Relativistic frozen core potential scheme with relaxation of core electrons

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Abstract

This letter proposes a relaxation scheme for core electrons based on the frozen core potential method at the infinite-order Douglas–Kroll–Hess level, called FCP-CR. The core electrons are self-consistently relaxed using frozen molecular valence potentials after the valence SCF calculation is performed. The efficiency of FCP-CR is confirmed by calculations of gold clusters. Furthermore, FCP-CR reproduces the results of the all-electron method for the energies of coinage metal dimers and the core ionization energies and core level shifts of vinyl acetate and three tungsten complexes at the Hartree–Fock and/or symmetry-adapted cluster configuration interaction levels.

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1. Introduction

The development of a highly accurate and efficient scheme to treat any elements in the periodic table is one of the most significant problems in quantum chemistry. One rigorous scheme is the four-component formalism based on the Dirac equation, which satisfies the Lorentz invariance for the motion of electrons [1]. This scheme automatically includes both the spin-free and spin-dependent relativistic effects. Recent theoretical and computational developments in the four-component method have enlarged its applicability for treating large molecules [2–4]. An alternative relativistic scheme is a two-component formalism that uses only electronic states. In the last decade, several schemes have been proposed, such as the normalized elimination of small component [5], exact two-component method [6], and infinite-order Douglas–Kroll–Hess (IODKH) [7] methods, which provide the same energies as the four-component method. From the viewpoint of efficiency in two-component formalisms, the locality of the relativistic effect has been considered [8–16]. Our group has also proposed a scheme, termed local unitary transformation (LUT), for both one- and two-electron relativistic transformations [10, 11]. Furthermore, the LUT scheme was combined with the divide-and-conquer method to achieve an overall linear-scaling technique from integral calculations to post-Hartree–Fock (HF) calculations [12–14]. These improvements can reduce the gap between non-relativistic and highly accurate relativistic methods in all-electron (AE) calculations.

A widely used method to reduce the number of electrons treated explicitly is the effective core

20 potential (ECP) method. The ECP method, which includes the pseudo-potential (PP) [17–23] and
21 model potential (MP) [24–27] methods, replaces the effect of the core electrons with a core poten-
22 tial. The ECP method includes part of the relativistic effects in the core potential. The PP method
23 introduces a smooth and nodeless potential function in the core region. On the other hand, the
24 MP method uses a nodal potential function to describe the valence orbital in the AE treatment.
25 Our group has also proposed another scheme for reducing the number of electrons treated explic-
26 itly, which is termed the frozen core potential (FCP) method [28]. The FCP method is based on
27 the same equation as the MP method but the core electrons obtained from atomic calculations
28 are treated explicitly. Another advantage of the FCP method is a seamless connection to the AE
29 method with an accurate two-component relativistic Hamiltonian. The ECP and FCP methods are
30 quite effective for determining valence electronic states and valence properties. However, the ECP
31 method has difficulties in describing core electron states and their properties because the core po-
32 tential is obtained by atomic calculations without the consideration of any chemical environment
33 effect.

34 In the present study, we propose a novel scheme based on the FCP method to describe core
35 properties using the relaxations of core electrons. This letter is organized as follows; the theory
36 and implementation are described in Sec. 2; numerical assessments are performed in Sec. 3; and
37 concluding remarks are given in Sec. 4.

2. Theory and implementation

2.1. FCP with relaxation of core electrons

This subsection provides the theory for core electron relaxations based on the FCP scheme. The FCP method is based on the Huzinaga–Cantu equation [29], which separates electrons into core and valence regions. Here, we discuss a closed-shell system for simplicity, though extension to an open-shell system is straightforward. The AE HF–Roothaan (HFR) equation is given by

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

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

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

and

$$D_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i}^*. \quad (3)$$

Here, $H_{\mu\nu}$ and $G_{\mu\nu}$ are non-relativistic (NR)/relativistic one- and two-electron integrals with respect to atomic orbitals $\{\mu, \nu\}$, respectively. The density matrix $\mathbf{D}$ is separated into core and valence contributions as

$$\mathbf{D} = \mathbf{D}^{\text{C}} + \mathbf{D}^{\text{V}}. \quad (4)$$

In the valence FCP method, two approximations are adopted. First, the total density matrix $\mathbf{D}$

55 is approximated in a block-diagonal form:

$$56 \quad \mathbf{D} \approx \mathbf{d}^C \oplus \mathbf{d}^V, \quad (5)$$

57 where $\mathbf{d}^C(\mathbf{d}^V)$ is a submatrix that includes only the core (valence) AO indices. This approximation
 58 is effective if a generally contracted basis set is adopted. Second, the molecular core density matrix
 59 $\mathbf{D}^C$ is approximated as the direct sum of the atomic contributions as follows,

$$60 \quad \mathbf{d}^C \approx \tilde{\mathbf{d}}^C = \tilde{\mathbf{d}}_A^C \oplus \tilde{\mathbf{d}}_B^C \oplus \cdots, \quad (6)$$

61 where $\{A, B, \cdots\}$ denote individual atoms. Using these two approximations, the valence-only HFR
 62 equation is expressed as

$$63 \quad \mathbf{f}^V(\mathbf{d}^V)\mathbf{c}^V = \mathbf{s}^V\mathbf{c}^V\boldsymbol{\varepsilon}^V \quad (7)$$

64 with

$$65 \quad \begin{aligned} f_{\mu\nu}^V = & h_{\mu\nu}^V + \frac{1}{2} \sum_{\lambda,\rho} d_{\lambda\rho}^V \left(\langle \chi_\mu^V \chi_\lambda^V | \chi_\nu^V \chi_\rho^V \rangle - \frac{1}{2} \langle \chi_\mu^V \chi_\lambda^V | \chi_\rho^V \chi_\nu^V \rangle \right) \\ & + \frac{1}{2} \sum_{\lambda,\rho} \sum_A (\tilde{d}_A^C)_{\lambda\rho} \left(\langle \chi_\mu^V \chi_\lambda^C | \chi_\nu^V \chi_\rho^C \rangle - \frac{1}{2} \langle \chi_\mu^V \chi_\lambda^C | \chi_\rho^C \chi_\nu^V \rangle \right) \\ & - 2 \sum_{l,m} s_{\mu l} w_{lm}^C s_{m\nu} \end{aligned} \quad (8)$$

66 and

$$67 \quad w_{\mu\nu}^C = \sum_c^{\text{core}} \varepsilon_c c_{\mu c} c_{\nu c}^*, \quad (9)$$

68 where $\langle \chi_\mu \chi_\lambda | \chi_\nu \chi_\rho \rangle$ is the two-electron integral, $\mathbf{S}$ is the overlap matrix, ε_c is the core orbital energy,
 69 and $\{c_{\mu c}\}$ is the core orbital coefficient. The last term is a projection operator that prevents electrons

70 from falling into core orbitals. The valence energy in the FCP scheme is defined as

$$71 \quad E^V = \frac{1}{2} \sum_{\mu,\nu} d_{\mu\nu}^V (h_{\mu\nu}^V + f_{\mu\nu}^V) + \sum_{A < B} \frac{(Z_A - n_A^C)(Z_B - n_B^C)}{R_{AB}} \quad (10)$$

72 where Z_A , n_A^C , and R_{AB} are the nuclear charge, the number of core electrons in atom A , and the
73 internuclear distance between atoms A and B , respectively.

74 After the valence SCF calculation, the core electron relaxations are performed. For the relax-
75 ation, the equation is derived using the above first approximation of Eq. (5) in the FCP method. A
76 similar derivation for the valence-only equation is performed to obtain a core-only equation. The
77 resulting equation is given by

$$78 \quad \mathbf{f}^C(\mathbf{d}^C)\mathbf{c}^C = \mathbf{s}^C\mathbf{c}^C\boldsymbol{\varepsilon}^C \quad (11)$$

79 with

$$\begin{aligned} f_{\mu\nu}^C = & h_{\mu\nu}^C + \frac{1}{2} \sum_{\lambda,\rho} d_{\lambda\rho}^C \left(\langle \chi_\mu^C \chi_\lambda^C | \chi_\nu^C \chi_\rho^C \rangle - \frac{1}{2} \langle \chi_\mu^C \chi_\lambda^C | \chi_\rho^C \chi_\nu^C \rangle \right) \\ & + \frac{1}{2} \sum_{\lambda,\rho} d_{\lambda\rho}^V \left(\langle \chi_\mu^C \chi_\lambda^V | \chi_\nu^C \chi_\rho^V \rangle - \frac{1}{2} \langle \chi_\mu^C \chi_\lambda^V | \chi_\rho^V \chi_\nu^C \rangle \right) \\ & - 2 \sum_{l,m} s_{\mu l} w_{lm}^V s_{m\nu} \end{aligned} \quad (12)$$

81 and

$$82 \quad w_{\mu\nu}^V = \sum_v \varepsilon_v c_{\mu\nu} c_{\nu\nu}^* \quad (13)$$

83
84 Using the fixed valence orbitals obtained from the valence FCP calculation, the core-only
85 equation in Eq. (11) is solved self-consistently to determine the relaxed core orbitals and their

86 energies.

87 A core energy is defined as

$$88 \quad E^C = \frac{1}{2} \sum_{\mu, \nu} d_{\mu\nu}^C (h_{\mu\nu}^C + f_{\mu\nu}^C) + \sum_{A < B} \frac{(Z_A - n_A^V)(Z_B - n_B^V)}{R_{AB}}, \quad (14)$$

89 where n_A^V is the number of valence electrons in atom A .

90 2.2. Implementation

91 This subsection gives the implementation of the FCP scheme with relaxations of core electrons
92 (hereinafter called FCP-CR). FCP-CR consists of three steps: an atomic calculation, a valence
93 calculation, and a core calculation as shown in Table 1. In atomic calculations, each atomic AE
94 calculation included in a target molecule is performed to determine the atomic core orbitals and
95 orbital energies. These are then used in the atomic core density matrix in Eq. (4) and the core
96 potential and projection matrices in Eq. (8). In a valence calculation, the valence-only equation
97 in Eq. (7) is solved using the information for the atomic core electrons. Here, valence–valence
98 two-electron integrals, which require smaller basis set dimensions than AE, are evaluated. In
99 addition, the computational scaling for calculations of the core–valence two-electron integrals is
100 theoretically reduced from $O(n^4)$ to $O(n^3)$. Finally, in a core calculation, we perform the SCF
101 calculation based on the core-only equation in Eq. (12) using a fixed valence potential, which
102 is determined using Eq. (12). Note that the core–core and core–valence two-electron integrals
103 with smaller computational costs than the total two-electron integral are evaluated. Throughout

this Letter, the calculations of the core–valence two-electron integrals for Eq. (12) are skipped because these integrals, which are the same as those used in Eq. (8), are stored on a disk.

3. Numerical assessments

3.1. Computational details

This section examines the performance of the FCP-CR scheme. The IODKH with LUT (LUT- IODKH) Hamiltonian was applied to all the calculations. Numerical assessments were performed to investigate the accuracy and efficiency of the FCP-CR scheme. The Core, valence, and total HF energies, as well as the orbital energies, of coinage metal dimers M_2 ($M = \text{Cu, Ag, and Au}$) were calculated for accuracy. The bond lengths were 2.55, 2.89, and 2.89 Å for Cu_2 , Ag_2 , and Au_2 , respectively [30, 31]. The core ionization energies (CIEs) and core level shifts (CLSs) of C 1s and W 4f orbitals were calculated to investigate differences between core electrons in various chemical environments at the HF and symmetry-adapted cluster configuration interaction (SAC-CI) levels [32, 33]. Vinyl acetate was employed for CIEs and CLSs of C 1s orbitals, whose geometry was optimized at the density functional theory (DFT) with the B3LYP functional using cc-pVTZ basis set [34]. In addition, $\text{W(CO)}_4\text{L}$ [$\text{L} = 1,2\text{-bis(diphenylphosphino)ethane (dppe), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis((pentafluorophenyl)phosphino)ethane (F-dppe)}$] was adopted for CIEs and CLSs of W 4f orbitals. The threshold sets (hartree) for the perturbation selection [35] were 1×10^{-6} for SAC and 1×10^{-7} for SAC-CI in vinyl acetate and 5×10^{-6} for SAC and 5×10^{-7} for SAC-CI in $\text{W(CO)}_4\text{L}$ with a non-direct algorithm. Their geometries were

optimized at DFT with the B3LYP functional using Sapporo-DZP-2012 basis set for main group elements [36] and the SDD relativistic small-core effective core potential for W [37]. Gold clusters were adopted to investigate the efficiency. In these clusters, an experimental lattice constant of 4.062 Å with a face-centered cubic structure was adopted [38]. The total numbers of atoms in the Au_n clusters were 14, 32, 50, 68, and 86, which correspond to 1 × 1 × 1, 1 × 1 × 3, 1 × 1 × 5, 1 × 1 × 7, 1 × 1 × 9 unit cells, respectively. In AE, the maximum number of the atoms in a cluster was 50. All the results were compared to those of the AE method.

The basis sets were DKH3-Gen-TK/NOSec-V-TZP [39–41] for C in vinyl acetate, Cu, Ag, W, and Au; Sapporo-DZP-2012 for H and O in vinyl acetate; and 6-31G [42, 43] for H, C, O, F, and P in tungsten complexes. In gold clusters the minimal third-order DKH basis set [44] was adopted. Note that a polarization function was added to the basis sets of the C and P atoms nearest to the central tungsten atom of these complexes. The valence orbitals were set to {2s,2p} for C, {3s,3p,3d,4s} for Cu, {4s,4p,4d,5s} for Ag, {5s,5p,5d} for W, and {5s,5p,5d,6s} for Au.

HF calculation was performed using our in-house relativistic quantum chemical program. A modified version of the Gaussian09 suite of programs [45] was employed for DFT and SAC-CI calculations.

3.2. Computational cost of FCP-CR

This subsection examines the efficiency of FCP-CR. Table 2 shows the CPU times of the HF calculation obtained with FCP-CR and AE for a Au₅₀ cluster at the following four steps: core

142 or valence potential (Potential), one-electron integral (OEI), two-electron integral (TEI), and SCF
143 procedure. Valence is the CPU time for the valence electron calculation, which corresponds to
144 FCP, whereas core is the CPU time for the relaxation of core electrons. All is a sum over both
145 the valence and core CPU times. A Xeon E5-2690/2.90 GHz (Octa-core) processor was used on a
146 single core.

147 The total CPU time of FCP-CR (all) was 34.4% of that for the AE case: 70816.3 and 203983.8
148 s for FCP-CR and AE, respectively. The total CPU time was mainly reduced by the TEI and
149 SCF calculations. In the TEI calculation, the number of integrals was decreased by treating only
150 valence or core electrons. The SCF calculation was performed with a smaller dimension basis set
151 in FCP-CR compared with AE. In addition, the CPU time for valence was dominant in FCP-CR
152 compared with that of core.

153 Figure 1 shows the system-size dependence of the CPU time in Au_n ($n = 14, 32, 50, 68$, and
154 86). The horizontal axis shows the number of gold atoms in the cluster. The vertical axis shows
155 the total CPU time of FCP-CR and AE. FCP-CR reduces the CPU time in comparison with AE.
156 The scalings are $O(n^{2.71})$ and $O(n^{2.28})$ for AE and FCP-CR, respectively.

157 To investigate the scaling for FCP-CR, Figure 2 shows the system-size dependence of the CPU
158 time for dominant steps: TEI, the SCF procedure, and construction of a potential (Potential). The
159 CPU times were measured at (a) AE, (b) FCP-CR for valence electrons (equal to FCP), and (c)
160 FCP-CR for core electrons. The scaling of the CPU time in each step is given in Figure 2. In the

AE, the TEI and SCF scalings are $O(n^{2.50})$ and $O(n^{4.32})$. Thus, the scaling of the total CPU time becomes $O(n^{2.71})$. In FCP-CR, the CPU time for the valence calculation is larger than that for the core calculation. This is because the dimension of the basis set is larger. Furthermore, the TEI steps in the valence and core calculations are dominant. The scalings are $O(n^{2.53})$ and $O(n^{2.18})$ for valence and core, respectively, and resulting scaling of the total CPU time is $O(n^{2.28})$.

3.3. Accuracy of FCP-CR

This subsection examines the accuracy of FCP-CR. Table 3 shows the core, valence, and total HF energies (in hartree) obtained with the LUT-IODKH Hamiltonian for M_2 ($M = \text{Cu, Ag, and Au}$), as well as the results of the FCP and molecular AE methods. The deviations from the molecular AEs are shown in parentheses. The energy components of the molecular AE are evaluated using the procedure described in a previous study [28].

The difference in the total energy of FCP is less than 0.09 hartree: 0.001430, 0.08759, and 0.007563 hartree for Cu_2 , Ag_2 , and Au_2 , respectively. For each molecule, the difference in the core part is smaller than that of the valence part because the core regions are similar to that in the atomic state. On the other hand, the total energies of FCP-CR give small deviations compared with FCP: 0.000188, 0.000117, and 0.001538 hartree for Cu_2 , Ag_2 , and Au_2 , respectively. The deviations in the valence energy are speculated to be canceled out by those in the core energy because the core electrons are relaxed self-consistently under the frozen valence potential.

Figure 3 shows the orbital energy differences (in hartree) from those of the AE method in

180 coinage metal dimers (Cu_2 , Ag_2 , and Au_2) obtained by FCP and FCP-CR. The vertical axis shows
181 the difference from AE in the orbital energy, $\Delta\epsilon$. The horizontal axis indicates the orbital species
182 from the core to the valence regions. The dotted line indicates the boundary between the core and
183 valence regions.

184 The values $\Delta\epsilon$ in the valence orbitals of FCP-CR are the same as those of FCP because these
185 schemes are common until the valence electrons are solved self-consistently. The mean absolute
186 deviations of both schemes are 0.04, 0.04, and 0.03 eV for Cu_2 , Ag_2 , and Au_2 , respectively, which
187 is consistent with the results of a previous study [28].

188 The $\Delta\epsilon$ values in the core orbitals of FCP-CR are smaller than those of FCP. The mean absolute
189 deviations of FCP-CR are 0.04, 0.0, and 0.02 eV for Cu_2 , Ag_2 , and Au_2 , respectively, while those
190 of FCP are 0.24, 0.22, and 0.04 eV for Cu_2 , Ag_2 , and Au_2 , respectively. Thus, the core orbitals
191 can be properly relaxed under a molecular valence potential.

192 3.4. Core ionization energy and core level shift

193 This subsection discusses the accuracies of the CIEs and CLSs. In HF calculations, the CIEs
194 and CLSs were estimated from the orbital energies based on Koopmans' theorem. In SAC-CI
195 calculations, these values were directly obtained.

196 Table 4 shows the CIEs (in eV) of C 1s and W 4f in vinyl acetate and $\text{W}(\text{CO})_4\text{L}$ complexes,
197 respectively. Vinyl acetate has four types of C 1s with different chemical environments: COO,
198 CHO, CH_3 , and CH_2 . In addition, $\text{W}(\text{CO})_4\text{L}$ has three types of W 4f with different ligands: dppe,

199 dmpe, and F-dppe. The CLSs (in eV), which are shown in parentheses, were estimated using the
200 differences from the reference values. As references, CH₃ and dppe were adopted for vinyl acetate
201 and W(CO)₄L, respectively. The experimental values for vinyl acetate and W(CO)₄L were taken
202 from Refs. 46 and 47, respectively.

203 In FCP, the CIEs at the HF level were always the same value in different chemical environ-
204 ments: 308.298 eV and 47.540 eV for vinyl acetate and W(CO)₄L, respectively. On the other
205 hand, in FCP-CR, the CIEs depended on the chemical environment. The CIEs and CLSs were
206 close to those of AE, within a deviation of 0.5 eV. Furthermore, the electron correlation effect,
207 which is the difference between HF and SAC-CI, contributed to reproducing the values of the ex-
208 perimental CIEs. The deviations from the experimental CIEs were less than 5.7 and 6.0 eV for
209 vinyl acetate and W(CO)₄L, respectively. Note that the deviations from the experimental values
210 are mainly caused by the incompleteness of the basis sets, which is shown in Appendix B.

211 In vinyl acetate, the tendency is explained by the characteristics of the atoms or bonds sur-
212 rounding a target atom. For COO, the carbon has bonds with two electronegative oxygen atoms,
213 which leads to a decrease of the electron density at C. For CHO, the shift is smaller than that of
214 COO because CHO has one C–O bond. For CH₂, the carbon has one double bond with a hybridized
215 sp² orbital. The hybridization expands the valence orbitals compared with the sp³ hybridization in
216 CH₃, which also leads to a decrease of the electron density at C.

217 In W(CO)₄L, the tendency is explained by the characteristics of the ligands. For dppe, the shift

218 is smaller than that of dmpe because of the screening capability of a core hole in the ligands. The
219 π electrons of the phenylphosphine group are likely polarized in comparison with the σ electrons
220 of the methylphosphine group, which leads to easy screening of core holes [47]. For F-dppe, the
221 pentafluorophenylphosphine group includes highly electronegative F, and thus the electron density
222 at W decreases.

223 4. Concluding remarks

224 In the present study, we have proposed the FCP-CR scheme for relaxation of core electrons
225 based on FCP at the IODKH level. The core-only HFR equation is derived using the same proce-
226 dure as that for a valence-only one. The molecular core orbitals and their energies are computed
227 under the frozen valence molecular potential, which is constructed on the fly. Numerical assess-
228 ments were performed with coinage metal dimers and small gold clusters to examine accuracy
229 and efficiency. The CIEs and CLSs of C 1s in vinyl acetate and W 4f in three tungsten complexes
230 were calculated with FCP-CR at the HF and SAC-CI levels. The results suggest that FCP-CR
231 sufficiently reproduces the corresponding AE results with high efficiency. The proposed scheme
232 has a high potential for becoming an alternative and efficient AE method, without loss of accuracy.

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240 on Relativistic Electronic Theory” of the Japan Science and Technology Agency (JST).

Figure 1: System-size dependence of CPU time (s) in Au_n ($n = 14, 32, 50, 68$, and 86) obtained with the AE and FCP-CR methods. A Xeon E5-2690/2.90 GHz (octa-core) processor was used on a single core.

Figure 2: System-size dependence of CPU time (s) for dominant steps with the AE and FCP-CR methods in Au_n ($n = 14, 32, 50, 68$, and 86): two-electron integral (TEI), SCF procedure, and construction of potential (Potential). (a) AE; (b) valence part in FCP-CR; and (c) core part in FCP-CR. A Xeon E5-2690/2.90 GHz (octa-core) processor was used on a single core.

Figure 3: Differences of between the FCP and FCP-CR orbital energies (in hartree) and those of the AE method in coinage metal dimers at the Hartree-Fock level: (a) Cu_2 , (b) Ag_2 , and (c) Au_2 . The orbitals are sorted in ascending order of energy.

Table 1: Calculation procedure for FCP-CR.

(I) Atomic calculations	(I.1) One- and two-electron integrals for each atom
	(I.2) All-electron HF calculation for each atom
	(I.3) Save core orbital, density matrix, and orbital energy
(II) Valence calculation	(II.1) Core-valence two-electron integrals of third term of r.h.s. in Eq. (8)
	(II.2) Construct core potential
	(II.3) Construct projection operator matrices of fourth term of r.h.s. in Eq. (8)
	(II.4) One- and two-electron integrals for valence
	(II.5) Add projection operator matrix and core potential
	(II.6) Solve valence-only equation of Eq. (7)
(III) Core calculation	(III.1) Construct fixed valence potential of second term of r.h.s. in Eq. (12)
	(III.2) Construct projection operator matrices in Eq. (12)
	(III.3) One- and two-electron integrals for core
	(III.4) Add projection operator matrix and fixed valence potential
	(III.5) Solve core-only equation of Eq. (11)

Table 2: CPU time for four steps in the Hartree–Fock calculation obtained with FCP-CR and AE for a Au₅₀ cluster: construction of core or valence potential (Potential), one-electron integral (OEI), two-electron integral (TEI), and SCF procedure (SCF). A Xeon E5-2690/2.90 GHz processor (octa-core) was used on a single core. The percentages of individual steps are given in parentheses.

Step	FCP-CR						AE	
	Valence		Core		All			
	Time (s)	%	Time (s)	%	Time (s)	%	Time (s)	%
Potential	20120.4	(44.5)	175.9	(0.7)	20296.3	(28.9)	0.0	(0.0)
OEI	328.4	(0.7)	719.0	(2.9)	1047.4	(1.5)	985.1	(0.5)
TEI	24363.1	(53.8)	23991.0	(96.2)	48354.1	(68.9)	149132.0	(73.1)
SCF	440.0	(1.0)	48.5	(0.2)	488.5	(0.7)	53866.7	(26.4)
Total	45251.9	(100.0)	24934.4	(100.0)	70186.3	(100.0)	203983.8	(100.0)

Table 3: Comparison of core, valence, and total HF energies (in hartree) of M_2 ($M = \text{Cu, Ag, and Au}$) obtained by the FCP, FCP-CR, and molecular AE methods. The deviations from the molecular AEs are given in parentheses.

		FCP		FCP-CR		Molecular AE
Cu_2	Core	−2913.534822	(−0.000063)	−2913.533204	(0.001555)	−2913.534759
	Valence	−392.856146	(−0.001367)	−392.856146	(−0.001367)	−392.854779
	Total	−3306.390968	(−0.001430)	−3306.389350	(0.000188)	−3306.389538
Ag_2	Core	−10332.790532	(−0.000150)	−10332.704656	(0.085726)	−10332.790382
	Valence	−293.119642	(−0.085609)	−293.119642	(−0.085609)	−293.034033
	Total	−10625.910174	(−0.085759)	−10625.824298	(0.000117)	−10625.824415
Au_2	Core	−37750.131480	(0.001660)	−37750.137505	(−0.004365)	−37750.133140
	Valence	−272.254111	(0.005903)	−272.254111	(0.005903)	−272.260014
	Total	−38022.385591	(0.007563)	−38022.391616	(0.001538)	−38022.393154

Table 4: Core ionization energies (in eV) obtained by FCP, FCP-CR, and AE of C 1s and W 4f for vinyl acetate and three tungsten complexes, respectively. Experimental values are taken from Ref. 46 for vinyl acetate and Ref. 47 for the tungsten complexes. Core level shifts from the reference molecules (CH_3 or dppe) are given in parentheses.

Molecule	type	HF			SAC-CI		Exptl.
		FCP	FCP-CR	AE	FCP-CR	AE	
vinyl acetate	COO	308.298	310.249	310.103	298.617	298.475	294.94
		(0.000)	(3.951)	(3.938)	(3.870)	(3.860)	(3.510)
	CHO	308.298	307.700	307.553	295.726	295.585	292.32
		(0.000)	(1.402)	(1.388)	(0.979)	(0.970)	(0.890)
	CH_3	308.298	306.298	306.165	294.747	294.615	291.43
		(0.000)	(0.000)	(0.000)	(0.000)	(0.000)	(0.000)
	CH_2	308.298	305.634	305.509	293.181	293.061	290.54
		(0.000)	(-0.664)	(-0.656)	(-1.566)	(-1.554)	(-0.890)
$\text{W}(\text{CO})_4\text{L}$	dppe	47.540	47.589	48.033	36.274	36.558	31.118
		(0.000)	(0.000)	(0.000)	(0.000)	(0.000)	(0.000)
	dmpe	47.540	47.588	48.030	36.963	37.236	31.296
		(0.000)	(-0.001)	(-0.003)	(0.689)	(0.678)	(0.178)
	F-dppe	47.540	48.316	48.773	37.403	37.742	31.931
		(0.000)	(0.727)	(0.740)	(1.129)	(1.184)	(0.813)

Appendix A. Accuracy of an iterative procedure between valence and core calculations

This appendix examines the effect of an iterative self-consistent procedure between the valence and core calculations. FCP-CR calculates core orbitals under a valence potential only once, after valence orbitals are calculated under an atomic core potential. However, the valence orbitals could be more accurate if the valence orbitals were recalculated under the core potential obtained by FCP-CR. Here, a procedure is iteratively performed between the valence and core calculations based on Eqs. (7), (8), (11), and (12). Table A.1 shows the iteration number dependence in total energy (hartree) of Au_2 . Iteration = 0 and 1 indicate FCP and FCP-CR, respectively. ΔE is the deviation in the total energy from the previous value. ΔE^{AE} is the deviation from the reference value obtained by molecular AE; the reference value is -38022.393154 hartree. The total energy was steeply converged with a small iteration number. The largest deviation in ΔE^{AE} is 0.001456 hartree at the fifth iteration. This deviation is due to the approximation of the basis set in Eq. (5). Furthermore, the largest deviation in ΔE is -0.006025 hartree at the first iteration, which is the difference between FCP and FCP-CR. This result indicates that FCP-CR, which requires only one calculations of core orbitals under a valence potential, is enough to describe the core electrons in a chemical environment.

Table A.1: Iteration number dependence in total energy (in hartree) of Au₂ obtained by the valence–core iterative procedure.

Iteration	Energy	ΔE	ΔE^{AE}
0 (FCP)	-38022.385591	–	0.007563
1 (FCP-CR)	-38022.391616	-0.006025	0.001537
2	-38022.391693	-0.000077	0.001461
3	-38022.391697	-0.000004	0.001457
4	-38022.391698	-0.000001	0.001456
5	-38022.391698	0.000000	0.001456

Appendix B. Dependence of core ionization potential energies

We examined core ionization potential energies by the standard SAC-CI calculations without a symmetry (C_1) as well as using different basis sets: cc-pCVXZ ($X = D, T, \text{ and } Q$) and special basis sets designed for a core ionization potential in the paper written by Kuramoto and Ehara [J. Chem. Phys. 122 (2005) 014304]. Table B.2 shows the core ionization energies (eV) of C 1s for vinyl acetate. Δ shows the difference from the experimental values. In the C_1 symmetry, Δ is almost the same as the C_S symmetry in Section 3. In the cc-pCVXZ types of basis sets, Δ gets systematically smaller as the cardinal number X increases. For cc-pCVQZ basis set, the maximum deviation is 1.34 eV compared with 4.93 eV for cc-pCVDZ and 1.55 for cc-pCVTZ. Moreover, the special basis set gives the best results among these basis sets. The maximum deviation is 1.04 eV although the size of the basis sets is smaller than cc-pCVQZ, because the special basis set includes the differential basis function for the primitive s-type of function. These indicate that the proper basis set selection requires for reproducing the experimental values.

Table B.2: Core ionization energies (in eV) of C 1s for vinyl acetate with C1 symmetry, cc-pCVXZ (X = D, T, and Q), and special basis sets.

type	C_1	Δ	cc-pCVDZ	Δ	cc-pCVTZ	Δ	cc-pCVQZ	Δ	Special	Δ	Exptl.
COO	298.492	3.55	299.871	4.93	296.491	1.55	296.284	1.34	295.984	1.04	294.94
CHO	295.701	3.38	297.536	5.22	293.600	1.28	293.428	1.11	293.012	0.69	292.32
CH ₃	294.523	3.09	295.851	4.42	292.521	1.09	292.330	0.90	291.866	0.44	291.43
CH ₂	293.247	2.73	295.822	5.28	291.644	1.10	291.499	0.96	291.021	0.48	290.54

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Graphical Abstract