SOiCI and iCISO: combining iterative configuration interaction with spin–orbit coupling in two ways

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Abstract

The near-exact iCIPT2 approach for strongly correlated systems of electrons, which stems from the combination of iterative configuration interaction (iCI, an exact solver of full CI) with configuration selection for static correlation and second-order perturbation theory (PT2) for dynamic correlation, is extended to the relativistic domain. In the spirit of spin separation, relativistic effects are treated in two steps: scalar relativity is treated by the infinite-order, spin-free part of the exact two-component (X2C) relativistic Hamiltonian, whereas spin–orbit coupling (SOC) is treated by the first-order, Douglas–Kroll–Hess-like SOC operator derived from the same X2C Hamiltonian. Two possible combinations of iCIPT2 with SOC are considered, i.e., SOiCI and iCISO. The former treats SOC and electron correlation on an equal footing, whereas the latter treats SOC in the spirit of state interaction, by constructing and diagonalizing an effective spin–orbit Hamiltonian matrix in a small number of correlated scalar states. Both double group and time reversal symmetries are incorporated to simplify the computation. Pilot applications reveal that SOiCI is very accurate for the spin–orbit splitting (SOS) of heavy atoms, whereas the computationally very cheap iCISO can safely be applied to the SOS of light atoms and even of systems containing heavy atoms when SOC is largely quenched by ligand fields.

Keywords: electron correlation, spin–orbit coupling, SOiCI, iCISO, sf-X2C + so-DKH1, double group, time reversal

(Some figures may appear in colour only in the online journal)

1. Introduction

It has long been recognized [1–3] that both relativistic and correlation effects ought to be accounted for in accurate quantum mechanical descriptions of the electronic structure not only of systems containing heavy elements (say, Z > 30) but also of systems composed only of light elements (Z ≤ 30). Literally, relativity is in the Hamiltonian, whereas correlation is in the wave function parameterized by a particular ansatz [4]. As the advent of the continuous and complete ‘Hamiltonian ladder’ [5, 6], the relativity problem in quantum chemistry can be regarded as solved, in the sense that one can just pick up the right Hamiltonian according to the target physics/chemistry and accuracy. In particular, all relativistic Hamiltonians [4, 7–12], including the effective quantum electrodynamics (QED) [5, 6, 13–20], can be written in the same second-quantized...
In this work, we extend the recently proposed iCIPT2 approach [112, 113] to the relativistic domain within the 1C framework. iCIPT2 stems from the combination of iterative configuration interaction (iCI, an exact solver of full CI) [114] with configuration selection for static correlation and second-order perturbation theory (PT2) for dynamic correlation, and belongs to the ‘modern family’ of selected CI methods [115–132] for strongly correlated systems of electrons. In particular, the use of configuration state functions (CSFs) as the many-electron basis and the tabulated unitary group approach (TUGA) [112] for fast evaluation and reuse of the basic coupling coefficients between randomly selected CSFs allows an easy extension of iCIPT2 to the treatment of SOC in two ways, one-step SOiCI and two-step iCISO, which are to be detailed in section 4, after introducing the spin-separated exact two-component (X2C) relativistic Hamiltonian [12, 133, 134] in section 2 and symmetry adaptation of the many-electron basis in section 3. Pilot applications are then presented in section 5, followed by concluding remarks in section 6.

The following notations are to be used throughout. A configuration of in total \( n \) ordered spatial orbitals \( \{ \phi_j \} \) with occupation numbers \( \{ n_j \} \) is denoted as \( | f \rangle \), which can generate CSFs of spin \( S \) if it has \( N_o \) singly occupied orbitals. Since each CSF is characterized uniquely by a vector \( d \) of the Shavitt step numbers \( \{ d_i \} \) \( d_i = 0 \) if orbital \( r \) is not occupied; \( d_i = 1 \) if orbital \( r \) is singly occupied and spin-up coupled with orbital \( r - 1; d_i = 2 \) if orbital \( r \) is singly occupied and spin-down coupled with orbital \( r - 1; d_i = 3 \) if orbital \( r \) is doubly occupied) [135], a CSF can be denoted simply as \( | d \rangle \). When necessary, the notation will be expanded to \( | d S \rangle \), even though the spin \( S \) can be derived automatically from \( d \). The components of \( | d \rangle \) are denoted accordingly as \( | d, S \rangle \) or \( | d, S, M \rangle \) with \( M \in \{ - S, S \} \). After double group and time reversal symmetry adaption (see section 3, appendices A and B), the Kramer paired components of \( | d \rangle \) will be denoted as \( | d, \mu \rangle \) (or \( | d, S, \mu \rangle \)) with \( \mu \in \{ 1, n_0^2 \} \), where \( n_0^2 \) is the dimension of an irreducible representation (irrep) \( \gamma \) of a double group.

2. Two-step relativistic Hamiltonian: sf-X2C + so-DKH1

A two-step relativistic Hamiltonian is needed to postpone the treatment of SOC to the correlation step. It has been shown [12, 133, 134] that the X2C Hamiltonian [136, 137], albeit defined only algebraically, can be separated into a spin-free part (sf-X2C) and a family of spin-dependent operators. Among the latter, the first-order Douglas–Kroll–Hess-like spin–orbit operator (so-DKH1) is the simplest variant. Without going into further details, the sf-X2C + so-DKH1 Hamiltonian reads

\[
H = H_{sf} + H_{so},
\]
\[ H_{df} = \sum_{pq} \left[ \frac{\hbar^2}{2m} \right] p_q e_{pq} + \frac{1}{2} \sum_{pqrs} (pq|rs) e_{pqrs}, \]  

(4)

\[ H_{so} = \sum_{pq} \sum_{l \in x,y,z} \left( H_{so}^l \right)_{pq} \tau_q^l, \quad H_{so}^l = h_{\text{SO},1e}^l + h_{\text{SO},2e}^l, \]  

(5)

\[ E_{pq} = \sum_{\sigma} d_{pq}^\dagger d_{pq}, \quad e_{pqrs} = E_{pq} - \delta_{pq} E_{rs}, \]  

\[ T_{pq}^l = a_{pq}^\dagger a_{pq} + a_{pq}^\dagger a_{pq}, \quad T_{pq}^L = -i (d_{pq}^\dagger a_{pq} - a_{pq}^\dagger d_{pq}), \]  

(7)

where \( p,q,r,s \) refer to real-valued MOs and the two-electron integrals have been written in the Mulliken notation. The one-electron term \( h_{\text{XC}}^{\text{NC}} \) in \( H_{df} \) (4) is obtained simply by block-diagonalizing the spin-free part of the one-electron Dirac equation represented in a kinetically balanced basis [138],

\[ h_{\text{XC}}^{\text{NC},df} = R_{+,0} \left( V_{\text{ne}} + TX_0 + X_1^T \right) \]  

(8)

\[ R_{+,0} = (S^{-1}S_{+,0})^{-\frac{1}{2}} \left( S^{-1}S_{+,0}S^{-\frac{1}{2}} \right), \]  

(9)

\[ S_{+,0} = S + \frac{\alpha^2}{4} X_1^T \]  

(10)

\[ X_0 = B_1 A_1^{-1} = B_1 A_1^{-1} (A_1 A_1^T)^{-1}, \]  

(11)

where \( \alpha \) is the fine-structure constant, \( S, T \) and \( V_{\text{ne}} \) are the respective matrices of the nonrelativistic metric, kinetic energy and nuclear attraction (\( V_{\text{ne}} \)), whereas \( W_{\text{df}} \) is the matrix of the ‘small-component potential’ \( W_{\text{df}} = \vec{\rho} \cdot V_{\text{ne}} \vec{\rho} \). The decoupling matrix \( X_0 (11) \) is simply the ratio between the coefficients of the small (\( B_1 \)) and large (\( A_1 \)) components of the scalar, two-component Dirac orbitals of positive energies. Note that scalar two-electron picture change corrections have been neglected here since this is known to be a very good approximation for valence properties [139]. The so-DKH1 operator \( H_{so} \) (5) is composed of a one-electron term \( h_{\text{SO},1e} \) [133] and a mean-field approximation \( f_{\text{SO},2e} \) [134] to the two-electron spin–orbit interaction, viz,

\[ h_{\text{SO},1e} = \frac{\alpha^2}{4} R_{+,0} X_1^T \]  

(12)

\[ f_{\text{SO},2e} = \frac{\alpha^2}{4} R_{+,0} \left[ g_{\text{LL}}^{\text{SL}} + g_{\text{LS}}^{\text{SL}} X_0 + X_1^T g_{\text{SLL}} \right] \]  

(13)

Here, \( w^l \) is the matrix of \( w^l = (\vec{p} V_{\text{ne}} \times \vec{p}) = \varepsilon_{lmn} P_m \vec{p}_n \) in the basis of atomic orbitals (AOs), viz,

\[ w_{l \mu}^l = \varepsilon_{lmn} (\mu n | V_{\text{ne}} V_{\text{ne}}) = -w_{l \mu}^l, \quad \varepsilon_{lmn} = \partial_{\mu n}, \]  

(14)

where \( \varepsilon_{lmn} \) is the Levi-Civita symbol. The effective one-body spin–orbit integrals \( g_{X,Y} ^{J,L} (X, Y \in \{E, S\}) \) are defined as [134]

\[ g_{\mu \nu}^{L,J} = -2 \sum_{\lambda, \kappa} K_{\mu \lambda, \nu \kappa} P_{\lambda \kappa} = -g_{\mu \nu}^{L,J}, \quad l \in \{x, y, z\}, \]  

(15)

\[ g_{\mu \nu}^{L,J} = -2 \sum_{\lambda, \kappa} (K_{\mu \lambda, \nu \kappa} + K_{\lambda \kappa, \nu \mu}) P_{\lambda \kappa} = -g_{\mu \nu}^{L,J}, \]  

(16)

\[ g_{\mu \nu}^{L,J} = -2 \sum_{\lambda, \kappa} (K_{\mu \lambda, \nu \kappa} - K_{\lambda \kappa, \nu \mu}) P_{\lambda \kappa} = -g_{\mu \nu}^{L,J}, \]  

(17)

\[ K_{\mu \nu, \lambda \kappa} = \sum_{mn} \varepsilon_{lmn} (\mu n | V_{\text{ne}} | \kappa \lambda), \]  

(18)

where \( P = \frac{1}{2} (P^o + P^s) \) is the real-valued, spin-averaged molecular density matrix, with \( P^o \) and \( P^s \) being the converged sf-X2C-restricted open-shell Hartree–Fock (ROHF) spin density matrices. The terms (16) and (17) as well as the first two terms in equation (18) arise from the Coulomb-exchange interaction and represent the so-called spin-same-orbit coupling, whereas the term (15) and the third term of equation (18) originate from the Gaunt-exchange interaction and hence represent the spin-other-orbit coupling. The Gaunt-direct interaction vanishes due to spin averaging. Note in passing that \( w^l \) (14) and \( g_{X,Y} ^{J,L} \) (15)–(18) are all real-valued and antisymmetric. It deserves to be mentioned that \( H_{so} \) (5) will reduce to [134] on the mean-field Breit–Pauli spin–orbit Hamiltonian or the original mean-field so-DKH1 [140, 141] if both the decoupling matrix \( X_0 (11) \) and the renormalization matrix \( R_{+,0} (9) \) are set to identity or the free-particle counterparts in \( h_{\text{SO},1e} \) (12) and \( f_{\text{SO},2e} \) (13). It is hence clear that so-DKH1 gains accuracy without overhead, as demonstrated before [89, 90, 133, 142].

To facilitate the use of the spin-dependent unitary group approach [80, 143] for SOC, we further convert the so-DKH1 operator \( H_{so} \) (5) from Cartesian to tensor form

\[ H_{so} = \sum_{pq} \left[ H_{so,1e}^l \right]_{pq} T_{pq}^l - 1 + \left[ H_{so}^0 \right]_{pq} T_{pq}^0 + \left[ H_{so}^{-1} \right]_{pq} T_{pq}^{-1}, \]  

(21)

\[ H_{so}^l = \frac{l}{2} H_{so}^l - H_{so}^l, \]  

(22)

\[ T_{pq}^{-1} = \frac{1}{2} (a_{pq}^l a_{pq} - a_{pq}^l a_{pq}), \]  

(23)

The matrix elements of the rank-1 tensor operator \( T_{pq}^{-1} \) over \{\{JdSM\} \} \_{M=-S} \text{ and } \{\{JdSM\} \}_{M=-S} \text{ then read}
where $|d_{n+1}\rangle$ refers to a CSF with $n + 1$ spatial orbitals, which can be characterized by padding the step number $d_{n+1}$ to the end of $d$. This means that such matrix elements can be calculated in terms of the $U(n+1)$ generators, by only slight modifications of the current implementation of TUGA [112]. The step numbers $d'_{n+1}$ and $d_{n+1}$ as well as the spin $S_{n+1}$ are determined by $S'$ and $S$ as follows:

\[
\begin{align*}
S_{n+1} &= S + \frac{1}{2}, & d'_{n+1} &= 1, d_{n+1} = 1, & \text{if } S' = S, \\
S_{n+1} &= S - \frac{1}{2}, & d'_{n+1} &= 2, d_{n+1} = 2, & \text{if } S' = S, \\
S_{n+1} &= S + \frac{1}{2}, & d'_{n+1} &= 2, d_{n+1} = 1, & \text{if } S' = S + 1, \\
S_{n+1} &= S - \frac{1}{2}, & d'_{n+1} &= 1, d_{n+1} = 2, & \text{if } S' = S - 1.
\end{align*}
\]

For the case of $S = S$, we adopt here $S_{n+1} = S + \frac{1}{2}$. In view of the Wigner–Eckart theorem, the left-hand side of equation (24) can further be simplified to

\[
\langle d'S'M'|T_{pq}^{1\gamma}|dS\rangle = \langle d'S'|T_{pq}^{1\gamma}|dS'\rangle - \langle d'S'|T_{pq}^{1\gamma}|dS\rangle.
\]

where the reduced matrix elements can be calculated as

\[
\langle d'S'|T_{pq}^{1\gamma}|dS\rangle = \frac{(-1)^{S'+M'}S^{1}\frac{1}{2}}{\sqrt{3}} \left( \begin{array}{c} S' \\ S \end{array} \right)
\]

\[
\times \left( \begin{array}{c} 1 \\ \frac{1}{2} \phi \end{array} \right) S^{n+1} \frac{1}{2} \left( \begin{array}{c} 1 \\ \phi \end{array} \right) S_{n+1}.
\]

\[
(27)
\]

3. Double group and time reversal symmetries

Unlike the spin-free case, the spin and spatial degrees of freedom are coupled in the presence of SOC. In particular, for a system of odd number of electrons, the eigenfunctions of the Hamiltonian (3) have a half-integral spin and hence change sign under a rotation $2\pi$ about an arbitrary axis. Such an operation (denoted as $E$) commutes with all symmetry operations and can hence be added into a single group $G$, thereby doubling the order $|G|$ of the group. The so-obtained group $G'$ is hence called double group, even though the number of irreps is not doubled (the original and extra irreps are called boson and fermion irreps, respectively). Consider $D_{2h}$, which is a non-abelian subgroup of $SU(2) \times C_2$, with $C_2 = \{E, i\}$ being the inversion point group. Since the elements of $SU(2)$ can be parameterized in the spin ($\alpha, \beta$) basis as

\[
R^\mp(\vec{n}, \varphi) = \exp \left(-\frac{i}{2} \varphi \vec{\sigma} \cdot \vec{n}\right), \quad \varphi \in [0, 4\pi]
\]

\[
= I_2 \cos \frac{\varphi}{2} - i (\vec{\sigma} \cdot \vec{n}) \sin \frac{\varphi}{2},
\]

where $\vec{\sigma}$ and $I_2$ being the vector of Pauli spin matrices and two-dimensional unit matrix, respectively, it is easy to see that every element $g$ of $D_{2h}$ can be factorized as

\[
g = abc, \quad a \in \{I_2, -I_2\}, \quad b \in \{I_2, -I_2\}, \quad c \in \{E, i\},
\]

\[
\text{where } -\sigma_i \text{ is just } R^\mp(\mu, \pi) \text{ with } \mu = x, y, z, \text{ whereas } -I_2 \text{ in group } B \text{ is just } E \text{ for it is equal to } R^\mp(\vec{n}, 2\pi) \text{ regardless of the rotation axis } \vec{n}. \text{ By definition, the inversion } i \text{ acts trivially on spin coordinates. Likewise, the elements in B act trivially on spatial coordinates. In contrast, the elements in A act on both spin and spatial coordinates and should be reinterpreted as operations } E, C_{2x}, C_{2y}, C_{2z}, \text{ respectively, when acting on spatial coordinates. That is, in the absence of } B, \text{ we will have } A = D_2 \text{ and hence } A \times C_i = D_{2h}. \text{ Since any element } g \text{ of } D_{2h} (\text{and its subgroups}) \text{ does not mix CSFs of different spins or of the same spin but different Shavitt step vectors, it is necessary to consider only the action of } g \text{ on the components } \{[d'dm]\},
\]

\[
|\text{d}| = [A([\phi_1 \otimes \phi_2 \otimes \cdots \otimes |\phi_{n} \otimes |\phi_{M}\rangle)], \quad M \in [-S,S],
\]

\[
\text{of a single CSF } |d|, \text{ Here, the spatial orbitals have been adapted to the 1D irreps of } G \text{ (and hence } G'). \text{ Since the anti-symmetrizer } A \text{ commutes with } g, \text{ the action of } g \text{ takes the following form}
\]

\[
g|\text{d}|M = A [(|\phi_1 \otimes \phi_2 \otimes \cdots \otimes |\phi_{n}\rangle)\otimes |\phi_0\rangle] \otimes |\phi_{M}\rangle, \quad M \in [-S,S].
\]

\[
(32)
\]

The spin rotation matrices $S^{(i)}$ are constructed explicitly in appendices A and B.

The so-constructed symmetric many-electron basis functions $\{[d|]\}$ can further be made to form Kramers pairs via time reversal symmetry (see appendix B), so as to make the Hamiltonian matrix well structured, viz. real for all binary double groups in the case of an even number of electrons and quaternion (for $C_d$ and $C_{2h}$, cf (B.8)), complex (for $C_{1v}$, $C_{2v}$ and $C_{2h}$, cf. (B.9)) or real (for $C_{2v}$, $D_2$ and $D_{2h}$, cf (B.10)) in the
case of an odd number of electrons. Compared with no use of any symmetry, the computational cost can be reduced by a factor of \( |G|^2 \) [NB: due to uneven distributions of the symmetrized functions among the irreps, the actual reduction of the computational cost may be somewhat less than this idea factor]. It has been shown [80] that, for an odd number of electrons, the Hamiltonian matrix can also be made real-valued for \( C_1, C_2, C_3, \) and \( C_5 \), by adding in a non-interacting electron. However, the CI space is then doubled (because of the spin-up and spin-down couplings of the extra electron, cf equation (25)) and hence has no particular advantage over the direct use of complex algebra.

### 4. SOCI and ICISO

Having introduced the two-step sf-X2C + so-DKH1 Hamiltonian and symmetrized many-electron basis functions, it is necessary to outline the icIPPT2 approach [112, 113] for accurate descriptions of strongly correlated electrons [144, 145]. Like other selected CI, icIPPT2 proceeds in two steps, selection of important configurations for static correlation and perturbative treatment of the first-order interacting space \( Q \) for dynamical correlation. As stated before, only slight modifications of the TUGA code [112] are necessary to handle SOC. Since different components of a CSF \(|Jd\rangle\) are generally mixed by spin–orbit interaction, it is natural to include all the components \(|J^\mu d\rangle\) of a double group and time reversal adapted CSF once one component is selected. Moreover, care should be taken of the invariance of a degenerate manifold \( \{ E_{k}^{(0)}; |\Psi_{k}^{(0)}\rangle = \sum_{d} |Jd\rangle |C_{(d);k}\rangle \}_{k=1}^{N_{d}} \) of state \( k \) upon a unitary transformation within the manifold. Keeping these restrictions to the reference space \( P_{0} \), the selection criteria can be set up as follows.

A configuration \(|Jd\rangle \in P_{0}\) of spin \( S \) can interact with a configuration \(|I\rangle \in Q = 1 - P_{0}\) of spin \( S' = S, S \pm 1\), with the interaction matrix elements being \( \langle Jd|H|Id\rangle \equiv H_{d}^{d' d'} \). Note that the diagonal elements \( H_{d}^{d' d'} \) reduce to \( (H_{d}^{d' d'})_{\mu' \mu'} = \frac{1}{N_{d}} \delta_{\mu' \mu'} \) (independent of \( \mu' \)), because \( (H_{so})_{\mu' \mu'} = 0 \) due to the antisymmetry of \( H_{so} \). To simplify the notation, we further define the following quantities:

\[
A_{d;\delta,k}^{d' d} = \frac{1}{N_{d}} \sum_{j=1}^{N_{d}} \sum_{\mu' = 1}^{\mu_{d}} |\langle Jd|H|Id\rangle (C_{(d);k}\rangle, C_{(d');j}\rangle)^{2} | \equiv \frac{1}{N_{d}} \sum_{j=1}^{N_{d}} (Jd|H|Id\rangle)_{\mu' \mu'} (C_{(d);k}\rangle, C_{(d');j}\rangle)^{2} \]

\[
A_{d;\delta,k}^{d' d} = \frac{1}{N_{d}} \sum_{j=1}^{N_{d}} \sum_{\mu' = 1}^{\mu_{d}} |\langle Jd|H|Id\rangle (C_{(d);k}\rangle, C_{(d');j}\rangle)^{2} | \equiv \frac{1}{N_{d}} \sum_{j=1}^{N_{d}} (Jd|H|Id\rangle)_{\mu' \mu'} (C_{(d);k}\rangle, C_{(d');j}\rangle)^{2} \]

which are obviously invariant with respect to unitary transformations of the degenerate manifold of state \( k \) due to the averaging. Following the previous iCI criteria [113], we then have

(a) If \(|I\rangle\) is identical with or singly excited from \(|J\rangle\), then

\[
\max_{d,k} A_{d;\delta,k}^{d' d} \geq C_{\min} \quad \text{and} \quad \max_{d,k} A_{d;\delta,k}^{d' d} \geq C_{\min}, \quad (37)
\]

(b) If \(|I\rangle\) is doubly excited from \(|J\rangle\), only \( H_{d} \) is involved, then

\[
\max_{d,k} H_{d} \geq C_{\min} \quad \text{and} \quad \max_{d,k} A_{d;\delta,k}^{d' d} \geq C_{\min}, \quad (38)
\]

In detail, for case (a), loop over all symmetry adapted CSFs \(|Jd\rangle\) associated with configuration \(|I\rangle \in Q \) and evaluate \( A_{d;\delta,k}^{d' d} \) and \( A_{d;\delta,k}^{d' d} \) for all CSFs \(|Jd\rangle \in P_{0}\). If \( \max_{d} \max_{k} A_{d;\delta,k}^{d' d} \) or \( \max_{d} \max_{k} A_{d;\delta,k}^{d' d} \) is larger than \( C_{\min} \) then evaluate the diagonal matrix elements \( H_{d}^{d' d'} \); otherwise discard \(|Jd\rangle\). If \( \max_{d} \max_{k} A_{d;\delta,k}^{d' d} \) is larger than \( C_{\min} \) then \(|Jd\rangle\) is selected.

As for case (b), only those doubly excited configurations \(|I\rangle\) with the estimated, CSF-independent two-body integrals \( \langle H_{d}^{d' d'} \rangle \) (see reference [112]) larger than \( C_{\min}/\max_{k} \sqrt{\frac{1}{N_{d}} \text{Tr}(C_{k}^{(d)\dagger} C_{k}^{(d)})} \) need to be generated (i.e., those unimportant ones are never touched, just like determinant-based heat-bath CI [122]). For such \(|I\rangle\), the remaining step is the same as case (a).

The above ranking procedure expands the reference \( P_{0} \) to \( P_{1} \), which is diagonalized by the iterative vector interaction (IVI) approach [146, 147]. Those CSFs of coefficients smaller in absolute value than \( C_{\min} \) are then pruned away, leading to \( P_{1} \). The procedure is iterated until \( P_{1} = P_{2} \) are sufficiently similar in compositions. It has been shown [113] that such combined integral- and coefficient-driven, ranking-pruning selection scheme is highly efficient in building up iteratively a compact variational space \( P \).

What has been described so far is a procedure that selects important CSFs for both static correlation and SOC. Given the weak interplay in between, one can simply invoke conditions (37) and (39) to select iteratively important CSFs of spins \( S - 1 \), \( S \) and \( S - 1 \) for static correlation alone and then invoke condition (38) to select non-iteratively additional singly excited CSFs important for SOC. Although not documented here, it has been confirmed numerically that such combined and separate selections lead to virtually identical results for systems considered here. Therefore, the latter will be used throughout.
Upon termination of the selection, the residual dynamic correlation is estimated by using the state-specific Epstein–Nesbet type of second-order perturbation theory (ENPT2):

$$E_{r,k}^{(2)} = \sum_{|\boldsymbol{j}^d\mu^k|\in Q} \left| \frac{\langle \boldsymbol{j}^d\mu^k|H|\Psi^{(0)}_{kl} \rangle}{E_k^{(0)} - \|\tilde{\boldsymbol{j}}\tilde{\mu}\tilde{r}\tilde{d}\|} \right|^2$$

$$= \sum_{|\boldsymbol{j}^d\mu^k|\in Q} \frac{\left| \sum_{|\boldsymbol{j}^d\mu^k|\in P,|\boldsymbol{j}^d\mu^k|\neq|\boldsymbol{j}^d\mu^k|\in P} H_{\tilde{j}\tilde{d}\tilde{r}\tilde{d}'} |C_{\tilde{j}\tilde{d}\tilde{r}\tilde{d}'}^{(0)}| \right|^2}{E_k^{(0)} - \|\tilde{\boldsymbol{j}}\tilde{\mu}\tilde{r}\tilde{d}\|}$$

(39) which can be reexpressed as [120]

$$E_{r,k}^{(2)} = \tilde{E}_{r,k}^{(2)} - E_{c,k}^{(2)}$$

(40)

$$\tilde{E}_{c,k}^{(2)} = \sum_{|\boldsymbol{j}^d\mu^k|\in P,|\boldsymbol{j}^d\mu^k|\neq|\boldsymbol{j}^d\mu^k|\in P} \frac{\left| \sum_{|\boldsymbol{j}^d\mu^k|\in P} H_{\tilde{j}\tilde{d}\tilde{r}\tilde{d}'} |C_{\tilde{j}\tilde{d}\tilde{r}\tilde{d}'}^{(0)}| \right|^2}{E_k^{(0)} - \|\tilde{\boldsymbol{j}}\tilde{\mu}\tilde{r}\tilde{d}\|}$$

(41)

$$\tilde{E}_{c,k}^{(2)} = \sum_{|\boldsymbol{j}^d\mu^k|\in P} \frac{\left| \sum_{|\boldsymbol{j}^d\mu^k|\in P} H_{\tilde{j}\tilde{d}\tilde{r}\tilde{d}'} |C_{\tilde{j}\tilde{d}\tilde{r}\tilde{d}'}^{(0)}| \right|^2}{E_k^{(0)} - \|\tilde{\boldsymbol{j}}\tilde{\mu}\tilde{r}\tilde{d}\|}$$

(42)

where the use of the relation $\langle \boldsymbol{j}^d\mu^k|H|\Psi^{(0)}_{kl} \rangle = C_{\tilde{j}\tilde{d}\tilde{r}\tilde{d}'}^{(0)} E_k^{(0)}$ has been made when going from equations (44) to (45). This reformulation avoids the expensive double-check of the excited CSFs belonging to $Q$ or $P$. The use of pre-ordered arrays [113] for Timsorting [148, 149] the residues [121, 150] involved in the constraint-based [120] ENPT2 allows a massive parallel implementation.

The above formulation defines SoIC and which treats electron correlation and SOC on an equal footing and hence leads to the one-step family of methods outlined in the Introduction. It can be simplified in two ways: (1) only those CSFs with coefficients larger in absolute value than $C^{\text{SO}_0}_{\text{min}}$ (e.g., $10^{-4}$, which is larger $C^{\text{min}}$) are employed as references to select additionally singly excited CSFs for SOC with condition (38). Although the ENPT2 correlation corrections have to be evaluated twice (one for sf-X2C-iCIPT2 with $C^{\text{min}}$ and the other for SoIC with $C^{\text{SO}_0}_{\text{min}}$), there is still a gain in efficiency when $C^{\text{min}}$ is much smaller than $C^{\text{SO}_0}_{\text{min}}$. Moreover, if wanted, only the sf-X2C-iCIPT2 energies need to be extrapolated with different $C_{\text{min}}$. This ansatz may be termed intermediate SoIC (iSoIC). (2) A more dramatic simplification follows directly the idea of state interaction, that is, an effective spin–orbit Hamiltonian matrix in the basis of a small number of correlated scalar states is constructed and diagonalized. More specifically, the diagonal elements herein are the sf-X2C-iCIPT2 energies, whereas the off-diagonal elements are the spin–orbit interactions between the zeroth-order wave functions within the $P$ space selected by the spin-free counterpart [113] of conditions (37) and (39). Note that iSoIC cannot be viewed simply as a contracted version of SoIC since the spin-dependent selection of configurations with condition (38) is not invoked therein. An illustration of SoIC and iSoIC is plotted in figure 1.

5. Results and discussion

5.1. Generality

It is well known that the heavy $p$-block elements in the periodic table are most challenging to the treatment of SOC, because the $np_{1/2}$ spinors are weakly singular in the vicinity of the nuclear position and have very different spatial extensions from $np_{3/2}$. While these features can readily be resolved if SOC is treated variationally already at the mean-field level, they do impose a serious issue when SOC is postponed to the correlation step, for the chosen (contracted) scalar $np$ orbitals are close to $np_{1/2}$ but are very different from $np_{3/2}$ in spatial extensions. This means essentially that single excitations to the ‘right’ virtual orbitals (e.g., those with nodes close to the maximum of $np$ and extrema on the two sides) ought to be captured, so as to bring in biased polarization of $np$ towards $np_{1/2}$ (i.e., spin-dependent orbital relaxation). The question is how to identify such ‘right’ virtual orbitals in an automatic manner. In principle, one can perform a selection of configuration with some criterion involving the SOC matrix elements, e.g., condition (38) adopted here. However, such selection may be dangerous. For instance, when working with an uncontracted basis with steep functions, very likely some virtual orbitals that are very high in energy but are very local (HELO) in space will be picked up (because of appreciable spin–orbit integrals), but they correspond to ‘anti-bonding’ orbitals of innermost core orbitals and therefore have nothing to do with the spin–orbit splitting (SOS) of a valence $np$ orbital. As a matter of fact, including such HELOs usually worsens the
result if the innermost core orbitals are not included in the treatment of electron correlation (which is usually the case). To avoid such situation, we borrow the idea of virtual space decomposition (VSD) [145] designed originally to reduce the correlation space. Specifically, a small set of orthonormal AO\(\{\chi_{\mu}\}_{\mu=1}^{N}\) derived by symmetric orthonormalization of, e.g., a scalar relativistic effective core potential (SRECP) DZP basis, can be used to map out a reduced set of virtual orbitals \(\{\psi_{b}^{\text{vir}}\}\)

from the all-electron virtual orbitals \(\{\psi_{b}^{\text{NS}}\}\) by a singular value decomposition of the overlap

\[
\langle \chi_{\mu} | \psi_{a} \rangle = (L\lambda R)_{\mu a},
\]

followed by the rotation of the virtual orbitals

\[
|\psi_{b}^{\text{vir}}\rangle = \sum_{b=1}^{N_{\text{vir}}} |\psi_{b}\rangle R_{ba}.
\]

Those \(\{|\psi_{b}^{\text{vir}}\rangle\}\) with \(N_{\text{vir}}^{C_{\text{vir}}} = N^{5} + N_{\text{core}} - N_{\text{occ}}\) largest singular values \(\lambda_{a}\) are then taken as the effective virtual orbitals. Here, \(N_{\text{occ}}\) is the total number of doubly occupied and active orbitals in the all-electron calculation. In this way, both the \(N_{\text{core}}\) innermost core orbitals (corresponding to those replaced by SRECP) and their ‘anti-bonding’ virtual orbitals are removed, leaving a set of all-electron orbitals that are suitable for both correlation and SOC. Another issue that deserves attention lies in that SOC and correlation require different configuration spaces to describe, for they have very different physical origins [one-body spin–orbit (magnetic) vs two-body Coulomb interaction]. For instance, it is often the case that a good result for the SOS of a valence \(np\) configuration can be obtained by correlating just a small number of electrons in a small number of valence orbitals, but the result may deteriorate significantly when the number of correlated electrons or orbitals is increased individually [84, 94, 98].

In short, the number of electrons (or occupied orbitals) as well as the number and character of virtual orbitals must be chosen carefully to achieve a balanced description of SOC and correlation in \(p\)-block elements. In contrast, the \(d\)-block elements are much easier as far as SOC is concerned, simply because the \(nd_{3/2}\) and \(nd_{5/2}\) spinors are very much the same in spatial extensions. However, electron correlation is the major issue therein, particularly when configurations of different \(d\) occupations are nearly degenerate.

To confirm the above points on one hand and test the proposed SOICl and iCISO methods on the other, we take atomic (section 5.2) and diatomic (section 5.3) \(p\)-block systems as well as the Os atom (section 5.4) as examples. Spin-free X2C state-averaged (SA) CASSCF calculations with the (contracted) relativistic ANO-RCC basis sets [151, 152] were performed to generate the MOs, under the \(D_{6h}\) and \(C_{2v}\) symmetries for the atoms and molecules, respectively. For CAS(12e, 12o) and smaller active spaces, no selection was performed, whereas for active spaces larger than CAS(12e, 12o), the iCISC approach [153] (which employs selected iCl [114] as the active space solver) was adopted to obtain near-exact CASSCF solutions. When necessary, the SOICl energies were extrapolated linearly with five \(C_{\text{min}}\) values \(\{10.0, 7.0, 5.0, 3.0, 1.5\} \times 10^{-5}\). The standard deviation for the extrapolated SOS is estimated according to

\[
\sigma = \sqrt{\sigma_{0}^{2} + \sigma_{1}^{2}},
\]

with \(\sigma_{0}\) and \(\sigma_{1}\) being the standard deviations for the extrapolated energies of the ground and excited states.

Table 1. SOS (in \(\text{cm}^{-1}\)) of halogen \(2^p\) calculated by SOICl(2) and iCISO(2) with the sf-X2C + so-DKH1 Hamiltonian and the ANO-RCC basis sets [152] and various active spaces. In parentheses are standard deviations of linear extrapolations (cf table 2).

| Atom | Method | Active space | Expt. |
|------|--------|--------------|-------|
|      | SOICl(2) | (7e, 8o)\(^a\) | (7e, 87o)\(^c\) | 405 |
|      | iCISO(2) | (7e, 8o)\(^b\) | (7e, 87o)\(^c\) | 398 |
| F    | SOICl(2) | 405 | 401 | 398(1) |
|      | iCISO(2) | 405 | 401 | 398 |
| Cl   | SOICl(2) | 829 | 837 | 807(3) |
|      | iCISO(2) | 829 | 835 | 805 |
| Br   | SOICl(2) | 3429 | 3479 | 3378(1) |
|      | iCISO(2) | 3429 | 3434 | 3298 |
| I    | SOICl(2) | 7024 | 7138 | 7144(1) |
|      | iCISO(2) | 7024 | 6938 | 6670 |

\(^a\)CASSCF(5e, 3o) orbitals (identical with CASSCF(7e, 4o)).

\(^b\)CASSCF(7e, 8o) orbitals.

\(^c\)Including all virtual orbitals from CASSCF(7e, 8o).

\(^d\)ICSCF(13e, 16o) orbitals.

\(^e\)Including all virtual orbitals from ICSCF(13e, 16o).

\(^f\)ICSCF(17e, 18o) orbitals.

\(^g\)Including all virtual orbitals from ICSCF(17e, 18o).

\(^h\)Experiment [158].

[Note: The rest of the table content is not transcribed here due to the page limit.]
spinor states, respectively. Following the previous notation [153], SOCl/\text{CiSO} will be denoted as SOCl(2)/\text{CiSO}(2) if ENPT2 is performed only within the active space. All calculations were performed with the BDF program package [154–157].

5.2. SOS of p-block atoms

The halogen atoms (F to I) as well as the Pb and Bi atoms have very simple ground states resulting from the open-shell np orbital and are therefore ideal systems for examining the previous general arguments. The simplest active space for np have very simple ground states resulting from the open-shell spinor states, respectively. Following the previous notation [153], SOCl/\text{CiSO} will be denoted as SOCl(2)/\text{CiSO}(2) if ENPT2 is performed only within the active space. All calculations were performed with the BDF program package [154–157].

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Figure 2. Linear extrapolations of the SO\textsubscript{C}(2) energies of \textsuperscript{2}P\textsubscript{1/2} and \textsuperscript{2}P\textsubscript{3/2} of iodine versus the absolute second-order correlation energies \(|E_{\text{c}}^{(2)}|\) (17 electrons in all virtual orbitals).

Table 3. SA-iCISCF(14e, 18o) orbital-based SO\textsubscript{C}(2) energies (in cm\(^{-1}\)) for the low-lying spinor states of Pb relative to the ground state \(^3\)P\textsubscript{0}. In parentheses are standard deviations of linear extrapolations.

| Active space | \(^3\)P\textsubscript{1} | \(^3\)P\textsubscript{2} | \(^1\)D\textsubscript{2} | \(^1\)S\textsubscript{0} |
|--------------|----------------|----------------|----------------|----------------|
| CAS(14e, 18o)\textsuperscript{a} | 6845(3) | 10606(2) | 21302(2) | 31877(2) |
| CAS(20e, 21o)\textsuperscript{b} | 6322(4) | 10012(4) | 20266(4) | 30776(3) |
| CAS(14e, 144o)\textsuperscript{c} | 8838(38) | 11704(40) | 23480(31) | 31557(27) |
| CAS(20e, 147o)\textsuperscript{d} | 7937(5) | 10826(15) | 20961(8) | 28711(39) |
| Expt.\textsuperscript{e} | 7819 | 10650 | 21458 | 29467 |

\textsuperscript{a}14 electrons in 5s\textsuperscript{6}d\textsuperscript{6}\textsuperscript{7}s\textsuperscript{7}\textsuperscript{7}p\textsuperscript{7} orbitals.
\textsuperscript{b}20 electrons in 5p\textsuperscript{5}d\textsuperscript{6}\textsuperscript{6}s\textsuperscript{6}\textsuperscript{7}p\textsuperscript{7}d\textsuperscript{7} orbitals.
\textsuperscript{c}14 electrons in 5d\textsuperscript{6}\textsuperscript{7}s\textsuperscript{7}\textsuperscript{7}p\textsuperscript{6} orbitals.
\textsuperscript{d}20 electrons in 5p\textsuperscript{5}d\textsuperscript{6}\textsuperscript{6}p\textsuperscript{7}d\textsuperscript{8} orbitals.
\textsuperscript{e}Experiment [158].

Table 4. SA-iCISCF(20e, 21o) orbital-based SO\textsubscript{C}(2) energies (in cm\(^{-1}\)) for the low-lying spinor states of Pb relative to the ground state \(^3\)P\textsubscript{0}. In parentheses are standard deviations of linear extrapolations.

| Active space | \(^3\)P\textsubscript{1} | \(^3\)P\textsubscript{2} | \(^1\)D\textsubscript{2} | \(^1\)S\textsubscript{0} |
|--------------|----------------|----------------|----------------|----------------|
| CAS(20e, 21o)\textsuperscript{a} | 6510(4) | 10170(4) | 20456(4) | 30647(4) |
| CAS(20e, 30o)\textsuperscript{b} | 6437(4) | 10040(4) | 20105(4) | 29610(3) |
| CAS(20e, 39o)\textsuperscript{c} | 6027(6) | 9443(5) | 19008(4) | 27824(3) |
| CAS(20e, 48o)\textsuperscript{d} | 6476(3) | 9905(3) | 19786(5) | 28393(9) |
| CAS(20e, 147o)\textsuperscript{e} | 8007(19) | 10825(13) | 21252(13) | 29019(13) |
| MRCISD\textsuperscript{f} | 7633 | 10683 | 21507 | 29707 |
| Expt.\textsuperscript{g} | 7819 | 10650 | 21458 | 29467 |

\textsuperscript{a}20 electrons in 5p\textsuperscript{5}d\textsuperscript{6}\textsuperscript{7}s\textsuperscript{7}\textsuperscript{7}p\textsuperscript{6}d\textsuperscript{8} orbitals.
\textsuperscript{b}20 electrons in 5p\textsuperscript{5}d\textsuperscript{6}\textsuperscript{7}s\textsuperscript{7}\textsuperscript{7}p\textsuperscript{6}d\textsuperscript{8}8\textsuperscript{8}s\textsuperscript{8}p\textsuperscript{7}d\textsuperscript{8} orbitals.
\textsuperscript{c}20 electrons in 5p\textsuperscript{5}d\textsuperscript{6}\textsuperscript{7}s\textsuperscript{7}\textsuperscript{7}p\textsuperscript{6}d\textsuperscript{8}9\textsuperscript{9}s\textsuperscript{9}p\textsuperscript{8}d\textsuperscript{10} orbitals.
\textsuperscript{d}20 electrons in 5p\textsuperscript{5}d\textsuperscript{6}\textsuperscript{7}s\textsuperscript{7}\textsuperscript{7}p\textsuperscript{6}d\textsuperscript{8}9\textsuperscript{9}s\textsuperscript{9}p\textsuperscript{10}d\textsuperscript{10} orbitals.
\textsuperscript{e}20 electrons in 5p\textsuperscript{5}d\textsuperscript{6}\textsuperscript{7}s\textsuperscript{7}\textsuperscript{7}p\textsuperscript{6}d\textsuperscript{8}10\textsuperscript{10}s\textsuperscript{10}p\textsuperscript{11}d\textsuperscript{11} orbitals.
\textsuperscript{f}Two-component large-core pseudopotential and core-polarization potential based MRCISD [159].
\textsuperscript{g}Experiment [158].

original ANO-RCC basis [151]. This is because the steepest p-functions in p-ANO-RCC have somewhat less contributions to the valence p orbitals than those in the ANO-RCC basis. Therefore, to keep a balance between correlation and SOC, the \((n-1)d^{10}ns^{2}np^{5}\) electrons of I (and Br) should be correlated in a generally contracted basis.
Table 5. SA-iCISCF(21e, 21o) orbital-based SOCl(2) energies (in cm⁻¹) for the low-lying spinor states of Bi relative to the ground state ⁴S₈/₅. In parentheses are standard deviations of linear extrapolations.

| Active space | ²D₃/₂ | ²D₅/₂ | ²P₁/₂ | ²P₃/₂ |
|--------------|-------|-------|-------|-------|
| CAS(21e, 21o)ᵃ | 11.997(2) | 16.344(2) | 23.920(2) | 32.114(2) |
| CAS(21e, 133o)ᵇ | 11.121(35) | 15.293(47) | 21.382(46) | 33.149(45) |
| Expt.ᶜ | 11.419 | 15.438 | 21.661 | 33.165 |

ᵃ21 electrons in 5p⁷5s⁶5p⁶5s²5p₆6p₁ orbitals.
ᵇ21 electrons in 5p⁷5s⁶5p₆6p and all virtual orbitals.
ᶜExperiment [158].

Table 6. SOS (in cm⁻¹) of halogen atoms calculated by different methods. In parentheses are standard deviations of linear extrapolations (cf table 2).

| Atom | SOCl(2) | SOS HCI(2)ᵃ | EOM-CCSD(SOC)b | X2Cmmf-FSCCSDᶜ | Expt.ᵈ |
|------|---------|-------------|----------------|----------------|-------|
| F    | 398(1)⁹ | 399         | 398            | 421            | 404   |
| Cl   | 871(1)  | 866(1)      | 876            | 907            | 882   |
| Br   | 3745(58) | 3454(93)    | 3649           | 3723           | 3685  |
| I    | 7416(38) | 7487(62)    | 7755           | 7752           | 7603  |

⁹Spin–orbit stochastic heat-bath CI [90].
ᵇReference [89] (SOC included perturbatively in the CCSD step).
ᶜReference [89] (spinor-based Fock space CCSD).
ᵈExperiment [158].

Table 7. SOS (in cm⁻¹) of XO and XF calculated by CAS (1e, 2o)-SOCl(2).

| Molecule | SOCl(2) | Expt.ᵃ | Molecule | SOCl(2) | Expt.ᵃ |
|----------|---------|--------|----------|---------|--------|
| NO       | 125     | 120    | CF       | 64      | 77     |
| PO       | 239     | 224    | SiF      | 135     | 156    |
| AsO      | 1234    | 1026   | GeF      | 976     | 934    |
| SbO      | 2614    | 2272   | SnF      | 2256    | 2317   |
| BiO      | 8655    | 7089   | PbF      | 7806    | 8264   |

ᵃExperiment [160].

For more details, the SOCl(2) results calculated with the largest active spaces in table 1 and different values for Cₘᵢₙ are shown in table 2. It is first seen that the SOS is very insensitive to Cₘᵢₙ, thereby substantiating the iSOCl approach (which is only briefly mentioned in the end of section 4 and will be discussed in more detail elsewhere). Moreover, the nearly perfect linear relations (cf figure 2 for 1) between the SOCl(2) energies of ²P₃/₂ and ²P₁/₂ and the absolute second-order correlation energies |E_cl²| allows accurate extrapolations to the zero Cₘᵢₙ limit.

As for iCISO(2), the very first choice is to project the so-DKH1 Hamiltonian onto the degenerate manifold of the lowest ²P⁻ state. Not surprisingly, as a very cheap method, iCISO(2) performs very well for the lightest atoms (F and Cl) but fails for the heaviest ones, with Br being the borderline. This is of course due to the lack of spin-dependent orbital relaxation, just like other two-step approaches. Nonetheless, iCISO(2) may perform well for heavy elements when SOC is quenched to a large extent by chemical bondings [89]. Another point that deserves to be addressed is the sensitivity of iCISO(2) on the number of scalar states. At first glance, the scalar states arising from 5s¹⁵p⁶ (²S) and/or 5p⁷6s⁶6p (²P, ²P, ²D, and ²S) should first be added. However, such states are inversion even and hence do not interact with ²P⁻ via SOC. On the other hand, both the ²P and ²D states of 5s¹⁵p⁶6p are energetically too high to have discernible couplings with ²P⁻.

The SOS of Pb is more difficult to describe. First of all, the ²P, ¹D, and ¹S states of 5d¹⁰6s²⁶p² are strongly coupled by SOC and should hence all be included during the selection procedure. Secondly, as indicated by the significant differences between the CAS(20e, 21o)-SOCl(2) results with orbitals optimized by SA-iCISCF(14e, 18o) (see table 3) and SA-iCISCF(20e, 21o) (see table 4), the ⁵P₅ shell should also be included in the orbital optimization, i.e., iCISCF(20e, 21o) averaged equally over the ⁵P, ¹D, and ¹S states of ⁵P₅⁵d¹⁰6s²⁶p². Including all virtual orbitals in the SOCl(2) calculations then yields the best estimate of the SOS of Pb, with the maximal error being ca. 2.5%. Similarly, the ²S, ²P, and ²D states of ⁵P₅⁵d¹⁰6s²⁶p³ should all be included in the SOCl(2) calculations of Bi. As can be seen from table 5, the SA-iCISCF(21e, 21o) orbital-based SOCl(2) SOS of Bi, with all virtual orbitals included, are in very good agreement with experiments.

Finally, a brief comparison should be made between SOCl(2) and other related approaches [89, 90]. As can be seen from table 6 for the halogen atoms, only the SOSHCl(2) (spin–orbit stochastic heat-bath CI) value [90] for the SOS of Br is an outlier to the good agreement in between. Since SOSHCl(2) employs the same two-step sf-X2C + so-DKH1 Hamiltonian (see section 2), their calculations on Br should
As a further test of SOI CI(2) and iCISO(2), we consider the agreement with the previous theoretical values [159].

Table 8. SOS of XO and XF calculated by different methods.

| Molecule | SOI CI(2)\(^a\) | iCISO(2)\(^a\) | EOMEA(SO)-CCSD\(^b\) | EOMEA-CCSD(SO)\(^c\) | Expt.\(^d\) |
|----------|-----------------|----------------|----------------------|----------------------|----------|
| NO       | 120             | 119            | 122                  | 122                  | 120      |
| PO       | 230             | 232            | 230                  | 218                  | 224      |
| AsO      | 958             | 954            | 1089                 | 967                  | 1026     |
| SbO      | 2326            | 2305           | 2518                 | 2142                 | 2272     |
| BiO      | 7542            | 7167           | 7598                 | 6171                 | 7089     |
| CF       | 75              | 75             | 75                   | 78                   | 77       |
| SiF\(^e\) | 166             | 166            | 163                  | 158                  | 156      |
| GeF      | 887             | 882            | 949                  | 907                  | 934      |
| SnF      | 2300            | 2212           | 2288                 | 2176                 | 2317     |
| PbF      | 8586            | 7561           | 7150                 | 6777                 | 8264     |
| PMAE\(^f\) | 3.7±2.0        | 4.1±2.3        | 5.3±3.3              | 5.8±3.9              |          |

\(^a\)ICISCF orbitals with contracted ANO-RCC basis (\(C_{mn} = 5 \times 10^{-6}\)).
\(^b\)Reference [108] (uncontracted ANO-RCC basis; SOC included perturbatively in the EOM step).
\(^c\)Reference [108] (uncontracted ANO-RCC basis; SOC included perturbatively in the CCSD step).
\(^d\)Experiment [160].
\(^e\)Percentage mean absolute error.

Table 9. Energies (in eV) of the low-lying scalar states of Os relative to the ground state 5\(d^66s^2\) (\(^2\)D).

| Configuration | State | CAS(8e, 6o)\(^a\) | CAS(16e, 19o)\(^b\) |
|---------------|-------|-------------------|---------------------|
|               |       | CASSCF             | iCIF2\(^c\)         |
| 5\(d^76s^1\)  | \(^3\)F | 0.93               | 0.451               |
| 5\(d^76s^1\)  | \(^3\)P | 1.157              | 1.211               |
| 5\(d^76s^2\)  | \(^3\)F | 1.466              | 1.371               |
| 5\(d^76s^2\)  | \(^3\)H | 1.716              | 1.784               |

\(^a\)Eight electrons in 5\(d\)f6s orbitals.
\(^b\)16 electrons in 5\(s\)p5\(d\)6s6p6d7f orbitals.
\(^c\)16 electrons in 5\(s\)p5\(d\)6s6p6d7f orbitals (i.e., CASSCF).

be repeated. As for Pb, the SOI CI(2) results are also in good agreement with the previous theoretical values [159].

5.3. SOS of p-block molecules

As a further test of SOI CI(2) and iCISO(2), we consider the isovalent \(^2\)H diatomic molecules XO (X = N, P, As, Sb, Bi) and XF (X = C, Si, Ge, Sn, Pb), at their experimental bond lengths (1.150 77 Å for NO, 1.476 Å for PO, 1.6236 Å for AsO, 1.825 Å for SbO, 1.934 Å for BiO, 1.601 Å for SiF, 1.745 Å for GeF, 1.944 Å for SnF, and 2.0575 Å for PbF) [160].

Following the previous atomic calculations, the minimal active space CAS(1e, 2o) was first considered here. As can be seen from table 7, the results are pretty off. However, unlike the atomic calculations, larger active spaces cannot readily be chosen solely by means of orbital energies. Instead, the iCAS (imposed automatic selection of CAS) approach [161] can be adopted here, which employs valence atomic orbitals (VAO) as probe to select precisely the same number of guess orbitals for CASSCF/iCISCF. Moreover, iCAS imposes the matching of the doubly occupied, active, and virtual subspaces between two adjacent iterations, so as to render the converged CASSCF orbitals as close to the guest orbitals as possible. Specifically, the 2s, 2p, 3s, 3p, 3d atom shells (13 VAOs) for the second row atoms, the 2s, 2p, 3s, 3p, 3d, 4s, 4p atomic shells (17 VAOs) for the third row atoms, and the \((n - 1)d, ns, np, (n + 1)s, (n + 1)p, (n + 1)d\) atomic shells (18 VAOs) for the nth row atoms (\(n > 3\)). Such VAOs can readily be obtained from sf-X2C-HF calculations of spherical, unpolarized atomic calculations. The corresponding active spaces are then CAS(11e, 26o), CAS(19e, 30o), and CAS(21e, 31o) for the 2–2, 3–2, and \(n - 2\) (\(n > 3\)) types of diatomic molecules, respectively (NB: \(n - m\) is short for nth row-mnth row). The so-calculated results are given in table 8. It can be seen that both iCISO(2) and SOI CI(2) work very well for these systems. The former is of course due to the fact that the SOC is quenched substantially as compared to the free atoms. The results are even better than those by the EOMEA-CCSD (equation-of-motion electron affinity coupled-cluster singles and doubles) [108] with all electrons correlated in the uncontracted ANO-RCC basis sets.

5.4. SOS of Os

As a final example, we consider the SOS of Os, a representative of 5\(d\) systems. It turns out that this is an extremely complicated system. According to the experimental data [162], the spiner states mainly of 5\(d^66s^2\) (\(^3\)D) are crossed in energy with those of 5\(d^76s^1\) (\(^3\)F), which are further crossed with those of 5\(d^76s^2\) (\(^3\)F), and the crossing keeps going up to even higher states such as \(^3\)P, \(^3\)F, and \(^3\)H of 5\(d^86s^1\). It should be clear from the outset that the difficulty here resides mainly in electron correlation (due to change in the number of 5\(d\) electrons) rather than SOC (due to proximate radial extensions of 5\(d_{3,2}\) and 5\(d_{5,2}\)). As such, the iCISO approach should work well here. However, the use of \(D_{2h}\) symmetry renders the calculation very difficult: the 5\(d\) orbitals cannot be made fully degenerate (due to the lack of SO(3) symmetry) and all degenerate components of the scalar/spinor states have to be calculated simultaneously (due to the lack of SO(3)/SU(2) symmetry). Specifically, there are in total 33/123 scalar/spinor components from \(^3\)D, \(^3\)F, \(^3\)P, \(^3\)F, and \(^3\)H. The relative
energies of these scalar states are first given in Table 9. It can be seen that the \( ^3F \) state is affected most strongly by dynamic correlation. The relative energies of the spinor states mainly of \( 5d^66s^2 \) (\(^5D\)) are documented in Table 10. The most striking point here is that the reversed ordering \([158, 162]\) of the \( J = 3 \) and \( J = 2 \) states is not reproduced correctly. One possible reason might be that the adopted ANO-RCC basis set (24s21p15d11f4g2h/11s10p9d8f4g2h) \([152]\) is not flexible enough. Anyhow, the present investigation of Os is only preliminary. More extensive and systematic investigations of atomic spectra will be reported in the future.

### 6. Conclusion

Two, two-step relativistic approaches, SOiCl and iCISO, have been proposed to treat scalar relativity and SOC separately. The former amounts to treating SOC and correlation on an equal footing, whereas the latter is rooted in quasi-degenerate perturbation theory and is hence applicable only when spin-dependent orbit relaxation is not significant or when SOC is quenched to a large extent by ligand fields in the case of heavy atoms. The use of both double group and time reversal adapted many-electron basis facilitates greatly not only the computation but also the analysis of spinor wave functions. Although only pilot calculations have been performed to elucidate mainly the conceptual aspects on the interplay between SOC and correlation, there is no doubt that the methods can widely be applied to investigate the SOC in general open-shell systems containing heavy elements.

### Postscript

This work is dedicated to the commemoration of Prof Dr Enrico Clementi, a good friend of one of the present authors (WL), both personally and scientifically. His expertise and ideas in relativistic quantum chemistry and computational chemistry had great influence on WL’s early research.

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### Data availability statement

The data that supports the findings of this study is available within the article.

### Appendix A. Double group symmetry

To complete the discussion of double group symmetry presented in the main text, the spin rotation matrices \( S^{(d)} \) in equation (34) should further be specified. Instead of the parametrization \([29]\), the following parametrization

\[
R^2(\alpha, \beta, \gamma) = \begin{pmatrix}
 e^{-i\frac{\alpha}{2}} & 0 & 0 \\
 0 & e^{i\frac{\beta}{2}} & 0 \\
 0 & 0 & e^{-i\frac{\gamma}{2}}
\end{pmatrix}
\]

\[
S^{(d)}(\alpha, \beta, \gamma) = R^2(\alpha, \beta, \gamma) S \ (\alpha, \beta, \gamma)
\]

where

\[
S^{(d)} = \langle \text{SM} | R^2(\alpha, \beta, \gamma) | \text{SM} \rangle = e^{-i\Omega_{\alpha}^{\beta} R^{(d)}_{MM}(\beta)} e^{-i\Omega_{\gamma}}
\]

in terms of the Euler angles \( \alpha, \beta, \gamma \) is more convenient for the construction of \( S^{(d)} \). Specifically,

\[
S^{(d)}_{MM} = \langle \text{SM} | R^2(\alpha, \beta, \gamma) | \text{SM} \rangle = e^{-i\Omega_{\alpha}^{\beta} R^{(d)}_{MM}(\beta)} e^{-i\Omega_{\gamma}}
\]
Table A1. Reducible spin rotation matrices \( S^{(l)} \) of \( D_5^\ast \) in the basis \( (\langle SM \rangle, |S - M|) \) with \( S \) being an integer.

| \( (\langle SM \rangle, |S - M|) \) | \( E \) | \( E \) | \( -\sigma_x \) | \( -\sigma_y \) | \( -\sigma_z \) | \( -\sigma_x E \) | \( -\sigma_y E \) | \( -\sigma_z E \) |
|-----------------|-------|-------|--------|--------|--------|--------|--------|--------|
| \( M = 0 \)     | 1     | 1     | 1      | 1      | 1      | -1     | 1      | 1      |
| \( M \) odd     | 1 0   | 1 0   | 0 -1   | 0 -1   | 0 1    | 0 1    | 0 1    | 0 1    |
| \( M \) even    | 1 0   | 0 1   | 0 -1   | 0 -1   | 0 1    | 0 1    | 0 1    | 0 1    |

Table A2. Irreducible spin rotation matrices \( S^{(l)} \) of \( D_5^\ast \) in the basis \( (\langle SM \rangle, |S - M|) \) with \( S \) being a half-integer.

\[
S = p + \frac{1}{2}, \ p \ odd
\]

\[
S = p + \frac{1}{2}, \ p \ even
\]

Table B1. The Frobenius–Schur classes (a), (b), and (c) of \( D_{2h} \) and its subgroups. In parentheses are the orders of the groups.

| Boson | Fermion | Point groups |
|-------|---------|--------------|
| a     | a       | \( C_1^\ast (2), C_1^\ast (4) \) |
| b     | b       | \( C_2^\ast (4), C_2^\ast (4), C_2^\ast (8) \) |
| c     | c       | \( C_2^\ast (8), D_5^\ast (8), D_{2h}^\ast (16) \) |

\[
d_{\beta}^{M}(\beta) = \left( (S + M!) (S - M !) (S + M!) (S - M !) \right)^{1/2} 
\times \sum_{s} \left( -1 \right)^{M-M+s} \left( \cos \frac{\beta}{2} \right)^{2M-M-M+2 s} \left( \sin \frac{\beta}{2} \right)^{M-M+2 s} (S + M - s) s ! (M' - M + s) ! (S - M' - s) ! .
\]

(A.3)

The calculation is simplified greatly by noticing that the operations of \( D_5^\ast \) can mix only two spin functions \( |SM\rangle \) and \( |S-M\rangle \). The corresponding matrix elements \( S_{M'M}^{(l)} \) are documented in tables A1 and A2 for even and odd numbers of electrons, respectively. The same spin rotation matrices apply also to \( D_{2h} \), because \( g \in D_{2h} \) can be written as \( g = g' c \) (\( g' \in D_5^\ast \), \( c \in C_1 = \{ E, i \} \)) and the spin rotation matrices of \( C_1 \) are simply unit matrices. The spin rotation matrices of other subgroups can be read from the tables by looking up the corresponding

Table B2. Irreducible spin rotation representations \( S^{(l)} \) of \( D_5^\ast \) in the basis \( |SM\rangle \) \( \text{(B.7)}^* \).

\[
E \ E \ -\sigma_x \ -\sigma_y \ -\sigma_z \ -\sigma_x E \ -\sigma_y E \ -\sigma_z E \ -\sigma_x E \ -\sigma_y E \ -\sigma_z E
\]

\[
S = p + \frac{1}{2}, \ p \ odd

M = q + \frac{1}{2}, \ q \ odd
\]

M = q + \frac{1}{2}, q even
\]

M = q + \frac{1}{2}, q even
\]

M = q + \frac{1}{2}, q even
\]

M = q + \frac{1}{2}, q even
\]

\[
M = q + \frac{1}{2}, q even
\]

M = q + \frac{1}{2}, q even
\]

The calculation is simplified greatly by noticing that the operations of \( D_5^\ast \) can mix only two spin functions \( |SM\rangle \) and \( |S-M\rangle \). The corresponding matrix elements \( S_{M'M}^{(l)} \) are documented in tables A1 and A2 for even and odd numbers of electrons, respectively. The same spin rotation matrices apply also to \( D_{2h} \), because \( g \in D_{2h} \) can be written as \( g = g' c \) (\( g' \in D_5^\ast \), \( c \in C_1 = \{ E, i \} \)) and the spin rotation matrices of \( C_1 \) are simply unit matrices. The spin rotation matrices of other subgroups can be read from the tables by looking up the corresponding
Appendix B. Time reversal symmetry

Double group adapted basis functions do not form naturally Kramers pairs, which can only be achieved by further incorporating properly the time reversal symmetry. As shown [163] before, this can actually be done by a simple unitary transformation of the symmetrized functions.

A set of functions \( \{ \tau \mu i \}, i = 1, \ldots, n_u \) spanning an irrep \( \mu \) of double group \( G' \) will transform among themselves according to

\[
gr{\tau \mu i} = \sum_j \langle \tau \mu j | D_{\mu}^{(i)}(g) \rangle, \tag{B.1}\]

where \( D^{(i)}(g) \) is an \( n_u \)-dimensional unitary matrix corresponding to operation \( g \). The index \( i \) in \( | \tau \mu i \rangle \) indicates that the function belongs to the \( i \)th column of irrep \( \mu \), whereas \( \tau \) serves to distinguish functions of the same \( \mu \) and \( i \). The Hamiltonian matrix over such symmetrized basis functions are block diagonal, i.e.,

\[
\langle \tau \mu i | H | \sigma \nu j \rangle = \delta_{\mu \nu} \delta_{ij} \langle \tau \mu i | H | \sigma \nu i \rangle = \delta_{\mu \nu} \delta_{ij} \langle \tau \mu i | H | \sigma \nu i \rangle. \tag{B.2}\]

Moreover, the fact that the time reversal operation \( T \) commutes with the Hamiltonian \( H \) imposes the following relations between the Hamiltonian matrix elements

\[
\left\langle T \psi_p | H | T \psi_q \right\rangle = \left\langle \psi_p | H | \psi_q \right\rangle^*, \tag{B.3}\]

\[
\left\langle T \psi_p | H | \psi_q \right\rangle = \pm \left\langle \psi_p | H | T \psi_q \right\rangle^*, \quad T^2 \psi_p = \pm \psi_p, \tag{B.4}\]
where the positive and negative signs apply to boson and fermion types of functions, respectively. In particular, it is easy to see from the action of $T$ on the spin functions $|SM⟩^T_{M = −S}$

$$T|SM⟩ = (−1)^{S−M}|S − M⟩,$$  \hspace{1cm} (B.5)

that the spin functions are either boson (if $S$ is an integer for an even number of electrons) or fermion functions (if $S$ is a half-integer for an odd number of electrons).

Since the irreducible representation matrices for the spaces spanned by $\{|τμi⟩\}$ and $\{T|τμi⟩\}$ are related simply by complex conjugation, viz,

$$gT|τμi⟩ = Tg|τμi⟩ = \sum_j D_j^{[τ]}(g)T|τμj⟩,$$  \hspace{1cm} (B.6)

where $M \geq 0$ for $|SM⟩$ and $M > 0$ for $|SM −⟩$. Both $|SM⟩$ and $|SM −⟩$ can serve as a basis for the 1D irreps of $D^g_2$. As such, the corresponding spin rotation matrices $S^{[τ]}$ of $D^g_2$ (obtained from the above transformation of those documented in table A1) become irreducible, see table B2. The associations of $|SM ≥⟩$ with the irreps of $D^g_2$ and its subgroups are further given in table B3. It is trivial to see that the Hamiltonian matrix elements in this basis and hence the CI vectors are real-valued. That is, time reversal symmetry itself will reduce the computational cost by a factor of two as compared with the complex algebra without time reversal symmetry. Further combined with spatial symmetry, a factor of $2G = |G⟩$ will be gained in efficiency.

As for the case of an odd number of electrons, the fermion irreps of $D^g_2$ and its subgroups may belong to class (a), (b) or (c) (cf table B1). Class (a) includes $C^1_g$ and $C^2_g$. In this case, every spin function $|SM⟩$ serves as the basis of a 1D irrep. So is every component $|JdM⟩$ of CSF $|Jd⟩$, see table B4. In particular, $|JdM⟩$ and $T|JdM⟩$ are already Kramers paired, such that the Hamiltonian matrix has the following (quaternion) structure

$$\langle |JdM⟩, T|JdM⟩ \rangle H(|JdM⟩, T|JdM⟩) = \begin{bmatrix} A & B \\ -B^* & A^* \end{bmatrix},$$  \hspace{1cm} (B.8)

in view of equations (B.3) and (B.4). This structure allows a reduction of the memory footprint by a factor of two. However, since the computational cost is dominated heavily by the spin-free two-body terms, there is no much gain in efficiency in the evaluation of the Hamiltonian matrix elements. On the other hand, although both $\{|JdM⟩\}$ and $\{T|JdM⟩\}$ are needed to expand the CI eigenvectors, the number of states is halved due to the Kramers degeneracy between states $|Ψ_k⟩$ and $T|Ψ_k⟩$. As such, the combined use of spatial and time reversal symmetries leads to an overall reduction of the computational cost by a factor of two ($= 2|C^1⟩ = |C^1⟩_0$) and four ($= 2|C^2⟩ = |C^2⟩_0$) for $C^1_g$ and $C^2_g$, respectively.

As can be seen from table B1, the fermion irreps of $C^2_g$ and $C^2_{g0}$ belong to class (b). In this case, every spin function $|SM⟩$ also serves as the basis of a 1D irrep. So is every component $|JdM⟩$ of CSF $|Jd⟩$, see tables B5–B7 for $C^2_g$, $C^2_{g0}$, and $C^2_{g0}$, respectively. Furthermore, if $|\{JdM⟩\}$ span irrep $μ_0$, $\{T|JdM⟩\}$ will span a different irrep $μ′$. In view of equation (B.2), the Hamiltonian matrix has the following structure

$$\langle |JdM⟩, T|JdM⟩ \rangle H(|JdM⟩, T|JdM⟩) = \begin{bmatrix} A & 0 \\ 0 & A^* \end{bmatrix},$$  \hspace{1cm} (B.9)

where $A$ is in general complex. Since $A$ and $A^*$ matrices have the same eigenvalues and complex conjugated eigenvectors, only matrix $A$ needs to be explicitly diagonalized so as to reduce the computational cost by a factor of two. Moreover, unlike the quaternion structure (B.8), only $\{|\{JdM⟩\}\}$ (or equivalently $\{T|JdM⟩\}$) are needed to expand the CI eigenvectors, thereby reducing the computational cost by another factor of two. As such, the combined use of spatial and time reversal symmetries leads to a reduction of the computational cost by a factor of $|G^1⟩$ (four for $C^2_g$ and $C^2_{g0}$ and eight for $C^2_{g0}$).

Finally, the fermion irreps of $C^2_g$, $D^g_2$, and $D^g_{2h}$ belong to class (c). Such irreps are all two-dimensional. $\{|\{JdM⟩\}\}$ and $\{T|JdM⟩\}$ can be arranged to different columns of the same irrep, i.e., $\langle |JdM⟩, J⟩|dM⟩2⟩$ with $|JdM2⟩ = T|JdM⟩$ and $M > 0$. The first-column functions $\{|\{JdM⟩\}\}$ are given in tables B8 and B9 for $D^g_2$ and $C^2_g$, respectively. Such functions are characterized by the irreps of the spatial part of $|JdM⟩$ as well as the odd and even characters of $M − \frac{1}{2}$, totaling up
to eight cases. The corresponding functions for $D_{2h}^1$ can be obtained from table B8 by replacing an irrep X of $D_2$ with $X_S$ or $X_A$. With the so-constructed Kramers-paired basis, the Hamiltonian matrix takes the following structure (cf equation (B.2))

$$(\langle JdM1 \rangle, \langle JdM1 \rangle)H(\langle JdM1 \rangle, \langle JdM1 \rangle) = \begin{bmatrix} A & 0 \\ 0 & A \end{bmatrix},$$

(3.10)

where matrix $A$ is real-valued and is independent of the column indices (cf equation (B.3)). This structure itself gives rise to a factor of 8 reduction of the computational cost. As such, the combined use of spatial and time reversal symmetries leads to a factor of 8 reduction of the computational cost. As such, the combined use of spatial and time reversal symmetries leads to a factor of 8 reduction of the computational cost.

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