



Research paper

Two-component transformation inclusive contraction scheme in the relativistic molecular orbital theory

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ABSTRACT

The incorporation of a two-component transformation into the contraction coefficients of basis functions is suggested. Such a contraction, referred to as “two-component transformation inclusive contraction (TIC)”, effectively eliminates the computational cost associated with the two-component transformation and can be readily implemented into conventional quantum chemistry programs. TIC was verified through numerical calculations using the second- and third-order unitarized Douglas–Kroll method, which is newly derived for the validation of TIC, and the infinite-order two-component method. The numerical validation results suggested that TIC could sufficiently reproduce the results of primitive basis sets for both atoms and molecules.

1. Introduction

One of the key goals of computational chemistry is the treatment of all the elements in the periodic table with uniformity and high accuracy. Achieving this goal would provide accurate information about all molecules uniformly. However, the heavy and superheavy elements contain a large number of electrons, and also require the consideration of relativistic effects, in particular in the description of their core electrons. Therefore, to treat heavy and superheavy elements with the same level of accuracy as light elements, in practical calculations, a low computational cost method that can incorporate relativistic effects with high accuracy is needed.

The relativistic effects are introduced into the molecular orbital theory by formulating it based on the Dirac equation instead of the nonrelativistic Schrödinger equation. However, the four-component formulation based on the Dirac equation includes negative kinetic energy solutions corresponding to positrons, as well as positive kinetic energy solutions corresponding to electrons. Most of the systems of interest in chemistry contain only electrons, and the description of positrons is not required. For this reason, in the relativistic molecular orbital theory, the relativistic two-component method, which transforms and

decouples the four-component equations and wave functions into those corresponding to only two components for electrons, is often used. For example, the following methods have been developed: the Breit–Pauli approximation (BPA) [1], the zeroth-order regular approximation (ZORA) [2–5], the infinite-order regular approximation (IORA) [6], the Douglas–Kroll (DK) method [7–14], the infinite-order two-component (IOTC) method [15], exact two-component (X2C) method [16–19], etc. The two-component method gives a one-electron Hamiltonian that is half the size of the four-component method; moreover, the theoretical framework does not include positron solutions, giving the Hamiltonian a structure similar to nonrelativistic theory. This provides significant implementation advantages.

Another way to reduce the size of the problems is an effective contraction of the basis functions. This contraction of basis functions was originally introduced to fit linear combinations of primitive Gaussian functions to Slater-type functions that are the exact solutions of one-center problems, and various contracted basis sets for nonrelativistic calculation [20,21] have been proposed. In addition to these nonrelativistic contracted basis sets, relativistic versions have also been proposed: a contracted basis set for two-component methods, the Sapporo-DK basis set [22–24], or the basis sets for four-component

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methods by Koga et al. [25–27], Tatewaki et al. [28,29], Dyall et al. [30–38], and Faegri [39]. In the framework of the nonrelativistic theory, a superior basis set is one that results in fewer contracted basis functions and a lower total energy. However, in the relativistic case, in some instances, inadequate contracted basis functions may produce a lower energy than the exact solution, primarily due to the incorrect mixing of negative kinetic energy solutions, a phenomenon known as “variational collapse”. Consequently, it is challenging to obtain a concise basis set that consistently yields a lower total energy in relativistic calculations.

To reduce the computational cost directly, we considered the possibility of combining the two-component method with basis function contraction. One idea for reducing the computational cost of the two-component transformation is to contract basis functions before the transformation. However, the division into positive and negative energy spaces by two-component transformation in a much smaller space of the contracted basis set can lead not only to the variational collapse described above, but also to a loss of accuracy of the resolution of identity. In other words, it is very important to adhere to the order of the two-component transformation first, followed by the basis function contraction. Here, we arrive at a different perspective by recognizing that both the two-component transformations that are expressible through unitary transformations and the contraction of basis functions can be seen as linear transformations on the Dirac Hamiltonian. From this perspective, we propose a scheme that uses a linear transformation that unifies the two-component transformation and the contraction of basis functions; in other words, this is a proposal of the contraction coefficients of the basis functions encapsulating the two-component transformation.

In this paper, we introduce a new scheme called the two-component transformation inclusive contraction coefficient (TIC) scheme. We describe the construction of the TIC basis functions in subsection 2.1. In subsection 2.2, we present a new two-component method, called the unitarized DK method, which recovers the complete unitarity of the DK method by not applying cutoffs. In section 3, we provide numerical verification for the methods proposed in subsections 2.1 and 2.2. In practical use, our scheme provides a means to obtain the two-component Hamiltonian by simply contracting the basis functions without explicitly performing the two-component transformation.

2. Theory

2.1. Two-component transformation inclusive contraction

In the relativistic two-component methods, the one-electron Dirac Hamiltonian operator H_D is block-diagonalized by a two-component transformation U to obtain the two-component one-electron Hamiltonian H_{2c}^+ :

$$U^\dagger H_D U = \begin{bmatrix} U_{LL}^\dagger & U_{SL}^\dagger \\ U_{LS}^\dagger & U_{SS}^\dagger \end{bmatrix} \begin{bmatrix} V & c(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \\ c(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) & V - 2c^2 \end{bmatrix} \begin{bmatrix} U_{LL} & U_{LS} \\ U_{SL} & U_{SS} \end{bmatrix} = \begin{bmatrix} H_{2c}^+ & 0 \\ 0 & H_{2c}^- \end{bmatrix}, \quad (1)$$

where V is the nuclear attraction potential, c is the speed of light, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is the Pauli matrices, and $\hat{\mathbf{p}}$ is the momentum operator. Using the two-component primitive basis functions $\{\chi_\mu^L\}$ and the strict kinetic balance (SKB) relation $|\chi_\mu^S\rangle \propto \alpha(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) |\chi_\mu^L\rangle$, the representation matrices of the Dirac Hamiltonian \mathbf{H}_D is expressed as

$$\mathbf{H}_D = \begin{bmatrix} \mathbf{V}_L & c\mathbf{\Pi}_{LS} \\ c\mathbf{\Pi}_{SL} & \mathbf{V}_S - 2c^2\mathbf{S}_S \end{bmatrix},$$

$$(\mathbf{V}_L)_{\mu\nu} = \langle \chi_\mu^L | V | \chi_\nu^L \rangle, (\mathbf{V}_S)_{\mu\nu} = \kappa_\mu \kappa_\nu \langle \chi_\mu^L | (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) V (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) | \chi_\nu^L \rangle, \quad (2)$$

$$(\mathbf{\Pi}_{SL})_{\mu\nu} = \kappa_\mu \langle \chi_\mu^L | \hat{\mathbf{p}}^2 | \chi_\nu^L \rangle, (\mathbf{\Pi}_{LS})_{\mu\nu} = \kappa_\nu \langle \chi_\nu^L | \hat{\mathbf{p}}^2 | \chi_\mu^L \rangle,$$

$$(\mathbf{S}_L)_{\mu\nu} = \langle \chi_\mu^L | \chi_\nu^L \rangle, (\mathbf{S}_S)_{\mu\nu} = \kappa_\mu \kappa_\nu \langle \chi_\mu^L | \hat{\mathbf{p}}^2 | \chi_\nu^L \rangle,$$

with $\kappa_\mu = 1/\sqrt{\langle \chi_\mu^L | \hat{\mathbf{p}}^2 | \chi_\mu^L \rangle}$. The representation matrices of U_{LL} and U_{SL} in the transformation operator U , which are required to construct the H_{2c}^+ , are expressed as

$$(\mathbf{U}_{LL})_{\mu\nu} = \mathbf{S}_L^{-1} \langle \chi_\mu^L | U_{LL} | \chi_\nu^L \rangle, \quad (3)$$

$$(\mathbf{U}_{SL})_{\mu\nu} = \kappa_\mu \mathbf{S}_S^{-1} \langle \chi_\mu^L | (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) U_{SL} | \chi_\nu^L \rangle.$$

From Eqs. (1), (2), and (3), the representation matrix of $(\mathbf{H}_{2c}^+)_{\mu\nu} = \langle \chi_\mu^L | H_{2c}^+ | \chi_\nu^L \rangle$ is written as

$$\mathbf{H}_{2c}^+ = [\mathbf{U}_{LL}^\dagger \quad \mathbf{U}_{SL}^\dagger] \mathbf{H}_D \begin{bmatrix} \mathbf{U}_{LL} \\ \mathbf{U}_{SL} \end{bmatrix}. \quad (4)$$

To apply the two-component Hamiltonian \mathbf{H}_{2c}^+ to the many-electron systems, a two-electron Hamiltonian is necessary along with \mathbf{H}_{2c}^+ . Because the relativistic effects on the two-electron Hamiltonian are relatively small compared with those on the one-electron Hamiltonian, in this work, the nonrelativistic Coulomb operator was used as the two-electron Hamiltonian. Using these one- and two-electron Hamiltonians for atomic Hartree–Fock (HF) calculations yields the atomic orbitals (AOs). In the case where the basis functions are primitive Gaussian functions, the AO coefficients can be used as the general contraction coefficients in the basis function contraction. Using matrix \mathbf{d}^A , the contracted basis functions $\chi_\alpha^{A(c)}$ of an atom A are represented by linear combinations of the primitive Gaussian basis functions χ_μ^A as

$$|\chi_\alpha^{A(c)}\rangle = \sum_\mu (\mathbf{d}^A)_{\mu\alpha} |\chi_\mu^A\rangle, \quad (5)$$

where the number of rows in \mathbf{d}^A is equal to that in \mathbf{U}_{LL}^A and \mathbf{U}_{SL}^A and larger than the number of columns in \mathbf{d}^A .

Let us discuss the contraction of the one-electron Hamiltonian in more detail. For atoms, the one-electron Hamiltonian in the primitive basis functions \mathbf{H}_{2c}^+ can be reduced into that of the contracted basis functions $\mathbf{H}_{2c}^{+(c)}$ using matrix \mathbf{d}^A :

$$\mathbf{H}_{2c}^{+(c)} = \mathbf{d}^{A\dagger} \mathbf{H}_{2c}^+ \mathbf{d}^A. \quad (6)$$

Substituting Eq. (4) into Eq. (6) yields

$$\mathbf{H}_{2c}^{+(c)} = \mathbf{d}^{A\dagger} [\mathbf{U}_{LL}^{A\dagger} \quad \mathbf{U}_{SL}^{A\dagger}] \mathbf{H}_D \begin{bmatrix} \mathbf{U}_{LL}^A \\ \mathbf{U}_{SL}^A \end{bmatrix} \mathbf{d}^A. \quad (7)$$

This equation shows that the two-component transformation and basis function contraction can be combined into a single transformation. Thus, we introduce TIC. In this TIC scheme, the TIC matrices are defined by

$$\mathbf{d}_L^{A(\text{TIC})} = \mathbf{U}_{LL}^A \mathbf{d}^A, \quad (8)$$

$$\mathbf{d}_S^{A(\text{TIC})} = \mathbf{U}_{SL}^A \mathbf{d}^A.$$

The contracted two-component Hamiltonian for atoms can be rewritten in simpler form:

$$\mathbf{H}_{2c}^{+(c)} = \begin{bmatrix} \mathbf{d}_L^{A(\text{TIC})\dagger} & \mathbf{d}_S^{A(\text{TIC})\dagger} \end{bmatrix} \mathbf{H}_D \begin{bmatrix} \mathbf{d}_L^{A(\text{TIC})} \\ \mathbf{d}_S^{A(\text{TIC})} \end{bmatrix}. \quad (9)$$

In other words, by preparing these TIC matrices as the coefficient matrix of the basis functions, the two-component transformation and basis function contraction can be performed simultaneously in advance. Here, when we use the nonrelativistic two-electron Hamiltonian mentioned above, \mathbf{d}^A should be used for the contraction of the two-electron Hamiltonian instead of $\mathbf{d}_L^{A(\text{TIC})}$ and $\mathbf{d}_S^{A(\text{TIC})}$.

The TIC matrices thus constructed can be applied to molecular calculations by combining the local unitary transformation (LUT) [40], which approximates the molecular two-component transformation by the direct sum of atomic two-component transformations. Suppose that a molecule consists of a set of atoms $\{A, B, \dots\}$. The contraction matrix $\mathbf{d}^{\text{Total}}$ and LUT-approximated two-component transformation $\mathbf{U}_{\text{LL}}^{\text{Total}}$ and $\mathbf{U}_{\text{SL}}^{\text{Total}}$ of the whole molecule can be written as

$$\mathbf{d}^{\text{Total}} = \begin{bmatrix} \mathbf{d}^A & 0 & \dots \\ 0 & \mathbf{d}^B & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}, \quad (10)$$

$$\mathbf{U}_{\text{LL}}^{\text{Total,LUT}} = \begin{bmatrix} \mathbf{U}_{\text{LL}}^A & 0 & \dots \\ 0 & \mathbf{U}_{\text{LL}}^B & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}, \quad (11)$$

$$\mathbf{U}_{\text{SL}}^{\text{Total,LUT}} = \begin{bmatrix} \mathbf{U}_{\text{SL}}^A & 0 & \dots \\ 0 & \mathbf{U}_{\text{SL}}^B & \dots \\ \vdots & \vdots & \ddots \end{bmatrix},$$

where \mathbf{U}_{LL}^A , \mathbf{U}_{LL}^B , \dots (\mathbf{U}_{SL}^A , \mathbf{U}_{SL}^B , \dots) are the LL (SL) blocks of the atomic two-component transformation for atom A , B , \dots , respectively. The TIC matrices of the molecule are constructed from the atomic TIC coefficient matrices:

$$\mathbf{d}_L^{\text{Total(TIC)}} = \mathbf{U}_{\text{LL}}^{\text{Total,LUT}} \mathbf{d}^{\text{Total}} = \begin{bmatrix} \mathbf{d}_L^{A(\text{TIC})} & 0 & \dots \\ 0 & \mathbf{d}_L^{B(\text{TIC})} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}, \quad (12)$$

$$\mathbf{d}_S^{\text{Total(TIC)}} = \mathbf{U}_{\text{SL}}^{\text{Total,LUT}} \mathbf{d}^{\text{Total}} = \begin{bmatrix} \mathbf{d}_S^{A(\text{TIC})} & 0 & \dots \\ 0 & \mathbf{d}_S^{B(\text{TIC})} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}. \quad (13)$$

Thus, under the LUT approximation, the TIC matrices obtained from the atomic calculations can be applied to molecular calculations. The LUT approximation provides a key idea in implementing the TIC scheme for molecules. The above discussion applies to any two-component transformation as long as the transformation is unitary.

In the TIC scheme, by applying Eqs. (10), (12), and (13) to the uncontracted one-electron Dirac Hamiltonian matrix \mathbf{H}_D and Eq. (10) to the uncontracted nonrelativistic two-electron integrals $(\chi_{\mu}^L \chi_{\nu}^L | \chi_{\lambda}^L \chi_{\sigma}^L)$, we can obtain the contracted one-electron integrals

$$\left(\mathbf{H}_{2c}^{+(\text{TIC})} \right)_{\alpha\beta} = \sum_{X,Y}^{\text{L,S}} \sum_{\mu\nu} \left(\mathbf{d}_X^{\text{Total(TIC)}} \right)_{\mu\alpha}^* \left(\mathbf{d}_Y^{\text{Total(TIC)}} \right)_{\nu\beta} \left([\mathbf{H}_D]_{XY} \right)_{\mu\nu}, \quad (14)$$

and the contracted two-electron integrals

$$(\alpha\beta|\gamma\delta)^{(\text{TIC(NR)})} = \sum_{\mu\nu\lambda\sigma} \left(\mathbf{d}^{\text{Total}} \right)_{\mu\alpha}^* \left(\mathbf{d}^{\text{Total}} \right)_{\nu\beta} \left(\mathbf{d}^{\text{Total}} \right)_{\lambda\gamma}^* \left(\mathbf{d}^{\text{Total}} \right)_{\sigma\delta} \left(\chi_{\mu}^L \chi_{\nu}^L | \chi_{\lambda}^L \chi_{\sigma}^L \right). \quad (15)$$

Here, α , β , γ , and δ are the indices for the contracted basis functions. Based on Eq. (14), we can construct the two-component Hamiltonian from the TIC coefficients without explicitly performing the two-component transformation. That is, unless the adopted two-component method or the set of primitive basis functions before contraction is replaced with another, the stored TIC coefficients can be reused and there is no need to compute them in each electronic structure calculation.

To obtain specific representations of the TIC matrices, explicit expressions of \mathbf{U}_{LL}^A and \mathbf{U}_{SL}^A are necessary. Taking IOTC [15,41] as an example, the explicit expressions of \mathbf{U}_{LL}^A and \mathbf{U}_{SL}^A are summarized as

$$\mathbf{U}_{\text{LL,IOTC}}^A = \mathbf{XQ} \tilde{\mathbf{A}} \left(\mathbf{I} - \tilde{\mathbf{B}} \tilde{\mathbf{p}} \tilde{\mathbf{Y}} \right) \tilde{\mathbf{Q}} \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \quad (16)$$

$$\mathbf{U}_{\text{SL,IOTC}}^A = \mathbf{S}_S^{-1} \mathbf{\Pi}_{\text{SL}} \mathbf{XQ} \tilde{\mathbf{A}} \tilde{\mathbf{B}} \left(\mathbf{I} + \tilde{\mathbf{B}}^{-1} \tilde{\mathbf{p}}^{-1} \tilde{\mathbf{Y}} \right) \tilde{\mathbf{Q}} \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \quad (17)$$

with

$$\tilde{\mathbf{E}}_p = \sqrt{c^2 \tilde{\mathbf{p}}^2 + c^4}, \quad \tilde{\mathbf{A}} = \sqrt{\frac{\tilde{\mathbf{E}}_p + c^2}{2\tilde{\mathbf{E}}_p}}, \quad \tilde{\mathbf{B}} = \frac{c}{\tilde{\mathbf{E}}_p + c^2}, \quad (18)$$

$$\tilde{\mathbf{Q}}_+ = \left(\mathbf{I} + \tilde{\mathbf{Y}}^\dagger \tilde{\mathbf{Y}} \right)^{-\frac{1}{2}}. \quad (19)$$

\mathbf{X} and \mathbf{Q} are an orthogonalized matrix satisfying $\mathbf{X}^\dagger \mathbf{S}_L \mathbf{X} = \mathbf{I}$ and a unitary matrix such that $\mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{\Pi}_{\text{LS}} \mathbf{S}_S^{-1} \mathbf{\Pi}_{\text{SL}} \mathbf{XQ}$ is a diagonal matrix $\tilde{\mathbf{p}}^2$, respectively. $\tilde{\mathbf{M}}$ is defined by $\tilde{\mathbf{M}} = \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{M} \mathbf{XQ}$ for an arbitrary representation matrix \mathbf{M} . \mathbf{Y} is the parameter of IOTC.

In contrast to IOTC, the original DK Hamiltonian cannot be expressed by a single linear transformation because of the finite-order truncation of the Hamiltonian. Restoration of the unitarity solves this problem, making the TIC scheme applicable to the DK method.

2.2. Unitarized DK transformation

In this subsection, we present a unitarized variant of the DK method, to which the TIC scheme is applicable. The second- and third-order DK Hamiltonian operators H_{DK2} and H_{DK3} are obtained by applying the transformations $[U_1^\dagger U_0^\dagger H_D U_0 U_1]_{\text{LL}}$ and $[U_2^\dagger U_1^\dagger U_0^\dagger H_D U_0 U_1 U_2]_{\text{LL}}$ to the Dirac Hamiltonian, and then truncating the result at the second and third orders, respectively. The unitary transformations U_0 , U_1 , and U_2 are given by

$$U_0 = \begin{bmatrix} A & -AB(\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \\ (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}})BA & A \end{bmatrix}, \quad (20)$$

$$U_1 = f \left(\begin{bmatrix} 0 & -W_1^\dagger \\ W_1 & 0 \end{bmatrix} \right), \quad (21)$$

and

$$U_2 = f \left(\begin{bmatrix} 0 & -W_2^\dagger \\ W_2 & 0 \end{bmatrix} \right), \quad (22)$$

respectively, where f is a function specifying the transformation. According to the function form of f , several parametrization types have been proposed, such as the exponential (exp) [10], the square root (sqrt) [7], McWeeny (McW) [42], Cayley (CA) [14], and Optimal (opt) [14]. In addition, a general treatment including all function forms is also

proposed [14]. The matrix representations of W_1 and W_2 are

$$\begin{aligned} (W_1)_{\mu\nu} &= \langle \chi_\mu^L | (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \hat{p}^{-1} W_1 | \chi_\nu^L \rangle = \mathbf{S}_L \mathbf{X} \mathbf{Q} \tilde{\mathbf{W}}_1 \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \\ (W_2)_{\mu\nu} &= \langle \chi_\mu^L | (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \hat{p}^{-1} W_2 | \chi_\nu^L \rangle = \mathbf{S}_L \mathbf{X} \mathbf{Q} \tilde{\mathbf{W}}_2 \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \end{aligned} \quad (23)$$

where $\tilde{\mathbf{W}}_1$ and $\tilde{\mathbf{W}}_2$ are defined as

$$\left(\tilde{\mathbf{W}}_1 \right)_{ij} = \frac{\left(\tilde{\mathbf{O}}_1 \right)_{ij}}{\left(\tilde{\mathbf{E}}_p \right)_{ii} + \left(\tilde{\mathbf{E}}_p \right)_{jj}}, \quad (24)$$

$$\left(\tilde{\mathbf{W}}_2 \right)_{ij} = \frac{\left(\tilde{\mathbf{E}}_1 \tilde{\mathbf{W}}_1 - \tilde{\mathbf{W}}_1 \tilde{\mathbf{E}}_1 \right)_{ij}}{\left(\tilde{\mathbf{E}}_p \right)_{ii} + \left(\tilde{\mathbf{E}}_p \right)_{jj}}, \quad (25)$$

with

$$\tilde{\mathbf{E}}_1 = \tilde{\mathbf{A}} \left(\tilde{\mathbf{V}}_L + \tilde{\mathbf{B}} \tilde{\mathbf{V}} \tilde{\mathbf{B}} \right) \tilde{\mathbf{A}}, \quad (26)$$

$$\tilde{\mathbf{O}}_1 = \tilde{\mathbf{A}} \left(\tilde{\mathbf{p}}^{-1} \tilde{\mathbf{V}} \tilde{\mathbf{B}} - \tilde{\mathbf{B}} \tilde{\mathbf{p}} \tilde{\mathbf{V}}_L \right) \tilde{\mathbf{A}}, \quad (27)$$

$$\tilde{\mathbf{E}}_1 = \tilde{\mathbf{A}} \left(\tilde{\mathbf{B}} \tilde{\mathbf{p}} \tilde{\mathbf{V}}_L \tilde{\mathbf{p}} \tilde{\mathbf{B}} + \tilde{\mathbf{p}}^{-1} \tilde{\mathbf{V}} \tilde{\mathbf{p}}^{-1} \right) \tilde{\mathbf{A}}, \quad (28)$$

and

$$\tilde{\mathbf{V}} = \mathbf{\Pi}_{LS} \mathbf{S}_S^{-1} \mathbf{V}_S \mathbf{S}_S^{-1} \mathbf{\Pi}_{SL}. \quad (29)$$

In the conventional DK method, the unitarity of the transformations does not hold because of the truncation of the Hamiltonian at a finite order. In other words, if we evaluate the Hamiltonian without truncating each unitary transformation at a finite order, we can construct a ‘‘unitarized’’ DK (uDK) method. Thus, the second- and third-order uDK Hamiltonians are obtained by the same derivation scheme without truncation, as follows:

$$\begin{aligned} \mathbf{H}_{\text{uDK2}} &= \mathbf{S}_L \mathbf{X} \mathbf{Q} \left\{ \tilde{\mathbf{G}}_1^e \left(\tilde{\mathbf{E}}_p - c^2 \mathbf{I} + \tilde{\mathbf{E}}_1 \right) \tilde{\mathbf{G}}_1^e + \tilde{\mathbf{G}}_1^{o\dagger} \tilde{\mathbf{O}}_1 \tilde{\mathbf{G}}_1^e \right. \\ &\quad \left. + \tilde{\mathbf{G}}_1^e \tilde{\mathbf{O}}_1^\dagger \tilde{\mathbf{G}}_1^e + \tilde{\mathbf{G}}_1^{o\dagger} \left(-\tilde{\mathbf{E}}_p - c^2 \mathbf{I} + \tilde{\mathbf{E}}_1 \right) \tilde{\mathbf{G}}_1^o \right\} \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \end{aligned} \quad (30)$$

and

$$\begin{aligned} \mathbf{H}_{\text{uDK3}} &= \mathbf{S}_L \mathbf{X} \mathbf{Q} \cdot \\ &\quad \left\{ \left(\tilde{\mathbf{G}}_2^e \tilde{\mathbf{G}}_1^e - \tilde{\mathbf{G}}_2^{o\dagger} \tilde{\mathbf{G}}_1^o \right) \left(\tilde{\mathbf{E}}_p - c^2 \mathbf{I} + \tilde{\mathbf{E}}_1 \right) \left(\tilde{\mathbf{G}}_1^e \tilde{\mathbf{G}}_2^e - \tilde{\mathbf{G}}_1^{o\dagger} \tilde{\mathbf{G}}_2^o \right) \right. \\ &\quad \left. + \left(\tilde{\mathbf{G}}_2^e \tilde{\mathbf{G}}_1^{o\dagger} + \tilde{\mathbf{G}}_2^{o\dagger} \tilde{\mathbf{G}}_1^e \right) \tilde{\mathbf{O}}_1 \left(\tilde{\mathbf{G}}_1^e \tilde{\mathbf{G}}_2^e - \tilde{\mathbf{G}}_1^{o\dagger} \tilde{\mathbf{G}}_2^o \right) \right. \\ &\quad \left. + \left(\tilde{\mathbf{G}}_2^e \tilde{\mathbf{G}}_1^e - \tilde{\mathbf{G}}_2^{o\dagger} \tilde{\mathbf{G}}_1^o \right) \tilde{\mathbf{O}}_1^\dagger \left(\tilde{\mathbf{G}}_1^o \tilde{\mathbf{G}}_2^e + \tilde{\mathbf{G}}_1^e \tilde{\mathbf{G}}_2^o \right) \right. \\ &\quad \left. + \left(\tilde{\mathbf{G}}_2^e \tilde{\mathbf{G}}_1^{o\dagger} + \tilde{\mathbf{G}}_2^{o\dagger} \tilde{\mathbf{G}}_1^e \right) \left(-\tilde{\mathbf{E}}_p - c^2 \mathbf{I} + \tilde{\mathbf{E}}_1 \right) \left(\tilde{\mathbf{G}}_1^o \tilde{\mathbf{G}}_2^e + \tilde{\mathbf{G}}_1^e \tilde{\mathbf{G}}_2^o \right) \right\} \\ &\quad \cdot \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \end{aligned} \quad (31)$$

where, \mathbf{G}_n^e , \mathbf{G}_n^o , and \mathbf{G}_n^e in Eqs. (30) and (31) are defined by

$$\begin{aligned} \mathbf{G}_n^e &= \langle \chi_\mu^L | g_{\text{even}}(W_n^\dagger W_n) | \chi_\nu^L \rangle, \\ \mathbf{G}_n^o &= \langle \chi_\mu^L | (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \hat{p}^{-1} W_n g_{\text{odd}}(W_n^\dagger W_n) | \chi_\nu^L \rangle, \\ \mathbf{G}_n^e &= \langle \chi_\mu^L | (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) \hat{p}^{-1} g_{\text{even}}(W_n W_n^\dagger) \hat{p}^{-1} (\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}) | \chi_\nu^L \rangle, \end{aligned} \quad (32)$$

with

$$\begin{aligned} g_{\text{even}}(x) &= \frac{f(i\sqrt{x}) + f(-i\sqrt{x})}{2}, \\ g_{\text{odd}}(x) &= \frac{f(i\sqrt{x}) - f(-i\sqrt{x})}{2i\sqrt{x}}. \end{aligned} \quad (33)$$

Here, $f(x)$ is the function in Eqs. (21) and (22). The evaluation of Eq. (32) requires the explicit expressions of $g_{\text{even}}(x)$ and $g_{\text{odd}}(x)$, which are derived from the even- and odd-order terms of $f(x)$, respectively (Table 1). The four types (exp, sqrt, McWeeny, Cayley) have their explicit forms, and hence, Eq. (32) can be evaluated directly. By contrast, the optimal type has no function form, being given only by coefficients of the Taylor series. However, for practical use, evaluation with double precision in the region of $|x| \leq 1$ is sufficient.

To construct TIC coefficients for the n -th-order uDK, we need to obtain not only the general contraction coefficients \mathbf{d}^A from a one-center HF calculation for each atom using $\mathbf{H}_{\text{uDK}n}$, but also the two-component transformation matrices $\mathbf{U}_{\text{LL,uDK}n}$ and $\mathbf{U}_{\text{SL,uDK}n}$. These transformation matrices for the second and third orders are obtained by $[U_0 U_1]_{\text{LL}}$, $[U_0 U_1]_{\text{SL}}$, $[U_0 U_1 U_2]_{\text{LL}}$, $[U_0 U_1 U_2]_{\text{SL}}$, and Eq. (3), as follows:

$$\mathbf{U}_{\text{LL,uDK2}} = \mathbf{X} \mathbf{Q} \tilde{\mathbf{A}} \left(\tilde{\mathbf{G}}_1^e - \tilde{\mathbf{B}} \tilde{\mathbf{p}} \tilde{\mathbf{G}}_1^o \right) \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \quad (34)$$

$$\mathbf{U}_{\text{SL,uDK2}} = \mathbf{S}_S^{-1} \mathbf{\Pi}_{\text{SL}} \mathbf{X} \mathbf{Q} \tilde{\mathbf{A}} \tilde{\mathbf{B}} \left(\tilde{\mathbf{G}}_1^e + \tilde{\mathbf{B}}^{-1} \tilde{\mathbf{p}}^{-1} \tilde{\mathbf{G}}_1^o \right) \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \quad (35)$$

$$\begin{aligned} \mathbf{U}_{\text{LL,uDK3}} &= \mathbf{X} \mathbf{Q} \tilde{\mathbf{A}} \left\{ \left(\tilde{\mathbf{G}}_1^e - \tilde{\mathbf{B}} \tilde{\mathbf{p}} \tilde{\mathbf{G}}_1^o \right) \tilde{\mathbf{G}}_2^e \right. \\ &\quad \left. - \left(\tilde{\mathbf{G}}_1^{o\dagger} + \tilde{\mathbf{B}} \tilde{\mathbf{p}} \tilde{\mathbf{G}}_1^e \right) \tilde{\mathbf{G}}_2^o \right\} \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L, \end{aligned} \quad (36)$$

$$\begin{aligned} \mathbf{U}_{\text{SL,uDK3}} &= \mathbf{S}_S^{-1} \mathbf{\Pi}_{\text{SL}} \mathbf{X} \mathbf{Q} \tilde{\mathbf{A}} \tilde{\mathbf{B}} \left\{ \left(\tilde{\mathbf{G}}_1^e + \tilde{\mathbf{B}}^{-1} \tilde{\mathbf{p}}^{-1} \tilde{\mathbf{G}}_1^o \right) \tilde{\mathbf{G}}_2^e \right. \\ &\quad \left. + \left(\tilde{\mathbf{B}}^{-1} \tilde{\mathbf{p}}^{-1} \tilde{\mathbf{G}}_1^e - \tilde{\mathbf{G}}_1^{o\dagger} \right) \tilde{\mathbf{G}}_2^o \right\} \mathbf{Q}^\dagger \mathbf{X}^\dagger \mathbf{S}_L. \end{aligned} \quad (37)$$

3. Results and discussion

3.1. Atomic calculations: Rn^{84+} ion and Rn atom

To verify the performance of the TIC scheme in atomic calculations, we performed HF calculations for the Rn helium-like cation (Rn^{84+}) and the Rn atom. The IOTC, conventional DK, and uDK based on five different function forms were applied to the two-component transformations. For the DK method, conventional and uDK at the second and third orders were considered. The basis functions for the Rn atom and its cation were constructed by adding three additional basis functions with large orbital exponents to the Gaussian functions of Tatewaki et al. [25–27]. This addition of large exponents was due to the use of the point charge model for the nucleus. Using these basis functions, we carried out two-component HF calculations to obtain the AO coefficients \mathbf{d}^A first, and then constructed the TIC coefficients from Eq. (8).

Table 2 and Table 3 show the HF energies and the energy errors of the TIC basis functions from the primitive basis functions for the Rn^{84+}

Table 1
Function forms used in the implementation of uDK transformations.

	exp	sqrt	McW	CA	opt
$f(x)$	exp x	$\sqrt{1+x^2} + x$	$\frac{1+x}{\sqrt{1-x^2}}$	$\frac{2+x}{2-x}$	$\sum_{i=0}^{\infty} a_i x^i$
$g_{\text{even}}(x)$	$\cos \sqrt{x}$	$\sqrt{1-x}$	$\frac{1}{\sqrt{1+x}}$	$\frac{4-x}{4+x}$	$\sum_{i=0}^{\infty} a_{2i} (-x)^i$
$g_{\text{odd}}(x)$	$\frac{\sin \sqrt{x}}{\sqrt{x}}$	1	$\frac{1}{\sqrt{1+x}}$	$\frac{4}{4-x}$	$\sum_{i=0}^{\infty} a_{2i+1} (-x)^i$

Table 2

HF energies by TIC scheme and errors from primitive basis set energies for the Rn⁸⁴⁺ ion (in Hartree).

Method	TIC	primitive ^a	Difference
IOTC	-8247.0076	-8247.0076	<10 ⁻⁸ ^b
exp-DK3	-8248.2263	-8248.2263	<10 ⁻⁸ ^b
sqrt-DK3	-8248.1222	-8248.1222	<10 ⁻⁸ ^b
McW-DK3	-8248.4454	-8248.4454	<10 ⁻⁸ ^b
CA-DK3	-8248.2797	-8248.2797	<10 ⁻⁸ ^b
opt-DK3	-8248.2135	-8248.2135	<10 ⁻⁸ ^b
exp-DK2	-8255.0896	-8255.0896	<10 ⁻⁸ ^b
sqrt-DK2	-8255.3458	-8255.3458	<10 ⁻⁸ ^b
McW-DK2	-8254.5988	-8254.5988	<10 ⁻⁸ ^b
CA-DK2	-8254.9644	-8254.9644	<10 ⁻⁸ ^b
opt-DK2	-8255.1203	-8255.1203	<10 ⁻⁸ ^b
DK3	-8248.1139	-8249.8238	1.7098
DK2	-8255.1690	-8220.4862	-34.6828

^a The “primitive” results were obtained by the two-component method without LUT, using primitive basis functions.

^b The notation “<10⁻⁸” indicates that the absolute value of the difference is less than 10⁻⁸.

Table 3

HF energies by TIC scheme and errors from primitive basis set energies for the Rn atom (in Hartree).

Method	TIC	primitive ^a	Difference
IOTC	-23598.6123	-23598.6123	<10 ⁻⁸ ^b
exp-DK3	-23600.1008	-23600.1008	<10 ⁻⁸ ^b
sqrt-DK3	-23599.9747	-23599.9747	<10 ⁻⁸ ^b
McW-DK3	-23600.3660	-23600.3660	<10 ⁻⁸ ^b
CA-DK3	-23600.1654	-23600.1654	<10 ⁻⁸ ^b
opt-DK3	-23600.0853	-23600.0853	<10 ⁻⁸ ^b
exp-DK2	-23608.5245	-23608.5245	<10 ⁻⁸ ^b
sqrt-DK2	-23608.8343	-23608.8343	<10 ⁻⁸ ^b
McW-DK2	-23607.9307	-23607.9307	<10 ⁻⁸ ^b
CA-DK2	-23608.3730	-23608.3730	<10 ⁻⁸ ^b
opt-DK2	-23608.5616	-23608.5616	<10 ⁻⁸ ^b
DK3	-23599.9897	-23602.1726	2.1830
DK2	-23608.6278	-23566.0769	-42.5509

^a The “primitive” results were obtained by the two-component method without LUT, using primitive basis functions.

^b The notation “<10⁻⁸” indicates that the absolute value of the difference is less than 10⁻⁸.

ion and Rn atom, respectively. As theoretically expected, for the IOTC and the 10 uDK methods, the TIC results agreed exactly with the results of the primitive basis functions for both the Rn⁸⁴⁺ ion and the Rn atom. These results were in contrast with the large errors of ≥ 1 Hartree for the conventional DK2 and DK3, the transformations of which are not unitary.

Moreover, the uDKs (DK2 and DK3) gave HF energies closer to those of IOTC in comparison to the conventional DKs in the primitive basis functions, indicating that they are more accurate than the conventional DKs. This and the abovementioned fact suggest the effectiveness of the combination of the TIC and uDK methods.

3.2. Molecular calculations: NaF, NaI, FrF, and FrI molecules

To verify the applicability of the TIC scheme to molecular systems, we constructed TIC basis functions for F, Na, I, and Fr, and performed HF calculations for NaF, NaI, FrF, and FrI molecules. The primitive basis functions for the atoms were the Gaussian basis functions of Tatewaki et al. [25–27] augmented by three additional functions with large orbital exponents. To construct the TIC basis functions, because these four atoms are open-shell atoms, the average-of-configuration approximation [43,44] was applied in the calculations. In addition, to describe the bonding of the molecules more accurately, some HF virtual orbitals (the *s*, *p* functions for F and Na, *s*, *p*, *d* functions for I, and *s*, *p*, *d*, *f*

functions for Fr) of the atoms were included in the TIC basis functions. The contents of the resulting basis functions are shown in Table 4. The term “Min. + *n* (*n* = 1, 2, 3)” in the table indicates that these are the basis functions with *n* lowest virtual orbitals in each angular momentum. Note also that the alkali metal atoms (Na and Fr) include one more *p* orbital in the outermost shell. In addition to these elements, we constructed “Min. + 3” TIC coefficients for IOTC for elements 1–103, which are presented in the supporting information.

Table 5 compares the results of the TIC basis functions with those of the primitive basis functions in terms of the equilibrium internuclear distance *R*_e and the HF energy at *R*_e of the FrI molecule. The equilibrium internuclear distance *R*_e was calculated using cubic curve fitting. The table shows that the inclusion of at least two virtual orbitals in each angular momentum, namely (Min. + 2), is necessary for obtaining an *R*_e error of less than 0.001 Å. The (Min. + 2) basis functions also calculate the energy with an error of less than 10⁻⁴ Hartree. These results indicate that the errors due to the LUT approximation and the contraction are both sufficiently small. By contrast, the (Min. + 1) and (Min.) TIC basis functions show errors of more than 0.02 Å for *R*_e and more than 0.001 Hartree for the energy. Table 6 shows the equilibrium internuclear distances and the HF energies calculated with the (Min. + 3) basis functions for the other three molecules. For all the three molecules, the errors are about 0.001 Å for *R*_e and less than 10⁻⁴ Hartree for the energy.

By including two or more virtual orbitals in each angular momentum in the TIC basis functions, the errors due to TIC are sufficiently small, indicating that the present scheme performs satisfactorily in molecular calculations.

4. Conclusion

We have proposed the TIC scheme, in which a two-component transformation is incorporated into the contraction coefficients of basis functions, to reduce the computational cost of relativistic two-component calculations. The TIC scheme is directly applicable to atoms, and can also be applied to molecules by utilizing the LUT approximation, with a treatment almost identical to the conventional basis function contractions. In addition to reducing the computational cost at runtime, TIC has a very low implementation cost owing to its similarity in form to the conventional basis function contraction. We have also introduced a new uDK method, which is a modification of the conventional DK method designed to maintain the unitarity of the two-component transformation. This ensures that TIC is in agreement with the original two-component method and does not require modification of the overlap integrals. To generate TIC coefficients, the contraction coefficients obtained by applying the original two-component method to atomic calculations with primitive basis functions and the specific matrix-form expressions for the two-component transformations are needed. Once TIC coefficients are generated and stored for a certain set of a two-component method and primitive basis functions, then we can obtain the contracted two-component Hamiltonian without two-component transformation using the stored TIC coefficients unless the set is changed. The explicit expressions and procedures for generating the TIC coefficients for the uDK and conventional IOTC methods were provided.

We have implemented programs for generating TIC coefficients and performing calculations using these coefficients. These programs were applied to study atomic (Rn⁸⁴⁺ and Rn) and several molecular systems

Table 4

Contents of primitive and TIC basis sets.

Atom	Primitive	Min. + 3	Min. + 2	Min. + 1	Min.
F	15s11p	5s4p	4s3p	3s2p	2s1p
Na	19s11p	6s5p	5s4p	4s3p	3s2p
I	25s21p15d	8s7p5d	7s6p4d	6s5p3d	5s4p2d
Fr	31s24p18d13f	10s9p6d4f	9s8p5d3f	8s7p4d2f	7s6p3d1f

Table 5

Equilibrium internuclear distances and HF energies for FrI calculated using TIC and primitive basis sets.

Method	$R_e/\text{\AA}$	$\Delta R_e/\text{\AA}$				$E_e/\text{Hartree}$	$\Delta E_e/\text{Hartree}$			
	primitive ^a	Min. + 3	Min. + 2	Min. + 1	Min. + 0	primitive ^a	Min. + 3	Min. + 2	Min. + 1	Min. + 0
IOTC	3.5874	0.0002	0.0004	0.0274	0.0952	-31421.9194	0.0000	0.0000	0.0021	0.0302
exp-DK3	3.5873	0.0001	0.0004	0.0274	0.0952	-31423.5768	0.0000	0.0000	0.0021	0.0302
sqrt-DK3	3.5873	0.0001	0.0004	0.0274	0.0952	-31423.4365	0.0000	0.0000	0.0021	0.0302
McW-DK3	3.5873	0.0001	0.0004	0.0274	0.0952	-31423.8719	0.0000	0.0000	0.0021	0.0302
CA-DK3	3.5873	0.0001	0.0004	0.0274	0.0952	-31423.6487	0.0000	0.0000	0.0021	0.0302
opt-DK3	3.5873	0.0001	0.0004	0.0274	0.0952	-31423.5595	0.0000	0.0000	0.0021	0.0302
exp-DK2	3.5870	0.0002	0.0004	0.0274	0.0952	-31433.0300	0.0000	0.0000	0.0021	0.0302
sqrt-DK2	3.5870	0.0002	0.0004	0.0274	0.0952	-31433.3751	0.0000	0.0000	0.0021	0.0302
McW-DK2	3.5870	0.0002	0.0004	0.0274	0.0952	-31432.3684	0.0000	0.0000	0.0021	0.0302
CA-DK2	3.5870	0.0002	0.0004	0.0274	0.0952	-31432.8612	0.0000	0.0000	0.0021	0.0302
opt-DK2	3.5870	0.0002	0.0004	0.0274	0.0952	-31433.0713	0.0000	0.0000	0.0021	0.0302

^a The "primitive" results were obtained by the two-component method without LUT, using primitive basis functions.**Table 6**

Equilibrium internuclear distances and HF energies for FrF, NaI, and NaF molecules calculated using TIC (Min. + 3) and primitive basis sets.

Method	$R_e/\text{\AA}$	$\Delta R_e/\text{\AA}$	$E_e/\text{Hartree}$	$\Delta E_e/\text{Hartree}$
	primitive ^a	Min. + 3	primitive ^a	Min. + 3
FrF				
IOTC	2.5231	0.0007	-24407.2191	0.0000
exp-DK3	2.5230	0.0007	-24408.8578	0.0000
sqrt-DK3	2.5230	0.0007	-24408.7189	0.0000
McW-DK3	2.5230	0.0007	-24409.1500	0.0000
CA-DK3	2.5230	0.0007	-24408.9290	0.0000
opt-DK3	2.5230	0.0007	-24408.8407	0.0000
exp-DK2	2.5229	0.0007	-24417.9764	0.0000
sqrt-DK2	2.5229	0.0007	-24418.3159	0.0000
McW-DK2	2.5229	0.0007	-24417.3261	0.0000
CA-DK2	2.5229	0.0007	-24417.8105	0.0000
opt-DK2	2.5229	0.0007	-24418.0170	0.0000
NaI				
IOTC	2.7728	0.0004	-7276.3638	0.0000
exp-DK3	2.7728	0.0004	-7276.3825	0.0000
sqrt-DK3	2.7728	0.0004	-7276.3811	0.0000
McW-DK3	2.7728	0.0004	-7276.3853	0.0000
CA-DK3	2.7728	0.0004	-7276.3832	0.0000
opt-DK3	2.7728	0.0004	-7276.3823	0.0000
exp-DK2	2.7729	0.0004	-7276.7170	0.0000
sqrt-DK2	2.7729	0.0004	-7276.7228	0.0000
McW-DK2	2.7729	0.0004	-7276.7058	0.0000
CA-DK2	2.7729	0.0004	-7276.7142	0.0000
opt-DK2	2.7729	0.0004	-7276.7177	0.0000
NaF				
IOTC	1.9479	0.0003	-261.6679	0.0000
exp-DK3	1.9479	0.0003	-261.6679	0.0000
sqrt-DK3	1.9479	0.0003	-261.6679	0.0000
McW-DK3	1.9479	0.0003	-261.6679	0.0000
CA-DK3	1.9479	0.0003	-261.6679	0.0000
opt-DK3	1.9479	0.0003	-261.6679	0.0000
exp-DK2	1.9479	0.0003	-261.6679	0.0000
sqrt-DK2	1.9479	0.0003	-261.6679	0.0000
McW-DK2	1.9479	0.0003	-261.6679	0.0000
CA-DK2	1.9479	0.0003	-261.6679	0.0000
opt-DK2	1.9479	0.0003	-261.6679	0.0000

^a The "primitive" results were obtained by the two-component method without LUT, using primitive basis functions.

(NaF, NaI, FrF, and FrI) for numerical validation. The calculations

Appendix

Appendix A. . TIC two-electron integrals

In this work, we used a many-body Hamiltonian composed of the one-electron Hamiltonian by TIC and the nonrelativistic two-electron Hamiltonian. However, the use of the nonrelativistic two-electron Hamiltonian is not essential to the TIC scheme, and the use of the two-electron Hamiltonian with TIC applied is also an available option. The TIC two-electron integrals are given by

confirmed that for the atomic systems, the results obtained using the TIC basis functions were in exact agreement with those derived from the two-component method using primitive basis functions. Additionally, for the molecular systems, we have demonstrated that the equilibrium internuclear distances (R_e) and the total energies at R_e , as calculated with primitive basis functions, could be accurately reproduced by extending the minimal basis set so as to include up to the third virtual orbital of each angular momentum. These results suggest that the TIC scheme proposed in this paper could be an effective approach in the field of relativistic molecular orbital calculations.

CRedit authorship contribution statement

Ippei Tsuzuki: Writing – original draft, Software, Methodology, Investigation, Formal analysis. **Nobuki Inoue:** Writing – original draft, Software, Methodology, Formal analysis, Conceptualization. **Yoshihiro Watanabe:** Supervision, Software, Resources. **Haruyuki Nakano:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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$$(\alpha\beta|\gamma\delta)^{(\text{TIC})} = \sum_{X,Y}^{\text{L,S}} \sum_{\mu\nu\lambda\sigma} \left(\mathbf{d}_X^{\text{Total(TIC)}} \right)_{\mu\alpha}^* \left(\mathbf{d}_X^{\text{Total(TIC)}} \right)_{\nu\beta} \left(\mathbf{d}_Y^{\text{Total(TIC)}} \right)_{\lambda\gamma}^* \left(\mathbf{d}_Y^{\text{Total(TIC)}} \right)_{\sigma\delta} \left(\chi_{\mu}^X \chi_{\nu}^X | \chi_{\lambda}^Y \chi_{\sigma}^Y \right). \quad (\text{A1})$$

Relativistic two-component electronic structure calculations using these integrals are expected to be highly accurate. However, the two-electron integrals in Eq. (A1) involving small components, namely $\left(\chi_{\mu}^S \chi_{\nu}^S | \chi_{\lambda}^L \chi_{\sigma}^L \right)$ and $\left(\chi_{\mu}^S \chi_{\nu}^S | \chi_{\lambda}^S \chi_{\sigma}^S \right)$, require a high computational cost compared with $\left(\chi_{\mu}^L \chi_{\nu}^L | \chi_{\lambda}^L \chi_{\sigma}^L \right)$. Therefore, other approaches, such as approximating small-component two-electron integrals [45–47], are essential for achieving efficient two-component method calculations using the two-electron integrals $(\alpha\beta|\gamma\delta)^{(\text{TIC})}$ in Eq. (A1).

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