Calculation of NMR chemical shifts of inorganic compounds by empirical molecular orbital methods

XIAO-ZENG YOU, WEI-XIONG WU* and AN-BANG DAI
Coordination Chemistry Institute,
Nanjing University, Nanjing, China

ABSTRACT- Empirical molecular orbital methods for calculation of NMR chemical shift have been introduced. The INDO perturbation theory including d and f orbitals with SOS and FPT method is emphasised. The methods have been applied to the study of C-13 nuclei in a representative set of inorganic compounds. The results of INDO/GIAO method generally agree well with the trends of experimental results.

INTRODUCTION

Nuclear magnetic resonance chemical shifts are both easily measured and sensitive to the electronic structure of a molecule (ref.1). It has become a useful tool in the study of structure and bonding of inorganic compounds. The numerical calculation of chemical shifts may be achieved by two different paths (ref.2). One is the sum-over-states perturbation theory (SOS), based on Ramsey's theory and developed by Schlichter. The other is the finite perturbation theory (FPT), developed by Karplus, Lipscomb, Ditchfield, Pople and Ellis' groups.

An INDO method of C-13 chemical shifts has been proposed by Ellis, Maciel and McIver to reduce the calculation CPU time (ref.3). A modified set of H-1, C-13 and F-19 INDO parameters lead to a good agreement of theoretical results with experimental data. Recently, we have developed the MNDO/GIAO method to calculate C-13, N-15 and O-17 NMR chemical shifts for a set of typical simple compounds (ref.4,5).

Most of these methods have only been used to calculate the chemical shifts of simple compounds with s and p orbitals. Since the 1950's, organometallic and coordination chemistry has undergone a tremendous growth in depth and breadth. It is evident, therefore, that approximate methods including d and f orbitals must be developed for inorganic and organometallic molecules. Some recent results in this field will be described.

THE X_α-SCATTERED WAVE METHOD

The Slater's self-consistent statistical exchange multiple scattering wave method is extensively used in dealing with the electronic structures of molecules. Fenske et al. have developed for the first time a quantum mechanical expression for the NMR chemical shifts via the X_α -SW method (ref.6,7).

With application of perturbation theory to a system with an electron and fixed nuclei within the X_α -framework, the following equations are obtained:

$$\sigma = \sigma^d + \sigma^p \tag{1}$$

$$\sigma^d = (a^2/3)2 \sum_{i=1}^{n} \langle \phi_i | 1/r_m | \phi_i \rangle \tag{2}$$

$$\sigma^p = -(a^2/3) \sum_{i=1}^{n} \sum_{k=n+1}^{} \left(\langle \phi_i | \overrightarrow{L_m} / r_m^3 | \phi_k \rangle \langle \phi_k | \overrightarrow{L_m} | \phi_i \rangle + \langle \phi_i | \overrightarrow{L_m} | \phi_k \rangle \langle \phi_k | \overrightarrow{L_m} / r_m^3 | \phi_i \rangle \right) / (E_k - E_i) \tag{3}$$

where ϕ_i represents the eigenfunctions of the ground state, r_m is the position vector of the electron relative to the magnetic nucleus whose chemical shift is being calculated, L_m is the angular momentum, a is a constant. The summation is over all occupied orbitals i and virtual orbital k. σ^d and σ^p are, respectively, the diamagnetic and paramagnetic contribution. The energy difference between the ground state i and an excited state k, $E_k - E_i$ in the denominator of the term is conveniently provided in X_α theory as the difference in eigenvalues of orbitals k and i as a half electron energy. The calculation of σ consists in evaluating the matrix elements of $1/r$, L_m and L_m/r_m .

---

* Present address: Shanghai Institute of Computer Technology, Shanghai, China.

The X_α-SW method has been extended to the calculation of C-13 NMR chemical shift in some transition metal complexes (ref.8). The results in Fig.1 show the trends in C-13 NMR experiments for the CO.CS,CN and C_5H_5 ligands in transition metal complexes $Ni(CO)_4$, $Cr(CO)_5CS$ and $Fe(C_5H_5)(CO)_2$ CN.

Usually, the σ^d of carbon in a complex is rather larger than that in the free ligand (our calculated σ^d for free CO and CS were 251.4 and 256.5 ppm. respectively). These facts constitute a reasonable support for the scheme of back-bonding of the metal to the carbon atom. Of all the diamagnetic and paramagnetic contributions, only σ^P shows pronounced difference between ligands that are free and metal bound. Thus the observed decrease in σ in the metal complexes may be explained on the basis of σ^P only. It has been pointed out that there may be some relationship between chemical shift and certain types of chemical reactivity (ref.9).

The chemical shift has some relation with π back bonding in transition metal complexes (ref.10). This is reflected in two aspects. Firstly, part of the contribution is involved directly in
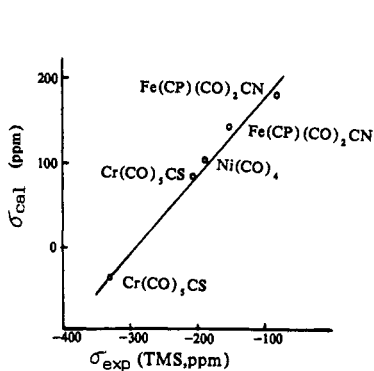

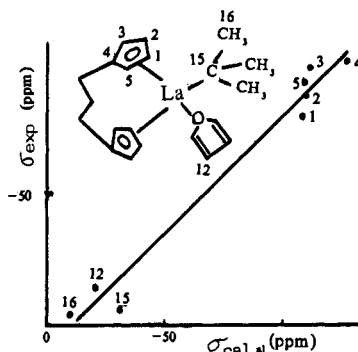Fig.1. σ for C-13 by X_α method

Fig.2. σ for C-13 by INDO/GIAO

a transition from metal to carbonyl π^* molecular orbital. The 33A'-35A' transition in $Fe(CP)(CO)_2$ CN is one of the largest contributions from M$\longrightarrow$ L. That is why some authors also observe a correlation between carbonyl chemical shift and the frequency of the lowest energy uv transition that involves a charge transfer from the metal to the carbonyl π^* orbital (ref.11,12). Secondly, the π^* orbital stabilized by metal bonding is lowered and its population reduces the CO bond order to between 2 and 3. This effect has been attributed to the fact that carbonyl chemical shift is observed to be linearly dependent on carbonyl stretching frequencies (ref.13). Both synergic effects make the σ^P in the complex rather lower than that of free ligands resulting in downfield shift as observed.

The Fenske-Hall MO model is also extended to calculate the NMR chemical shifts for these complexes. It can predict the C-13 exprerimantal trend with less computer time (ref.14).

THE INDO CALCULATION BASED ON THE SOS METHOD

For theoretical calculation of NMR chemical shifts in inorganic molecules, we have extended the INDO method to include d and f orbitals which was not attempted before. The details of our INDO/σ method have been dealt with elsewhere (ref.15,16), so here we only discuss the basic features of the method. Firstly, the eigenfunction and eigenvalue are calculated by the Hartree-Fock equation without external magnetic field.

$$\sum \left(F_{\mu\nu}^{\alpha} - \varepsilon \, S_{\mu\nu} \right) C_{\mu i} = 0 \tag{4}$$

The INDO method has been extended by Prof. G.X.Xu et al. to include f orbitals (ref.17).

The chemical shift parameters are then considered. We take the SOS perturbation theory formulated by Pople using independent-electron MO(ref.18).

The local diamagnetic screening σ_A^d comes from the circulation of electrons in the orbitals of atom A:

$$\sigma_A^d = (e^2/2mc^2) \sum_\mu P_{\mu\mu} \langle \phi_\mu | r^{-1} | \phi_\mu \rangle \tag{5}$$

The contribution from local paramagnetic term that arises from mixing of ground and excited states in the external field is given as:

$$\sigma_A^p = (2e^2h/3\,m^2c^2)\sum_i^{occ}\sum_j^{vac}(\epsilon_j-\epsilon_i)^{-1}\sum_{\mu<\nu}^A\sum_{\lambda<\sigma}^B\Big(C_{i\mu}C_{iv}-C_{iv}C_{j\mu}\Big)\Big[C_{i\lambda}C_{j\sigma}-C_{i\sigma}C_{j\lambda}\Big]\Big(\Big\langle\phi_\mu\Big|L_x\,/\,r^3\Big|\phi_v\Big\rangle$$

$$\Big\langle\phi_\lambda\Big|L_x\Big|\phi_\sigma\Big\rangle + \Big\langle\phi_\mu\Big|L_y\,/\,r^3\Big|\phi_v\Big\rangle\;\Big\langle\phi_\lambda\Big|L_y\Big|\phi_\sigma\Big\rangle + \Big\langle\phi_\mu\Big|L_z\,/\,r^3\Big|\phi_v\Big\rangle\;\Big\langle\phi_\lambda\Big|L_z\Big|\phi_\sigma\Big\rangle\Big] \tag{6}$$

where C_{iv} is the LCAO coeffcent of molecular orbital, and L_x , L_y , L_z are the components of the angular momentum operators. The paramagnetic contribution of neighboring atoms is estimated by using a classical dipolar field. We have obtained all integrals for these operators by using STO bases. With the known matrix elements, calculation of chemical shifts for different atoms in a molecule could be carried out readily by equations (5-6). It differs from the general INDO method in that it includes d and f orbitals and considers the contribution from neighbouring atoms but disregards the approximation of average energy.

The best values of INDO/σ parameters have been adopted by minimizing the discrepancy between calculated and experimental values of chemical shifts for several representative compounds.

We have chosen $Fe(\eta^5\text{-}C_5H_5)(CO)_2CN$ as a model complex in which various carbon atoms are bonded to a transition metal (ref.19). Compared with simple molecules, the paramagnetic contribution

Table 1. C-13 Chemical Shifts for $Fe(\eta^5\text{-}C_5H_5)(CO)_2CN$ complex (ppm)

Ligands	Net Charge on C Atom	σ^d	$-\sigma^p$	σ_{cal}	σ_{exp} (Rel. TMS)
CP	-0.16	58.735	102.267	-42.809	-85.9
CN	-0.13	58.540	106.485	-48.300	-154.7
CO	0.097	57.043	110.542	-53.251	-211.1

σ^p of the complex molecule is considerably larger. The overall agreement between the calculated and observed values of chemical shifts is demonstrated in Table 1 which also shows a good linear relationship.

INDO CALCULATION BASED ON FPT METHOD

The INDO/GIAO semiempirical scheme extended by us seems to be attractive. The serious problem that comes from the dependence of theoretical results upon the origin of coordination could be solved by using gauge invariant atomic orbitals χ .

$$\chi_v = \Big\{\exp\Big[-(i/c)\,\vec{A}_v\cdot\vec{\gamma}\Big]\Big\}\chi_v = f_v\chi_v \tag{7}$$

where $\vec{A}$ is a vector potential at nucleus, $\vec{A} = \vec{B}\times\vec{R}$, with $\vec{R}$ as the position vector of the atom upon which unperturbed atomic orbital is centered. The Fock matrix F is represented as

$$F = H + G = (H^r + G^r) + i(H^i + G^i) \tag{8}$$

the H and G matrices being generated to include calculations of transition metal complexes.

The shielding tensor $\sigma_{AB}(M)$ can be obtained from the definition via Eqs. (9-11).

$$\sigma_{\alpha\beta}(M) = \alpha_{\alpha\beta}^d(M,M) + \alpha_{\alpha\beta}^p(M,M) + \sum_{K\neq M}\Big|\sigma_{\alpha\beta}^d(M,K) + \sigma_{\alpha\beta}^p(M,K)\Big| \tag{9}$$

$$\sigma_{\alpha\beta}^d(M,K) = 2\sum_\mu^k\sum_v^k R_{\mu v}(0)\Big\langle\chi_\mu^0\Big|h_{\alpha\beta}^v(M)\Big|\chi_v^0\Big\rangle \tag{10}$$

$$\alpha_{\alpha\beta}^p(M,K) = 2\sum_\mu^k\sum_v^k(\delta R_{\mu v}/\delta B_\alpha)_0\Big\langle\chi_\mu\Big|h_{\alpha\beta}(M)\Big|\chi_v\Big\rangle \tag{11}$$

where $\sigma_{\alpha\beta}^d(M,K)$ and $\sigma_{\alpha\beta}^p(M,K)$ are the diamagnetic and paramagnetic contribution of chemical shift respectively, and $R_{\mu v}(0)$ is the unperturbated density matrix elements.

On the basis of the above principle, the Fock equation with complex coefficient for eigenvalues is solved first, then the pertubation coefficients are obtained by using difference methods. In practice, the (I+A)/2's and β 's parameters are obtained by minimizing the average difference of theoretical values for a representative set of compounds.

The σ^p and σ^d values listed in Table 2 for a ferrocene again show that the change in chemical shifts is mainly decided by paramagnetic terms (ref.20).
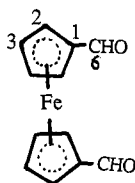
Table 2.   C-13 Chemical Shifts of $(C_5H_4CHO)_2Fe$ (ppm)

NO.of C	ρ (M)	σ^d(M)	σ^p(M)	σ(M)	σ_{exp}
C_1	0.1053	56.93	-120.22	-63.30	-80.10
C_2	0.0707	57.18	-120.31	-63.13	-74.05
C_3	0.0539	57.30	-119.06	-61.76	-70.75
C_6	0.3598	54.98	-231.66	-176.68	-192.71

We have also calculated the C-13 chemical shift for diamagnetic complex $C_5H_4(CH_2)_3C_5H_4$ La (Bu^t)·THF. containing the f orbital (Fig.2,ref.21).

Generally, an excellent linear relationship between the calculated diamagnetic term σ^d and the corresponding atomic net charge ρ on discussed atoms is obtained, which is explained by the fact that the diamagnetic part is due mainly to the core electrons.

The INDO/GIAO calculated results are much better than those of INDO/σ method in absolute magnitude and the range of shifts. It is indicated by our calculation for this complicated organolanthanide complex with 54 atoms and 124 valence electrons that the INDO/GIAO method is an available semiempirical method of NMR chemical shift calculations and bonding studies for coordination compounds.

CONCLUSION

Most of our calculation may reproduce experimentally observed trends in the chemical shifts and provide some useful qualitative results. The molecules treated here cover a wide range of chemical environments, especially for a series of molecules including some metallorganic compounds containing d and f orbitals.

The calculation of chemical shifts for the transition metal complexes is still at the development stage.   Usually, the contribution of the transition between the orbitals in complexes is more complicated than that in simple organic compounds. That is why some author stated that it is not a convincing explanation for the C-13 shielding constant in the transition metal complexes (ref.22).

REFERENCES

(1) R.Ditchfield and P.D. Ellis, in Topics in Carbon-13 NMR Spectroscopy, edited by G.C.Levy, Wiley, New York (1977).
(2) G.A. Segal, Semiempirical method of electronic structure calculation. part B. Plenum Press, New York (1977).
(3) P.D.Ellis, G.E.Maciel and J.W.McIver, Jr., J.Am.Chem.Soc. 94, 4069 (1972); 95, 5857 (1973).
(4) W.X.Wu, X.Z.You and A.B.Dai, Sicence Sinica. 5, 451 (1988).
(5) You Xiao-zeng and Wu Wei-xiong, Magn. Reson. Chem. 25, 860 (1987).
(6) D.F.Freier, R.F.Fenske and You Xiao-zeng, J.Chem.Phys. 83 (7). 3526 (1985).
(7) You Xiao-zeng, J. of Mol. Sci (China). 2, 67 (1984).
(8) You Xiao-zeng, R.F.Fenske, D.G.Freier, Chem.J. of Chinese Univ. 6, 146 (1985).
(9) T.F.Block, R.F.Fenske and C.P.Casey., J.Am.Chem.Soc. 98, 441 (1976).
(10) O.A.Gansow, B.Y.Kimura, G.R.Dobson and R.A.Brown, J.Amer.Chem.Soc. 93, 5922(1971).
(11) G.M.Bodner and L.J.Todd, Inorg.Chem. 13, 1335 (1974).
(12) P.S.Brarerman, D.W.Milne., E.W.Randall and E.Rosenberg J.Chem.Soc.Dalton, 1027 (1973).
(13) O.A.Gansow. A.Schexnayder and B.Y.Kimura, J.Amer.Chem.Sco. 17, 3406 (1972).
(14) You Xiao-zeng, R.F.Fenske, D.G.freier, J. of Mol.Sci. (China), 1, No.2, 42 (1983).
(15) You Xiao-zeng, Wu Wei-xiong, Feng Xing-hong, Zhu Long-gen, and Dai An-Bang, J.Mol.Sci. (China), No.2, 189 (1985).
(16)Wu Wei-xiong, Feng Xing-hong, Zhu Long-gon, You Xiao-zeng and Dai An-bang, Chem.J.Chin.Univ. 7 No.8, 725 (1986).
(17) Ren Jing-qing , Li Le-min , Xu Guang-Xian and Wang Xiu-zhen , Acta Sci. Natur.Univ.Pekinensis, No.3, 30, 49 (1982).
(18) J.A.Pople, J.Chem.Phys. 37 60 (1962); Mol.Phys. 1, 301 (1964).
(19) Wu Wei-xiong, You Xiao-zeng, Dai An-bang, Scientia Sinica, 30, No.12, 1253 (1987).
(20) Wu Wei-xiong, You Xiao-zeng, Dai An-bang, J. Inorg. Chem. (China), 4, 84 (1986).
(21) You Xiao-zeng, Wu Wei-xiong, Li Cun, Dai An-bang, Sci. Bull., No.4 , 265 (1988).
(22) J.A.Evans and I.R.Norton., Inorg.Chem. 13, 3042 (1974).