

GENERALIZED-UHF THEORY FOR MAGNETIC PROPERTIES WITH QUASI-RELATIVISTIC HAMILTONIAN

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The generalized-UHF (GUHF) theory is reviewed in the framework of two-component quasi-relativistic molecular orbital theory. The GUHF orbitals in which alpha and beta spin functions have independent complex spatial functions can describe the magnetic interactions of spinning electrons, which are important for magnetic chemistry. Spin-orbit (SO) and Zeeman interactions are examples. This study presents the SO-GUHF theory in which the SO interaction is considered and the quasi-relativistic (QR)-GUHF theory in which the DKH (Douglas-Kroll-Hess) quasi-relativistic Hamiltonian is used. We review theories on the magnetic shielding constants based on the SO-GUHF and QR-GUHF methods and explain the applications to the ^1H shielding constants of hydrogen halides, the ^{13}C chemical shifts of methyl halides, ^{119}Sn chemical shifts of tin halides, the shielding constants of noble gas atoms, and the ^{199}Hg shielding constants of mercury halides.

1. Introduction

The periodic table is one of the greatest manifestations of quantum theory as a governing principle of atomic and molecular systems. The chemical properties of an element can be predicted from its position in the periodic table. For example, the nuclear magnetic shielding constants and the chemical shifts in nuclear magnetic resonance (NMR) can be predicted.¹ Our systematic study shows that the mechanism of the chemical shift is an intrinsic atomic property that can be understood from its position in the periodic table.¹⁻³ When the elements are in an upper row of the table, the basic principle is explained from the non-relativistic theory but as the elements becomes heavier, the relativistic effects becomes very important.⁴ Magnetic properties are sensitive to relativistic effects. Since our purpose here is to provide quantitatively correct predictions and the underlying

concepts for the magnetic properties of molecules including all the elements in the periodic table, our intended theory should be based on the relativity.⁵

The basic aspects of the relativistic quantum theory is described by the four-component Dirac theory.⁵ Many recent studies attempting to develop relativistic quantum chemistry are based on the four-component Dirac theory.⁶⁻⁹ However, despite such developments, the four-component theory has actually been applied only to small molecules. The main problem arose from a subtle balance between the large- and small-component spaces, which were necessary for obtaining a solution satisfying the variational principle.^{10,11} Many different quasi-relativistic theories, two-component approximate versions of the Dirac theory, have been proposed in recent years. A traditional quasi-relativistic theory is based on the Pauli approximation: the non-relativistic Schrödinger Hamiltonian is modified to include the mass-velocity, Darwin, and the spin-orbit (SO) terms.⁴ The Pauli SO operator has been widely used in quantum chemistry, for example to investigate spin-forbidden processes.¹² A more systematic quasi-relativistic theory was introduced by Hess to quantum chemistry,^{13,14} and is known as the Douglas-Kroll-Hess (DKH) theory.¹³⁻¹⁶ The DKH theory is based on the unitary transformation¹³⁻¹⁶ that separates the positive and negative energy parts of the Dirac Hamiltonian; it was formerly called “no-pair theory”.^{13,14,16} The ability of the successive higher order transformation had been suggested by Douglas and Kroll,¹⁵ however, only the second-order transformation has been actually used for the calculation until recently. Nakajima and Hirao adopt an exponential unitary operator to derive the higher order Douglas-Kroll (DK) transformed Hamiltonian.¹⁷ The third order DK (DK3) is applied for various systems.^{17,18}

Another method based on the “normalized elimination of the small-component” (NESC) was developed by van Lenthe and co-workers as “regular approximation”.¹⁹ Among a series of regular approximations, the zeroth-order regular approximation (ZORA)^{19,20} is the most widely applied for quantum chemical calculations. In the category of NESC, Nakajima and Hirao proposed a new scheme of quasi-relativistic method, namely “relativistic scheme by eliminating of small components” (RESC).^{21,22} In order to eliminate the small-component, without involving the infinite series expansion, the RESC method assumes the denominator, $E-V$, to be the classical relativistic kinetic energy. For various molecules including heavy elements, the RESC method works well.²¹⁻²³ These quasi-relativistic approaches are widely used today in quantum chemistry as a useful theoretical tool. In addition, the relativistic effective core potential (ECP) and relativistic model potential²⁴⁻²⁶ methods have

been used frequently because they include the relativistic effect at low computational cost.

Relativistic theory is important for studies of magnetic properties: the fact that an electron has an internal freedom known as “spin” is most naturally described by the Dirac theory.²⁷ The magnetic shielding constant is an important magnetic property and is measured mainly in NMR spectroscopy. It reflects the angular momentum of valence electrons in the vicinity of the nuclei,⁴ so that the relativistic effect becomes important for molecules that include heavy elements.

The importance of the SO interaction in the magnetic shielding constant have been demonstrated with a semi-empirical perturbation calculation by Morishima, Endo, and Yonezawa in 1973 (Ref. 28). Similar results are also given by Ref. 29. The importance of the relativistic effect on the magnetic shielding constant for atoms was shown with Dirac-RPA calculation by Kolb, Johnson, and Shorer in 1982 (Ref. 30). The relativistic theory for NMR parameters was formulated by Pyper,³¹ Pyykkö,³² and Zhang and Webb³³ by extending the Ramsey’s formula³⁴ to Dirac theory. No *ab-initio* reliable calculations on the relativistic effects had been published until 1995, when an *ab-initio* calculations of the SO effects on the magnetic shielding constants were presented by this laboratory by developing the UHF formalism for calculating the SO effects.³⁵ Although this SO-UHF method is only an approximate method for calculating the SO effects, it is easy and simple and was developed later to become the generalized UHF (GUHF) method in this laboratory,^{41,45-48} which is the topic of this review. The well-known GUHF method⁴⁹⁻⁵¹ not only describes the SO effects accurately within the orbital theory, but also represents a general quasi-relativistic theory as an extreme of the non-relativistic molecular orbital theory.

The SO-UHF method has clearly demonstrated that the SO interaction is an essential source of the chemical shifts even for proton chemical shifts in hydrogen halides and for ¹³C chemical shifts in methyl halides:³⁵ the chemical shifts actually observe the SO effect in these molecules. The SO-UHF method has been applied to a number of molecules, such as the halides of main-group elements, Si,³⁶ Sn,³⁷ Al,³⁸ Ga,³⁹ and In,³⁹ and the importance of the SO effects on the nuclear magnetic shielding constants has been shown. It has been shown that “normal halogen dependence” (NHD)⁵² is essentially due to the SO effect. In the compounds of the transition metals, Ti⁴⁰ and Nb,⁴⁰ the chemical shifts were mainly determined by the paramagnetic term and the SO effect was relatively small. Many subsequent studies^{53,54} have recognized the importance of the SO interaction on the NMR chemical shifts.

For the magnetic shielding constants of heavy resonant nuclei, not only the SO interaction but also the spin-free relativistic (SFR) effects, such as

mass-velocity and Darwin terms, are important:⁴²⁻⁴⁴ they further interact strongly with each other.^{43,44} Relativistic increase of magnetic shielding constants of heavy atoms has been shown by Kolb *et al.*³⁰ Pyykkö and his co-workers pointed out that such relativistic effect is significantly important in the NMR of heavy resonant nuclei.⁵¹ They distinguished between the effect of the “heavy atom shift of heavy atom” itself (HAHA),⁵⁵ in contrast to “heavy atom shift induced by a neighboring heavy atom” which is observed as the NHD. This laboratory recently shown that the HAHA effect originates from the relativistic effect, mainly the mass-velocity correction, on the magnetic interaction term of the Hamiltonian.⁴⁵⁻⁴⁸

Thus, a relativistic theory that covers all elements of the periodic table, yet is of very rigid foundation and is still very usable is necessary. As the correlation effects are not as large for the chemical shifts,^{56,57} we do not consider them in this article. Some benchmark calculations of the NMR parameters based on the Dirac-Hartree-Fock (DHF) theory have been performed only for small molecules.⁵⁸⁻⁶¹ On the other hand, the quasi-relativistic NMR theories have been applied to various molecules within the frameworks of the DKH⁴⁵⁻⁴⁸ and ZORA^{62,63} formalisms. We recently developed the quasi-relativistic theory⁴⁷ based on the DKH transformation for the Hamiltonian including magnetic interactions. The resultant Hamiltonian was quite complicated compared with the non-relativistic Hamiltonian or the Dirac Hamiltonian;⁵⁸ however, once the Hamiltonian matrix elements are obtained, the method can be handled within the well known molecular orbital (MO) theory of the GUHF framework. Therefore, the quasi-relativistic MO theory can be considered as a natural extension of the non-relativistic MO theory. The GUHF based quasi-relativistic NMR theory has been successfully applied to the NMR chemical shifts of the various nuclei such as ¹H,⁴⁸ ¹³C,⁴¹ ¹²⁵Te,⁴⁶ and ¹⁹⁹Hg.^{45,48}

The quasi-relativistic GUHF method can be applied to NMR parameters other than the magnetic shielding constant and also to magnetic properties other than the NMR parameters. The magnetic circular dichroism (MCD) is an important field of relativistic quantum chemistry. The quasi-relativistic GUHF method had been applied to the theoretical study of the MCD spectra of CH₃I.⁶⁴ The quasi-relativistic GUHF/SECI calculation showed the importance of the relativistic effect to explain the experimentally observed spectra.

The relativistic study of molecular properties other than energy is a new field of quantum chemistry. Consideration of the change of picture effect^{47,65,66} has enabled us to conduct relativistic study in an appropriate manner. As relativistic quantum chemistry progress, the importance of relativistic effect on the molecular properties will become more widely recognized.

In this article, we examine the relativistic molecular orbital theory in terms of the unrestricted Hartree-Fock (UHF) theory and its generalization. The relativistic effects on the molecular magnetic properties, especially the magnetic shielding constants, are discussed and we present our recent results of the relativistic study on the magnetic shielding constants and NMR chemical shifts. First, we address the conventional UHF wavefunction. The UHF wavefunction describes the spin-polarization. Although there are certain limitations, the UHF wavefunction can approximately treat the SO effect. We discuss the applicability and limitation of the SO-UHF theory. To accurately include the SO effect, the UHF wavefunction has to be generalized. The GUHF theory for SO interaction [GUHF is also called the general HF (GHF)^{49,50}] is introduced here. A theoretical outline of the NMR magnetic shielding constant with the SO-GUHF theory is presented in Section 2. The relation between the UHF, GUHF, and the two-component quasi-relativistic theories is discussed in Section 3. The GUHF orbital, which is introduced from the nonrelativistic theory, is corresponding to the two-component quasi-relativistic orbital. In Section 5, an example of the magnetic shielding constants and chemical shifts including SO and relativistic effects is shown. The SO effect of SO-UHF and SO-GUHF methods and the heavy atom shift using the quasi-relativistic GUHF method are explained. Section 6 gives a summarize this article.

2. Magnetic shielding constant with spin-orbit interaction

2.1. Hamiltonian and operators

The electronic Hamiltonian for molecules in a uniform magnetic field \mathbf{B} with nuclear magnetic moment $\boldsymbol{\mu}_N$ is written as³⁵

$$H(\mathbf{B}, \boldsymbol{\mu}_N) = \sum_j \left[\frac{1}{2} \left(\mathbf{p}_j + \frac{1}{c} \mathbf{A}_j \right)^2 + \sum_N \frac{-Z_N}{r_{Nj}} \right] + \sum_{j>k} \frac{1}{r_{jk}} + H^{\text{SO}} + \frac{1}{2c} \sum_j \boldsymbol{\sigma}_j \cdot (\nabla_j \times \mathbf{A}_j). \quad (1)$$

where Z_N denotes the charge of atom N , \mathbf{A}_j and H^{SO} are the magnetic vector potential and SO operator; they are given by

$$\mathbf{A}_j = \frac{1}{2} \mathbf{B} \times (\mathbf{r}_j - \mathbf{d}) + \sum_N \frac{\boldsymbol{\mu}_N \times \mathbf{r}_{Nj}}{r_{Nj}^3}, \quad (2)$$

$$H^{\text{SO}} = \frac{1}{4c^2} \sum_j \left[\sum_N \frac{(\mathbf{r}_{Nj} \times \mathbf{p}_j) \cdot \boldsymbol{\sigma}_j}{r_{Nj}^3} - \sum_{k \neq j} \frac{(\mathbf{r}_{jk} \times \mathbf{p}_j) \cdot \boldsymbol{\sigma}_j + 2(\mathbf{r}_{kj} \times \mathbf{p}_j) \cdot \boldsymbol{\sigma}_j}{r_{jk}^3} \right]. \quad (3)$$

Here \mathbf{d} denotes the gauge origin of the vector potential. Expanding the Hamiltonian in powers of \mathbf{B} and $\boldsymbol{\mu}_N$, we obtain

$$H(\mathbf{B}, \boldsymbol{\mu}_N) = H^{(0,0)} + \sum_t^{x,y,z} B_t H_t^{(1,0)} + \sum_N \sum_u^{x,y,z} \mu_{Nu} H_{Nu}^{(0,1)} + \sum_N \sum_{t,u}^{x,y,z} B_t H_{Ntu}^{(1,1)} \mu_{Nu} + \dots, \quad (4)$$

where

$$H^{(0,0)} = \sum_j \left(\frac{1}{2} p_j^2 + \sum_N \frac{-Z_N}{r_{Nj}} \right) + \sum_{j>k} \frac{1}{r_{jk}} + H^{\text{SO}}, \quad (5)$$

$$H_t^{(1,0)} = \frac{1}{2c} \sum_j [(\mathbf{r}_j - \mathbf{d}_j) \times \mathbf{p}_j]_t + \frac{1}{2c} \sum_j \sigma_{jt}, \quad (6)$$

$$\begin{aligned} H_{Nu}^{(0,1)} &= H_{Nu}^{(0,1)}(\text{para}) + H_{Nu}^{(0,1)}(\text{SD}) + H_{Nu}^{(0,1)}(\text{FC}) \\ &= \frac{1}{c} \sum_j \frac{(\mathbf{r}_{Nj} \times \mathbf{p}_j)_u}{r_{Nj}^3} \\ &+ \frac{1}{2c} \sum_j \left[\frac{3r_{Nj,u} (\boldsymbol{\sigma}_{Nj} \cdot \mathbf{r}_{Nj})}{r_{Nj}^5} - \frac{\sigma_{ju}}{r_{Nj}^3} \right] + \frac{4\pi}{3c} \sum_j \delta(\mathbf{r}_{Nj}) \sigma_{ju}, \end{aligned} \quad (7)$$

$$H_{Ntu}^{(1,1)} = \frac{1}{2c^2} \sum_j \frac{[(\mathbf{r}_j - \mathbf{d}) \cdot \mathbf{r}_{Nj}] \delta_{tu} - (\mathbf{r}_j - \mathbf{d})_u r_{Njt}}{r_{Nj}^3}. \quad (8)$$

Eq. (5) represents the Hamiltonian without magnetic field including the SO interaction. Eq. (6) denotes the magnetic Zeeman interaction. The first term of Eq. (7) is the paramagnetic shielding term. The second and third terms of Eq. (7) are the spin-dipolar (SD) and the Fermi-contact (FC) term: these terms arise from the SO effect. Eq. (8) is the diamagnetic shielding term.

The magnetic shielding constant is given by

$$\sigma_{N,tu} = \left[\frac{\partial^2 E}{\partial B_t \partial \mu_{Nu}} \right]_{\mathbf{B}=\boldsymbol{\mu}_N=0}. \quad (9)$$

Using the Hellmann-Feynman theorem, the magnetic shielding tensor is written as

$$\begin{aligned}\sigma_{N,tu} &= \langle \Psi(0) | H_{Ntu}^{(1,1)} | \Psi(0) \rangle + \frac{\partial}{\partial B_t} [\langle \Psi(B_t) | H_{Nu}^{(0,1)} | \Psi(B_t) \rangle]_{\mathbf{B}=0} \\ &= \sigma_{N,tu}^{\text{dia}} + \sigma_{N,tu}^{\text{para}} + \sigma_{N,tu}^{\text{SO}}(\text{SD}) + \sigma_{N,tu}^{\text{SO}}(\text{FC}).\end{aligned}\quad (10)$$

In the presence of the SO interaction, the magnetic shielding tensor is described by the sum of the diamagnetic term, paramagnetic term, SD term and FC term. The wavefunctions $\Psi(0)$ and $\Psi(B_t)$ are defined by

$$H^{(0,0)} |\Psi(0)\rangle = E(0) |\Psi(0)\rangle, \quad (11)$$

$$(H^{(0,0)} + B_t H_t^{(1,0)}) |\Psi(B_t)\rangle = E(B_t) |\Psi(B_t)\rangle. \quad (12)$$

To apply the Hellmann-Feynman theorem, the wavefunctions have to satisfy the variational principle.

The wavefunctions of $\Psi(0)$ and $\Psi(B_t)$ in Eqs. (11) and (12) may be expressed by the sum of the singlet and triplet functions because the Hamiltonians $H^{(0,0)}$ and $H_t^{(1,0)}$ include spin-dependent operators.

$$\Psi(0) = \sum_I C_I^S(0) \Phi_I^S(0) + \sum_I \sum_s^{x,y,z} C_I^{Ts}(0) \Phi_I^{Ts}(0), \quad (13)$$

$$\Psi(B_t) = \sum_I C_I^S(B_t) \Phi_I^S(B_t) + \sum_I \sum_s^{x,y,z} C_I^{Ts}(B_t) \Phi_I^{Ts}(B_t). \quad (14)$$

Here Φ_I^S denotes singlet functions, Φ_I^{Ts} ($s = x, y, z$) triplet functions in x, y , and z components, C_I their coefficients, and the sum of I runs all over the states. We label the triplet functions with x, y , and z components: the recombination by the unitary transformation of $m_s = +1, 0, -1$ functions. Explicitly using Eqs (13) and (14) leads to the sum-over-state perturbation formalism. Because the magnetic shielding constant is a second order property, the SO effect on the magnetic shielding constant comes to the third order perturbation. For easier treatment of SO interaction, we adopt different approach. We used a method that includes the effect of SO interaction as an orbital theory of the single Slater determinant, without expanding the configuration state functions.

2.2. SO-UHF method

The finite-perturbation method with UHF wavefunction is used for the spin-spin coupling constants.⁶⁷ Spin-spin coupling is the coupling of nuclear and electron spin. The electron spin-polarization is induced by the magnetic moment of the other nucleus. The mechanism is similar to the SD and FC terms of the magnetic shielding constant, in which electron spin is induced by the SO and Zeeman interactions. So we first consider the UHF wavefunction to describe the SO effect. For the closed shell system with $2n$ electron, the UHF wavefunction is written as

$$\Psi^{\text{UHF}} = \mathcal{N} |\varphi_1^\alpha \alpha \varphi_2^\alpha \alpha \cdots \varphi_n^\alpha \alpha \varphi_1^\beta \beta \varphi_2^\beta \beta \cdots \varphi_n^\beta \beta|. \quad (15)$$

Here we use the corresponding orbital, which was obtained by the unitary transformation of the SCF orbitals. The corresponding orbitals $\{\varphi^\alpha\}$ and $\{\varphi^\beta\}$ are orthonormal in each sets but have overlap between them when $i = j$,

$$\int d\mathbf{r} \varphi_i^\alpha \varphi_j^\beta = T_i \delta_{ij}. \quad (16)$$

These corresponding orbitals are connected with the natural orbitals λ and ν of the UHF wavefunction as

$$\varphi_i^\alpha = a_i \lambda_i + b_i \nu_i, \quad (17)$$

$$\varphi_i^\beta = a_i \lambda_i - b_i \nu_i, \quad (18)$$

where a and b are the normalization constants. Using Eqs. (17) and (18) the UHF wavefunction can be expanded in the form of limited configuration interaction (CI) and to the first order it is written as⁶⁸

$$\Psi^{\text{UHF}} = C^{\text{RHF}} \Phi^{\text{RHF}} + \sum_i C_i^{Tz} \Phi_i^{Tz}, \quad (19)$$

where Φ^{RHF} denotes the RHF configuration,

$$\Phi^{\text{RHF}} = |\lambda_1 \alpha \lambda_1 \beta \cdots \lambda_n \alpha \lambda_n \beta| \quad (20)$$

and Φ^{Tz} is the triplet configuration of z component

$$\Phi_i^{Tz} = \frac{1}{\sqrt{2}} |\lambda_1 \alpha \lambda_1 \beta \cdots \nu_i \lambda_i (\alpha \beta + \beta \alpha) \cdots \lambda_n \alpha \lambda_n \beta|. \quad (21)$$

The UHF wavefunction is an eigenfunction of S_z and satisfies the relation $S_z |\Psi^{\text{UHF}}\rangle = 0$ for closed-shell molecules: it includes only the triplet $m_s = 0$ component and the other x and y components are not included.

The matrix elements of the spin-linear operators between singlet and triplet functions are shown in Table I. It is diagonal in the x , y , and z representation. Using this diagonal nature, we can study the effect of the SO interaction on the magnetic shielding constant by the UHF wavefunction up-to the first-order in the perturbation.³⁵

For calculating the diagonal and off-diagonal elements of the magnetic shielding tensors, we need all the terms in Eqs. (13) and (14). The term $\sum C_I^{Ts}(0)\Phi_I^{Ts}(0)$ ($s = x, y, \text{ or } z$) for zero magnetic field is obtained by calculating the UHF wavefunction in the s -component of the SO interaction operator. It is the eigenfunction of the S_s operator and is written as

$$\Psi_x^{\text{UHF}}(0) = C^{\text{RHF}}(0)\Phi^{\text{RHF}}(0) + \sum C^{Tx}(0)\Phi^{Tx}(0), \quad (22)$$

$$\Psi_y^{\text{UHF}}(0) = C^{\text{RHF}}(0)\Phi^{\text{RHF}}(0) + \sum C^{Ty}(0)\Phi^{Ty}(0), \quad (23)$$

$$\Psi_z^{\text{UHF}}(0) = C^{\text{RHF}}(0)\Phi^{\text{RHF}}(0) + \sum C^{Tz}(0)\Phi^{Tz}(0). \quad (24)$$

Since the SO matrix elements are diagonal as shown in Table I, the terms $\sum C^{Tx}(0)\Phi^{Tx}(0)$ etc. in Eqs. (22) to (24) are exactly the same as the corresponding terms of the first order in the SO perturbation.

In the presence of the magnetic field, we first applied the magnetic field in the same direction as the SO interaction and calculate the UHF wavefunction for each direction:

$$\Psi_x^{\text{UHF}}(B_x) = C^{\text{RHF}}(B_x)\Phi^{\text{RHF}}(B_x) + \sum C^{Tx}(B_x)\Phi^{Tx}(B_x), \quad (25)$$

$$\Psi_y^{\text{UHF}}(B_y) = C^{\text{RHF}}(B_y)\Phi^{\text{RHF}}(B_y) + \sum C^{Ty}(B_y)\Phi^{Ty}(B_y), \quad (26)$$

$$\Psi_z^{\text{UHF}}(B_z) = C^{\text{RHF}}(B_z)\Phi^{\text{RHF}}(B_z) + \sum C^{Tz}(B_z)\Phi^{Tz}(B_z). \quad (27)$$

The diagonal elements ($t = u$) of the diamagnetic, paramagnetic, and FC term can be calculated with the six UHF wavefunctions corresponding to Eqs. (22) to (27). For the diagonal elements of the SD term, we can perform the UHF calculation for the u component of the SO interaction and for the t component of the magnetic field,

$$\Psi_u^{\text{UHF}}(B_t) = C^{\text{RHF}}(B_t)\Phi^{\text{RHF}}(B_t) + \sum C^{Tu}(B_t)\Phi^{Tu}(B_t). \quad (28)$$

However, if we neglect the coupling between the magnetic field and the SO interaction, we have

$$\sum C^{Tu}(B_t)\Phi^{Tu}(B_t) = \sum C^{Tu}(0)\Phi^{Tu}(0). \quad (29)$$

Therefore, no new UHF calculation is necessary for obtaining the SD term. Using Eq. (29), the off-diagonal terms of the shielding tensor ($t \neq u$) can be obtained with using the six UHF wavefunctions of Eqs. (22) to (27).

The matrix elements of the spin-linear operator,

$$F_t = \sum_j f_t(j) S_t(j) \quad (t = x, y, z), \quad (30)$$

are calculated as

$$\langle \Psi(B_t) | F_u | \Psi(B_t) \rangle = \langle \Psi_t^{\text{UHF}}(B_t) | F_t | \Psi_t^{\text{UHF}}(B_t) \rangle \quad (t = u) \quad (31)$$

$$= \langle \Psi_t^{\text{UHF}}(B_t) | F_u | \Psi_u^{\text{UHF}}(B_u) \rangle \quad (t \neq u). \quad (32)$$

The SD and FC terms of the shielding constant is obtained with Eq. (10). Note in the calculation of the matrix element of Eq. (32), we have to handle two different UHF wavefunctions and so the problem of -non-orthogonal orbitals arise. However, this can be circumvented by calculating the corresponding orbitals of the two-UHF wavefunctions.

Eqs (22) to (32) summarizes the SO-UHF method for the magnetic shielding constant.³⁵ In the SO-UHF method we used the nature of each component where the spin-linear operator can be calculated by the UHF wavefunction for each direction. The effect of the first-order perturbation of SO interaction can be calculated using the conventional UHF wavefunctions. For the higher-order effect of SO interaction, we need the matrix elements between the different component of triplet functions as $\langle \Phi^{Tt} | F_s | \Phi^{Tu} \rangle$ ($t \neq u$). To include such terms within the HF orbital theory, we have to extend the UHF wavefunctions to the GUHF form.

2.3. SO-GUHF method

The UHF wavefunction includes triplet functions of $S_z | \Psi^{\text{UHF}} \rangle = 0$, but other components are not involved. To include all the x , y , and z components of triplet functions in the single determinant, the spin-functions are generalized to the linear combination of α and β functions as

$$\Psi^{\text{GUHF}} = \mathcal{N} |\varphi_1(a_1\alpha + b_1\beta) \varphi_2(a_2\alpha + b_2\beta) \cdots \varphi_{2n}(a_{2n}\alpha + b_{2n}\beta)|. \quad (33)$$

Eq. (33) is known as the GUHF wavefunction. The limited CI form of the GUHF wavefunction is

$$\Psi^{\text{GUHF}} = C^{\text{RHF}} \Phi^{\text{RHF}} + \sum C^{Tx} \Phi^{Tx} + \sum C^{Ty} \Phi^{Ty} + \sum C^{Tz} \Phi^{Tz}. \quad (34)$$

The GUHF wavefunction is no longer the eigenfunction of S_t ($t = x, y, z$).

The single Slater determinant of Eq. (33) for the $2n$ electron system can be re-written as

$$\Psi^{\text{GUHF}} = \|\psi_1 \psi_2 \dots \psi_{2n}\|. \quad (35)$$

The GUHF orbital, the linear combination of α and β spin-orbitals as

$$\psi_p = \phi_p^\alpha \alpha + \phi_p^\beta \beta, \quad (36)$$

is defined by the GUHF equation

$$(F_j - \varepsilon_j)(\phi_j^\alpha \alpha + \phi_j^\beta \beta) = 0. \quad (37)$$

Projecting Eq.(37) on $\langle \alpha |$ and $\langle \beta |$ and using the orthonormal condition of spin-functions, yields

$$\begin{pmatrix} \langle \alpha | F_j | \alpha \rangle - \varepsilon_j & \langle \alpha | F_j | \beta \rangle \\ \langle \beta | F_j | \alpha \rangle & \langle \beta | F_j | \beta \rangle - \varepsilon_j \end{pmatrix} \begin{pmatrix} \phi_j^\alpha \\ \phi_j^\beta \end{pmatrix} = 0. \quad (38)$$

The orthonormal condition of GUHF orbitals is given by

$$\langle \psi_j | \psi_k \rangle = \langle \phi_j^\alpha | \phi_k^\alpha \rangle + \langle \phi_j^\beta | \phi_k^\beta \rangle = \delta_{jk}. \quad (39)$$

The spatial orbitals are expanded by the conventional one-electron basis functions as

$$\psi_p = \sum_{\lambda} C_{\lambda p}^{\alpha} \chi_{\lambda} \alpha + \sum_{\lambda} C_{\lambda p}^{\beta} \chi_{\lambda} \beta. \quad (40)$$

The GUHF based LCAO-MO approach. The orbital expansion coefficients, C , are complex in general. The matrix GUHF-Roothaan equation has the form

$$\begin{pmatrix} \mathbf{F}^{\alpha\alpha} & \mathbf{F}^{\alpha\beta} \\ \mathbf{F}^{\beta\alpha} & \mathbf{F}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix} = \boldsymbol{\varepsilon} \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \mathbf{S} \end{pmatrix} \begin{pmatrix} \mathbf{C}^{\alpha} \\ \mathbf{C}^{\beta} \end{pmatrix}, \quad (41)$$

where \mathbf{S} is the overlap matrix, $S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle$, and $\boldsymbol{\varepsilon}$ is the orbital energy. The Fock matrix can be written as

$$\mathbf{F}^{\omega\omega'} = \mathbf{h}^{\omega\omega'} + (\mathbf{J}_{\mathbf{C}}^{\omega\omega'} - \mathbf{K}_{\mathbf{C}}^{\omega\omega'}) + (\mathbf{J}_{\mathbf{SO}}^{\omega\omega'} - \mathbf{K}_{\mathbf{SO}}^{\omega\omega'}). \quad (42)$$

If the magnetic field is not applied, the matrix elements of \mathbf{h} are

$$h_{\mu\nu}^{\omega\omega'} = \delta_{\omega\omega'} \left\langle \mu \left| \left(\frac{1}{2} p^2 - \sum_A \frac{Z_A}{r_A} \right) \right| \nu \right\rangle$$

$$-\frac{i}{4c^2} \sum_A \sum_{s=x,y,z} \left\langle \mu \left| \frac{Z_A (r_A \times \nabla)_s}{r_A^3} \right| \nu \right\rangle \langle \omega | \sigma_s | \omega' \rangle. \quad (43)$$

\mathbf{J}_C and \mathbf{K}_C denote Coulomb and exchange operators of the electron-electron repulsion; their matrix elements are

$$\mathbf{J}_{C,\mu\nu}^{\omega\omega'} = \delta_{\omega\omega'} \sum_{\tau=\alpha,\beta} \sum_{\rho\lambda} (\mu\nu | r_{12}^{-1} | \rho\lambda) D_{\rho\lambda}^{\tau\tau}, \quad (44)$$

$$\mathbf{K}_{C,\mu\nu}^{\omega\omega'} = \sum_{\rho\lambda} (\mu\lambda | r_{12}^{-1} | \rho\nu) D_{\rho\lambda}^{\omega'\omega}, \quad (45)$$

and

$$(\mu\lambda | r_{12}^{-1} | \rho\nu) = \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_\mu^*(1) \chi_\lambda(1) r_{12}^{-1} \chi_\rho^*(2) \chi_\nu(2). \quad (46)$$

The density matrix is

$$D_{\rho\lambda}^{\omega\omega'} = \sum_k^{\text{occ}} C_{\rho k}^{\omega*} C_{\lambda k}^{\omega'}. \quad (47)$$

\mathbf{J}_{SO} and \mathbf{K}_{SO} represent Coulomb and exchange operators of the two-electron SO interaction. The matrix elements are given by

$$\begin{aligned} \mathbf{J}_{\text{SO},\mu\nu}^{\omega\omega'} &= \sum_{s=x,y,z} \sum_{\tau\tau'=\alpha,\beta} \sum_{\rho\lambda} [(\mu\nu | g_{12}^s | \rho\lambda) \delta_{\tau\tau'} \langle \omega | \sigma_s | \omega' \rangle \\ &\quad + (\mu\nu | g_{21}^s | \rho\lambda) \langle \tau | \sigma_s | \tau' \rangle \delta_{\omega\omega'}] D_{\rho\lambda}^{\tau\tau'}, \end{aligned} \quad (48)$$

$$\begin{aligned} \mathbf{K}_{\text{SO},\mu\nu}^{\omega\omega'} &= \sum_{s=x,y,z} \sum_{\tau=\alpha,\beta} \sum_{\rho\lambda} [(\mu\lambda | g_{12}^s | \rho\nu) \langle \omega | \sigma_s | \tau \rangle D_{\rho\lambda}^{\omega\tau} \\ &\quad + (\mu\lambda | g_{21}^s | \rho\nu) \langle \tau | \sigma_s | \omega' \rangle D_{\rho\lambda}^{\tau\omega'}], \end{aligned} \quad (49)$$

and

$$(\mu\lambda | g_{12}^s | \rho\nu) = -\frac{1}{4c^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_\mu^*(1) \chi_\lambda(1) \left(\frac{l_{12}^s + 2l_{21}^s}{r_{12}^{-3}} \right) \chi_\rho^*(2) \chi_\nu(2). \quad (50)$$

The GUHF-Roothaan equation is solved iteratively, by the same procedure as that in the usual non-relativistic HF method.

The magnetic shielding constant is calculated with the finite perturbation method.^{35,69} The finite-field GUHF equation is written as

$$(F_j + B_i H_i^{(1,0)} - \varepsilon_j^{(B_i)}) \psi_j^{(B_i)} = 0. \quad (51)$$

To quantize the electron spin in the direction of the magnetic field, we choose the principal axis of spin-angular momentum as $\sigma_t = \sigma_z$. The magnetic shielding constant is calculated by Eq. (10). For calculating all the components of the magnetic shielding tensor, we need one GUHF wavefunction without magnetic field and three GUHF wavefunctions with each direction of magnetic field B_t ($t = x, y, z$).

3. Relation between quasi-relativistic theory and GUHF theory

3.1. Orbital space for the general two-component Hamiltonian

Here we study what kind of one-particle orbital is necessary for the quasi-relativistic theory. We consider an arbitral one-body operator \hat{O} which is represented by 2×2 matrix form. \hat{O} can be written with identity operator \hat{I} and Pauli matrix $\boldsymbol{\sigma}$ as

$$\hat{O} = o_0 \hat{I} + \mathbf{o} \cdot \boldsymbol{\sigma} = o_0 \hat{I} + \sum_{s=x,y,z} o_s \sigma_s \quad (52)$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (53)$$

and

$$\hat{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (54)$$

Here, o_s ($s = 0, x, y, z$) represents the usual one-dimensional operator which acts on spatial functions. The one-particle orbital space $\{\psi_p\} = \{\psi_1, \psi_2\}$ on which \hat{O} acts must have the direct product of $\{\omega\}$ and $\{\chi\}$; χ is a spatial function on which o_s acts and ω is the two-dimensional column vector as

$$\{\omega\} = \left\{ \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right\}. \quad (55)$$

ω is the eigenfunction of σ_z and \hat{I} . Thus, ψ has the form

$$\psi_p = \sum_k \left[c_{kp} \chi_k \begin{pmatrix} 1 \\ 0 \end{pmatrix} + c'_{kp} \chi_k \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] \quad (56)$$

with complex coefficient c and c' . Generally, operators in the two-component quasi-relativistic theory have 2×2 matrix form, thus, the two-component quasi-relativistic orbital is expressed by Eq. (56).

The Pauli matrix relates the spin-operator as

$$\mathbf{s} = \frac{1}{2} \boldsymbol{\sigma} \quad (57)$$

The spin functions, eigenfunction of \mathbf{s}^2 and s_z , are

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (58)$$

Therefore, the two-component quasi-relativistic orbital can be written as

$$\begin{aligned} \psi_p &= \sum_k [c_{kp} \chi_k \alpha + c'_{kp} \chi_k \beta] \\ &= \phi_p^\alpha \alpha + \phi_p^\beta \beta \end{aligned} \quad (59)$$

Eq. (59) is identical to the GUHF orbital. The quasi-relativistic orbital theory is not special; it can be handled in the frameworks of GUHF theory⁴⁹⁻⁵¹ with modification of operators into relativistic theory. Eq. (59), is also known as the LCASO-MS approach.⁷⁰

The orbital space for the spin free operator,

$$\hat{O} = o_0 \hat{I} = \begin{pmatrix} o_0 & 0 \\ 0 & o_0 \end{pmatrix}, \quad (60)$$

has an RHF form expressed as

$$\psi^\alpha = \sum_k c_k^\alpha \chi_k \alpha, \quad \psi^\beta = \sum_k c_k^\beta \chi_k \beta \quad (61)$$

with

$$c_k^\alpha = c_k^\beta, \quad (62)$$

because the spatial functions are completely decoupled from the spin function. An interesting example is the conventional UHF orbital which is expressed as Eq. (61), but

$$c_k^\alpha \neq c_k^\beta. \quad (63)$$

The operator corresponding to UHF orbital space has a form expressed as

$$\hat{O} = \begin{pmatrix} x & 0 \\ 0 & y \end{pmatrix} \quad (64)$$

where $x \neq y$. This operator can be rewritten as follows:

$$\begin{aligned} \hat{O} &= \frac{1}{2} \begin{pmatrix} (x+y) + (x-y) & 0 \\ 0 & (x+y) - (x-y) \end{pmatrix} \\ &= o_0 \hat{I} + o_z \sigma_z. \end{aligned} \quad (65)$$

Here

$$o_0 = \frac{1}{2}(x+y) \quad (66)$$

and

$$o_z = \frac{1}{2}(x-y). \quad (67)$$

Eqs. (64) to (67) show that the conventional UHF orbital describes the spin-dependent operator of \mathbf{s}_z direction.

Similarly to Eq. (52), the two-body operator, $V(1,2)$, of the two-component theory can be written as

$$\begin{aligned} V(1,2) &= \hat{I}(1)v_0(1,2)\hat{I}(1) + \hat{I}(1)\mathbf{v}(1,2) \cdot \boldsymbol{\sigma}(2) + \hat{I}(2)\mathbf{v}(1,2) \cdot \boldsymbol{\sigma}(1) \\ &\quad + \boldsymbol{\sigma}(2) \cdot \hat{\mathbf{x}}(1,2) \cdot \boldsymbol{\sigma}(1) \end{aligned} \quad (68)$$

where $\hat{I}(1)$, $\boldsymbol{\sigma}(1)$, etc., denote an operator acting on the spin part of electron 1. $v_0(1,2)$ represents the scalar two-body operator i.e. Coulomb repulsion. $\mathbf{v}(1,2)$ represents the vector operator: the two-electron SO interaction⁴ is categorized in this type. $\hat{\mathbf{x}}(1,2)$ is the tensor operator and the spin-spin interaction⁴ having this form.

3.2. Quasi-relativistic GUHF method

The outline of the GUHF theory including the SO interaction is given in Sections 2.3. In this section, we consider further relativistic correction within the GUHF theory. In the quasi-relativistic theory, the Hamiltonian is written as

$$H(\mathbf{B}, \boldsymbol{\mu}_N) = \sum_j (H^{\text{SF}}(j) + H^{\text{SO}}(j) + H^{\text{mag}}(j))$$

$$+\sum_{j>k}(V^C(j,k)+V^{SO}(j,k)), \quad (69)$$

where H^{SF} and H^{SO} denote the spin-free and spin-orbit parts of Hamiltonian without magnetic field. V^C and V^{SO} are electron-electron interaction of Coulomb repulsion and the SO interaction, respectively. H^{mag} represents the magnetic interaction.

Since the spin-free relativistic (SFR) effect strongly couples with the SO interaction,⁴²⁻⁴⁴ the SO-GUHF method is insufficient for the magnetic shielding constant of heavy elements. The relativistic correction to the magnetic interaction, especially the mass-velocity correction is also important.⁴⁵⁻⁴⁸ The quasi-relativistic- (QR-) GUHF theory is necessary to explain the magnetic shielding constant of heavy elements. The quasi-relativistic theory can be handled within the frame of the SO-GUHF only changing the operators into the quasi-relativistic form.⁴⁵⁻⁴⁸

The DKH theory is a quasi-relativistic theory whose accuracy has been examined in detail and has been widely accepted in quantum chemistry.¹³⁻¹⁶ We have extended the DKH theory to the systems in which the magnetic vector potential is present, and adapted it for the QR-GUHF theory,^{47,48} namely we use the Hamiltonian,

$$H^{\text{SF}}(j) = c\sqrt{p_j^2 + c^2} + K_j(V_j + R_j\mathbf{p}_jV_j \cdot \mathbf{p}_jR_j)K_j + H_j^{\text{SF}2}, \quad (70)$$

$$H^{\text{SO}}(j) = i\boldsymbol{\sigma}_j \cdot [K_jR_j(\mathbf{p}_jV_j \times \mathbf{p}_j)R_jK_j], \quad (71)$$

$$H^{\text{mag}}(j) = K_j[R_j\boldsymbol{\sigma}_j \cdot \mathbf{p}_j(c\boldsymbol{\sigma}_j \cdot \mathbf{A}_j) + (c\boldsymbol{\sigma}_j \cdot \mathbf{A}_j)\boldsymbol{\sigma}_j \cdot \mathbf{p}_jR_j]K_j + H_j^{\text{mag}2}, \quad (72)$$

where, K_j and R_j are kinetic factors, V_j and \mathbf{A}_j are the scalar and vector potentials, $H_j^{\text{SF}2}$ and $H_j^{\text{mag}2}$ are the second-order terms. The detailed form of the above operators is given in Ref. 47. The first term in Eq.(70) is the relativistic kinetic energy involving mass-velocity correction. The third term, appears as $\mathbf{p}V \cdot \mathbf{p}$ in Eq.(70), is the Darwin term of the DK form. The kinetic factors, K_j and R_j , in Eq.(72) relate to the mass-velocity correction to the magnetic interaction. Expanding Eq.(72), we obtain the diamagnetic, paramagnetic, spin-dipolar, and Fermi contact terms in the DK form: each term corresponds to it of the SO-GUHF in the non-relativistic limit.

If we are interested in the heavy atom effect on the chemical shift of light resonant nucleus, we can use the relativistic ECP^{24,25} for the sake of convenience. Using the ECP is based on the assumption that the chemical shift is mainly

determined by the valence electronic structure and that the relativistic effect is local in heavy elements.

4. Computational aspects

4.1. Basis sets

Basis sets for NMR properties in the non-relativistic level have been discussed in the literature (for example, see Ref. 57). Here, we turn our attention to the basis sets for heavy elements in relativistic calculations.⁷¹ The orbitals of a heavy atom shrink to the nucleus by the relativistic effect; therefore, functions with a large exponent are necessary compared with the non-relativistic function.⁷¹ For the contracted basis sets, contraction coefficients should be determined by the relativistic calculations.^{48,69} Because the orbital shapes differ between $p_{1/2}$ and $p_{3/2}$ or $d_{3/2}$ and $d_{5/2}$ orbitals in a heavy element, the inner orbital should be contracted in two patterns or sufficient freedom should be given. Because of the FC term which sensitively reflects the electron density at the nucleus, a sufficient degree of freedom is necessary for the 1s orbital of the heavy element from which the shielding constant is calculated.

Our laboratory uses the well-tempered Gaussian basis function (WTBF)⁷². The WTBF covers a sufficient range of exponents, and the parameters for almost all elements are available. Because the primitive WTBF is too large to apply to molecular calculations, our laboratory uses the segment contraction scheme based on the proposal by Davidson⁷³ and Dunning.⁷⁴ The coefficient of the inner most p orbitals ($2p_{1/2}$ and $2p_{3/2}$) is determined by primitive basis calculation of atom or small molecule includes the SO interaction, and the primitive functions are contracted with the resulting coefficients. The coefficients of outer orbitals are determined by the atomic ROHF calculation with the SFR Hamiltonian. For the 6s6p block elements the second inner p orbital ($3p_{1/2}$ and $3p_{3/2}$) and inner most d orbital ($3d_{3/2}$ and $3d_{5/2}$) are contracted with two patterns considering the SO interaction. The obtained basis function is used in a certain splitting pattern according to the purpose.

4.2. Gauge-origin problem

Gauge-origin dependence is problematic in the finite-basis calculation. Here we propose two methods to overcome the origin dependence. The first approach is systematic augmentation of the basis function. This can be achieved by adding the FOBFs (first-order higher angular momentum basis functions).⁷⁵ The FOBFs

method can be used without modifying the previous formulation, and conserves the traditional picture of NMR theory.⁷⁸⁻⁸⁰ The second approach is using GIAOs (Gauge invariant atomic orbitals).^{76,77} To adapt to the GIAO, we have to modify the previous formula (in details, see Ref. 48), and some additional terms from gauge-error arise. In the molecule including heavy elements, the computation dimension of FOBFs method becomes very large to diminish the gauge-error; therefore, the GIAO method was mainly used in the following calculations.

We should note that the decomposition of the total magnetic shielding constant into the diamagnetic and paramagnetic shielding terms depends on the gauge-origin,^{57,79} however, the total shielding constant is invariant at the infinite basis limit. The conventional basis and GIAO calculations provide the different shielding pictures in terms of diamagnetic contributions.

5. Results

5.1. SO-UHF results

The first report of the SO-UHF calculation is the proton shielding constants of hydrogen halides and ¹³C shielding constants of methyl halides.³⁵ In that study, we demonstrated that the origin of the chemical shifts of heavy halides is the SO interaction with the *ab-initio* calculation. The proton chemical shifts are discussed in a following section, and the result of the ¹³C chemical shifts is shown in Fig.1. The result clearly shows that the chemical shifts of CH₃I and CH₃Br are entirely the SO effects. The ¹³C NMR is a common research tool in chemistry and alkyl iodides are also familiar reagents. In other word, the measurement of ¹³C NMR is measurement of the magnitude of the relativistic effect.

The SO-UHF method has been applied for the NMR of various elements and the chemical shifts of main-group and transition metal halides, Al,³⁸ Si,³⁶ Ga,³⁹ In,³⁹ Sn,³⁷ Ti,⁴⁰ and Nb.⁴⁰ The ¹¹⁹Sn chemical shifts calculated with the SO-UHF method are shown in Fig.2 with a comparison of the experimental value. The chemical shifts of the main-group of metals are mostly determined from the electronegativity of ligands.⁶⁸ However, the large NHD has pointed out.⁴⁸ The NHD has been explained by the substituent effect in the diamagnetic term or by the $\langle r_N^{-3} \rangle$ value of the paramagnetic term affected with the overlap of ligand orbitals.⁸¹

Our series of SO-UHF studies shows that the origin of the NHD is the SO interaction. The diamagnetic and paramagnetic terms are also an important origin of the chemical shifts in certain cases. We can conclude from our RHF^{1,2} and

SO-UHF^{35-40,42-44} studies that the NMR chemical shifts are determined from the various contributions of the electronic structure. The chemical shifts contain rich chemical information. This information reflects the valence electronic structure as well as the core electron density.

5.2. *SO-GUHF results*

Hydrogen halides (HX, X = F, Cl, Br, and I) are the simplest molecular system that clearly shows the relativistic effect on the magnetic shielding constant. The experimentally observed chemical shifts show the typical NHD: the high field shift according to the increase in the atomic number of halogen. The pioneering report of semi-empirical work by Morishima *et al.*²⁸ has indicated that this halogen dependence originates from the SO effect. The first *ab-initio* calculation with the SO-UHF method was carried out by Nakatsuji *et al.*,³⁶ and the result clearly shows that the origin of the chemical shift is the SO interaction. Several groups are applying various methods of calculating these molecules.^{53,54,61,82,83}

Table II shows the SO-GUHF and QR-GUHF results of proton magnetic shielding constants of hydrogen halides.⁴⁸ For the comparison, the non-relativistic (NR) results and the experimental values are also indicated. We use the uncontracted cc-pVTZ^{84,85} for H, F, and Cl, and the even-tempered sets of Visscher *et al.*⁸⁶ for Br and I. The GIAO method was used, and the experimental bond lengths were used.

In the GUHF calculation $\sigma^{\text{dia+para}}$ is almost the same as the NR value. The SO contribution becomes as large in the heavy halides as bromide and iodide. In σ^{SO} , the spin-dipolar term is 1 ppm or less and the Fermi contact term is dominant. The QR-GUHF method in which the DKH Hamiltonian was used gives slightly large value in HI compared with the SO-GUHF method in which the Pauli SO term is included. We can conclude that in the proton shielding constants in hydrogen halides the most of relativistic effects can be taken into account by considering the SO interaction with the GUHF method.

The calculated proton chemical shifts compared with the experimental values are shown in Fig. 3. Without SO interaction, no chemical shifts are observed in HCl, HBr, and HI. In other word, observing the proton chemical shifts in these molecules is measuring the SO interaction itself.

5.3. *Magnetic Shielding Constants of Heavy Elements: noble gases*

Kolb *et al.* calculated several properties of various closed shell atoms and ions with the four-component relativistic RPA.³⁰ They showed that the magnetic

shielding constants of heavy elements increase substantially by the relativistic effect. In the non-relativistic theory, the magnetic shielding constant of a closed shell atom can be written as

$$\sigma_{NR} = \frac{1}{2c^2} \left\langle \frac{1}{r} \right\rangle. \quad (73)$$

This formula is derived from the diamagnetic shielding term. In the non-relativistic formula, the paramagnetic shielding term does not contribute to the shielding constant of atoms because of their spherical symmetry. Kolb *et al.* have shown that this formula does not hold in a system with large atomic charge, even though the expectation value was calculated using the four-component relativistic wavefunction.³⁰

Their results strongly suggest that we have to consider the relativistic correction to the magnetic interaction. Our recent study shows that the origin of the relativistic increase of the magnetic shielding constant is the relativistic correction to the magnetic interaction.⁴⁷

Table III shows the magnetic shielding constants of noble gas atoms at the non-relativistic RHF, the QR-GUHF, and the DHF theory.⁴⁷ We used (9s4p) and (12s8p) basis sets for Ne and Ar: the exponents were taken from cc-pVDZ.^{84,85} Dyllal's (15s11p6d), (19s15p9d), and (24s20p13d8f) basis sets⁸⁷ were used for Kr, Xe, and Rn.

The results clearly show that the relativistic effect substantially increases the magnetic shielding constants of heavy elements: the effect is about 400 ppm in Kr and 1600 ppm in Xe. It becomes about 8500 ppm in Rn. The relativistic molecular orbital method is indispensable for studying the magnetic shielding of heavy elements. Using the DHF method is the most favorable approach. However, the DHF calculation of magnetic shielding constant is still very costly and it can be applied only to very small molecules. The QR-GUHF method well reproduces the results of the DHF method; moreover, the QR-GUHF calculation is much easier than the DHF calculation. The QR-GUHF method is a strong theoretical tool for studying the magnetic shielding constants of molecules including heavy elements.

5.4. Mercury-199 NMR

As discussed in the previous section, the relativistic molecular orbital theory is necessary for the theoretical study of the NMR parameters of heavy resonant nuclei. In this section, we present the study of ¹⁹⁹Hg NMR of HgXY (X, Y = Me, Cl, Br, and I) compounds, the NMR chemical shifts of a heavy atom.⁴⁸

We used Huzinaga-Dunning DZ basis for H,⁸⁸ Ahlrich's TZ basis⁸⁹ with polarization functions⁹⁰ for C and Cl. In the non-relativistic calculation, Huzinaga's TZ basis with polarization functions⁹⁰ were used for Hg, I, and Br. In the relativistic calculation, contracted WTBFs^{72,48} of [18s15p8d3f], [12s10p6d], and [10s8p5d] are used for Hg, I, and Br. Experimental molecular geometries were used. All calculations were performed using the GIAO method.

Table IV shows the calculated magnetic shielding constants. Comparing the $\sigma^{\text{d+p}}$ of the QR-GUHF with the NR value, we can see the significant relativistic effect in the spin-free terms: the effect is about 1000 ppm in HgI₂. Moreover, σ^{SO} is large even in HgMe₂: the heavy atom is only Hg itself. Consequently, the magnetic shielding constants of the QR-GUHF are largely increased compared with the NR values. Such heavy atom shift of heavy atom itself (HAHA) effect was pointed out by Pyykkö and co-workers.⁵⁵ Our study shows that the origin of the HAHA effect is the mass-velocity correction of the magnetic interaction in the QR Hamiltonian⁴⁵⁻⁴⁸ and such correction relates to the change of picture effect.^{47,48,65,66}

The theoretical and experimental ¹⁹⁹Hg chemical shifts are shown in Table III. The comparison between theoretical and experimental chemical shifts is displayed in Fig. 5. The halogen dependence of the chemical shifts clearly originated from the relativistic effect. The origin of the chemical shift is σ^{para} and $\sigma^{\text{SO}}(\text{FC})$. However, unlike ¹H and ¹³C chemical shifts, considering only the SO interaction is insufficient for ¹⁹⁹Hg chemical shift. The coupling of the SO and SFR effect is quite important for heavy elements; the relativistic correction to the magnetic interaction is also important. Without these effects, the experimental values cannot be reproduced.⁴⁸

6. Summary

This review article explains the two-component quasi-relativistic theory from the viewpoint of the Generalized UHF molecular orbital theory. In terms of MO, the GUHF-MO in which the freedom of electron spin is considered is equivalent to the relativistic two-component molecular spinor. The GUHF-MO gives α and β spin to a single electron and gives an independent degree of freedom to the spatial function of α and β furthermore. This GUHF-MO provides a complete space for the spinning electron in the presence of a magnetic field. Thus, the GUHF theory is suited to study of the magnetic properties of atoms and molecules. We applied the GUHF theory to the study of magnetic shielding constants: it is a fundamental property in chemistry and physics, and the importance of the relativistic effect on it is known. The SO-GUHF theory with

the SO interaction and the QR-GUHF theory, with the DKH quasi-relativistic Hamiltonian have been explained. The SO-GUHF theory is our fundamental theory; its quasi-relativistic extension, the QR-GUHF theory, and adaptation to the relativistic ECP can be easily achieved by modification of Hamiltonian matrix elements.

In this article, we classified the relativistic effect on the magnetic shielding constant into two types. The first type is where the relativistic effect from the bonding heavy elements affects the magnetic shielding constant of the resonant nucleus. These “heavy atom shift induced by bonding heavy elements” mainly originate from the SO interaction of heavy elements. The second type is the relativistic effect of the heavy resonant nucleus itself. To study this “heavy atom shift of the heavy atom itself”, a high-level relativistic theory is required. The mass-velocity correction to the magnetic interaction term is an important source of this shielding effect, but the SFR and SO are also needed.

The proton shielding constants of hydrogen halides and ^{13}C shielding constants of methyl halides are examples of the first type. The SO interaction is the essential origin of the chemical shifts. The magnetic shielding constants of noble gas atoms are important examples of the “heavy atom shift of the heavy atom itself”, since the four-component DHF results are available. The relativistic effect significantly increases the magnetic shielding constants of heavy atoms, Kr, Xe, and Rn. The DKH based QR-GUHF theory has been able to accurately reproduce the DHF results. The theoretical study of the ^{199}Hg NMR chemical shifts, the NMR of heavy resonant nucleus, has been presented. Although, without relativistic theory we have not been able to clarify the mechanism of the ^{199}Hg NMR chemical shifts. The QR-GUHF study has shown that the origin of the chemical shift is the paramagnetic shielding and Fermi contact term.

QR-GUHF theory is a good starting point of electron correlation theory because it includes relativistic effect in the zero-th order Hamiltonian. In addition, many of the developments that have been accumulated with non-relativistic quantum chemistry can be applied with some modifications. For example, QR-GUHF theory can be adapted to the properties of excited state molecules, such as the MCD spectra. Thus, QR-GUHF is a fundamental theory of the relativistic quantum chemistry of molecular magnetic properties.

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TABLE I. Matrix elements of the spin-linear operator between singlet and triplet functions.

Operator	$\langle \Phi^S O \Phi^{Tx} \rangle$	$\langle \Phi^S O \Phi^{Ty} \rangle$	$\langle \Phi^S O \Phi^{Tz} \rangle$
$\sum_i f_{xi} s_{xi}$	$\langle \Phi^S \sum_i f_{xi} s_{xi} \Phi^{Tx} \rangle$	0	0
$\sum_i f_{yi} s_{yi}$	0	$\langle \Phi^S \sum_i f_{yi} s_{yi} \Phi^{Ty} \rangle$	0
$\sum_i f_{zi} s_{zi}$	0	0	$\langle \Phi^S \sum_i f_{zi} s_{zi} \Phi^{Tz} \rangle$

$$O = \sum_i \mathbf{f}_i \cdot \mathbf{s}_i = \sum_i (f_{xi} s_{xi} + f_{yi} s_{yi} + f_{zi} s_{zi})$$

TABLE II. Proton magnetic shielding constants and chemical shifts of hydrogen halides (ppm).

	Magnetic shielding constant								Chemical shift ^c				
	NR ^a		SO-GUHF ^b			QR-GUHF ^b			exp.	δ^{theory}			δ^{exp}
	σ^{total}	$\sigma^{\text{d+p}}$	σ^{so}	σ^{total}	$\sigma^{\text{d+p}}$	σ^{so}	σ^{total}	σ^{total}	NR	SO	QR		
HF	28.09	28.15	0.18	28.09	28.17	0.17	28.34	29.20	0.00	0.00	0.00	0.00	
HCl	30.54	30.55	1.02	31.57	30.54	1.01	31.56	31.78	-2.45	-3.48	-3.22	-2.58	
HBr	30.74	30.73	5.95	36.68	30.71	6.43	37.15	35.65	-2.65	-8.59	-8.81	-6.45	
HI	31.15	31.08	16.07	47.15	30.95	18.77	49.72	44.54	-3.06	-19.06	-21.38	-15.34	

^aNon-relativistic calculation (NR): $\sigma^{\text{total}} = \sigma^{\text{dia}} + \sigma^{\text{para}}$.

^bGUHF calculation: $\sigma^{\text{total}} = \sigma^{\text{d+p}} + \sigma^{\text{SO}}$, $\sigma^{\text{d+p}} = \sigma^{\text{dia}} + \sigma^{\text{para}}$, $\sigma^{\text{SO}} = \sigma^{\text{SO}}(\text{SD}) + \sigma^{\text{SO}}(\text{FC})$.

^c $\delta(\text{HX}) = \sigma(\text{HF}) - \sigma(\text{HX})$

TABLE III. Magnetic shielding constants of noble gas atoms (ppm).

	NR	QR-GUHF	DHF
Ne	552.0	560.5	557.5
Ar	1233.7	1284.4	1271.8
Kr	3154.5	3624.0	3571.6
Xe	5326.6	7044.7	6957.8
Rn	10727.1	19074.6	19162.9

TABLE IV. ^{199}Hg magnetic shielding constants and chemical shifts of mercury compounds (ppm).

Molecule	Magnetic shielding constant				Chemical shift ^c		
	NR	QR-GUHF		σ^{total}	δ^{theory}		Exptl δ^{exp}
	σ^{total}	$\sigma^{\text{d+p}}$	σ^{so}		NR	QR	
HgMe ₂	6666.6	6064.0	6708.2	12772.2	0.0	0.0	0
HgMeCl	7228.4	7066.1	6191.3	13257.4	-561.8	-485.2	-814
HgMeBr	7205.5	6972.8	6797.7	13725.5	-538.9	-953.3	-915
HgMeI	7021.0	6619.1	7564.2	14183.3	-354.4	-1411.1	-1097
HgCl ₂	7525.6	7473.1	6467.8	13940.0	-859.0	-1168.7	-1594
HgBr ₂	7729.9	7625.0	8609.3	16234.3	-1063.3	-3462.1	-2209
HgI ₂	7233.6	6297.1	10910.7	17551.6	-567.0	-4779.4	-3430

^aNon-relativistic calculation (NR): $\sigma^{\text{total}} = \sigma^{\text{dia}} + \sigma^{\text{para}}$.

^bGUHF calculation: $\sigma^{\text{total}} = \sigma^{\text{d+p}} + \sigma^{\text{SO}}$, $\sigma^{\text{d+p}} = \sigma^{\text{dia}} + \sigma^{\text{para}}$, $\sigma^{\text{SO}} = \sigma^{\text{SO}}(\text{SD}) + \sigma^{\text{SO}}(\text{FC})$.

^c $\delta(\text{HgXY}) = \sigma(\text{HgMe}_2) - \sigma(\text{HgXY})$

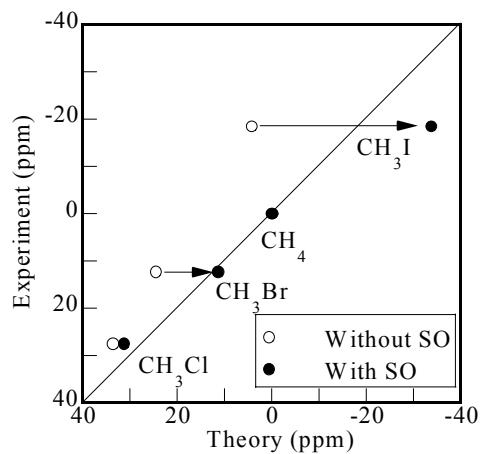


Fig. 1. Comparison between theoretical and experimental ^{13}C chemical shifts in methyl halides with and without the spin-orbit interaction.

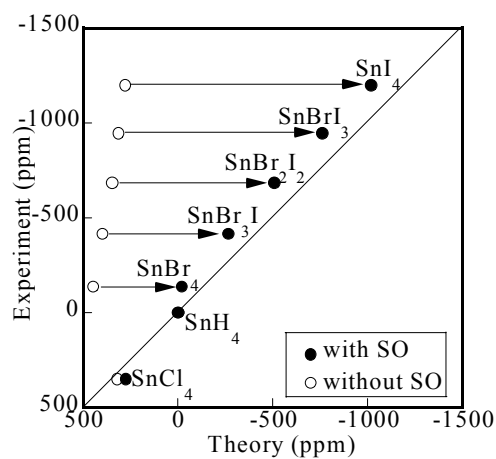


Fig. 2. Comparison between theoretical and experimental ^{119}Sn chemical shifts in tin tetrahydride and tetrahalides.

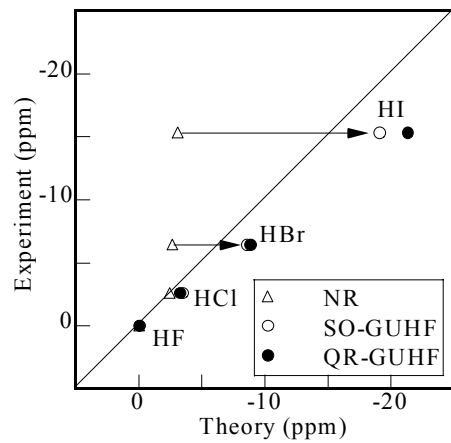


Fig. 3. Comparison between theoretical and experimental ^1H chemical shifts in hydrogen halides.

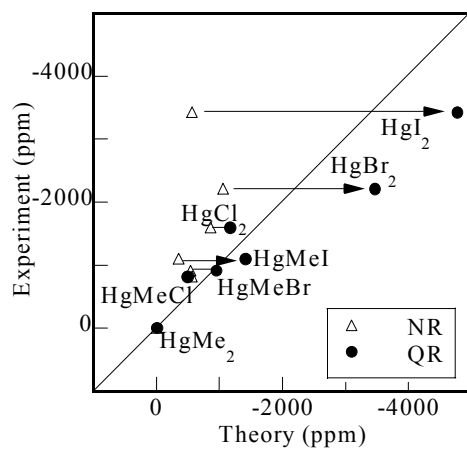


Fig. 4. Comparison between theoretical and experimental ^{199}Hg chemical shifts in HgXY (X, Y = Me, Cl, Br, and I).