Calculation of Magnetic Shielding and Susceptibility of H_2O and FOH with Gauge Invariant Gaussian Basis Set

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Susceptibility and magnetic shieldings of all nuclei are calculated for water and hypofluorous acid. A finite perturbation SCF method with gauge invariant gaussian basis set is used. Results calculated with a slightly extended basis set agree well with experimental values.

The finite perturbation self-consistent field (SCF) method has been used for the calculation of magnetic properties of some linear molecules [1, 2]. The aim of the present calculations has been to prove this method on non-linear molecules calculating the susceptibility and magnetic shieldings of FOH and H_2O.

In the Hamiltonian describing the closed shell molecule in the presence of a uniform magnetic field the vector potential of this field is included. Gauge invariant atomic orbitals are chosen as a basis set to provide the minimal or slightly extended sets to have enough flexibility to describe the induced electronic motion. The single determinant MO wavefunctions in the presence and in the absence of external magnetic field are determined by solving Roothaan-type equations for several finite magnetic field strenghts. The susceptibility is deduced by numerical differentiation of the molecular energy. Magnetic shieldings are calculated by means of Ditchfield's [3] expression, where the derivatives of the density matrix are calculated numerically. Within such a model there only remains to specify the basis set. In this work we have used two types of basis sets. The first one (I) is a slightly extended basis set composed by Dunning's [3s 2p] set [4] on oxygen and by STO-4G functions [5] on hydrogen. The total SCF energy of H_2O calculated with this basis set in the absence of the magnetic field is $E = -75.9859$ a.u. The experimental geometry ($R(O-H) = 1.8111$ a.u., $\sphericalangle HOH = 104.5°$) was used. The second basis set (II) used is the minimal STO-3G set [5]: With this set we calculated the magnetic properties of H_2O and FOH at fixed geometry for H_2O ($R(O-H) = 1.8100$ a.u., $\sphericalangle = 105°$) and for FOH ($R(F-O) = 2.7250$ a.u., $R(O-H) = 1.8217$ a.u., $\sphericalangle FOH = 97.200°$). The calculated energies are $E = -75.0012$ a.u. and $E = -172.3622$ a.u., respectively.

The calculated susceptibilities are shown in Table 1. Components of both molecules are given for comparison in the O – H bond axis framework. Susceptibilities of H_2O calculated with basis set I are comparable with those of Thomsen and Swanstrøm [6] calculated with the near Hartree-Fock basis set without gauge invariant orbitals. STO-3G basis set gives about 20% too small absolute values as was noticed before [2]. It is supposed that the susceptibility of FOH calculated with the same basis set (II) is for roughly the same amount too low. Also by Pascal additivity rule it should be about 16.10^{-6} erg gauss^{-2} mole^{-1}. Nevertheless, basis set II shows the anisotropy of FOH susceptibility, which is much greater than in H_2O, as expected.

Magnetic shieldings calculated with the first basis set (I) are given in Table 2. The magnetic shieldings of both oxygen and hydrogen are nearly the same as those of Thomsen and Swanstrøm [6], the differences are not greater than some percents, though the geometries of both calculations are slightly different. There are some differences between our values and those of Ditchfield [10] which by our oppinion are due to the different geometries of H_2O used in both calculations and less to the different extended basis sets.

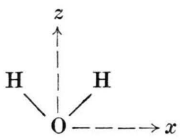
Table 3 shows the magnetic shieldings of all nuclei in FOH and H_2O calculated with basis II. As it is seen from the values for water, the basis set (and geometry) dependence is much more pronounc-

Table 1. Magnetic susceptibilities of H_2O and FOH [a].

z↑ →x	χ_{xx}	χ_{yy}	χ_{zz}	χ_{izo}	$\Delta\chi$ [b]	
H \ O–H	−13.81	−13.77	−13.84	−13.81	−0.11	basis I
	−11.41	−11.77	−11.52	−11.57		basis II
F \ O–H	−13.96	−14.06	−14.04	−14.02	−0.18	Ref. [6]
				−13.0 ± 0.1		Ref. [7] (expt.)
	−16.74	−11.53	−11.30	−13.19		basis II

[a] Units are 10^{-6} erg gauss^{-2} mole^{-1} (cgs ppm). [b] $\Delta\chi = \chi_{11} \cdot \frac{1}{2}(\chi_{22} + \chi_{33})$ in the principal axis system.

Table 2. Magnetic shieldings of H_2O calculated with basis set I.



Nucleus	σ_{xx}	σ_{yy}	σ_{zz}	$\Delta\sigma$	σ_{iso}	
O	343.7	290.6	298.8	49.0	311.1	present work
	349.0	272.7	291.2	67.1	304.3	Ref. [6] (column EC)
	360.9	325.3	307.0	44.8	331.1	Ref. [8]
H	38.86	24.96	31.38	10.69	31.73	present work
	39.2	23.5	29.5	12.7	30.7	Ref. [6] (column EC)
	36.7	12.0	24.3	18.6	24.3	Ref. [9]

Table 3. Comparison of magnetic shieldings of FOH with those of H_2O.

Nucleus of interest	σ_{xx}	σ_{yy}	σ_{zz}	σ_{iso}	Ref.
F	474.5	−5.1	102.1	190.5	
				187±20	[11] (expt.)
				−81.5	[7]
O	340.9	181.8	−5.4	172.4	
H	31.7	25.3	27.6	28.2	
	27.7	20.4	24.2	24.1	[10]
O	371.5	356.1	374.7	367.5	
	315.7	290.6	326.9	311.1	*
H′	29.2	25.5	43.3	32.7	
	27.6	25.2	42.2	31.6	[10]
		25.0		31.7	*

* Calculated values with basis set I (Table 1) transformed to O−H bond axis fromework.

ed for the shielding of oxygen than for that of hydrogen. Unfortunately no reliable values have been published about fluorine and oxygen shieldings in hypofluorous acid. But the agreement of fluorine shift with the experimental value [11] is good. Comparing the values of both molecules a pronounced diminution of oxygen shielding going from H_2O to FOH can be seen.

We may conclud that the finite perturbation method combined with gauge invariant basis sets gives reliable results for magnetic susceptibilities as well for magnetic shieldings.

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