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Large-Scale Two-Component Relativistic Quantum-Chemical Theory: Combination of the Infinite-Order Douglas–Kroll–Hess Method with the Local Unitary Transformation Scheme and the Divide-and-Conquer Method

Junji Seino^[a] and Hiromi Nakai^{*[a,b,c,d]}

Large-scale two-component (2c) relativistic quantum-chemical (RQC) theory is reviewed. We briefly discuss the theories, advantages, and extensibilities of an overall linear-scaling scheme in 2c relativistic theory. The theory is based on the infinite-order Douglas–Kroll–Hess method, with the local unitary transformation scheme to produce the 2c relativistic Hamiltonian, and the divide-and-conquer method to achieve linear-

scaling of Hartree–Fock and electron correlation methods. Furthermore, perspectives for large-scale RQC are explained to bring the practical usage and treatment of light and heavy elements in 2c relativistic calculations close to those in non-relativistic methods. © 2014 Wiley Periodicals, Inc.

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Introduction

Relativistic quantum chemistry (RQC) provides both qualitative and quantitative understandings of any element in the periodic table, and thus helps to design substances and materials with innovative functions. However, in terms of practical usage, the methodology still has significant differences from non-relativistic (NR) QC, even though both theories were proposed in the 1920s. Based on the Schrödinger equation, NRQC has developed considerably over about 90 years because of developments in theories, computational techniques, and computers. Nowadays, theoretical and experimental chemists can perform black-box large-scale QC calculations on tens of thousands of atoms.

Conversely, RQC, which is based on the four-component (4c) Dirac equation (or more accurately, quantum electrodynamics), has developed slowly because of difficulties in treatment, such as variational collapse,^[1] and the enormous computational costs due to the small-component (or positronic state) wavefunction. Initially, relativistic effects were added to NRQC perturbatively by lowest-order relativistic corrections from the Breit–Pauli approximation.^[2] In the 1980s, however, several techniques were proposed to avoid problems such as the no-pair approximation^[3] or the kinetic balance between large- and small-component wavefunctions.^[4] Furthermore, two-component (2c) relativistic methods, which describe only the electronic state of a molecule, have been developed for the variational treatment of higher-order relativistic effects, for example, the Douglas–Kroll–Hess (DKH) transformation^[5,6] and the regular approximation.^[7] These developments increased the system size that can be treated computationally. However, there are differences in accuracy between the 4c and 2c relativistic methods, because the 2c method is derived from approxi-

mations of the 4c method. In the 2000s, however, an exact 2c scheme, which gives equivalent results to 4c, was proposed for the one-electron 4c Dirac,^[8–10] many-electron Dirac–Coulomb,^[11–13] and Dirac–Coulomb–Gaunt^[13] Hamiltonians. Thus, in terms of accuracy, the theoretical gap between 2c and 4c is closed.

There is still a large difference in computational cost between 2c and NR. Accurate 2c relativistic calculations have been limited to small- or medium-sized molecules because of the large computational cost associated with the transformation from 4c to 2c and complications with the 2c relativistic Hamiltonian. Thus, it has been difficult to perform calculations with hundreds or thousands of atoms, even after extension of the method to large-scale molecular theories.

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In this article, we review methods to lower the computational cost of accurate 2c methods to approach that of NR. In addition, we described the problems associated with large-scale calculations of any element or electronic effect, along with proposed solutions. Realization of the suggested theory will make 2c similar to NR in terms of practical usage and treatment of light and heavy elements, and make 2c as accurate as 4c.

Overall Linear-Scaling Scheme in the 2c Relativistic Method

This section provides an overall explanation of the linear-scaling scheme in the 2c relativistic method, which can bring the computational cost closer to that of NR. In our research, we have adopted the 2c infinite-order Douglas–Kroll–Hess (IODKH) method^[8] for the many-electron Dirac–Coulomb Hamiltonian, termed IODKH/IODKH,^[14] which reproduces the Hartree–Fock (HF) energies obtained from the 4c Dirac–Coulomb Hamiltonian up to superheavy elements. We start with the many-electron 4c Dirac Hamiltonian, given by

$$\mathbf{H}_4^{\text{DH}} = \sum_i \mathbf{h}_4^{\text{D}}(i) + \sum_{i>j} \mathbf{g}_4(i, j). \quad (1)$$

Here, \mathbf{h}_4^{D} is the one-electron Dirac Hamiltonian and $\mathbf{g}_4(i, j)$ is the general expression for the two-electron operator. For the Dirac–Coulomb Hamiltonian, the Coulomb interaction is adopted as $\mathbf{g}_4(i, j)$, that is, $\mathbf{g}_4(i, j) = 1/r_{ij}$. With straightforward programming of the 4c relativistic calculations, the computational cost is very high in large molecular systems containing heavy elements. For example, in HF calculations with the Dirac–Coulomb Hamiltonian, the estimated prefactor of computational cost is more than 70 times that of NR calculations because of the treatments of large- and small-component wavefunctions, and spins, although the theoretical scaling is the same as that of NR. In addition, to describe the core and

valence regions of heavy-element systems accurately, a large number of orbitals are required. These are serious obstacles to large-scale molecular theories. Recent developments, with some approximations, have realized molecular calculations with more than 100 atoms using a parallel computation technique.^[15]

In 2c relativistic schemes, a many-electron unitary transformation $\mathbf{U}(i, j, \dots)$ is applied to \mathbf{H}_4^{DH} to completely decouple the electronic and positronic states. However, the many-body problem must be solved to obtain an exact $\mathbf{U}(i, j, \dots)$ because of the existence of electron–electron interactions in \mathbf{H}_4^{DH} . The IODKH/IODKH method avoids the many-body problem by approximating $\mathbf{U}(i, j, \dots)$ as the product of one-particle unitary transformations \mathbf{U} , expressed as

$$\mathbf{U}(i, j, \dots) \approx \mathbf{U}(i) \otimes \mathbf{U}(j) \otimes \dots, \quad (2)$$

where \mathbf{U} is determined by the block diagonalization of the one-particle Dirac Hamiltonian. Then, the approximately block diagonalized $\tilde{\mathbf{H}}_4^{\text{DH}}$ is written as

$$\begin{aligned} \tilde{\mathbf{H}}_4^{\text{DH}} &\approx \left[\dots \mathbf{U}^\dagger(j) \mathbf{U}^\dagger(i) \dots \right] \left[\sum_i \mathbf{h}_4^{\text{D}}(i) + \sum_{i>j} \mathbf{g}_4(i, j) \right] [\mathbf{U}(i) \mathbf{U}(j) \dots] \\ &= \sum_i \begin{pmatrix} \mathbf{h}_2^+(i) & 0 \\ 0 & \mathbf{h}_2^-(i) \end{pmatrix} + \sum_{i>j} \begin{pmatrix} \mathbf{g}_2^{++}(i, j) & \mathbf{g}_2^{+-}(i, j) \\ \mathbf{g}_2^{-+}(i, j) & \mathbf{g}_2^{--}(i, j) \end{pmatrix}, \end{aligned} \quad (3)$$

where $\mathbf{h}_2^+(\mathbf{h}_2^-)$ and $\mathbf{g}_2^{++}(\mathbf{g}_2^{--})$ are the electronic (positronic) components of the one- and two-particle operators, respectively. Furthermore, \mathbf{g}_2^{+-} and \mathbf{g}_2^{-+} are the off-diagonal components of the two-particle operator, which correspond to the electron–positron coupling terms. However, the off-diagonal components are negligible because the relativistic effect due to the two-particle operator is typically smaller than that of the one-particle Hamiltonian. Finally, the many-electron equation can be expressed as

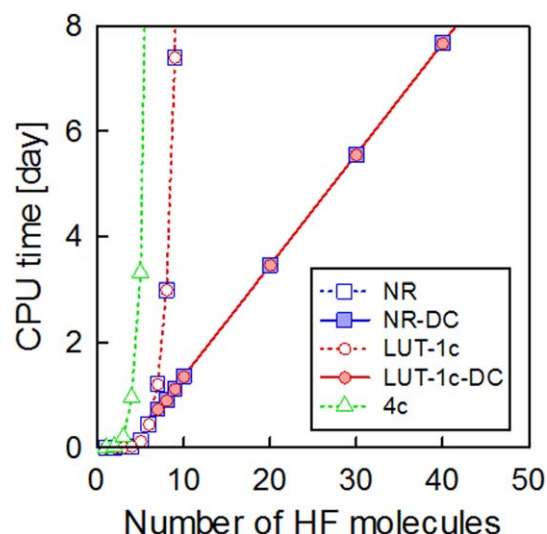


Figure 1. System-size dependence on the total CPU time for $(\text{HF})_n$ ($n = 1, 2, \dots, 50$) as calculated with the conventional and DC-based CCSD(T) methods using the NR, LUT-1c, and Dirac-Coulomb (4c) Hamiltonians. The basis set for H was (5s1p), while that for F was (10s5p1d). Calculated with a single core of a Hexa Core Xeon/3.33 GHz processor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\left(\sum_i \mathbf{h}_2^+(i) + \sum_{i>j} \mathbf{g}_2^{++}(i,j) \right) \Psi_2 = E \Psi_2, \quad (4)$$

where Ψ_2 is the 2c many-electron wavefunction of the electronic state.

Although Eq. (4) eliminates the small-component wavefunction, calculating the unitary transformation can become a bottleneck because the unitary transformations for one- and two-electron Hamiltonians scale as $O(n^3)$ and $O(n^5)$, respectively. To reduce the unitary transformation scaling, we have developed the local unitary transformation (LUT) scheme.^[16,17] The LUT scheme approximates the one-particle unitary transformation \mathbf{U} as a block-diagonal form of the subsystem contributions:

$$\mathbf{U} \approx [\mathbf{U}^A \oplus \mathbf{U}^B \oplus \dots], \quad (5)$$

where $\{A, B, \dots\}$ denotes subsystems that do not intersect, which are normally adopted as each atom. Furthermore, the LUT scheme is designed based on the locality of relativistic interactions. The relativistic effect is dominant in each atom and in interatomic interactions with their nearest-neighbor atoms. The other interactions behave like those in NR methods.

The LUT method has three characteristic features: accuracy, efficiency, and extensibility. In terms of accuracy, the LUT scheme reproduces the total HF energy obtained by conventional spin-free 2c [or one-component (1c)] relativistic methods with millihartree deviations in both light- and heavy-element systems. In regards to efficiency, the LUT scheme drastically reduces the computational cost in comparison with the conventional method. The scaling becomes $O(n^1)$ with a small pre-

factor. Finally, in terms of extensibility, a well-defined unitary transformation can provide high applicability, as shown below.

One of the largest extensions of this theory is the combination with large-scale molecular theories. In a NR framework, we have developed fragmentation-based linear-scaling methods for ground- and excited-state theories based on the divide-and-conquer (DC) scheme.^[18,19] Unlike other fragmentation-based schemes, the DC scheme demands no artificial prediction associated with the positions of the spin and/or charge because the distribution of electrons in the system is uniformly solved by the common Fermi level. Thus, the DC scheme can treat delocalized metallic systems accurately. The DC scheme is available for closed-shell and open-shell HF,^[20] and electron correlation methods, such as the second-order Møller-Plesset (MP2)^[21] and coupled cluster (CC) theories.^[22]

To introduce the DC scheme to a relativistic framework, we have combined the spin-free LUT scheme^[23,24] with the DC-based HF, MP2, and CC theories. Note that in a spin-free framework, the extension only requires the replacement of NR one- and two-electron integrals by the transformed relativistic integrals. This combination realizes quasi-linear-scaling in the construction and diagonalization of the Fock matrix, and MP2/CC correlation calculations, as well as the 2c relativistic transformations for one- and two-electron integrals. For example, Figure 1 shows the system-size dependence of the central processing unit (CPU) time in total CCSD(T) calculations using NR, 1c LUT-1c, and 4c Dirac-Coulomb Hamiltonians at a spin-free level. LUT-1c drastically reduces the CPU time in comparison with 4c. In addition, the DC-based scheme achieves linear-scaling. Note that the CPU time of LUT-1c is extremely close to that of NR both with and without DC. Thus, this method has made spin-free relativistic schemes similar to NR in terms of computational cost.

Another extension is the application of the 2c relativistic Hamiltonian to analytical energy gradients. Analytical expressions with respect to the nuclear coordinates of the IODKH Hamiltonian and an extension to the LUT method have been proposed.^[25] The derivative of the conventional IODKH Hamiltonian requires many complicated calculations due to the use of Hess' numerical matrix transformation technique.^[6] However, the LUT scheme simplifies the calculations because the gradient of the atomic unitary transformation is commonly zero, which eliminates the complicated analytical derivatives required in Hess' technique. With the LUT scheme, bond length deviation of several diatomic molecules containing heavy elements is less than 0.01 Å compared with the conventional scheme. Furthermore, the computational scaling for the derivative of the spin-free 2c relativistic Hamiltonian is linear and the computational cost is close to that of NR. Note that the relativistic treatment of nucleus-electron interactions in interatomic interactions with their nearest-neighbor atoms plays an essential role, as does the energy calculation.

The LUT scheme is applicable to the spin-dependent 2c relativistic Hamiltonian with little effort because the spin-dependent integrals for both one- and two-electron systems are more localized than the spin-free integrals. In long-range

interactions, the spin-orbit effect is thought to appear through the coupling of local spin-orbit integrals and long-range changes in the electron density. Note that a spin-dependent 2c relativistic calculation commonly demands more computational cost than NR or corresponding 1c calculations because the molecular orbitals have a complex form and are doubled in number.

Furthermore, parallelization of the calculation of the 2c relativistic Hamiltonian matrix is easily applicable to the LUT method. The 2c atomic transformation, including kinetic energy, nucleus–electron, and electron–electron potentials, can be calculated independently for each atom. Once we obtain the atomic unitary transformations, the transformation of the interatomic nucleus–electron interactions can be performed independently for sets of atoms. Furthermore, the parallelization of other calculations, including the NR one- and two-electron integrals, HF, and electron correlations with or without the DC scheme, can be easily implemented in the same manner as in the NR or 4c relativistic scheme.

Perspectives

Although the difference in computational cost between NR and relativistic theories has diminished with our schemes, there is still a variance in its applicability to molecular systems. For example, reliable calculations of metal clusters containing heavy elements with high density can be difficult, even if the LUT-iodkh/iodkh Hamiltonian is combined with the DC technique. The obstacle in the calculation is the large number and high density of electrons in the system. As a solution, we have proposed the frozen core potential (FCP) scheme, which utilizes the frozen atomic core orbitals without any loss of accuracy in relativistic effects.^[26] The FCP scheme is based on the valence-only Huzinaga–Cantu equation,^[27] which uses two approximations in comparison with the all-electron (AE) scheme.

The first approximation is that the total density matrix **D** with a generally contracted (GC) basis set can be approximated in a block-diagonal form:

$$\mathbf{D} \approx \mathbf{d}^C \oplus \mathbf{d}^V, \quad (6)$$

where \mathbf{d}^C (\mathbf{d}^V) is a submatrix that includes only the core (valence) atomic orbital (AO) indices. The second approximation is that the molecular core density matrix \mathbf{d}^C is assumed to be close to the individual atomic core density matrices, which is defined by a direct sum of those atomic contributions:

$$\mathbf{d}^C \approx \mathbf{d}_A^C \oplus \mathbf{d}_B^C \oplus \dots \quad (7)$$

This second approximation is called the frozen atomic-core approximation. The FCP scheme enables the use of accurate 2c relativistic methods such as IODKH/IODKH. In addition, the LUT scheme allows for a seamless connection between model potential and AE calculations. FCP calculations achieve high accuracy with only millihartree deviations from the AE methods. The computational cost is less than that of the AE method, especially for heavy elements.

Another problem in realizing large-scale calculations for heavy-element systems is that the computational algorithm is not optimized. In the LUT-iodkh/iodkh method, which relativistically transforms only the one-center electron–electron integrals, the most time-consuming step is the electron repulsive integral (ERI) calculations for the multicenter integrals in the HF calculation, similar to the bottleneck in the NR method. For heavy-element systems, the ERI algorithm should be suitable for basis sets with higher angular momenta and larger numbers of primitive functions. We have extended the accompanying coordinate expansion (ACE) algorithm^[28] and the recurrence relation (RR) scheme^[29] to the GC scheme, termed GC-ACE-RR.^[30] The ACE algorithm is advantageous in ERI calculations with a large number of primitive functions, and the RR technique has the advantage when using basis sets with high angular momenta. When we adopt GC basis sets, the algorithm reduces the computational cost compared with the conventional ACE-RR algorithm for segmented basis sets. For example, in three-dimensional gold clusters with a GC basis set, the GC-ACE-RR computations are more than 10 times faster.^[30] Thus, the GC-ACE-RR scheme is preferable in calculations of molecules containing many heavy elements, such as metal clusters and polynuclear metal complexes.

We should also consider the computational treatment of several electronic effects that become important in heavy-element systems. First, the static electron correlation effect is extremely important in molecules that have many degenerate states, such as polynuclear metal complexes. So far, however, no linear-scaling static electron correlation scheme has been proposed. The second treatment is for delocalized electronic systems. Most linear-scaling techniques based on spatial fragmentation do not represent the precise electronic state of the system. Although the DC scheme can accurately calculate a delocalized system, the size of subsystem, including environmental effects, will be much larger than that in a localized system. For example, from our experience with metal clusters, the subsystem for the electron correlation calculation should encompass a radius of at least 10–20 Å from the central region for accurate calculations with less than 1-millihartree deviation. This means molecules with hundreds of atoms could be calculated in a conventional manner. Thus, improved techniques using the DC scheme or an alternative linear-scaling scheme is desirable for delocalized systems.

The above theoretical extensions can reduce the computational cost of relativistic methods to resemble that of NR methods and increase the accuracy of 2c to be nearer to that of 4c, and make the practical usage of heavy elements close to light elements. Once achieved, the field will undergo a paradigm shift to using relativistic quantum-chemical theory, which will allow reliable calculations of systems with thousands of atoms containing both light and heavy elements.

Finally, an applicability of the present theory to the density functional theory, routinely used for practical calculations, should be discussed. In the LUT-iodkh/C method, the application can be easy as we have shown calculations of bond distances in diatomic molecules^[25] because the two-electron interaction is the same as that of NR, that is, Coulomb

interaction. Therefore, the standard exchange-correlation (XC) functionals developed within the NR framework are applicable. However, in the LUT-IODKH/IODKH method, the XC functionals should be reconstructed because of the picture change of the two-electron interaction.

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