Frozen core potential scheme with a relativistic electronic Hamiltonian: theoretical connection between the model potential and all-electron treatments

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Abstract

This Letter proposes an accurate scheme using frozen core orbitals, called the frozen core potential (FCP) method, to theoretically connect model potential calculations to all-electron (AE) ones. The present scheme is based on the Huzinaga-Cantu equation combined with spin-free relativistic Douglas-Kroll-Hess Hamiltonians. The local unitary transformation scheme for efficiently constructing the Hamiltonian produces a seamless extension to the FCP method in a relativistic framework. Numerical applications to coinage diatomic molecules illustrate the high accuracy of this FCP method, as compared to AE calculations. Furthermore, the efficiency of the FCP method is also confirmed by these calculations.

1. Introduction

The development of large-scale molecular theory which includes accurate relativistic effects is one of the most important research areas in quantum chemistry. Relativistic effects are essential for describing the behavior of electrons in any element on the periodic table. A fundamental relativistic treatment of molecules is based on a four-component (4c) Dirac theory with electronic and positronic states [1], which adopts a one-particle Dirac operator that satisfies the Lorentz invariance only in terms of the motion of each electron. Another approach is a two-component (2c) relativistic theory with an electronic state [2-16], which is derived from a proper transformation of the 4c Dirac theory. Recent developments in the 4c and 2c treatments have achieved accurate calculations for small molecules. However, there remain many problems when applying this work to large molecular systems, i.e., the large dimensions of the basis set in the 4c treatment, the large computational cost for transformation in the accurate 2c treatment, and the slow convergence of the self-consistent field (SCF) procedure due to the many electrons of heavy-element systems in all-electron (AE) calculations.

Recent attempts to reduce the computational cost of the 2c treatment include the local unitary transformation (LUT) scheme proposed by our group [17, 18] and the diagonal local approximation to the unitary transformation (DLU) scheme of Peng and Reiher [19, 20], both being focused on the locality of the relativistic effect. Furthermore, the combination of the divide-and-conquer (DC) based Hartree-Fock (HF) [21, 22] and the electron correlation methods [23-25] achieve an overall linear

scaling of the computational cost [26].

Widely accepted approaches for treating heavy-element systems are the pseudo-potential (PP) and model potential (MP) methods [27, 28], which reduce the number of electrons treated explicitly by replacing the core electrons with the potential. The PP and MP methods have the advantage of being able to easily include relativistic effects of the core electrons. The PP method, which includes the norm-conserving PP [29] and the ultrasoft PP [30, 31] for the plane-wave basis and the effective core potential (ECP) [32-35] for the Gaussian basis, introduces a smooth and nodeless potential function in the core region. The inner valence orbital of the PP treatment does not agree with that of the AE treatment. The MP method, which involves the model core potential (MCP) [36, 37] and the ab initio model potential (AIMP) [38, 39], adopts a nodal potential function in order to reproduce the valence orbital in the AE treatment. In general, the MP method is expected to be more accurate than the PP one.

Although the PP and MP approaches have demonstrated reasonable results for the spectroscopic constants in comparison with the 4c treatment [27, 28], there is still room for further examination of the molecular properties of heavy-element systems, including chemical reactions and their electric/magnetic properties, as well as for investigating the theoretical connection of the PP and MP methods with the relativistic AE treatments. In this Letter, we focus on the MP method. To achieve a seamless combination between the MP and accurate AE approaches, two effects should be included: (a) the valence relativistic effect and (b) the accurate core-valence relativistic effect using an

electronic Hamiltonian. In the former effect, the AIMP method has already been extended to use the valence relativistic Hamiltonian within the relativistic scheme by eliminating the small component [40] and third-order Douglas-Kroll-Hess (DKH) methods [37]. In the latter effect, two conditions should be satisfied. The first condition is the use of the one- and two-particle relativistic Hamiltonians in a (quasi-)infinite-order manner. The second is that the scheme should utilize an electronic wavefunction without a positronic one. The most accurate relativistic treatment that satisfies above two conditions is the infinite-order DKH (IODKH) transformation [11] applied to the Dirac-Coulomb Hamiltonian [41].

The present study attempts to develop a scheme based on the frozen core potential (FCP) method using several levels of spin-free 2c relativistic Hamiltonians to examine the limitations of the MP approach. In addition, the effectiveness of the FCP scheme is also discussed. This Letter is organized as follows. Section 2 presents the theoretical aspects of this scheme. The presented scheme is then numerically assessed in Sec. 3. Concluding remarks are given in Sec. 4.

2. Theory

2.1. FCP method with a non-relativistic Hamiltonian

The present study proposes a scheme that seamlessly connects the AE method to the MP method. Here, we consider a closed-shell system for simplicity, while noting that the extension to an open-shell system is straightforward. The AE HF-Roothaan (HFR) equation in a closed-shell system is written as

$$\mathbf{F}(\mathbf{D})\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}, \quad (1)$$

where $\mathbf{F}$, $\mathbf{D}$, $\mathbf{C}$, $\mathbf{S}$, and $\mathbf{E}$ are the Fock, density, orbital coefficient, overlap, and orbital energy matrices, respectively. The Fock matrix is expressed as

$$F_{\mu\nu}(\mathbf{D}) = H_{\mu\nu} + G_{\mu\nu}(\mathbf{D}), \quad (2)$$

with

$$G_{\mu\nu}(\mathbf{D}) = \sum_{\lambda\rho} D_{\lambda\rho} \left[\langle \chi_\mu \chi_\rho | \hat{g} | \chi_\nu \chi_\lambda \rangle - \frac{1}{2} \langle \chi_\mu \chi_\rho | \hat{g} | \chi_\lambda \chi_\nu \rangle \right], \quad (3)$$

and

$$D_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i}^*. \quad (4)$$

Here $H_{\mu\nu}$ and $\langle \chi_\mu \chi_\rho | \hat{g} | \chi_\nu \chi_\lambda \rangle$ are non-relativistic (NR) one- and two-electron integrals, respectively. The density matrix $\mathbf{D}$ can be divided into core and valence contributions as follows:

$$\mathbf{D} = \mathbf{D}^{\text{c}} + \mathbf{D}^{\text{v}}, \quad (5)$$

with

$$D_{\mu\nu}^{\text{c}} = 2 \sum_c^{\text{core}} C_{\mu c} C_{\nu c}^*, \quad (6)$$

and

$$D_{\mu\nu}^V = 2 \sum_v^{\text{val}} C_{\mu\nu} C_{\nu\nu}^* . \quad (7)$$

Note that D^C and D^V include all atomic orbital (AO) indices as well as D . The total energies can also be separated as

$$E = E^C + E^V , \quad (8)$$

with

$$E^C = \frac{1}{2} \text{tr} \left[D^C (H + F(D^C)) \right] + \sum_{A < B} \frac{n_A^C (Z_B - n_B^C) + n_B^C Z_A}{R_{AB}} , \quad (9)$$

and

$$E^V = \frac{1}{2} \text{tr} \left[D^V (H + F(D^V)) \right] + \frac{1}{2} \text{tr} \left[D^C G(D^V) + D^V G(D^C) \right] + \sum_{A < B} \frac{(Z_A - n_A^C)(Z_B - n_B^C)}{R_{AB}} , \quad (10)$$

where Z_A , n_A^C , and R_{AB} are the nuclear charge, the number of core electrons in atom A , and the internuclear distance between atoms A and B , respectively. E^C and E^V denote the core and valence energies, respectively. The first and second terms of Eq. (10) are the intra-valence and core-valence energies, respectively.

Here, let us consider the properties of D^C and D^V . In the case of segmented-contraction basis sets, D^C and D^V are supposed to be as follows:

$$D_{\mu\nu}^C = \begin{cases} \text{large} & (\mu, \nu \in \text{core AO}) \\ \text{small} & (\mu \text{ or } \nu \in \text{val. AO}) \end{cases} , \quad (11)$$

and

$$D_{\mu\nu}^V = \begin{cases} \text{moderate} & (\mu \text{ or } \nu \in \text{core AO}) \\ \text{large} & (\mu, \nu \in \text{val. AO}) \end{cases} . \quad (12)$$

In contrast, $\mathbf{D}^C$ and $\mathbf{D}^V$ in the general-contraction basis sets are expected to be as follows:

$$D_{\mu\nu}^C = \begin{cases} \text{large} & (\mu, \nu \in \text{core AO}) \\ (\text{negligibly}) \text{ small} & (\mu \text{ or } \nu \in \text{val. AO}) \end{cases}, \quad (13)$$

and

$$D_{\mu\nu}^V = \begin{cases} (\text{negligibly}) \text{ small} & (\mu \text{ or } \nu \in \text{core AO}) \\ \text{large} & (\mu, \nu \in \text{val. AO}) \end{cases}. \quad (14)$$

The apparent difference is the off-diagonal term in $D_{\mu\nu}^V$, which arises because the core AOs are used to describe the nodal picture of the valence molecular orbitals when adapting the segmented contraction. From the above property in the general contraction, the total density matrix $\mathbf{D}$ can be approximated in a block-diagonal form:

$$\mathbf{D} \approx \mathbf{d}^C \oplus \mathbf{d}^V, \quad (15)$$

where $\mathbf{d}^C$ ($\mathbf{d}^V$) is a submatrix that includes only the core (valence) AO indices.

Furthermore, the molecular core density matrix $\mathbf{D}^C$ as well as its submatrix $\mathbf{d}^C$ is supposed to be close to the individual atomic core density matrices. Thus, the matrices can be described by the direct sum of their atomic contributions as follows:

$$\mathbf{D}^C \approx \tilde{\mathbf{D}}^C = \tilde{\mathbf{D}}_A^C \oplus \tilde{\mathbf{D}}_B^C \oplus \dots, \quad (16)$$

and

$$\mathbf{d}^C \approx \tilde{\mathbf{d}}^C = \tilde{\mathbf{d}}_A^C \oplus \tilde{\mathbf{d}}_B^C \oplus \dots, \quad (17)$$

where $\{A, B, \dots\}$ denotes each atom. The approximation of Eqs. (16) or (17) is called the frozen atomic-core approximation (FACA). Here, the atomic core density $\tilde{\mathbf{D}}_A^C$ is obtained by solving the atomic HFR equation, which is given by

$$\mathbf{F}_A(\mathbf{D}_A)\mathbf{C}_A = \mathbf{S}_A\mathbf{C}_A\mathbf{E}_A, \quad (18)$$

with

$$F_{\mu\nu,A}(\mathbf{D}_A) = H_{\mu\nu,A} + \sum_{\lambda\rho \in A} D_{\lambda\rho,A} \left[\langle \chi_{\mu,A} \chi_{\rho,A} | \hat{g} | \chi_{\nu,A} \chi_{\lambda,A} \rangle - \frac{1}{2} \langle \chi_{\mu,A} \chi_{\rho,A} | \hat{g} | \chi_{\lambda,A} \chi_{\nu,A} \rangle \right], \quad (19)$$

and

$$\mathbf{D}_A = \mathbf{D}_A^C + \mathbf{D}_A^V. \quad (20)$$

Here, we consider a closed-shell system for simplicity as well as the molecular HFR equation in Eq. (1), while an open-shell equation is adopted for calculations of open-shell atoms. Note that the tilde in Eqs. (16) and (17) means that the core density matrices determined by the atomic calculations in Eq. (18) are frozen for the molecular calculations.

Using the above two approximations, the valence-only HFR equation, which corresponds to the so-called Huzinaga-Cantu (HC) equation [42], is expressed as

$$\mathbf{f}^V(\mathbf{d}^V)\mathbf{c}^V = \mathbf{s}^V\mathbf{c}^V\mathbf{\varepsilon}^V, \quad (21)$$

with

$$\begin{aligned} f_{\mu\nu}^V(\mathbf{d}^V) &= H_{\mu\nu} + \sum_{\lambda\rho}^{\text{val}} d_{\lambda\rho}^V \left[\langle \chi_{\mu}^V \chi_{\rho}^V | \hat{g} | \chi_{\nu}^V \chi_{\lambda}^V \rangle - \frac{1}{2} \langle \chi_{\mu}^V \chi_{\rho}^V | \hat{g} | \chi_{\lambda}^V \chi_{\nu}^V \rangle \right] \\ &\quad + \sum_A \sum_{\lambda\rho \in A}^{\text{core}} (\tilde{d}_{\lambda\rho}^C)_A \left[\langle \chi_{\mu}^V \chi_{\rho}^V | \hat{g} | \chi_{\nu}^V \chi_{\lambda}^V \rangle - \frac{1}{2} \langle \chi_{\mu}^V \chi_{\rho}^V | \hat{g} | \chi_{\lambda}^V \chi_{\nu}^V \rangle \right] \\ &\quad + \sum_A \sum_{c \in A}^{\text{core}} (-2\varepsilon_{c,A}) \langle \chi_{\mu}^V | \varphi_{c,A} \rangle \langle \varphi_{c,A} | \chi_{\nu}^V \rangle \\ &= H_{\mu\nu} + (2J_{\mu\nu}^V - K_{\mu\nu}^V) + \sum_A (2J_{\mu\nu,A}^C - K_{\mu\nu,A}^C) + \sum_A P_{\mu\nu,A} \end{aligned} \quad (22)$$

This scheme is called the FCP method. Here $|\varphi_{c,A}\rangle$ and $\varepsilon_{c,A}$ are the core orbital and its energy, respectively, which are obtained in advance by solving Eq. (18). $\mathbf{J}^C$ ($\mathbf{J}^V$) and $\mathbf{K}^C$ ($\mathbf{K}^V$) stand for the

Coulomb and exchange terms for the core (valence) region. $\mathbf{P}$ is the projection/shift term that prevents the valence electrons from collapsing into the core, which retains the inner nodes of the radial valence orbitals. For example, the projection operator $\mathbf{P}$ makes the definition of core density more flexible: namely, $\tilde{\mathbf{d}}^c$ can be replaced by $\tilde{\mathbf{D}}^c$. In addition, the one-particle Hamiltonian $\mathbf{H}$ is the same as that used in the AE treatment. $\mathbf{J}^c$ and $\mathbf{K}^c$ are explicitly obtained by the atomic AE calculations in the FCP method, although both the MCP and AIMP methods adopt a linear combination of Gaussian-type functions with a local spherically symmetric model potential and/or a non-local exchange interaction with spectral representation. Finally, the valence energy in the FCP method is defined as

$$E^v = \frac{1}{2} \text{tr} \left[\mathbf{d}^v \left(\mathbf{H} + \mathbf{f}^v(\mathbf{d}^v) \right) \right] + \sum_{A < B}^N \frac{(Z_A - n_A^c)(Z_B - n_B^c)}{R_{AB}}. \quad (23)$$

2.2. Connectivity to the 2c relativistic Hamiltonian

This subsection discusses the connectivity between the FCP method and the 2c relativistic calculations. In the case of the NR Hamiltonian, the intra-atomic part of the molecular Hamiltonian is the same as the corresponding part of the atomic one. Thus, the FCP method can seamlessly extend to the molecular calculation without any loss of accuracy in the Hamiltonian. However, the use of a relativistic Hamiltonian, such as DKH or IODKH, replacement of the NR Hamiltonian causes two problems. The first problem appears in a numerical calculation using Hess' technique. In practical molecular calculations, basis functions, $\{ \chi_\mu \}$, such as Gaussian-type orbitals, are commonly adopted. Because direct evaluation of the matrix elements of $H_{\mu\nu} = \langle \chi_\mu | \hat{H} | \chi_\nu \rangle$ in the DK transformation is remarkably difficult, Hess proposed a matrix transformation method that adopts the resolution of identity (RI) technique [4]. The first step in Hess' technique is the generation of the eigenvectors, $\{k\}$, for the operator $\hat{p}^2$ using the linear combination of $\{ \chi_\mu \}$,

$$|k\rangle = \sum_\mu | \chi_\mu \rangle C_{\mu k} , \quad (24)$$

where the coefficients, $\{C_{\mu k}\}$, are determined by diagonalizing the matrix with the elements $\langle \chi_\mu | \hat{p}^2 | \chi_\nu \rangle$. The obtained (pseudo) eigenvectors, $\{k\}$, satisfy

$$\langle k' | \hat{p}^2 | k \rangle = w_k \delta_{k'k} , \quad (25)$$

where w_k is a (pseudo) eigenvalue. By using Eq. (25) and the appropriate RI, expressed as

$$1 \approx \sum_k |k\rangle \langle k| , \quad (26)$$

the explicit matrix representation of the one-particle IODKH Hamiltonian, $H_{kk'} = \langle k | \hat{H} | k' \rangle$, which

is derived using two-step transformations, is given by

$$H_{kk'} = \sum_{k''k'''} \Omega_{kk''}^\dagger W_{k''k'''} \Omega_{k'''k'}, \quad (27)$$

where $\mathbf{W}$ is the effective first-step transformed Hamiltonian matrix and $\mathbf{\Omega}$ is the effective second-step transformation matrix. Explicit representations of $\mathbf{W}$ and $\mathbf{\Omega}$ are defined in Ref. [11]. Note that the RI approximation is used in the summations of k'' and k''' in Eq. (27) as well as in the constructions of $\mathbf{W}$ and $\mathbf{\Omega}$. In general, a larger RI space gives more accurate results. In the FCP calculation, however, the atomic RI space needed to obtain information about the core electron is smaller than the molecular one. Therefore, the difference in accuracy between the atomic and molecular RI spaces should be investigated.

The second problem appears in the unitary transformation for the production of a 2c relativistic Hamiltonian. The transformation in a molecular system is defined as

$$\begin{pmatrix} U^{AA\dagger} & U^{BA\dagger} & \dots \\ U^{AB\dagger} & U^{BB\dagger} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \mathbf{H}_D^{AA} & \mathbf{H}_D^{AB} & \dots \\ \mathbf{H}_D^{BA} & \mathbf{H}_D^{BB} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} U^{AA} & U^{AB} & \dots \\ U^{BA} & U^{BB} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \mathbf{h}_D^{AA} & \mathbf{h}_D^{AB} & \dots \\ \mathbf{h}_D^{BA} & \mathbf{h}_D^{BB} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}, \quad (28)$$

where $\mathbf{H}_D^{AB}$, U^{AB} , and $\mathbf{h}_D^{AB}$ are the Dirac Hamiltonian, the unitary transformation, and the block-diagonalized Hamiltonian with respect to the electronic and positronic states between atoms A and B . Thus, the block-diagonal terms of $\mathbf{h}_D$, such as $\mathbf{h}_D^{AA}$ and $\mathbf{h}_D^{BB}$, contain molecular information through U^{AB} , U^{BA} , etc. On the other hand, the transformation in an atomic system is given by

$$U^{A\dagger} \mathbf{H}_D^A U^A = \mathbf{h}_D^A. \quad (29)$$

Apparently, $\mathbf{h}_D^A$ only contains atomic information. In the FCP calculation, the relativistic

Hamiltonian used in the atomic HFR equation of Eq. (18) is different from the corresponding term of the relativistic Hamiltonian used in the molecular HFR equation of Eq. (1). Therefore, the difference in accuracy between the atomic and molecular relativistic Hamiltonians should also be examined numerically.

The LUT method, which is based on the locality of the relativistic effect, can solve the problems of the 2c relativistic calculation. In the LUT scheme, the relativistic unitary transformation in the whole system is approximated as a block-diagonal form of the subsystem contributions:

$$\begin{pmatrix} \mathbf{U}^{AA} & \mathbf{U}^{AB} & \dots \\ \mathbf{U}^{BA} & \mathbf{U}^{BB} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \approx \begin{pmatrix} \mathbf{U}^A & \mathbf{0} & \dots \\ \mathbf{0} & \mathbf{U}^B & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}. \quad (30)$$

Using this approximation, the transformation of Eq. (27) in a molecular system changes to

$$\begin{pmatrix} \mathbf{U}^{A\dagger} & \mathbf{0} & \dots \\ \mathbf{0} & \mathbf{U}^{B\dagger} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \mathbf{H}_D^{AA} & \mathbf{H}_D^{AB} & \dots \\ \mathbf{H}_D^{BA} & \mathbf{H}_D^{BB} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \mathbf{U}^A & \mathbf{0} & \dots \\ \mathbf{0} & \mathbf{U}^B & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \mathbf{h}_{LUT}^{AA} & \mathbf{h}_{LUT}^{AB} & \dots \\ \mathbf{h}_{LUT}^{BA} & \mathbf{h}_{LUT}^{BB} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}. \quad (31)$$

Note that the diagonal terms of $\mathbf{h}_{LUT}^{AA}$ and $\mathbf{h}_{LUT}^{BB}$ are the same as the corresponding terms of $\mathbf{h}_D^A$ and $\mathbf{h}_D^B$, respectively. Furthermore, each transformation is performed in the atomic RI space. The numerical assessments of the LUT scheme have exhibited high accuracy, with less than 1 millihartree deviations from the conventional methods for the total HF energies and orbital energies [17, 18]. Thus, the combination of the LUT scheme with the FCP method is consistent without loss of accuracy in the Hamiltonian, as in the case of NR.

2.3. Implementation

The calculation procedure for the FCP method based on both the IODKH and LUT-IOCKH schemes as well as the AE scheme is summarized in Table 1. The entire process of the FCP method is divided into three categories: (I) the atomic calculation, (II) the FCP construction, and (III) the molecular calculation. In the atomic calculation, an AE HF calculation for each atom with the relativistic Hamiltonian is performed in Eq. (18). In the case of the relativistic calculation, LUT-IOCKH is equivalent to IODKH. Here, the core density matrix $\mathbf{D}_A^C$, core orbitals $|\varphi_{c,A}\rangle$, and its energy $\varepsilon_{c,A}$ are obtained.

In the FCP construction, the necessary core-valence two-electron integral calculations are performed first. When the approximate valence density $\mathbf{d}^V$ is adopted, the core basis functions needed to describe frozen core orbitals are eliminated. In the case of IODKH, the integrals are relativistic ones. On the other hand, in the case of LUT-IOCKH, the integrals that should be calculated are multi-center NR core-valence ones because the one-center relativistic integrals have been obtained in the atomic calculation. Then, using the integrals, the core-valence Coulomb and exchange terms of the third term in Eq. (22) are calculated. Finally, the projection operator $\mathbf{P}$ of the fourth term in Eq. (22) is constructed using the core orbital $|\varphi_{c,A}\rangle$.

In the molecular calculation, the one- and two-electron integrals are calculated first. In the case of IODKH, the relativistic transformation is applied to one- and two-electron integrals, which is the same procedure as in the AE calculation. In the case of LUT-IOCKH, three-step calculations are

performed because relativistic one-center one- and two-electron integrals have already been obtained in the atomic calculations: the LUT transformed one-electron interatomic integrals within the cutoff distance, the NR one-electron interatomic integrals beyond the cutoff distance, and the multi-center NR valence two-electron integrals. Then, the valence Coulomb and exchange terms of the second term in Eq. (22) are calculated. Next, the one-electron matrix, projection matrix, and valence Coulomb and exchange terms are summed up to construct the Fock matrix of Eq. (22). Finally, a valence SCF calculation of Eq. (21) for the molecule is performed. The difference between the NR and LUT-iodkh procedures is observed in the numerical values in parts of the one- and two-electron integrals. Thus, the procedure and concept of LUT-iodkh is very similar to that of NR.

3. Numerical assessment

3.1. Computational details

This section assesses the performance of the FCP scheme combined with several levels of the relativistic Hamiltonians. The one-particle Hamiltonians adopted here were the NR, first- (DKH1), second- (DKH2), third- (DKH3), and IODKH methods in a spin-free formalism. The two-particle Hamiltonians were the NR Coulomb interaction (/C) and the IODKH transformed interaction (/IODKH). Furthermore, the LUT scheme was applied to the one- and two-particle IODKH Hamiltonian. A cutoff distance of 3.5 Å was adopted for the one-particle LUT calculation. All calculations were performed by a modified version of the GAMESS program [43].

Numerical tests were performed for diatomic molecules M_2 (where $M = \text{Cu, Ag, and Au}$). The following experimental bond distances for diatomic molecules were chosen for Cu, Ag, and Au: 2.55, 2.89, and 2.89 Å [44, 45]. The basis sets for the NR and relativistic calculations were the DKH3-Gen-TK/NOsec-V-TZP basis sets [46, 47], whose general contraction coefficients were optimized by the DKH3/C method. The sizes of the basis sets were (24s13p10d3f)/[5s3p3d1f] for Cu, (26s17p22d3f)/[6s4p4d1f] for Ag, and (26s24p19d16f)/[7s5p6d2f] for Au. The frozen orbitals in FACA and FCP were $[\text{He}](2s)^2(2p)^6$, $[\text{Ne}](3s)^2(3p)^6(3d)^{10}$, and $[\text{Zn}](4p)^6(4d)^{10}(4f)^{14}$ for Cu, Ag, and Au, respectively. In the FCP method, the eliminated core functions for constructing d^V are [2s1p] to describe 1s, 2s, and 2p orbitals for Cu, [3s2p] to describe 1s, 2s, 3s, 2p, and 3p orbitals for Ag, and [4s3p2d1f] to describe 1s, 2s, 3s, 4s, 2p, 3p, 4p, 3d, 4d, and 4f orbitals for Au.

3.2. Accuracy of the FCP scheme

This subsection examines the accuracy of the FCP method. Table 2 shows the comparison of the core, valence, and total HF energies (in hartrees) with the LUT-iodkh/LUT-iodkh Hamiltonian of M_2 ($M = \text{Cu, Ag, and Au}$). The deviations of two approximations from the molecular AE calculations, i.e., FACA and FCP, are investigated. Note that FCP means the approximation of eliminating the core AOs with FACA. Comparisons between the molecular and atomic AE calculations are also given. The total energies are divided into the core and valence contributions as defined in Eq. (8). The energy components in the molecular AE calculation are given in Eqs. (9) and (10). The energy components in FACA are defined as

$$E^c = \frac{1}{2} \text{tr} \left[\tilde{D}^c \left(H + F \left(\tilde{D}^c \right) \right) \right] + \sum_{A < B}^N \frac{n_A^c (Z_B - n_B^c) + n_B^c Z_A}{R_{AB}}, \quad (32)$$

and

$$E^v = \frac{1}{2} \text{tr} \left[D^v \left(H + F \left(D^v \right) \right) \right] + \frac{1}{2} \text{tr} \left[\tilde{D}^c G \left(D^v \right) + D^v G \left(\tilde{D}^c \right) \right] + \sum_{A < B}^N \frac{(Z_A - n_A^c)(Z_B - n_B^c)}{R_{AB}}. \quad (33)$$

In the case of elimination of the core AOs with FACA, the core and valence energies of Eqs. (32) and (23) are adopted. Finally, in the case of the atomic AE calculation, each energy component for an atom is doubled and compared with the corresponding molecular AE value.

The FACA method produces small deviations in the core and valence energies. Interestingly, the valence deviations have the opposite sign from the comparable values of the core deviations. This means that the valence deviations compensate for the core deviations caused by a lack of relaxation

of the core orbitals in the molecular calculations. In consequence, the deviations in the total energies are significantly lower than those in the energy components: -0.003, -0.008, and -0.019 millihartrees for Cu₂, Ag₂, and Au₂, respectively. The core deviations using FCP are theoretically equivalent with the FACA case as well as the atomic AE calculations. On the other hand, the valence deviations produced by FCP are positive and larger than those of FACA, because the variational space is reduced by eliminating core basis functions. However, the deviations of the total energies are one or two orders of magnitude smaller than those produced by the atomic AE calculations.

Table 3 shows the orbital energies of M₂ (M = Cu, Ag, and Au) obtained with the molecular AE scheme at the NR/C and LUT-IODKH/LUT-IODKH levels, respectively. The differences between the NR/C and LUT-IODKH/LUT-IODKH cases are given in brackets, and correspond to the relativistic effect. The relativistic effects on the orbital energies are apparent. The differences for s- and p-type orbitals are commonly positive in all diatomic molecules due to the shrinking of these orbitals. In contrast, the differences for d-type orbitals are negative because the orbitals are expanded as a result of being shielded from nuclear charges by the inner s- and p-type orbitals.

Table 4 shows the deviations of the orbital energies of M₂ (M = Cu, Ag, and Au) obtained with FACA and FCP from AE at the LUT-IODKH/LUT-IODKH levels. The absolute deviations of FACA are extremely small: less than 0.052 millihartree. The absolute deviations of FCP are somewhat large, but still less than 1.6 millihartree. The numerical assessment confirmed that the FCP method is accurate enough to discuss the relativistic effects in the total and orbital energies.

3.3. Dependence of the 2c relativistic Hamiltonian

Table 5 shows the deviations of the valence HF energies of M_2 ($M = \text{Cu}, \text{Ag}, \text{and Au}$) using AE, FACA, and FCP at the NR/C, DKH1/C, DKH2/C, DKH3/C, LUT-IODKH/C, IODKH/C, and LUT-IODKH/LUT-IODKH levels. The reference values are obtained with the LUT-IODKH/LUT-IODKH Hamiltonian in the AE calculations; the valence energies are -392.879515, -293.065111, and -272.326823 hartrees for Cu_2 , Ag_2 , and Au_2 , respectively. The energy deviation from the AE calculation at each Hamiltonian level is also shown in parentheses.

The NR/C results show the total relativistic correction energies for one- and two-electron interactions with/without the errors of FACA or FCP. In AE, the total relativistic effects increase when the system gets heavier; the relativistic correction energies are 1.39438, 3.053454, and 12.456076 hartrees for Cu_2 , Ag_2 , and Au_2 , respectively. This is because the valence orbitals of heavier atoms have higher electron densities in the inner valence region, which stabilize the energies by the direct relativistic effects. In addition, the FACA and FCP results produce large deviations from AE in comparison with the other Hamiltonians. This is because the approximations in Eqs. (13) and (14) are not satisfied at the NR/C level due to the use of contracted basis sets optimized at the DKH3/C level.

The results of the DKH series, DKH1/C, DKH2/C, DKH3/C, and IODKH/C, show the relativistic correction energies for two-electron interactions and the deficiencies of the finite-order DKH methods from IODKH/C. In AE, the relativistic correction energies for two-electron

interactions also increase when the system gets heavier for the same reason as in the case of the total relativistic ones. The deficiencies of the finite-order DKH series produce an oscillation behavior compared with the deviations of IODKH/C; DKH1/C produces a large stabilization, DKH2/C a small destabilization, and DKH3/C an extremely small stabilization. The differences in the DKH series between FACA/FCP and AE are close to those with LUT-IOCKH/LUT-IOCKH, except for DKH1. The exception of DKH1 is also because the approximations in Eqs. (13) and (14) are not satisfied at the DKH1/C level. Furthermore, the DKH3/C does not always give the most accurate results in FACA/FCP because the contraction coefficients of the basis sets were determined by the DKH3/C calculations including electron correlation effects. The differences between IODKH/C and LUT-IOCKH/C illustrate the error in the LUT scheme as the differences should be negligibly small in all diatomic molecules.

3.4. Efficiency of the FCP scheme

We here examine the efficiency of the FCP scheme focusing on the molecular calculation step, which is a time-consuming step except for small molecules, because the atomic calculation step can be done only once in the same set of element and basis set. The two-electron integrals (TEIs) calculated in the FCP construction step are limited as shown in Eq. (22).

Table 6 shows the central processing unit (CPU) times for the coinage metal diatomic molecules M_2 ($M = \text{Cu, Ag, and Au}$) using AE, FACA, and FCP at the LUT-IODKH/LUT-IODKH level. The CPU times for four steps are shown as well as the total CPU times: one-electron integral (OEI), TEI, and construction and diagonalization of Fock matrix. The CPU times were measured with the use of a Quad Core Xeon/2.8 GHz processor on a single core. The ratios in the individual steps with respect to the AE calculations, namely $t(\text{FACA})/t(\text{AE})$ and $t(\text{FCP})/t(\text{AE})$, are shown in parentheses. The ratios for FACA are close to 1 for all steps, because the orbital spaces are not reduced in the molecular calculations. Although the ratio in OEI is approximately equal to 1 due to the use of the uncontracted basis sets, the other ratios for FCP decrease for heavier systems: the ratios in the total CPU times are 0.47, 0.23, and 0.02 for Cu_2 , Ag_2 , and Au_2 , respectively. That is because the eliminated core basis functions increase as $[2s1p]$ in Cu, $[3s2p]$ in Ag, and $[4s3p2d1f]$ in Au. Thus, the CPU time in TEI, which is the most time-consuming step, is largely reduced. The efficiency using FCP is expected to increase in larger systems with heavier elements. From the point of view of both efficiency and accuracy, the FCP treatment is extremely promising for practical

relativistic calculations.

4. Concluding remarks

In the present study, we have developed an accurate relativistic scheme with frozen core orbitals based on the HC equation to seamlessly connect MP calculations to AE calculations. The method can utilize several levels of 2c relativistic DKH transformations in a spin-free formalism at the HF level. The most accurate Hamiltonian presented here is based on the IODKH transformation applied to the Dirac-Coulomb Hamiltonian. Two approximations are discussed in comparison with the AE method. The first is the usage of frozen core density matrix obtained from atomic calculation, which is called FACA. The second is the usage of an approximated valence density matrix constructed by eliminating core basis functions. In addition, the local unitary transformation scheme for the relativistic Hamiltonian allows a seamless extension to the FCP method in a relativistic framework. The accuracies and efficiencies in terms of the core, valence, and total energies as well as the orbital energies are numerically assessed for diatomic molecules M_2 ($M = \text{Cu}, \text{Ag}, \text{and Au}$). The FCP calculations have achieved a high accuracy with only millihartree deviations from the AE methods. The computational costs of the FCP scheme were smaller than those of the AE methods. The proposed scheme is highly promising for large-system calculations including heavy elements while maintaining high accuracy.

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Table 1. Calculation procedures for FCP and AE using the IODKH scheme with/without the LUT method.

	(x) FCP		(y) AE	
	(a) IODKH	(b) LUT-IODKH	(c) IODKH	(d) LUT-IODKH
(I) Atomic calculation	(x.1) Relativistic one-electron integrals for each atom A		—	(d.1) Relativistic one-electron integrals for each atom A
	(x.2) Relativistic two-electron integrals for each atom A		—	
	(x.3) All-electron HF calculation for each atom A in Eq. (18)		—	(d.2) Relativistic two-electron integrals for each atom A
	(x.4) Save core orbital $\phi_{c,A}$, density matrix D_A^C , and energy $\varepsilon_{c,A}$		—	
(II) FCP construction	(a.1) Relativistic core-valence two-electron integrals	(b.1) NR core-valence two-electron integrals without (x.2)	—	—
	(x.5) Core-valence Coulomb and exchange terms of third term in Eq. (22)		—	—
	(x.6) Projection operator obtained from core orbital $\phi_{c,A}$ of fourth term in Eq. (22)		—	—
(III) Molecular calculation	(a.2) Relativistic one-electron integrals	(b.2) LUT transformed one-electron interatomic integrals	(c.1) Relativistic one-electron integrals	(d.3) LUT transformed one-electron interatomic integrals
	—	(b.3) NR one-electron interatomic integrals	—	(d.4) NR one-electron interatomic integrals
	(a.3) Relativistic valence two-electron integrals	(b.4) Multi-center NR valence two-electron integrals	(c.2) Relativistic two-electron integrals	(d.5) Multi-center NR two-electron integrals
	(x.7) Valence Coulomb and exchange terms of second term in Eq. (22)		(y.1) Coulomb and exchange terms in Eq. (3)	
	(x.8) Sum up one-electron matrix, projection matrix, and Coulomb and exchange terms		(y.2) Add Coulomb and exchange terms to one-electron matrix in Eq. (2)	
	(x.9) Solve valence SCF equation in Eq. (21)		(y.3) Solve total SCF equation in Eq. (1)	

Table 2. Comparison of the core, valence, and total HF energies (in hartrees) of M_2 ($M = \text{Cu, Ag, and Au}$) obtained by the LUT-IODKH/LUT-IODKH Hamiltonian ^{a,b}.

		Molecular AE	FACA	FCP ^c	Atomic AE
Cu ₂	Core	−2914.000431	−2914.000240 (0.000192)	−2914.000240 (0.000192)	−2914.000240 (0.000192)
	Valence	−392.879515	−392.879709 (−0.000194)	−392.879292 (0.000223)	−392.861921 (0.017594)
	Total	−3306.879946	−3306.879949 (−0.000003)	−3306.879532 (0.000415)	−3306.862161 (0.017786)
Ag ₂	Core	−10335.233874	−10335.233922 (−0.000048)	−10335.233922 (−0.000048)	−10335.233922 (−0.000048)
	Valence	−293.065111	−293.065054 (0.000056)	−293.064324 (0.000787)	−293.049259 (0.015852)
	Total	−10628.298985	−10628.298977 (0.000008)	−10628.298246 (0.000739)	−10628.283181 (0.015804)
Au ₂	Core	−37765.489421	−37765.488088 (0.001333)	−37765.488088 (0.001333)	−37765.488088 (0.001333)
	Valence	−272.326823	−272.328174 (−0.001352)	−272.324502 (0.002321)	−272.296790 (0.030033)
	Total	−38037.816243	−38037.816262 (−0.000019)	−38037.812590 (0.003654)	−38037.784878 (0.031366)

^a Doubled values of the atomic AE calculations, i.e., $2E(M)$, are also shown for comparison.

^b Energy deviations from the molecular AE calculations are shown in parentheses.

^c Eliminated core basis functions are [2s1p] in Cu, [3s2p] in Ag, and [4s3p2d1f] in Au.

Table 3. Comparison of the orbital energies (in hartrees) of M_2 ($M = \text{Cu, Ag, and Au}$) combined with the NR/C and LUT-IODKH/LUT-IODKH Hamiltonians in the molecular AE calculations ^a.

Molecule	Cu ₂			Ag ₂			Au ₂		
1e Hamil.	LUT-IODKH	NR		LUT-IODKH	NR		LUT-IODKH	NR	
2e Hamil.	LUT-IODKH	C		LUT-IODKH	C		LUT-IODKH	C	
$(n-1)s\sigma$	-5.142411	-4.943754	[0.198657]	-4.265700	-3.826421	[0.439279]	-4.685253	-3.229408	[1.455845]
$(n-1)s\sigma^*$	-5.142281	-4.943577	[0.198704]	-4.265538	-3.826214	[0.439324]	-4.685124	-3.228877	[1.456247]
$(n-1)p\sigma$	-3.349282	-3.309783	[0.039499]	-2.736359	-2.669991	[0.066368]	-2.746112	-2.430654	[0.315458]
$(n-1)p\sigma^*$	-3.347463	-3.308017	[0.039446]	-2.733639	-2.667700	[0.065939]	-2.741810	-2.404904	[0.336906]
$(n-1)p\pi$	-3.347389	-3.307998	[0.039391]	-2.734139	-2.667797	[0.066342]	-2.740710	-2.401808	[0.338902]
$(n-1)p\pi^*$	-3.347255	-3.307888	[0.039367]	-2.733900	-2.667729	[0.066171]	-2.740361	-2.393138	[0.347223]
$(n-1)d\sigma$	-0.479671	-0.494595	[-0.014924]	-0.521539	-0.561029	[-0.039490]	-0.479200	-0.612312	[-0.133112]
$(n-1)d\pi$	-0.474591	-0.489004	[-0.014413]	-0.511892	-0.551186	[-0.039294]	-0.466483	-0.598148	[-0.131665]
$(n-1)d\delta$	-0.466952	-0.481655	[-0.014703]	-0.502465	-0.542471	[-0.040006]	-0.449409	-0.585672	[-0.136263]
$(n-1)d\delta^*$	-0.463625	-0.478483	[-0.014858]	-0.499063	-0.539479	[-0.040416]	-0.443760	-0.581978	[-0.138218]
$(n-1)d\pi^*$	-0.455738	-0.470843	[-0.015105]	-0.490917	-0.532111	[-0.041194]	-0.433498	-0.573853	[-0.140355]
$(n-1)d\sigma^*$	-0.448207	-0.463723	[-0.015516]	-0.482985	-0.524313	[-0.041328]	-0.423495	-0.563299	[-0.139804]
$ns\sigma$	-0.230139	-0.222772	[0.007367]	-0.221040	-0.200006	[0.021034]	-0.272789	-0.176606	[0.096183]

^a Energy deviations between NR/C and LUT-IODKH/IODKH are given in square brackets.

Table 4. Comparison of the orbital energies (in hartrees) of M_2 ($M = \text{Cu, Ag, and Au}$) combined with the LUT-IODKH/LUT-IODKH Hamiltonian ^a.

Molecule	Cu_2		Ag_2		Au_2	
1e Hamil.	LUT-IODKH		LUT-IODKH		LUT-IODKH	
2e Hamil.	LUT-IODKH		LUT-IODKH		LUT-IODKH	
Method	FACA	FCP ^b	FACA	FCP ^b	FACA	FCP ^b
$(n-1)s\sigma$	-0.000006	0.001483	-0.000007	-0.000232	-0.000051	0.001170
$(n-1)s\sigma^*$	-0.000006	0.001484	-0.000007	-0.000233	-0.000052	0.001167
$(n-1)p\sigma$	0.000004	0.001586	0.000005	-0.000207	-0.000012	0.000750
$(n-1)p\sigma^*$	0.000004	0.001584	-0.000002	-0.000216	-0.000012	0.000792
$(n-1)p\pi$	0.000000	0.001576	-0.000002	-0.000217	-0.000034	0.000891
$(n-1)p\pi^*$	0.000000	0.001576	0.000005	-0.000213	-0.000034	0.000892
$(n-1)d\sigma$	-0.000002	0.001544	-0.000001	-0.000151	-0.000006	0.000751
$(n-1)d\pi$	0.000000	0.001500	0.000000	-0.000170	-0.000001	0.000741
$(n-1)d\delta$	-0.000002	0.001460	-0.000002	-0.000185	-0.000011	0.000919
$(n-1)d\delta^*$	-0.000002	0.001460	-0.000002	-0.000188	-0.000011	0.000947
$(n-1)d\pi^*$	0.000000	0.001477	0.000000	-0.000206	0.000001	0.000859
$(n-1)d\sigma^*$	0.000000	0.001432	0.000001	-0.000235	0.000002	0.000962
$ns\sigma$	0.000001	0.000852	0.000001	0.000356	-0.000002	0.001338

^aEnergy deviations using FACA and FCP from the molecular AE calculations are shown.

^bEliminated core basis functions are [2s1p] in Cu, [3s2p] in Ag, and [4s3p2d1f] in Au.

Table 5. Comparison of the deviations of valence HF energies (in hartrees) obtained by NR, DKH1, DKH2, DKH3, LUT-IODKH, and IODKH for the one-particle part, and C and LUT-IODKH for the two-particle part combined with molecular AE, FACA, and FCP methods in M₂ (M = Cu, Ag, and Au). The reference values are obtained by LUT-IODKH for the one- and two-particle parts in the molecular AE calculation ^a.

	1e Hamil.	NR	DKH1	DKH2	DKH3	LUT-IODKH	IODKH	LUT-IODKH
	2e Hamil.	C	C	C	C	C	C	LUT-IODKH
Cu ₂	AE	1.397438	−0.027390	0.025952	0.024701	0.024798	0.024790	0.000000
	FACA	1.398995	−0.027544	0.025789	0.024539	0.024634	0.024639	−0.000194
		(0.001557)	(−0.000154)	(−0.000163)	(−0.000162)	(−0.000165)	(−0.000151)	(−0.000194)
	FCP ^b	1.499997	−0.026500	0.026188	0.024936	0.025032	0.025037	0.000223
		(0.102559)	(0.000891)	(0.000236)	(0.000235)	(0.000233)	(0.000247)	(0.000223)
Ag ₂	AE	3.053454	−0.096055	0.036243	0.031019	0.031211	0.031212	0.000000
	FACA	3.054855	−0.095916	0.036381	0.031157	0.031329	0.031330	0.000057
		(0.001401)	(0.000139)	(0.000138)	(0.000138)	(0.000118)	(0.000118)	(0.000057)
	FCP ^b	3.967565	−0.089849	0.037019	0.031803	0.031968	0.031970	0.000787
		(0.914111)	(0.006206)	(0.000776)	(0.000784)	(0.000757)	(0.000758)	(0.000787)
Au ₂	AE	12.456076	−0.549564	0.105914	0.064493	0.066921	0.066922	0.000000
	FACA	12.429320	−0.551602	0.104279	0.062844	0.065592	0.065593	−0.001351
		(−0.026756)	(−0.002038)	(−0.001636)	(−0.001649)	(−0.001329)	(−0.001329)	(−0.001351)
	FCP ^b	22.152742	−0.399033	0.109919	0.068143	0.068938	0.068939	0.002321
		(9.696667)	(0.150531)	(0.004004)	(0.003650)	(0.002017)	(0.002017)	(0.002321)

^a Energy deviations using FACA and FCP from the molecular AE calculations are also shown in parentheses.

^b Eliminated core basis functions are [2s1p] in Cu, [3s2p] in Ag, and [4s3p2d1f] in Au.

Table 6. CPU times (in seconds) for four steps and total SCF in the AE, FACA, and FCP calculations for M_2 ($M = \text{Cu, Ag, and Au}$) molecules at the LUT-IODKH/LUT-IODKH level: one-electron integral (OEI), two-electron integral (TEI), construction of Fock matrix (Const.), and diagonalization of Fock matrix (Diag.). A single core of a Quad Core Xeon/2.80 GHz processor was used.

Mole.	Step	AE	FACA		FCP ^a	
		<i>t</i>	<i>t</i>	Ratio ^b	<i>t</i>	Ratio ^b
Cu ₂	OEI	0.33	0.33	(1.00)	0.33	(1.00)
	TEI	12.84	12.83	(1.00)	5.69	(0.44)
	Const.	0.34	0.40	(1.18)	0.32	(0.95)
	Diag.	0.04	0.03	(0.75)	0.02	(0.50)
	SCF Total	13.55	13.59	(1.00)	6.36	(0.47)
	[SCF Iter.]	14		14		15
Ag ₂	OEI	1.05	1.03	(0.98)	1.04	(0.99)
	TEI	83.93	84.35	(1.01)	18.55	(0.22)
	Const.	0.99	1.00	(1.01)	0.51	(0.52)
	Diag.	0.12	0.11	(0.92)	0.04	(0.33)
	SCF Total	86.09	86.49	(1.00)	20.14	(0.23)
	[SCF Iter.]	22		22		14
Au ₂	OEI	5.72	5.71	(1.00)	5.70	(1.00)
	TEI	1693.54	1671.56	(0.99)	32.59	(0.02)
	Const.	4.43	4.29	(0.97)	0.60	(0.14)
	Diag.	0.11	0.14	(1.27)	0.04	(0.36)
	SCF Total	1703.80	1681.70	(0.99)	38.93	(0.02)
	[SCF Iter.]	15		15		15

^a Eliminated core basis functions are [2s1p] in Cu, [3s2p] in Ag, and [4s3p2d1f] in Au.

^b Ratio in each step is estimated by $t(\text{FACA})/t(\text{AE})$ or $t(\text{FCP})/t(\text{AE})$ in parentheses.

Graphical Abstract

All-Electron Scheme

Seamless Connection to Accurate All-Electron
(Scalar) Two-Component Relativistic Calculations