Research paper

Relativistic two-electron repulsion operator formulas for the Douglas–Kroll method

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ABSTRACT

Two-electron repulsion operator formulas for the second- and third-order Douglas–Kroll (DK2 and DK3) method were derived and implemented. The formulas were applied to helium-like ions with $Z = 10, 20, \ldots, 130$, and to rare gas atoms. The energies obtained for the DK2 and DK3 two-electron operators showed differences from the four-component method that were one order of magnitude smaller than those of the nonrelativistic and DK1 two-electron operators. Approximation formulas for the small component-type two-electron integrals were also derived; they were applied to the helium-like ions with $Z = 80$ and 130 and were numerically confirmed to reproduce unapproximated values very accurately.

1. Introduction

A relativistic treatment is essential for the accurate description of electronic structures of molecules that include heavy atoms. This effect is taken into account most naturally via the Dirac equation, which is the basic equation in relativistic quantum mechanics. The Dirac equation provides four-component spinors as solutions that describe the electrons and their anti-particles, positrons. The method based on the Dirac equation is known as the four-component method, and is now widely used in quantum chemistry [1]. The two-component method is also widely used. The components of the four-component spinors can be classified into large and small parts, each of which is characterized by a large and a small contribution to the electronic solution. The two-component method uses only the degree of freedom of electrons decoupled from that of positrons. The two-component spinors used in this method are transformed spinors that are decoupled from the degrees of freedom of positrons and thus are not identical to any parts of the original four components. Today, there are several versions of the two-component method depending on the transformation: the Breit–Pauli approximation (BPA) [2], the zeroth-order regular approximation (ZORA) [3], the infinite-order regular approximation (IORA) [4], the relativistic scheme for eliminating small components (RESC) [5], the Douglas–Kroll (DK) method [6–12], the infinite-order two-component (IOTC) method [13], and the exact-two-component (X2C) method [14–16]. These methods are now included in various program packages and are commonly used in research in this field.

In the many-body problem in relativistic theory, the way of defining the many-body Hamiltonian is a very important issue. In the most common formulation, for the one-particle part, the sum of the Dirac one-particle Hamiltonian is used. By contrast, to satisfy the Lorentz and gauge invariances, the electron interaction effect is formulated through a perturbation calculation using quantum electrodynamics (QED). However, because the effects at high perturbation orders are known to be usually very small, in relativistic quantum chemistry, the Dirac–Coulomb (DC) or the Dirac–Coulomb–Breit (DCB) Hamiltonians [17] truncated at the zeroth or second order, respectively, are commonly used. Of these two, the DCB Hamiltonian approximately includes the effect of the quantized electromagnetic field in the QED. Thus, the DCB Hamiltonian is a better approximation of the QED than the DC Hamiltonian, but is more complicated. Under these circumstances, the DC Hamiltonian is mainly used as the many-body Hamiltonian in electronic structure calculations in current relativistic quantum chemistry. However, in approximating the four-component method into a two-component method, the DC Hamiltonian designed according to each two-component method needs to be transformed. Such transformed DC Hamiltonians have been derived for the BP, IOTC [18], DK1 [19–21], and NESC [22] approximations, but the expressions for orders higher than the first-order DK approximation have not been explicitly given.

In the present Letter, we derive explicit expressions for the DK2 and DK3 two-electron operators and, using the derived formulas, we numerically assess the accuracy of several two-electron Hamiltonians, including DK2 and DK3. In addition, to evaluate the value of the two-

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component transformed two-electron operator, the two-electron integrals that are not used in the calculation of the nonrelativistic molecular orbital calculation (small component-type two-electron integrals) need to be calculated. Such a two-electron integral demands a larger calculation cost than the ordinary two-electron integral of the nonrelativistic theory, which is not much different from that of the four-component method. To develop a two-component method with a computational cost that is sufficiently cheaper than the conventional four-component method, the computational method for the small component-type two-electron integrals is important. Low-cost methods have been proposed to incorporating a part of the electron–electron interaction described by small-component type two-electron integrals into the one-electron Hamiltonian or the Fock operator as effective electron repulsion [23,24]. While these are useful methods, a direct approximation for the small component type two-electron integrals is also effective in performing post-Hartree–Fock methods and systematically improving their accuracy.

2. Theory

2.1. Two-electron repulsion operator formulas for the second- and third-order DK method

Let $\boldsymbol{U}$ be a unitary transformation that transforms the Dirac spinor $\Psi(1)$ as $\boldsymbol{U}(1)\Psi(1)$. The transformation for an arbitrary one-electron operator $\widehat{O}(1)$ is given by

$$\boldsymbol{U}(1)\widehat{O}(1)\boldsymbol{U}^\dagger(1) . \tag{2.1}$$

It is useful to introduce a notation in which the upper and the lower two components of the four components are described separately:

$$\Psi(1) = \begin{bmatrix} \Psi^L(1) \\ \Psi^S(1) \end{bmatrix}, \boldsymbol{U}(1) = \begin{bmatrix} U^{LL}(1) & U^{LS}(1) \\ U^{SL}(1) & U^{SS}(1) \end{bmatrix} \tag{2.2}$$

Because we consider $\boldsymbol{U}$ to be a transformation from the Dirac Hamiltonian to a two-component effective Hamiltonian, the corresponding operator in the two-component method is obtained from the upper-left part (LL) of the 2×2 blocks of Eq. (2.1) as:

$$\widehat{O}^{2c} = \left(\boldsymbol{U}\widehat{O}\boldsymbol{U}^\dagger \right)^{LL}. \tag{2.3}$$

The two-electron operator of the DC Hamiltonian, namely the Coulomb repulsion operator, is expressed in the four-component method as:

$$g^{4c}(1,2) = \frac{\mathbf{1}_4(1)\mathbf{1}_4(2)}{r_{12}} \tag{2.4}$$

By sequentially performing a two-component transformation on electrons 1 and 2, we obtain the Coulomb repulsion operator in the two-component method as:

$$g^{2c}(1,2) = \left[\boldsymbol{U}(2)\left[\boldsymbol{U}(1)\frac{\mathbf{1}_4(1)}{r_{12}}\boldsymbol{U}^\dagger(1) \right]^{LL} \mathbf{1}_4(2)\boldsymbol{U}^\dagger(2) \right]^{LL}, \tag{2.5}$$

where the "LL" marks on the inner and outer parentheses in the right-hand side (rhs) represent the upper-left part of the matrix (see eq. (2.2)) for electrons 1 and 2, respectively. Defining $\widehat{V}^{2e}(1;2)$ and $\widehat{V}^{2e'}(2;1)$ as a shorthand notation:

$$\widehat{V}^{2e}(1;2) = \frac{1}{r_{12}},$$
$$\widehat{V}^{2e'}(2;1) = \left[\boldsymbol{U}(1)\frac{\mathbf{1}_4(1)}{r_{12}}\boldsymbol{U}^\dagger(1) \right]^{LL}, \tag{2.6}$$

it becomes clear that eq. (2.5) requires two matrix operations,

$\boldsymbol{U}(1)\widehat{V}^{2e}(1;2)\mathbf{1}_4(1)\boldsymbol{U}^\dagger(1)$ and $\boldsymbol{U}(2)\widehat{V}^{2e'}(2;1)\mathbf{1}_4(2)\boldsymbol{U}^\dagger(2)$, which are formally identical transformations that do not depend on the electron variables. Hence, we only need an expression for $\boldsymbol{U}\widehat{V}^{2e}\mathbf{1}_4\boldsymbol{U}^\dagger$.

Let us explicitly show the process by using the DK1 example instead of DK2 and DK3, although the DK1 formula is already known [21], because the intermediate expressions in the derivation of the two-electron repulsion operators for DK2 and DK3 are quite lengthy. DK1 is equivalent to the free-particle Foldy–Wouthuysen (fpFW) transformation, which ignores the external field $V^{\text{ext.}}$.

$$\boldsymbol{U}_0 = \begin{bmatrix} A & A\kappa \\ -A\kappa & A \end{bmatrix} \tag{2.7}$$

Here, A and κ are given by

$$A = \sqrt{\frac{E_p + c^2}{2E_p}} \quad \text{and} \quad \kappa = \frac{c\boldsymbol{\sigma}\cdot\boldsymbol{p}}{E_p + c^2}, \tag{2.8}$$

respectively, where $E_p = \sqrt{p^2c^2 + c^4}$ is the relativistic kinetic energy. Applying the fpFW transformation to the pseudo one-electron operator $\widehat{V}^{2e}$ (eq. (2.6)), we obtain

$$\begin{aligned} &\begin{bmatrix} A & A\kappa \\ -A\kappa & A \end{bmatrix} \begin{bmatrix} \widehat{V}^{2e} & 0 \\ 0 & \widehat{V}^{2e} \end{bmatrix} \begin{bmatrix} A & -\kappa A \\ \kappa A & A \end{bmatrix} \\ &= \begin{bmatrix} A\widehat{V}^{2e}A + A\kappa\widehat{V}^{2e}\kappa A & -A\widehat{V}^{2e}\kappa A + A\kappa\widehat{V}^{2e}A \\ A\widehat{V}^{2e}\kappa A - A\kappa\widehat{V}^{2e}A & A\widehat{V}^{2e}A + A\kappa\widehat{V}^{2e}\kappa A \end{bmatrix} \end{aligned} \tag{2.9}$$

We can obtain the coefficients of the two-electron repulsion operator $1/r_{12}$ from the upper-left block of the rhs. The relativistic two-electron operators in the DK2 and DK3 can be derived in the same manner using the transformation matrices $\boldsymbol{U}_1\boldsymbol{U}_0$, and $\boldsymbol{U}_2\boldsymbol{U}_1\boldsymbol{U}_0$, respectively, instead of $\boldsymbol{U}_0$. For simplicity, we use the following exponential-type [9] operators among several variants of the DK transformation matrices $\boldsymbol{U}_1$, $\boldsymbol{U}_2$, …,

$$\boldsymbol{U}_i = exp(\boldsymbol{W}_i), \tag{2.10}$$

where $\boldsymbol{W}_i$ is an anti-Hermitian operator of the i-th order with respect to the external field. Therefore, the terms in the second- and higher-order terms with respect to $\boldsymbol{W}_1$ are cut off to ensure the consistency with the one-electron term of DK2 because $\widehat{V}^{2e}$ is regarded as a first-order term.

$$\begin{aligned} &\boldsymbol{U}_1\boldsymbol{U}_0\widehat{V}^{2e}\mathbf{1}_4\boldsymbol{U}_0^\dagger\boldsymbol{U}_1^\dagger \\ &= \left(\mathbf{1}_4 + \boldsymbol{W}_1 + o(\boldsymbol{W}_1^2) \right)\boldsymbol{U}_0\widehat{V}^{2e}\mathbf{1}_4\boldsymbol{U}_0^\dagger\left(\mathbf{1}_4 - \boldsymbol{W}_1 + o(\boldsymbol{W}_1^2) \right) \\ &\simeq \boldsymbol{U}_0\widehat{V}^{2e}\mathbf{1}_4\boldsymbol{U}_0^\dagger + \boldsymbol{W}_1\boldsymbol{U}_0\widehat{V}^{2e}\mathbf{1}_4\boldsymbol{U}_0^\dagger - \boldsymbol{U}_0\widehat{V}^{2e}\mathbf{1}_4\boldsymbol{U}_0^\dagger\boldsymbol{W}_1 \end{aligned} \tag{2.11}$$

The terms $\boldsymbol{W}_1, \boldsymbol{W}_2,…$ that generate $\boldsymbol{U}_1, \boldsymbol{U}_2,…$ are determined order-by-order from a one-electron DK transformation.

$$\begin{aligned} \boldsymbol{W}_1 &= \begin{bmatrix} 0 & o_1 \\ o_1 & 0 \end{bmatrix}, \\ o_1 &= A\kappa\frac{V^{\text{ext.}}(p,p')}{E_p + E_{p'}}A - A\frac{V^{\text{ext.}}(p,p')}{E_p + E_{p'}}\kappa A \end{aligned} \tag{2.12}$$

$$\begin{aligned} \boldsymbol{W}_2 &= \begin{bmatrix} 0 & [o_1, E_1]/(E_p + E_{p'}) \\ -[o_1, E_1]/(E_p + E_{p'}) & 0 \end{bmatrix}, \\ E_1 &= AV^{\text{ext.}}A + A\kappa V^{\text{ext.}}\kappa A \end{aligned} \tag{2.13}$$

Using these quantities, we obtain the DK2 and DK3 two-electron repulsion operators $g^{\text{DK2}}(1,2)$ and $g^{\text{DK3}}(1,2)$

$$g^{\text{DK2}}(1,2) = \sum_{i=0}^{1}\sum_{j=0}^{1} N_i^L(1)N_j^L(2)\frac{1}{r_{12}}\left(N_{1-i}^L(1)\right)^{\dagger}\left(N_{1-j}^L(2)\right)^{\dagger}$$

$$+ \sum_{i=0}^{1}\sum_{j=0}^{1} N_i^L(1)N_j^S(2)\kappa(2)\frac{1}{r_{12}}\kappa(2)\left(N_{1-i}^L(1)\right)^{\dagger}\left(N_{1-j}^S(2)\right)^{\dagger}$$

$$+ \sum_{i=0}^{1}\sum_{j=0}^{1} N_i^S(1)N_j^L(2)\kappa(1)\frac{1}{r_{12}}\kappa(1)\left(N_{1-i}^S(1)\right)^{\dagger}\left(N_{1-j}^L(2)\right)^{\dagger}$$

$$+ \sum_{i=0}^{1}\sum_{j=0}^{1} N_i^S(1)N_j^S(2)\kappa(1)\kappa(2)\frac{1}{r_{12}}\kappa(1)\kappa(2)\left(N_{1-i}^S(1)\right)^{\dagger}\left(N_{1-j}^S(2)\right)^{\dagger}$$

$$\text{, (2.14)}$$

$$g^{\text{DK3}}(1,2) = \sum_{i=0}^{2}\sum_{j=0}^{2} L_i^L(1)L_j^L(2)\frac{1}{r_{12}}\left(L_{2-i}^L(1)\right)^{\dagger}\left(L_{2-j}^L(2)\right)^{\dagger}$$

$$+ \sum_{i=0}^{2}\sum_{j=0}^{2} L_i^L(1)L_j^S(2)\kappa(2)\frac{1}{r_{12}}\kappa(2)\left(L_{2-i}^L(1)\right)^{\dagger}\left(L_{2-j}^S(2)\right)^{\dagger}$$

$$+ \sum_{i=0}^{2}\sum_{j=0}^{2} L_i^S(1)L_j^L(2)\kappa(1)\frac{1}{r_{12}}\kappa(1)\left(L_{2-i}^S(1)\right)^{\dagger}\left(L_{2-j}^L(2)\right)^{\dagger}$$

$$+ \sum_{i=0}^{2}\sum_{j=0}^{2} L_i^S(1)L_j^S(2)\kappa(1)\kappa(2)\frac{1}{r_{12}}\kappa(1)\kappa(2)\left(L_{2-i}^S(1)\right)^{\dagger}\left(L_{2-j}^S(2)\right)^{\dagger}$$

$$\text{, (2.15)}$$

where the operators N_i^X and L_i^X are defined by

$$N_0^L = N_0^S = L_0^L = L_0^S = A, \tag{2.16}$$

$$N_1^L = \left(\frac{1}{2} + A\nu AR^2 p^2 - AR\omega RA\right)A$$

$$N_1^S = \left(\frac{1}{2} + AR\omega RAR^{-2}p^{-2} - A\nu A\right)A, \tag{2.17}$$

$$L_1^L = \left(A\nu AR^2 p^2 - AR\omega RA\right)A$$

$$L_1^S = \left(A\nu A - AR\omega RAR^{-2}p^{-2}\right)A$$

$$L_2^L = \left\{\frac{1}{2} + A\nu AR^2 p^2 - AR\omega RA + \frac{1}{2}W_1^2 + \frac{(E_1 o_1 \kappa)}{E_p + E_{p'}} - \frac{(o_1 E_1 \kappa)}{E_p + E_{p'}}\right\}A$$

$$L_2^S = \left\{\frac{1}{2} + AR\omega RAR^{-2}p^{-2} - A\nu A + \frac{1}{2}W_1^2 - \frac{(E_1 o_1 \kappa^{-1})}{E_p + E_{p'}} + \frac{(o_1 E_1 \kappa^{-1})}{E_p + E_{p'}}\right\}A. \tag{2.18}$$

Here, $E_1 o_1 \kappa$, $o_1 E_1 \kappa$, $E_1 o_1 \kappa^{-1}$, $o_1 E_1 \kappa^{-1}$, R, ν, and ω are given by

$$E_1 o_1 \kappa = \left(AV^{\text{ext.}}A + AR\Omega RA\right)\left(AR\omega RA - A\nu AR^2 p^2\right),$$
$$o_1 E_1 \kappa = \left(AR\omega RAR^{-2}p^{-2} - A\nu A\right)\left(AR\Omega RA + p^2 R^2 AV^{\text{ext.}}AR^2 p^2\right),$$
$$E_1 o_1 \kappa^{-1} = \left(AV^{\text{ext.}}A + AR\Omega RA\right)\left(AR\omega RAR^{-2}p^{-2} - A\nu A\right),$$
$$o_1 E_1 \kappa^{-1} = \left(AR\omega RAR^{-2}p^{-2} - A\nu A\right)\left(AR\Omega RAR^{-2}p^{-2} + p^2 R^2 AV^{\text{ext.}}A\right), \tag{2.19}$$

$$R = \frac{c}{E_p + c^2},\ \nu(p,p') = \frac{V^{\text{ext.}}(p,p')}{E_p + E_{p'}}$$
$$\text{and}\quad \omega(p,p') = \frac{\Omega(p,p')}{E_p + E_{p'}} \tag{2.20}$$

with

$$\Omega(p,p') = \boldsymbol{\sigma}\cdot\boldsymbol{p}V^{\text{ext.}}(p,p')\boldsymbol{\sigma}\cdot\boldsymbol{p}.$$

The transformations for the two-electron operators used here are determined only for the one-electron operator. Therefore, for many-electron systems, there remains some difference from the four-component method. If the transformation is determined using the two-electron repulsion energy, this difference is eliminated. However, the transformation must be repeated for each self-consistent field step in a

Hartree–Fock calculation. Such a transformation for the DK method has already been reported by Nakajima et al. [21]. In their method, the entire Fock operator is transformed and only the Coulomb and exchange integrals of DK2 or DK3 are obtained. In contrast, because all the two-electron integrals are obtained explicitly, the formula derived here enabled us to perform electron correlation calculations directly.

2.2. Approximate formula for the small component-type two-electron integrals

The four components of the Dirac spinor can be divided into two: upper (large) and lower (small) components. When the small components are expanded using the set $\{p^{-1}\boldsymbol{\sigma}\cdot\boldsymbol{p}|\varphi^L\rangle\}$ (strict kinetic balance), the execution using the Dirac–Hartree–Fock method requires the calculation of the following two-electron integrals.

$$[(\boldsymbol{\sigma}\cdot\boldsymbol{p}\mu)(\boldsymbol{\sigma}\cdot\boldsymbol{p}\nu)|\kappa\lambda],\ [(\boldsymbol{\sigma}\cdot\boldsymbol{p}\mu)(\boldsymbol{\sigma}\cdot\boldsymbol{p}\nu)|(\boldsymbol{\sigma}\cdot\boldsymbol{p}\kappa)(\boldsymbol{\sigma}\cdot\boldsymbol{p}\lambda)] \tag{2.21}$$

Here, $\{|\varphi^L\rangle\}$ is the basis set used to expand the large component. We refer to the former and latter integrals as (SS|LL)- and (SS|SS)-type, respectively. In the two-electron operator of DK2 and DK3, the second and third terms on the rhs of eqs. (2.14) and (2.15) correspond to (SS|LL)-type integrals and the fourth terms on the rhs of eqs. (2.14) and (2.15) correspond to (SS|SS)-type integrals. Thus, to compute the relativistic two-electron repulsion integrals in the four-component, IOTC, and DK methods, it is necessary to evaluate the two-electron integrals with a base function composed of a small component of the Dirac equation. Compared with the nonrelativistic two-electron integrals, more computational time and three times the amount of storage are necessary even under the spin-free approximation. However, as previously shown by Filatov and Cremer [22], it is possible to approximate the spin-free (SS|LL)- or (SS|SS)-type integrals by integrals used in nonrelativistic methods ((LL|LL)-type two-electron integrals and nonrelativistic kinetic energy integrals). As a part of this approximation, a term is neglected as being of small value. In Ref. [22], the (SS|LL)-type two-electron integral is first approximated by

$$[(\boldsymbol{p}\mu)\cdot(\boldsymbol{p}\nu)|\kappa\lambda] = \sum_{\rho}\{[\mu\rho|\kappa\lambda]Y_{\rho\nu} + Y_{\rho\mu}[\rho\nu|\kappa\lambda]\} + \frac{1}{2}\left[\mu\nu|\nabla_1^2\frac{1}{r_{12}}|\kappa\lambda\right]. \tag{2.22}$$

and then the second rhs term is dropped as negligible. Here, $Y = S^{-1}T$, where T is the nonrelativistic kinetic energy and S^{-1} is the inverse matrix of the overlap matrix. However, the value is not necessarily so small (see next section). To compensate the term, a more accurate approximation is necessary. Note that the left and right sides of eq. (2.22) are exactly equal only for a complete basis set. In the practical calculations, the intermediate sum for ρ requires a sufficiently large basis set such as primitive basis sets. The same is true for the sums in the following resolution of identities (RI).

Here, we take both the terms of eq. (2.22) into consideration without dropping the second. The second derivative of the Coulomb potential gives a delta function, and a set of two-electron integrals with a delta function potential is identical to four-center overlap integrals. Furthermore, the four-center overlap integrals $\langle\mu\nu\kappa\lambda\rangle$ can be decomposed into three-center overlap integrals $\langle\mu\nu\rho\rangle$ using the RI technique.

$$\frac{1}{2}\left[\mu\nu|\nabla_1^2\frac{1}{r_{12}}|\kappa\lambda\right] = -2\pi\langle\mu\nu\kappa\lambda\rangle = -2\pi\sum_{\rho\sigma}\langle\mu\nu\rho\rangle S_{\rho\sigma}^{-1}\langle\sigma\kappa\lambda\rangle \tag{2.23}$$

Thus, all the terms in the (SS|LL)-type two-electron integral are approximated by the formula

$$[(\boldsymbol{p}\mu)\cdot(\boldsymbol{p}\nu)|\kappa\lambda] = \sum_{\rho}\{[\mu\rho|\kappa\lambda]Y_{\rho\nu} + Y_{\rho\mu}[\rho\nu|\kappa\lambda]\} - 2\pi\sum_{\rho\sigma}\langle\mu\nu\rho\rangle S_{\rho\sigma}^{-1}\langle\sigma\kappa\lambda\rangle$$

$$\tag{2.24}$$

We refer to the terms that include the two-electron integrals on the rhs as

ERISL (where ERI stands for electron repulsion integral) and the terms that include the three-center overlap integrals as DWSL.ERI (where DW stands for Darwin). The ERISL term corresponds to the approximation of the paper by Filatov and Cremer [22].

We also consider an approximation for (SS|SS)-type two-electron integrals. These are of the c^{-4} order and hence smaller than the (SS|LL)-type by the c^{-2} order, but the next section will show that they are important for an accurate approximation. The procedure of approximation is the same as for the (SS|LL)-type integrals. The approximate formula is given by

$$
\begin{aligned}
&[(\boldsymbol{p}\mu)\cdot(\boldsymbol{p}\nu)|(\boldsymbol{p}\kappa)\cdot(\boldsymbol{p}\lambda)]\\
&= \sum_{\rho\sigma}\{[\mu\rho|\kappa\sigma]Y_{\rho\nu}Y_{\sigma\lambda} + Y_{\rho\mu}[\rho\nu|\kappa\sigma]Y_{\sigma\lambda}\\
&+ Y_{\sigma\kappa}[\mu\rho|\sigma\lambda]Y_{\rho\nu} + Y_{\rho\mu}Y_{\sigma\kappa}[\rho\nu|\sigma\lambda]\}\\
&-2\pi\sum_{\rho\eta\tau}\{\langle\mu\rho\eta\rangle S_{\eta\tau}^{-1}\langle\tau\kappa\lambda\rangle Y_{\rho\nu} + Y_{\rho\mu}\langle\rho\nu\eta\rangle S_{\eta\tau}^{-1}\langle\tau\kappa\lambda\rangle\\
&+ Y_{\rho\kappa}\langle\mu\nu\eta\rangle S_{\eta\tau}^{-1}\langle\tau\rho\lambda\rangle + \langle\mu\nu\eta\rangle S_{\eta\tau}^{-1}\langle\tau\kappa\rho\rangle Y_{\rho\lambda},\\
&- \langle\mu\nu\eta\rangle S_{\eta\tau}^{-1}Y_{\rho\tau}\langle\rho\kappa\lambda\rangle\}
\end{aligned}
\tag{2.25}
$$

We refer to the terms that include the two-electron integrals as ERISS and those that include the three-center overlap integrals as DWSS. Here, three-center overlap integrals including derivatives that appeared during the derivation of eq. (2.25) are deformed as:

$$
\begin{aligned}
\langle\tau(\nabla\kappa)\cdot(\nabla\lambda)\rangle &= -\frac{1}{2}\langle\tau(\nabla^2\kappa)\lambda\rangle - \frac{1}{2}\langle\tau\kappa(\nabla^2\lambda)\rangle + \frac{1}{2}\langle(\nabla^2\tau)\kappa\lambda\rangle\\
&= \sum_{\rho}\{Y_{\rho\kappa}\langle\tau\rho\lambda\rangle + \langle\tau\kappa\rho\rangle Y_{\rho\lambda} - Y_{\rho\tau}\langle\rho\kappa\lambda\rangle\}
\end{aligned}
\tag{2.26}
$$

Although eqs. (2.24) and (2.25) can be also used in the four-component method, these formulas are more suitable for use in the two-component methods, because the coefficients $1/r_{12}$ in the two-electron operator of DK1 [21], eqs. (2.14) and (2.15) and the coefficients Y in eqs. (2.24) and (2.25) can be multiplied simultaneously.

Note that the present method reduces the computational cost for the small-component type two-electron integrals, but does not change the scaling of the electronic structure calculations. The advantage of the present method is rather in implementation cost, which is easily implemented by modifying programs of nonrelativistic or relativistic two-component methods.

3. Results and discussion

3.1. Helium-like ions

To illustrate the performance of the two-electron repulsion operators, $g^{\mathrm{DK2}}(1,2)$ and $g^{\mathrm{DK3}}(1,2)$, we performed Hartree–Fock (HF) calculations for the simplest multielectron systems, namely the helium-like ions ($Z = 10, 20, 30, …, 130$). The basis sets used were even-tempered

Gaussian functions with their exponents given by $\{\zeta = 0.01(Z/45)^3(2.0)^{n-1}, n = 1, 2, …, 45\}$. The speed of light used was 137.0359895 a.u.

The results are shown in Table 1. In the table, we use the abbreviation A/B, which means that the one- and two-electron Hamiltonians were transformed by methods A and B, respectively. The difference in energy of each two-component method from that of the four-component method increases with the increase in Z. First, let us consider the case of transforming the one-electron Hamiltonian at the infinite order (IOTC). This case exclusively extracts the effect of the two-electron Hamiltonian approximation. The energy differences of IOTC/DK2, IOTC/DK3, and IOTC/IOTC from the four-component method are 1.8119, 2.0358, and −0.0210 a.u., respectively, for $Z = 130$, where the difference is largest. These differences are one order of magnitude smaller than the values calculated by IOTC/NR (51.7365 a.u.) and IOTC/DK1 (14.7670 a.u.) methods, where NR denotes for "nonrelativistic". Similarly, for $Z = 80$, with the typical atomic number of heavy atoms, the energy differences of IOTC/NR, IOTC/DK1, IOTC/DK2, IOTC/DK3, and IOTC/IOTC methods from the four-component method are 4.2906, 0.7894, 0.0150, 0.0169, and −0.0014 a.u., respectively. These results indicate that the transformation of the two-electron Hamiltonian, in particular the DK transformation at the second order or higher, is important. Even IOTC/IOTC, which is the most accurate two-component method used in the present paper, still presents some differences from the four-component method, because the IOTC transformation is determined by using only the one-electron Hamiltonian. However, this difference is only about 0.02 a.u. even for $Z = 130$. Therefore, for the helium-like ions, determining the two-component transformation using only the one-electron Hamiltonian is appropriate. The difference between IOTC/DK3 and the four-component method (2.0358 a.u.) is larger than that between IOTC/DK2 and the four-component method (1.8119 a.u.). This strange result, which does not obey the order of the DK method, is due to the cancellations caused by the different transformations for one- and two-electron Hamiltonians. To avoid such behavior, it is desirable to use the same transformation for the one- and two-electron Hamiltonians, such as DK3/DK3 or DK2/DK2. However, the results show that in the latter cases, the difference due to the one-electron Hamiltonian is not small.

3.2. Noble gases

As a second illustration of the performance of $g^{\mathrm{DK2}}(1,2)$ and $g^{\mathrm{DK3}}(1,2)$, we performed HF calculations for the atoms of noble gases (He, Ne, Ar, Kr, Xe, Rn, and Og). The basis sets used were taken from Ref. [25] for He, Ne, Ar, Kr, and Xe, Ref. [26] for Rn, and Ref. [27] for Og. The calculated total energies are shown in Table 2. As with the helium-like ions, the difference in energy of each two-component method from that of the four-component method increases with increase in Z. The tendency observed for the helium-like ions is also observed for the noble gases. In Og, which has the largest atomic number, the energy differences of IOTC/DK2, IOTC/DK3, and IOTC/

Table 1
Total energy of helium-like ions calculated using the two- and four-component methods (in a.u.)

Z	IOTC/NR	IOTC/DK1	IOTC/DK2	IOTC/DK3	IOTC/IOTC	4-comp.	DK2/DK2	DK3/DK3
10	−93.9767	−93.9827	−93.9828	−93.9828	−93.9828	−93.9828	−93.9827	−93.9828
20	−389.6154	−389.6652	−389.6668	−389.6668	−389.6668	−389.6668	−389.6591	−389.6670
30	−891.8956	−892.0643	−892.0743	−892.0743	−892.0743	−892.0743	−891.9982	−892.0782
40	−1609.4690	−1609.8687	−1609.9053	−1609.9053	−1609.9054	−1609.9053	−1609.5280	−1609.9301
50	−2555.5699	−2556.3545	−2556.4523	−2556.4522	−2556.4528	−2556.4525	−2555.1597	−2556.5547
60	−3749.3822	−3750.7577	−3750.9745	−3750.9743	−3750.9764	−3750.9759	−3747.4439	−3751.2945
70	−5218.3442	−5220.5889	−5221.0152	−5221.0146	−5221.0212	−5221.0204	−5212.7176	−5221.8406
80	−7002.1561	−7005.6573	−7006.4317	−7006.4298	−7006.4481	−7006.4467	−6988.8477	−7008.2726
90	−9160.1841	−9165.5073	−9166.8434	−9166.8390	−9166.8848	−9166.8826	−9132.1356	−9170.4769
100	−11786.4871	−11794.5177	−11796.7599	−11796.7498	−11796.8598	−11796.8563	−11731.2516	−11803.0762
110	−15044.9287	−15057.2089	−15060.9606	−15060.9371	−15061.1995	−15061.1937	−14939.4470	−15069.8987
120	−19272.0528	−19291.7930	−19298.2987	−19298.2366	−19298.8974	−19298.8874	−19067.1056	−19302.9923
130	−25440.8934	−25477.8629	−25490.8180	−25490.5941	−25492.6509	−25492.6299	−24981.6403	−25432.2375

Table 2

Total energy of noble gas atoms calculated using the two- and four-component methods (in a.u.)

	He	Ne	Ar	Kr	Xe	Rn	Og
4-comp.	−2.8613	−128.6912	−528.6832	−2788.8791	−7447.1272	−23610.2167	−55023.8229
IOTC/IOTC	−2.8613	−128.6912	−528.6832	−2788.8795	−7447.1302	−23610.2466	−55024.0018
IOTC/DK3	−2.8613	−128.6912	−528.6832	−2788.8794	−7447.1288	−23610.1909	−55022.8541
IOTC/DK2	−2.8613	−128.6912	−528.6832	−2788.8795	−7447.1295	−23610.2215	−55023.4073
IOTC/DK1	−2.8613	−128.6912	−528.6819	−2788.8422	−7446.8666	−23607.4932	−55004.1531
IOTC/NR	−2.8613	−128.6841	−528.6324	−2788.3812	−7445.1893	−23600.2171	−54982.9784
DK3/DK3	−2.8613	−128.6912	−528.6833	−2788.8931	−7447.3171	−23613.7313	−55045.5417
DK2/DK2	−2.8613	−128.6911	−528.6789	−2788.6477	−7444.8844	−23578.0562	−54770.4997

IOTC from the four-component method are 0.4156, 0.9688, and −0.1789 a.u., respectively. The differences are one order of magnitude smaller than the values calculated by the IOTC/NR (40.8445 a.u.) and IOTC/DK1 (19.6698 a.u.) methods. As observed for the helium-like ions, the IOTC/DK2 difference is smaller than the IOTC/DK3 difference. For Rn, which is in the same sixth period as typical heavy elements such as Au and Pb, the energy differences of IOTC/NR, IOTC/DK1, IOTC/DK2, IOTC/DK3, and IOTC/IOTC from the four-component method were 9.9996, 2.7235, −0.0048, 0.0258, and −0.0299 a.u., respectively. These results suggest the importance of transforming the two-electron Hamiltonian, as well as the one-electron Hamiltonian in multielectron systems, as in the case of helium-like ions.

Tables 3 and 4 show the orbital energies of Rn and Og, respectively. The accuracy of the approximation in orbital energy is similar to the total energy. For Rn in Table 3, the differences in $1s$ orbital energy from the four-component method of IOTC/IOTC, IOTC/DK3, IOTC/DK2, IOTC/DK1, and IOTC/NR are −0.014, 0.028, 0.015, 1.609, and 6.294 a. u., respectively, and the differences in spin-splitting energy of $2p$ are 0.002, −0.002, 0.007, −0.187, and 2.869 a.u., respectively. The former three methods have clearly a smaller difference than the latter two. For the spin–orbit splitting of $4f$ orbitals, the values of IOTC/IOTC, IOTC/DK3, IOTC/DK2, and DK3/DK3 are very close to the four-component value of 0.2657 a.u., while the value of IOTC/NR is 0.3998 a.u.,

which is rather different. IOTC/DK1 shows almost the same spin–orbit splitting, but the orbital energies themselves of $4f_{5/2}$ and $4f_{7/2}$ are different from the four-component method. A similar trend is seen for Og in Table 4. The differences in $1s$ orbital energy from the four-component method of IOTC/IOTC, IOTC/DK3, IOTC/DK2, IOTC/DK1, and IOTC/NR are −0.079, 0.692, 0.461, 10.422, and 26.553 a.u., respectively, and the differences in the spin-splitting energy of $2p$ are 0.023, −0.136, 0.033, −2.683, and 10.410 a.u., respectively. The trend of the $5f$ orbital energies is the same as that of the $4f$ orbitals in Rn. Thus, the results for orbital energy also indicate that the transformation of the two-electron Hamiltonian at the second- or higher-order DK transformation is important. In particular, the spin–orbit splitting of the highest angular momentum electrons such as $4f$ and $5f$ electrons shows that to estimate the two-electron operators with DK2 or higher is important.

3.3. Approximation of (SS|LL)- and (SS|SS)-type ERIs

To assess the accuracy of the approximate formulas for (SS|LL)- and (SS|SS)-type ERIs eqs. (2.24) and (2.25), we performed HF calculations for the helium-like ions $Z = 80$ and 130. The HF energies calculated using the four-component, IOTC/IOTC, DK2/DK2, and DK3/DK3 methods are shown in Table 5. In the column of the method in the table, among the ERISL, DWSL, ERISS, and DWSS, the terms not shown were

Table 3

Orbital energies of the Rn atom calculated using the two- and four-component methods (in a.u.)

Rn	4-comp.	IOTC/IOTC	IOTC/DK3	IOTC/DK2	IOTC/DK1	IOTC/NR	DK3/DK3	DK2/DK2
$1s_{1/2}$	−3644.4297	−3644.4432	−3644.4017	−3644.4152	−3642.8206	−3638.1357	−3645.7655	−3631.6603
$2s_{1/2}$	−669.3239	−669.3271	−669.3237	−669.3256	−669.1483	−668.3869	−669.5126	−667.8446
$3s_{1/2}$	−166.9501	−166.9508	−166.9501	−166.9505	−166.9151	−166.7452	−166.9931	−166.6223
$4s_{1/2}$	−41.3416	−41.3417	−41.3415	−41.3416	−41.3333	−41.2923	−41.3526	−41.2576
$5s_{1/2}$	−8.4126	−8.4126	−8.4125	−8.4126	−8.4110	−8.4032	−8.4149	−8.3945
$6s_{1/2}$	−1.0695	−1.0695	−1.0695	−1.0695	−1.0694	−1.0685	−1.0699	−1.0668
$2p_{1/2}$	−642.3424	−642.3478	−642.3432	−642.3524	−642.0571	−643.9135	−642.4221	−641.6852
$3p_{1/2}$	−154.8951	−154.8961	−154.8950	−154.8971	−154.8379	−155.2882	−154.9140	−154.7363
$4p_{1/2}$	−36.0165	−36.0167	−36.0164	−36.0169	−36.0030	−36.1275	−36.0211	−35.9770
$5p_{1/2}$	−6.4050	−6.4051	−6.4050	−6.4051	−6.4026	−6.4318	−6.4059	−6.3977
$6p_{1/2}$	−0.5362	−0.5362	−0.5362	−0.5362	−0.5359	−0.5398	−0.5362	−0.5354
$2p_{3/2}$	−541.0802	−541.0836	−541.0832	−541.0831	−540.9815	−539.7824	−541.0745	−541.1448
$3p_{3/2}$	−131.7218	−131.7224	−131.7223	−131.7223	−131.7036	−131.4252	−131.7197	−131.7415
$4p_{3/2}$	−30.1153	−30.1154	−30.1154	−30.1153	−30.1116	−30.0422	−30.1145	−30.1220
$5p_{3/2}$	−5.1717	−5.1717	−5.1717	−5.1717	−5.1713	−5.1575	−5.1714	−5.1741
$6p_{3/2}$	−0.3813	−0.3813	−0.3813	−0.3813	−0.3814	−0.3800	−0.3813	−0.3819
$3d_{3/2}$	−112.5581	−112.5586	−112.5587	−112.5586	−112.5571	−112.9610	−112.5561	−112.5796
$4d_{3/2}$	−21.5430	−21.5431	−21.5431	−21.5431	−21.5436	−21.6465	−21.5423	−21.5497
$5d_{3/2}$	−2.1858	−2.1858	−2.1858	−2.1858	−2.1862	−2.2045	−2.1855	−2.1877
$3d_{5/2}$	−107.7506	−107.7511	−107.7511	−107.7510	−107.7512	−107.4443	−107.7486	−107.7709
$4d_{5/2}$	−20.4338	−20.4338	−20.4339	−20.4338	−20.4347	−20.3646	−20.4331	−20.4401
$5d_{5/2}$	−2.0128	−2.0128	−2.0128	−2.0128	−2.0132	−2.0027	−2.0125	−2.0146
$4f_{5/2}$	−9.1892	−9.1891	−9.1892	−9.1891	−9.1910	−9.2715	−9.1885	−9.1941
$4f_{7/2}$	−8.9235	−8.9235	−8.9235	−8.9235	−8.9253	−8.8717	−8.9229	−8.9283

Table 4

Orbital energies of the Og atom calculated using the two- and four-component methods (in a.u.)

Og	4-comp.	IOTC/IOTC	IOTC/DK3	IOTC/DK2	IOTC/DK1	IOTC/NR	DK3/DK3	DK2/DK2
$1s_{1/2}$	−8286.9765	−8287.0558	−8286.2850	−8286.5158	−8276.5542	−8260.4232	−8292.7379	−8195.5597
$2s_{1/2}$	−1742.9125	−1742.9354	−1742.8625	−1742.9140	−1741.3902	−1737.6783	−1745.1251	−1730.4992
$3s_{1/2}$	−477.3242	−477.3296	−477.3128	−477.3244	−477.0035	−476.1024	−477.8730	−474.5099
$4s_{1/2}$	−142.8125	−142.8138	−142.8090	−142.8123	−142.7264	−142.4752	−142.9728	−142.0096
$5s_{1/2}$	−40.4472	−40.4475	−40.4461	−40.4471	−40.4230	−40.3531	−40.4957	−40.2070
$6s_{1/2}$	−9.1357	−9.1358	−9.1354	−9.1356	−9.1297	−9.1130	−9.1490	−9.0703
$7s_{1/2}$	−1.3207	−1.3207	−1.3206	−1.3206	−1.3197	−1.3177	−1.3233	−1.3076
$2p_{1/2}$	−1664.3075	−1664.3464	−1664.1846	−1664.3537	−1661.1143	−1670.4484	−1665.2458	−1653.2733
$3p_{1/2}$	−446.9688	−446.9768	−446.9422	−446.9731	−446.3290	−448.5048	−447.1694	−444.5148
$4p_{1/2}$	−129.6226	−129.6246	−129.6150	−129.6232	−129.4503	−130.1050	−129.6771	−128.9394
$5p_{1/2}$	−34.7632	−34.7637	−34.7609	−34.7633	−34.7147	−34.9217	−34.7784	−34.5672
$6p_{1/2}$	−6.9583	−6.9584	−6.9577	−6.9583	−6.9466	−7.0027	−6.9620	−6.9095
$7p_{1/2}$	−0.7127	−0.7127	−0.7126	−0.7127	−0.7109	−0.7205	−0.7133	−0.7046
$2p_{3/2}$	−1138.7331	−1138.7495	−1138.7460	−1138.7466	−1138.2224	−1134.4643	−1138.6846	−1139.1086
$3p_{3/2}$	−318.4664	−318.4701	−318.4693	−318.4690	−318.3646	−317.3890	−318.4483	−318.5992
$4p_{3/2}$	−92.0724	−92.0733	−92.0731	−92.0729	−92.0477	−91.7612	−92.0652	−92.1236
$5p_{3/2}$	−23.6726	−23.6728	−23.6728	−23.6727	−23.6672	−23.5842	−23.6697	−23.6930
$6p_{3/2}$	−4.2101	−4.2101	−4.2102	−4.2101	−4.2097	−4.1916	−4.2090	−4.2179
$7p_{3/2}$	−0.3003	−0.3003	−0.3003	−0.3003	−0.3004	−0.2989	−0.3000	−0.3019
$3d_{3/2}$	−286.7835	−286.7869	−286.7884	−286.7876	−286.7622	−288.1419	−286.7666	−286.9310
$4d_{3/2}$	−76.3205	−76.3212	−76.3217	−76.3214	−76.3191	−76.7337	−76.3139	−76.3727
$5d_{3/2}$	−16.6729	−16.6730	−16.6732	−16.6731	−16.6743	−16.7955	−16.6704	−16.6918
$6d_{3/2}$	−1.7581	−1.7581	−1.7582	−1.7581	−1.7591	−1.7826	−1.7574	−1.7638
$3d_{5/2}$	−265.8142	−265.8167	−265.8181	−265.8171	−265.8123	−264.8006	−265.7986	−265.9479
$4d_{5/2}$	−70.4015	−70.4019	−70.4024	−70.4021	−70.4055	−70.1210	−70.3954	−70.4495
$5d_{5/2}$	−15.0790	−15.0791	−15.0793	−15.0791	−15.0817	−15.0064	−15.0767	−15.0964
$6d_{5/2}$	−1.4865	−1.4865	−1.4865	−1.4865	−1.4876	−1.4760	−1.4858	−1.4915
$4f_{5/2}$	−49.6647	−49.6648	−49.6653	−49.6649	−49.6757	−50.0147	−49.6592	−49.7058
$5f_{5/2}$	−6.4654	−6.4654	−6.4656	−6.4654	−6.4693	−6.5495	−6.4637	−6.4783
$4f_{7/2}$	−47.9791	−47.9792	−47.9796	−47.9793	−47.9902	−47.7428	−47.9738	−48.0186
$5f_{7/2}$	−6.1131	−6.1131	−6.1132	−6.1131	−6.1170	−6.0657	−6.1114	−6.1255

Table 5

Total energy of helium-like ions calculated using the (SS|LL)- and (SS|SS)-type ERI approximation formulas (in a.u.) (The numbers are the differences from the energies calculated using exact ERIs.)

Method	4-comp.	IOTC/IOTC	DK3/DK3	DK2/DK2
Z = 80				
Exact ERI	−7006.446732	−7006.448075	−7008.272602	−6988.847659
NR[a]	n/a	4.292012	4.275570	4.246199
ERISL[b]	3.694689	3.694782	3.692405	3.639315
ERISL + DWSL	−0.503793	−0.504516	−0.502226	−0.484536
ERISL + ERISS	5.062748	5.062623	5.053403	4.959310
ERISL + DWSL + ERISS	0.867072	0.867815	0.863229	0.839731
ERISL + DWSL + ERISS + DWSS	$< 10^{-8}$	$< 10^{-8}$	$< 10^{-8}$	$< 10^{-8}$
Z = 130				
Exact ERI	−25492.629941	−25492.650861	−25432.237501	−24981.640255
NR[a]	n/a	51.757433	48.962468	47.027483
ERISL[b]	22.987116	22.956290	23.915805	21.326244
ERISL + DWSL	−19.265127	−19.300015	−18.040075	−16.951297
ERISL + ERISS	85.148199	85.104456	81.708043	76.293713
ERISL + DWSL + ERISS	43.306775	43.308100	40.181257	38.396141
ERISL + DWSL + ERISS + DWSS	0.000002	0.000002	0.000001	0.000002

[a] NR denotes DK2/NR, DK3/NR, or IOTC/NR.
[b] Ref. [22].

ignored, i.e., were treated as zero. For example, (ERISL + DWSL) means that only ERISL and DWSL are approximated, whereas ERISS and DWSS are ignored. Let us take for example the DK3/DK3 results of $Z = 80$. The difference of DK3/NR from exact DK3/DK3 is 4.27556970876 a.u. When the ERISL term is included (see Table 5), this difference decreases to 3.692405 a.u. The ERISL formula derived by Filatov and Cremer [22]

surely improves the HF energy from NR. When the DWSL term is further included (ERISL + DWSL), the difference becomes −0.502226 a.u. That is, the DWSL term makes a significant contribution to energy and greatly improves total energy. In Ref. [22], the DWSL term is neglected as being quite small together with the (SS|SS) integrals, but in fact we can see that neglecting the DWSL term is not necessarily a proper

approximation. By contrast, when the ERISS term is further included instead of the DWSL term to ERISL (ERISL + ERISS) the difference from the exact ERI rather increases to 5.053403 a.u. Thus, the DWSL term is more important than ERISS. The difference when using the ERISL, DWSL, and ERISS terms (ERISL + DWSL + ERISS) is 0.863229 a.u., and the absolute value of the difference becomes larger than when only the ERISL and DWSL terms are used. However, further including the DWSS term gives a value very close to the exact ERI, and much smaller than 10^{-8} a.u. These trends are the same for the four-component method, IOTC/IOTC, and DK2/DK2. Even in the cases of $Z = 130$, the differences from exact have the almost same tendency. Although there is an approximation error in ERISL + DWSL + ERISS + DWSS, it is very small. From these results, we can conclude that the DWSL term in eq. (2.24) is very important and that the use of both eqs. (2.24) and (2.25) (ERISL + DWSL + ERISS + DWSS) provides a fairly good approximation.

4. Conclusions

We have derived and implemented the explicit formulas for the two-electron operator of the second- and third-order DK method. Using these formulas, we performed a range of numerical verifications to the helium-like ion ($Z = 10, 20, 30, …, 130$) and all noble gas atoms. In the comparison using the fixed one-electron Hamiltonian transformation (IOTC), the energies obtained for the DK2 and DK3 two-electron operators showed differences from the four-component method that were one order of magnitude smaller than those of the nonrelativistic and DK1 two-electron operators. These results showed that for the transformation of the two-electron Hamiltonian, in particular, the DK transformation at the second order or higher is important. We also found that in some cases, the DK2 two-electron Hamiltonian gives better results than the DK3 two-electron Hamiltonian, which is due to the error cancellation with the one-electron Hamiltonian.

We have also derived approximation formulas for the small component-type two-electron integrals. These formulas were applied to the helium-like ions with $Z = 80$ and 130 and were numerically confirmed to reproduce unapproximated values very accurately. We expect that the formulas can achieve high-accuracy calculations that are comparable with the four-component method, using only two-component methods without the implementation of any small component-type two-electron integrals.

CRediT authorship contribution statement

Nobuki Inoue: Conceptualization, Methodology, Software, Formal analysis, Investigation, Writing - original draft, Funding acquisition. **Yoshihiro Watanabe:** Supervision, Writing - review & editing. **Haruyuki Nakano:** Supervision, Writing - review & editing, 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.

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