

Quasirelativistic theory for the magnetic shielding constant.

III. Quasirelativistic second-order Møller–Plesset perturbation theory and its application to tellurium compounds

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The quasirelativistic (QR) generalized unrestricted Hartree–Fock method for the magnetic shielding constant [R. Fukuda, M. Hada, and H. Nakatsuji, *J. Chem. Phys.* **118**, 1015 (2003); **118**, 1027 (2003)] has been extended to include the electron correlation effect in the level of the second-order Møller–Plesset perturbation theory (MP2). We have implemented the energy gradient and finite-perturbation methods to calculate the magnetic shielding constant at the QR MP2 level and applied to the magnetic shielding constants and the NMR chemical shifts of ¹²⁵Te nucleus in various tellurium compounds. The calculated magnetic shielding constants and NMR chemical shifts well reproduced the experimental values. The relations of the chemical shifts with the natures of ligands, and the tellurium oxidation states were investigated. The chemical shifts in different valence states were explained by the paramagnetic shielding and spin-orbit terms. The tellurium 5*p* electrons are the dominant origin of the chemical shifts in the Te I and Te II compounds and the chemical shifts were explained by the *p*-hole mechanism. The tellurium *d* electrons also play an important role in the chemical shifts of the hypervalent compounds. © 2005 American Institute of Physics.
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I. INTRODUCTION

The NMR spectrum involves rich information on the electronic structure of molecules.¹ The NMR spectrum reflects the electronic structure rather local near the resonance nucleus: for example, the *d*-electron structure of transition-metal complexes. The mechanisms of chemical shifts of transition metals as well as main-group elements have been studied by our laboratory and we concluded that the electronic mechanisms of the chemical shifts are characterized by the positions of the resonant nuclei in the Periodic Table.^{1–3}

While the Hartree–Fock self-consistent field (HFSCF) calculations give us a great deal of knowledge about the NMR chemical shifts, electron correlation effect must also be considered for quantitative predictions of NMR chemical shifts. The progress in the energy gradient methods has enabled the calculation of magnetic shielding constants with electron correlation methods. The first study of magnetic shielding constants with the energy derivative approach of a correlated method was reported by Gauss.^{4,5} He adapted the analytical energy derivative of the second-order many-body perturbation theory [MBPT(2)] to magnetic shielding constants with the gauge-including atomic orbital (GIAO). Almost at the same time, Cybulski and Bishop have applied the MBPT energy derivative for magnetic shielding constants

within conventional AO basis,⁶ and van Wüllen and Kutzelnigg have adapted their individual gauges for localized orbitals (IGLO) method for the multiconfiguration SCF (MCSCF) wave functions.⁷ Now, the methods for calculating magnetic shielding constants have been developed up to more accurate wave functions, e.g., GIAO-CCSD (Ref. 8) and GIAO-CCSD(T).⁹ An alternative method for including the electron correlation is the density-functional theory (DFT). The DFT calculation for magnetic shielding constants has been proposed by Malkin *et al.* as DFT-IGLO.¹⁰ The DFT-GIAO method has also been developed by Schreckenbach and Ziegler.¹¹

In spite of the progress in electron correlation methods for magnetic shielding constants, we have to address another important issue, namely, relativistic effect.¹² Multinuclear NMR research deals with almost all the elements in the Periodic Table,^{13,14} so the relativistic effect could be important even more than the electron correlation effect. The relativistic effects on magnetic properties are significant and many NMR experiments cannot be understood without the relativistic theory.

Ramsey's original theory of the magnetic shielding constant¹⁵ is based on the nonrelativistic Schrödinger equation; therefore, the relativistic effects are not included. The relativistic theory of NMR parameters had been investigated by two different approaches. The first approach intends to adapt Ramsey's theory to the four-component Dirac

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equation.^{16–18} Although the *ab initio* four-component calculations^{19–21} have been reported for the magnetic shielding constant of molecules, the four-component method can be applied only for small systems. The second approach is appending the spin-orbit (SO) interaction to the nonrelativistic theory. The importance of the SO interaction had been recognized many years ago.²² Our laboratory proposed the NMR theory including the SO interaction using the *ab initio* unrestricted Hartree–Fock (UHF) wave function.²³ This SO-UHF method has been applied to H, C,²³ Ga, In,²⁴ Si,²⁵ Al,²⁶ Sn,²⁷ Nb, and Ti²⁸ chemical shifts of various compounds. The series of studies of this approach have shown the importance of the SO effect, particularly the Fermi contact (FC) term. Heavy atom effects, for example, “normal halogen dependence,” are clearly explained with the SO effect which appears as the FC term. However, including only the SO interaction is insufficient for the magnetic shielding constants of heavy resonant nuclei.

Recently, the third approach based on the quasirelativistic (QR) method has been receiving increasing attention. In the previous articles of this series,^{29,30} we have developed the QR theory for magnetic properties based on the Douglas–Kroll (DK) transformation and applied it to the magnetic shielding constants of noble gas atoms²⁹ and NMR chemical shifts of ¹⁹⁹Hg (Refs. 30 and 31) and ¹²⁵Te.³² We extended the DK theory to include the “change of picture effect,” which ensures consistency with the Hellmann–Feynman theorem for the QR theory.²⁹ Our QR theory for magnetic shielding constants was adapted for the generalized-UHF (GUHF) wave function and GIAO method.³⁰ Other QR methods, particularly the zeroth-order regular approximation (ZORA), have been successfully used to study the magnetic shielding constants of molecules including heavy elements.^{33,34} The QR methods can be extensively applied for the magnetic shielding constants of heavy nuclei. The history and recent studies of the relativistic effect on NMR parameters are summarized in review articles.^{35–37}

The purpose of the present study is to extend our QR-GUHF method^{29,30} to include the electron correlation effect. The QR theories are essentially a no-pair theory³⁸ in which positronlike states are not involved. Thus, the electron correlation can be considered by the usual nonrelativistic manner, but the molecular orbitals and electron repulsion operators are replaced by the relativistic form. We present the second-order Møller–Plesset perturbation theory (MP2) for the GUHF orbitals (GUMP2) in this study. The magnetic shielding constant at the MP2 level is calculated by the relaxed density approach based on the energy derivative method. We use the formulation similar to the GIAO-MBPT(2) method,^{4,5} but we calculate the derivatives of the relaxed density matrix by numerical differentiation. Solving the coupled perturbative (CPHF) equations and the first-order Z-vector equations is avoided, but the finite-field SCF and the finite-field Z-vector equations are solved. We adapt the energy gradient of the QR-GUMP2 method including the frozen-core orbitals.

The presented QR-GUMP2 method is applied to ¹²⁵Te magnetic shielding constants and NMR chemical shifts. Because the experimental research had proposed the magnetic

shielding constant of tellurium,³⁹ several relativistic methods have been applied to calculate ¹²⁵Te magnetic shielding constants.^{40–42} However, there is still room for further research on the accuracy of the experimental value of the magnetic shielding constant. To give a theoretical prediction of the shielding constant of heavy elements, we have to consider both the relativistic and electron correlation effects.

The ¹²⁵Te NMR chemical shifts of various compounds have been systematically studied by Ruiz-Morales *et al.* using the DFT-GIAO method and scalar relativistic Hamiltonian.⁴⁰ Although their results generally reproduced the experimental findings, the SO effect on the tellurium chemical shifts is still an open question. Tellurium can take various oxidation states and coordination numbers; the compounds with formal oxidation states Te II to Te VI are well known.⁴³ Many experimental and theoretical studies indicate the relations of the chemical shifts with the electronegativity of ligands.^{13,40,44} Because the valence electronic configuration of a tellurium atom is s^2p^4 , the *p*-hole mechanism is suggested for tellurium NMR chemical shifts.^{1,45} We know that this mechanism explains the relation of chemical shifts with the electronegativity of ligands.^{1,41} Only a few studies have pointed out the relations of the chemical shifts with the oxidation states of tellurium. Zumbulyadis and Gysling have reported that an increase in the oxidation state causes the low-field shift of the Te chemical shift;⁴⁶ on the other hand, this relation has not been observed in telluropyranes.⁴⁷ To elucidate the relations of the chemical shifts with the oxidation states of a resonant atom is significant for predicting molecular structure using the NMR spectroscopy.

The relations between the coordination number and the chemical shift are studied with the relativistic *ab initio* calculations. The paramagnetic shielding term mainly rules the chemical shifts; additionally, the SO interaction is significant for the chemical shifts of molecules in different oxidation states of tellurium. The chemical shifts mainly depend on the electron-withdrawing ability of ligands. The nature of ligand reflects the chemical shift through the tellurium *p* orbitals. The *d* orbital is important in hypervalent compounds. The importance of the SO term induced by the neighboring heavy elements is well recognized. The present results show the SO effect of the heavy resonant atom itself.

II. THEORY

A. QR-GUHF method for the magnetic shielding constant

The detailed formulation of the QR-GUHF method on the magnetic shielding constant was given in Refs. 29 and 30. Here we give a brief outline of the method. The electronic Hamiltonian obtained by the second-order DK transformation^{38,48–50} with magnetic field is written as²⁹

$$H = \sum_j (E_{p_j} + V_j^{\text{eff}}) + \sum_{j>k} V_{jk} + \sum_j H_j^{\text{mag}}, \quad (1)$$

where $E_{p_j} = c\sqrt{p_j^2 + c^2}$ is the relativistic kinetic-energy operator and c denotes the speed of light. V_j^{eff} represents the effective scalar potential. The two-electron terms used in the present study are

$$V_{jk} = \frac{1}{r_{jk}} - \frac{1}{4c^2} \left[\frac{[(\mathbf{r}_{jk} \times \mathbf{p}_j) + 2(\mathbf{r}_{jk} \times \mathbf{p}_k)] \cdot \boldsymbol{\sigma}_j}{r_{jk}^3} + \frac{[(\mathbf{r}_{kj} + \mathbf{p}_k) + 2(\mathbf{r}_{jk} \times \mathbf{p}_k)] \cdot \boldsymbol{\sigma}_k}{r_{kj}^3} \right], \quad (2)$$

where $\boldsymbol{\sigma}_j$ denotes the Pauli matrix. The magnetic interaction H_j^{mag} is given by

$$\begin{aligned} H_j^{\text{mag}} &= K_j [R_j \boldsymbol{\sigma}_j \cdot \mathbf{p}_j (c \boldsymbol{\sigma}_j \cdot \mathbf{A}_j) + (c \boldsymbol{\sigma}_j \cdot \mathbf{A}_j) \boldsymbol{\sigma}_j \cdot \mathbf{p}_j R_j] K_j \\ &+ \frac{1}{2} [(W_j^V W_j^A - W_j^A W_j^V) E_j + 2(W_j^V E_j W_j^A - W_j^A E_j W_j^V) \\ &+ E_j (W_j^V W_j^A - W_j^A W_j^V)] + \frac{1}{2} [(W_j^A)^2 E_j + 2W_j^A E_j W_j^A \\ &+ E_j (W_j^A)^2]. \end{aligned} \quad (3)$$

The vector potential generated by a uniform magnetic field \mathbf{B} and magnetic moment $\boldsymbol{\mu}_A$ of nucleus A is written as

$$\mathbf{A}_j = \frac{1}{2} \mathbf{B} \times \mathbf{r}_j - \frac{1}{c^2} \sum_A^{\text{nuc}} \boldsymbol{\mu}_A \times \int \frac{w_A(R_A)}{|\mathbf{r}_j - \mathbf{R}|} d\mathbf{R}. \quad (4)$$

Here w_A represents the distribution of nuclear magnetic moment.⁵¹ The Gaussian nucleus model for the nuclear charge and magnetic moment is used in the present study.⁵²

The HF wave function has the GUHF form in order to describe spin-dependent properties. The GUHF molecular orbital is a direct product of spatial and spin functions, and the spatial function is a linear combination of atomic orbitals with complex coefficients. To allow origin-independent calculations, we utilize the GIAO function,^{53,54} which is defined by

$$\chi_\lambda^{\text{GIAO}} = \exp \left[-\frac{1}{2} i (\mathbf{B} \times \mathbf{R}_\lambda) \cdot \mathbf{r} \right] \chi_\lambda^{(0)}, \quad (5)$$

where $\chi_\lambda^{(0)}$ denotes the usual real AO function that centered at \mathbf{R}_λ . The QR-GUHF orbitals

$$\phi_k^{\text{GUHF}} = \sum_\lambda^{\text{AO}} (C_{\lambda k}^\alpha \chi_\lambda^{\text{GIAO}} \alpha + C_{\lambda k}^\beta \chi_\lambda^{\text{GIAO}} \beta) \quad (6)$$

are obtained by solving the QR-GUHF-SCF equations,

$$\begin{aligned} (E_p + V^{\text{eff}} + B_i H_i^{(1,0)} + \mathbf{J} + \mathbf{K}) |\phi_k^{\text{GUHF}}\rangle \\ = F |\phi_k^{\text{GUHF}}\rangle = \varepsilon_k |\phi_k^{\text{GUHF}}\rangle, \end{aligned} \quad (7)$$

under the orthonormality condition

$$\langle \phi_j^{\text{GUHF}} | \phi_k^{\text{GUHF}} \rangle = \delta_{jk}. \quad (8)$$

Here \mathbf{J} and \mathbf{K} are Coulomb and exchange operators, respectively.

The magnetic shielding tensor of nucleus A in the tu component is given by Ramsey as

$$\sigma_{A,tu} = \left. \frac{\partial^2 E}{\partial B_t \partial \mu_{A,u}} \right|_{B_t = \mu_{A,u} = 0}, \quad (9)$$

where E is the total energy. Using the Hellmann–Feynman theorem and finite-perturbation method, we obtain the QR-GUHF magnetic shielding tensor in the form

$$\begin{aligned} \sigma_{A,tu} &= \sum_{\lambda\nu}^{\text{AO}} \sum_{\omega\omega'}^{\alpha\beta} \left[\left(\frac{D_{\lambda\nu}^{\omega\omega'}(B_t) - D_{\lambda\nu}^{\omega\omega'}(0)}{B_t} \right) \right. \\ &\times \langle \chi_\nu^{(0)} \omega' | H_{A,u}^{(0,1)} | \chi_\lambda^{(0)} \omega \rangle + D_{\lambda\nu}^{\omega\omega'}(0) \\ &\left. \times \langle \chi_\nu^{(0)} \omega' | H_{A,u}^{(1,1)} | \chi_\lambda^{(0)} \omega \rangle \right]. \end{aligned} \quad (10)$$

The GUHF-SCF density matrix is given by

$$D_{\lambda\nu}^{\omega\omega'} = \sum_k^{\text{occ}} C_{\lambda k}^\omega C_{\nu k}^{\omega'*}, \quad (11)$$

the density matrix $D(0)$ is obtained by solving Eq. (7) in $B=0$, and $D(B_t)$ is obtained from the equation with finite-magnetic field.

B. QR-GUMP2 method for the magnetic shielding constant

In the many-body perturbation theory, the Hamiltonian is split into the unperturbed part and perturbation. In this study, we work with the Møller–Plesset partitioning and the canonical orbital, namely,

$$H = F + V. \quad (12)$$

The QR-GUHF wave function, $|\Phi_0^{\text{GUHF}}\rangle \equiv |\Phi_0\rangle$, satisfy the Brillouin theorem; the second-order MP perturbation energy is then given by

$$E^{(2)} = \frac{1}{4} \sum_{ij}^{\text{O}} \sum_{ab}^{\text{V}} \langle \Phi_0 | V | \Phi_{ij}^{ab} \rangle a_{ij}^{ab} = \frac{1}{4} \sum_{ij}^{\text{O}} \sum_{ab}^{\text{V}} (ai||bj) a_{ij}^{ab}. \quad (13)$$

The first-order doubly substitution amplitudes are given by

$$a_{ij}^{ab} = -\frac{(ia||jb)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \quad (14)$$

The molecular-orbital (MO) base integrals are defined by

$$(ai||bj) = (ai|bj) - (aj|bi) \quad (15)$$

and

$$\begin{aligned} (ai|bj) &= \sum_{\mu\nu\lambda\rho}^{\text{AO}} \sum_{\omega\omega'\tau\tau'}^{\alpha\beta} (\chi_\mu^{(0)} \omega' \chi_\nu^{(0)} \omega | V_{12} | \chi_\lambda^{(0)} \tau' \chi_\rho^{(0)} \tau) \\ &\times C_{\mu a}^{\omega'*} C_{\nu i}^\omega C_{\lambda b}^{\tau'*} C_{\rho j}^\tau, \end{aligned} \quad (16)$$

where V_{12} is given by Eq. (2). The following index conventions are used: i, j, k, \dots are occupied orbitals, a, b, c, \dots are virtual orbitals, and p, q, r, \dots refer to either occupied or virtual orbitals. We also label orbital groups as follows: ‘‘C’’ (core) denotes frozen occupied orbitals, ‘‘O’’ (occupied) and ‘‘V’’ (virtual) are used for active occupied and virtual orbitals, and ‘‘F’’ (frozen) denotes frozen virtual orbitals.

Here we note that the spin functions are already integrated at the integral transformation step. The MO base integrals obtained by Eq. (16) are represented by the same form as ordinary spin-orbital integrals; although, they are complex numbers. Therefore, we can adapt the nonrelativis-

tic MP2 energy and energy gradient theories to the QR-GUMP2 method after some modification for handling complex numbers.

We will calculate the magnetic shielding tensor of the QR-GUMP2 by the finite-perturbation method. Our strategy for the calculation of the QR-GUMP2 magnetic shielding tensor is in analogy to that of QR-GUHF. The derivatives of GUMP2 energy with respect to $\mu_{A,u}$ can be written as

$$\left. \frac{\partial E^{(2)}}{\partial \mu_{A,u}} \right|_{\mu_{A,u}=0} = \sum_{pq}^{\text{MO}} D_{pq}^{(2)} \left\langle P \left| \frac{\partial H}{\partial \mu_{A,u}} \right| q \right\rangle. \quad (17)$$

Since the Hellmann–Feynman theorem does not hold in the MP2 wave function, $D_{pq}^{(2)}$ in Eq. (17) has to be the relaxed density that is derived by the GUMP2 energy gradient formula. The QR-GUMP2 relaxed density can be derived as the nonrelativistic one that has been reported by Gauss.^{4,5} In the present study, we use the frozen orbital approximation; therefore, we extend the Gauss formulation to include frozen orbitals. With using frozen orbitals $\mathbf{D}^{(2)}$, the hermitial matrix, has the following individual blocks:

$$\mathbf{D}^{(2)} = \begin{bmatrix} \mathbf{D}^{\text{CC}(2)} & \dots & & & \\ \mathbf{D}^{\text{OC}(2)} & \mathbf{D}^{\text{OO}(2)} & \dots & & \\ \mathbf{D}^{\text{VC}(2)} & \mathbf{D}^{\text{VO}(2)} & \mathbf{D}^{\text{VV}(2)} & \dots & \\ \mathbf{D}^{\text{FC}(2)} & \mathbf{D}^{\text{FO}(2)} & \mathbf{D}^{\text{FV}(2)} & \mathbf{D}^{\text{FF}(2)} & \end{bmatrix}. \quad (18)$$

The occupied–occupied blocks are given by

$$D_{kl}^{\text{OO}(2)} = -\frac{1}{2} \sum_i^{\text{O}} \sum_{ab}^{\text{V}} a_{ik}^{ab} a_{il}^{ab*}, \quad (19)$$

$$D_{kl}^{\text{OC}(2)} = -\frac{1}{2} \sum_l^{\text{O}} \sum_{ab}^{\text{V}} a_{ik}^{ab} \frac{(ia||lb)}{\varepsilon_l - \varepsilon_k}, \quad (20)$$

and

$$D_{kl}^{\text{CC}(2)} = 0. \quad (21)$$

The virtual–virtual blocks are given by

$$D_{ab}^{\text{VV}(2)} = \frac{1}{2} \sum_{ij}^{\text{O}} \sum_c^{\text{V}} a_{ik}^{ac*} a_{ij}^{bc}, \quad (22)$$

$$D_{ab}^{\text{FV}(2)} = \frac{1}{2} \sum_{ij}^{\text{O}} \sum_c^{\text{V}} \frac{(ia||jc)}{\varepsilon_b - \varepsilon_a} a_{ij}^{bc}, \quad (23)$$

and

$$D_{ab}^{\text{FF}(2)} = 0. \quad (24)$$

The remaining virtual–occupied blocks are obtained as the solution of the Z -vector equations,

$$D_{ai}^{(2)}(\varepsilon_a - \varepsilon_i) + \sum_j^{\text{C,O}} \sum_b^{\text{V,F}} [D_{bj}^{(2)}(bj||ai) + D_{jb}^{(2)}(jb||ia)] = -L_{ai}. \quad (25)$$

The GUMP2 Lagrangian is

$$L_{ai} = \sum_{jk}^{\text{C,O}} D_{jk}^{(2)}(jk||ia) + \sum_{bc}^{\text{V,F}} D_{bc}^{(2)}(bc||ia) + \frac{1}{2} \sum_j^{\text{O}} \sum_{bc}^{\text{V}} (ba||cj) a_{ij}^{bc*} - \frac{1}{2} \sum_{jk}^{\text{O}} \sum_b^{\text{V}} (ij||bk) a_{jk}^{ab*}, \quad (26)$$

where $a_{jk}^{ab} = 0$ if a is a frozen orbital and $a_{ij}^{bc} = 0$ if i is a frozen orbital.

The MP2 contribution to the magnetic shielding tensor is defined by the differentiation of Eq. (17) with respect to B_t ,

$$\sigma_{A,tu}^{(2)} = \sum_{pq}^{\text{MO}} \left[\frac{\partial D_{pq}^{(2)}}{\partial B_t} \left\langle P \left| \frac{\partial H}{\partial \mu_{A,u}} \right| q \right\rangle + D_{pq}^{(2)} \left\langle P \left| \frac{\partial^2 H}{\partial B_t \partial \mu_{A,u}} \right| q \right\rangle \right]. \quad (27)$$

The finite-perturbation method obtains the derivative of $D^{(2)}$ by numerical differentiation as

$$\frac{\partial D_{pq}^{(2)}}{\partial B_t} \approx \frac{D_{pq}^{(2)}(B_t) - D_{pq}^{(2)}(0)}{B_t}. \quad (28)$$

Here $D_{pq}^{(2)}(0)$ denotes the relaxed density matrix without magnetic field. The perturbed density $D_{pq}^{(2)}(B_t)$ is evaluated with the GUHF orbitals which are obtained by Eq. (7) under finite B_t . The MO integrals used for evaluating $D_{pq}^{(2)}(B_t)$ are given by

$$(ai|bj) = B_t(ai|bj)^{(B_t)} + (a^{(B_t)}|i^{(B_t)}|b^{(B_t)}|j^{(B_t)}). \quad (29)$$

The second term of Eq. (29) is defined by Eq. (16) with MO coefficients involving finite perturbation. The first term is the AO derivative part, which involves the GIAO contribution as

$$(ai|bj)^{(B_t)} = \sum_{\mu\nu\lambda\rho}^{\text{AO}} \sum_{\omega\omega'\tau\tau'}^{\alpha\beta} \frac{\partial(\chi_\mu^{\text{GIAO}} \omega' \chi_\nu^{\text{GIAO}} \omega | V_{12} | \chi_\lambda^{\text{GIAO}} \tau' \chi_\rho^{\text{GIAO}} \tau)}{\partial B_t} \times C_{\mu a}^{\omega'*} C_{\nu i}^{\omega} C_{\lambda b}^{\tau'*} C_{\rho j}^{\tau}. \quad (30)$$

The AO base relaxed density is obtained by

$$D_{\lambda\nu}^{(2)\omega\omega'} = C_{\lambda q}^{\omega} D_{pq}^{(2)} C_{\nu p}^{\omega'*}. \quad (31)$$

The MP2 contribution to the magnetic shielding tensor is finally obtained as

$$\sigma_{A,tu}^{(2)} = \sum_{\lambda\nu}^{\text{AO}} \sum_{\omega\omega'}^{\alpha\beta} \left[\left(\frac{D_{\lambda\nu}^{(2)\omega\omega'}(B_t) - D_{\lambda\nu}^{(2)\omega\omega'}(0)}{B_t} \right) \times \langle \chi_\nu^{(0)} \omega' | H_{A,u}^{(0,1)} | \chi_\lambda^{(0)} \omega \rangle + D_{\lambda\nu}^{(2)\omega\omega'}(0) \times \langle \chi_\nu^{(0)} \omega' | H_{A,u}^{(1,1)} | \chi_\lambda^{(0)} \omega \rangle \right]. \quad (32)$$

The total QR-GUMP2 magnetic shielding tensor is

$$\sigma_{A,tu}^{\text{MP2}} = \sigma_{A,tu}^{\text{SCF}} + \sigma_{A,tu}^{(2)}. \quad (33)$$

In accordance with our previous analysis, σ_A will be decomposed as

TABLE I. Basis sets used in the present calculation.

| | | |
|-------------------|-----------------|--|
| Te, Sn | [12s11p6d] | WTBF ^a |
| Se | [11s10p4d] | WTBF |
| Si, Cl | [7s5p2d] | Ahlrichs VTZ+polarization ^{b,d} |
| C, ^c F | [5s3p1d]/[3s2p] | Ahlrichs+polarization ^{b,d} |
| H ^c | [2s]/[3s1p] | Huzinaga–Dunning ^f |

^aReference 55.^bReference 57.^cFor carbon in SiMe₃ and SnMe₃ group, [3s2p] set is used.^dReference 58.^e[3s1p] set is used for TeH₂.^fReference 59.

$$\sigma_{A,tu} = \sigma_{A,tu}^{\text{dia}} + \sigma_{A,tu}^{\text{para}} + \sigma_{A,tu}^{\text{SO}} \quad (34)$$

The first term is the diamagnetic shielding term which is calculated with $D(0)$. The second one is the paramagnetic shielding term, a spin-free contribution from $D(B)$. The third term is the SO effect, the contribution from the SO interaction; this involves the FC term and spin-dipolar term.

III. COMPUTATIONAL DETAILS

For the proper description of relativistic effects, we have to use the basis functions sufficiently large to describe the relativistic effects or the functions optimized by the relativistic method. In this study, the well-tempered Gaussian basis functions (WTBFs) proposed by Huzinaga and Klobukowski⁵⁵ are used for heavy elements. The WTBF covers the sufficient range of exponents for relativistic calculations. The WTBFs have been originally proposed in primitive functions. However, it is difficult to apply the primitive WTBF to molecular calculations, particularly to correlated calculations. Therefore, we contracted the WTBFs and used them for molecular calculations. Our strategy to contract the basis functions is as follows:

- (1) The coefficients were obtained by spin-averaged QR-SCF calculation of atomic ground state. For 1s, 2s, and 2p orbitals, the coefficients were obtained by the QR-GUHF calculation of a hydride molecule including the SO effect. Consequently, 2p_{1/2} and 2p_{3/2} orbitals have different contraction coefficients.
- (2) The length of contraction was reduced by using Davidson's elimination scheme.⁵⁶ Here we neglected small coefficients ($< \sim 10^{-4}$).
- (3) The contraction coefficients were polished up by energy optimization of small molecules with QR-GUHF calculations to minimize the energy loss due to contraction.
- (4) The obtained AO functions were used in split form. In this study, the valence functions are quadruple and the inner functions are double.

The basis functions used in this study are summarized in Table I. Experimental molecular geometry has been used if it is available; otherwise, the geometry has been optimized with the LANL2DZ/MP2 method.

First, we examined the accuracy of numerical differentiation. Because we have not yet developed a program for the

analytical second derivative of the QR-GUMP2 method, we checked the accuracy at the nonrelativistic level. The analytical method was carried out by the GAUSSIAN98 program.⁶⁰ We selected TeH₂, TeMe₂, TeMe₄, and TeF₆ for test molecules. The largest error, 1.3 ppm, was observed in the calculation of TeF₆, with $B=10^{-3}$ a.u. We concluded that the numerical method has enough accuracy for our purpose.

The frozen-core approximation was tested on the same molecules. The core orbitals of the 1s, 2s, 2p, 3s, 3p, and 3d shells of Te were treated as frozen-core orbitals. The virtual orbitals whose orbital energy is over 5.0 a.u. were also excluded in the MP2 calculations. The largest error is 18 ppm in TeF₆; it is equal to 6% of MP2 contributions. Because the MP2 contribution is small, the frozen-core orbital will not cause serious error in this study: the qualitative trend of chemical shifts can be reproduced at the SCF level. We used full MOs in the study of absolute shielding constants, while the frozen core was used for the study of chemical shifts because of the limitation of our computers. The core orbitals of Sn were the 3d and the lower shells. The core orbitals of Se contained the 1s, 2s, and 2p shells. The 1s orbitals of Cl were also treated as frozen core.

IV. ABSOLUTE MAGNETIC SHIELDING CONSTANTS OF ¹²⁵Te NUCLEUS

Tellurium is one of the heaviest elements whose absolute value of magnetic shielding constants has been proposed by the experimental research. Experimentally, magnetic shielding constants are obtained indirectly from the relation of Gierke and Flygare⁶¹

$$\sigma \approx \sigma^{\text{SR}} + \sigma(\text{free atom}). \quad (35)$$

σ^{SR} can be obtained by the observed spin-rotation constant, and $\sigma(\text{free atom})$ is estimated by *ab initio* calculation. The relation is based on Ramsey's nonrelativistic formula. In the nonrelativistic theory, atoms only have the diamagnetic shielding term and the term can be calculated in high accuracy. In the relativistic theory, however, the spin and orbital angular momenta are not separable. Most atoms are open shell in their ground state, thus, there will be a large contribution from the paramagnetic shielding term. Moreover, the separation of the diamagnetic shielding and paramagnetic shielding terms is not obvious in the Dirac theory.^{16–18} Thus, Eq. (35) cannot be applied to heavy atoms and the relativistic theory is necessary for the magnetic shielding constant of heavy atoms.

Jameson and Jameson proposed the following method to estimate the magnetic shielding constant of heavy atoms:³⁹

$$\sigma \approx \sigma^{\text{SR}} + \sigma^{\text{NR}}(\text{free atom}) + \Delta\sigma^{\text{rel}}(\text{free atom}). \quad (36)$$

Here, $\sigma^{\text{NR}}(\text{free atom})$ is the magnetic shielding constant of a free atom calculated with the nonrelativistic method and $\Delta\sigma^{\text{rel}}(\text{free atom})$ denotes the relativistic correction for the shielding constant of a free atom. In their study, $\Delta\sigma^{\text{rel}}(\text{free atom})$ was estimated by the interpolation of the relativistic random-phase approximation (RPA) results of closed-shell atoms.⁶² They obtained the absolute shielding

TABLE II. Absolute magnetic shielding constants of ^{125}Te nucleus (ppm).

| Molecule | This work | | | | Dirac-Fock | Expt. ^a |
|-------------------|-----------|--------|---------|----------|---------------------|--|
| | NR-SCF | NR-MP2 | QR-GUHF | QR-GUMP2 | | |
| TeF ₆ | 2798 | 2543 | 4163 | 3873 | | 3790±130 |
| TeMe ₂ | 3087 | 3092 | 4504 | 4511 | | 4333±130 |
| TeMe ₄ | 3339 | 3307 | 4631 | 4561 | | 4400±130 |
| TeH ₂ | 3644 | 3809 | 5094 | 5297 | 4769.4 ^b | 5638.8 ^c (4954) ^d |

^aReference 39.^bReference 41.^cReference 42.^dEstimated value (Refs. 63 and 64).

constant of TeF₆ as $\sigma=3790$ ppm using $\Delta\sigma^{\text{rel}}$ (free atom) = 1220 ppm.

The results of our calculations are given in Table II. The magnetic shielding constant of TeF₆ calculated by the QR-GUMP2 method is 83 ppm larger than the experimental value; the deviation is within experimental error. In TeMe₂, the deviation from the experimental value is 178 ppm and exceeds the range of experimental error. The relativistic effect on TeF₆ is 1365 ppm at the SCF level and 1330 ppm at the MP2 level. From our calculations, the relativistic correction of 1230 ppm used by Jameson and Jameson can be regarded as a good approximation. The uncertainty of the estimated relativistic effect is in the same magnitude as of the experimental error. The relativistic effect on magnetic shielding constants is not constant; it depends on molecular structure. The relativistic effect of TeMe₂ in the MP2 level is 1429 ppm, while the effect of TeMe₄ is 1254 ppm. The relativistic effect mainly arises from the σ^{SO} term and the effect is discussed in Sec. V.

Dirac-Fock calculations for the magnetic shielding constant of TeH₂ have been reported. The results are shown in Table II. The ^{125}Te NMR measurement of isolated tellurium hydride has not been reported. The shielding constant was estimated from the ^{77}Se NMR measurement of SeH₂ under the assumption of $\delta(\text{Te})/\delta(\text{Se})=1.8$.^{63,64} It is not clear why the two reported values of the Dirac-Fock calculations are so different. Due to the lack of the electron correlation and the gauge-origin dependence, these calculations could not appropriately provide a theoretical prediction. The ratio $\delta(\text{Te})/\delta(\text{Se})=1.8$ was obtained by the organotellurium compounds.⁶³ The QR-GUMP2 result suggests that the ratio should be larger than 2.0, as it has been pointed out.³⁹ Adopting $\delta(\text{Te})/\delta(\text{Se})=2.1$, the revised value of the estimated magnetic shielding constant of TeH₂ is 5057 ppm.

V. ^{125}Te NMR CHEMICAL SHIFTS

A. Comparison between theory and experiment

The calculated ^{125}Te NMR chemical shifts are summarized in Table III. The chemical shift is defined as the relative value of the magnetic shielding constant from the reference compound,

$$\delta(\text{compound}) = \sigma(\text{ref}) - \sigma(\text{compound}). \quad (37)$$

The reference of this study is TeMe₂. According to the decomposition of the magnetic shielding constant, chemical shifts were decomposed into the diamagnetic, paramagnetic, and SO terms. We also show the results of the QR-GUHF SCF calculations and experimental data in Table III. The absolute value of the magnetic shielding constant of TeMe₂ is 4499 ppm, where $\sigma^{\text{dia}}=5369$ ppm, $\sigma^{\text{para}}=-2291$ ppm, $\sigma^{\text{SO}}=1422$ ppm, and $\sigma^{\text{SCF}}=4505$ ppm.

Figure 1 displays the correlation among the QR-GUMP2, QR-GUHF, and experimental chemical shifts. The QR-GUMP2 calculation almost quantitatively reproduces the experimental values; the mean absolute deviation is 83 ppm. If we take TeH₂ out of the data set, the mean absolute deviation is 70 ppm. The mean absolute deviation of the QR-GUHF results is 147 ppm; if we take TeH₂ out of the data set, the mean absolute deviation is 144 ppm. The QR-GUHF can explain the qualitative trends and the MP2 contribution improves the quantitative agreement with experiments. Because the SO term was not negligible, the QR-GUMP2 method reproduced the experimental values better than the previous study with the DFT-GIAO.⁴⁰ Even with the QR-GUMP2 method, the disagreement with experiment exceeds 100 ppm in some molecules. The discrepancy can be attributed to the following reasons. As we have discussed in Sec. IV, the experimental data of TeH₂ are the estimated values and involve uncertainty. The NMR measurement of TeMe₃Cl was carried out in the aqueous solution; therefore, we expect larger solvent effects than other data. In Te(CF₃)₂, electron correlation effect is particularly large, probably because the correlation effect considered at the MP2 level is insufficient for this molecule. The cause of the discrepancy of Te(SnMe₃)₂ is not so clear. The incompleteness of the basis function is one possible reason; a larger active space may also be required to consider core electron correlation. However, calculation with larger basis sets and active orbitals is impossible due to the computer limitation.

B. Mechanism of the chemical shifts

The chemical shifts depend on the nature of substituents. Figure 2 shows the correlation between the chemical shift and the gross charge of the Te atom. Because the trend of chemical shifts can be explained by the QR-GUHF calcula-

TABLE III. ¹²⁵Te NMR chemical shifts (ppm).

| Molecule | QR-GUHF δ | QR-GUMP2 | | | δ | δ | Experiment | | | | | | |
|----------|---------------------|---------------|-------|----|----------|----------|------------|------|------------------------------------|-------|--------------------|--------------|--|
| | | Decomposition | | | | | Solvent | Ref. | Mulliken population analysis on Te | | | Gross charge | |
| | | Dia. | Para. | SO | | | | | 5s AO | 5p AO | 5d AO ^a | | |
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^aThe outermost *d* AO.

^bOptimized structure with the LANL2DZ/MP2 method.

^cStructural data from Ref. 66.

^dStructural data from Ref. 67.

^eStructural data from Ref. 68.

^fStructural data from Ref. 69.

^gStructural data from Ref. 70.

^hStructural data from Ref. 39.

ⁱStructural data from Ref. 71.

tion, the orbital picture will clarify the essential origin of chemical shifts. So we will discuss on the Mulliken population analysis of the QR-GUHF wave functions.

For Te I and Te II compounds, we found an approximately linear correlation between the chemical shift and gross charge. The same correlation was observed for Te IV compounds. The slopes of the two lines in Fig. 3 are equivalent, but the intercepts are different. The correlations in

Fig. 2 suggest that Te I, Te II, and Te IV compounds have similar electronic origin of the chemical shifts; however, the origin of the chemical shift in Te VI compounds will be different.

Table III shows that the diamagnetic shielding term changes only by 24 ppm. This is a negligible origin of the chemical shifts. The ¹²⁵Te NMR chemical shifts result from changes of the paramagnetic shielding and SO terms.

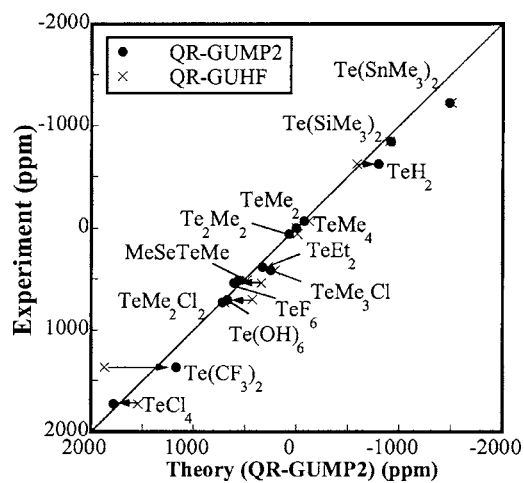


FIG. 1. Correlation between theoretical and experimental ¹²⁵Te NMR chemical shifts.

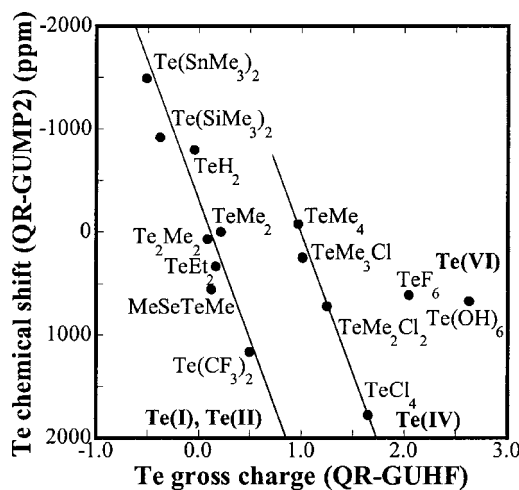


FIG. 2. Correlation between ¹²⁵Te magnetic shielding constant and Te gross charge.

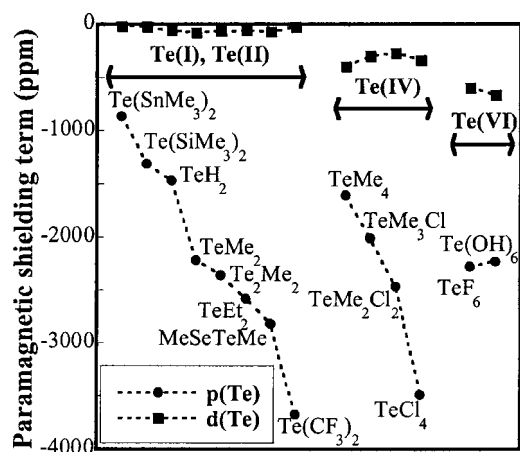
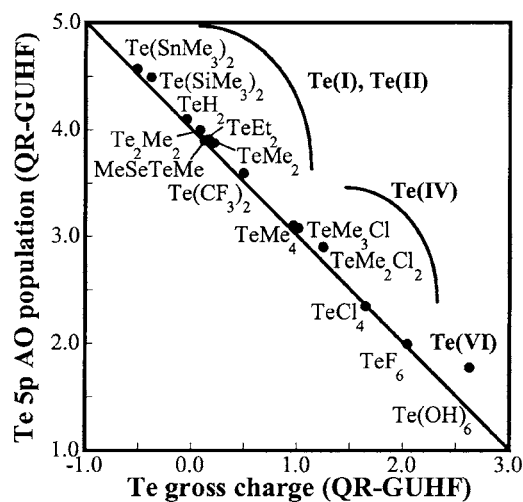


FIG. 3. AO contributions to the paramagnetic shielding terms.

1. Paramagnetic shielding term

We decompose the paramagnetic shielding term to the AO contributions and the contributions from Te p - and d AOs are shown in Fig. 3. Other AO contributions were small and they were minor origin of the chemical shifts. In Te I and Te II compounds, the p -AO contribution is predominant. The d -AO contribution is small and changes little. In Te IV compounds, the p -AO contributions are still dominant; however, the d -AO contributions are not negligible. In Te VI compounds, the changes of p - and d -AO contributions are almost the same in magnitude.

To understand the nature of the AO contributions, we made the Mulliken AO population analysis for Te and the valence AO populations are summarized in Table III. We show the population of the outermost d AO (the exponent is 0.263 422 91) as $5d$ AO. Because the sum of the d -AO populations except for the outermost d orbital is approximately 20.000 and the values are almost constant for all molecules, we considered these d AOs as core ($3d$ and $4d$) orbitals. We found an approximately linear relation between the gross charge of Te and the $5p$ -AO population; the relation is shown in Fig. 4. The charge of the Te atom mainly reflects the population on valence p orbitals. The atomic charge can be attributed to the electron-withdrawing abilities of ligands.

FIG. 4. Correlation between Te gross charge and Te p -AO population.

The order of the atomic electronegativity, $\text{Sn} < \text{Si} < \text{H} < \text{C} < \text{F}$, agrees with the order of the electron-withdrawing abilities of ligands, $\text{SnMe}_3 < \text{SiMe}_3 < \text{H} < \text{Me} < \text{CF}_3$. The $5p$ -electron population of Te IV compounds is approximately 1.0 a.u. smaller than that of Te II compounds. The formation of a three-center four-electron ($3c-4e$) bond moves the $5p(\pi)$ electron to axial ligands and reduces the gross charge of the Te atom. The formation of other $3c-4e$ bonds further reduces the Te gross charge of Te VI compounds.

In Te I and Te II compounds, the decrease of the $5p$ -electron population increases the absolute value of the paramagnetic term: the Te atom is deshielded by the paramagnetic term in accordance with the increase of the $5p$ -hole population, due to the electron-withdrawing ligands. The picture has been proposed as the p -hole mechanism to explain the selenium chemical shifts of Se II compounds.⁴⁴ The relations between Se and Te can be predicted by their position in the Periodic Table. The valence electron configurations of selenium and tellurium are s^2p^4 . Chemical shifts, particularly the paramagnetic shielding terms, reflect the valence p -electron structure.

The d -AO contributions are significant in the hypervalent compounds. Within Te VI compounds, the chemical shifts can be explained by the p -hole mechanism; however, to explain the shifts between Te IV and Te II compounds, we have to consider the role of Te d electrons. The chemical shifts of Te VI compounds cannot be explained only by the $5p$ electron. The increase of the d -electron contribution to the paramagnetic term can be explained by the hybrid orbital picture. Te I and Te II compounds have the sp^3 valence and the d -electron contribution is very small. Te IV compounds have the dsp^3 orbital and the valence of Te VI compounds is d^2sp^3 . The valence d character increases the d -AO contribution to the paramagnetic term. The increase in the valence d -AO population is also explained by the electron donation from ligands to the empty $5d$ orbital of Te. The π -back bonding ability is large in halides, TeCl_4 and TeF_6 , due to the lone pairs of halogens. The d -electron contributions are small for the chemical shifts within the same oxidation states, while the contributions are important for the shifts between molecules in different oxidation states.

The paramagnetic shielding of tellurium compounds is explained by the p -hole mechanism and d -electron mechanism. The mechanism is closely related to the NMR chemical shifts of d^{10} transition metals.^{2,3} The mechanism of d^{10} metal chemical shifts has been explained by the p -electron- d -hole mechanism. In those compounds, d orbitals are occupied and p orbitals are empty. In this work, we studied only two molecules of Te VI compounds. To elucidate the details of the d -electron mechanism of tellurium compounds, further study for Te VI compounds is necessary. As a result of this study, anyway, we can say the importance of d electrons for the tellurium chemical shifts of hypervalent compounds.

2. Spin-orbit term

It has been well studied that the FC term is the origin of chemical shifts of halides of main-group elements including heavy halogens.²³⁻²⁸ The shift has been known as normal halogen dependence.⁶⁵ The molecules of the present study do

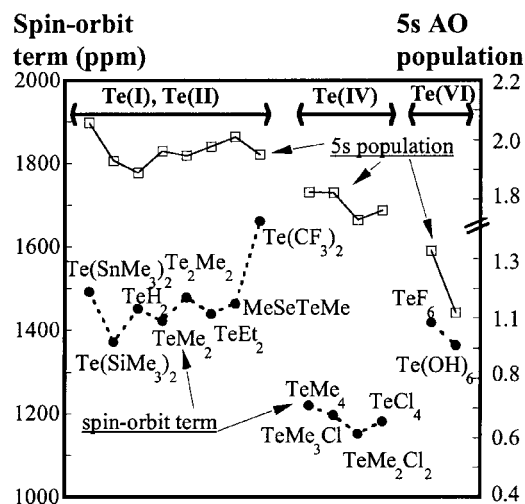


FIG. 5. Spin-orbit term of magnetic shielding constant (●) and 5s-AO population (□).

not contain heavy halogens; however, the SO terms take large values, 1200–1600 ppm. Figure 5 displays the change of the SO terms; the SO term significantly contributes to the chemical shifts. The value of the SO term largely depends on the oxidation states of tellurium and also depends on the nature of ligands.

The SO term of $\text{Te}(\text{SnMe}_3)_2$ has increased by 120 ppm in comparison with $\text{Te}(\text{SiMe}_3)_2$. We regard this increase of the SO term as the heavy atom effect. The large SO shift was calculated in $\text{Te}(\text{CF}_3)_2$. The valence p -electron population was significantly reduced in this molecule; consequently, the s character of the sp^3 orbital was enhanced. The origin of the FC term is the spin polarization at the nucleus which is induced by the SO interaction and Zeeman term; therefore, the s electrons of tellurium exclusively contribute to the FC term. The increase of s character of valence orbitals is the origin of the SO shifts in the $\text{Te}(\text{CF}_3)_2$ molecule.

The SO terms of Te IV compounds are approximately 200 ppm smaller than those of Te II compounds. This is one origin of the low-field shift of Te IV molecules. In the same series, TeMe_2 and TeMe_4 , this SO term diminishes by 287 ppm. The SO shifts induced by the neighboring heavy atoms are well recognized. In these molecules, the heavy atom is tellurium itself. This is an example of the heavy atom shift due to the SO interaction of the heavy resonant atom itself. The decrease in the SO term of Te IV compounds can be explained by the hybrid orbital picture. The valence s characters of Te IV, the dsp^3 molecules, are smaller than those of sp^3 molecules. Because of the spherical symmetry, the SO terms of Te VI compounds, which have d^2sp^3 valence, would be larger than those of Te IV compounds. To show the relation graphically, we plotted the 5s-AO populations in Fig. 5. We can see the hybridization of d orbitals to the sp^3 orbital reduces the valence s -AO population. The quantitative relation between the s -AO population and spin-orbit term is not monotonous, but the qualitative trend can be explained with the hybrid orbital model. Without the SO effect, the chemical shifts between the different oxidation states of tellurium cannot be explained properly.

VI. CONCLUSIONS

In the present study, we have developed the quasirelativistic electron correlation method for the magnetic shielding constants and chemical shifts. The basis of the presented method is the QR-GUHF method and we adapted it with the second-order Møller-Plesset perturbation theory and its energy derivative method. The magnetic shielding constant was calculated with the relaxed density method by solving the finite-field Z -vector equations.

The calculated ^{125}Te magnetic shielding constants agreed well with the experimental values proposed by Jameson and Jameson. The experimental shielding constant was obtained indirectly from the observed spin-rotation constant, the calculated diamagnetic shielding term, and the estimated relativistic correction. The present study showed the reliability of the experiment value.

The QR-GUMP2 method well reproduced the experimental ^{125}Te NMR chemical shifts of various molecules. The overall trend of chemical shifts can be explained by the QR-GUHF level and the MP2 contribution improves the quantitative agreement with the experiment.

The tellurium chemical shifts are mainly originated in the paramagnetic term; the mechanism is explained with the p -hole mechanism. The similarity to the selenium NMR was observed. The d -electron contributions are also important for hypervalent compounds. We proposed the p -hole and d -electron mechanisms for the tellurium chemical shifts including hypervalent compounds.

The SO effect is also an important origin of the chemical shifts, in particular the shifts between the molecules of different oxidation states. The SO term in Te IV compounds are about 200 ppm smaller than that in Te II compounds. This SO shift is an origin of the low-field shift of the Te IV compounds. The SO effect from the neighboring heavy elements has been well studied. The present study showed the SO effect originated in the heavy resonant atom itself.

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