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## MCSCF calculations of nitrogen NMR shielding constants using London atomic orbitals

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### Abstract

The MCSCF method is used to calculate the nitrogen shielding constants in  $\text{HN}_3$  and four isomers of  $\text{CH}_2\text{N}_2$ . The calculations are performed using SCF and RAS SCF wavefunctions, in both cases using London atomic orbitals. For some of the shielding constants the correlation corrections exceed 100 ppm and lead to much closer agreement with experiment.

### 1. Introduction

Ab initio calculations of NMR shielding constants are now becoming feasible for large polyatomic molecules. Although the theory has been known for many years, several obstacles have previously prevented accurate calculations. Finite basis set results obtained from standard perturbation theory are gauge-origin dependent. For small molecules this problem can be circumvented by increasing the basis set until the gauge dependence is so small that it is irrelevant compared to the accuracy of the calculated constants. However, for larger systems this approach cannot be applied as a prohibitively large number of basis functions is required. There have been efficient implementations of approaches in which the gauge-origin problem has been overcome [1-4]. These methods include the LAO (London atomic orbitals) approach [5,6] also known as the GIAO (gauge invariant atomic orbitals) [7,8] approach, the IGLO approximation [9,10] and the LORG scheme [11,12] (for the most recent reviews, see refs. [1-4]). We shall

use the LAO approach, which was recently presented in a form suitable for application to any wavefunction approximation [13].

London atomic orbitals (LAOs) are formed by multiplying AOs with a field-dependent phase factor. For the one-electron, one-center problem the LAOs formed from the AO eigenfunctions of the field-free problem are eigenfunctions to first order in the magnetic field  $B$ . Therefore the use of LAOs in molecular applications has several advantages. Numerous calculations (see e.g. refs. [8,14]) have shown that the LAO scheme converges to the basis set limit faster than perturbation theory and other gauge-origin independent methods [15,16]. This is particularly important for correlated wavefunctions when large molecules are studied since the largest manageable basis sets in these cases will be far from saturated.

Once the gauge dependence problem has been solved, accurate results can be obtained in the SCF (self-consistent field) scheme for molecules well described by a single configurational wavefunction. Numerical experience has shown that the shielding

constants often agree well with experiment for the C and H nuclei in saturated molecules, whereas this is usually not the case for atoms with lone pairs of electrons and molecules with multiple bonds [17–19]. In these cases the correlation corrections must be included in order to obtain reasonable agreement with experiment. Methods that include correlation effects have been developed both within the IGLO approach (the MC IGLO scheme [3,20]) and within the LORG approximation (the SOLO scheme [2,21]). Second-order perturbation theory (MP2) calculations [22] and MCSCF (multiconfigurational self-consistent field) calculations [16] have also been presented with LAOs. The LAO MCSCF [23] method has been demonstrated to be efficient in describing the main correlation corrections to the shielding constants for smaller molecules [16], where the correlation effects are described using CAS (complete active space) SCF reference functions. However, CAS wavefunctions cannot be used for large active orbital spaces and/or for a large number of active electrons. In this work we consider four isomers of  $\text{CH}_2\text{N}_2$  and  $\text{HN}_3$ . We would have liked to use full valence shell CAS SCF wavefunctions but this is not possible with our current programs as the wavefunctions would then contain several million determinants. Instead, we have used RAS (restricted active space) SCF wavefunctions, and it appears that these can be chosen to approximate well the analogous valence CAS SCF results.

## 2. Calculations

All shielding constants have been computed using the ABACUS program <sup>#1</sup>. The calculations include the analytical evaluation of MCSCF response equations with the magnetic field as the perturbation. The integrals required in the LAO calculations are evaluated using the HERMIT integral program <sup>#2</sup>, which employs the McMurchie–Davidson scheme [24]. The reference SCF and MCSCF wavefunctions have

<sup>#1</sup> ABACUS, a program for calculation of time-independent properties for MCSCF wavefunctions, T. Helgaker, H.J.Aa. Jensen, P. Jørgensen, J. Olsen, P. Taylor, H. Koch, K. Ruud, K.L. Bak and R. Kobayashi.

<sup>#2</sup> T. Helgaker, P. Taylor and K. Ruud, Hermit-molecular integral program.

been calculated using the SIRIUS program <sup>#3</sup>. We refer to refs. [15,16] for details and for a number of numerical applications using LAOs. These papers demonstrate the advantages of LAO basis sets in the calculations of magnetizabilities [15] at the SCF level, and for NMR shielding constants [16] and AATs (atomic axial tensors) (see footnote 3) at the SCF and CASSCF levels.

We apply the MCSCF approach to study the nitrogen shielding constants of four isomers of  $\text{CH}_2\text{N}_2$  and  $\text{HN}_3$ . We have calculated the shielding constants for all atoms, but as expected the correlation corrections for the carbon and hydrogen nuclei are in most cases small. We use the following symbols for the  $\text{CH}_2\text{N}_2$  compounds:  $\text{H}_2\text{CN}_2$  for diazirine (C, N and N form a triangle),  $\text{H}_2\text{CNN}$  for diazomethane ( $\text{H}_2\text{C}=\text{N}=\text{N}$  structure),  $\text{H}_2\text{NCN}$  for cyanamide ( $\text{H}_2\text{N}-\text{C}\equiv\text{N}$ ) and finally  $\text{HNCNH}$  for carbodiimide ( $\text{HN}=\text{C}=\text{NH}$ ). The  $\text{HN}_3$  molecule and the isomers of  $\text{CH}_2\text{N}_2$  are isoelectronic, and we have used a set of identical systematically constructed wavefunctions for all these compounds. The geometries at which the calculations are carried out are described later.

We have used two basis sets, H II and H III. The smaller H II basis is (9s5p1d/5s1p) contracted to (5s4p1d/3s1p), the larger H III basis set is (11s7p2d/6s2p) contracted to (7s6p2d/4s2p). Both the primitive sets are taken from Huzinaga's [26] compilation and have previously been used in IGLO MCSCF shielding calculations on smaller molecules [27].

For the smallest basis set, we have performed two different RAS SCF calculations with the active spaces selected according to the natural orbital occupation numbers of second-order perturbation theory (MP2). In both RAS SCF wavefunctions the three 1s orbitals on N and C are kept inactive. The MP2 calculations indicate that each of the molecules has two virtual orbitals with large occupation numbers. If we consider an idealized linear X–Y–Z (X, Y, Z=C or N) isoelectronic system, it has six orbitals of  $\pi$  symmetry, four occupied and two unoccupied. To a good approximation the considered molecules have a similar structure. In the first RAS SCF function, we have incorporated in RAS2 (arbitrarily occupied active space) the valence SCF and in addition the two above

<sup>#3</sup> SIRIUS, an MCSCF program, H.J.Aa. Jensen and H. Ågren.

virtual  $\pi$  orbitals, and in the RAS3 subspace (containing no more than two electrons) the rest of the valence orbitals. This wavefunction will be called RAS-I. In the other RAS wavefunction, called RAS-II, we include only the valence SCF orbitals in RAS2, and all the remaining valence orbitals in RAS3. In addition, we allow up to quadrupole excitations into RAS3. With the active spaces and the electron distributions defined in this way, we have obtained for both RAS SCF functions configuration expansions of 80000–200000 determinants, the length depending primarily on the molecular symmetry.

We wish to point out that in the molecules studied there are several nitrogen atoms which from a chemical point of view are very different, and therefore their chemical shifts differ significantly. Nevertheless, we have used the same basis set for each nitrogen atom, and in defining the RAS-I and RAS-II wavefunctions we have only considered the general features of the electronic structure of the molecules. This is consistent with our aim which is to analyse the performance of systematically constructed wavefunctions for the calculation of NMR shielding constants for a variety of nuclei.

The molecular electronic energies are listed in Table 1. The H II results indicate that the differences between the RAS-I and RAS-II correlation energies are small. Although there is a systematic lowering of all energies going from H II to H III, the correlation energies are not affected significantly. Also, the relative energies of the  $\text{CH}_2\text{N}_2$  isomers do not change significantly with the basis set. The differences between the isomers of  $\text{CH}_2\text{N}_2$  have been considered by several authors (see e.g. refs. [28,29]) and our energies are similar to the previously obtained values, e.g., the relative energies in ref. [28] vary from 42.45 to 208.48 kJ/mol at the SCF level, and from 39.20 to 152.57 kJ/mol in an MP3 calculation. As illustrated by the results in Table 1, significant changes are found in the relative stabilities at the SCF level and at the correlated level, but the effect of the basis set is small at both levels.

The H II nitrogen NMR shielding constants are shown in Table 2. The energies obtained at the RAS-I and RAS-II levels are similar and the same is true for the shielding constants. The largest difference is 2.6 ppm, and we have therefore carried out only RAS-I calculations of the shielding constants for the larger

Table 1  
Electronic energies (in atomic units) and differences with respect to the lowest isomer,  $\text{H}_2\text{NCN}$  (in kJ/mol)

	SCF	RAS-I	RAS-II
$\text{HN}_3$ energy			
H II basis	–163.8752	–164.1002	–164.1015
H II basis	–163.9040	–164.1271	–
$\text{H}_2\text{CN}_2$ energy			
H II basis	–147.8639	–148.0729	–148.0761
diff.	228.2	199.0	199.8
energy			
H III basis	–147.8858	–148.0948	–
diff.	228.4	198.2	–
$\text{H}_2\text{CNN}$ energy			
H II basis	–147.8779	–148.0962	–148.0989
diff.	191.4	137.8	139.9
energy			
H III basis	–147.9004	–148.1179	–
diff.	190.1	137.6	–
$\text{H}_2\text{NCN}$ energy			
H II basis	–147.9508	–148.1487	–148.1522
diff.	0.0	0.0	0.0
energy			
H III basis	–147.9728	–148.1703	–
diff.	0.0	0.0	–
$\text{HNCNH}$ energy			
H II basis	–147.9335	–148.1333	–148.1364
diff.	45.4	40.4	41.5
energy			
H III basis	–147.9605	–148.1579	–
diff.	32.3	32.6	–

Table 2  
Nitrogen shielding constants, basis H II (absolute values in ppm)

	SCF	RAS-I	RAS-II
$\text{HN}_a\text{N}_b\text{N}_c$ $\text{N}_a$	191.2	207.2	207.2
$\text{N}_b$	–23.9	19.3	18.9
$\text{N}_c$	–31.2	56.7	55.2
$\text{H}_2\text{CN}_2$ N	–271.2	–127.0	–127.0
$\text{H}_2\text{CN}_a\text{N}_b$ $\text{N}_a$	–1.7	–11.8	–11.8
$\text{N}_b$	–302.8	–120.2	–122.8
$\text{H}_2\text{N}_a\text{CN}_b$ $\text{N}_a$	255.9	260.3	260.2
$\text{N}_b$	29.3	72.7	72.3
$\text{HNCNH}$ N	185.1	198.8	198.3



reported for the molecules studied here. Our SCF results for diazirine are  $-271.2$  and  $-275.2$  ppm for basis H II and H III respectively, which may be compared with the LORG value of  $-271.45$  ppm by Hansen and Bouman [32] <sup>\*\*</sup>. In our calculations, we used the same geometry as Hansen and Bouman. We also carried out a calculation using their basis set and obtained  $-268.3$  ppm.

The two nitrogen shielding constants of  $\text{H}_2\text{CNN}$  are in good agreement with IGLO results [33] ( $-12.0$  and  $-303$  ppm, respectively). For  $\text{H}_2\text{NCN}$ , both values compare well with another GIAO calculation [34], which gives  $256.9$  and  $28.6$  ppm. For  $\text{HNCNH}$ , there is a significant difference between the GIAO value of  $241.0$  ppm in ref. [34] and our result, presumably due to differences in geometry and/or basis set.

### 3.2. Correlation effects

As mentioned above, both RAS-I and RAS-II yield an approximate description of valence shell correlation. In the MCSCF approach it is difficult to estimate the role of dynamic correlation. In a test calculation for diazirine,  $\text{H}_2\text{CN}_2$ , we have used a larger active space. We have extended the RAS-I function by including in the RAS3 subspace two additional orbitals. The result is similar to RAS-I,  $\sigma(\text{N}) = -139.8$  ppm.

We have also calculated the shielding constants for the carbon and hydrogen atoms. The changes in the shielding constants due to correlation are generally so small that they are irrelevant for a systematic comparison with experimental results. The correlation correction to  $\sigma(^{13}\text{C})$  is largest for  $\text{HNCNH}$ , where the SCF value is  $22.8$  ppm and the RAS-I value is  $46.4$  ppm, in much better agreement with the experimental value of  $45.9$  ppm (for  $\text{RNCNR}$ , R = isopropyl [35], and using for C shielding  $\sigma_{\text{abs}} = 185.4 - \sigma_{\text{rel}}$ ).

### 3.3. Geometry dependence

It is well known that  $\sigma(\text{N})$  varies strongly with the molecular geometry. The tabulated results were obtained using geometries taken from the following references:  $\text{HN}_3$  [36],  $\text{H}_2\text{CN}_2$  [37],  $\text{H}_2\text{CNN}$  [38],

$\text{H}_2\text{NCN}$  [39], and  $\text{HNCNH}$  [40]. For the two molecules where the shielding constants deviate most from experiment, we have also calculated the shielding constants at other geometries. For  $\text{H}_2\text{CN}_2$ , we have used the slightly different theoretical geometry of ref. [41]. The change observed at the H II SCF level is large, from  $-271.2$  to  $-216.6$  ppm. In the RAS-I calculation using the H III basis we obtained  $-108.9$  ppm, in much better agreement with the experimental value. The difference between our results and experiment becomes  $-21.9$  ppm, instead of  $-48.2$  ppm. The results in the tables and in the figure are for the experimental geometry but the above calculation indicates that a significant part of the differences between the calculated and experimental shieldings may be due to the molecular geometry dependence. This is in agreement with previous data that show a very strong geometry dependence of nitrogen shielding constants. For example, in LAO and MBPT(2) calculations for the nitrogen molecule, Gauss [22] obtained for  $\delta\sigma/\delta r - 1135$  ppm/Å at the SCF level,  $-506$  ppm/Å at the correlated level, with the experimental value estimated to be in between these two.

For  $\text{HNCNH}$ , we have carried out additional calculations with the geometries of refs. [42,43]. The SCF results for basis H II ( $190.8$  and  $208.9$  ppm, respectively) did not differ significantly from the value in Table 3. We therefore did not carry out further correlated calculations. Moreover, for this molecule the experimental data are estimated from the substituted compound NMR spectra, so a direct comparison is not possible.

### 3.4. Experimental data

The comparison of experimental and calculated data is not a trivial matter. Measurements are done in various solvents, at different concentrations, temperatures, and different reference compounds are applied to define  $\sigma(\text{N})$ . We have mainly used the tabulation of Witanowski et al. [44], where all shieldings refer to the nitromethane standard. To convert the experimental nitrogen shielding for this standard to absolute values we have used  $\sigma_{\text{abs}} = 135.0 - \sigma_{\text{rel}}$ . Most of the data we use were originally obtained by Mason et al. [45,46]. Considering the difficulties in defining absolute values of experimental shielding con-

<sup>\*\*</sup> The authors have communicated that an error was reported in the shielding constant. The correct constant is the one given.

stants, we have estimated the accuracy of the conversion of the experimental data to be  $\pm 10$  ppm. In addition, there may be differences of the order of 20 ppm or more between the shielding constants of a nucleus in experimental conditions (solution) and for an isolated molecule (gas phase) representing the analogue of the calculations. Unfortunately, there is presently no simple way to estimate the role of solvent or rovibrational contributions in polyatomic molecules.

#### 4. Summary

The accuracy of the computed nitrogen shielding constants depends crucially on the incorporation of correlation effects. The polyatomic molecules studied in this work were treated with standard basis sets using the LAO method. The LAO method can be applied for general wavefunctions and gives gauge-origin independent results, which rapidly converge with basis set size.

The RAS SCF wavefunctions we have used provide a good estimate of the valence shell correlation contributions to the shielding constants. At this level of approximation, the results are in much better agreement with experimental data than the SCF values. The next steps would be to use optimized molecular geometries and to estimate the role of the dynamic correlation. However, it appears that to obtain good agreement with experimental data it is even more important to determine the rovibrational contributions since the geometry dependence of the shielding constants is very large. It is also important to consider the molecule–solvent interactions.

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