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Generalized Foldy–Wouthuysen transformation for relativistic two-component methods: Systematic analysis of two-component Hamiltonians

Nobuki Inoue [ORCID] | Yoshihiro Watanabe [ORCID] | Haruyuki Nakano [ORCID]

Department of Chemistry, Graduate School of Science, Kyushu University, Fukuoka, Japan

Correspondence
Nobuki Inoue and Haruyuki Nakano, Department of Chemistry, Graduate School of Science, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.
Email: ion@ccl.scc.kyushu-u.ac.jp and nakano@chem.kyushu-univ.jp

Abstract

The generalized Foldy–Wouthuysen (GFW) transformation was proposed as a generic form that unifies four types of transformations in relativistic two-component methods: unnormalized GFW(UN), and normalized form 1, form 2, and form 3 (GFW(N1), GFW(N2), and GFW(N3)). The GFW transformation covers a wide range of transformations beyond the simple unitary transformation of the Dirac Hamiltonian, allowing for the systematic classification of all existing two-component methods. New two-component methods were also systematically derived based on the GFW transformation. These various two-component methods were applied to hydrogen-like and helium-like ions. Numerical errors in energy were evaluated and classified into four types: the one-electron Hamiltonian approximation, the two-electron operator approximation, the newly defined "picture difference error (PDE)," and the error in determining the transformation, and errors in multi-electron systems were discussed based on this classification.

KEYWORDS

exact two-component (X2C) method, Foldy–Wouthuysen (FW) transformation, picture difference error (PDE), relativistic two-component method

1 | INTRODUCTION

The importance of relativistic effects in understanding the chemical properties of systems containing heavy and superheavy elements is now well recognized. Relativistic effects on atoms and molecules are naturally introduced by the formalism based on the Dirac equation. The wave function, the solution of the Dirac equation, is a four-component spinor, where the four components correspond to electrons and positrons with up and down spins. The relativistic electronic structure methods that use this four-component spinor as an orbital are known as four-component methods. They can handle relativistic effects accurately, but their computational cost is significant compared with nonrelativistic (NR) methods. In the field of chemistry, we are often only interested in solutions corresponding to electrons, and therefore it is useful if the components corresponding to the up and down spins of positrons can be separated. To date, two-component methods that

explicitly handle only the two components corresponding to the up and down spins of electron were developed with this motivation. To effectively reduce computational costs, some approximations are required in the process of obtaining the two-component equation from the four-component equation, and various two-component methods have been developed for the different approximation types, including the Breit–Pauli approximation (BPA),[1] the zeroth order regular approximation (ZORA),[2–5] the infinite order regular approximation (IORA),[6] the Douglas–Kroll method (DK; also known as the Douglas–Kroll–Hess method (DKH)),[7–14] the infinite order two-component method (IOTC; also known as the Barysz–Sadlej–Snijders method (BSS)),[15] and the exact two-component method (X2C).[16–19]

The method to obtain two-component equations from the four-component equation is to apply a transformation that block-diagonalizes the four-component Hamiltonian to the Hamiltonian and the wave function. One such transformation is the Foldy–Wouthuysen

(FW)[2,3,20–23] transformation, and some two-component methods can be derived as approximations to this transformation. In addition, similar transformations, such as unnormalized elimination of the small component (UESC)[16,24] and normalized elimination of the small component (NESC)[16] have been proposed. However, there are also several two-component methods that are not formulated as approximations of the FW transformation, UESC, or NESC. A transformation that generalizes the FW transformation, UESC, and NESC, systematically derives the existing two-component methods under appropriate approximations, and allows for systematic error analysis of the two-component methods from the four-component methods would be useful. In the present article, we present such a transformation, the generalized FW (GFW) transformation.

The present article is structured as follows. In Section 2, the GFW transformation for the one-electron Dirac Hamiltonian in operator and matrix forms is introduced in subsection 2.1, existing and new two-component Hamiltonians are classified using the GFW transformation in subsection 2.2, and the GFW transformation for the two-electron operator is shown and existing two-component transformations for the two-electron operator are classified in subsection 2.3. In Section 3, various two-component methods based on the GFW transformation are applied to a hydrogen-like ion and to helium-like ions, and the accuracy of these methods is discussed. In Section 4, conclusions are presented.

2 | THEORY

2.1 | GFW transformation

The starting point of the discussion is the Dirac equation, the relativistic wave equation of an electron:

$$\widehat{H}_D \Psi^D = \Psi^D E, \tag{1}$$

where the Hamiltonian is a 4×4 matrix operator:

$$\widehat{H}_D = \begin{bmatrix} V & c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} \\ c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} & V - 2c^2 \end{bmatrix}, \tag{2}$$

and the wave function is a four-component spinor:

$$\Psi^D = \begin{bmatrix} \phi^D \\ \chi^D \end{bmatrix}. \tag{3}$$

Here, the operators V and $c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}$ in $\widehat{H}_D$ and the functions ϕ^D and χ^D in Ψ^D are two-component operators and spinors, respectively. The two-component spinors ϕ^D and χ^D in the electronic solutions are called the large and small components, respectively.

The FW transformation.[2,3,20–23]

$$\widehat{U}_N^\dagger \widehat{H}_D \widehat{U}_N = \begin{bmatrix} \widehat{H}_{FW}^{LL} & \widehat{H}_{FW}^{LS} \\ \widehat{H}_{FW}^{SL} & \widehat{H}_{FW}^{SS} \end{bmatrix}, \tag{4}$$

with $\widehat{H}_{FW}^{LS} = \widehat{H}_{FW}^{SL} = 0$ is widely known as the transformation that decouples the four-component Dirac equation to a two-component equation. Note that several different formulations are currently known as FW transformations, and in this paper, we refer to Kutzelnigg's formulation simply as "FW transformation"[21–23] to avoid readers' confusion. The FW transformation $\widehat{U}_N$ and the operator $\widehat{X}$ in $\widehat{U}_N$ are operators satisfying

$$\widehat{U}_N = \begin{bmatrix} \widehat{\omega}_+ & -\widehat{X}^\dagger \widehat{\omega}_- \\ \widehat{X}\widehat{\omega}_+ & \widehat{\omega}_- \end{bmatrix}, \tag{5}$$

$$\widehat{X}\phi^D = \chi^D. \tag{6}$$

The FW transformation $\widehat{U}_N$ consists of two steps, that is, the block-diagonalization step $\widehat{U}_U$ and the renormalization step $\widehat{\Omega}_{FW}$:

$$\widehat{U}_U = \begin{bmatrix} 1 & -\widehat{X}^\dagger \\ \widehat{X} & 1 \end{bmatrix}, \tag{7}$$

$$\widehat{\Omega}_{FW} = \begin{bmatrix} \widehat{\omega}_+ & 0 \\ 0 & \widehat{\omega}_- \end{bmatrix}, \tag{8}$$

with

$$\widehat{\omega}_+ = \left(1 + \widehat{X}^\dagger \widehat{X}\right)^{-1/2}, \tag{9}$$

$$\widehat{\omega}_- = \left(1 + \widehat{X}\widehat{X}^\dagger\right)^{-1/2}. \tag{10}$$

The spinor is transformed in the same manner:

$$\widehat{U}_N^\dagger \Psi^D = \begin{bmatrix} \widehat{\omega}_+^{-1} \phi^D \\ 0 \end{bmatrix}, \tag{11}$$

where only the upper two components remain from Equation (6). The transformation is specified so that the transformed off-diagonal block $\widehat{H}_{FW}^{SL}$ is null, and therefore $\widehat{X}$ satisfies the following equation[2,3,21]:

$$-\widehat{X}V - \widehat{X}c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}\widehat{X} + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} + (V - 2c^2)\widehat{X} = 0. \tag{12}$$

Equation (12) and the two-component equations resulting from the FW transformation

$$\widehat{H}_{FW} \phi^{FW} = \phi^{FW} E, \tag{13}$$

when combined, are equivalent to the four-component Dirac equation and are the basic equations of the two-component method, where $\widehat{H}_{FW}\left(= \widehat{H}_{FW}^{LL}\right)$ and ϕ^{FW} are

$$\widehat{H}_{FW} = \widehat{\omega}_+ \left(V + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}}\widehat{X} + \widehat{X}^\dagger c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} \right. \\ \left. + \widehat{X}^\dagger (V - 2c^2)\widehat{X}\right)\widehat{\omega}_+, \tag{14}$$

$$\phi^{FW} = \widehat{\omega}_+^{-1} \phi^D.$$

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It should be noted here that transformations have been previously proposed that use the same operators as the FW transformation but have different formulation. One of them is UESC[16,24]:

$$\widehat{H}_{\text{UESC}}\phi^{\text{UESC}} = \phi^{\text{UESC}}E, \tag{15}$$

$$\widehat{H}_{\text{UESC}} = V + c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{X}, \ \phi^{\text{UESC}} = \phi^{\text{D}}, \tag{16}$$

another is NESC[16]:

$$\widehat{H}_{\text{NESC}}\phi^{\text{NESC}} = \widehat{\omega}_+^{-2}\phi^{\text{NESC}}E, \tag{17}$$

$$\widehat{H}_{\text{NESC}} = V + c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{X} + \widehat{X}^\dagger c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}} + \widehat{X}^\dagger(V - 2c^2)\widehat{X}, \ \phi^{\text{NESC}} = \phi^{\text{D}}, \tag{18}$$

and yet another is the formulation by Heully et al.,[3] which is also known as the FW transformation:

$$\widehat{H}_{\text{FW(Heully)}}\phi^{\text{FW(Heully)}} = \phi^{\text{FW(Heully)}}E, \tag{19}$$

$$\widehat{H}_{\text{FW(Heully)}} = \widehat{\omega}_+^{-1}\left(V + c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{X}\right)\widehat{\omega}_+, \ \phi^{\text{FW(Heully)}} = \widehat{\omega}_+^{-1}\phi^{\text{D}}. \tag{20}$$

The operator $\widehat{X}$ in Equations (15)–(20) are all the same as $\widehat{X}$ of the FW transformation, determined from Equation (12).

These four decoupling methods of the Dirac Hamiltonian mentioned above, FW, UESC, NESC, and FW (Heully), have much in common and can be described in a common framework. However, several existing two-component methods cannot be derived from this framework. To describe such two-component methods in a single framework, an additional transformation used along with the decoupling transformation is necessary. Thus, we introduce an additional unitary transformation $\widehat{U}_{\text{G}}$ within the diagonal blocks:

$$\widehat{U}_{\text{G}} = \begin{bmatrix} \widehat{U}_+ & 0 \\ 0 & \widehat{U}_- \end{bmatrix}. \tag{21}$$

This transformation does not break the block-diagonality, and hence it does not affect $\widehat{X}$ already determined from Equation (12).

Incorporating the new additional transformation into the four forms, FW, UESC, NESC, and FW (Heully), we propose a GFW transformation:

$$\left(\widehat{U}_{\text{GFW}}^\times \widehat{H}_{\text{D}}\widehat{U}_{\text{GFW}}\right)\left(\widehat{U}_{\text{GFW}}^{-1}\Psi^{\text{D}}\right) = \left(\widehat{U}_{\text{GFW}}^\times\widehat{U}_{\text{GFW}}\right)\left(\widehat{U}_{\text{GFW}}^{-1}\Psi^{\text{D}}\right)E. \tag{22}$$

Here, according to the two options for the product representation of $\widehat{U}_{\text{GFW}}$, we have four choices

$$\widehat{U}_{\text{GFW}} : \widehat{U}_{\text{GFW}} = \widehat{U}_{\text{N}}\widehat{U}_{\text{G}} \text{ or } \widehat{U}_{\text{GFW}} = \widehat{U}_{\text{U}}\widehat{U}_{\text{G}}, \tag{23}$$

and two possibilities for $\widehat{U}_{\text{GFW}}^\times$

$$\widehat{U}_{\text{GFW}}^\times = \widehat{U}_{\text{GFW}}^\dagger \text{ or } \widehat{U}_{\text{GFW}}^\times \neq \widehat{U}_{\text{GFW}}^\dagger. \tag{24}$$

The two-component wave equation resulting from these four GFW transformations can be written in a common form:

$$\widehat{H}_{\text{GFW}}\phi^{\text{GFW}} = \widehat{S}_{\text{GFW}}\phi^{\text{GFW}}E, \tag{25}$$

and when combined with Equation (12), they are equivalent to the four-component Dirac equation and hence are the basic equations of the two-component methods. Here,$\widehat{H}_{\text{GFW}}$ and $\widehat{S}_{\text{GFW}}$ are the two-component Hamiltonian and the normalization factor, respectively. Using this normalization factor, we define the normalization condition:

$$\left\langle\Psi^{\text{D}}|\Psi^{\text{D}}\right\rangle = \left\langle\phi^{\text{GFW}}\left|\widehat{S}_{\text{GFW}}\right|\phi^{\text{GFW}}\right\rangle, \tag{26}$$

which means that the norm in the four-component method is preserved in the two-component method.

Let us examine the four forms more specifically. The first is the transformation using the combination of $\widehat{U}_{\text{GFW}} = \widehat{U}_{\text{U}}\widehat{U}_{\text{G}}$ and $\widehat{U}_{\text{GFW}}^\times \neq \widehat{U}_{\text{GFW}}^\dagger$, which we call "unnormalized form (UN)." Here, $\widehat{U}_{\text{GFW}}^\times$ is written as

$$\widehat{U}_{\text{GFW}}^\times = \widehat{U}_{\text{G}}^\dagger. \tag{27}$$

The resulting two-component wave equation of the GFW(UN) is given by setting

$$\begin{aligned} \widehat{H}_{\text{GFW}} &= \widehat{H}_{\text{UN}} \equiv \widehat{U}_+^\dagger\left(V + c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{X}\right)\widehat{U}_+, \\ \widehat{S}_{\text{GFW}} &= \widehat{S}_{\text{UN}} \equiv \widehat{1}, \\ \phi^{\text{GFW}} &= \phi^{\text{UN}} \equiv \widehat{U}_+^\dagger\phi^{\text{D}}, \end{aligned} \tag{28}$$

in Equation (25). This form includes UESC[16,24] as a special case, $\widehat{U}_{\text{G}} = \widehat{1}$. GFW(UN) is characterized by the fact that it does not satisfy the normalization condition:

$$\begin{aligned} \left\langle\Psi^{\text{D}}|\Psi^{\text{D}}\right\rangle &= \left\langle\phi^{\text{D}}\left|\widehat{\omega}_+^{-2}\right|\phi^{\text{D}}\right\rangle \\ &= \left\langle\phi^{\text{UN}}\left|\widehat{U}_+^\dagger\widehat{\omega}_+^{-2}\widehat{U}_+\right|\phi^{\text{UN}}\right\rangle \\ &\neq \left\langle\phi^{\text{UN}}\left|\widehat{S}_{\text{UN}}\right|\phi^{\text{UN}}\right\rangle. \end{aligned} \tag{29}$$

The second is the transformation using the combination of $\widehat{U}_{\text{GFW}} = \widehat{U}_{\text{N}}\widehat{U}_{\text{G}}$ and $\widehat{U}_{\text{GFW}}^\times = \widehat{U}_{\text{GFW}}^\dagger$, which we call "normalized form 1 (N1)." The resulting two-component wave equation of the GFW(N1) is given by setting

$$\begin{aligned} \widehat{H}_{\text{GFW}} &= \widehat{H}_{\text{N1}} \equiv \widehat{U}_+^\dagger\widehat{\omega}_+\left(V + c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{X} + \widehat{X}^\dagger c\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}} + \widehat{X}^\dagger(V - 2c^2)\widehat{X}\right)\widehat{\omega}_+\widehat{U}_+, \\ \widehat{S}_{\text{GFW}} &= \widehat{S}_{\text{N1}} \equiv \widehat{1}, \\ \phi^{\text{GFW}} &= \phi^{\text{N1}} \equiv \widehat{U}_+^\dagger\widehat{\omega}_+^{-1}\phi^{\text{D}}, \end{aligned} \tag{30}$$

in Equation (25). This form includes the FW transformation[21–23] as a special case, $\widehat{U}_G = \widehat{1}$. The GFW(N1) satisfies the normalization condition:

$$\langle \Psi^D | \Psi^D \rangle = \left\langle \phi^D \left| \widehat{\omega}_+^{-2} \right| \phi^D \right\rangle$$
$$= \left\langle \phi^D \left| \widehat{\omega}_+^{-1} \widehat{U}_+ \widehat{U}_+^{\dagger} \widehat{\omega}_+^{-1} \right| \phi^D \right\rangle \qquad (31)$$
$$= \left\langle \phi^{N1} \left| \widehat{S}_{N1} \right| \phi^{N1} \right\rangle.$$

The third is the transformation using the combination of $\widehat{U}_{GFW} = \widehat{U}_U \widehat{U}_G$ and $\widehat{U}_{GFW}^{\times} = \widehat{U}_{GFW}^{\dagger}$, which we call "normalized form 2 (N2)." The resulting two-component wave equation of the GFW(N2) is given by setting

$$\widehat{H}_{GFW} = \widehat{H}_{N2} \equiv \widehat{U}_+^{\dagger} \left(V + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} \widehat{X} + \widehat{X}^{\dagger} c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} + \widehat{X}^{\dagger} (V - 2c^2) \widehat{X} \right) \widehat{U}_+,$$
$$\widehat{S}_{GFW} = \widehat{S}_{N2} \equiv \widehat{U}_+^{\dagger} \widehat{\omega}_+^{-2} \widehat{U}_+, \qquad (32)$$
$$\phi^{GFW} = \phi^{N2} \equiv \widehat{U}_+^{\dagger} \phi^D,$$

in Equation (25). This form includes NESC[16] as a special case, $\widehat{U}_G = \widehat{1}$. The GFW(N2) satisfies the normalization condition:

$$\langle \Psi^D | \Psi^D \rangle = \left\langle \phi^D \left| \widehat{\omega}_+^{-2} \right| \phi^D \right\rangle$$
$$= \left\langle \phi^D \left| \widehat{U}_+ \widehat{U}_+^{\dagger} \widehat{\omega}_+^{-2} \widehat{U}_+ \widehat{U}_+^{\dagger} \right| \phi^D \right\rangle \qquad (33)$$
$$= \left\langle \phi^{N2} \left| \widehat{S}_{N2} \right| \phi^{N2} \right\rangle.$$

The fourth is the transformation using the combination of $\widehat{U}_{GFW} = \widehat{U}_N \widehat{U}_G$ and $\widehat{U}_{GFW}^{\times} \neq \widehat{U}_{GFW}^{\dagger}$, which we call "normalized form 3 (N3)." Here, $\widehat{U}_{GFW}^{\times}$ is written as

$$\widehat{U}_{GFW}^{\times} = \widehat{U}_G^{\dagger} \widehat{U}_N^{\dagger} \widehat{U}_U. \qquad (34)$$

The resulting two-component wave equation of the GFW(N3) is given by setting

$$\widehat{H}_{GFW} = \widehat{H}_{N3} \equiv \widehat{U}_+^{\dagger} \widehat{\omega}_+^{-1} \left(V + c\boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} \widehat{X} \right) \widehat{\omega}_+ \widehat{U}_+,$$
$$\widehat{S}_{GFW} = \widehat{S}_{N3} \equiv \widehat{1}, \qquad (35)$$
$$\phi^{GFW} = \phi^{N3} \equiv \widehat{U}_+^{\dagger} \widehat{\omega}_+^{-1} \phi^D,$$

in Equation (25). This form includes FW (Heully)[3] as a special case, $\widehat{U}_G = \widehat{1}$. The GFW(N3) satisfies the normalization condition:

$$\langle \Psi^D | \Psi^D \rangle = \left\langle \phi^D \left| \widehat{\omega}_+^{-2} \right| \phi^D \right\rangle$$
$$= \left\langle \phi^D \left| \widehat{\omega}_+^{-1} \widehat{U}_+ \widehat{U}_+^{\dagger} \widehat{\omega}_+^{-1} \right| \phi^D \right\rangle \qquad (36)$$
$$= \left\langle \phi^{N3} \left| \widehat{S}_{N3} \right| \phi^{N3} \right\rangle.$$

The GFW transformation can describe the existing two-component methods by setting $\widehat{X}$ and $\widehat{U}_+$ properly. In some cases, however,

method-specific approximations may be necessary to achieve a full match, such as truncation of a series expansion and Hermitization of the Hamiltonian:

$$\left(\widehat{H}^{\dagger} + \widehat{H} \right) / 2. \qquad (37)$$

The Hermitization is in effect for the GFW(UN) or GFW(N3), where the resulting Hamiltonian may not be Hermitian.

In the last part of this subsection, we rewrite the GFW transformations in operator form into a matrix form, which has the strong advantage of being directly implementable in the computational programs. The matrix form is a representation of equations by the basis functions $\{|\mu\rangle\}$, but in some cases, it differs from direct expression of operators in matrices. For example, the matrix representation of $\widehat{X}$, a key operator of the GFW transformation, differs from the direct expression and is given by

$$(\mathbf{X})_{\mu\nu} = c \sum_{\lambda} \left(\mathbf{T}^{-1} \right)_{\mu\lambda} \left\langle \lambda \left| \boldsymbol{\sigma} \cdot \widehat{\mathbf{p}} \widehat{X} \right| \nu \right\rangle. \qquad (38)$$

The two-component wave Equation (25) is rewritten in matrix form:

$$\mathbf{H}_{GFW} \mathbf{C}^{GFW} = \mathbf{S}_{GFW} \mathbf{C}^{GFW} \mathbf{E}, \qquad (39)$$

with

$$(\mathbf{H}_{GFW})_{\mu\nu} = \left\langle \mu \left| \widehat{H}_{GFW} \right| \nu \right\rangle, \quad (\mathbf{S}_{GFW})_{\mu\nu} = \left\langle \mu \left| \widehat{S}_{GFW} \right| \nu \right\rangle. \qquad (40)$$

Applying Equations (28), (30), (32), and (35) to Equations (39) and (40), we obtain the two-component wave equation in matrix form for GFW(UN), GFW(N1) GFW(N2), and GFW(N3), respectively. The resulting two-component Hamiltonian and overlap matrices are

$$\mathbf{H}^{UN} = \mathbf{U}_+^{\dagger} (\mathbf{V} + \mathbf{TX}) \mathbf{U}_+, \quad \mathbf{S}^{UN} = \mathbf{S}, \qquad (41)$$

$$\mathbf{H}^{N1} = \mathbf{U}_+^{\dagger} \boldsymbol{\Omega}_+^{\dagger} \left(\widetilde{\mathbf{V}} + \widetilde{\mathbf{T}} \right) \boldsymbol{\Omega}_+ \mathbf{U}_+, \quad \mathbf{S}^{N1} = \mathbf{S}, \qquad (42)$$

$$\mathbf{H}^{N2} = \mathbf{U}_+^{\dagger} \left(\widetilde{\mathbf{V}} + \widetilde{\mathbf{T}} \right) \mathbf{U}_+, \quad \mathbf{S}^{N2} = \mathbf{U}_+^{\dagger} \widetilde{\mathbf{S}} \mathbf{U}_+, \qquad (43)$$

$$\mathbf{H}^{N3} = \mathbf{U}_+^{\dagger} \mathbf{S} \boldsymbol{\Omega}_+^{-1} \mathbf{S}^{-1} (\mathbf{V} + \mathbf{TX}) \boldsymbol{\Omega}_+ \mathbf{U}_+, \quad \mathbf{S}^{N3} = \mathbf{S}. \qquad (44)$$

Here, $\mathbf{S}$, $\mathbf{T}$, and $\mathbf{V}$ are the NR overlap, kinetic energy, external potential matrices given by

$$(\mathbf{S})_{\mu\nu} = \langle \mu | \nu \rangle, \quad (\mathbf{T})_{\mu\nu} = \langle \mu | p^2/2 | \nu \rangle, \quad (\mathbf{V})_{\mu\nu} = \langle \mu | V | \nu \rangle, \qquad (45)$$

respectively. $\mathbf{V}^p$ defined here is the matrix used to the relativistic correction of external potential, and given by

$$(\mathbf{V}^p)_{\mu\nu} = \langle\mu|\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}V\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}|\nu\rangle. \tag{46}$$

The matrices $\widetilde{\mathbf{S}}$, $\widetilde{\mathbf{T}}$, and $\widetilde{\mathbf{V}}$ are defined from $\mathbf{X}$, $\mathbf{S}$, $\mathbf{T}$, $\mathbf{V}$, and $\mathbf{V}^p$ as

$$\widetilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2c^2}\mathbf{X}^\dagger\mathbf{T}\mathbf{X}, \ \widetilde{\mathbf{T}} = \mathbf{T}\mathbf{X} + \mathbf{X}^\dagger\mathbf{T} - \mathbf{X}^\dagger\mathbf{T}\mathbf{X}, \ \widetilde{\mathbf{V}} = \mathbf{V} + \frac{1}{4c^2}\mathbf{X}^\dagger\mathbf{V}^p\mathbf{X}, \tag{47}$$

and $\boldsymbol{\Omega}_+$ and $\mathbf{U}_+$ are the matrix representations of operators $\widehat{\omega}_+$ and $\widehat{U}_+$:

$$(\boldsymbol{\Omega}_+)_{\mu\nu} = \sum_\lambda \left(\mathbf{S}^{-1}\right)_{\mu\lambda}\langle\lambda|\widehat{\omega}_+|\nu\rangle, \tag{48}$$

$$(\mathbf{U}_+)_{\mu\nu} = \sum_\lambda \left(\mathbf{S}^{-1}\right)_{\mu\lambda}\left\langle\lambda\left|\widehat{U}_+\right|\nu\right\rangle. \tag{49}$$

Using the definitions in Equations (9), (47), and (48), $\boldsymbol{\Omega}_+$ is explicitly represented as

$$\boldsymbol{\Omega}_+ = \mathbf{S}^{-1/2}\left[\mathbf{S}^{-1/2}\widetilde{\mathbf{S}}\mathbf{S}^{-1/2}\right]^{-1/2}\mathbf{S}^{1/2}. \tag{50}$$

The matrix representations for FW, UESC, NESC, and FW (Heully) are given by Equations (41–44) with $\mathbf{U}_+ = \mathbf{I}$ applied, respectively. The normalized modified FW (NMFW),[25]

$$\mathbf{H}^{\text{NMFW}} = \mathbf{S}^{1/2}\widetilde{\mathbf{S}}^{-1/2}\left(\widetilde{\mathbf{V}} + \widetilde{\mathbf{T}}\right)\widetilde{\mathbf{S}}^{-1/2}\mathbf{S}^{1/2}, \ \mathbf{S}^{\text{NMFW}} = \mathbf{S}, \tag{51}$$

is the case with $\mathbf{U}_+ = \boldsymbol{\Omega}_+^{-1}\widetilde{\mathbf{S}}^{-1/2}\mathbf{S}^{1/2}(\neq\mathbf{I})$ applied in Equation (42) and is not identical to the matrix representation of FW.

2.2 | Classification of two-component methods using GFW transformation

In the previous subsection, we proposed a new GFW transformation. In this subsection, we classify the various existing two-component methods to the four-types of GFW transformation or approximations thereof. Table 1 shows the classification of existing two-component methods. First, consider the case $\widehat{U}_+ = \widehat{1}$. For $\widehat{X}$, several approximations are known. One approximation for $\widehat{X}$ is the "low-order (LO) approximation"[26,27]:

$$\widehat{X} = \frac{1}{2c}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}. \tag{52}$$

For this $\widehat{X}$, if we use GFW(UN), we obtain the NR Schrödinger equation, and if we use GFW(N1) and truncate the Taylor series of the Hamiltonian for $1/c$ at the second order ($1/c^2$), we obtain BPA[1]; if we use GFW(N2), we obtain the low-order NESC (LO-NESC).[26,27] Another approximation for $\widehat{X}$ is "regular approximation (RA)":

$$\widehat{X} = \frac{c}{2c^2 - V}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}. \tag{53}$$

For this $\widehat{X}$, if we use GFW(UN), GFW(N1), and GFW(N2), we obtain ZORA,[5] RFW,[6] and IORA,[6] respectively. GFW(N3) has not been reported previously, and thus we obtained a new approximation, which we named RA(N3). The methods, such as the newly derived RA(N3) for method comparison in this work, are summarized in Table 2. Here, although ZORA is based on GFW(UN), it gives a Hermitian Hamiltonian. However, in general, RA(N3) can give a non-Hermitian Hamiltonian, and we named the RA(N3) with Hermitization in such a case "RA(N3)-H." If we set $V = 0$ in Equation (12) (the free particle FW (fpFW)), we have another $\widehat{X}$:

TABLE 1 Classification of existing two-component methods.

	GFW type	Approximation of $\widehat{X}$	Series truncation	Hamiltonian Hermitization	$\widehat{U}_G$
NR	UN	LO	–	–	$\widehat{1}$
LO-NESC	N2	LO	–	–	$\widehat{1}$
BPA	N1	LO	$1/c^2$	–	$\widehat{1}$
ZORA	UN	RA	–	–	$\widehat{1}$
IORA	N2	RA	–	–	$\widehat{1}$
RFW	N1	RA	–	–	$\widehat{1}$
FORA	UN	RA and Equation (71)	–	✓	$\widehat{1}$
NESC-SORA	N2	RA and Equation (75)	–	–	$\widehat{1}$
RESC	N3	Equation (55)	$1/c^2$ only for $\widehat{\omega}_+^{-1}, \widehat{\omega}_+$	✓	$\widehat{1}$
DK1	N1	fpFW	–	–	$\widehat{1}$
DKn ($n > 1$)	N1	Equation (61)	V^n	–	Equation (62)
IOTC	N1	exact solution of Equation (12)	–	–	Equation (56)
X2C	N1	exact solution of Equation (12)	–	–	$\widehat{1}$

TABLE 2 Classification of newly derived two-component methods.

	GFW Type	Approximation of $\widehat{X}$	Series truncation	Hamiltonian Hermitization	$\widehat{U}_G$
X2C(UN)	UN	exact solution of Equation (12)	–	×	$\widehat{1}$
X2C(N2)	N2	exact solution of Equation (12)	–	–	$\widehat{1}$
X2C(N3)	N3	exact solution of Equation (12)	–	×	$\widehat{1}$
X2C(UN)-*H*	UN	exact solution of Equation (12)	–	✓	$\widehat{1}$
X2C(N3)-*H*	N3	exact solution of Equation (12)	–	✓	$\widehat{1}$
RA(N3)	N3	RA	–	×	$\widehat{1}$
RA(N3)-*H*	N3	RA	–	✓	$\widehat{1}$
RESC-*NH*	N3	Equation (55)	$1/c^2$ only for $\widehat{\omega}_+^{-1}, \widehat{\omega}_+$	×	$\widehat{1}$

$$\widehat{X} = \widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}, \ \widehat{B} = \frac{c}{c^2 + \widehat{E}_p}, \ \widehat{E}_p = \sqrt{c^2\widehat{p}^2 + c^4}. \tag{54}$$

For this $\widehat{X}$, if we use GFW(N1), we obtain the first-order Douglas–Kroll method (DK1).[7] Furthermore, if we use the following $\widehat{X}$ (which is Equation (54) with additional terms)

$$\widehat{X} = \widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}} + c^{-1}\widehat{B}^2 V\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}} - c^{-1}\widehat{p}^{-2}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}} V\widehat{B}^2\widehat{p}^2, \tag{55}$$

and use GFW(N3), the relativistic scheme with small component elimination (RESC)[28] is obtained. In RESC, as further approximations, the second and third terms in rhs of Equation (55) are neglected in evaluating $\widehat{\omega}_+$ and $\widehat{\omega}_+^{-1}$ in the Hamiltonian (Equation (35)), and Hermitization (Equation (37)) is applied. We also considered RESC with no Hermitization for comparison, which was named "RESC-*NH*."

Next, consider the case of $\widehat{U}_+ \neq \widehat{1}$. If we use $\widehat{X}$, the exact solution of Equation (12), and following $\widehat{U}_+$:

$$\widehat{U}_+ = \left[\widehat{A}\left(1 - \widehat{B}\widehat{p}\widehat{Y}\right)\widehat{\omega}_{\text{IOTC}}\widehat{\omega}_{\text{IOTC}}\left(1 - \widehat{Y}^\dagger\widehat{p}\widehat{B}\right)\widehat{A}\right]^{-1/2}\widehat{A}\left(1 - \widehat{B}\widehat{p}\widehat{Y}\right)\widehat{\omega}_{\text{IOTC}}, \tag{56}$$

and use GFW(N1), we obtain IOTC.[15] Here, $\widehat{A}$ and $\widehat{\omega}_{\text{IOTC}}$ are

$$\widehat{A} = \sqrt{\frac{E_p + c^2}{2E_p}}, \quad \widehat{\omega}_{\text{IOTC}} = \left(1 + \widehat{Y}^\dagger\widehat{Y}\right)^{-1/2}, \tag{57}$$

and $\widehat{Y}$ is the solution of the nonlinear equation:

$$\begin{aligned}\widehat{Y} = \sum_{p,p'}|p\rangle\frac{1}{E_p + E_{p'}}\langle p|\widehat{p}^{-1}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{O}_1 \\ + \widehat{p}^{-1}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{E}_1\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{p}^{-1}\widehat{Y} - \widehat{Y}\widehat{E}_1 \\ + \widehat{Y}\widehat{O}_1\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{p}^{-1}\widehat{Y}|p'\rangle\langle p'|,\end{aligned} \tag{58}$$

with

$$\widehat{E}_1 = \widehat{A}V\widehat{A} + \widehat{A}\widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}V\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{B}\widehat{A}, \tag{59}$$

$$\widehat{O}_1 = \widehat{A}V\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{B}\widehat{A} - \widehat{A}\widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}V\widehat{A}. \tag{60}$$

Moreover, if we use the following $\widehat{X}$ and $\widehat{U}_+$:

$$\widehat{X} = \widehat{A}\widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\left(\widehat{U}_{\text{DK}n}^{LL} + \widehat{B}^{-1}\widehat{p}^{-2}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{U}_{\text{DK}n}^{SL}\right)\left(\widehat{U}_{\text{DK}n}^{LL} - \widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{U}_{\text{DK}n}^{SL}\right)^{-1}\widehat{A}^{-1}, \tag{61}$$

$$\widehat{U}_+ = \left[\widehat{A}\left(\widehat{U}_{\text{DK}n}^{LL} - \widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{U}_{\text{DK}n}^{SL}\right)\left(\widehat{U}_{\text{DK}n}^{LL\dagger} - \widehat{U}_{\text{DK}n}^{SL\dagger}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{B}\right)\widehat{A}\right]^{-1/2}\widehat{A}\left(\widehat{U}_{\text{DK}n}^{LL} - \widehat{B}\boldsymbol{\sigma}\cdot\widehat{\mathbf{p}}\widehat{U}_{\text{DK}n}^{SL}\right), \tag{62}$$

with

$$\widehat{U}_{\text{DK}n} = \prod_{i=1}^{n-1}\widehat{U}_i, \quad \widehat{U}_i = f\left(\begin{bmatrix} 0 & -\widehat{W}_i^\dagger \\ \widehat{W}_i & 0 \end{bmatrix}\right), \tag{63}$$

use GFW(N1), and truncate the transformed Hamiltonian up to the n-th order of V, we obtain the n-th order DK (DKn).[9–14] This truncation is done based on the Taylor series of $f(x)$ and $\widehat{W}_k$ being k-th order with respect to V. Here, the function $f(x)$ characterizes the variants of DK and should satisfy

$$f(x)f(-x) = 1, \tag{64}$$

for $\widehat{U}_i$ to be unitary. Several function forms have been proposed (e.g., square root type function,[7] Cayley transform type,[14,21] McWeeny choice,[29] exponential type,[10] optimal unitary type[14]) and a general treatment[14] that covers all the function forms is also proposed. Each $\widehat{W}_k$ are determined by the condition that the k-th order terms of V in the *LS*-part of the transformed four-component Hamiltonian cancel out. The low-order operators $\widehat{W}_1$ and $\widehat{W}_2$ can be determined regardless of the choice of $f(x)$ and they have a common form:

$$\widehat{W}_1 = \sum_{p,p'}|p\rangle\frac{\langle p|\widehat{O}_1|p'\rangle}{E_p + E_{p'}}\langle p'|, \tag{65}$$

$$\widehat{W}_2 = \sum_{p,p'} |p\rangle \frac{\left\langle p \left| \widehat{E}_1 \widehat{W}_1 - \widehat{W}_1 \widehat{E}_1 \right| p' \right\rangle}{E_p + E_{p'}} \langle p'|. \tag{66}$$

On the other hand, $\widehat{W}_k (k \geq 3)$ are different depending on the function $f(x)$. The DK2, DK3, and DK4 Hamiltonians are common[14] regardless of the choice of $f(x)$, while the DKn $(n \geq 5)$ Hamiltonians differ depending on the choice of $f(x)$.

In the following, we discuss the two-component methods that were not mentioned in first half of this subsection; first-order regular approximation (FORA), second-order regular approximation to NESC (NESC-SORA), and X2C. It is more straightforward to consider these methods in matrix form than in operator form. The starting point of the discussion is the matrix form of Equations (52–54),

$$\mathbf{X} = \mathbf{I}, \tag{67}$$

$$\mathbf{X} = \left(\mathbf{T} - \frac{1}{4c^2} \mathbf{V}^p \right)^{-1} \mathbf{T}, \tag{68}$$

and

$$\mathbf{X} = 2c\mathbf{S}^{-1}\mathbf{B}, \tag{69}$$

respectively. Here, matrix $\mathbf{B}$ is defined by $(\mathbf{B})_{\mu\nu} = \langle \mu | \widehat{B} | \nu \rangle$. To enhance the approximation of $\mathbf{X}$ in Equations (67–69), an $\mathbf{X}$ matrix that is closer to the exact solution of Equation (12) needs to be adopted. The matrix form can be used to systematically provide such $\mathbf{X}$. In matrix form, Equation (12) is written as

$$\mathbf{X} = \mathbf{X}_0 \left[\mathbf{I} - \frac{1}{2c^2} \mathbf{X} \mathbf{S}^{-1} (\mathbf{V} + \mathbf{T}\mathbf{X}) \right], \tag{70}$$

where $\mathbf{X}_0$ is equal to $\mathbf{X}$ of Equation (68). One way to use Equation (70) is to create a recurrence formula, for example,

$$\mathbf{X}_{k+1} = \mathbf{X}_0 \left[\mathbf{I} - \frac{1}{2c^2} \mathbf{X}_k \mathbf{S}^{-1} (\mathbf{V} + \mathbf{T}\mathbf{X}_k) \right], \tag{71}$$

where $\mathbf{X}$ converges to the exact solution of Equation (70), unless it diverges. Therefore, it is expected that a better approximation of $\mathbf{X}$ is obtained from $\mathbf{X}_0$ by the recurrence formula. From the first step of the recurrence relation (Equation (71)),

$$\mathbf{X}_1 = \mathbf{X}_0 \left[\mathbf{I} - \frac{1}{2c^2} \mathbf{X}_0 \mathbf{S}^{-1} (\mathbf{V} + \mathbf{T}\mathbf{X}_0) \right], \tag{72}$$

is obtained. Substituting this $\mathbf{X}_1$ into UESC yields the FORA Hamiltonian[4] after Hermitization (Equation (37)):

$$\mathbf{H}^{FORA} = \frac{1}{2} \left[(\mathbf{V} + \mathbf{T}\mathbf{X}_1) + (\mathbf{V} + \mathbf{X}_1^\dagger \mathbf{T}) \right]. \tag{73}$$

Equation (70) is also transformed to another equivalent form:

$$\mathbf{X} = \mathbf{X}_0 \left[\mathbf{I} - \frac{1}{2c^2} \mathbf{X} \widetilde{\mathbf{S}}^{-1} (\widetilde{\mathbf{V}} + \widetilde{\mathbf{T}}) \right]. \tag{74}$$

This equation is similarly used to create a recurrence formula:

$$\mathbf{X}_{k+1} = \mathbf{X}_0 \left[\mathbf{I} - \frac{1}{2c^2} \mathbf{X}_k \widetilde{\mathbf{S}}^{-1} (\widetilde{\mathbf{V}} + \widetilde{\mathbf{T}}) \right]. \tag{75}$$

$\mathbf{X}_1'$ obtained from the first step of the recurrence relation (75) is

$$\mathbf{X}_1' = \mathbf{X}_0 \left[\mathbf{I} - \frac{1}{2c^2} \mathbf{X}_0 \widetilde{\mathbf{S}}_0^{-1} (\widetilde{\mathbf{V}}_0 + \widetilde{\mathbf{T}}_0) \right], \tag{76}$$

with

$$\widetilde{\mathbf{S}}_0 = \mathbf{S} + \frac{1}{2c^2} \mathbf{X}_0^\dagger \mathbf{T} \mathbf{X}_0, \quad \widetilde{\mathbf{T}}_0 = \mathbf{T}\mathbf{X}_0 + \mathbf{X}_0^\dagger \mathbf{T} - \mathbf{X}_0^\dagger \mathbf{T} \mathbf{X}_0, \quad \widetilde{\mathbf{V}}_0 = \mathbf{V} + \frac{1}{4c^2} \mathbf{X}_0^\dagger \mathbf{V}^p \mathbf{X}_0, \tag{77}$$

and substituting $\mathbf{X}_1'$ into NESC yields the NESC-SORA[30] Hamiltonian. Thus, both FORA and NESC-SORA are derived from the first step of the recurrence relations. In this manner, the recurrence Equations (71) and (75) can be formally used to obtain $\mathbf{X}$ with sequential approximation, but they can also be used to obtain the solution of Equation (70) numerically by the iterative method. However, the convergence of the recurrence Equations (71) and (75) is not good, and special numerical processing is often required[31] to make them converge.

The solution of Equation (70) can also be obtained through the direct diagonalization of the one-electron Hamiltonian and such a scheme is called X2C.[16–19] The X2C scheme can also be derived within the framework of the GFW transformation as follows. Using the basis function expansion by $\{|\mu\rangle\}$, the matrix forms of the Dirac Hamiltonian and the four-component overlap are given by

$$\mathbf{H}_D = \begin{bmatrix} \mathbf{V} & 2c\mathbf{T}\boldsymbol{\kappa} \\ 2c\boldsymbol{\kappa}\mathbf{T} & \boldsymbol{\kappa}\mathbf{V}^p\boldsymbol{\kappa} - 4c^2\boldsymbol{\kappa}\mathbf{T}\boldsymbol{\kappa} \end{bmatrix}, \tag{78}$$

and

$$\mathbf{S}_D = \begin{bmatrix} \mathbf{S} & 0 \\ 0 & 2\boldsymbol{\kappa}\mathbf{T}\boldsymbol{\kappa} \end{bmatrix}, \tag{79}$$

respectively, with

$$(\boldsymbol{\kappa})_{\mu\nu} = \delta_{\mu\nu} / \sqrt{2T_{\mu\mu}}. \tag{80}$$

By solving the generalized eigenvalue problem for the Hamiltonian $\mathbf{H}_D$, the eigenvector matrix

$$\begin{bmatrix} \mathbf{C}_+^L & \mathbf{C}_-^L \\ \mathbf{C}_+^S & \mathbf{C}_-^S \end{bmatrix}, \tag{81}$$

is obtained, where the eigenvectors with positive and negative energy are divided between the left and right half columns, respectively. On the other hand, the transformation GFW(N1) is represented in matrix form as

$$
\begin{bmatrix}
\mathbf{\Omega}_+ \mathbf{U}_+ & -c^{-1}\mathbf{S}^{-1}\boldsymbol{\kappa}\mathbf{T}\mathbf{X}\mathbf{\Omega}_-\mathbf{U}_- \\
(2c)^{-1}\boldsymbol{\kappa}^{-1}\mathbf{X}\mathbf{\Omega}_+\mathbf{U}_+ & \mathbf{\Omega}_-\mathbf{U}_-
\end{bmatrix},
\tag{82}
$$

with

$$
\begin{aligned}
(\mathbf{\Omega}_-)_{\mu\nu} &= \sum_\lambda \left(\mathbf{S}^{-1}\right)_{\mu\lambda} \langle\lambda|\widehat{\omega}_-|\nu\rangle, \\
(\mathbf{U}_-)_{\mu\nu} &= \sum_\lambda \left(\mathbf{S}^{-1}\right)_{\mu\lambda} \left\langle\lambda\left|\widehat{U}_-\right|\nu\right\rangle.
\end{aligned}
\tag{83}
$$

Assuming that the expressions in Equations (81) and (82) are equivalent, two equations are obtained from the matrix correspondence:

$$
\mathbf{X} = -c\mathbf{T}^{-1}\boldsymbol{\kappa}^{-1}\left(\mathbf{C}_-^S \mathbf{C}_-^{S\dagger}\right)^{-1}\mathbf{C}_-^S \mathbf{C}_-^{L\dagger}\mathbf{S},
\tag{84}
$$

$$
\mathbf{X} = 2c\boldsymbol{\kappa}\mathbf{C}_+^S \mathbf{C}_+^{L\dagger}\left(\mathbf{C}_+^L \mathbf{C}_+^{L\dagger}\right)^{-1}.
\tag{85}
$$

The two $\mathbf{X}$ matrices determined from Equations (84) and (85) are identical. Equations (84) and (85) obtained from GFW(N1) are identical to the equations shown in the original X2C papers,[17–19] indicating that the X2C method is actually derived in the framework of the GFW transformation. The derivation based on the GFW transformation is straightforward, because the FW transformation only describes the block diagonalization, whereas the GFW transformation can represent more general transformations, including full diagonalization. This favorable feature of the GFW transformation allowed us a direct comparison of Equations (81) and (82) to obtain Equations (84) and (85).

The $\mathbf{X}$ matrix determined from Equation (84) (or Equation (85)) can also be applied to GFW(UN), GFW(N2), and GFW(N3). We refer to GFW(UN), GFW(N2), and GFW(N3) with Equation (84) (or Equation (85)) and $\mathbf{U}_+ = \mathbf{I}$ applied as X2C(UN), X2C(N2), and X2C(N3), respectively. Furthermore, we refer to the Hermitized X2C (UN) and X2C(N3) as X2C(UN)-*H* and X2C(N3)-*H*, respectively. The Hermitization is important because these transformations may lead to non-Hermitian Hamiltonians.

2.3 | GFW transformation of two-electron operator

For higher accuracy of the two-component methods, the transformations of the two-electron operator are essential as well as the one-electron Hamiltonian. The two-component methods involving the transformation of the two-electron operator have already been developed for BPA,[1,32] DK1,[33–35] DK2,[36] DK3,[36] and IOTC.[37] Moreover, without specification of $\widehat{X}$, the two-electron operator for NESC[26,30]

has been developed. Here, the transformation of the two-electron operator is discussed in the framework of the GFW transformation.

The two-component two-electron operator obtained by applying the GFW transformation to the four-component two-electron Coulomb interaction operator is

$$
\widehat{g}^{\text{GFW}}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{X,Y}^{L,S} \left(\widehat{K}^{X(l)}(\mathbf{r}_1)\right)^\dagger \left(\widehat{K}^{Y(l)}(\mathbf{r}_2)\right)^\dagger \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \widehat{K}^{X(l)}(\mathbf{r}_1)\widehat{K}^{Y(l)}(\mathbf{r}_2),
\tag{86}
$$

where the transformation operators $\widehat{K}^{L(l)}$, $\widehat{K}^{L(r)}$, $\widehat{K}^{S(l)}$, and $\widehat{K}^{S(r)}$ used in Equation (86) are

$$
\begin{aligned}
\widehat{K}^{L(l)} &= \widehat{K}^{L(r)} = \widehat{U}_+, \\
\widehat{K}^{S(l)} &= \widehat{K}^{S(r)} = 0,
\end{aligned}
\tag{87}
$$

for GFW(UN),

$$
\begin{aligned}
\widehat{K}^{L(l)} &= \widehat{K}^{L(r)} = \widehat{\omega}_+\widehat{U}_+, \\
\widehat{K}^{S(l)} &= \widehat{K}^{S(r)} = \widehat{X}\widehat{\omega}_+\widehat{U}_+,
\end{aligned}
\tag{88}
$$

for GFW(N1),

$$
\begin{aligned}
\widehat{K}^{L(l)} &= \widehat{K}^{L(r)} = \widehat{U}_+, \\
\widehat{K}^{S(l)} &= \widehat{K}^{S(r)} = \widehat{X}\widehat{U}_+,
\end{aligned}
\tag{89}
$$

for GFW(N2), and

$$
\begin{aligned}
\widehat{K}^{L(l)} &= \widehat{\omega}_+^{-1}\widehat{U}_+, \\
\widehat{K}^{L(r)} &= \widehat{\omega}_+\widehat{U}_+, \\
\widehat{K}^{S(l)} &= \widehat{K}^{S(r)} = 0,
\end{aligned}
\tag{90}
$$

for GFW(N3). The Hermitization can also be defined for two-electron operators. Because only GFW(N3) gives a non-Hermitian two-electron operator, the Hermitization is effective only for GFW(N3):

$$
\begin{aligned}
\widehat{g}^{\text{GFW(N3)}-H}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{4}\Bigg[& \left(\widehat{K}^{L(l)}(\mathbf{r}_1)\right)^\dagger \left(\widehat{K}^{L(l)}(\mathbf{r}_2)\right)^\dagger \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \widehat{K}^{L(r)}(\mathbf{r}_1)\widehat{K}^{L(r)}(\mathbf{r}_2) \\
+ & \left(\widehat{K}^{L(l)}(\mathbf{r}_1)\right)^\dagger \left(\widehat{K}^{L(r)}(\mathbf{r}_2)\right)^\dagger \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \widehat{K}^{L(r)}(\mathbf{r}_1)\widehat{K}^{L(l)}(\mathbf{r}_2) \\
+ & \left(\widehat{K}^{L(r)}(\mathbf{r}_1)\right)^\dagger \left(\widehat{K}^{L(l)}(\mathbf{r}_2)\right)^\dagger \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \widehat{K}^{L(l)}(\mathbf{r}_1)\widehat{K}^{L(r)}(\mathbf{r}_2) \\
+ & \left(\widehat{K}^{L(r)}(\mathbf{r}_1)\right)^\dagger \left(\widehat{K}^{L(r)}(\mathbf{r}_2)\right)^\dagger \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} \widehat{K}^{L(l)}(\mathbf{r}_1)\widehat{K}^{L(l)}(\mathbf{r}_2) \Bigg].
\end{aligned}
\tag{91}
$$

The two-electron operators of various two-component methods are derived from Equation (86) by the same procedure as for the two-component one-electron Hamiltonian. Take the $\widehat{U}_+ = \widehat{1}$ case as an

example. Applying GFW(UN) and Equation (52) to Equation (86) yields the NR approximation:

$$\widehat{g}^{NR}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{92}$$

and applying GFW(N1) and Equation (52) to Equation (86) and truncating the Taylor series for $1/c$ of the two-electron operator up to the second order $(1/c^2)$ yield the BPA.

Let us consider the matrix form of the two-component two-electron operator. The matrix representation of the two-electron operator is the two-electron integral, which is given by

$$(\alpha\beta|\gamma\delta)^{GFW} = \sum_{X,Y}^{L,S} \sum_{\mu\nu\lambda\rho} K_{\alpha\mu}^{X(l)\dagger} K_{\gamma\lambda}^{X(l)\dagger} (\mu^X \nu^X | \lambda^Y \rho^Y) K_{\nu\beta}^{Y(r)} K_{\rho\delta}^{Y(r)}, \tag{93}$$

where the bases $|\mu^L\rangle$ and $|\mu^S\rangle$ denote $|\mu\rangle$ and $\boldsymbol{\sigma} \cdot \mathbf{p}|\mu\rangle$, respectively. The transformation matrices $\mathbf{K}^{L(l)}$, $\mathbf{K}^{L(r)}$, $\mathbf{K}^{S(l)}$, and $\mathbf{K}^{S(r)}$ are

$$\begin{aligned} \mathbf{K}^{L(l)} = \mathbf{K}^{L(r)} &= \mathbf{U}_+, \\ \mathbf{K}^{S(l)} = \mathbf{K}^{S(r)} &= \mathbf{0}, \end{aligned} \tag{94}$$

for GFW(UN),

$$\begin{aligned} \mathbf{K}^{L(l)} = \mathbf{K}^{L(r)} &= \boldsymbol{\omega}_+ \mathbf{U}_+, \\ \mathbf{K}^{S(l)} = \mathbf{K}^{S(r)} &= \frac{1}{2c} \mathbf{X} \boldsymbol{\omega}_+ \mathbf{U}_+, \end{aligned} \tag{95}$$

for GFW(N1),

$$\begin{aligned} \mathbf{K}^{L(l)} = \mathbf{K}^{L(r)} &= \mathbf{U}_+, \\ \mathbf{K}^{S(l)} = \mathbf{K}^{S(r)} &= \frac{1}{2c} \mathbf{X} \mathbf{U}_+, \end{aligned} \tag{96}$$

for GFW(N2), and

$$\begin{aligned} \mathbf{K}^{L(l)} &= \mathbf{S}^{-1} \boldsymbol{\omega}_+^{-1} \mathbf{S} \mathbf{U}_+, \\ \mathbf{K}^{L(r)} &= \boldsymbol{\omega}_+ \mathbf{U}_+, \\ \mathbf{K}^{S(l)} = \mathbf{K}^{S(r)} &= \mathbf{0}, \end{aligned} \tag{97}$$

for GFW(N3). In the matrix form, the NR approximation to the two-component two-electron operator corresponds to the replacement of $(\alpha\beta|\gamma\delta)^{GFW}$ with $(\alpha\beta|\gamma\delta)$.

For multi-electron systems, even using the two-component transformation of the two-electron operator discussed here and applying the exact $\widehat{X}$ in Equation (12) to the two-component transformation does not give the same results as the four-component method. This is because Equation (12) is a condition for block diagonalization of the one-electron Hamiltonian, in which the two-electron operator is not taken into account. Such errors can be eliminated by applying a two-component transformation to the Dirac–Fock operator instead of the one-electron Hamiltonian in, for example, the Hartree–Fock method.[35,38]

3 | NUMERICAL RESULTS AND DISCUSSION

As shown in subsection 2.2, the GFW transformation framework systematically derives various existing two-component methods. In this section, we numerically examine the accuracy of the approximations of the various two-component methods described in the framework of the GFW transformation.

3.1 | Calculations by a single Gaussian function

First, consider the calculation on a very simple model. We calculated the energy of the hydrogen-like ion with nuclear charge $Z = 96$ using a single normalized s-type Gaussian functions: $N\exp(-\zeta r^2)$. The specific form of this "single Gaussian function" for the four-component method is given by

$$N^L \begin{bmatrix} \exp(-\zeta r^2) \\ 0 \end{bmatrix}, \quad N^S \boldsymbol{\sigma} \cdot \mathbf{p} \begin{bmatrix} \exp(-\zeta r^2) \\ 0 \end{bmatrix}, \tag{98}$$

where N^L and N^S are the normalization constants. Figure 1 shows the energy E plotted against the exponent ζ of the Gaussian function. This plot follows the method used in Refs.26,27 The vertical axis represents the modified logarithmic scale of E, and the horizontal axis represents the logarithmic scale of ζ.

Three important pieces of information can be observed from Figure 1. First, the asymptotic behavior in the large ζ region indicates the p-dependent form of the kinetic energy. For a single Gaussian function, the expectation value $\langle p^2 \rangle$ is 3ζ, and in the large ζ region, the kinetic energy is dominant in the total energy relative to the nuclear attraction potential energy. Therefore, the behavior of the curve in the large ζ region represents the $\langle p^2 \rangle$ dependence of the relativistic kinetic energy $\sqrt{c^2\langle p^2 \rangle + c^4} - c^2 \sim \sqrt{3c^2\zeta}$. Because the graph in Figure 1 is bi-logarithmic, the slope of the curve should be 1/2. This condition is not satisfied in the NR, BPA, FORA, and LO-NESC approximations (Figure 1). Second, the existence of a minimum value indicates the possibility of a stable variational calculation. The absence of a minimum value implies that the more the Gaussian basis functions with larger exponents added, the lower the total energy. Thus, the existence of the minimum value is essential for the solution of the linear variational problem using basis function expansion. The BPA, FORA, and LO-NESC approximations, which do not have the minimum value, are not suitable for variational calculations (Figure 1). Third, the graphs give a rough indication of the approximation accuracy of the methods. The four-component method is the reference for the X2C methods. The RESC curve deviates slightly from the four-component method curve; the ZORA, IORA, and RFW curves are also good approximations of the four-component method curve. For the entire ζ region, the NESC-SORA, DK, IOTC, and X2C closely follow the four-component method curve. The IOTC and X2C theoretically give the
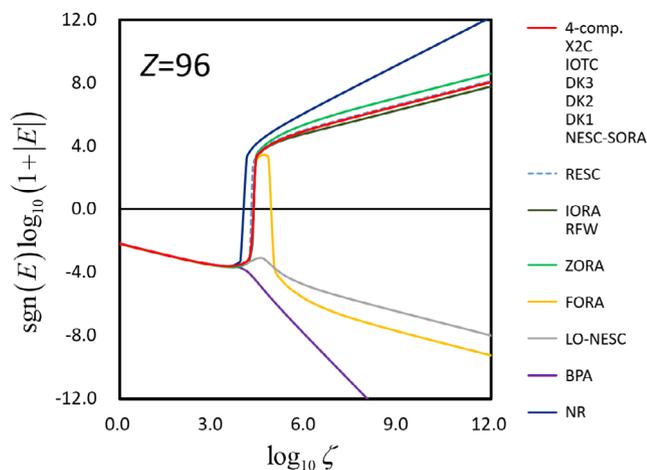
FIGURE 1 Energy of a hydrogen-like ion ($Z = 96$) computed with a single Gaussian basis function. Curves that overlap due to the same or close numerical values are represented by a single line.

FIGURE 2 Energy of a hydrogen-like ion ($Z = 0$) computed with a single Gaussian basis function. Curves that overlap due to the same or close numerical values are represented by a single line.

same curve as the four-component method for the one-electron system (Figure 1).

Figure 2 shows the results for the $Z = 0$ case, that is, no external potential $V = 0$; ZORA is consistent with NR. The BPA and FORA curves show divergence, which is due to the collapse of the Taylor expansion (or the asymptotic expansion) for $1/c$ of the kinetic energy, and IORA, RFW, LO-NESC, and NESC-SORA are also ill behaved. By contrast, the RESC, DK, IOTC, and X2C curves are almost identical to the four-component method curve; hence, the relativistic kinetic energy is properly computed by these methods.

3.2 | Calculations by multiple Gaussian functions

3.2.1 | Hydrogen-like ion

Next, consider a hydrogen-like ion using multiple Gaussian functions. We calculated the total energy of the hydrogen-like ion ($Z = 100$) using even-tempered s orbital-type basis functions expanded with 45 Gaussian functions.[37] Both two- and four-component methods were used for comparison. However, the two-component methods, which were shown to be unsuitable for variational calculations (see Section 3.1), were excluded. Table 3 shows the computed total energies and the square of the norm $\langle \Psi^D | \Psi^D \rangle$ defined by Equation (26). The forms satisfy the normalization condition with the exception of GFW(UN), that is, $\langle \Psi^D | \Psi^D \rangle = 1$ is always satisfied. The energies of X2C and IOTC are identical to that obtained using the four-component method because of the theoretical equivalence to the four-component method for one-electron systems. Similarly, the energies of X2C(UN), X2C(N2), and X2C(N3) are also identical to that obtained using the four-component method. However, the X2C(UN) energy divided by $\langle \Psi^D | \Psi^D \rangle$, that is, the normalized energy, has a difference of 939.1944 a.u. from the four-component method. By contrast, the normalized ZORA energy (ZORA energy divided by $\langle \Psi^D | \Psi^D \rangle$) has a very
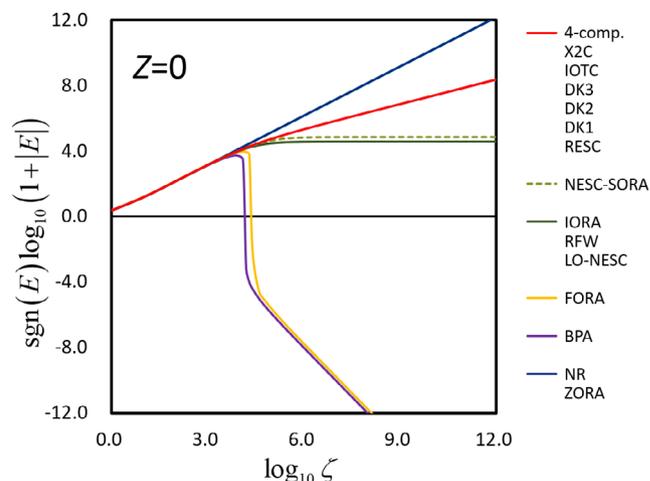
TABLE 3 Energy and the square of the wave function norm (Equation (26)) for the $Z = 100$ hydrogen-like ion.

	ΔE (a.u.) from $E^{\text{4-comp.a}}$	Square of the norm (equation (26))
IOTC	0.0000	1
X2C	0.0000	1
X2C(UN)	0.0000	1.1878
X2C(N2)	0.0000	1
X2C(N3)	0.0000	1
X2C(UN)-H	−123.9186	1.2312
X2C(N3)-H	0.0000	1
ZORA	−1115.6115	1.1878
RFW	−103.3898	1
IORA	−103.3898	1
RA(N3)	−1115.6115	1
RA(N3)-H	−58242725.5868	1
NESC-SORA	−140691.2280	1
RESC-NH	432.2560	1
RESC	−202738.3711	1
DK1	−533.1619	1
DK2	33.0021	1
DK3	−3.1754	1

[a]The reference energy of the four-component method is $E^{\text{4-comp.}} = -5939.1935$ a.u.

small difference of −0.0001 a.u. from the four-component method, but this improvement may be due to error cancelation. This is because the energy of X2C(UN), which uses $\widehat{X}$ with no approximation in one-electron systems, is deteriorated by the normalization.

The total energies of RESC and RA(N3)-H (both approximations of X2C(N3)-H) are extremely low and their errors are far beyond

100%. By contrast, the total energy differences of RESC-*NH* and RA(N3) from the four-component method (both approximations of X2C(N3)) are 432.2560 and −1115.6115 a.u., respectively, and their errors are within 20%. These results indicate that the Hermitization (Equation (99)) of the X2C(N3) Hamiltonian after the approximation is not effective. The NESC-SORA energies are also extremely low. This poor performance is probably ascribed to the point-charge nucleus model in the large atomic number region. In fact, the total energy under the finite-size nuclear model is −5924.190743 a.u., which is rather favorable. The truncation of the $1/c$ series in the BPA system was such a poor approximation that it could not be used for variational calculations. By contrast, the energy differences for DK1, DK2, and DK3 from the four-component method were −533.1619, 33.0021, and −3.1754 a.u., respectively, indicating that truncation did not lead to poor behavior and provided rather good approximations. These findings indicated that truncation of *V* was a good approximation, and truncation of a series itself was not necessarily a bad strategy in deriving the two-component methods.

3.2.2 | Helium-like ions

Finally, consider many-electron systems. We performed Hartree–Fock calculations for the helium-like ions ($Z = 10, 20,...,130$) using the basis functions expanded by even-tempered *s* orbital-type 45 Gaussian functions.[37] In these calculations, the two-component methods, the values of which collapsed in the previous subsection, were further excluded. The GFW transformations were first applied and determined for the one-electron Hamiltonian, and then applied to the relativistic two-electron operator using Equation (93). The calculations applying the NR approximation to the two-electron operator were also performed for comparison.

Figure 3 shows the Hartree–Fock energy plotted against the nuclear charge *Z*. The energies were adjusted so that the energy of the four-component method represents the origin. The results for NR/NR, DK1/NR, DK2/NR, DK3/NR, and IOTC/NR show that the energy difference from the four-component method was greatly reduced as the level of approximation for the one-electron Hamiltonian increased. At first glance, it appears that DK3/NR gave better results than IOTC/NR, but it was due to the cancelation of the underestimated contribution from the one-electron Hamiltonian and the overestimated contribution from the two-electron operator in DK3/NR. In fact, IOTC/NR gave a better result at $Z = 130$, where the relativistic effect was the largest. The results of IOTC/NR, IOTC/DK1, IOTC/DK2, IOTC/DK3, and IOTC/IOTC showed that the energy difference from the four-component method was also reduced as the level of approximation for the two-electron operator increased. However, the effect was much smaller than for the one-electron Hamiltonian. Therefore, when selecting the approximation to be used for the one-electron Hamiltonian and the two-electron operator, the one-electron Hamiltonian approximation should be chosen preferentially.

The total energies of the helium-like ion with $Z = 100$ obtained using several selected methods are shown in Table 4. IOTC/IOTC,
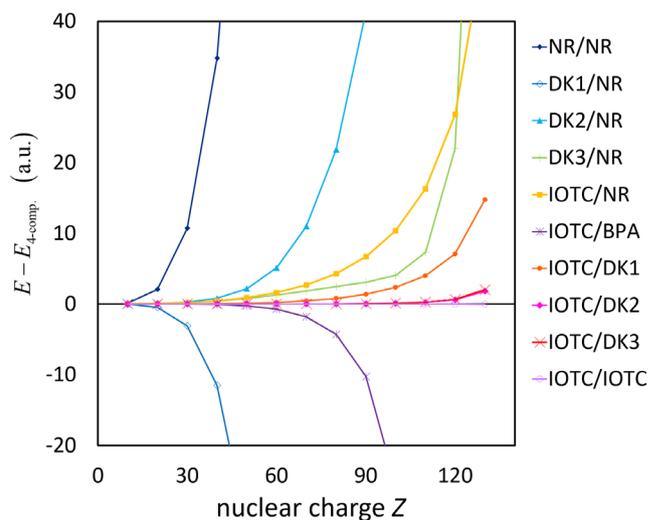
FIGURE 3 Hartree–Fock total energy difference of helium-like ions from the four-component method computed with several selected two-component methods. The symbol A/B means (method for one-electron Hamiltonian)/(method for two-electron operator).

X2C/X2C, and X2C(N2)/X2C(N2), in which the one-electron Hamiltonian and the two-electron operator were transformed by the same method, gave identical energies. Although these three methods apply the exact $\hat{X}$ in Equation (12), the error mentioned in the last paragraph of Section 2.3 remains. In fact, IOTC/IOTC, X2C/X2C, and X2C(N2)/X2C(N2) have quite a small but non-zero difference of −0.0035 a.u. from the four-component method.

Let us consider the errors that arise when the two-electron operator approximation was changed to the NR approximation for IOTC/IOTC, X2C/X2C, and X2C(N2)/X2C(N2), that is, IOTC/NR, X2C/NR, and X2C(N2)/NR. In these cases, at first glance, it appears that the only new error arising is the error from the NR approximation of the two-electron operator. However, this does not explain the fact that IOTC/NR, X2C/NR, and X2C(N2)/NR gave different total energies. The errors were 10.3692, 9.4853, and −23.6423 a.u., respectively. This indicates that the NR approximation of the two-electron operator introduced another new error in addition to the error directly introduced by this approximation. This new error, which gave different energies even when exact transformations for the one-electron Hamiltonian and the common transformation for the two-electron operator were used, was due to the difference of the transformations applied to the one-electron Hamiltonian and the two-electron operator and can be viewed as picture change errors in the two-electron operator with respect to the one-electron Hamiltonian picture. We refer to these differences caused by the different transformations between the one-electron Hamiltonian and the two-electron operator as the "picture difference error (PDE)." The PDE always occurs when the transformation methods used for the one- and two-electron integrals are different. In particular, the PDE can occur even when any of $\hat{X}$, $\hat{U}_+$, and the GFW types are different. In fact, X2C/IOTC and IOTC/X2C gave different total energies despite having the same $\hat{X}$ and GFW type. Thus, PDE even resulted only from the $\hat{U}_+$ difference. The

TABLE 4 Hartree–Fock energy of the $Z = 100$ helium-like ion by several selected two-component methods.

Method[a]	ΔE (a.u.) from $E^{\text{4-comp.}}$[b]
IOTC/IOTC	−0.0035
X2C/X2C	−0.0035
X2C(N2)/X2C(N2)	−0.0035
X2C/IOTC	−0.6734
IOTC/X2C	0.6772
IOTC/DK3	0.1065
IOTC/DK2	0.0964
IOTC/DK1	2.3386
IOTC/BPA	−25.5287
IOTC/NR	10.3692
X2C/NR	9.4853
X2C(N2)/NR	−23.6423
ZORA/NR	−2215.8968
RFW/NR	−196.5770
IORA/NR	−225.4527
DK3/NR	4.0459
DK2/NR	75.7278
DK1/NR	−1045.3359

[a]The symbol A/B means (method for one-electron Hamiltonian)/(method for two-electron operator).
[b]The reference total energy of the four-component method is $E^{\text{4-comp.}} = -11796.8563$ a.u.

PDE lead a larger error (−0.6734 a.u. for X2C/IOTC and 0.6772 a.u. for IOTC/X2C) than the approximation for determining $\hat{X}$ without considering the two-electron operator (−0.0035 a.u. for IOTC/IOTC and X2C/X2C).

The effect on accuracy of the two-electron operator Hermitization was not examined in this paper, but the following considerations predict that the two-electron operator Hermitization has a negative impact on accuracy. The two-electron operator Hermitization is necessary only for GFW(N3), and to prevent PDE, Hermitization is also necessary for the one-electron Hamiltonian. However, we have seen that Hermitization is not a good treatment for approximating a two-component transformation of the one-electron Hamiltonian. Moreover, there is no practical reason to actively use X2C(N3) instead of X2C or X2C(N2) for the one-electron Hamiltonian. Thus, it is theoretically predicted that the Hermitization of the two-electron operator and PDE prevention are incompatible.

4 | SUMMARY

We have proposed the GFW transformation, which is a generalization of the FW transformation for the Dirac Hamiltonian. The GFW transformation is a generic term for four types of transformations (the combinations of unitary/nonunitary and Hermitian/non-Hermitian transformations) and includes an additional transformation rotating only positive energy orbitals. This transformation form can express all existing two-component methods. We showed that the existing two-component methods are derived from the GFW-transformed Hamiltonian and furthermore systematically derived two-component methods that have not been previously derived based on this transformation.

We then applied various two-component methods to the hydrogen-like ion ($Z = 100$) and the helium-like ions ($Z = 10, 20, …, 130$) and systematically evaluated the numerical errors in the two-component method by organizing the approximations based on the GFW transformation. The results showed that the errors of the two-component methods could be classified as follows:

1. An error due to the approximation of the one-electron Hamiltonian transformation, resulting from (a) the approximation of $\hat{X}$, (b) series truncation, or (c) Hamiltonian Hermitization,
2. an error due to the approximation of the two-electron operator transformation, resulting from (a) the approximation of $\hat{X}$, (b) series truncation, and (c) Hamiltonian Hermitization,
3. the PDE, and
4. the error from the determination of the transformation using only the one-electron Hamiltonian.

The additional transformation $\hat{U}_+$ in the GFW transformation does not directly affect the accuracy of the two-component methods. To reduce the error in the transformed one-electron Hamiltonian and ensure high accuracy of the two-component methods, it is required that the methods have correct relativistic kinetic energy when the potential is zero. The LO-NESC, BPA, and RA methods do not satisfy this requirement. Furthermore, the Hermitization of non-Hermitian Hamiltonians amplifies the approximation error in $\hat{X}$.

The accuracy of the approximation for multi-electron systems is mostly determined by the transformation applied to the one-electron Hamiltonian. By contrast, applying a high-accuracy method to the two-electron operator has little effect when a low-accuracy method is applied to the one-electron Hamiltonian. Different transformations for the one-electron Hamiltonian and the two-electron operator result in PDE and, in some cases, produce not a small error. When two different methods are used unavoidably, it should be noted that PDE occurs. The fourth error in the aforementioned classification resulting from the transformation to the two components by the one-electron Hamiltonian is quite smaller compared with errors 1–3.

In conclusion, the GFW transformation is a powerful tool that can represent all existing two-component methods and can be used to systematically derive new two-component methods. In the future, it is expected to be applicable to the analysis of two-component method calculations for practical molecules with a large number of atoms.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Nobuki Inoue https://orcid.org/0000-0002-6116-1735
Yoshihiro Watanabe https://orcid.org/0000-0001-9729-6810
Haruyuki Nakano https://orcid.org/0000-0002-7008-0312

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