Implementation of Efficient Two-component Relativistic Method Using Local Unitary Transformation to GAMESS Program

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This Letter provides an implementation of an efficient and accurate relativistic method based on the infinite-order two-component scheme with the local unitary transformation (LUT-IOTC) to the GAMESS program. The sample input and major capabilities in GAMESS are shown as well as the accuracies and efficiencies in energy and analytical energy gradient calculations. The scheme realizes calculations of molecules containing heavy elements with four-component relativistic accuracy and the non-relativistic computational cost.

Keywords: Relativistic effect, Linear-scaling, Infinite–order Douglas–Kroll–Hess transformation, Divide-and-conquer method, Local unitary transformation

1 Introduction

Relativistic effects are essential for highly accurate calculations of molecular structures and properties for molecules containing heavy elements. To describe the relativistic effects, two-component (2c) relativistic schemes are one of the most practical methods. Actually, most quantum chemical packages contain various 2c relativistic schemes. For example, the GAMESS program package [1] implements the normalized elimination of the small component scheme [2], the relativistic elimination of the small component scheme [3], the first- to third-order Douglas–Kroll–Hess scheme [4–6], and the infinite-order two-component (IOTC) scheme [7]. Especially, IOTC gives equivalent results to the four-component (4c) relativistic calculations in one-electron systems.

Our group has developed an efficient 2c relativistic method, which is termed the local unitary transformation (LUT) scheme based on IOTC (LUT-IOTC) [8,9]. Furthermore, LUT-IOTC was extended to the analytical gradient method [10,11] and combined with a large-scale molecular theory, namely, the divide-and-conquer (DC) method [12–14]. This Letter explains implementation of LUT-IOTC to GAMESS. The package including LUT-IOTC will be released in the next version of GAMESS.

2 Theory and implementation

This section briefly summarizes the theoretical aspects of LUT-IOTC. In IOTC, the one-electron 4c Dirac Hamiltonian $\hat{h}^D$ is completely block-diagonalized by unitary transformation $U$ to separate the electronic and positronic parts independently, which is written as

$$U\hat{h}^D U^\dagger = \begin{pmatrix} \hat{h}^+ & 0 \\ 0 & \hat{h}^- \end{pmatrix}$$

In atomic/molecular calculations, only the electronic part $\hat{h}^+$ is adopted, which reduces a dimension in a calculation.
However, the computational cost in the transformation is non-negligible when the system is large. The LUT scheme is based on the locality of the relativistic effect. The unitary transformation for an entire system is approximated by a direct sum of the individual subsystem contributions,

$$U \approx \bigoplus U_A \otimes U_B \otimes U_C \ldots$$  (2)

where $A$, $B$, and $C$ are the subsystems. Normally, atom is adopted as a subsystem. The interatomic interaction such as a nuclear attraction is transformed using the combination of these unitary transformations. The resulting LUT-IOTC Hamiltonian matrix with basis functions $\{\chi\}$ is defined as

$$H_{LUT} = \sum_{T} \sum_{V} \sum_{R} \chi^{\mu\nu}_T \chi^{\mu\nu}_V + \sum_{C} V^{NR}_C \chi^{\mu\nu}_C$$  (3)

where $T$ and $V$ are the kinetic energy and the nuclear attraction. The superscripts NR and $+$ mean the nonrelativistic and relativistic operators, respectively. $\tau$ is the threshold of cutoff for the relativistic interaction. LUT-IOTC reduces the cost from $(nN)^3$ to $n^3N$, where $n$ and $N$ are the basis set dimension and the number of atoms, respectively. Note that a one-center atomic transformation only adopts the $A = B$ part in equation (3), which leads to loss of accuracy qualitatively and quantitatively [8]. The analytical gradient of LUT-IOTC is also derived by the direct differentiation of equation (3) with respect to a nuclear coordinate.

Figure 1 shows the sample input in GAMESS for an energy calculation by LUT-IOTC at the Hartree–Fock (HF) level. We only select "relwfn = lut-iotc" in the name list of $\text{SCONTRL}$. Table 1 summarizes the major capabilities combined with LUT-IOTC. Any levels of theory such as the second-order Möller-Plesset (MP2) and coupled-cluster with singles and doubles (CCSD) are applicable because only one-electron integrals are modified in an analogous way of other 2c relativistic methods. Furthermore, the DC method is also applicable.

### 3 Performances

This section provides performances of LUT-IOTC in GAMESS from the viewpoints of accuracy and efficiency. For comparison, the NR and 4c calculations were adopted. The 4c calculations were performed by the DiRac12 program [15].

Figure 2 shows the differences in bond lengths (Å) of diatomic molecules from 4c at the HF level. The Sapporo-dZP-2012 and the dkh3-Gen-tk-NoSe c-V-tZP basis sets were used in an uncontracted form. LUT-IOTC reproduces the bond lengths in all diatomic molecules: the maximum deviation is 0.004 Å. In addition, Figure 3 shows the percentage differences in frequencies of DFT calculations with the PBE0 functional from the experimental values. LUT-IOTC also agrees well with the experimental values within 10% deviations.

Figure 4 shows the system-size dependence of a central processing unit (CPU) time (s) in (HF), molecules. HF, MP2, and CCSD with the 6-311G (d,p) basis sets were adopted with...
or without DC. A Xeon E5-2637v3/3.50 GHz (quad-core) was used on a single core. All DC methods realize molecular calculations with a quasi-linear scaling with a small prefactor.

4 Conclusion

We explain theoretical aspects and performances of an accurate and efficient 2c relativistic LUT-IOTC method newly implemented in GameSS. The computational costs of the LUT-IOTC scheme is close to those of NR. Thus, we strongly recommend the users to select LUT-IOTC for any all-electron calculations instead of NR without any hesitation.

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