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The Douglas−Kroll−Hess Approach

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1. INTRODUCTION

It is common knowledge that relativistic effects are important in the chemistry of heavy elements. As a result, polyatomic systems that contain heavy elements are involved in a variety of interesting chemical and physical phenomena. The consideration of relativistic effects is essential for the theoretical description of the molecular structures, chemical activities, and properties of heavy-element systems.[1] The continuing development of relativistic molecular orbital (MO) theory is reaching rows of the periodic table that are nearly impossible to treat with nonrelativistic approaches. To theoretically treat the relativistic effect, the Dirac equation is usually used instead of the nonrelativistic Schrödinger equation. The one-electron Dirac Hamiltonian with an external potential is written as

$$\mathbf{H}_{\mathrm{D}} = c\boldsymbol{\alpha}\cdot\mathbf{p} + \boldsymbol{\beta}c^2 + V \qquad (1)$$

where the constant c is the speed of light, V is the external potential, and $\mathbf{p}$ $(= -i\nabla)$ is the momentum operator. Hereafter, atomic units are used (e.g., $c \cong 137.036$). The 4×4 Dirac matrices $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ in eq 1 are given by

$$\alpha_t \equiv \begin{pmatrix} 0_2 & \boldsymbol{\sigma}_t \\ \boldsymbol{\sigma}_t & 0_2 \end{pmatrix}, t = (x, y, z), \quad \boldsymbol{\beta} \equiv \begin{pmatrix} \mathbf{I}_2 & 0_2 \\ 0_2 & -\mathbf{I}_2 \end{pmatrix} \qquad (2)$$

where $\boldsymbol{\sigma}_t$ represents 2×2 Pauli spin matrices comprising

$$\boldsymbol{\sigma}_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (3)$$

Since the Dirac equation is only valid for a one-electron system, the one-electron Dirac Hamiltonian has to be extended to a many-electron Hamiltonian to treat the chemically interesting

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many-electron systems. A straightforward way to construct the relativistic many-electron Hamiltonian is to augment the one-electron Dirac operator, eq 1, with a Coulomb or Breit (or its approximate Gaunt) operator or both as a two-electron term to yield Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) Hamiltonians. Recently, the Hartree–Fock (HF) and the Kohn–Sham (KS) methods, which use the DC(B) Hamiltonians, have become familiar and powerful relativistic approaches as efficient computational algorithms are developed.[2−8]

However, despite recent implementations of an efficient algorithm for a four-component relativistic approach, the DC(B) equation with four-component spinors composed of large (upper) and small (lower) components still demands intensive computational efforts to solve and is difficult to apply to large-sized molecules. Chemists' attentions are devoted to the electronic solution even though the four-component calculations provide eigenstates for not only the electronic state but also the negative-energy eigenstate. As an alternative to solving the four-component relativistic equation, several two-component quasi-relativistic approximations have been proposed and applied to chemically interesting systems containing heavy elements. The motivation of the two-component relativistic approximation is to obtain the electronic state without explicitly treating the negative-energy solution Since the relativistic effects that appear in the electronic state are closely related to the negative-energy state in four-component language, the primary problem of the two-component relativistic approach is the effective retrieval of those effects that are lost by neglecting the negative-energy solution. Therefore, an approximate relativistic approach should include the following features:

(1) It should be accurate enough to give a result close to that of the one- and many-electron four-component approaches.
(2) It should be efficient and effective when applied to polyatomic molecular systems containing heavy elements.
(3) It should be well balanced in that it is able to describe molecular systems that contain a wide variety of atoms in the periodic table with the same quality.
(4) It should be variationally stable in order to avoid variational collapse in the sense that at least the nonrelativistic limit is correctly determined.
(5) It should be variational and nonperturbative in order to evaluate various energy values and one-electron properties.

The Douglas–Kroll (DK) approach decouples the large and small components of the Dirac spinors in the presence of an external potential by repeating several unitary transformations. The DK transformation is a variant of the Foldy–Wouthuysen (FW) transformation[9] and adopts the external potential, V, as an expansion parameter instead of the speed of light, c, that is using in the FW transformation. Several excellent comprehensive reviews of the DK method have appeared so far.[10−13] The DK method satisfies almost all of the criteria mentioned above: it avoids the high singularity in the FW transformation by adopting the external potential as an expansion parameter resulting in the DK Hamiltonian having variational stability. In contrast to the Breit–Pauli (BP) Hamiltonian, the DK Hamiltonian can be applied to variational calculations. Criterion 1 is also satisfied by the higher-order DK method for one- and many-electron systems. In the present review, we will describe both the theoretical and practical aspects of the DK approach.

2. THEORETICAL ASPECTS

2.1. Douglas–Kroll Transformation

The one-electron Dirac equation including the Dirac Hamiltonian, eq 1, is given by

$$\mathbf{H}_{\mathrm{D}}\begin{pmatrix}\Psi^{\mathrm{L}}\\ \Psi^{\mathrm{S}}\end{pmatrix} = \begin{pmatrix}V+c^2 & c\boldsymbol{\sigma}\cdot\mathbf{p}\\ c\boldsymbol{\sigma}\cdot\mathbf{p} & V-c^2\end{pmatrix}\begin{pmatrix}\Psi^{\mathrm{L}}\\ \Psi^{\mathrm{S}}\end{pmatrix} = E\begin{pmatrix}\Psi^{\mathrm{L}}\\ \Psi^{\mathrm{S}}\end{pmatrix} \quad (4)$$

where Ψ^{L} and Ψ^{S} are the large and small components, respectively, and E is the energy of a particle. The two-component relativistic approach can be obtained by block-diagonalization of the Dirac Hamiltonian with a suitable unitary operator, $\mathbf{U}$, that removes the off-diagonal blocks as follows:

$$\mathbf{U}\mathbf{H}_{\mathrm{D}}\mathbf{U}^{\dagger} = \begin{pmatrix}H_{+} & 0\\ 0 & H_{-}\end{pmatrix} \quad (5)$$

The eigenvalues of H_+ and H_- form the positive- and negative-energy branches of the full Dirac spectrum, respectively. Consequently, the two-component equation can be solved as

$$H_{+}\Phi = E\Phi \quad (6)$$

which gives the eigenvalues for the electronic solution of the original Dirac equation. Douglas and Kroll[14] proposed a procedure to decompose the overall transformation, $\mathbf{U}$, into a sequence of simpler unitary transformations,

$$\mathbf{U} = \ldots\mathbf{U}_3\mathbf{U}_2\mathbf{U}_1\mathbf{U}_0 \quad (7)$$

The first step in the DK transformation is a free-particle FW transformation in momentum space because it is difficult to obtain an analytical form of the unitary operator, $\mathbf{U}$, except in the free particle case. Using the free-particle eigensolutions of the Dirac Hamiltonian associated with the positive-energy eigenvalues, the unitary operator in the free-particle FW transformation is given as

$$\mathbf{U}_0 = \begin{pmatrix}A & AR\\ -AR & A\end{pmatrix} \quad (8)$$

where A and R are kinematical operators defined by

$$A = \left(\frac{E_0+c^2}{2E_0}\right)^{1/2} \quad (9)$$

$$R = \frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E_0+c^2} \quad (10)$$

with

$$E_0 = (p^2c^2+c^4)^{1/2} \quad (11)$$

If Ω is an eigenfunction of p^2 with an eigenvalue of κ^2, then

$$E_0|\Omega\rangle = (\kappa^2c^2+c^4)^{1/2}|\Omega\rangle = \varepsilon(\kappa^2)|\Omega\rangle \quad (12)$$

$$A|\Omega\rangle = \left[\frac{\varepsilon(\kappa^2) + c^2}{2\varepsilon(\kappa^2)}\right]^{1/2} |\Omega\rangle \quad (13)$$

and so forth. The application of the unitary operator, eq 8, to the Dirac Hamiltonian in an external field, $\mathbf{H}_D$, gives

$$\mathbf{H}_1 = \mathbf{U}_0 \mathbf{H}_D \mathbf{U}_0^{\dagger} = \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{O}_1 \quad (14)$$

where

$$\mathbf{E}_0 = \begin{pmatrix} E_0 & 0 \\ 0 & -E_0 \end{pmatrix} \quad (15)$$

$$\mathbf{E}_1 = \begin{pmatrix} E_1 & 0 \\ 0 & E_1 \end{pmatrix} \quad (16)$$

$$\mathbf{O}_1 = \begin{pmatrix} 0 & O_1 \\ -O_1 & 0 \end{pmatrix} \quad (17)$$

with

$$E_1 = AVA + ARVRA \quad (18)$$

$$O_1 = ARVA - AVRA \quad (19)$$

The $\mathbf{E}_0$ and $\mathbf{E}_1$ blocks are even (i.e., only diagonal blocks) and $\mathbf{O}_1$ is odd; only off-diagonal blocks are nonzero. The resulting Hamiltonian yields the free-particle FW Hamiltonian, which is also referred to as the no-pair Hamiltonian[15−17] or the first-order DK (DK1) Hamiltonian in the context of the DK approximation. The resultant DK Hamiltonian still maintains four-component formalism. The reduction from four-component formalism to the electronic two-component formalism is carried out by keeping the upper diagonal block of all operators. In order to correspond to the nonrelativistic limit, the resulting two-component Hamiltonian is shifted by $-2c^2$. Therefore, the DK1 Hamiltonian in the two-component form is given as

$$H_{\mathrm{DK1}} = E_0 - c^2 + E_1 \quad (20)$$

Douglas and Kroll suggested that it is possible to remove odd terms of arbitrary orders in the external potential through successive unitary transformations as follows:

$$\mathbf{U}_n = (1 + \mathbf{W}_n{}^2)^{1/2} + \mathbf{W}_n \quad (21)$$

where

$$\mathbf{W}_n = -\mathbf{W}_n^{\dagger} = \begin{pmatrix} 0 & W_n \\ -W_n^{\dagger} & 0 \end{pmatrix} \quad (22)$$

Here, W_n is an anti-Hermitian operator of the nth order in V. The DK transformation correct to second order in the external potential has been extensively studied by Hess and co-workers[18,19] and has become one of the most familiar quasi-relativistic approaches. The Douglas−Kroll−Hess (DKH) method is another frequently used term for the DK method in honor of the pioneering work of Hess. The second-order DK (DK2) Hamiltonian in the two-component form is given as

$$H_{\mathrm{DK2}} = H_{\mathrm{DK1}} - \frac{1}{2}[W_1, [W_1, E_0]_+]_+ \quad (23)$$

where $[a,b]_+$ denotes the anticommutator and W_1 is determined by

$$W_1 E_0 + E_0 W_1 = O_1 \quad (24)$$

Equation 24 cannot be directly inverted to give W_1; however, the matrix elements of W_1 between two eigenfunctions, Ω_i and Ω_j, of p^2 with eigenvalues, κ_i^2 and κ_j^2, are

$$\langle \Omega_i | W_1 | \Omega_j \rangle = \frac{\langle \Omega_i | O_1 | \Omega_j \rangle}{\varepsilon(\kappa_i^2) + \varepsilon(\kappa_j^2)} \quad (25)$$

since Ω_i and Ω_j are eigenfunctions of E_0 with eigenvalues of $\varepsilon(\kappa_i^2)$ and $\varepsilon(\kappa_j^2)$, respectively, which are defined by eq 12. Hess and co-workers reported various DK2 applications. In addition to the atomic and molecular systems that contain heavy elements, the DK2 method was applied to crystalline systems with the crystal orbital approach under periodic boundary conditions.[20] Their applications include the calculation of spectroscopic constants[21−26] such as molecular geometries, frequencies, and dissociation energies, fine structure splittings,[27,28] electronic excitation energies,[29−38] laser-induced chemiluminescence,[39,40] ionization potentials, and electron affinities,[41] as well as electrical properties such as dipole moments,[42] dynamic multipole polarizabilities, dispersion coefficients,[43−45] and nuclear quadrupole coupling tensors.[46,47] Independent of the work in the Hess group, the DK2 approach was implemented in the framework of the linear combination of Gaussian-type orbitals (LCGTO) approach to density functional theory (DFT) by the Rösch group.[48] Rösch and co-workers applied their LCGTO−DFT approach using the DK2 method to the electronic structure investigations of large molecular systems[49−51] and diatomic molecules.[52−56]

2.2. Higher-Order/Arbitrary-Order Douglas−Kroll Hamiltonians

For ordinary chemical problems, the DK2 approach gives satisfactory results. A numerical analysis by Molzberger and Schwarz[57] shows that the DK2 method recovers energy up to the order of $Z^6\alpha^4$ ($\alpha = 1/c$) to a large extent and also includes a significant part of the higher-order terms. However, the DK2 approach does not completely recover the stabilizing higher-order energy contributions, as shown in Figure 1. The straightforward way to include higher-order relativistic effects is to apply further unitary transformations.

Nakajima and Hirao[58,59] proposed a higher-order DK method based on exponential parametrization of the unitary transformation,

$$\mathbf{U}_n = \exp(\mathbf{W}_n) \quad (26)$$

This exponential-type unitary operator leads to more compact formulas than the unitary operator defined by Douglas and Kroll. The third-order DK (DK3) Hamiltonians in the two-component form are given as

$$H_{\mathrm{DK3}} = H_{\mathrm{DK2}} + \frac{1}{2}[W_1, [W_1, E_1]] \quad (27)$$

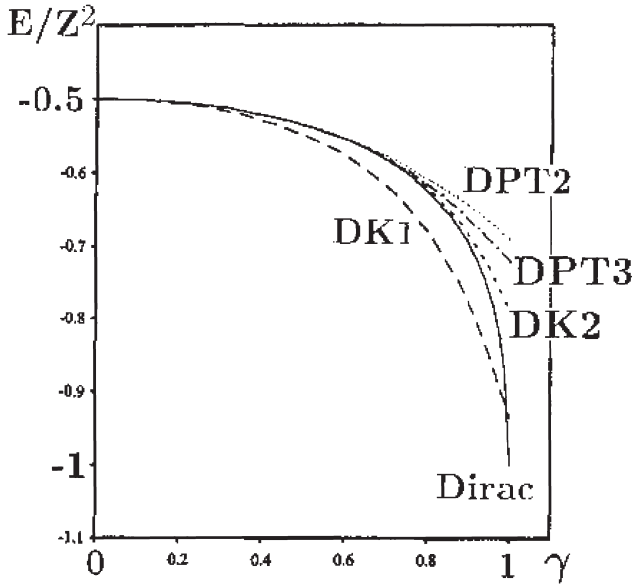


Figure 1. E/Z^2 versus $\gamma = Z\alpha$ for hydrogen-like ions.Reprinted with permission from ref 57. Copyright 1996 Springer.

where $[a,b]$ denotes the commutator. The DK3 method has been applied in various studies by Nakajima and co-workers to the electronic structures and spectroscopic properties of ground and excited states including spectroscopic constants,[60−62] excitation energies,[63] potential energy curves in ground and excited states,[64] photoelectron spectra,[65] and electric properties such as polarizabilities and hyperpolarizabilities.[66] Thereafter, Wolf et al.[67] introduced a generalized DK method with Hamiltonians up to the fifth order by adapting a power series expansion, as follows:

$$\mathbf{U}_n = f(\mathbf{W}_n) = \sum_{k=0}^{\infty} a_k \mathbf{W}_n{}^k \tag{28}$$

where the unitary condition, $f(\mathbf{W}_n)f(-\mathbf{W}_n) = 1$, imposes constraints on the coefficients a_k. Without a loss of generality, the condition $a_0 = a_1 = 1$ can be imposed, from which it follows that $a_2 = {}^1/_2$. Wolf et al. found that the DK Hamiltonian is independent of the chosen parametrization of the unitary transformation up to the fourth order; higher-order DK Hamiltonians depend slightly on the chosen parametrization of the unitary transformations. van Wüllen[68,69] extended the DK transformation to the sixth order (DK6) and discussed the differences among the various choices of parametrization. His numerical findings show that the fifth- and sixth-order DK results are quite insensitive to the parametrization for the unitary transformation steps involved in the DK procedure. Later, the DK protocol was extended to arbitrary-order DK Hamiltonians by Reiher and Wolf.[70−73] The form of the nth transformed four-component Hamiltonian is generally given by

$$\mathbf{H}_n = \sum_{i=0}^{2n+1} \mathbf{E}_i + \sum_{i\,\geq\, 2n+2} \mathbf{E}_i^{(n)} + \sum_{i\,\geq\, n+1} \mathbf{O}_i^{(n)} \tag{29}$$

There is no superscript in the even terms of an order of no more than $2n + 1$ because they remain unchanged in the following unitary transforms. This is the $2n + 1$ rule that was first mentioned in ref 58. The kth order $\mathbf{W}_k$ operator is obtained by solving

$$[\mathbf{W}_k, \mathbf{E}_0] + \mathbf{O}_k^{(k-1)} = 0. \tag{30}$$

The matrix elements of its two-component part can be evaluated by

$$\langle \Omega_i | W_k | \Omega_j \rangle = \frac{\langle \Omega_i | O_k^{(k-1)} | \Omega_j \rangle}{\varepsilon(\kappa_i{}^2) + \varepsilon(\kappa_j{}^2)} \tag{31}$$

The block structures of these four-component operators are

$$\mathbf{E}_k = \begin{pmatrix} E_k & 0 \\ 0 & (-1)^{k+1} E_k \end{pmatrix} \tag{32}$$

$$\mathbf{O}_k = \begin{pmatrix} 0 & O_k \\ (-1)^k O_k & 0 \end{pmatrix} \tag{33}$$

$$\mathbf{W}_k = \begin{pmatrix} 0 & W_k \\ (-1)^{k+1} W_k & 0 \end{pmatrix} \tag{34}$$

The two-component DK Hamiltonian truncated at the nth order is finally given by

$$H_{\mathrm{DK}k} = \sum_{i=0}^{k} E_i \tag{35}$$

Due to the form of the transformed four-component operator (eq 29), it is sufficient to calculate the nth order DK Hamiltonian with only $[n/2]$ unitary transformations, where $[a]$ denotes the integer part of number a. Reiher and co-workers applied the higher-order DK method to various properties including spectroscopic constants,[74] potential energy curves in ground and excited states,[75,76] electric field gradients,[77,78] nuclear quadrupole moments,[79] and electron densities at an atomic nucleus.[80]

There is significant freedom for the selection of parametrizations of the unitary transformation in the DK method. It is noted that all choices converge to the same spectrum although this does not mean that the various DK Hamiltonians are the same; therefore, the truncation of such an expansion can yield different spectra. As already mentioned, van Wüllen[68] has shown that the DK5 and DK6 results are almost independent of the selections for parametrization in the DK transformation. Recently, Peng and Hirao[81] also found that differences in the various parametrizations of the unitary transformation are negligible and that various choices converge to the same eigenvalues in the total energy. Table 1 indicates the ground-state energies for one-electron hydrogen-like atoms with $Z = 80$ computed by the DK methods employing various parametrizations of the unitary transformation. In this table, five types of parametrization are considered: (i) exponential parametrization, eq 26, (ii) the traditional square-root form, eq 28, (iii) the McWeeny choice, (iv) the Cayley-type expression, and (v) optimal unitary parametrization, eq 21. At this accuracy, the energies do not converge up to DK20; however, the various parametrizations converge to an accuracy of 12 digits. Consequently, they concluded that exponential parametrization is recommended due to its simple formulation and lower computational cost.

Table 1. One-Electron ($Z = 80$) Ground-State Energies for the DK Scheme Employing Various Parameterizations of the Unitary Transformation[a]

	exp	sqrt-exp	McW-exp	CA-exp	opt-exp
DK2	−3523.324 89				
DK3	−3533.119 62				
DK4	−3531.708 61				
DK5	−3532.462 660 97	0.009 351 55	−0.0187 143 9	−0.004 677 19	0.001 134 73
DK6	−3532.101 216 73	−0.001 297 20	0.002 592 91	0.000 648 41	−0.000 157 35
DK7	−3532.225 419 34	0.000 071 46	0.000 021 47	−0.000 012 22	0.000 004 92
DK8	−3532.177 057 38	0.000 038 88	−0.000 113 98	−0.000 024 58	0.000 005 53
DK9	−3532.200 248 65	0.000 005 71	0.000 007 09	−0.000 000 07	0.000 000 24
DK10	−3532.188 489 71	−0.000 008 28	0.000 016 86	0.000 004 10	−0.000 000 99
DK11	−3532.193 768 23	0.000 000 10	−0.000 000 21	−0.000 000 04	0.000 000 01
DK12	−3532.191 321 15	0.000 000 71	−0.000 001 50	−0.000 000 37	0.000 000 09
DK13	−3532.192 566 62	0.000 000 14	−0.000 000 30	−0.000 000 07	0.001 134 73
DK14	−3532.191 909 97	−0.000 000 25	0.000 000 50	0.000 000 12	0.000 000 02
DK15	−3532.192 234 41	0.000 000 02	−0.000 000 04	−0.000 000 01	−0.000 000 03
DK16	−3532.192 072 64	0.000 000 02	−0.000 000 05	−0.000 000 01	0.000 000 00
DK18	−3532.192 111 88	−0.000 000 01	0.000 000 03	0.000 000 01	0.000 000 00
DK19	−3532.192 135 64	0.000 000 00	0.000 000 00	0.000 000 00	0.000 000 00
DK20	−3532.192 123 33	0.000 000 00	0.000 000 00	0.000 000 00	0.000 000 00

[a] All results are in atomic (hartree) units and are obtained with an even-tempered Gaussian basis set of 50 exponents. DK2−DK4 and DK5−DK20 results are taken from refs 68 and 81, respectively.

2.3. Related Two-Component Approaches

Recently, the interest of many quantum chemists has been devoted to the calculation and treatment of the electronic structures of polyatomic systems that include heavy elements. However, even now, the DC(B) equation with four-component spinors demands intensive computational efforts to solve, and its applications are currently limited to small- to medium-size molecular systems. In addition to the DK method, to improve efficiency and cost-effectiveness, several quasi-relativistic approximations have been proposed that ignore the relativistic correction to the electron−electron or the spin−orbit interactions. Here, we will briefly introduce several quasi-relativistic approaches other than the DK method.

2.3.1. Breit−Pauli Approximation. From eq 4, the Schrödinger−Pauli equation including only the large components is obtained as

$$\left[V + (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{2c^2 - (V - E)}(\boldsymbol{\sigma}\cdot\mathbf{p})\right]\Psi^{\mathrm{L}} = E\Psi^{\mathrm{L}} \qquad (36)$$

with the normalization condition of

$$\langle\Psi^{\mathrm{L}}|1 + X^{\dagger}X|\Psi^{\mathrm{L}}\rangle = 1 \qquad (37)$$

where the X operator is defined by

$$X = \frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{2c^2 - (V - E)}. \qquad (38)$$

Note that no approximation has been made so far. The Breit−Pauli (BP) approximation[82] is introduced by expanding the inverse operators in the Schrödinger−Pauli equation in powers of $(V - E)/(2c^2)$ and ignoring the higher-order terms. Alternatively, the BP approximation can be obtained by truncating the Taylor expansion of the FW-transformed Dirac Hamiltonian up to the $(p/c)^2$ term. The one-electron BP Hamiltonian for the Coulomb potential $V = Z\mathbf{r}/r^3$ is represented by

$$H_{\mathrm{BP}} = T + V - \frac{\mathbf{p}^4}{8c^2} + \frac{Z\delta(r)}{8c^2} + \frac{Z\mathbf{s}\cdot\mathbf{l}}{2c^2r^3} \qquad (39)$$

where $\mathbf{r} \times \mathbf{p} = \mathbf{l}$ and $\boldsymbol{\sigma} = 2\mathbf{s}$ and the T operator is the nonrelativistic kinetic energy. The BP equation has the well-known mass-velocity, Darwin, and spin−orbit operators. Although the BP equation gives reasonable results in the first-order perturbation calculation, it cannot be used in the variational treatment.

2.3.2. Regular Approximation. One of the shortcomings of the BP approach is that the expansion in $(p/c)^2$ is not justified when the electronic momentum is too large, for example, for a Coulomb-like potential. The zeroth-order regular approximation (ZORA) avoids this disadvantage by expanding $E/(2c^2 - V)$ up to the first order so that the ZORA Hamiltonian is variationally stable. The ZORA Hamiltonian was first derived by Chang et al. in 1986[83] and later rediscovered as an approximation to the FW transformation by van Lenthe et al.[84−86] The ZORA Hamiltonian of one electron in an external potential V is given by

$$H_{\mathrm{ZORA}} = V + (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{2c^2 - V}(\boldsymbol{\sigma}\cdot\mathbf{p}) \qquad (40)$$

The higher-order RA Hamiltonians such as the first-order RA (FORA) have been derived; however, they cannot be used variationally because of the higher-order derivatives. Instead, starting from an un-normalized FW transformation, Dyall and van Lenthe[87] introduced the infinite-order RA (IORA) equation,

$$H_{\mathrm{ZORA}}\Phi_{\mathrm{IORA}} = E_{\mathrm{IORA}}(1 + X_0^{\dagger}X_0)\Phi_{\mathrm{IORA}} \qquad (41)$$

with

$$X_0 = \frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{2c^2 - V} \qquad (42)$$

The IORA equation corresponds to the ZORA equation with a modified metric operator. The numerical results using the IORA method are considerably improved over those obtained using ZORA and are superior to those of FORA for a many-electron system. The RA approach has the advantage of being easier to implement than the DK approach because the RA Hamiltonians are simple and are evaluated numerically in direct space. One of the disadvantages of the ZORA and IORA methods is an incorrect dependence of the energy eigenvalues on the choice of gauge in the electrostatic potential.

2.3.3. Relativistic Scheme by Eliminating Small Components. It is difficult to solve the Schrödinger−Pauli eq 36 with the normalization condition (eq 37) since eq 36 has both energy and potential in the denominator. One appropriate approximation is *the relativistic substitutive correction*, which involves the replacement of the $E - V$ in the denominator by classical relativistic kinetic energy,

$$T_{\mathrm{R}} = (c^4 + p^2c^2)^{1/2} - c^2 \tag{43}$$

The relativistic approach based on this approximation is referred to as the relativistic scheme by eliminating small components (RESC).[88−91] The resulting RESC Hamiltonian, H_{RESC}, can be separated into spin-free (sf) and spin-dependent (sd) parts, as follows:

$$H_{\mathrm{RESC}} = H_{\mathrm{RESC}}^{\mathrm{sf}} + H_{\mathrm{RESC}}^{\mathrm{sd}} \tag{44}$$

where

$$H_{\mathrm{RESC}}^{\mathrm{sf}} = T_{\mathrm{R}} + OQ\mathbf{p}\cdot V\mathbf{p}QO^{-1} + 2cOQ^{1/2}VQ^{1/2}O^{-1} \tag{45}$$

$$H_{\mathrm{RESC}}^{\mathrm{sd}} = iOQ\boldsymbol{\sigma}\cdot(\mathbf{p}V)\times\mathbf{p}QO^{-1} \tag{46}$$

Here, the O and Q operators are defined by

$$O = \frac{1}{E_0 + c^2}\left[1 + \frac{p^2c^2}{(E_0 + c^2)^2}\right]^{1/2} \tag{47}$$

$$Q = \frac{c}{E_0 + c^2} \tag{48}$$

For practical calculations, H_{RESC} is symmetrized to be Hermitian for mathematical convenience instead of due to physical significance. It is known that the RESC method works well for a number of systems[92−95] and gives similar results for chemical properties as the DK method. However, very large exponents in the basis set can lead to variational collapse in a low-order RESC approximation, which includes only the lowest truncation of the O operator.

2.3.4. Direct Perturbation Theory. To separate the positive- and negative-energy eigenstates, the direct perturbation theory (DPT) was originally proposed by Rutkowski[96,97] and later developed by Kutzelnigg.[98,99] In DPT, the bispinor in the Dirac equation,

$$\Psi = \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix} \tag{49}$$

is replaced by the modified bispinor,

$$\tilde{\Psi} = \begin{pmatrix} \Psi^{\mathrm{L}} \\ \tilde{\Psi}^{\mathrm{S}} \end{pmatrix} = \begin{pmatrix} \Psi^{\mathrm{L}} \\ c\Psi^{\mathrm{S}} \end{pmatrix} \tag{50}$$

This defines the modified Dirac equation, which is shifted by $-c^2$,

$$\left[\mathbf{D}^{(0)} + \frac{1}{c^2}\mathbf{D}^{(2)}\right]\tilde{\Psi} = E\left[\mathbf{S}^{(0)} + \frac{1}{c^2}\mathbf{S}^{(2)}\right]\tilde{\Psi} \tag{51}$$

where

$$\mathbf{D}^{(0)} = \begin{pmatrix} V & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & -2 \end{pmatrix} \tag{52}$$

$$\mathbf{D}^{(2)} = \begin{pmatrix} 0 & 0 \\ 0 & V \end{pmatrix} \tag{53}$$

$$\mathbf{S}^{(0)} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{54}$$

$$\mathbf{S}^{(2)} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{55}$$

The zeroth-order equation is the Lévy−Leblond equation,[100]

$$\mathbf{D}^{(0)}\Psi^{(0)} = E^{(0)}\mathbf{S}^{(0)}\Psi^{(0)} \tag{56}$$

which is equivalent to the nonrelativistic Schrödinger equation. To derive the high-order corrections in DPT, the perturbation parameter is chosen to be $1/c$ and the expansion is performed in even powers. The lowest-order relativistic correction to the energy is given by

$$\begin{aligned} E^{(2)} &= \langle\Psi^{(0)}|\mathbf{D}^{(2)} - E^{(0)}\mathbf{S}^{(2)}|\Psi^{(0)}\rangle \\ &= \langle\Psi^{\mathrm{S}(0)}|V - E^{(0)}|\Psi^{\mathrm{S}(0)}\rangle \end{aligned} \tag{57}$$

2.3.5. Normalized Elimination of the Small Component. Dyall[101,102] proposed the normalized elimination of the small component (NESC) method based on the modified Dirac equation. In the NESC method, the pseudo-large component, Φ^{L}, is defined by

$$\Psi^{\mathrm{S}} = \frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2c}\Phi^{\mathrm{L}} \tag{58}$$

The modified Dirac equation in the NESC approach is given by

$$T\Phi^{\mathrm{L}} + V\Psi^{\mathrm{L}} = E\Psi^{\mathrm{L}} \tag{59}$$

$$T\Psi^{\mathrm{L}} + \frac{1}{4c^2}(\boldsymbol{\sigma}\cdot\mathbf{p})(V - E)(\boldsymbol{\sigma}\cdot\mathbf{p})\Phi^{\mathrm{L}} = T\Phi^{\mathrm{L}} \tag{60}$$

The elimination of the pseudo-large component, Φ^{L}, from eqs 59 and 60 leads to the one-electron NESC equation,

$$\left[T-(I-U^{\dagger})T(I-U)+V+\frac{1}{4c^{2}}U^{\dagger}(\boldsymbol{\sigma}\cdot\mathbf{p})V(\boldsymbol{\sigma}\cdot\mathbf{p})U\right]\Psi^{L}=E\left(1+\frac{U^{\dagger}TU}{2c^{2}}\right)\Psi^{L} \quad (61)$$

with the relationship between the large and pseudo-large components being defined by

$$\Phi^{L}=U\Psi^{L} \quad (62)$$

where the U operator is generally energy-dependent. The approximation $U = I$ leads to a low-order approximation of the NESC approach,

$$\left[T+V+\frac{1}{4c^{2}}(\boldsymbol{\sigma}\cdot\mathbf{p})V(\boldsymbol{\sigma}\cdot\mathbf{p})\right]\Psi=E\left(1+\frac{T}{2c^{2}}\right)\Psi \quad (63)$$

which was found to be variationally unstable by Dyall. Filatov and Cremer[103−105] improved the low-order NESC method by introducing the effective potential (EP), V_{eff},

$$\left[T+V+\frac{1}{4c^{2}}(\boldsymbol{\sigma}\cdot\mathbf{p})V_{\mathrm{eff}}(\boldsymbol{\sigma}\cdot\mathbf{p})\right]\Psi=E\left(1+\frac{T}{2c^{2}}\right)\Psi \quad (64)$$

The NESC-EP method gives satisfactory results for equilibrium bond lengths, vibrational frequencies, and dissociation energies, as well as the magnetic shielding constants,[106] for molecules that contain heavy elements.

2.3.6. Infinite-Order Two-Component Method. The approach that is most closely related to the DK method was proposed by Barysz, Sadlej, and Snijders (BSS)[107] and is called the infinite-order two-component (IOTC) method. Similar to the DK approach, the first step is the transformation of $\mathbf{H}_{\mathrm{D}}$ with the free-particle FW transformation. Instead of block-diagonalizing the Dirac Hamiltonian using sequential unitary transformations, they proposed a different approach to block-diagonalize $\mathbf{H}_1 = \mathbf{U}_0\mathbf{H}_{\mathrm{D}}\mathbf{U}_0^{\dagger}$ in one step by employing a unitary transformation similar to the form of the FW transformation. They presented the results for the leading order contribution in their first paper and later extended it to an infinite order by adopting an iterative scheme.[108,109] This approach is often called the BSS method in the family of the IOTC method. An efficient implementation of the IOTC method was proposed by Iliaš and Saue.[110] In contrast to the BSS approach, they avoid the preliminary free-particle FW transformation and generate the IOTC Hamiltonian through a one-step decoupling transformation starting from the Dirac operator in the finite basis representation. Their IOTC approach provides the decoupled Hamiltonian from a similarity transformation, as follows:

$$\mathbf{H}_{\mathrm{IOTC}}=\mathbf{X}^{\dagger}\mathbf{H}_{\mathrm{D}}\mathbf{X}=\begin{pmatrix}H_{+\mathrm{IOTC}} & 0\\ 0 & H_{-\mathrm{IOTC}}\end{pmatrix} \quad (65)$$

where $\mathbf{X} = \mathbf{VUV}^{\dagger}\mathbf{S}$ and the matrix $\mathbf{V}$ is the orthogonalization matrix for the atomic basis, namely, satisfying $\mathbf{V}^{\dagger}\mathbf{SV} = 1$. Iliaš and Saue formulated the matrix $\mathbf{U}$ as the unitary decoupling matrix given by $\mathbf{U} = \mathbf{W}_1\mathbf{W}_2$ with

$$\mathbf{W}_1=\begin{pmatrix}1 & -R^{\dagger}\\ R & 1\end{pmatrix} \quad (66)$$

$$\mathbf{W}_2=\begin{pmatrix}\sqrt{1+R^{\dagger}R} & 0\\ 0 & \sqrt{1+RR^{\dagger}}\end{pmatrix} \quad (67)$$

The detailed algorithm to obtain the picture-change operator, R, through a one-step procedure is shown in ref 110. The two-component approach closely related to the IOTC method was proposed by Kutzelnigg and Liu.[111−114]

2.4. Electron−Electron Interaction in the DK Hamiltonian

The derivation of the DK transformation is only valid for the one-electron Dirac equation with an external potential. Thus, the theory must be extended to obtain the relativistic many-electron DK Hamiltonian with the electron−electron Coulomb or Breit interaction. Most of the DK applications developed so far for many-electron systems are based on the no-pair approximation[15] to a greater or lesser extent. In the no-pair DK approach, the electron−electron interaction is transformed only in the first-order DK (or free-particle FW) step, that is, only the one-electron potential is transformed in the sequence DK transformation and the two-electron term is kept in the free-particle FW transformed form, as follows:[115,116]

$$V_{\mathrm{np}}(i,j)=A_iA_j\left[\frac{1}{r_{ij}}+R_i\frac{1}{r_{ij}}R_i+R_j\frac{1}{r_{ij}}R_j+R_iR_j\frac{1}{r_{ij}}R_iR_j\right]A_iA_j \quad (68)$$

$$A_i=\left(\frac{E_i+c^{2}}{2E_i}\right)^{1/2} \quad (69)$$

$$R_i=\frac{c\boldsymbol{\sigma}_i\cdot\mathbf{p}_i}{E_i+c^{2}}=K_i\boldsymbol{\sigma}_i\cdot\mathbf{p}_i \quad (70)$$

In eq 68, we omit the two-electron terms derived from the Breit operator, which are given explicitly in ref 15. A further approximation to the two-electron DK term is to neglect the relativistic kinematics correction to the electron−electron interaction in the no-pair DK Hamiltonian, which yields the simplest many-electron DK Hamiltonian, that is, the one-electron DK Hamiltonian with the electron−electron Coulomb operator in the nonrelativistic form. This approximation is usually implemented in the variety of program packages and is often adopted in the practical scalar DK calculations.

The effects of the relativistic correction to the electron−electron interaction in the DK Hamiltonian have been argued. Matveev and Rösch[117] proposed an extension of the DK2 approach to the pure DFT problem that accounts for the second-order DK correction to the classical Hartree portion of the electron−electron interaction. In their approach, the exchange−correlation contribution is untransformed because the electron charge density fitting scheme with auxiliary basis functions is adopted. They show that first-order DK treatment of the two-electron term is

Table 2. Spin−Orbit Splittings (in au) of the Hg Atom[a]

	DK2+DK2	DK3+NR	DK3+DK1	DK3+DK2	DK3+DK3	DC
2p	71.1300 (−1.07)	74.1102 (3.07)	71.4960 (−0.56)	72.0377 (0.19)	71.9654 (0.09)	71.9008
3p	15.9073 (−1.39)	16.6891 (3.45)	16.0073 (−0.77)	16.1829 (0.32)	16.1546 (0.14)	16.1318
4p	3.8847 (−1.51)	4.0938 (3.79)	3.9042 (−1.01)	3.9604 (0.41)	3.9506 (0.16)	3.9442
5p	0.6867 (−1.55)	0.7269 (4.22)	0.6890 (−1.22)	0.7007 (0.46)	0.6986 (0.16)	0.6975
3d	3.4373 (−0.01)	3.9576 (15.12)	3.4208 (−0.49)	3.4377 (−0.00)	3.4374 (−0.01)	3.4378
4d	0.7480 (−0.03)	0.8689 (16.13)	0.7421 (−0.82)	0.7482 (0.00)	0.7480 (−0.03)	0.7482
5d	0.0759 (0.26)	0.0895 (18.23)	0.0751 (−0.79)	0.0758 (0.13)	0.0757 (0.00)	0.0757
4f	0.1629 (0.00)	0.2501 (53.53)	0.1620 (−0.55)	0.1629 (0.00)	0.1629 (0.00)	0.1629

[a] Values in parentheses are deviations (%) of DK spin−orbit splittings relative to the DC values, $[(\Delta E^{\mathrm{SO}}_{\mathrm{DK}nl-\mathrm{DK}n2} - \Delta E^{\mathrm{SO}}_{\mathrm{DC}})/\Delta E^{\mathrm{SO}}_{\mathrm{DC}}] \times 100$.

often sufficient and that the second-order correction is much less important. Nakajima and Hirao[118] also developed an extended DK approach for the relativistic many-electron Hamiltonian including the electron−electron interaction. In their approach, HF-exchange, exchange−correlation potentials, and the Coulomb interaction are relativistically corrected. To consider the higher-order DK transformation to the two-electron interaction, the approach of Nakajima and Hirao adopts the effective one-electron potential in the Dirac−Hartree−Fock (DHF)/Dirac−Kohn−Sham (DKS) operator as an expansion parameter in the DK transformation. The DHF or DKS operator is generally written as

$$\mathbf{F}_{\mathrm{DHF/DKS}} = \begin{pmatrix} V_{\mathrm{nuc}} + c^2 + J^{\mathrm{LL}} + J^{\mathrm{SS}} - t_{\mathrm{ex}}K^{\mathrm{LL}} - t_{\mathrm{xc}}V_{\mathrm{xc}} & c\boldsymbol{\sigma}\cdot\mathbf{p} - t_{\mathrm{ex}}K^{\mathrm{LS}} \\ c\boldsymbol{\sigma}\cdot\mathbf{p} - t_{\mathrm{ex}}K^{\mathrm{SL}} & V_{\mathrm{nuc}} - c^2 + J^{\mathrm{LL}} + J^{\mathrm{SS}} - t_{\mathrm{ex}}K^{\mathrm{SS}} - t_{\mathrm{xc}}V_{\mathrm{xc}} \end{pmatrix} \quad (71)$$

Here, V_{nuc} is the nuclear potential and V_{xc} is the exchange−correlation potential. The matrix elements for the Coulomb and exchange operators, J^{XX} and K^{XY} (X, Y = L or S), respectively, are given by

$$J^{\mathrm{XX}}\phi(1) = \left[\sum_i \int \frac{\varphi_i^{\mathrm{X}*}(2)\varphi_i^{\mathrm{X}}(2)}{r_{12}}\,\mathrm{d}\tau_2\right]\phi(1) \quad (72)$$

$$K^{\mathrm{XY}}\phi(1) = \left[\sum_i \int \frac{\varphi_i^{\mathrm{Y}*}(2)\phi(2)}{r_{12}}\,\mathrm{d}\tau_2\right]\varphi_i^{\mathrm{X}}(1) \quad (73)$$

where φ_i^{L} and φ_i^{S} are the two-component large and small spinors, respectively, and ϕ is an arbitrary two-component function. The parameter t_{xc} is set to zero and one for the DHF and DKS approaches, respectively, and the constant t_{ex} is the parameter for the hybrid DFT approach and is usually set to zero for the pure DFT approach. The DHF/DKS operator, eq 71, can be written in the same form as the one-electron Dirac Hamiltonian in eq 4 through the following replacements:

$$V_{\mathrm{nuc}} + J^{\mathrm{LL}} + J^{\mathrm{SS}} - t_{\mathrm{ex}}K^{\mathrm{XX}} - t_{\mathrm{xc}}V_{\mathrm{xc}} \rightarrow V \quad (74)$$

$$\boldsymbol{\sigma}\cdot\mathbf{p} - \frac{t_{\mathrm{ex}}}{c}K^{\mathrm{XY}} \rightarrow \boldsymbol{\sigma}\cdot\mathbf{p} \quad (75)$$

By substituting these relations into the one-electron DK terms, it is straightforward to obtain the DKn−Fock operators with the DK transformation to the DHF/DKS potential in the two-component DKn−HF/KS equation,

$$F_{\mathrm{DK}n}\psi_i = \varepsilon_i\psi_i \quad (76)$$

where ψ_i is the (orthonormalized) two-component DKn spinor and ε_i is its spinor energy. From Table 2, it is evident that the improvement of the two-electron treatment makes the orbital energy values closer to the four-component DC results. The numerical calculations show that the third-order DK transformation to both the one-electron and two-electron Hamiltonians gives excellent agreement with the four-component relativistic approach. The first-order DK correction to the two-electron interaction has also been shown to be satisfactory for both atomic and molecular systems. van Wüllen and Michauk[119] developed an efficient and accurate approximation to the DK transformation of the two-electron term. Their approach adopts a model potential, which is determined by an atomic calculation, to estimate the relativistic correction to the electron−electron interaction in molecules; their approach involves a single DK transformation and negligible computational effort.

2.5. Spin−Orbit Effects

The two-component DK Hamiltonian can be separated into the spin-free and spin-dependent parts by using the Dirac relation,

$$(\boldsymbol{\sigma}\cdot\mathbf{u})(\boldsymbol{\sigma}\cdot\mathbf{v}) = \mathbf{u}\cdot\mathbf{v} + i\boldsymbol{\sigma}\cdot\mathbf{u}\times\mathbf{v} \quad (77)$$

The spin-dependent part includes the DK-transformed one- and two-electron spin−orbit (SO) terms. Since the cost of the DK transformation to the two-electron SO term is high, usual applications of the SO term adopt the no-pair approximation. In this context, Pestka and Sadlej pointed out that an approximation in which the different order DK transformations are inconsistently applied to one- and two-electron terms gives an incorrect long-range limit,[120] while, to our knowledge, such treatment has successfully been applied to most atomic and molecular calculations. The DK-transformed SO Hamiltonian with the no-pair approximation is given by

$$H^{\mathrm{SO}}_{\mathrm{np}} = \sum_i \sum_A A_i K_i \frac{Z_A}{{r_{iA}}^3}(\mathbf{r}_{iA} \times \mathbf{p}_i)\cdot\boldsymbol{\sigma}_i K_i A_i - \sum_{i \neq j} A_i K_i A_j \left(\frac{\mathbf{r}_{ij}}{{r_{ij}}^3} \times \mathbf{p}_i\right).(\boldsymbol{\sigma}_i + 2\boldsymbol{\sigma}_j) A_j K_i A_i \quad (78)$$

The two-electron SO terms are the spin−same-orbit (SSO) and spin−other-orbit (SOO) terms, respectively. The no-pair SO Hamiltonian corresponds to the DK1 SO Hamiltonian. In contrast to the BP-type SO Hamiltonian, the DK-type SO Hamiltonian is variationally stable.

For scalar relativistic effects, it is usually sufficient to only include the one-electron term and neglect the spin-free contribution of the DK transformation for the two-electron interaction. On the other hand, it is known that the contribution of the two-electron SO term to a variety of property calculations is important. For the magnetic shielding constants, for example, the two-electron SO contribution is almost 30% of the one-electron SO contribution for fluorine substituents.[121,122] However, the evaluation of the two-electron SO integral is costly. To reduce the computational effort for evaluating the full SO Hamiltonian, several approximations have been proposed. Hess et al.[123] introduced a pseudo-one-electron Fock-type SO operator based on a mean-field (MF) approximation to the full SO Hamiltonian. Following the idea of the MF approximation to the SO Hamiltonian, Schimmelpfennig[124] implemented an atomic mean-field integral (AMFI) program with additional approximations: (1) only the atomic one-center term is retained, and (2) the atomic orbitals obtained from the spherically averaged atomic SCF calculations with predetermined valence-shell occupations are used as the mean-field orbitals. The Cartesian components of the matrix element of the no-pair AMFI Hamiltonian are given by

$$\langle\mu|(H_{\mathrm{np}}^{\mathrm{AMFI}})_t|\nu\rangle = \langle\mu|(H_{\mathrm{np}}^{\mathrm{SO1}})_t|\nu\rangle + \frac{1}{2}\sum_{M}^{\text{mf-orbs}} n_M[2\langle\mu M|(H_{\mathrm{np}}^{\mathrm{SO2}})_t|\nu M\rangle - \langle\mu M|(H_{\mathrm{np}}^{\mathrm{SO2}})_t|M\nu\rangle - \langle M\mu|(H_{\mathrm{np}}^{\mathrm{SO2}})_t|\nu M\rangle], \quad t = (x, y, z) \tag{79}$$

where $H_{\mathrm{np}}^{\mathrm{SO1}}$ and $H_{\mathrm{np}}^{\mathrm{SO2}}$ are the one- and two-electron SO terms, respectively, with the no-pair approximation. The summation of the two-electron part runs over occupied (mean-field) spatial $M(l, m_l)$ atomic orbitals with the occupation number n_M. The computational efficiency and accuracy of the AMFI approximation with the spin-free DK Hamiltonian have been demonstrated in a variety of applications such as spin−orbit splittings,[125−127] excitation energies,[128−130] spectroscopic constants for molecules,[131] and phosphorescent radiative lifetimes.[132] By adoption of the AMFI technique, Gagliardi et al.[133] implemented the variational two-component SODFT program in which the spin-free relativistic part is treated by the DK2 method. Iliaš et al.[134] proposed a two-component extension of the electron correlation methods including second-order Møller−Plesset perturbation (MP2), coupled-cluster (CC), and configuration-interaction (CI) methods based on the spin-free DK2 method with the MFSO approximation. Table 3 shows the efficiency of the AMFI approximation through a comparison of the computational timings between the two-component DK-AMFI and four-component DC calculations using the MOLFDIR[2] program package. Clearly, the AMFI approximation gives better timing than the four-component DC calculation, especially in the integral generation and HF steps.

Table 3. Comparison of Timing (in s) of Two- And Four-Component Calculations for TlH Molecule

step	DK2+AMFI[a]	DC[b]
2e integrals	391 (0.086)	4 538
SCF	1 822 (0.059)	30 801
integral transform	44 689 (0.256)	174 265
CCSD	19 724 (1.038)	19 002
total	66 626 (0.291)	228 606

[a] Fraction of the four-component DC timing in parentheses. [b] SS two-electron integrals discarded.

Boettger[135] proposed a simple approximation that adopts only one-electron SO integrals with modification of the nuclear charge, Z, in the one-electron SO Hamiltonian. The approach is called the screened-nuclear spin−orbit (SNSO) approximation. The two-electron SO effect is altered by the replacement of the nuclear charge, Z, with the effective charge, $Z_{\mathrm{eff}}(l)$, which depends on the angular momentum, l,

$$Z_{\mathrm{eff}}(l) = Z - Q(l) \tag{80}$$

with $Q(l) = 0, 2, 10, 28$ for $l = 0, 1, 2, 3$, respectively. The computational cost of the construction of the SNSO Hamiltonian is negligible because only the evaluation of the one-electron SO integrals is required. It was found that the SNSO approximation improves the fine structure of heavy atoms.

Beyond the no-pair approximation to the SO Hamiltonian, Majumder et al.[136] proposed the DK2-transformed SO Hamiltonian using the SNSO approximation. Their approximation implicitly includes the second-order DK effect on the SO interaction. They applied their approximation to various atomic and molecular properties such as spin−orbit splittings, **g**-tensor shifts, bond lengths, vibrational frequencies, and binding energies. Their calculations show that the original SNSO Hamiltonian is insufficient for an accurate estimation of the fine structure, although it is attractive for determining approximate molecular **g**-values. Despite the success of their approach with the DK2-SNSO approximation, van Wüllen[137] pointed out that it is inconsistent because the spin-dependent part, $(\boldsymbol{\sigma}\cdot\mathbf{p})V$, in the W_1 term is screened. Instead, van Wüllen and Michauk[119] proposed another higher-order SNSO approximation in which the screening is applied to the spin-dependent part of the matrix elements of $(\boldsymbol{\sigma}\cdot\mathbf{p})V(\boldsymbol{\sigma}\cdot\mathbf{p})$ in the E_1 term before the DK transformation. Peralta and Scuseria[138] developed the two-component noncollinear spin-density functional method based on the higher-order DK-transformed SNSO approximation. The inclusion of the DK4-SNSO Hamiltonian considerably improves the orbital energy splittings obtained by the unscreened one-electron SO Hamiltonian.

3. PRACTICAL ASPECTS

3.1. Implementation of the DK Hamiltonian

For a practical calculation, the matrix elements of the DK Hamiltonian are evaluated using the resolution of identity (RI) with finite basis functions in the space spanned by the eigenfunctions of the squared momentum, $\mathbf{p}^2$, following Buenker et al.[139] The procedure is usually adopted with the basis functions in an uncontracted form inside the Douglas−Kroll machine. Let us consider an evaluation of the matrix elements containing any function $f(\mathbf{p}^2)$ in momentum space,

$$\mathbf{M}_{\mu\nu}[f(\mathbf{p}^2)] \equiv \langle\chi_\mu|f(\mathbf{p}^2)|\chi_\nu\rangle \tag{81}$$

This can be achieved by the following procedure:

(1) Transformation of $\mathbf{M}[\mathbf{p}^2]$ to an orthonormal basis:

$$\tilde{\mathbf{M}}[\mathbf{p}^2] = \mathbf{X}^{\dagger}\mathbf{M}[\mathbf{p}^2]\mathbf{X} \tag{82}$$

where

$$\mathbf{X}^{\dagger}\mathbf{S}\mathbf{X} = 1 \tag{83}$$

(2) Diagonalization of $\tilde{\mathbf{M}}[\mathbf{p}^2]$:

$$\tilde{\mathbf{M}}[\mathbf{p}^2]\mathbf{U} = \mathbf{U}\boldsymbol{\lambda} \tag{84}$$

where $\mathbf{U}$ is unitary and $\boldsymbol{\lambda}$ is diagonal, which results in

$$\tilde{\mathbf{M}}[\mathbf{p}^2] = \mathbf{U}\boldsymbol{\lambda}\mathbf{U}^{\dagger} \tag{85}$$

(3) Evaluation of the function of the eigenvalues:

$$\tilde{\mathbf{M}}[f(\mathbf{p}^2)] = \mathbf{U}f(\boldsymbol{\lambda})\mathbf{U}^{\dagger} \tag{86}$$

(4) Back-transformation to the original basis:

$$\begin{aligned}\mathbf{M}[f(\mathbf{p}^2)] &= (\mathbf{X}^{\dagger})^{-1}\tilde{\mathbf{M}}[f(\mathbf{p}^2)](\mathbf{X})^{-1} \\ &= (\mathbf{SXU})f(\boldsymbol{\lambda})(\mathbf{SXU})^{\dagger}\end{aligned} \tag{87}$$

The evaluation is exact only for complete basis functions, but it was shown by numerical calculations that the RI scheme in momentum space with the uncontracted basis functions is sufficiently accurate. In this context, Kutzelnigg and Liu[112] pointed out that the eigenfunctions of approximate quasi-relativistic operators are more singular than the Dirac solutions so that additional errors may occur in the quasi-relativistic approach if it is used with regular basis functions. Indeed, Saito[140] showed that the RI scheme in the momentum space overestimates the total DK3 energies for superheavy atoms in comparison with the *B*-spline calculation although the differences are small (i.e., on the order of millihartree). On the other hand, the spherical wave results of van Wüllen[141] show no indication that the use of Douglas−Kroll operators with regular basis sets introduces errors larger than those of a four-component treatment. Thus, the argument of Kutzelnigg and Liu remains an open question.

To calculate the matrix elements of DK Hamiltonians, the terms, including both W_1 and E_1, have to be calculated from scratch. For example, $W_1E_1W_1$ is given by

$$\begin{aligned}W_1E_1W_1 &= A(RvR)AR^{-2}(RE_1R)AvA \\ &\quad - A(RvR)AR^{-2}(RE_1R)R^{-2}A(RvR)A \\ &\quad - AvA(RE_1R)AvA + AvA(RE_1R)R^{-2}A(RvR)A\end{aligned} \tag{88}$$

Here, R^{-2} is calculated by

$$R^{-2} = \frac{(E_0 + c^2)^2}{c^2p^2} \tag{89}$$

and RE_1R is given by

$$RE_1R = A(RVR)A + AR^2VR^2A \tag{90}$$

This standard approach to the matrix construction of the DK Hamiltonian requires a huge number of matrix multiplications. Since the computational cost increases exponentially with the order of DK transformation, it is difficult to obtain results for very high-order DK Hamiltonians. Several groups have proposed approximations to efficiently construct the DK Hamiltonian matrix. Gagliardi et al.[142] introduced the two-center approximation, in which the matrix elements of the DK Hamiltonian are evaluated within basis sets of two atoms at a time. Matveev and Rösch[143] avoided the full transformation by adopting an atomic ansatz for the relativistic projection transformation. In their approximation, the kinematic factors were taken from some approximate relativistic calculations on atoms. The merit is that its matrix representation becomes independent of the molecular geometry so that the DK gradient and Hessian are simplified. Thar and Kirchner[144] proposed a scheme that confines the DK transformation to either each molecule, atom, or heavy atom. Instead of using the locality or sparsity, Peng and Hirao[81] reduced the number of matrix multiplications by applying a simple transformation to all DK intermediate operators instead of complicated step-by-step symbolic manipulations. The number of matrix multiplications in their approach scales with only polynomial behavior with respect to the DK order and the computational cost is much less than that of the standard approach.

3.2. Energy Derivatives

An analytical derivative technique for the scalar DK2 approach was proposed by Rösch and co-workers.[145,146] Since the matrix elements of the relativistic kinetic and potential operators in the DK Hamiltonian are practically calculated by the RI technique, the analytical expression for the DK energy derivatives is complicated in comparison with the nonrelativistic case. For example, the first derivative of the relativistic kinetic energy integral, $E_0 - c^2$, is derived from the following procedure. The explicit expression for the relativistic kinetic energy integral in AO basis is given by (note, small letters denote diagonal matrices):

$$\tilde{T} = (SXB)t(SXB)^{\dagger} \tag{91}$$

where $X = Us^{-1/2}$; U and s are eigenvectors and eigenvalues, respectively, of the overlap matrix S; $t_{\nu\nu} = (p^2c^2 + c^4)^{1/2} - c^2$; and B is the eigenvector of the doubled nonrelativistic kinetic energy. By taking the derivative by a nuclear coordinate a,

$$\begin{aligned}\frac{\partial\tilde{T}}{\partial a} &= \left[\left(\frac{\partial S}{\partial a}XB\right)t(SXB)^{\dagger} + h.c.\right] + \left[\left(S\frac{\partial X}{\partial a}B\right)t(SXB)^{\dagger} + h.c.\right] \\ &\quad + \left[\left(SX\frac{\partial B}{\partial a}\right)t(SXB)^{\dagger} + h.c.\right] + (SXB)\frac{\partial t}{\partial a}(SXB)^{\dagger}\end{aligned} \tag{92}$$

with

$$\frac{\partial t}{\partial a} = \frac{c^2}{2E_0}\frac{\partial[p^2]}{\partial a} \tag{93}$$

$\partial[p^2]/\partial a$ is readily computed using the technique described in ref 145. The derivatives, such as $\partial X/\partial a$ and $\partial B/\partial a$, are computed by differentiating the eigenvalue equation $U^{\dagger}SU = s$ and using the diagonal structure of the eigenvalue matrix, $\mathbf{s}$, to obtain $\partial U/\partial a$ and $\partial s/\partial a$. The displacement derivatives of the matrix elements of the effective nuclear potential are calculated similarly to the derivatives of the kinetic energy matrix. Instead of this complicated procedure, de Jong et al.[147] proposed an efficient and accurate mixed analytical/numerical method to calculate DK gradients. In their approach, the gradients of the nonrelativistic integrals are computed analytically and the gradient of the difference between the nonrelativistic and DK one-electron integrals is computed numerically. The DK gradients are obtained by the addition of the relativistic correction to the nonrelativistic term. Wahlgren et al.[148] proposed a similar approach for the gradient calculation in which the one-center approximation is adopted for the difference between the nonrelativistic and DK Hamiltonians. Their approximation works well, provided that the core electrons are frozen. Vallet et al.[149] and Thar and Kirchner[144] simply evaluated the DK gradients by adopting relativistic densities in the nonrelativistic gradient routine. The assessment of Thar and Kirchner for halogen dimers shows that the geometries obtained by this approach are in excellent agreement (error smaller than 0.02 pm) with the geometries obtained from numerical gradients; therefore, the approach leads to an acceptable approximation of relativistic DK gradients.

3.3. Basis Sets

One-particle basis sets determine the accuracy of quantum chemical calculations. It is widely recognized that the Gaussian-type orbital (GTO) is particularly attractive for *ab initio* MO calculations mainly because it has the advantage that multicenter two-electron integrals can be evaluated easily. The Gaussian basis sets have reached a high level of sophistication and are capable of achieving excellent results for molecular calculations. The nonrelativistic contracted basis sets can produce erroneous results for elements beyond the first row. To appropriately incorporate relativistic effects, several relativistic basis sets constructed by the DK method have been proposed.

The simple construction of relativistic basis sets with the DK method retains the nonrelativistic exponents and determines the contraction coefficients of the basis function from atomic calculations. Kellö and Sadlej developed basis sets including the polarization functions for the relativistic calculations of atomic and molecular electric properties in the DK2 approximation. Their basis sets are devised for atoms of groups Ib and IIb[150] and groups Ia and IIa[151] of the periodic table. The excellent performance of their basis sets has been shown in the case of the calculations for atomic and molecular electric properties such as polarizabilities and dipole moments. de Jong et al. proposed the generation of DK2 correlation consistent basis sets, cc-pVXZ (X = D, T, Q, and 5) for H, He, B−Ne, Al−Ar, and Ga−Br.[147] Roos et al. have also developed relativistic basis sets contracted by the use of the atomic natural orbital (ANO) with the DK2 method for the main group and rare gas atoms,[152] alkaline and alkaline-earth atoms,[153] actinide atoms Ac−Cm,[154] and lanthanide atoms La−Lu.[155] The basis sets developed by de Jong et al. and Roos et al. can be retrieved from the EMSL Gaussian Basis Set Library.[156] Haiduke et al.[157] proposed the DK2 version of the relativistic-adapted Gaussian basis sets (RAGBSs), which were contracted with the general contraction scheme at the HF level. In their RAGBSs, Gaussian exponents were generated by using a technique with a polynomial version of the Generator Coordinate. Polarization functions were determined by optimizing with the CI method including single and double excitations. While these four families are generally contracted basis sets, Pantazis et al. constructed the segmented-contracted DK2 basis sets for the elements La−Lu[158] and Hf−Hg.[159] Jorge and co-workers also proposed segmented-contracted basis sets with the inclusion of the scalar DK2 effect at the DZP, TZP, and QDP levels for the elements H−Kr[160] and Rb−Xe.[161] Significant computational advantages can be realized owing to the loose contraction of their basis sets compared with the generally contracted basis sets. The basis sets of the Jorge group are provided on their Web site,[162] while the DK2 basis sets (Hf−Hg) of Pantazis et al. are available at the EMSL Gaussian Basis Set Library.

As well as the contraction coefficients, the exponents of GTOs can be optimized with the inclusion of the DK Hamiltonian. The first attempt, by Chandra and Hess, was for basis sets with point-nucleus and finite-nucleus models for the gold atom.[163] Nakajima and co-workers proposed the relativistic GTO basis sets covering the elements H−Lr (atomic numbers $Z = 1-103$) using the DK3 method with point-charge[164] and finite-nucleus[165] models. The exponents and contraction coefficients in their DK3 basis sets are determined by atomic HF calculations. Peterson and co-workers systematically developed the correlation-consistent family of basis sets including the scalar DK2 effect, cc-pwCVXZ (X = T, Q, and 5) for main group elements (Ga−Kr),[166] cc-pVXZ (X = T, Q, and 5) for 3d transition metals (Sc−Zn),[167] and cc-pVTZ for groups 11 (Cu, Ag, and Au) and 12 (Zn, Cd, and Hg)[168] and 4d (Y−Pd)[169] and 5d (Hf−Pt) transition metals.[170] Their basis sets are available on the Web site of the Peterson group,[171] as well as the EMSL Gaussian Basis Set Library. Noro and co-workers also developed the natural-orbital-based relativistic correlating basis sets. The spin-free relativistic effects are considered through the DK3 approximation with the finite nucleus model. A segmented contraction scheme is adopted so that their basis sets attain both efficiency and compactness while maintaining a high-quality method of describing correlation energies in various atoms and molecules. Their DK3 basis sets cover the elements H to Lr.[172−177] Their basis sets are provided at the Web site of their basis set library.[178]

3.4. Model Potentials

The effective core potential (ECP) approach is one of the most successful techniques for the calculation of computationally demanding molecular systems. It greatly reduces the computational effort for systems with a large number of electrons by replacing the chemically inert core electrons with a potential acting on the valence electrons. In addition, the ECPs can be derived to include a relativistic treatment. Two families are recognized from the base ECP method. The first family is called the pseudopotential, which originates from the Phillips−Kleinman equation[179] and results in the use of nodeless valence pseudo-orbitals. The second family is the model potential, which originates from the Huzinaga−Cantu equation[180] in which the valence orbitals retain exact nodal properties.

In the ECP approximation with the DK Hamiltonian, the core electrons can be modeled by the potential determined by the atomic DK calculation, and the relativistic effects on the valence orbitals are directly taken into account by the valence DK Hamiltonian with the predetermined potential. *Ab initio* core model potentials (AIMPs) based on the DK2 and DK3 methods have been proposed for the third row transition metal elements from La to Pt,[181] the transition metal elements from Sc to Hg,[182,183] the lanthanide series from Ce to Lu,[184] and the actinide elements from Th to Lr.[185] The AIMP of a nucleus is represented by[186,187]

$$V^{\mathrm{AIMP}}(i) = V^{\mathrm{MP}}_{\mathrm{Coul}}(i) + V^{\mathrm{MP}}_{\mathrm{exch}}(i) + P(i) \quad (94)$$

The V_{Coul} operator represents the Coulomb interactions of one valence electron with the Z_{core} electrons and the same number of protons located at the nucleus. It is convenient to fit V_{Coul} with a linear combination of Gaussian functions as follows:

$$\begin{aligned} V_{\text{Coul}}(i) &= -\frac{Z_{\text{core}}}{r_i} + 2\sum_c^{\text{core}} J_c(i) \cong V_{\text{Coul}}^{\text{MP}}(i) \\ &= \sum_k C_k \frac{\exp(-\alpha_k r_i^2)}{r_i} \end{aligned} \tag{95}$$

Similarly, the V_{exch} operator represents the exchange interaction between one valence electron and the core electrons. Its spectral representation operator replaces this operator as

$$\begin{aligned} V_{\text{exch}}(i) &= -\sum_c^{\text{core}} K_c(i) \cong V_{\text{exch}}^{\text{MP}}(i) \\ &= \sum_l \sum_{m=-l}^{l} \sum_{a,b} |a;\, lm\rangle A_{l;ab} \langle b;\, lm| \end{aligned} \tag{96}$$

where a and b are arbitrary Gaussian functions and $A_{l,ab}$ is an element in the following matrix:

$$A = S^{-1}KS^{-1} \quad \text{where} \quad K_{ij} = \langle i|V_{\text{exch}}|j\rangle \quad \text{and} \quad S_{ij} = \langle i|j\rangle \tag{97}$$

By use of these operators, all of the one-electron exchange integrals become those of the all-electron calculation if $\langle i|$ and $|j\rangle$ belong to the $\{a;lm\}$ and $\{b;lm\}$ basis functions. The operator $P(i)$ is obtained by the core−valence orthogonality and consists of the core orbitals, ϕ_c, and the core orbital energies, ε_c. The nodal structures of the valence orbitals are ensured through the operator

$$P(i) = -\sum_c^{\text{core}} 2\varepsilon_c |\phi_c\rangle\langle\phi_c| \tag{98}$$

The direct relativistic effects on the valence electrons are explicitly taken into account by using one-component relativistic kinetic energy and DK-transformed nuclear attraction interaction operators. The corresponding valence basis sets were optimized by the minimization of the valence SCF total energies. Several applications of DK-AIMPs to atomic and molecular systems in ground and excited states show that the DK-AIMP results satisfactorily reproduce the all-electron DK results.[188−190] The model core potential (MCP) approach,[191,192] which is another family of model potential methods, has also been extended to the relativistic case with the DK Hamiltonian. The MCP is generally written as

$$V^{\text{MCP}}(i) = -\frac{Z - Z_{\text{core}}}{r_i} \sum_k C_k r_i^{n_k} \exp(-\alpha_k r_i^2) + P(i) \tag{99}$$

Recently, Zeng et al.[193−195] developed MCPs with the scalar-relativistic effect at the DK3 level combined with the DK1 Hamiltonian for spin−orbit couplings and their basis sets. The comparison between the DK-MCP and all-electron DK calculations of atomic and ionic term and level energies and spectroscopic constants indicate the chemical accuracy of new DK-MCPs in reproducing all-electron properties. A timing study using DK-MCPs demonstrates the computational savings.

3.5. Program Packages

The DK method is currently implemented in several quantum chemical program packages. The DK2 method can be used in official Gaussian,[196] Dalton,[197] and ParaGauss[198] programs. The NWChem[199] and GAMESS[200] programs are able to treat the DK3 method, as well as the DK2 method. The arbitrary-order DK method is also available in the MOLCAS[201] and MOLPRO[202] programs, and first- to fifth-order DK methods can be used in the TURBOMOLE,[203] ORCA,[204] and CP2k[205] programs by the use of the DK module developed by the Reiher group. Most of these program packages currently treat the scalar DK Hamiltonian with the nonrelativistic two-electron term in the SCF calculation or the sequential electron correlation calculation. The spin−orbit couplings are usually treated in a perturbative fashion (for example, see ref 206). The spin−orbit eigenstates are obtained by the diagonalization of the spin−orbit Hamiltonian over a basis consisting of all the spin components of wave functions constructed using the spin-free eigenstates.

4. MAGNETIC PROPERTIES WITH THE DK METHOD

The DK approach has successfully been applied to relativistic calculations for a variety of atomic and molecular systems that contain heavy elements. The applications include calculations of spectroscopic constants such as molecular geometries, frequencies, dissociation energies, fine structure splittings, excitation energies, ionization potentials, and electron affinities, as well as electric properties such as dipole moments, polarizabilities, hyperpolarizabilities, and nuclear quadrupole coupling tensors. Most of these calculations are referred to in the excellent recent review of Iliaš et al.[207] Static dipole polarizabilities for the electronic ground states of the neutral elements, which are calculated by several relativistic approaches including the DK method, are compiled by Schwerdtfeger.[208] To avoid overlap with these accounts as much as possible, in this review we will focus on the magnetic properties calculated by the DK method. Since most of the magnetic properties such as nuclear magnetic shielding and spin−spin coupling constants are the properties that are mainly derived from the electrons in the region close to the nuclei, changes in the electronic structure due to relativistic effects are important for magnetic properties. In addition, the so-called "picture-change" effect is important for the calculation of second-order magnetic properties such as magnetic shielding constants because of a huge contribution of the negative-energy states. The picture-change effect is derived from the change in representation from the Dirac picture to the Schrödinger−Pauli picture. In a quasi-relativistic theory, the four-component wave function is transformed into the two-component form so that a perturbation operator should be transformed into the same representation as the wave function. We will point out the importance of the picture-change effect for individual magnetic properties in the following subsections.

4.1. NMR Magnetic Shielding Constants

The first application of the DK approach to the calculation for the NMR magnetic shielding constants was proposed by Ballard et al.[209−211] They used the two-component unrestricted HF (generalized UHF, GUHF) method with the DK2 Hamiltonian. Only the spin-free part of the DK2 Hamiltonian was considered, and the spin−orbit term and the magnetic interaction term remained in the Breit−Pauli form. Fukui and Baba[212] also applied the DK2 method to the calculation of NMR chemical shifts with fixed gauge origins at the HF level. In their calculation, the relativistic corrections to the spin−orbit part of the zeroth-order

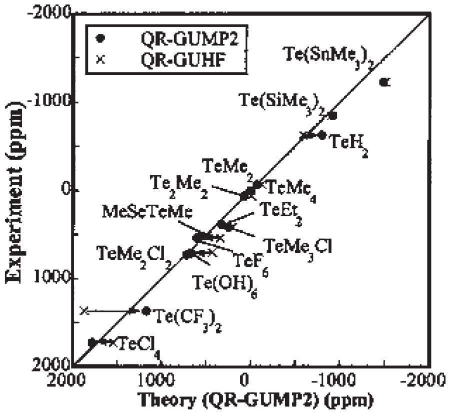


Figure 2. Correlation between theoretical and experimental ^{125}Te NMR chemical shifts.Reprinted with permission from ref 217. Copyright 2005 American Institute of Physics.

Hamiltonian and the spin-free term were considered. They pointed out that the relativistic DK transformation including the magnetic vector potential is important, and they still used the magnetic interaction term in the Breit−Pauli form in their practical calculations. Baba and Fukui[213] proposed a gauge-origin independent expression for the nuclear magnetic shielding derived from the DK2 transformation with the gauge-including atomic orbital (GIAO) approach. However, since their implementation ignored the spin−orbit contribution, the computed values were too small to interpret the very large upshield proton shifts observed in HBr and HI molecules. Later, to reproduce the full relativistic effect, Baba and Fukui[214] introduced the mass-velocity effect on the magnetic perturbation Hamiltonians in their GIAO treatment. They found that the inclusion of the mass−velocity effects into all of the perturbation Hamiltonians greatly improves the results. Fukuda et al. proposed the DK2-transformed Hamiltonian including the relativistic magnetic vector potential.[215] They applied it to the calculation of the magnetic shielding constants with the GIAO approach at generalized UHF (QR-GUHF)[216] and generalized unrestricted second-order Møller−Plesset (QR-GUMP2)[217] levels. Figure 2 displays the correlation among the QR-GUMP2, QR-GUHF, and experimental ^{125}Te NMR chemical shifts in several Te compounds. The DK2-GUMP2 method quantitatively reproduces the experimental findings. In contrast, the QR-GUHF method can qualitatively explain the experimental trends, while the electron-correlation contribution improves the quantitative agreement with experiment findings. A series of the calculations of the Nakatsuji group[215−219] show that the picture-change effect on the magnetic interaction terms is significant for the magnetic shielding constant of heavy elements. For example, Table 4 shows the shielding constant values for hydrogen halides computed by three approximations for the picture-change effect on the magnetic terms: QR-0, which is the DK2 calculation with nonrelativistic magnetic interaction; QR-1, which is the DK2 calculation with the first-order DK magnetic interaction and the nonrelativistic diamagnetic shielding term; and QR-2, which is the full DK2 calculation with the second-order DK magnetic interaction. The relativistic correction of the magnetic interaction almost does not affect the shielding constants of hydrogen. On the other hand, for the halogen magnetic shielding constants, the relativistic correction of the magnetic interaction is important. The relativistic effect on the magnetic interaction and the picture-change effect are the dominant sources of the heavy atom shifts of the magnetic shielding constants of the heavy halogens. Recently, for the nuclear magnetic shielding of HX (X = F, Cl, Br, and I), H_2X (X = O, S, Se, and Te), and noble gas X (X = He, Ne, Ar, Kr, and Xe) systems, Kudo and Fukui[220] compared the DK2 results with those of the infinite-order BSS. The results show that the relativistic corrections of higher than second order are negligibly small, except for the paramagnetic parts of I, Te, and Xe shieldings.

Table 4. Proton and Halogen Magnetic Shielding Constants (in ppm) of Hydrogen Halides

	nuc[a]	NR	QR-0	OQ-1	QR-2	4-comp
HF	H	28.09	28.61	28.23	28.34	27.87
HCl	H	30.54	31.64	31.56	31.56	31.00
HBr	H	30.74	37.17	37.13	37.15	36.08
HI	H	31.15	49.57	49.49	49.72	47.98
HF	F	416.8	415.9	430.6	423.4	423.3
HCl	Cl	957.5	968.8	1035.0	1018.9	1020.1
HBr	Br	2634.9	2754.9	3280.3	3164.9	3224.6
HI	I	4540.4	5393.6	6902.6	6508.5	6768.4

[a] Resonance nucleus.

Table 5. Calculated One-Bond ^1J(X,H) Spin−Spin Couplings (in Hz) for the Series of Tetrahydrides Using the Hartree−Fock Approximation

	CH_4	SiH_4	GeH_4	SnH_4
nonrel.	158.4	−243.5	−108.2	−1930.6
DK1-sf	150.6	−229.1	−110.3	−2371.0
DK1-SO	150.6	−229.1	−109.9	−2392.3
DK2-sf	157.1	−245.9	−122.5	−2616.0
DK2-SO	157.1	−245.9	−121.9	−2629.3

4.2. NMR Spin−Spin Couplings

Melo et al.[221] applied the DK approximation to the calculation of NMR spin−spin couplings. The first- and second-order DK-transformed Hamiltonians of the magnetic interaction terms were derived following Fukuda et al., while, in the practical calculation, the diamagnetic contribution is kept in the Breit−Pauli form. As shown in Table 5, the numerical results calculated at the HF level for one-bond spin−spin couplings for a series of tetrahydrides (CH_4, SiH_4, GeH_4, and SnH_4) show that the first-order DK gives relativistic corrections that are too large even for tetrahydrides containing the lighter elements while the second-order DK considerably improves the agreement with relativistic corrections given by four-component DHF calculations. The SO effect seems to be negligible for the one-bond couplings of this series of tetrahydrides.

4.3. Magnetizabilities

The calculations of the magnetizabilities of noble gas atoms (He, Ne, Ar, Kr, and Xe) were carried out at the HF level with the DK2 Hamiltonian including the picture-change effect on the magnetic term.[222] The calculated and experimental magnetizabilities of He, Ne, Ar, Kr, and Xe are shown in Table 6. It was found that the picture-change effect gives a correction in the magnetizabilities of Kr and Xe. The picture-change effect on the magnetizabilities is larger than any other relativistic effects such as the SO interaction. The approach has been extended to the MP2 case.[223] These results demonstrate that the total relativistic

Table 6. Calculated and Experimental Magnetizabilities (in units of 10^{-30} J T^{-2}) of He, Ne, Ar, Kr, and Xe

atom	method[a]	dia-ξ_{zz}	para-ξ_{zz}	total iso-ξ_{zz}	PC effect
He	NR	−31.2	0.000	−31.2	
	sf DK2(V)	−31.2	0.000	−31.2	
	DK2(V)	−31.2	0.000	−31.2	
	DK2($V + \mathbf{A}$)	−31.0	0.000	−31.0	0.2
	exptl			−33.5	
Ne	NR	−123.3	0.000	−123.3	
	sf DK2(V)	−123.2	0.000	−123.2	
	DK2(V)	−123.2	0.000	−123.2	
	DK2($V + \mathbf{A}$)	−120.3	0.000	−120.3	2.9
	exptl			−116	
Ar	NR	−342.4	0.000	−342.4	
	sf DK2(V)	−341.6	0.000	−341.6	
	DK2(V)	−341.6	0.004	−341.6	
	DK2($V + \mathbf{A}$)	−331.0	0.004	−331.0	10.6
	exptl			−321	
Kr	NR	−519.9	0.000	−519.9	
	sf DK2(V)	−514.3	0.000	−514.3	
	DK2(V)	−514.4	0.062	−514.3	
	DK2($V + \mathbf{A}$)	−470.1	0.137	−470.0	44.3
	exptl			−482	
Xe	NR	−823.9	0.000	−823.9	
	sf DK2(V)	−804.6	0.000	−804.6	
	DK2(V)	−804.9	0.370	−804.5	
	DK2($V + \mathbf{A}$)	−719.5	0.531	−719.0	85.5
	exptl			−756	

[a] NR, nonrelativistic; sf DK2(V), spin-free DK2; DK2(V), full DK2 calculation without the PC effect on the magnetic term; DK2($V + \mathbf{A}$), full DK2 calculation with the PC effect on the magnetic term.

effects for singlet hydrides are small, whereas the total relativistic effect for IF is as high as 22% because of the coupling between the high electronegativity of F and the SO interaction. Consequently, relativistic contributions to magnetizabilities should not be neglected. The relativistic−correlation interferences for the magnetizabilities were insignificant for the investigated molecules other than SbH. The calculation of the frequency-dependent magnetizabilities at the HF level with the DK2 Hamiltonian has also been reported,[224] although the dependence of the origin of the coordinate axes, as well as that of the gauge-origin, are ignored in the calculations. The frequency-dependent calculations of H_2X (X = O, S, Se, and Te), noble gases (He, Ne, Ar, Kr, and Xe), and small open-shell molecules (CH_2, CH_3, and O_2) show that scalar relativistic and spin−orbit interactions affect mainly the diamagnetic magnetizabilities and paramagnetic magnetizabilities, respectively.

4.4. Zero-Field Splittings

Zero-field splitting (ZFS) originates from two interactions, that is, the spin−orbit interaction and the direct dipolar spin−spin interaction. While the direct dipolar spin−spin coupling dominates the ZFS parameters for organic radicals, the spin−orbit interaction generally dominates the ZFS parameters for transition metal complexes. Reviakine et al. applied the two-component DK approach including the spin−orbit term to the density-functional calculation of the spin−orbit contributions to the ZFS parameters of high-spin molecular systems[225] The ZFS parameters are computed directly from energy differences between different relativistic states. They found that their approach systematically underestimates the zero-field splitting, D, by a factor of 2 probably because of the use of a single-determinant wave function.

By using the variational approach of Reviakine et al. in addition to the second-order perturbation approach, van Wüllen[137] estimated the magnetic anisotropy energy, which is closely related to ZFS. The DK Hamiltonian, ZORA, and ECP are adopted in his calculations. The magnetic anisotropy of the Mn_{12} molecule is reproduced reasonably by all-electron DK and ZORA calculations. He proposed that the magnetic anisotropy energy should be divided by $S(S - {}^1/_2)$ (with spin S) instead of the conventional factor, S^2, to extract the ZFS parameter, D, from the (axial) magnetic anisotropy energy. The factor $S(S - {}^1/_2)$ is derived from the quantum mechanical treatment of spin rather than the classical treatment. It is expected that his approach will automatically correct the underestimated ZFS results of Reviakine et al.

4.5. EPR g-Tensors

Neyman et al.[226] and Malkin et al.[227] developed a two-component density functional approach with the two-component DK2 approach including the spin−orbit effect to calculate EPR **g**-tensor values. Since their approaches employ two-component eigenfunctions when spin−orbit effects are taken into account self-consistently, the **g**-tensor can be treated as a first-order property with respect to the external magnetic field. To consider the picture-change effect of the DK transformation properly, both groups use the first-order DK-transformed Zeeman operators. Following the work of Lenthe et al. based on the ZORA Hamiltonian,[228] Neyman et al. adopted spin-restricted two-component density functional treatments for the calculation of the electronic **g**-tensors. In the spin-restricted case, the expression for the **g**-tensor can simply be given by using Kramers doublet functions. Majumder et al.[136] investigated the effect of the first- and second-order SNSO approximations on the **g**-tensor values by using the approach of Neyman et al. They found that the first- and second-order results agree in the number of digits, so the first-order SNSO method is attractive for determining approximate molecular **g**-shifts using the first-order perturbation approach. Malkin et al. applied the spin-polarized noncollinear DFT method to the calculation of electronic **g**-tensors. In their approach, the diagonal elements of the **g**-matrix are obtained by three self-consistent-field calculations with orthogonal orientation of the total magnetization. By comparing the spin-restricted result of Neyman et al. with their spin-polarized results, they showed that the spin polarization effect is important for the evaluation of **g**-tensor values, as shown in Table 7. The approach of Malkin et al. was recently applied to electronic **g**-tensor calculations for transition metal complexes such as molybdenum and tungsten enzyme-active sites.[229] Their results indicate the substantial importance of the spin-polarized two-component treatment that includes higher-order spin−orbit effects.

4.6. Hyperfine Coupling Tensors

The scalar relativistic DK2 method with picture-change transformation of the hyperfine operators was applied to the calculation of hyperfine coupling tensors with point-charge[230] and finite-nucleus[231] approximations. While neglect of the transformation of the operators leads to meaningless hyperfine results, DFT

Table 7. Comparison of Different Approaches for the DFT (BP86) Calculation of g-Shift Components (in ppm) for Small Radicals

molecule		exptl.	spin-restricted[a]	spin-polarized[b]
CO^+	$\Delta g_\perp$	−2 400	−3 500	−2 550
CN	$\Delta g_\perp$	−2 000	−2 700	−1 990
HCO	Δg_x	1 500	3 030	2 072
	Δg_y	0	−200	−290
	Δg_z	−7 500	−10 760	−7 834
NF_2	Δg_x	−100	−370	−783
	Δg_y	6 200	10 270	6 135
	Δg_z	2 800	6 030	3 735
NO_2	Δg_x	3 900	4 720	3 195
	Δg_y	−11 300	−15 130	−11 579
	Δg_z	−300	−720	−792
C_3H_5	Δg_x	0	−130	−181
	Δg_y	400	760	380
	Δg_z	800	960	417

[a] Reference 227. [b] Reference 228.

calculations with operators transformed to the first order agree relatively well with previous ZORA results.[232] While nonrelativistic calculations increasingly underestimate the isotropic hyperfine couplings with increasing nuclear charge, scalar relativistic calculations with point nucleus provide somewhat overestimated values. The effect of the finite nuclear size is small for lighter atoms like Cu but reduces the computed values by up to 20% for heavy elements like Au or Hg. Its effect improves the agreement with experimental findings.

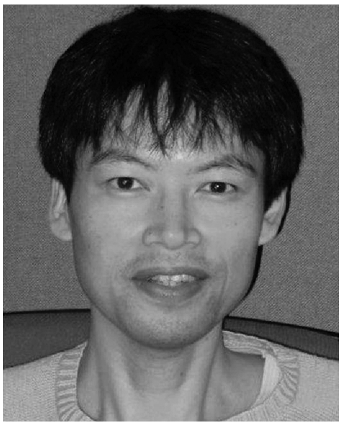
4.7. Magnetic Circular Dichroisms

The two-component DK2 formulation of magnetic circular dichroism (MCD) has been proposed using the finite perturbation method and the sum-over-state perturbation method at the HF level.[233,234] Relativistic effects are shown to be important for the MCD spectra of molecules that contain heavy elements. The relativistic effects on the Faraday term are mainly due to the one-electron spin−orbit term rather than the spin-free relativistic and the two-electron spin−orbit terms.

5. CONCLUSIONS AND PERSPECTIVES

The scalar variant of the DK method has successfully been applied to a variety of systems that contain elements across the periodic table. Among many relativistic approximations to the four-component approach with the DC(B) Hamiltonian, currently it is the most widely used relativistic all-electron approximation. This is partly because the DK approach has continuously been developed and has been implemented in various publicly available program packages. One of the goals of the next-generation molecular theory is to offer a computational approach for the electronic structure that is applicable to molecular systems that contain a wide variety of atoms in the periodic table with the same quality and accuracy. The approximate variant of the two-component relativistic molecular theory with the DK approach can become a foundation for the next-generation molecular theory. To this end, we need further improvements to the theoretical work on the DK method. In addition, we need to develop a widely used program suite based on the two-component spin−orbit SCF approach and its electron-correlation approach with the DK method. The current establishment of quantum chemistry largely depends on the development of the (one-component) program packages that are widely available and user-friendly. When two-component versions of program packages are established and widely used in place of the current scalar programs, we will switch to the next stage of theoretical chemistry.

BIOGRAPHIES



Takahito Nakajima was born in Yonago, Japan, in 1967. He received Ph.D in engineering from Kyoto University, Kyoto, in 1997, having carried out work in the area of theoretical chemistry under the supervision of Professor Hiroshi Nakatsuji. In 1998, he joined Professor Kimihiko Hirao's group in theoretical chemistry in the University of Tokyo, Japan. He became Research Associate at the University of Tokyo in 1999 and Associate Professor in 2004. In 2010, he moved to Advanced Institute for Computational Science, RIKEN, where he became a team leader of the computational molecular science research team. He has over 70 publications in the field of computational quantum chemistry, including work on the development of relativistic molecular theory, accurate molecular theory, and large-scale molecular theory.

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