Calculation of NMR Shielding Constants with Optimized Numerical Basis Function

Katsumi NAKAGAWA

MO BASICS Research, 3-1-201 Hiyoshi-Honcho, Kohoku-ku, Yokohama, Kanagawa 223-0062 Japan
e-mail: nakagawa.katsumi@nifty.com

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Isotropic NMR shielding constants $\sigma_{iso}$ were calculated for hydrogen, carbon, nitrogen, oxygen, fluorine and phosphorous atoms in small molecules by using numerical basis functions, which were based on AOs of Discrete Variational $X\alpha$ (DV-X$\alpha$) method and were modified to London atomic orbitals to avoid the gauge-origin-dependence when magnetic field exists. In DV-X$\alpha$ method AOs are prepared by solving the Hartree-Fock-Slater (HFS) equation substantially equivalent to that used to calculate MOs and are very accurate around each nucleus. However, $\sigma_{iso}$ calculated in the default condition of DV-X$\alpha$ method don’t agree well to experimental ones. By optimizing AOs in a reasonable way, $\sigma_{iso}$ were highly improved and agreed with experimental ones far better than results by Hartree-Fock (HF) method having conventional basis functions. The usefulness of MOs constructed with optimized numerical basis functions was clearly demonstrated.

Key words : NMR shielding constant, Chemical shift, Basis function, DV-X$\alpha$ method, London atomic orbital

1 Method

NMR chemical shift $\delta$ is a powerful tool to investigate local structure of molecules and non-single-crystal substances. The author tried to calculate isotropic NMR shielding constant $\sigma_{iso}$ which can be simply related with $\delta$, by entirely numerical way. Basis functions $\chi_i$, suitable for existence of uniform external magnetic field $H_0$ is

$$\chi_i = e^{-i\alpha u_i},$$

where $\alpha$ is fine structure constant, $u_i$ is AO prepared by DV-X$\alpha$ method [1] without magnetic field and $\theta_i$ is a function of $H_0$ and the position of atom $A$ to which $u_i$ belongs and the last term in [ ] represents the interaction of $H_0$ and $L_A$, the angular momentum around atom $B$.

Fock matrix element $F_{\alpha\beta}$ of HFS equation in the existence of $H_0$ is approximated like

$$F_{\alpha\beta} = \left[ \chi^* \chi F^e dz \right] = \left[ e^{\alpha(u_i-u_\beta)} H_0 \right] \left[ e^{-\alpha u_i} u_\beta d\rho \right]$$

where $\alpha$ is a function of $H_0$ and the position of atom $A$ to which $u_i$ belongs and the last term in [ ] represents the interaction of $H_0$ and $L_A$, the angular momentum around atom $B$.

Anti magnetic field $aH$ at the position of each nucleus can be calculated by eq.(3) and Biot-Savart law and $\sigma_{iso}$ is defined as the ratio of $H_0$ to $H_1$.

In DV-X$\alpha$ method, MOs are given their values discretely on sample points in 3D space. To suppress numerical error, the sample point system improved for energy gradient calculation [3] was adopted and angular part of differentiation of $\phi_i$ in eq.(3)
were replaced by the recurrence relation of Legendre functions. Even with complex factor, eq.(2) can be integrated as easily as the case without complex factor, which is one of the advantages of the numerical way when magnetic field is treated.

2 Results

By using AOs obtained by DV-Xα default conditions, \( \sigma_{\text{iso}} \) for several kinds of atom were calculated. It was confirmed that numerical errors of \( \sigma_{\text{iso}} \) were suppressed below 0.2 ppm and \( \sigma_{\text{iso}} \) were completely independent of the position of molecule. These \( \sigma_{\text{iso}} \) are listed in the column "default" in Table 1. As they didn't agree well to experimental ones in the column "exp.", calculation conditions of AOs of DV-Xα method were re-examined.

In DV-Xα method, parameter \( \alpha \) included in \( E_x \) in eq.(2) (different from \( \alpha \) in eq.(1)) designates electron exchange interaction. This \( \alpha \) is 0.7 in default condition but was optimized for each atom, like 0.7802 for hydrogen and 0.7532 for carbon. By these optimization, calculated total energies of these atoms agree to ones strictly calculated by HF method.

In default condition, necessity minimum natural AOs, like 1s, 2s, 2p\(_x\), 2p\(_y\), 2p\(_z\) for carbon, are used as basis functions, but they were extended, like 1s-2p + 3s, 3p\(_x\), 3p\(_y\), 3p\(_z\) for carbon. The AOs used in the optimized condition are listed in the column "basis" of Table 1. At each SCF step of MO calculation, AOs are recalculated by HFS equation based on charge distribution for each AO. The method to estimate charge distribution was improved for this research. In the SCF process AOs of the cation atom lose charge and AOs of the anion atom gain charge and finally all AOs fit adaptively to actual MOs of molecules.

But extended AOs are apt to spread too widely. To compress them, "well potential" is added supplementary only in AO calculation. Depth of well potential is \(-2.0 \text{ au} \) as default condition but was optimized in order that total energy of the molecule may have the minimum according to the variational principle. Total energies of the molecule are listed in the row "energy" of Table 1.

In Table 1, \( \sigma_{\text{iso}} \) by optimized conditions are listed in column "optimized." Their agreements to experimental ones in the column "exp." were highly improved. In the columns of "RHF" and the "CCSD(T)", \( \sigma_{\text{iso}} \) calculated by RHF and by CCSD (T) are cited from the literature [4]. Optimized \( \sigma_{\text{iso}} \) are far closer to experimental ones and CCSD (T) ones than RHF results.

3 Discussion

Although most physical quantities can be calculated well by DV-Xα method in default conditions, \( \sigma_{\text{iso}} \) isn't the case and seems to be very sensitive to the accuracy of MOs or the degree of fitness of MOs to the exact solutions of HFS equation at each point in 3D space. LCAO approximation, which DV-Xα method adopts together with other practical Molecular Orbital methods, may degrade accuracy of MOs.

By not only using HFS equation to obtain AOs but also reshaping them adaptively, the author tried to fit MOs as closely as possible to exact solutions of HFS equation within the limitation of LCAO approximation. Resultant \( \sigma_{\text{iso}} \) by optimized AOs were highly improved and seem even similar to those by CCSD (T). The author's trial was rewarded. However, this finding is surprising because HFS equation is an approximation of HF equation and doesn't consider electron correlation interaction, which is properly considered in CCSD (T).

References