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Quantum Chemical Calculation of NMR for Tetramethylsilane (TMS) *

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Abstract: The chemical shift δ is the most important parameter in analyzing NMR spectra. It is the relative value of the sample's shielding (σ) related to the reference's shielding (σ_{ref}). The reference (standard) is usually tetramethylsilane (TMS) for ^1H and ^{13}C . In quantum chemistry *ab initio* calculation, it is necessary to calculate the absolute shielding (σ_{ref}), which has been calculated by different levels of theory and methods. The calculated results are fundamentally consistent with the experimental values.

Key words: NMR, Quantum chemistry, Shielding constant, Chemical shift, TMS

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1 Introduction

Over the past decades, nuclear magnetic resonance (NMR) spectroscopy has revealed itself to be invaluable tool in areas of chemistry, biology and medicine. Especially in organic chemistry, for some compounds, it is difficult to prepare their single crystals. Their structures and geometries are usually determined by their MS, IR, UV and NMR spectra. From the 1970's, quantum chemical calculation for NMR has been becoming one of fascinating areas of researches in the world. Especially, from the late 1990's, with the development of the theory and computer technology, quantum chemical calculation of NMR has made great progress^[1-8].

2 Theory

2.1 The condition of NMR

Any nucleus has a spin angular momentum associ-

ated with nuclear spin quantum number I and a magnetic moment as follows

$$M = \sqrt{I(I+1)}\hbar, \quad \mu_n = \gamma m\hbar$$

Where M is the spin angular momentum, γ is the magnetogyric ratio, and m is the magnetic spin quantum number, which can have any of the following values.

$$m = I, I-1, I-2, \dots, -I+2, -I+1, -I$$

A nuclear moment can interact with an applied external magnetic field to produce an additional energy, which can be presented as follows

$$E = -\vec{\mu}_n \cdot \vec{B}_0 = -\mu_n \cdot B_0 = -\gamma m\hbar B_0$$

Where B_0 is the strength of the external magnetic field applied along the z -axis. For the case of $I = \frac{1}{2}$ (such as ^1H and ^{13}C), m can either be $+\frac{1}{2}$ or $-\frac{1}{2}$. The energy difference between these two states can be presented as follows

$$\Delta E = \gamma\hbar B_0$$

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The oscillating frequency of a transition between these two energy levels can be derived as follows

$$\nu = \frac{\gamma B_0}{2\pi}$$

If the frequency of the external electromagnetic wave is equal to this frequency, we can observe the NMR phenomenon.

2.2 The shielding

The applied field causes electronic currents, which, in turn, induce a secondary local field at any given nuclear site. A nucleus in a molecule henceforth sees a local field that may be less (shielding) or greater (deshielding) in magnitude as compared with the applied field, depending on the behaviour and distributions of the electrons in its immediate vicinity. The local or actual field experienced by the nucleus can be expressed as follows

$$B^{\text{loc}} = (1 - \sigma) B^{\text{ext}}$$

The first use of SCF wavefunctions in computing shielding was introduced by Stevens *et al.*^[9]. The nuclear magnetic shielding tensor is expressed as the mixed second derivative of the molecular energy with respect to the external magnetic field B and the magnetic moment of nucleus μ ^[10].

$$\sigma_{\alpha\beta} = \frac{\partial^2 E}{\partial \mu_\alpha \partial B_\beta}$$

where β and α are the components of the external magnetic field and induced magnetic moment, respectively. The shielding is actually a tensor of rank two, and the shielding tensor is composed of nine independent components. In most cases, molecules do not prefer a single orientation so the averaging which takes place is isotropic. The observed value is the average of the principal components^[11].

$$\sigma_{\text{iso}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

2.3 The chemical shift

As far as the same nucleus is concerned, the absorption peaks of its NMR are in different positions because of its different environment in the molecule. This difference is called the chemical shift. Usually, the chemical shift is presented as follows

$$\delta = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6$$

$$\begin{aligned} &= \frac{\sigma_{\text{ref}} - \sigma}{1 - \sigma_{\text{ref}}} \times 10^6 \\ &= (\sigma_{\text{ref}} - \sigma) \times 10^6 \end{aligned}$$

Shielding constants reported in experimental values are usually shifts relative to a standard compound (reference), which is often tetramethylsilane.

3 Quantum chemical calculation

3.1 The levels of theory and the methods

Theoretical calculation of NMR is dependent on HF level of theory, DFT (B3LYP) level and Post-Hartree-Fock level. Furthermore, there are several methods at each theory level, for example, GIAO (gauge including atomic orbital), IGAIM (individual gauges for atoms in molecules), CSGT (continuous set of gauge transformation), LORG (localized orbital local origin), IGLO (individual gauge for localized orbitals), SOLO (second-order LORG), GIAO-MBPT(2) (GIAO-second-order many-body perturbation theory), and so on.

3.2 Theoretical calculation for NMR

In most cases, TMS is the standard (reference) for ^1H and ^{13}C . In order to compare calculated values of samples with experimental results, we need to calculate the absolute shielding value of TMS. We have studied all kinds of absolute shielding of TMS at different levels and by different methods.

In Table 1, the calculation is based on Hartree-Fock and DFT levels of theory. In geometric optimization, as 4-31G basis set isn't suitable for Si, so we use 4-31G basis set for C, H, 6-21G for Si, which does not affect on the calculated results. We take Gaussian Program's four methods to calculate NMR for TMS.

From Table 1, it is known that the calculation accuracy can be improved by adding polarization function and diffusion function to the basis set. One can simply increase the size of the basis set used until no noticeable change is observed in the calculated shielding at the point, the system has already been saturated with basis set. We have calculated a series of compounds synthesized by ourself by quantum chemical calculation of NMR, which has get the same conclusion^[13,14]. Namely, an 'saturated' basis set can be obtained.

Table 1 Data of TMS (Opt. HF/4-31G(Si = 6-21G))

Methods	Basis sets	σ_c	σ_H	σ_c (exp.)
GIAO	HF/4-31G	205.5864	33.3651	188.1 ^[12]
	HF/6-31G(D)	197.0192	32.7194	
	HF/6-31 ++ G(D,P)	189.0408	31.7798	
	HF/6-311 ++ G(D,P)	192.0460	32.2996	
	B3LYP/4-31G	192.4181	32.8585	
	B3LYP/6-31G(D)	185.7440	32.2622	
	B3LYP/6-31 ++ G(D,P)	189.0406	31.7798	
	B3LYP/6-311 ++ G(D,P)	180.6645	32.0251	
IGAİM	HF/4-31G	175.7262	30.0804	
	HF/6-31G(D)	192.5695	29.6752	
	HF/6-31 ++ G(D,P)	190.5618	29.7199	
	HF/6-311 ++ G(D,P)	189.5005	31.0944	
	B3LYP/4-31G	164.7481	29.8616	
	B3LYP/6-31G(D)	183.3986	29.3141	
	B3LYP/6-31 ++ G(D,P)	190.5618	29.7199	
	B3LYP/6-311 ++ G(D,P)	178.8737	30.9270	
CSGT	HF/4-31G	175.7264	30.0804	
	HF/6-31G(D)	192.5695	29.6751	
	HF/6-31 ++ G(D,P)	190.5612	29.7200	
	HF/6-311 ++ G(D,P)	189.5007	31.0945	
	B3LYP/4-31G	164.7484	29.8616	
	B3LYP/6-31G(D)	183.3987	29.3140	
	B3LYP/6-31 ++ G(D,P)	190.5612	29.7200	
	B3LYP/6-311 ++ G(D,P)	178.8739	30.9270	
Single gauge origin	HF/4-31G	222.0016	23.2637	
	HF/6-31G(D)	235.8761	23.4496	
	HF/6-31 ++ G(D,P)	219.3234	28.0018	
	HF/6-311 ++ G(D,P)	201.7592	29.9642	
	B3LYP/4-31G	209.5342	22.4607	
	B3LYP/6-31G(D)	224.4131	23.0980	
	B3LYP/6-31 ++ G(D,P)	219.3234	28.0018	
	B3LYP/6-311 ++ G(D,P)	189.8636	29.5434	

In Table 2, B3LYP/6-31G(D) is used for geometric optimization. From Table 1 and Table 2, we know that accuracy of calculating NMR by Single Gauge Origin is not good. Since CSGT takes each point in the space as the different gauge origin for correlating IGAİM, the calculated result of CSGT is similar to that

of IGAİM. For geometric optimization, HF/4-31G is used in Table 1, and B3LYP/6-31G(D) is used in Table 2. The calculated results show that the better the geometric optimization is, the more accuracy the calculated value is. The effect of the basis set on calculated results is the same as the conclusion in Table 1.

Table 2 Data of TMS (Opt. B3LYP/6-31G(D))

Methods	Basis sets	σ_C	σ_H	σ_C (exp.)
GIAO	HF/6-31G(D)	195.1183	32.3668	188.1 ¹²
	HF/6-31 ++ G(D,P)	197.1368	31.7714	
	HF/6-311 ++ G(D,P)	190.0552	31.9320	
	HF/6-311 + G(2D,P)	188.7867	31.8416	
	B3LYP/6-31G(D)	183.7642	31.9195	
	B3LYP/6-31 ++ G(D,P)	187.0472	24.5529	
	B3LYP/6-311 ++ G(D,P)	178.5416	31.6700	
	B3LYP/6-311 + G(2D,P)	177.5834	31.5518	
IGAIM	HF/6-31G(D)	190.8528	29.3610	
	HF/6-31 ++ G(D,P)	196.8777	29.6052	
	HF/6-311 ++ G(D,P)	187.5937	30.7289	
	HF/6-311 + G(2D,P)	188.6013	31.4512	
	B3LYP/6-31G(D)	181.6083	29.0134	
	B3LYP/6-31 ++ G(D,P)	188.5990	24.0227	
	B3LYP/6-311 ++ G(D,P)	176.8061	30.5749	
	B3LYP/6-311 + G(2D,P)	177.2790	31.2107	
CSGT	HF/6-31G(D)	190.8529	29.3610	
	HF/6-31 ++ G(D,P)	196.8780	29.6053	
	HF/6-311 ++ G(D,P)	187.5939	30.7289	
	HF/6-311 + G(2D,P)	188.6013	31.4512	
	B3LYP/6-31G(D)	181.6083	29.0134	
	B3LYP/6-31 ++ G(D,P)	188.5993	24.0225	
	B3LYP/6-311 ++ G(D,P)	176.8063	30.5749	
	B3LYP/6-311 + G(2D,P)	177.2791	31.2107	
Single gauge origin	HF/6-31G(D)	235.3958	23.3457	
	HF/6-31 ++ G(D,P)	228.2143	28.1943	
	HF/6-311 ++ G(D,P)	200.0147	29.7085	
	HF/6-311 + G(2D,P)	195.5927	29.2591	
	B3LYP/6-31G(D)	223.8136	23.0106	
	B3LYP/6-31 ++ G(D,P)	218.4123	27.7777	
	B3LYP/6-311 ++ G(D,P)	187.9743	29.3003	
	B3LYP/6-311 + G(2D,P)	183.3400	28.9490	

In Table 3, B3LYP/6-31G is used for geometric optimization. From Table 3, it is shown that the calculated σ_C values of GIAO and IGAIM have a little difference. But, these two methods are used for δ_C and δ_H of the organic compounds synthesized by us, the results show that GIAO is better than IGAIM in calculating δ_H ^[13,14]. A diffusion function is added to carbon (C)

of Table 2 in geometric optimization, so the calculated result is obviously better than that of Table 3.

In Table 4, HF/6-31G is used for geometric optimization. Table 4 shows that when the geometry is optimized by HF/6-31G and the NMR is calculated by B3LYP/6-31 ++ G(D,P), the result is much better.

Table 3 Data of TMS (Opt. B3LYP/6-31G)

Methods	Basis sets	σ_C	σ_H	$\sigma_C(\text{exp.})$
GIAO	HF/6-31G	200.1919	33.0588	188.1 ^[12]
	HF/6-31G(D)	194.4534	32.3253	
	HF/6-31 ++ G(D,P)	186.1199	31.3843	
	HF/6-311 + G(2D,P)	177.6388	32.6218	
	HF/6-311 ++ G(D,P)	189.4209	31.8878	
	B3LYP/6-31G	187.3965	32.4910	
	B3LYP/6-31G(D)	182.8703	31.8728	
	B3LYP/6-31 ++ G(D,P)	186.1199	31.3843	
	B3LYP/6-311 ++ G(D,P)	177.6388	31.6218	
	B3LYP/6-311 + G(2D,P)	176.6693	31.5046	
ICAIM	HF/6-31G	184.9587	29.2073	
	HF/6-31G(D)	190.4787	29.3331	
	HF/6-31 ++ G(D,P)	187.8740	29.3454	
	HF/6-31 ++ G(D,P)	186.7553	30.6732	
	HF/6-311 + G(2D,P)	175.7286	30.5166	
	B3LYP/6-31G	174.2816	28.8921	
	B3LYP/6-31G(D)	181.0128	28.9770	
	B3LYP/6-31 ++ G(D,P)	188.8848	29.3447	
	B3LYP/6-311 ++ G(D,P)	175.7380	30.5158	
	B3LYP/6-311 + G(2D,P)	176.2670	31.1560	

Table 4 Data of TMS (Opt. HF/6-31G)

Methods	Basis sets	σ_C	σ_H	$\sigma_C(\text{exp.})$
GIAO	HF/6-31G(D)	196.7129	32.6934	188.1 ^[12]
	HF/6-31 + G(D,P)	196.7129	32.6934	
	HF/6-31 ++ G(D,P)	198.7629	32.1062	
	HF/6-311 + G(2D,P)	191.7410	32.2721	
	HF/6-311 + G(D,P)	191.7410	32.2721	
	B3LYP/6-31G(D)	185.3588	32.2345	
	B3LYP/6-31 + G(D,P)	185.3588	32.2345	
	B3LYP/6-31 ++ G(D,P)	188.6418	31.7512	
	B3LYP/6-311 + G(2D,P)	180.2649	31.9964	
	B3LYP/6-311 ++ G(D,P)	180.2649	31.9964	

In Table 5, MP2/6-31G(D) is used for geometric optimization. Second-order-many-body perturbation theory (MP2) is also used for shielding in Table 5. MP2 is the simplest level of theory which includes electron correlation. But owing to the additional MP2 treatment the computational requirements of a shielding cal-

ulation have also increased. So GIAO-MP2 is limited^[11], we only calculated the absolute shielding of TMS moreover. Because of restriction of MP2 itself, we have not further calculated the relative shielding for the compound with MP2. Its accuracy will be further discussed in another paper.

Table 5 Data of TMS (Opt. MP2/6-31G(D))

Methods	Basis sets	σ_c	σ_H	σ_c (exp.)
GIAO	HF/6-31G(D)	195.5882	32.4469	188.1 ^[2]
	HF/6-31 ++ G(D,P)	197.6190	31.8536	
	HF/6-311 ++ G(D,P)	190.5136	32.0153	
	HF/6-311 + G(2D,P)	189.2575	31.9228	
	B3LYP/6-31G(D)	184.3048	31.9986	
	B3LYP/6-31 ++ G(D,P)	187.5915	31.5149	
	B3LYP/6-311 ++ G(D,P)	179.0902	31.7514	
	B3LYP/6-311 + G(2D,P)	178.1317	31.6309	
	MP2/STO-3G	239.0803	33.1359	
	MP2/3-21G	208.6473	33.3379	
	MP2/4-31G	200.8595	33.3223	
	MP2/6-31G	201.7348	33.2702	
	MP2/6-31G(D)	195.8065	32.6509	
	MP2/6-31 ++ G(D,P)	196.2740	32.0078	

4 Conclusion

1. As far as the theory levels are concerned, DFT (B3LYP) is usually better than HF.

2. At the same level of theory, GIAO method is better than others.

3. As for the same method, to a certain extent, the larger the basis sets are, the more accurate the calculated values are. One can simply increase the size of the basis set used until no noticeable change is observed in the calculated shielding at the point, the system has already been saturated with basis set.

4. From Table 1 to Table 5, we see that for different levels of theory, different methods and basis sets, the calculated values of GIAO/6-31 ++ G(d,p) are 'saturated' with basis set. They are fundamentally consistent with the experimental value.

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TMS 的 NMR 量子化学计算*

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摘要: 分别用 HF/4-31G(Si=6-21G)、B3LYP/6-31G(D)、B3LYP/6-31G、HF/6-31G、MP2/6-31G(D)对 TMS 进行了结构优化, 在此基础上, 用 Hartree-Fock、B3LYP 理论水平下, 分别用不同的基组 6-31G、6-31++G(D,P)、6-311+G(2D,P)、6-311++G(D,P)进行 NMR 的计算; 在 MP2 理论水平上, 用 STO-3G、3-21G、4-31G、6-31G、6-31G(D)、6-31++G(D,P)等基组进行 NMR 的计算. 并用 GAUSSION98 程序所给出的四种计算 NMR 的方法: GIAO、IGAIM、CSGT、SINGLE GAUGE ORIGIN, 分别在上述基础上进行了 TMS 的屏蔽值的计算. 研究表明, 就理论水平而言, DFT(B3LYP) 比 HF 计算结果要好, 而且基组越大, 计算精度越高, 但有一饱和基组存在. 就计算方法而言, 用 GIAO 有利于计算精度的提高. 计算结果与实验值基本上吻合.

关键词: NMR; 量子化学; 屏蔽常数; 化学位移; TMS

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