*trace(ATensC_Energy)/3
FCShiftC = 3.5159e+04
```

To calculate the pseudocontact shift (in ppm):

```
>PCShiftC =
(10^6)*(S*(S+1))/(9*k*T)*Be/(gnC*BN)*trace(ATensC_Corr_Dip_Energy*GTens)
PCShiftC = -1.9008
```

From the shielding calculation in NWChem,

```
>OrbShldC = 83.7136
```

Putting it all together, the total chemical shielding in ppm is:

```
>TotShldC = OrbShldC – FCShiftC – PCShiftC
TotShldC =  -3.5074e+04
```

Subtract this value from the appropriate reference to obtain the chemical shift.

We can repeat these steps for the hydrogen atom. The proton nuclear g-factor is:

```
>gnH = 5.5856947
```

The hyperfine A tensor for the hydrogen atom from the NWChem output is:

```
>ATensH = [-39.8498 -17.0675  5.2453; -17.0675  0.9102  23.3706; 5.2453
23.3706  -46.3284];
```

Correct this tensor by transforming it into the reference frame of the g-tensor:

```
>ATensH_Corr = (ATensH/ge)*GTens

  -39.85584  -17.07752    5.25143
  -17.07196    0.90977   23.38053
    5.25445   23.37695  -46.34308
```

Calculate the dipolar form of the corrected A tensor for the H atom:

```
>ATensH_Corr_Dip = ATensH_Corr - (trace(ATensH_Corr))/3*eye(3)
  -11.4261  -17.0775    5.2514
  -17.0720   29.3395   23.3805
    5.2545   23.3770  -17.9134
```

Convert the hyperfine tensors units from MHz to J:

```
>ATensH_Energy = (10^6)*h*ATensH
  -2.6405e-26  -1.1309e-26   3.4756e-27
  -1.1309e-26   6.0310e-28   1.5486e-26
   3.4756e-27   1.5486e-26  -3.0698e-26
>ATensH_Corr_Energy = (10^6)*h*ATensH_Corr
  -2.6409e-26  -1.1316e-26   3.4796e-27
  -1.1312e-26   6.0282e-28   1.5492e-26
   3.4816e-27   1.5490e-26  -3.0707e-26
>ATensH_Corr_Dip_Energy =(10^6)*h*ATensH_Corr_Dip
  -7.5710e-27  -1.1316e-26   3.4796e-27
```

```
  -1.1312e-26   1.9441e-26   1.5492e-26
   3.4816e-27   1.5490e-26  -1.1870e-26
```

Calculate the Fermi Contact Shift:

```
>FCShiftH =
(10^6)*trace(GTens)/3*Be/(gnH*BN)*(S*(S+1))/(3*k*T)*trace(ATensH_Energy)/3
FCShiftH = -735.76
```

Calculate the pseudocontact shift:

```
>PCShiftH =
(10^6)*(S*(S+1))/(9*k*T)*Be/(gnH*BN)*trace(ATensH_Corr_Dip_Energy*GTens)
PCShiftH =  0.0032218
```

From the NWChem output, the orbital shielding is:

```
>OrbShldH = 28.1923
```

Putting it all together, the total chemical shielding in ppm is:

```
>TotShldH = OrbShldH - FCShiftH – PCShiftH
TotShldH =  763.95
```