Quasirelativistic theory for the magnetic shielding constant. I. Formulation of Douglas–Kroll–Hess transformation for the magnetic field and its application to atomic systems

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A two-component quasirelativistic theory based on the Douglas–Kroll–Hess (DKH) transformation has been developed to study magnetic properties of molecules. The proposed Hamiltonian includes the relativistic magnetic vector potential in the framework of the DKH theory, and is applicable to the calculations of magnetic properties without further expansion in powers of c^{-1}. By combining with the finite-perturbation theory and the generalized-UHF method, new pictures of the magnetic shielding constant are derived. We apply the theory to calculations of the magnetic shielding constants of He isoelectronic systems, Ne isoelectronic systems, and noble gas atoms. The results of the present theory compare well with those of the four-component Dirac–Hartree–Fock calculations; the differences were within 3%. We note that the quasirelativistic theory that handles the magnetic vector potential at a nonrelativistic level greatly underestimates the relativistic effect. The so-called "picture change" effect is quite important for the magnetic shielding constant of heavy elements. The change in the orbital picture plays a significant role in the valence-orbital magnetic response as well as the core-orbital one. The effect of the finite nucleus is also studied using Gaussian nucleus model. The present theory reproduces the correct behavior of the finite-nucleus effect that has been reported with the Dirac theory. In contrast, the nonrelativistic theory and the quasirelativistic theory with the nonrelativistic vector potential underestimate the finite-nucleus effect. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1528933]

I. INTRODUCTION

Magnetic shielding constants observed by nuclear magnetic resonance (NMR) spectroscopy sensitively reflect the valence electronic structures of molecules. Multinuclear NMR experiments have been conducted for almost all of the elements in the Periodic Table, and a large body of experimental data has been accumulated.[1,2] A series of studies by our group on the electronic mechanism of NMR chemical shifts have shown that the major electronic mechanism of the chemical shifts is an intrinsic property of the resonance atom itself,[3,4] and therefore is closely related to its position in the Periodic Table. To elucidate the mechanism of the chemical shift for various nuclei, we need a quantitative theory that can deal with all of the elements in the periodic table *seamlessly* in a sufficient accuracy. Since magnetic shielding constants strongly reflect the contributions from the angular momenta of valence electrons in the vicinity of the nuclei, the relativistic effect is quite important for molecules that include heavy elements.[5]

Since the relativistic electronic structures of molecules are described by the four-component Dirac theory, it is favorable to use this theory for theoretical studies of NMR parameters. The theory of NMR parameters in a nonrelativistic framework was developed by Ramsey.[6] Pyper,[7] Pyykkö,[8] Zhang and Webb[9] have formulated the relativistic theory for magnetic shielding constants based on the Dirac theory, but until recently these theories have actually been applied only in the semiempirical framework.[10]

Ab initio four-component relativistic calculations of the magnetic shielding constants of molecules were performed by Ishikawa *et al.*[11] and Quiney *et al.*[12] in 1998. Ishikawa *et al.* developed a theory of magnetic shielding constants using finite-perturbation theory in the Dirac–Hartree–Fock method, and calculated hydrides of group 16 and group 17 elements.[13,14] Quiney *et al.* used sum-over-state formalism with a gauge invariant orbital and calculated H_2O molecules.[12] Another method using relativistic random phase approximation for magnetic shielding constants was proposed by Visscher *et al.* and applied to hydrogen halides.[15]

Despite such theoretical developments, the four-component theory has actually been applied only to small molecules. The main problem in the four-component calculations arises from the requirement for a small-component space. Since the magnetic vector potential is an odd operator, which directly connects the large-component space with the small-component one, the small components should be accurately described to obtain reliable magnetic properties.[7,16] Consequently, the computational size becomes large even for relatively small molecules.

One way to avoid this problem is to use a quasirelativistic formalism in which the small-component contribution is described in an explicit operator form. In the quasirelativistic theories, the relativistic effects are usually classified into

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spin-free (scalar) relativistic (SFR) term and spin-dependent term.[17] Among the spin-dependent terms, the spin–orbit (SO) interaction is often discussed separately. In 1973, Morishima, Endo, and Yonezawa showed the importance of the SO interaction for magnetic shielding constants by a semiempirical method,[18] but this study has been overlooked for a long time. In 1995, Nakatsuji et al. presented an ab initio UHF formalism for calculating the SO effect on the magnetic shielding constant[19] and showed that the SO interaction is certainly an essential source of the chemical shifts in hydrogen halides and methyl halides.[19] A series of studies have confirmed this findings.[20–23] Theoretical calculations including electron-correlation and the SO effect have been developed using density functional theory (DFT) (Ref. 24) and multiconfiguration self-constant field (MC-SCF) theory.[25]

Regarding the magnetic shielding constants of heavy elements such as mercury[26] and tungsten,[27] the SFR terms are very important as well as the SO term, and furthermore, these two effects couple strongly with each other.[26] Therefore, the theory that includes both the SO and SFR terms is necessary for calculating the magnetic shielding constants of heavy elements. Fukui et al.[28] and Wolff and Zieglar[29] developed a quasirelativistic theory for magnetic shielding constants at the Pauli approximation level. However, such theory is not reliable for calculations of magnetic shielding constants of heavy elements.

Douglas–Kroll transformation[30] of the Dirac Hamiltonian into a two-component form gives a variationally stable formalism.[32–34] Sucher provided a theoretical background of quantum electrodynamics for this Douglas–Kroll (DK) transformation.[31] Hess[32,33] developed the DK transformation in quantum chemistry and presented a method for evaluating the matrix elements in the DK transformation.[34] Thus, the Douglas–Kroll–Hess (DKH) method has an attractive feature in the relativistic quantum chemistry. Ballard et al. applied the DKH method to the calculation of magnetic shielding constants,[35] but used only the spin-free parts of the DKH Hamiltonian and the SO term and the magnetic interaction term remained in the Pauli form. Fukui and Baba also suggested a DKH transformation including magnetic vector potential,[36] but they did not propose an explicit working equation for the magnetic shielding constant. In these studies, the relativistic corrections to the zeroth order Hamiltonian were considered, but the magnetic interaction term remained nonrelativistic. Our recent studies[37,38] have shown that the relativistic correction to the magnetic interaction is significant for the magnetic shielding constants of heavy elements. Therefore, the magnetic vector potential should be addressed in the DKH theory to formulate a consistent quasirelativistic theory of magnetic shielding constants.

The difficulty in adapting the DKH transformation to the magnetic field lies in the presence of the magnetic vector potential in a square-root operator. Therefore, an additional expansion becomes necessary to extract the terms in the desired order in the magnetic perturbations.[39] In this study, we propose a different formulation of the DKH transformation to calculate magnetic properties that avoids the presence of the magnetic vector potential in a square-root operator. A

feature of the DKH transformation is that the operator is expanded in powers of an external potential V. In this study, we choose the electromagnetic potential, $V+\mathbf{A}$ as an expansion parameter. With this choice, linear and quadratic terms in $V+\mathbf{A}$ appear within the second-order transformation, and the vector potential does not appear in square-root form. We treat $\mathbf{A}$ as an external perturbation and our formula is closely related to the method proposed by Kellö et al.,[40] who calculated the electrostatic property. The choice of $\mathbf{A}$ as an expansion parameter is natural for the theory of magnetic properties. The so-called ''picture change'' effect,[41] which is the change in the representation from the Dirac picture to the Schrödinger–Pauli picture, is taken into account in the present formula. All of the terms in the Pauli approximation are involved in the present formula as its nonrelativistic limit. The Hamiltonian derived by our formula is analogous to that in the nonrelativistic theory and the NMR parameters are obtained as second-order properties. Consequently, the theoretical and computational methods for calculating magnetic properties, for example, the coupled-perturbed Hartree–Fock method[42] and the finite-perturbation method,[43] developed in nonrelativistic studies can also be adapted to the present relativistic formalism.

A finite size of the nucleus may also affect the magnetic shielding constant in the relativistic theory. It has been reported that the finite nucleus model affects the hyperfine structures of heavy atoms.[44] In the relativistic theory, the magnetic shielding constant includes the spin-dipolar and Fermi contact terms and the mechanisms of these terms are similar to those in the hyperfine structure. The Gaussian nucleus model[45] is used in this study, and the effect of the nucleus model on the magnetic shielding constant is examined.

In this paper, we formulate a quasirelativistic theory for magnetic properties based on the DKH transformation including magnetic field. We utilize the generalized-UHF (GUHF) formalism[46,47] to accurately describe the SO interaction and the magnetic field effect at the Hartree–Fock level. We use the Gaussian nucleus model. The resultant theory is are applied to several atomic systems to calculate their magnetic shielding constants. The calculated results are compared with the results of the four-component theory, and the reliability of the present theory is confirmed. We also perform the calculations with the previous DKH quasirelativistic model in which the magnetic interaction is treated in the nonrelativistic level and thereby show the importance of the relativistic effect on the magnetic interaction term.

II. THEORY

A. Douglas–Kroll–Hess transformation including the magnetic field

In the DKH formulation of magnetic properties, two different transformations are possible, depending on how we deal with the vector potential $\mathbf{A}$.

In our first approach, we regard $\mathbf{A}$ as an external potential, like V, and expand the operator in powers of the external potentials $\mathbf{A}$ and V together. This formulation leads to the DKH Hamiltonian in powers of V and $\mathbf{A}$. For the present purpose to calculate the magnetic shielding constant, a

second-order property, we need the Hamiltonian which is correct up to the second order in $\mathbf{A}$. For this purpose, we start from the one-electron Dirac Hamiltonian including V and $\mathbf{A}$,

$$H_D = c\,\boldsymbol{\alpha}\cdot\mathbf{p} + \beta c^2 + V + c\,\boldsymbol{\alpha}\cdot\mathbf{A}, \tag{1}$$

where $\boldsymbol{\alpha}$ and β represent the usual Dirac matrices and c is the velocity of light. First, we apply free-particle Foldy–Wouthuysen transformation of the Dirac Hamiltonian using the unitary operator[48]

$$U_0 = K(1 + \beta R\,\boldsymbol{\alpha}\cdot\mathbf{p}), \tag{2}$$

where K and R are the operators defined by

$$K = \left(\frac{E_p + c^2}{2E_p}\right)^{1/2}, \tag{3}$$

$$R = \frac{c}{E_p + c^2}, \tag{4}$$

with

$$E_p = c(p^2 + c^2)^{1/2}. \tag{5}$$

The transformed Hamiltonian is written as

$$U_0 H_D U_0^{-1} = \beta E_p + \mathcal{E}_1^V + \mathcal{E}_1^{\mathbf{A}} + \mathcal{O}_1^V + \mathcal{O}_1^{\mathbf{A}} \equiv H_1. \tag{6}$$

Here, $\mathcal{E}_1^V$ and $\mathcal{E}_1^{\mathbf{A}}$ are, respectively, the first-order even operators in the scalar potential V and the vector potential $\mathbf{A}$ as given by

$$\mathcal{E}_1^V = K(V + R\,\boldsymbol{\alpha}\cdot\mathbf{p}V\boldsymbol{\alpha}\cdot\mathbf{p}R)K, \tag{7}$$

$$\mathcal{E}_1^{\mathbf{A}} = \beta K[R\,\boldsymbol{\alpha}\cdot\mathbf{p}(c\,\boldsymbol{\alpha}\cdot\mathbf{A}) + (c\,\boldsymbol{\alpha}\cdot\mathbf{A})\boldsymbol{\alpha}\cdot\mathbf{p}R]K. \tag{8}$$

Similarly, $\mathcal{O}_1^V$ and $\mathcal{O}_1^{\mathbf{A}}$ are the first-order odd operators in the potentials V and $\mathbf{A}$ as

$$\mathcal{O}_1^V = \beta K(R\,\boldsymbol{\alpha}\cdot\mathbf{p}V - V\boldsymbol{\alpha}\cdot\mathbf{p}R)K, \tag{9}$$

$$\mathcal{O}_1^{\mathbf{A}} = K[c\,\boldsymbol{\alpha}\cdot\mathbf{A} - R\,\boldsymbol{\alpha}\cdot\mathbf{p}(c\,\boldsymbol{\alpha}\cdot\mathbf{A})\boldsymbol{\alpha}\cdot\mathbf{p}R]K. \tag{10}$$

The generalization of the second-order DKH transformation[33] for the magnetic vector potential is realized by introducing the term W_1, which arises from the second unitary transformation using the operator,

$$U_1 = [1 + (W_1^V + W_1^{\mathbf{A}})^2]^{1/2} + (W_1^V + W_1^{\mathbf{A}}). \tag{11}$$

The transformed Hamiltonian is written as

$$\begin{aligned}
U_1 H_1 U_1^{-1} = {} & \beta E_p + \mathcal{E}_1^V + \mathcal{E}_1^{\mathbf{A}} + \mathcal{O}_1^V + \mathcal{O}_1^{\mathbf{A}} + [(W_1^V \\
& + W_1^{\mathbf{A}}), \beta E_p] + [(W_1^V + W_1^{\mathbf{A}}), (\mathcal{O}_1^V + \mathcal{O}_1^{\mathbf{A}})] \\
& + \tfrac{1}{2}(W_1^V + W_1^{\mathbf{A}})^2 \beta E_p + (W_1^V + W_1^{\mathbf{A}})\beta E_p(W_1^V \\
& + W_1^{\mathbf{A}}) + \tfrac{1}{2}\beta E_p(W_1^V + W_1^{\mathbf{A}})^2 + \cdots.
\end{aligned} \tag{12}$$

To eliminate the odd terms, $\mathcal{O}_1^X$ ($X = V, \mathbf{A}$), in the transformed Hamiltonian, W_1^X should satisfy the relation,

$$\beta E_p W_1^X - W_1^X \beta E_p = \mathcal{O}_1^X. \tag{13}$$

Substituting this relation into Eq. (12) and collecting terms up to the second-order in the external potential $V + \mathbf{A}$, we obtain the transformed Hamiltonian that is correct to second order in $\mathbf{A}$ and V,

$$\begin{aligned}
H_2 = {} & \beta E_p + \mathcal{E}_1^V + \mathcal{E}_1^{\mathbf{A}} + \tfrac{1}{2}(W_1^V + W_1^{\mathbf{A}})^2 \beta E_p \\
& + (W_1^V + W_1^{\mathbf{A}})\beta E_p(W_1^V + W_1^{\mathbf{A}}) + \tfrac{1}{2}\beta E_p(W_1^V + W_1^{\mathbf{A}})^2.
\end{aligned} \tag{14}$$

Since the term $[W_1^X, \mathcal{O}_1^X]$ is odd, such terms are not included in H_2; they are involved in the next-order (third order) term of the DKH transformation.[33,61] For magnetic properties, the term up to the second order in $\mathbf{A}$ is sufficient, but for the potential V, the contribution of the third and higher order terms may not be negligible.[61,62] However, in the present paper, we terminate our DKH transformation only up to the second order. Then, the two-component positive energy Hamiltonian valid to second-order DKH transformation is obtained by taking only the upper two components of H_2 give by Eq. (14).

Thus, in this approximation, the total Hamiltonian for a many-electron system is given by

$$H = \sum_j (E_j + V_j^{\mathrm{eff}} + H_j^{\mathrm{mag}}) + \sum_{j>k} V_{jk}, \tag{15}$$

where E_j denotes the kinetic energy,

$$E_j = E_{p_j} = c(p_j^2 + c^2)^{1/2}, \tag{16}$$

and V_j^{eff} denotes the effective scalar potential term[32–34] given by

$$\begin{aligned}
V_j^{\mathrm{eff}} = {} & K_j(V_j + R_j\boldsymbol{\sigma}_j\cdot\mathbf{p}_j V_j\boldsymbol{\sigma}_j\cdot\mathbf{p}_j R_j)K_j \\
& - \tfrac{1}{2}[(W_j^V)^2 E_j + 2W_j^V E_j W_j^V + E_j(W_j^V)^2].
\end{aligned} \tag{17}$$

The magnetic interaction H_j^{mag} with the relativistic correction, which involves the first-order term H_{1j}^{mag} and the second-order term H_{2j}^{mag}, is given by

$$\begin{aligned}
H_j^{\mathrm{mag}} = H_{1j}^{\mathrm{mag}} + H_{2j}^{\mathrm{mag}} = {} & K_j(R_j\boldsymbol{\sigma}_j\cdot\mathbf{p}_j(c\,\boldsymbol{\sigma}_j\cdot\mathbf{A}_j) \\
& + (c\,\boldsymbol{\sigma}_j\cdot\mathbf{A}_j)\boldsymbol{\sigma}_j\cdot\mathbf{p}_j R_j)K_j + \tfrac{1}{2}[(W_j^V W_j^{\mathbf{A}} - W_j^{\mathbf{A}} W_j^V)E_j \\
& + 2(W_j^V E_j W_j^{\mathbf{A}} - W_j^{\mathbf{A}} E_j W_j^V) + E_j(W_j^V W_j^{\mathbf{A}} - W_j^{\mathbf{A}} W_j^V)] \\
& + \tfrac{1}{2}[(W_j^{\mathbf{A}})^2 E_j + 2W_j^{\mathbf{A}} E_j W_j^{\mathbf{A}} + E_j(W_j^{\mathbf{A}})^2].
\end{aligned} \tag{18}$$

V_{jk} denotes the electron–electron interaction term that includes the electron repulsion and the two-electron spin–orbit interaction in the present approximation,

$$V_{jk} = \frac{1}{r_{jk}} - \frac{1}{4c^2}\frac{(\mathbf{r}_{jk}\times\mathbf{p}_j)\cdot\boldsymbol{\sigma}_j - (\mathbf{r}_{jk}\times\mathbf{p}_k)\cdot\boldsymbol{\sigma}_k}{r_{jk}^3}, \tag{19}$$

where the Breit–Pauli form for the two-electron spin–orbit interaction is used for simplicity, though the electron–electron interaction in the DKH form is more favorable. W is the integral operator defined in the momentum space representation with the kernel as follows:

$$W^V(p,p')=\langle p|W^V|p'\rangle$$

$$=K_p R_p(\boldsymbol{\sigma}\cdot\mathbf{p}\bar{V}_{pp'})K_{p'}$$

$$-K_p(\bar{V}_{pp'}\boldsymbol{\sigma}\cdot\mathbf{p})R_{p'}K_{p'}, \tag{20}$$

$$W^{\mathbf{A}}(p,p')=K_p(c\boldsymbol{\sigma}\cdot\bar{\mathbf{A}}_{pp'})K_{p'}-K_p R_p \boldsymbol{\sigma}\cdot\mathbf{p}(c\boldsymbol{\sigma}\cdot\bar{\mathbf{A}}_{pp'})$$

$$\times\boldsymbol{\sigma}\cdot\mathbf{p}R_{p'}K_{p'}, \tag{21}$$

with

$$\bar{V}_{pp'}=\frac{\langle p|V|p'\rangle}{E_p+E_{p'}}, \tag{22}$$

$$\bar{\mathbf{A}}_{pp'}=\frac{\langle p|\mathbf{A}|p'\rangle}{E_p+E_{p'}}. \tag{23}$$

Another approach to treat magnetic vector potential $\mathbf{A}$ in the DKH transformation is to replace the momentum operator $\mathbf{p}$ with the mechanical momentum operator $\boldsymbol{\pi}=\mathbf{p}+\mathbf{A}$, according to Dirac's original proposal,[49] and so this formulation may seem to be more natural than the above one in the first sight. Using this replacement, we obtain the magnetic field-dependent kinetic operator as

$$E_p(\mathbf{A})=[(c\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2+c^4]^{1/2}$$

$$=c[(p^2+c^2)+(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}+A^2)$$

$$+\boldsymbol{\alpha}\cdot(\mathbf{p}\times\mathbf{A}+\mathbf{A}\times\mathbf{p})]^{1/2}. \tag{24}$$

If there is no scalar potential ($V=0$), this operator reproduces exactly the relativistic positive energy. However, in order to apply Eq. (24) to calculate derivative properties such as the magnetic shielding constant, we have to expand Eq. (24) in terms of $\mathbf{A}$. Expansion of Eq. (24) in powers of $\mathbf{A}$ is not obvious because the operators do not commute. With the use of a momentum space representation in which E_p is diagonal, Eq. (24) may be expanded in powers of $\mathbf{A}$ as

$$(a+b)^{1/2}=\langle p|a|p\rangle+\frac{\langle p|b|p'\rangle}{\langle p|a|p\rangle+\langle p'|a|p'\rangle}+\cdots, \tag{25}$$

where

$$a=p^2+c^2, \tag{26}$$

$$b=(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}+A^2)+\boldsymbol{\alpha}\cdot(\mathbf{p}\times\mathbf{A}+\mathbf{A}\times\mathbf{p}). \tag{27}$$

Replacing all the momentum operators in the usual DKH Hamiltonian by Eq. (25), we can obtain the operators for the magnetic perturbation in the DKH theory. However, since the kinetic operator E_p appears everywhere in the DKH Hamiltonian and we have to take special care for commutation relation of the operators, this approach is quite tedious, and moreover, the physical simplicity will be lost, though the two methods should finally give the same results. Thus, choosing the potential $\mathbf{A}$ as an expansion parameter in the DKH transformation is natural for the theory of magnetic properties.

B. Magnetic shielding constant

To study nuclear magnetic shielding constants, the magnetic vector potentials generated from the uniform magnetic field $\mathbf{B}$ and the nuclear magnetic moment $\boldsymbol{\mu}_A$ of nucleus A should be considered. Then, the vector potential is written as

$$\mathbf{A}=\mathbf{A}^0+\mathbf{A}^N, \tag{28}$$

with

$$\mathbf{A}^0=\tfrac{1}{2}\mathbf{B}\times\mathbf{r}_d, \tag{29}$$

$$\mathbf{A}^N=-\frac{1}{c^2}\sum_A^{\text{nuc}}\boldsymbol{\mu}_A\times\nabla G_A, \tag{30}$$

where

$$G_A=\int\frac{w_A(R_A)}{|\mathbf{r}-\mathbf{R}|}d\mathbf{R}. \tag{31}$$

Here, $\mathbf{r}_d=\mathbf{r}-\mathbf{d}$ is the position vector from the gauge origin $\mathbf{d}$, nucleus A is located at position $\mathbf{A}$, and $R_A=|\mathbf{R}-\mathbf{A}|$. The weight function $w_A(R_A)$ is related to the finite size of the nucleus.[50] In this study, we use Gaussian nucleus model, where the nucleus has the following finite distribution:

$$w_A(R_A)=(\eta_A/\pi)^{3/2}\exp(-\eta_A R_A^2). \tag{32}$$

The nuclear exponent η_A is taken from Ref. 51. The point nucleus model, which has a delta function distribution, is also used for comparison,

$$w_A(R_A)=\delta(R_A) \tag{33}$$

and we obtain

$$-\nabla\int\frac{\delta(R_A)}{|\mathbf{r}-\mathbf{R}|}d\mathbf{R}=-\nabla\frac{1}{|\mathbf{r}-\mathbf{A}|}=\frac{\mathbf{r}_A}{r_A^3}. \tag{34}$$

We also consider the nuclear charge distribution in the Gaussian model according to Chandra and Hess.[52] The Gaussian charge distribution affects not only the effective scalar potential V^{eff} but also the magnetic interaction H^{mag} through the vector-scalar cross terms in H_2^{mag}.

The magnetic shielding tensor of nucleus A in the tu component ($t,u=x,y,z$) is given by Ramsey[6] as a second-order property,

$$\sigma_{A,tu}=\frac{\partial^2 E}{\partial B_t\partial\mu_{A,u}}\bigg|_{\mu_{A,u}=B_t=0}. \tag{35}$$

To calculate this property, we adopt the finite perturbation theory along with the Hellmann–Feynman theorem.[19,43] Expanding the Hamiltonian of Eq. (15) in powers of $\mathbf{B}$ and $\boldsymbol{\mu}_A$, we obtain

$$H=H^{(0,0)}+\sum_t H_t^{(1,0)}B_t+\sum_A\sum_u H_{A,u}^{(0,1)}\mu_{A,u}$$

$$+\sum_A\sum_u B_t H_{A,tu}^{(1,1)}\mu_{A,u}+\cdots. \tag{36}$$

For variational wave functions, such as the Hartree–Fock SCF wave function used in this study, the Hellmann–Feynman theorem holds and Eq. (35) becomes

$$\sigma_{A,tu}=\langle\Psi^{(0)}|H_{A,tu}^{(1,1)}|\Psi^{(0)}\rangle$$

$$+\frac{\partial}{\partial B_t}[\langle\Psi^{(B_t)}|H_{A,u}^{(0,1)}|\Psi^{(B_t)}\rangle]_{B_t=0}, \tag{37}$$

where $\Psi^{(0)}$ is the unperturbed wave function and $\Psi^{(B_t)}$ is the wave function under the external magnetic field B_t. In a quasirelativistic theory, the four-component wave function is transformed into the two-component form, and accordingly, the perturbation operator should be transformed into the same representation as the wave function. This transformation is known as the "change of picture" effect.[41] To use the Hellmann–Feynman theorem in the quasi relativistic framework, the change of the picture effect should be considered. Thus, $H^{(0,1)}$ and $H^{(1,1)}$ in Eq. (37) [and also $H^{(1,0)}$] are different from the nonrelativistic operators used in the previous studies.[26,27] These terms are derived from H^{mag} in Eq. (18) which involves the quasirelativistic transformation operators K, R, and W^X. The operators $H^{(1,0)}$, $H^{(0,1)}$, and $H^{(1,1)}$ also involve these transformation operators [e.g., K and R appear in Eqs. (38), (45), and (48)]. Thus, the change of picture effect of the magnetic perturbation is taken into account and the Hellmann–Feynman theorem holds in our formula within the quasirelativistic framework.

In our derivation of the Hamiltonian, the kinetic factor E_p does not include the vector potential and our H includes the terms up to quadratic in $\mathbf{B}$ and $\boldsymbol{\mu}$. $H^{(0,0)}$ is the DKH Hamiltonian without the magnetic field.[32–34] The magnetic Zeeman term $H^{(1,0)}$ is given as

$$H_t^{(1,0)} = \sum_j \ (H_{1,jt}^{(1,0)} + H_{2,jt}^{(1,0)})$$

$$= \sum_j \ K_j(R_j h_{jt}^{(1,0)} + h_{jt}^{(1,0)\dagger} R_j)K_j + \sum_j \ H_{2,jt}^{(1,0)}, \quad (38)$$

with

$$h_{jt}^{(1,0)} = -\frac{1}{2}c(\mathbf{p}_j \times \mathbf{r}_{jd})_t + \frac{i}{2}c[\sigma_{jt}(\mathbf{p}_j \cdot \mathbf{r}_{jd}) - p_{jt}(\boldsymbol{\sigma}_j \cdot \mathbf{r}_{jd})]. \quad (39)$$

The term $H_1^{(1,0)}$ corresponds to the Zeeman term in the nonrelativistic theory and involves the mass–velocity correction through the R_j term. The term $H_2^{(1,0)}$ arises from the operators that include both W^V and $W^{\mathbf{A}}$ in Eq. (18). Using an anticommutator, $\{X,Y\} = XY + YX$, this term can be written as

$$H_{2,jt}^{(1,0)} = -\tfrac{1}{2}(\{\bar{U}_j, E_j\}\bar{h}_{jt}^{(1,0)} + \bar{U}_j\{\bar{h}_{jt}^{(1,0)}, E_j\}$$

$$+ \bar{h}_{jt}^{(1,0)\dagger}\{\bar{U}_j^\dagger, E_j\} + \{\bar{h}_{jt}^{(1,0)\dagger}, E_j\}\bar{U}_j^\dagger)$$

$$+ \tfrac{1}{2}(\bar{h}_{jt}^{(1,0)}\{\bar{T}_j, E_j\} + \{\bar{h}_{jt}^{(1,0)}, E_j\}\bar{T}_j$$

$$+ \{\bar{T}_j^\dagger, E_j\}\bar{h}_{jt}^{(1,0)\dagger} + \bar{T}_j^\dagger\{\bar{h}_{jt}^{(1,0)\dagger}, E_j\}), \quad (40)$$

where the momentum space integral operators are defined by

$$\bar{U}(p,p') = K_p\bar{V}_{pp'}K_{p'} - K_pR_p\boldsymbol{\sigma}\cdot\mathbf{p}\bar{V}_{pp'}\boldsymbol{\sigma}\cdot\mathbf{p}R_{p'}K_{p'}X_{p'}^{-1}, \quad (41)$$

$$\bar{T}(p,p') = X_pK_p\bar{V}_{pp'}K_{p'} - K_pR_p\boldsymbol{\sigma}\cdot\mathbf{p}\bar{V}_{pp'}\boldsymbol{\sigma}\cdot\mathbf{p}R_{p'}K_{p'}, \quad (42)$$

$$\bar{h}_t^{(1,0)}(p,p') = \frac{K_pR_p\langle p|h_t^{(1,0)}|p'\rangle K_{p'}}{E_p + E_{p'}}, \quad (43)$$

with

$$X_p = R_p\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\mathbf{p}R_p = R_pp^2R_p. \quad (44)$$

$H_2^{(1,0)}$ includes the magnetic correction to the SO interaction. The paramagnetic shielding term $H^{(0,1)}$ is given as

$$H_{A,u}^{(0,1)} = \sum_j \ (H_{1,jAu}^{(0,1)} + H_{2,jAu}^{(0,1)})$$

$$= \sum_j \ K_j(R_j h_{jAu}^{(0,1)} + h_{jAu}^{(0,1)\dagger} R_j)K_j + \sum_j \ H_{2,jAu}^{(0,1)}, \quad (45)$$

with

$$h_{jAu}^{(0,1)} = \frac{1}{c}(\mathbf{p}_j \times \nabla_j G_{jA})_u + \frac{i}{c}[\sigma_{ju}(\mathbf{p}_j \cdot \nabla_j G_{jA})$$

$$- p_{ju}(\boldsymbol{\sigma}_j \cdot \nabla_j G_{jA})]. \quad (46)$$

The first term in Eq. (46) is spin-free and corresponds to the usual one of the paramagnetic shielding. The second term is the SO-induced shielding term and it can be decomposed into two terms as follows:

$$\frac{2i}{3c}\sigma_{ju}(\mathbf{p}_j \cdot \nabla_j G_{jA}) - \frac{i}{c}\left[p_{ju}(\boldsymbol{\sigma}_j \cdot \nabla_j G_{jA}) - \frac{1}{3}\sigma_{ju}(\mathbf{p}_j \cdot \nabla_j G_{jA})\right]. \quad (47)$$

The first term is isotropic and corresponds to the Fermi contact term in its nonrelativistic limit;[53] the second term corresponds to the spin-dipolar term. Similar to $H_2^{(1,0)}$, the cross terms of W^V and $W^{\mathbf{A}}$ give $H_2^{(0,1)}$; the explicit form of this term is the same as Eq. (40), but $h^{(1,0)}$ is replaced by $h^{(0,1)}$. $H_2^{(0,1)}$ can be decomposed into the paramagnetic shielding, Fermi contact, and spin-dipolar terms similarly to Eqs. (46) and (47). The diamagnetic shielding term $H^{(1,1)}$ arises from the cross terms of $W^{\mathbf{A}_0}$ and $W^{\mathbf{A}_N}$. Since $\mathbf{A}^0$ can be commuted with the momentum operator $\mathbf{p}$, the diamagnetic shielding term can be written as

$$H_{A,tu}^{(1,1)} = \sum_j \ (-E_jK_j^2\bar{h}_{1,jAtu}^{(1,1)} - \bar{h}_{1,jAtu}^{(1,1)}K_j^2E_j + E_jK_j^2\bar{h}_{2,jAtu}^{(1,1)}$$

$$+ \bar{h}_{2,jAtu}^{(1,1)}K_j^2E_j - E_jK_j^2R_j^2\bar{h}_{3,jAtu}^{(1,1)} - \bar{h}_{3,jAtu}^{(1,1)}R_j^2K_j^2E_j), \quad (48)$$

where the momentum space integral operators are defined by

$$\bar{h}_{1,Atu}^{(1,1)}(p,p') = \frac{K_p\langle p|h_{Atu}^{(1,1)}|p'\rangle K_{p'}}{(E_p + E_{p'})^2}, \quad (49)$$

$$\bar{h}_{2,Atu}^{(1,1)}(p,p') = \frac{K_pR_p\langle p|p^2h_{Atu}^{(1,1)} + h_{Atu}^{(1,1)}p^2|p'\rangle R_{p'}K_{p'}}{(E_p + E_{p'})^2}, \quad (50)$$

$$\bar{h}_{3,Atu}^{(1,1)}(p,p') = \frac{K_pR_p\langle p|p^2h_{Atu}^{(1,1)}p^2|p'\rangle R_{p'}K_{p'}}{(E_p + E_{p'})^2}, \quad (51)$$

with

$$h_{Atu}^{(1,1)} = \tfrac{1}{2}[\delta_{tu}(\mathbf{r}_d \cdot \nabla G_A) - r_{d,u}(\nabla G_A)_t]. \quad (52)$$

Equation (52) corresponds to the nonrelativistic diamagnetic shielding operator with the Gaussian nucleus model except

for the constant c^{-2}. In the Dirac theory, the factor c^{-2} in the diamagnetic shielding arises from the energy gap between positive and negative energy states.[54] In this theory, this factor arises due to the free-particle kinetic energy E_p in the denominator of Eq. (49) and Eq. (48). The first and second terms in Eq. (48) correspond to the diamagnetic shielding term in its nonrelativistic limit. The next two terms correspond to the mass–velocity correction to the diamagnetic shielding term in the Pauli approximation. The last two terms are in the order of c^{-6}, and therefore there are no analogs in the Pauli approximation.[28,29]

To evaluate the matrix elements, we use the matrix transformation technique and adopt the resolution of identity method developed by Hess *et al.*[34] An operator $\langle p|O|p'\rangle$ represented in the eigenvector of p^2 is transformed from the representation in the coordinate space basis $\chi(\mathbf{r})$ as

$$\langle p|O|p'\rangle = \sum_{\chi,\chi'} \langle p|\chi\rangle\langle\chi|O|\chi'\rangle\langle\chi'|p'\rangle. \tag{53}$$

The matrix elements are calculated in p space and the resulting matrix elements are back-transformed to the $\chi(\mathbf{r})$ space.

Since the Hamiltonian includes the spin operator, the wave function must have the generalized UHF (GUHF) (Refs. 45, 46) form in the Hartree–Fock approximation. For an N electron system, the GUHF wave function can be written using a single Slater determinant as

$$\Psi^{\mathrm{GUHF}} = \|\phi_1\phi_2\cdots\phi_N\|, \tag{54}$$

where ϕ_j is a general spin–orbital,

$$\phi_j = \phi_j^\alpha\alpha + \phi_j^\beta\beta. \tag{55}$$

The above orbital is allowed to be occupied by a single electron. The spatial part of the orbital is described by a linear combination of the basis function χ as

$$\phi_j^\omega = \sum_\lambda C_{\lambda j}^\omega \chi_\lambda \qquad (\omega = \alpha,\beta), \tag{56}$$

where C is the orbital expansion coefficient, which is a complex number, determined by the SCF procedure. To calculate the magnetic shielding constant, we use the finite perturbation theory.[19,43] In the finite perturbation theory, the unperturbed SCF procedure

$$F_j\phi_j^{(0)} = \varepsilon_j^{(0)}\phi_j^{(0)} \tag{57}$$

and the SCF procedure with finite perturbation, B_t,

$$(F_j + B_t H_{jt}^{(1,0)})\phi_j^{(B_t)} = \varepsilon_j^{(B_t)}\phi_j^{(B_t)} \tag{58}$$

are performed, and ϕ_j is differentiated numerically with respect to B_t. The magnetic shielding tensor is expressed as a sum of the occupied orbital contributions,

$$\sigma_{A,tu} = \sum_j^{\mathrm{occ}} \left\{ \langle\phi_j^{(0)}|H_{jAtu}^{(1,1)}|\phi_j^{(0)}\rangle \right.$$
$$\left. + \frac{\partial}{\partial B_t}[\langle\phi_j^{(B_t)}|H_{jAu}^{(0,1)}|\phi_j^{(B_t)}\rangle]_{B_t=0} \right\}. \tag{59}$$

III. NUMERICAL CALCULATIONS AND THE RESULTS

To study the relativistic effect on the magnetic interaction operator H^{mag}, we use three different levels of approximations of the quasirelativistic (QR) calculations. At the QR level 0 (QR-0) approximation, the DKH transformation is applied to the nonmagnetic Hamiltonian $H^{(0,0)}$ and the magnetic interaction is treated in the nonrelativistic manner, H_0^{mag} which includes the spin-dipolar and Fermi contact terms. At the QR level 1 (QR-1) approximation, we used the first-order DKH magnetic interaction H_1^{mag} and the nonrelativistic diamagnetic term. At the QR level 2 (QR-2) approximation, we used the second-order DKH magnetic interaction $H_1^{\mathrm{mag}} + H_2^{\mathrm{mag}}$. The QR Hamiltonians used in this section are thus summarized as follows:

QR level 0,

$$H^{\mathrm{QR-0}} = \sum_j (E_j + V_j^{\mathrm{eff}}) + \sum_{j>k} V_{jk} + \sum_j H_{0j}^{\mathrm{mag}}; \tag{60}$$

QR level 1,

$$H^{\mathrm{QR-1}} = \sum_j (E_j + V_j^{\mathrm{eff}}) + \sum_{j>k} V_{jk} + \sum_j H_{1j}^{\mathrm{mag}}$$
$$+ \frac{1}{2c^2}\sum_j h_j^{(1,1)}; \tag{61}$$

QR level 2,

$$H^{\mathrm{QR-2}} = \sum_j (E_j + V_j^{\mathrm{eff}}) + \sum_{j>k} V_{jk} + \sum_j (H_{1j}^{\mathrm{mag}} + H_{2j}^{\mathrm{mag}}). \tag{62}$$

The explicit form of the nonrelativistic magnetic term H_0^{mag} is given in Ref. 19. The nonrelativistic diamagnetic term $h^{(1,1)}$ is given by Eq. (52). The QR-0 approximation has been used by our laboratory in studies of the $^1\mathrm{H}$,[35] $^{199}\mathrm{Hg}$,[26] and $^{183}\mathrm{W}$ (Ref. 27) chemical shifts within the SO-UHF framework; in this study, the GUHF wave function was used for all levels of approximations. The DKH transformation is applied only to the one-electron terms; the two-electron terms used in this study are

$$V_{jk} = \frac{1}{r_{jk}} - \frac{1}{4c^2}\frac{(\mathbf{r}_{jk}\times\mathbf{p}_j)\cdot\boldsymbol{\sigma}_j - (\mathbf{r}_{jk}\times\mathbf{p}_k)\cdot\boldsymbol{\sigma}_k}{r_{jk}^3}. \tag{63}$$

The first term is the contribution from conventional electron–electron repulsion; the second term represents the two-electron SO interaction. For comparison with the Dirac–Coulomb calculation, the spin–other–orbit interaction, which originates from the Breit interaction, is not included in the QR calculation. Dirac–Hartree–Fock (DHF) (Ref. 11) and the nonrelativistic (NR) calculations are also performed. The Breit interaction is not considered in the DHF calculation. A kinetic balanced small-component basis, a derivative of the large-component basis, is used for the DHF calculation.

A. Helium and neon isoelectronic systems

The magnetic shielding constants of He isoelectronic two-electron systems and Ne isoelectronic 10-electron systems with various nuclear charges were calculated. $32s$ and $32s30p$ universal Gaussian basis functions[55] were used for

TABLE I. Magnetic shielding constants of He isoelectronic systems (ppm).

System	Z[a]	Point nucleus model					Gaussian nucleus model				
			QR					QR			
		DHF	Level 2	Level 1	Level 0	NR	DHF	Level 2	Level 1	Level 0	NR
He	2	60.0	60.0	60.0	59.9	59.9	60.0	60.0	60.0	59.9	59.9
Ca^{18+}	20	738.8	752.1	770.7	713.5	698.9	738.6	752.0	768.2	713.5	698.9
Zr^{38+}	40	1762.7	1811.2	2109.6	1527.5	1408.9	1757.5	1805.8	2053.7	1526.1	1408.9
Nd^{58+}	60	3569.7	3617.0	5372.2	2529.5	2118.6	3513.4	3558.4	4819.9	2524.9	2118.5
Yb^{68+}	70	5123.9	5131.2	8611.2	3158.9	2474.3	4962.2	4964.1	7402.3	3141.4	2474.1
Hg^{78+}	80	7552.7	7470.9	14048.4	3927.9	2828.4	7107.6	7015.8	11586.0	3904.2	2828.0
Th^{88+}	90	11610.2	11356.8	23690.1	4914.3	3184.3	10393.5	10131.7	17769.8	4853.4	3183.7
Fm^{98+}	100	18953.8	18374.9	40922.6	6283.2	3539.0	15608.3	15062.8	28581.3	6105.4	3538.1

[a]Nuclear charge.

He- and Ne-isoelectronic systems, respectively. A Gaussian nucleus model and point nucleus model were used for calculations at each level of approximation.

The magnetic shielding constants calculated for He-isoelectronic systems are summarized in Table I. In Fig. 1, we plot the magnetic shielding constants against the nuclear charge Z. The magnetic shielding constants calculated at all levels of relativistic methods are larger than the corresponding nonrelativistic values. However, the amount of the relativistic correction is quite different at each level of approximations.

By comparing the full relativistic DHF results with the NR results, we can see the contributions of the total relativity to the magnetic shielding constants. In heavy systems of $Z > 70$, the contribution of relativity to the magnetic shielding constant is greater than the nonrelativistic contribution, and a significant relativistic effect can be seen even for the light

FIG. 1. Magnetic shielding constants (ppm) calculated for helium isoelectronic systems with the (a) point nucleus model and (b) Gaussian nucleus model plotted against the nuclear charge Z.

systems of $Z = 20–40$. The magnetic shielding constants calculated with the DHF theory increase exponentially with an increase in Z, whereas those calculated by the NR theory increase almost linearly. This relativistic increase in the magnetic shielding constants of heavy elements is the simplest example of a ''heavy-atom shift of the heavy atom'' (HAHA) effect that was pointed out by Pyykkö and co-workers.[56]

By comparing the QR-0 approximation with the NR results, we can see the relativistic effect on $H^{(0,0)}$ for magnetic shielding constants. This approximation includes the SO interaction and orbital shrinkage due to the SFR term, but does not include the relativistic effect on magnetic interaction. The relativistic effect on $H^{(0,0)}$ is only around 20% of the total relativistic effect at $Z = 100$. The remaining relativistic correction results from the relativistic effect on the magnetic interaction H^{mag}, which has been formulated by the DKH transformation applied to the magnetic field proposed in the preceding section. To study the effects of the first- and second-order DKH transformations, QR-1 and QR-2 calculations were carried out. At the QR-1 level, where the first-order transformation is considered, a mass–velocity correction is taken into account in the R_j term in Eqs. (38) and (45). This effect greatly increases the magnetic shielding constants of the heavy systems. The results clearly show that the HAHA effect dominantly arises from the mass–velocity correction of H^{mag}. However, the relativistic correction in the QR-1 approximation is twice as large as the true correction by the DHF theory. This overestimation of the relativity from the first-order transformation is corrected by including the second-order transformation. The magnetic shielding constants calculated by the QR-2 approximation agree well with the DHF results, with differences of 3% or less.

The relativistic magnetic term H^{mag} takes into account the so-called ''picture change'' effect suggested by Barysz and Sadlej;[41] the change in the operator representation resulting from the DKH (relativistic to quasirelativistic, in general) transformation. Kellö and Sadlej found that the picture change had a pronounced effect on the electric field gradient.[57] Our results are consistent with their findings and confirm the importance of the picture change for the electrostatic and magnetic properties. Generally, the wave function correction through the relativistic effect on $H^{(0,0)}$ significantly affects the total energy of the system and furthermore,
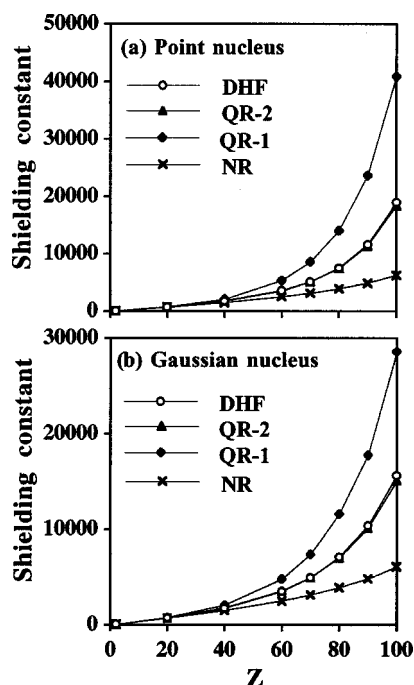
TABLE II. Magnetic shielding constants of Ne isoelectronic systems (ppm).

System	Z^a	Point nucleus model					Gaussian nucleus model				
		DHF	QR			NR	DHF	QR			NR
			Level 2	Level 1	Level 0			Level 2	Level 1	Level 0	
Ne	10	558.1	561.0	565.5	554.2	554.2	558.1	561.0	565.3	554.2	552.3
Ca^{10+}	20	1312.4	1328.0	1373.7	1281.7	1264.0	1312.2	1327.8	1370.6	1281.6	1264.0
Zr^{30+}	40	3123.8	3179.9	3703.7	2839.6	2684.3	3117.9	3174.0	3627.6	2839.2	2684.3
Nd^{50+}	60	5920.3	5975.3	8439.6	4681.2	4104.3	5856.6	5908.4	7856.9	4675.8	4104.1
Yb^{60+}	70	8142.7	8144.2	12870.3	5795.5	4814.1	7957.2	7951.1	11480.7	5779.4	4813.9
Hg^{70+}	80	11479.7	11356.9	20034.9	7134.6	5524.3	10962.8	10824.0	16921.4	7081.1	5523.9
Th^{80+}	90	16915.7	16534.5	32148.7	8870.8	6234.4	15481.8	15076.8	25280.8	8688.7	6233.8
Fm^{90+}	100	26642.1	25732.2	51838.2	11474.8	6944.4	22636.1	21712.1	37087.5	10806.7	6943.4

^{a}Nuclear charge.

the picture change of perturbation operators should be considered for the properties.

The direction of the deviation of the QR-2 result from the DHF result is not constant. For the systems of $Z = 2–70$, the magnetic shielding constants calculated in the QR-2 approximation are larger than those of the DHF theory, whereas for the systems of $Z = 80–100$, the QR2 approximation underestimates the magnetic shielding constants compared to the DHF results. This trend is due to the difference in the effects of H_1^{mag} and H_2^{mag}. The first-order term H_1^{mag} always increases the magnetic shielding constant. The mass correction in H_1^{mag} has a significant effect even in relatively light systems. The second-order term H_2^{mag}, which contains cross terms of the scalar and vector potentials, diminishes the shielding constant. The effect of this term increases with an increase in the nuclear potential. The deviations from the DHF results can be corrected by considering the higher-order DKH transformation.

The calculated magnetic shielding constants of the Ne-isoelectronic systems are summarized in Table II. In Fig. 2, we plot the magnetic shielding constants against the nuclear charge Z. The differences between QR-0 and NR in the Ne-isoelectronic systems are larger than those in He-isoelectronic systems. This difference is 4530 ppm for $Z = 100$ in the Ne-isoelectronic system with a point nucleus model, which is about 65% larger than the value in the He-isoelectronic system. In contrast, the differences between QR-1 and QR-0 in the Ne-isoelectronic systems are not so large compared to those in the He-isoelectronic systems. This difference is 40363 ppm for $Z = 100$ in a Ne-isoelectronic system with a point nucleus model, which is about 14% larger than that in the He-isoelectronic system. The difference between QR-2 and QR-1 is also about 14% greater than that in the He-isoelectronic system. This result indicates that the relativistic correction of the $2s$- and $2p$-orbitals, which is considered by the QR-0 approximation through $H^{(0,0)}$, is also significant compared to that of the $1s$-orbitals. The relativistic effect on H^{mag}, which is considered by the QR-1 and QR-2 approximations, is quite important for the $1s$ electrons, but not so much for the $2s$ and $2p$ electrons, even though there is a large effect on the absolute value. The relativistic effect on H^{mag} arises mainly near the nuclear region and dominantly affects the Fermi contact term. The contribution

of the $2s$ electron to the Fermi contact term is smaller than that of the $1s$ electron, and the contribution of the $2p$ electrons is zero because they have a nodal plane at the nucleus. Thus, the relativistic effects of H^{mag} on the $2s$ and $2p$ electrons are relatively small.

Figure 3 shows the effect of the finite nucleus model. The finite nucleus correction factor ε is defined by $\sigma^g = (1 + \varepsilon)\sigma^p$, where σ^p and σ^g are the magnetic shielding constants of the point nucleus and Gaussian finite nucleus model, respectively. The QR-2 results agree well with the DHF results and the plots of ε in Fig. 3 using both methods almost overlap. With both methods, ε increases exponentially with an increase in Z. A similar trend has been reported in the hyperfine coupling constants of one-electron atoms with large Z values.[44] In the magnetic shielding constant, the finiteness of nuclei dominantly affects the Fermi contact
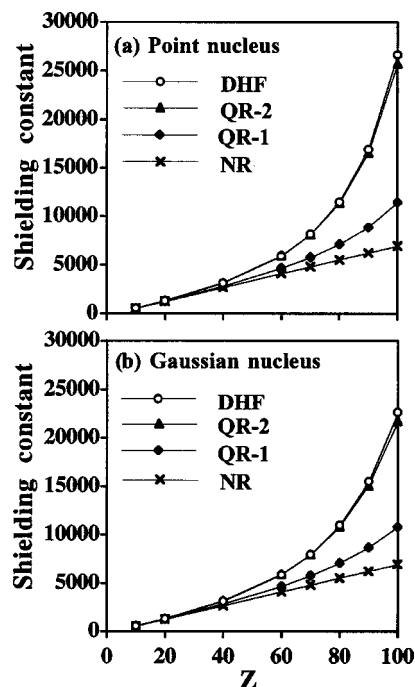
FIG. 2. Magnetic shielding constants (ppm) calculated for neon isoelectronic systems with the (a) point nucleus model and (b) Gaussian nucleus model plotted against the nuclear charge Z.
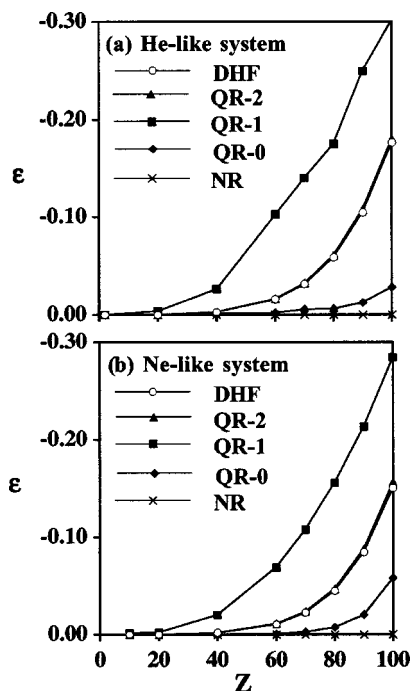
FIG. 3. Finite nucleus correction (see text) plotted against the nuclear charge Z. (a) Helium isoelectronic systems and (b) neon isoelectronic systems.

term. The Fermi contact term originates from the hyperfine coupling of the electron spin-polarization and the nuclear magnetic moment caused by SO interaction and magnetic Zeeman interaction.[10,18] This mechanism is closely related to that of the hyperfine coupling constant. In the NR theory, the Fermi contact term is zero for closed-shell systems because there is no SO interaction. Only the diamagnetic shielding term contributes to the NR magnetic shielding constants and the nucleus model has very little effect. The QR-1 approximation largely overestimates the ε value and the QR-0 approximation underestimates the ε value. Relativistic correction of the magnetic interaction strongly affects the magnetic response of electrons at the nucleus. A finite nucleus effect can not be neglected for the accurate calculation of a large nuclear charge system with a few electrons such as the present models in which $1s$ electrons account for a significant amount of the total magnetic shielding constant. This effect would be less important in many-electron systems in which the valence electrons have a significant contribution.

B. Noble gas atoms

The $9s4p$ Gaussian basis set for Ne, the $12s8p$ set for Ar, the $15s11p6d$ set for Kr, the $19s15p9d$ set for Xe, and the $24s20p13d8f$ set for Rn were used for calculations. The exponent parameters for Ne and Ar were taken from cc-pVDZ sets.[58,59] For Kr, Xe, and Rn, the exponent parameters were taken from Dyall's relativistic double-zeta sets.[60]

The calculated magnetic shielding constants of noble gas atoms are summarized in Table III. By comparing the DHF results with the NR values, we can see the magnitude of the HAHA effect that originates in relativity in heavy atoms. If we consider the point nucleus model, the effect gives an increase of 1500 ppm in the magnetic shielding constant of Xe, and an increase of 9000 ppm in that of Rn. Even with Kr, we cannot neglect the effect of relativity. The magnetic shielding constants calculated with the QR-2 approximation are in good agreement with the DHF values. The differences between the QR-2 results and the DHF results are 1.5% or less. Even though the basis sets used for these calculations are insufficient, and an accurate comparison should be carried out with a complete basis limit, our results suggest that QR-2 is a good approximation of the DHF theory.

The QR-1 approximation overestimates the magnetic shielding constants of heavy elements and QR-0 underestimates. The QR-0 result for Rn with a point nucleus model seem to be adequate compared to the DHF results. However, at the QR-0 approximation, the Gaussian nucleus model gives a decrease of 2385 ppm in the magnetic shielding constant of Rn. In comparison to the DHF and QR-2 values, the effect of the Gaussian nucleus on Rn seems to be too large at the QR-0 approximation.

To provide detailed insight into the magnetic shielding constants of heavy noble gases, the total shielding constant was decomposed into the contributions from each occupied orbital according to Eq. (59). The orbital contributions to the magnetic shielding constants of Xe and Rn are shown in Tables IV and V, respectively. In the magnetic shielding constant of Xe, relativity predominantly affects the inner s- and p-orbitals. In contrast, relativity only slightly affects the contribution of the d-orbital. In comparison to the DHF results, QR-0 underestimates the contribution of the 1s orbital by about 700 ppm and QR-1 overestimates the contribution of the 1s orbital by about 1000 ppm. On the other hand, the QR-0 approximation overestimates the contribution of the outer s-orbitals, particularly that of the 5s-orbital.

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

| System | Z^a | Point nucleus model | | | | | Gaussian nucleus model | | | | |
| | | | QR | | | | | QR | | | |
		DHF	Level 2	Level 1	Level 0	NR	DHF	Level 2	Level 1	Level 0	NR
Ne	10	557.5	560.5	560.3	554.1	552.0	557.5	560.5	560.3	554.1	552.0
Ar	18	1271.8	1284.4	1288.4	1250.6	1233.7	1271.8	1284.4	1288.3	1250.6	1233.7
Kr	36	3572.6	3625.0	3772.9	3367.8	3155.2	3571.6	3624.0	3768.7	3367.7	3154.5
Xe	54	6982.2	7070.1	8176.1	6180.8	5328.2	6957.8	7044.7	7956.7	6166.9	5326.6
Rn	86	19906.1	19959.8	31877.4	18895.1	10728.2	19162.9	19074.6	26888.6	16510.4	10727.1

^{a}Nuclear charge.

TABLE IV. Orbital contribution in the magnetic shielding constant of the Xe atom (ppm).

| | Point nucleus model | | | | | Gaussian nucleus model | | | | |
| | | QR | | | | | QR | | | |
Orbital	DHF	Level 2	Level 1	Level 0	NR	DHF	Level 2	Level 1	Level 0	NR
1s	2882.5	2953.9	3885.7	2182.0	1623.1	2861.6	2932.7	3701.7	2181.6	1621.7
2s	583.7	600.7	719.9	497.8	402.6	580.9	597.8	695.3	497.5	402.4
3s	196.9	206.8	238.6	183.5	151.6	196.3	206.1	232.2	182.4	151.5
4s	75.1	83.3	95.6	91.8	62.4	74.9	83.1	93.3	88.7	62.4
5s	25.9	37.4	47.1	87.5	21.9	25.9	37.2	45.2	78.4	21.9
2p	1413.1	1403.7	1392.5	1364.7	1311.9	14130	1403.7	1392.5	1364.7	1312.0
3p	503.1	487.5	497.2	490.4	474.5	503.1	487.5	497.2	490.4	474.5
4p	194.4	193.1	192.8	190.1	186.0	194.4	193.1	192.8	190.4	186.0
5p	59.8	59.6	59.9	59.4	58.6	59.8	59.6	59.9	59.4	58.6
3d	777.8	774.7	777.0	766.8	766.3	777.8	774.7	777.0	766.8	766.4
4d	270.0	269.3	269.8	266.9	296.3	270.0	269.3	269.8	260.9	269.2
Total	6982.2	7070.1	8176.1	6180.8	5328.2	6957.8	7044.7	7956.7	6166.9	5326.6

In Rn, the relativity affects the contributions of the inner s- and p-orbitals, and is also important for the contribution of the 3d-orbital. Relativity only slightly affects the contribution of the 4f-orbital. Compared to the DHF results, QR-0 underestimates the contribution of the 1s-orbital by about 5000 ppm. This approximation also underestimates the contribution of the 2s-orbital by about 700 ppm. On the other hand, the contributions of the outer 5s- and 6s-orbitals are overestimated by 1000 ppm. The finite nucleus effects on these orbitals are too large compared to the DHF results, and the finite nucleus effects on outer s-orbitals are larger than those on inner orbitals. The QR-0 approximation underestimates the contribution of the 2p-orbital by about 400 ppm and greatly underestimates the contribution of the 6p-orbital. This suggests that the QR-0 approximation cannot correctly treat the orbital response to a magnetic field at the nucleus position. Since the errors from the inner and outer orbitals are cancelled, the total shielding constant happens to be close to the DHF value in case of the point nucleus model.

The QR-2 approximation, which also considers a relativistic effect on H^{mag}, increases the contributions of the inner orbital and diminishes the contributions of the outer s-orbital; thus, the total shielding constant of QR-2 approaches the DHF values. This result clearly shows the importance of the relativistic effect on the magnetic interaction term to the magnetic shielding constants of heavy elements. It is inadequate to consider only the relativistic effect on the wave function. The change in the orbital picture due to DKH transformation significantly changes the magnetic response of orbitals. An approximation such as QR-0, in which the picture change effect on the magnetic perturbation is neglected, introduces errors not only to core electrons but also to valence electrons. Using the QR-0 approximation for theoretical studies of the chemical shifts of heavy elements will lead to serious error because the valence electrons play important roles in the chemical shifts of molecules. A theory that considers the picture changes of H^{mag} and $H^{(0,0)}$ equally

TABLE V. Orbital contribution in the magnetic shielding constant of the Rn atom (ppm).

| | Point nucleus model | | | | | Gaussian nucleus model | | | | |
| | | QR | | | | | QR | | | |
Orbital	DHF	Level 2	Level 1	Level 0	NR	DHF	Level 2	Level 1	Level 0	NR
1s	9566.6	9491.2	18827.7	4445.0	3033.3	8975.1	8810.5	14945.4	4417.5	3032.3
2s	1856.2	1929.1	3420.0	1103.0	717.7	1753.8	1806.7	2765.5	1075.8	717.6
3s	590.4	645.9	1081.6	611.5	281.2	563.7	610.8	891.6	515.1	281.1
4s	232.0	293.0	494.5	720.8	125.5	223.3	277.9	409.1	494.9	125.5
5s	86.4	168.6	309.6	1368.5	54.8	84.0	158.8	251.4	849.8	54.8
6s	48.3	250.7	538.0	3813.0	20.8	46.0	230.8	419.3	2309.4	20.8
2p	2792.5	2628.5	2572.4	2403.0	2154.2	2786.4	2625.3	2572.0	2404.4	2154.2
3p	1029.9	913.4	967.2	923.8	837.8	1027.7	913.8	967.1	924.5	837.8
4p	436.5	416.6	416.0	393.8	367.5	435.7	416.4	416.0	394.6	367.5
5p	174.2	163.7	167.6	153.6	154.3	174.0	163.9	167.7	155.4	154.3
6p	52.5	48.6	49.8	5.9	52.8	52.5	49.0	50.2	15.8	52.8
3d	1461.1	1439.3	1452.2	1412.6	1383.3	1461.1	1439.3	1454.2	1412.6	1383.3
4d	611.3	603.8	608.4	592.1	582.6	611.3	603.9	608.4	592.1	582.6
5d	221.3	219.4	220.0	215.5	217.6	221.3	219.4	220.1	215.6	217.6
4f	747.1	748.1	750.6	732.9	744.8	747.2	748.1	750.7	732.9	744.8
Total	19906.1	19959.8	31877.4	18895.1	10728.2	19162.9	19074.6	26888.6	16510.4	10727.1

TABLE VI. Computational time and SCF dimension for DHF and quasire-lativistic (QR-2) calculations.

System	Method	CPU seconds	Dimension	Iteration
Xe	DHF	4080	776	20
	QR-2	862	218	24
Rn	DHF	63900	1492	24
	QR-2	10300	410	32

is essential for studying the chemical shifts of heavy elements.

The QR-2 approximation greatly improves the magnetic shielding constants and their orbital contributions in heavy elements. However, in Rn, the contributions of the $5s$- and $6s$-orbitals still overshoot the DHF results. One reason for this difference may be the lack of the higher-order relativistic effect: the third- or higher-order DKH transformation may describe the effect.[61,62] The basis set incompleteness error may also be a reason. The basis sets used in the calculations for noble gases are double-zeta quality, and the basis set-dependence is different between the QR approximation and the DHF; the results of different theories should be compared in a complete basis limit. Calculations using a large even-tempered basis should be performed for a more reliable comparison. However, such a large-scale DHF calculation for magnetic shielding constants is still very difficult at present.

At the end of this section, we refer to the computation time. The calculations were performed on a COMPAQ XP1000 workstation. The CPU times (in seconds) and SCF dimensions (dimension of the Fock matrix) are summarized in Table VI. The dimension of the QR calculation is the same as the large-component dimension of the corresponding DHF calculation. Any symmetry reduction is not used. The convergence of QR method may be accelerated by using extrapolation method; the DIIS extrapolation[63] was used in DHF calculation to accelerate the convergence.

IV. CONCLUSIONS

We have proposed a quasirelativistic theory for calculating NMR magnetic shielding constants. The present theory is based on the second-order Douglas–Kroll transformation that was extended to include the magnetic vector potential. The present theory expands the Hamiltonian in terms of the electromagnetic potential $V + \mathbf{A}$, instead of V. The resulting Hamiltonian includes both linear and quadratic terms in the external magnetic field; it is suitable for calculations of magnetic properties. The present formulation of the DKH transformation including the magnetic field is combined with the matrix-transformation method developed by Hess *et al.*, the GUHF-SCF method, and the finite perturbation method together with the Hellmann–Feynman theorem, and applied to the calculations of the nuclear magnetic shielding constants. We have obtained the various terms as the origins of the nuclear shielding constants in a change of picture framework; their physical meanings are of considerable interests.

We applied the present theory to the magnetic shielding constants of helium-isoelectronic ions, neon-isoelectronic ions, and noble gas atoms. We also performed the calcula-tions using the four-component Dirac–Hartree–Fock theory, the nonrelativistic theory, and the DKH transformation of the lower level in which the magnetic interaction was approximated at the nonrelativistic level. The results of the present calculations may be summarized as follows:

(1) The results of the present two-component quasi relativistic theory compare well with those of the four-component Dirac–Hartree–Fock theory; the differences were within only 3%.

(2) In the helium isoelectronic systems of $Z > 70$, the contribution of the relativity to the magnetic shielding constant is larger than the nonrelativistic contribution. The relativistic wave function correction arising from the relativistic terms in $H^{(0,0)}$ is not the dominant origin of this relativistic increase in the magnetic shielding constants. Instead, the dominant origin of this relativistic increase is the relativistic correction to the magnetic interaction operator, H^{mag}. The effect of the so-called "picture change" is quite important for the magnetic shielding constant of the heavy nucleus.

(3) In the neon isoelectronic systems, the relativistic correction of H^{mag} mainly affects the $1s$ electrons. The effects of relativistic H^{mag} on the $2s$ and $2p$ electrons are relatively small.

(4) The finite nucleus effect on magnetic shielding constants was studied using the Gaussian nucleus model. The present theory reproduces well the DHF results. The effect on helium isoelectronic systems of $Z > 90$ is 10% or more. The finite nucleus model has almost no effect in the nonrelativistic theory.

(5) The present theory can well reproduce the relativistic increase in the magnetic shielding constants of noble gas atoms. The differences between the present theory and the DHF results are $< 1.5\%$. The change in the orbital picture due to the DKH transformation affects the valence orbitals as well as the cores.

The present theory provides a foundation for the relativistic study of molecular magnetic properties. Adaptation of the present theory to other magnetic properties such as spin–spin coupling constant and hyperfine structure should be straightforward with only some modifications on the one-electron matrix elements according to the DKH transformation. To apply this method to the study of molecular NMR chemical shifts, we need a gauge-origin-independent theory. The electron correlation effects may also be important. In a subsequent paper,[64] London's gauge-including atomic orbitals (GIAOs) are incorporated into the present DKH transformation, and the resultant theory is applied to the calculations of the NMR chemical shifts of molecular systems. An inclusion of the electron correlation effect, using the energy gradient method for the many-body theory developed in the nonrelativistic framework, is also straightforward because the present theory keeps the framework of the nonrelativistic theory.

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