
Quasirelativistic Study of ^{125}Te Nuclear Magnetic Shielding Constants and Chemical Shifts

MASAHIKO HADA,¹ JIAN WAN,^{1,2} RYOICHI FUKUDA,¹
HIROSHI NAKATSUJI¹

¹Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-Ku, Kyoto 606-8501, Japan

²Department of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China

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ABSTRACT: Calculations for ^{125}Te magnetic shielding constants and chemical shifts were carried out using a quasirelativistic Hamiltonian including the spin-free relativistic, one- and two-electron spin-orbit, and relativistic magnetic interaction terms. For the tellurium-containing series $\text{Te}(\text{CH}_3)_2$, TeH_2 , TeF_6 , $\text{Te}(\text{CH}_3)_4$, and $\text{Te}(\text{CH}_3)_2\text{Cl}_2$, the relativistic effects amounted to as much as 1300 ppm and were very important for qualitatively reproducing the absolute value of the ^{125}Te shielding constants obtained experimentally. On the other hand, for the ^{125}Te chemical shifts the relativistic effects were less important, because they cancelled each other between the sample and reference compounds. © 2001 John Wiley & Sons, Inc. *J Comput Chem* 22: 1502–1508, 2001

Keywords: tellurium magnetic shielding constant; NMR chemical shift; relativistic effect; tellurium compound; spin-orbit

Introduction

The shielding tensor in NMR spectroscopy is probably one of the most important second-order response properties in molecular spectroscopy. Much progress was made in the last

decade toward a correct description of this shielding by first-principles electronic structure theory. Calculations of the shielding were carefully reviewed in an annual series.¹ Recently, a good survey of the state of the art was provided by Helgaker et al.² One of the most important developments in the last few years was the inclusion of electron-correlation effects^{2–7} and relativistic effects^{8–27} into shielding calculations.

Over the years, many workers investigated the effects of relativity on NMR shieldings. Early inves-

Correspondence to: H. Nakatsuji; e-mail: hiroshi@sbchem.kyoto-u.ac.jp

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tigations studied the effects of relativity using perturbation theory.^{8–10} Recently, calculations of nuclear magnetic shieldings considered the effects of relativity without perturbation.^{11–19, 22–25} The range of theoretically accessible nuclei was only recently extended to gradually include compounds of heavier elements. Such calculations with various levels of theory are still comparatively rare. We proposed a simple method for including the spin–orbit (SO) interaction term into the *ab initio* unrestricted Hartree–Fock method¹¹ (UHF), which we called the SO-UHF method, and showed that the SO effect is very important for the chemical shift of a light nucleus bonded to heavy atoms.^{11–16}

When the resonant nucleus is heavy, the spin-free relativistic (SFR) effect, which includes the mass–velocity and Darwin terms in the lowest order (c^{-2}), becomes important. Hence, we introduced the SFR correction using the Douglas–Kroll–Hess method^{28–30} with the SO-UHF method to calculate the magnetic shielding constant and chemical shift of heavy elements. This approach is referred to as the quasirelativistic (QR)-SO-UHF method.¹⁶

Recently, we generalized this approach by introducing the QR-SO generalized UHF (QR-SO-GUHF) method¹⁹ in which the orbitals are general spin–orbital. Further, we adopted a more sophisticated QR Hamiltonian that includes a relativistic correction to the magnetic interaction term, the one-electron SO term in Douglas–Kroll³⁰ (DK) form and the two-electron SO term in Breit–Pauli (BP) form. This method was used to calculate NMR shielding constants and chemical shifts of a series of mercury compounds [Hg(XH₃)₂ (X = C, Si, and Ge), Hg(CH₃)₂Y, and HgY₂ (Y = Cl, Br, and I)], and it gave much closer agreement with the experimental values than the previous method.¹⁸ Moreover, we presented matrix Dirac–Fock calculations for heavy-element magnetic shielding constants using a finite perturbation method.^{20, 21}

Other important studies in NMR calculations are presented by Ziegler and coworkers.^{22–25} They carried out a density functional theory (DFT) calculation in which the scalar–relativistic and SO coupling effects were taken into account, and gauge-including atomic orbitals (GIAO) and a frozen-core approximation were used. More recently, they used the zeroth-order regular approximation^{31–34} to incorporate the effects of relativity into the calculation of NMR shielding tensors.^{22, 23} Kaupp et al.^{26, 27} extended the DFT-based individual gauge for localized orbitals method of Malkin et al.³⁵ to include scalar relativistic effects. Generally speaking, DFT calculations are relatively inexpensive and numer-

ical evidence indicates that the self-consistent field and DFT results differ significantly, especially when the correlation effects are large. However, we should keep in mind that “although DFT has a rigorous base, in application it is semiempirical” and that there is “no way to systematically converge to the exact result.”³⁶ This contrasts with conventional *ab initio* approaches in which we can estimate *a priori* the quality of a calculation and improve the calculation systematically by extending the basis set and improving the correlation treatment.

The purpose of the present study was to test the performance of the QR-SO-GUHF method for even heavier fourth-row main group compounds by calculating the ¹²⁵Te absolute shielding constants and relative chemical shifts of tellurium-containing complexes. Rodriguez-Fortea and coworkers²⁵ also systematically calculated the tellurium shieldings and shifts, taking into account the scalar relativistic two-component Pauli-type Hamiltonian. However, their calculations did not consider SO effects. We compared their results with our present calculations.

Computational Details

QR HAMILTONIAN AND GUHF WAVE FUNCTION

In order to introduce a two-component QR_Hamiltonian, we start with the one-electron Dirac_Hamiltonian including scalar potential V and vector potential \mathbf{A} :

$$H_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V + c\boldsymbol{\alpha} \cdot \mathbf{A} \quad (1)$$

where $\boldsymbol{\alpha}$ and β represent the Dirac 4×4 matrices. The last term $c\boldsymbol{\alpha} \cdot \mathbf{A}$ is separated from the mechanical momentum operator $\boldsymbol{\pi} = c\boldsymbol{\alpha}(p + \mathbf{A})$. The free-particle Foldy–Wouthuysen transformation (U_0) is applied to eq. (1) and the first-order Hamiltonian is obtained as

$$U_0 H_D U_0 = \beta E_p + H^{\text{int}}(\mathbf{V}) + H^{\text{int}}(\mathbf{A}) + O(\mathbf{V}) + O(\mathbf{A}) \equiv H_1 \quad (2)$$

where

$$E_p = c(p^2 + c^2)^{1/2} \quad (3)$$

$$H^{\text{int}}(\mathbf{V}) = \mathbf{K} \mathbf{V} \mathbf{K} + \mathbf{R}(c^2 \mathbf{p} \mathbf{V} \cdot \mathbf{p}) \mathbf{R} + \mathbf{R}[ic^2 \boldsymbol{\alpha} \cdot (\mathbf{p} \mathbf{V} \times \mathbf{p})] \mathbf{R} \quad (4)$$

$$H^{\text{int}}(\mathbf{A}) = \beta \left[\mathbf{K} \frac{2c\mathbf{A} \cdot \mathbf{p}}{E_p + c^2} \mathbf{K} - \mathbf{K} \frac{ic\boldsymbol{\alpha} \cdot (\mathbf{p} \times \mathbf{A})}{E_p + c^2} \mathbf{K} \right] \quad (5)$$

$$O(\mathbf{V}) = \beta [\mathbf{R}(c\boldsymbol{\alpha} \cdot \mathbf{p} \mathbf{V}) \mathbf{K} - \mathbf{K}(c\mathbf{V}\boldsymbol{\alpha} \cdot \mathbf{p}) \mathbf{R}] \quad (6)$$

$$O(\mathbf{A}) = \mathbf{K}\boldsymbol{\alpha} \cdot \mathbf{A} \mathbf{K} + \mathbf{R}[c^2 \boldsymbol{\alpha} \cdot \mathbf{p} (\boldsymbol{\alpha} \cdot \mathbf{p}) \boldsymbol{\alpha} \cdot \mathbf{p}] \mathbf{R} \quad (7)$$

and

$$U_0 = \mathbf{K} + \boldsymbol{\beta} \mathbf{R} \boldsymbol{\alpha} \cdot \mathbf{p} \quad (8)$$

Two scalar factors \mathbf{K} and \mathbf{R} are respectively expressed as

$$\mathbf{K} = \left[\frac{E_p + c^2}{2E_p} \right]^{1/2} \quad (9)$$

and

$$\mathbf{R} = [2E_p(E_p + c^2)]^{-1/2} \quad (10)$$

To remove the remaining odd terms $O(\mathbf{V})$ and $O(\mathbf{A})$, we used the second-order DK transformation³⁰ as

$$U_1 = \{1 + [W(\mathbf{V}) + W(\mathbf{A})]^2\}^{1/2} + [W(\mathbf{V}) + W(\mathbf{A})] \quad (11)$$

where W is the momentum space integral operator, and the kernel is expressed as

$$W(X_{pp'}) = \boldsymbol{\beta} O(X_{pp'}) / (E_p + E_{p'}) \quad (12)$$

and $X_{pp'}$ is $\mathbf{V}_{pp'}$ or $\mathbf{A}_{pp'}$. The transformed Hamiltonian is written as

$$\begin{aligned} U_1 H_1 U_1 = & \hat{a} E_p + H^{\text{int}}(\mathbf{V}) + H^{\text{int}}(\mathbf{A}) \\ & + \frac{1}{2} [W(\mathbf{V}), O(\mathbf{V})] + \frac{1}{2} [W(\mathbf{A}), O(\mathbf{A})] \\ & + \frac{1}{2} [W(\mathbf{V}), O(\mathbf{A})] + \frac{1}{2} [W(\mathbf{A}), O(\mathbf{V})] \\ & + \dots \end{aligned} \quad (13)$$

A two-component QR one-electron Hamiltonian can be achieved by taking only the upper two components from eq. (13).

The two-electron repulsion term ($1/r_{ij}$) and two-electron SO term ($\mathbf{V}_{ij}^{\text{SO}}$) are added to the one-electron two-component QR Hamiltonian obtained from eq. (13). For the two-electron SO term, we used a BP form as

$$\mathbf{V}_{ij}^{\text{SO}} = -\frac{1}{2c^2} \sum_j \sum_{i \neq j} \frac{L_{ij} \cdot s_j + 2L_{ij} \cdot s_j}{r_{ij}^3}, \quad (14)$$

where L and s denote orbital and spin angular momentum, respectively.

In this formulation the \mathbf{A} is relativistically treated up to the second-order expansion of \mathbf{V} and \mathbf{A} . When the \mathbf{A} consists of the uniform external magnetic field (\mathbf{B}) and the nuclear magnetic moment ($\boldsymbol{\mu}_N$), the resultant Hamiltonian can be expanded with regard to the powers of B and μ_N , and it can therefore be applied to the NMR theory. The magnetic shielding tensor for nucleus N can be written as the sum of the diamagnetic term (σ_N^{dia}), the paramagnetic term (σ_N^{para}), the spin-dipolar term [$\sigma_N^{\text{SO}}(\text{SD})$] and the Fermi contact term [$\sigma_N^{\text{SO}}(\text{FC})$]:^{11, 16, 19}

$$\sigma_N^{\text{total}} = \sigma_N^{\text{dia}} + \sigma_N^{\text{para}} + \sigma_N^{\text{SO}}(\text{SD}) + \sigma_N^{\text{SO}}(\text{FC}). \quad (15)$$

The terms $H^{\text{int}}(\mathbf{A})$, $[W(\mathbf{V}), O(\mathbf{A})]$, and $[W(\mathbf{A}), O(\mathbf{V})]$ give σ_N^{para} , $\sigma_N^{\text{SO}}(\text{SD})$, and $\sigma_N^{\text{SO}}(\text{FC})$, respectively, while $[W(\mathbf{A}), W(\mathbf{A})]$ gives σ_N^{dia} .

At the HF level the general spin dependence of the relativistic wave function is best expressed by using the GUHF method because of the presence of the spin-dependent operator in the magnetic field. In the GUHF method, the one-electron spin-space function is expressed as

$$\phi_i(x) = c_i^\alpha \phi_i^\alpha(r) \alpha(\sigma) + c_i^\beta \phi_i^\beta(r) \beta(\sigma) \quad (16)$$

where $x = (r, \sigma)$ is a spin-space coordinate and α and β are eigenfunctions of spin operators S_z and S^2 , respectively, in this equation.

BASIS SET AND MOLECULAR GEOMETRY

We used an uncontracted well-tempered Gaussian basis set (28s23p17d)³⁷ for the tellurium atom. The Gaussian basis set used for hydrogen was Huzinaga–Dunning³⁸ (4s)/[2s]. An uncontracted triple- ζ -quality valence basis of Huzinaga³⁹ (10s7p)/[4s3p] was used for carbon and fluorine atoms and (11s8p)/[5s4p]³⁹ was used for the chlorine atom. For hydrogen, carbon, and fluorine atoms the basis sets were augmented by the first-order higher angular momentum basis functions (FOBFs), which make the calculations approximately gauge invariant.^{40, 41} Two p-FOBFs of the s orbitals were added for hydrogen. Three d-FOBFs of the valence p orbitals were added for carbon, fluorine, and chlorine atoms. We used experimental geometries^{42–44} for all molecules. The common gauge origin was located on the Te nucleus throughout our calculations.

Results and Discussion

ABSOLUTE SHIELDINGS

Jameson and Jameson⁴⁸ reported an experimental absolute shielding scale for Te magnetic shielding constants, which was determined by observing the simultaneous nuclear spin-relaxation time and combining the spin-rotation constant with the calculated diamagnetic shielding of the atom. A direct comparison between calculated and observed shielding constants straightforwardly validated the present QR-GUHF method.

The calculated absolute shielding constants for several molecules are presented in Table I. The correlation between the theoretical and experimental results for the ¹²⁵Te absolute shielding constant is

TABLE I. Calculated and Experimental ¹²⁵Te Absolute Shielding Constants (ppm) for Selected Tellurium-Containing Compounds.

System	Nonrelativistic		Relativistic		Expt
	RHF	DFT-GIAO ^a	QR-SO-GUHF	DFT-GIAO ^a	
Te(CH ₃) ₂	3208 (-1125)	2968 (-1465)	4725 [1517] (392)	3050 [182] (-1283)	4333 ^b
TeH ₂	3772 (-1182)		5310 [1538] (356)	3762 (-1192)	4954 ^c
TeF ₆	3006 (-784)	2260 (-1530)	4455 [1449] (665)	2448 [188] (-1342)	3790 ± 130 ^b
Te(CH ₃) ₄	3310	3019	4768 [1458]	3189 [170]	
Te(CH ₃) ₂ Cl ₂	2906		4258 [1352]	2615	

The differences from experimental absolute shieldings are shown in parentheses, and differences between relativistic and nonrelativistic results are given in brackets.

^a From ref. 25.

^b From refs. 45 and 46.

^c From ref. 47.

illustrated in Figure 1. Here we focused on the influence of the inclusion of relativity compared with nonrelativistic calculations. There are several points to note about the results in Table I. First, the resultant relativistic effects were 1517, 1538, and 1449 ppm for Te(CH₃)₂, TeH₂, and TeF₆, respectively. This means that the relativistic effects made a considerable contribution to the calculated absolute shielding.

Furthermore, note from Table I that the maximal changes due to the inclusion of relativity were only 182 and 188 ppm for Te(CH₃)₂ and TeH₂, respectively, in the DFT-GIAO calculations. These values

were more than 1000 ppm smaller than those obtained by the QR-SO-GUHF method. One possible explanation for this underestimation was the lack of SO terms or the inclusion of a frozen-core approximation and the use of a different basis set in the DFT-GIAO calculations. In the QR-SO-GUHF calculations the total contributions of the SO terms were more than 1700 ppm for all tellurium-containing molecules of interest. With regard to this underestimation of the DFT-GIAO, Ruiz-Morales and coworkers⁵⁰ suggested that the absolute scale in the experiment for ¹²⁵Te by Jameson and Jameson⁴⁵ should be reduced by 945 ppm. Our calculations did not validate this suggestion.

Compared with the experimental absolute ¹²⁵Te shielding constants listed in Table I, the average deviation of the present QR-SO-GUHF method was an approximate 471-ppm overestimation. The electron-correlation effect, which was not included in the present calculations, might have been responsible for this deviation. Therefore, for a more accurate description of Te shielding constants in these molecules, relativistic and electron-correlation treatments were both necessary. Note from Table I that the DFT-GIAO results, which included the electron-correlation effect, were on average 459 ppm lower than the restricted HF results at the nonrelativistic level. This difference may be the electron-correlation effect.

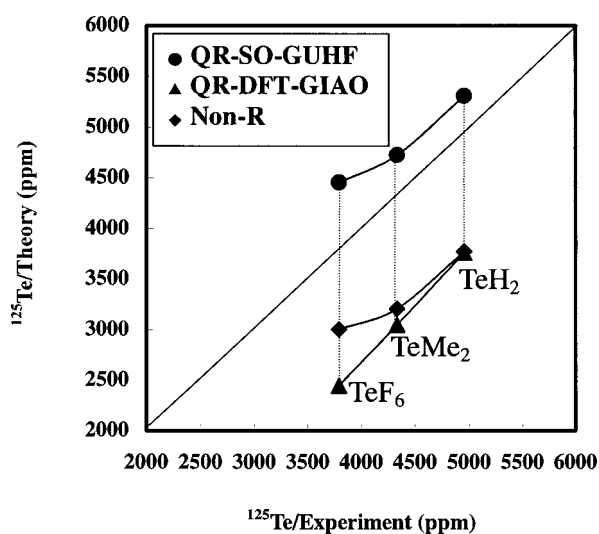


FIGURE 1. The correlations between the theoretical and experimental ¹²⁵Te absolute shielding constants.

CHEMICAL SHIFTS

The calculated ¹²⁵Te chemical shifts for our QR-SO-GUHF method are summarized in Tables II

TABLE II. QR-SO-GUHF Calculated and Experimental ^{125}Te Chemical Shifts (ppm) for Various Tellurium-Containing Compounds.

System	Level	σ^{para}	σ^{dia}	σ^{SO}			σ^{total}	δ_{calc}	δ_{expt}
				SD	FC	Total			
$\text{Te}(\text{CH}_3)_2$	Non-R	-2228	5436				3208	0	0 ^a
	QR	-2334	5161	-7.5	1906	1898.5	4725.5	0	
TeH_2	Non-R	-1602	5374				3772	-564	-621 ^b
	QR	-1684	5099	+7.5	1888	1895.5	5310.5	-585	
TeF_6	Non-R	-2626	5633				3007	201	543 ± 130 ^a
	QR	-2859	5358	-86	2042	1956	4455	270.5	
$\text{Te}(\text{CH}_3)_4$	Non-R	-2195	5505				3310	-102	-67 ^c
	QR	-2247	5230	-43	1828	1785	4768	-42.5	
$\text{Te}(\text{CH}_3)_2\text{Cl}_2$	Non-R	-2657	5563				2906	302	733.8 ^d
	QR	-2804	5288	-64	1838	1774	4258	467.5	

^a From refs. 45 and 46.^b From ref. 47.^c From ref. 48.^d From ref. 49.

and III. The correlation between the theoretical and experimental results for the ^{125}Te chemical shift is illustrated in Figure 2. We compare our results with the experimental shifts and the DFT-GIAO results in

Tables II and III. The experimentally accepted standard for ^{125}Te chemical shifts is dimethyl telluride, $\text{Te}(\text{CH}_3)_2$. Therefore, we included it in our investigations and used it as reference compound.

TABLE III. Decomposition of Calculated ^{125}Te Chemical Shifts (ppm).

Molecule	Level	Chemical Shift (ppm)							δ_{expt}
		DFT-GIAO ^a			QR-SO-GUHF				
		δ^{para}	δ^{dia}	δ^{total}	δ^{para}	δ^{dia}	δ^{SO}	δ^{total}	
$\text{Te}(\text{CH}_3)_2$	Non-R				0	0	0	0	0 ^b
	QR	0	0	0	0	0	0	0	
TeH_2	Non-R				-626	+62		-564	-621 ^c
	QR	-706.5	-4.9	-711.4	-650	+62	+3	-585	
TeF_6	Non-R				(-24)	(0)		(-21)	
	QR	+596.6	+5.5	+602.0	+398	-197		+201	543 ± 130 ^b
$\text{Te}(\text{CH}_3)_4$	Non-R				+525	-197	-57.5	+270.5	
	QR	-141.8	+2.8	-139.0	(127)	(0)		(+69.5)	
$\text{Te}(\text{CH}_3)_2\text{Cl}_2$	Non-R				-33	-69		-102	-67 ^d
	QR	+431.4	+4.0	+435.4	-87	-69	+113.5	-42.5	
$\text{Te}(\text{CH}_3)_2\text{Cl}_2$	Non-R				(-54)	(0)		(+59.5)	
	QR				+429	-127		+302	733.8 ^e
$\text{Te}(\text{CH}_3)_2\text{Cl}_2$	Non-R				+470	-127	+124.5	+467.5	
	QR				(+41)	(0)		(+65.5)	

The contributions of the relativistic effects to the ^{125}Te chemical shifts are listed in parentheses.

^a From ref. 25.^b From refs. 45 and 46.^c From ref. 47.^d From ref. 48.^e From ref. 49.

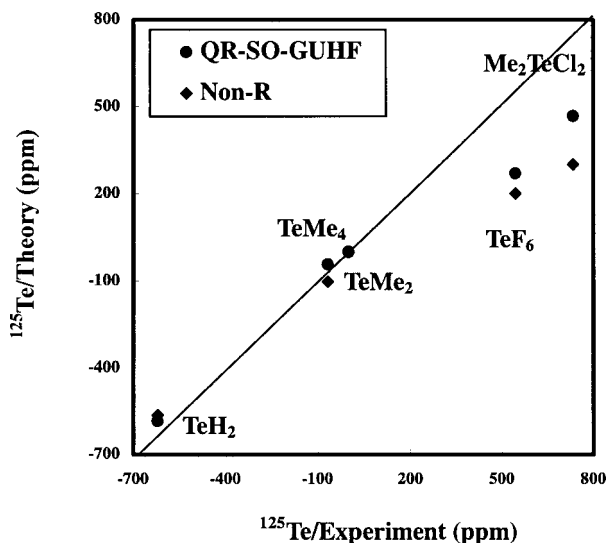


FIGURE 2. The correlations between the theoretical and experimental ¹²⁵Te relative chemical shifts.

Here we note that, when comparing theoretical results with experimental observations, we should keep in mind that the experimental values were influenced by thermal motion and solvent effects. These effects reportedly amount to as much as ± 100 ppm.²⁴

Table III also shows a decomposition of the ¹²⁵Te chemical shift (Δ) into its paramagnetic, diamagnetic, and SO components as

$$\delta^{\text{total}} = \delta^{\text{para}} + \delta^{\text{dia}} + \delta^{\text{SO}}, \quad (17)$$

where δ^{total} and its components are defined as

$$\delta^{\text{term}} = \sigma_{\text{TeMe}_2}^{\text{term}} - \sigma^{\text{term}} \quad (18)$$

and term refers to total, dia, para, and SO.

It is clear from Table III that the total δ was predominantly determined by the paramagnetic contribution δ^{para} . In the QR-SO-GUHF calculations the contributions of the diamagnetic and SO terms were relatively large. However, in the DFT-GIAO calculations the contribution of the diamagnetic term was very small. The reason for this difference is complicated. Some part was due to the different Hamiltonian approximations in these two methods: one- and two-electron SO terms were included in QR-SO-GUHF calculations but not in DFT-GIAO calculations and a frozen-core approximation was used in DFT-GIAO calculations but not in QR-SO-GUHF calculations. However, some part was due to the difference between GIAO and common gauge, especially in δ^{dia} .

Further, note from Table III that the relativistic effects cancelled each other in the calculations of the

chemical shift. The relativity improved the calculated chemical shifts by 21 ppm for TeH₂, 69.5 ppm for TeF₆, 59.5 ppm for Te(CH₃)₄, and 65.5 ppm for Te(CH₃)₂Cl₂. These numerical magnitudes were much smaller than those in the absolute shielding constant calculations. Interestingly, the contribution from the diamagnetic term to the relative chemical shift in QR-SO-GUHF calculations was exactly the same as that in nonrelativistic calculations for all of the molecules of interest. The relativistic effects increased the contribution of the paramagnetic term to chemical shifts. The SO contribution to the chemical shifts was almost the same magnitude as the diamagnetic contribution. In Te(CH₃)₄ the SO contribution (113.5 ppm) was the largest. Our numerical results showed that the σ^{SO} and δ^{SO} contributions were both important for accurately calculating the absolute shielding constants and the relative chemical shifts.

Conclusion

A two-component QR method was used to calculate the ¹²⁵Te NMR absolute shielding constants and relative chemical shifts. General trends in the observed spectra were well reproduced by the QR-SO-GUHF method for the ¹²⁵Te relative chemical shifts and the ¹²⁵Te absolute shielding constants. A direct comparison of the calculated and observed ¹²⁵Te absolute shieldings demonstrated the validity and the reliability of the present QR-SO-GUHF method. The electron-correlation effect should be further taken into account for a more accurate theoretical study of the NMR parameters.

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