

# **NMR spectroscopy**

[http://physchem.ox.ac.uk/~hill/tutorials/nm3\\_tutorial/nucspin/index.html](http://physchem.ox.ac.uk/~hill/tutorials/nm3_tutorial/nucspin/index.html)

<http://www.cis.rit.edu/htbooks/nmr/inside.htm>

## Calculation of NMR spectra

1. (Optimize) the geometry of your molecule (complex)
2. Calculate the NMR spectrum of the molecule  
#P NMR(Giao) Iop33(10=1) B3LYP/6-31G(d)
3. Extract the isotropic part of the magnetic shielding tensors found under the heading:  
**SCF GIAO Magnetic shielding tensor (ppm):**  
in the output file

SCF GIAO Magnetic shielding tensor (ppm):				TMS, B3LYP/6-31G(d)							
1 C	Isotropic =	45.3289	Anisotropy =	156.8247	7 H	Isotropic =	23.4596	Anisotropy =	6.5072		
XX=	25.5011	YY=	23.0027	ZX=	-8.0232	XX=	27.7156	YY=	1.1221	ZX=	-0.3373
XY=	43.3078	YY=	-20.0688	ZY=	57.2719	XY=	0.0997	YY=	22.6856	ZY=	-0.6154
XZ=	-14.4223	YZ=	57.3422	ZZ=	130.5545	XZ=	-0.0278	YZ=	-0.7572	ZZ=	19.9774
Eigenvalues:	-54.6746	40.7828	149.8787			Eigenvalues:	19.8133	22.7677	27.7977		
Eigenvectors:						Eigenvectors:					
(1)	-0.400111	0.868398	-0.292911			(1)	0.004579	0.231465	0.972832		
(2)	0.916467	0.379244	-0.127525			(2)	-0.127599	0.965025	-0.229007		
(3)	-0.000343	0.319467	0.947597			(3)	0.991815	0.123084	-0.033954		

4. Calculate the NMR spectrum of the reference (TMS) using the same method and basis set as for the molecule of interest
5. Extract the isotropic part of the magnetic shielding tensors of the reference molecule

2 C	Isotropic =	189.7001	Anisotropy =	7.0702	
XX=	189.1129	YY=	0.0980	ZX=	-3.0921
XY=	0.0890	YY=	187.3612	ZY=	-0.1613
XZ=	-3.0517	YZ=	-0.1773	ZZ=	192.6262
Eigenvalues:	187.3302	187.3565	194.4135		
3 H	Isotropic =	32.1867	Anisotropy =	9.3933	
XX=	29.7975	YY=	2.7634	ZX=	-2.1606
XY=	2.6566	YY=	35.4879	ZY=	-2.9663
XZ=	-2.1866	YZ=	-3.1550	ZZ=	31.2747
Eigenvalues:	28.1930	29.9183	38.4489		

6. Obtain the chemical shifts of your nuclei by subtracting their isotropic part of the magnetic shielding tensors from the calculated value for the corresponding nucleus in the reference molecule

$$\delta(\text{C1}) = 189.7 - 45.33 = 144.4 \text{ ppm}$$

$$\delta(\text{C1}) = 32.18 - 23.46 = 8.72 \text{ ppm}$$

7. If you want the spin-spin splittings, use the following keyword:

NMR(spinspin)

and find the spin-spin splittings in the output file under the heading:

Total nuclear spin-spin coupling J (Hz):

	1	2	3	4	5
1	0.000000D+00				
2	0.362024D+01	0.000000D+00			
3	-0.247358D+02	-0.229863D+02	0.000000D+00		
4	0.129198D+02	0.121468D+02	0.759584D-01	0.000000D+00	
5	-0.159667D+01	0.797070D+01	0.808829D+00	0.652205D+02	0.000000D+00
6	-0.867140D+00	-0.145790D+01	-0.754367D+00	0.755919D+01	-0.682201D+01
7	-0.214125D+02	-0.229658D+00	0.536527D+00	-0.492603D+00	-0.844361D+00
8	-0.124914D+01	0.350284D+00	0.266637D+01	0.167164D+00	0.360979D-01
9	0.462571D+00	-0.370440D+02	-0.313916D+01	-0.151217D+01	-0.412696D+00
	6	7	8	9	
6	0.000000D+00				
7	0.917323D-01	0.000000D+00			
8	0.150346D+01	0.247247D+02	0.000000D+00		
9	-0.740995D+00	-0.127195D+00	-0.133087D+00	0.000000D+00	

$$J_{24} = J_{42} = 12.14 \text{ Hz}$$

8. If you want to model solvent effects by using discrete models, construct the molecular complex by adding solvent molecule(s) in the vicinity of your molecule of interest.

Repeat steps 1-6.

Calculate the NMR spectrum for different tautomers of uracil.

Simulate the solvent effects on chemical shifts by using a discrete model.

# **ESR spectroscopy**

<http://www.chemistry.nmsu.edu/studntres/chem435/Lab7/intro.html>

## Calculation of ESR spectra

1. (Optimize) the geometry of your molecule (complex)

2. Calculate the ESR spectrum of the molecule

#P B3LYP/6-31G(d) Prop=EPR

by default, for open-shell systems, isotropic hyperfine coupling constants (hfcc's of the non-zero spin nuclei (isotopes) will be calculated

If you need the hyperfine coupling tensors, you must add in the route section [Prop=EPR](#)

3. Find the isotropic coupling constants in the output file under the heading:

Atom	Isotropic Fermi Contact Couplings			
	a.u.	MegaHertz	Gauss	10(-4) cm-1
1 C(13)	-0.01373	-15.43092	-5.50614	-5.14720
2 C(13)	-0.00581	-6.53089	-2.33039	-2.17847
3 C(13)	-0.01373	-15.43092	-5.50614	-5.14720
4 C(13)	0.05577	62.69550	22.37132	20.91297
5 C(13)	-0.03232	-36.33054	-12.96364	-12.11856
6 C(13)	0.05577	62.69550	22.37132	20.91297
7 O(17)	0.02363	-14.32257	-5.11065	-4.77749
8 H	0.00012	0.53720	0.19169	0.17919
9 O(17)	0.02363	-14.32257	-5.11065	-4.77749
10 H	-0.00790	-35.32797	-12.60590	-11.78414
11 H	0.00207	9.23790	3.29631	3.08143
12 H	-0.00790	-35.32797	-12.60590	-11.78414

3. Find the dipolar part of the hyperfine coupling tensors (principal values) in the output file under the heading:

----- Anisotropic Spin Dipole Couplings in Principal Axis System -----								
Atom		a.u.	MegaHertz	Gauss	10(-4) cm-1	Axes		
1 C(13)	Baa	-0.1986	-26.652	-9.510	-8.890	0.2421	0.9669	0.0804
	Bbb	-0.1858	-24.939	-8.899	-8.319	0.9097	-0.2550	0.3277
	Bcc	0.3845	51.590	18.409	17.209	-0.3374	0.0062	0.9413
14 H	Baa	-0.0026	-1.408	-0.503	-0.470	0.2540	0.8902	0.3782
	Bbb	-0.0015	-0.813	-0.290	-0.271	-0.1990	-0.3345	0.9211
	Bcc	0.0042	2.221	0.793	0.741	0.9465	-0.3092	0.0922
15 H	Baa	-0.0052	-2.800	-0.999	-0.934	-0.3608	0.0321	0.9321
	Bbb	-0.0013	-0.709	-0.253	-0.237	-0.2752	0.9513	-0.1393
	Bcc	0.0066	3.509	1.252	1.170	0.8911	0.3067	0.3344

4. Simulate the solvent effects by using discrete or continuum solvation models

Calculate the ESR spectrum for the glycine  $\cdot\text{CH}_2\text{COO}^-$  free radical