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A study of the relative importance of one and two-electron contributions to spin-orbit coupling

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The existing methods to estimate the magnitude of spin-orbit coupling for arbitrary molecules and multiconfigurational wave functions are reviewed. The form-factor method is extended from the original singlet-triplet formulation into arbitrary multiplicities. A simplified version of the mean-field method (the partial two-electron method, P2E) is formulated and tested versus the full two-electron operator on a set of representative molecules. The change of the one and two-electron spin-orbit coupling down the Periodic Table is investigated, and it is shown that the computationally much less demanding P2E method has an accuracy comparable to that of the full two-electron method. © 2000 American Institute of Physics. [S0021-9606(00)30107-6]

I. INTRODUCTION

As computational capabilities improve, the ability to do more accurate calculations and study finer features of molecular structure is facilitated. One of the features that has begun to be widely studied relatively recently for molecules rather than atoms is spin-orbit coupling (SOC). It is one of several interactions violating the commonly used adiabatic approximation, since SOC allows mixing states with different spin multiplicity, and it is the adiabatic approximation that introduces the conservation of electron spin. As such, it provides valuable information about dynamics of processes otherwise forbidden (such as transitions at energy surface crossings). As a consequence of relativistic effects, as can be seen directly from the reduction of the full relativistic Dirac equation, it provides a correction to the energy levels, generally growing with the nuclear charge. Whereas the general theoretical aspects of spin-orbit coupling have been known for a long time, there has been a lack of generally available tools with which it can be calculated.

In this work a general hierarchy of spin-orbit coupling methods is described. These methods have been developed and implemented into the electronic structure code GAMESS.¹ An approximate one-electron method developed by Koseki in GAMESS was previously described for both main group² and transition elements.³ The early studies by Blume *et al.*⁴ considered the one- and two-electron contributions to spin-orbit coupling in atoms. Veseth⁵ and Ross *et al.*⁶ studied spin-orbit coupling for a number of atoms. Langhoff studied core and valence contributions to spin-orbit coupling in molecular oxygen.⁷ A recent direct determinantal approach to spin-orbit coupling has been suggested by Sjøvoll⁸ *et al.* Although full two-electron Pauli-Breit SOC calculations (*vide infra*) have been done by many researchers,⁹⁻¹¹ their codes have not been generally available. As a result of the present work general SOC calculations can now be performed with GAMESS, as described below. Several advances

in calculation methods have been made. The code is fully capable of running in parallel with TCGMSG¹² and MPI¹³ libraries.

II. GENERAL DESCRIPTION OF THE METHODS

The Pauli-Breit spin-orbit coupling operator is given by¹⁴

$$\hat{H}_{so} = \frac{\Omega^2}{2} \left\{ \sum_{i=1}^{N_{el}} \sum_{\alpha=1}^{N_{atoms}} \frac{Z_{\alpha}}{|\vec{r}_j - \vec{r}_{\alpha}|^3} [(\vec{r}_i - \vec{r}_{\alpha}) \times \vec{p}_i] \cdot \vec{S}_i - \sum_{i=1}^{N_{el}} \sum_{j \neq i}^{N_{el}} \frac{1}{|\vec{r}_i - \vec{r}_j|^3} [(\vec{r}_i - \vec{r}_j) \times \vec{p}_i] \cdot [\vec{S}_i + 2\vec{S}_j] \right\}, \quad (1)$$

where Ω is the fine structure constant, Z_{α} are the nuclear charges, r_i and r_{α} are the electron and nuclear coordinates respectively, \hat{p}_i is the electron momentum operator, \hat{S}_i is the electron spin operator.

The first double sum is known as the one and the second as the two-electron SOC operators. The computational expenses of SOC calculations are considerably different (by one order of magnitude) for one- and two-electron operators. In addition, due to the local nature of the operator and the explicit dependence of the one-electron operator upon the nuclear charges, the one-electron contribution to SOC tends to grow rapidly with the nuclear charge, whereas the two-electron part grows much more slowly, due to increased electron density in the regions close to the nuclei. This has motivated the development of several approaches wherein the complexity grows from just one-electron (1E) to the full one- and two-electron (2E) operators through an intermediate partial two-electron contribution method (P2E).

The following quantity based upon the Fermi golden rule is useful for the description of the dynamics of SOC-induced transitions (such as reaction dynamics).

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$$\begin{aligned}
C_{S,S'} &\equiv \sum_{M_s=-S}^S \sum_{M'_s=-S'}^{S'} |\langle S M_s | \hat{H}_{so} | S' M'_s \rangle|^2 \\
&= \frac{2S+1}{3} \{ \langle S | \mathbf{L}_x | S' \rangle^2 + \langle S | \mathbf{L}_y | S' \rangle^2 + \langle S | \mathbf{L}_z | S' \rangle^2 \} \\
&= \frac{2S+1}{3} \langle S | \mathbf{L} | S' \rangle^2. \tag{2}
\end{aligned}$$

(Dirac notation is used throughout, \hat{L} denotes the molecular angular momentum operator, defined below.) This quantity is hence called the SOC constant (SOCC). Note that S' is either equal to S or to $S+1$, so there is no real asymmetry in the formula. More details are given below.

Since many modern quantum-chemical methods are based upon Slater determinants, with the total wave function being a linear combination thereof, the methods below are based on calculation of spin-orbit coupling matrix elements between two determinants. Spin-adapted linear combinations of determinants are known as configuration state functions (CSFs). Two different approaches can be taken. Given the total wave function and an operator \hat{A} , consider $\langle \Psi_1 | \hat{A} | \Psi_2 \rangle$:

- *Direct approach* $|\Psi\rangle = \sum_I C_I D_I$. The individual matrix elements between two determinants or CSFs $\langle D_I | \hat{A} | D_J \rangle$ are calculated one by one using the Slater rules, which reduces a matrix element to a sum of MO integrals.

- *Indirect approach* $\langle \Psi_1 | \hat{A} | \Psi_2 \rangle = \text{Tr}[AP] = \sum_{i,j} A_{ij} P_{ji}$ or $\sum_{ijkl} A_{ijkl} P_{lkji}$ for one- and two-electron operators. Here, Ψ can be a single determinant, a CSF or their linear combination, A are integrals in the basis of molecular orbitals (MOs) (i.e., $A_{ij} = \langle \varphi_i | \hat{A} | \varphi_j \rangle$) and P is the generalized density.

The advantage of the indirect method is that it does not require storing of the $2e$ integrals usually kept in memory in the direct method. The penalty for this advantage is having to calculate, sort, and store the form-factors (*vide infra*), from which the generalized density is calculated. This effectively restricts the practical applicability of the indirect approach to the complete active space (CAS) type of wave function. Thus, the indirect method is best used with small active spaces and large basis sets, whereas the direct approach may not be able to handle large basis sets due to limited computer memory.

A recent determinant approach by Sjøvoll *et al.*⁸ could be classified as indirect in the terminology of this paper. This approach provides considerable advantage over the previously existing form-factor method briefly discussed below, as it provides the means of effectively calculating the generalized density factors without having to sort them. On the other hand, it takes no advantage of avoiding adding negligible contributions as discussed in the threshold section below and is limited to orthogonal orbitals. Nevertheless, this determinantal approach appears very promising, especially for wave functions consisting of a large number of determinants.

An intermediate method also exists, known as the symbolic matrix element method,¹⁵ wherein the CSFs are divided into classes according to occupation schemes, and each scheme is then treated with the indirect approach. While

TABLE I. Summary of SOC code development in GAMESS.

	In GAMESS originally			In GAMESS after this work		
	1E	P2E	2E	1E	P2E	2E
direct	general	none	none	general	general	general
indirect	none	none	limited	none	none	general(*)

found to work well, this method is not considered below as its practical implementation requires an appropriate underlying configuration interaction (CI) scheme currently not available in GAMESS. The foregoing discussion is summarized in Table I.

Except for computation of the full $1e$ and $2e$ matrix elements, the indirect approach is at a disadvantage compared with the direct method, so it has not been implemented for the other approaches. The indirect one- and two-electron operator approach requires exponentially growing resources as the number of active orbitals (i.e., all variably occupied orbitals) increases, so the actual implementation is still limited to 26 active orbitals at most (denoted by*in Table I).

Throughout this work, it is assumed that the two sets of molecular orbitals (MOs) (the sets for bra and ket) are biorthogonal with identical core (doubly occupied space in all configurations). It is only possible to biorthogonalize MO sets for a pair of multiplicities in the CAS case¹⁶(or full CI, FCI). In all other cases identical MO sets have to be used to avoid having to deal with nonorthogonal orbitals. In principle, it is possible to work with nonorthogonal orbitals,¹⁷ with the computational expense increased by an order of magnitude. Then a one-electron SOC nonorthogonal calculation would cost as much as a two-electron one with orthogonal orbitals.

III. SYMMETRY SUMMARY

By application of the Wigner–Eckhart theorem¹⁸ and by using the hermiticity of \hat{H}_{so} , it is possible to reduce the number of matrix elements to be calculated from $(2S+1) \times (2S'+1)$ where S and S' are the bra and ket \hat{S}^2 quantum numbers, to at most two.¹⁹ Application of symmetry selection rules can further reduce this number. It has been found that the double group does not offer any advantage over the point group formalism,¹⁹ if the matrix elements are calculated in the real-valued CI state basis. The matrix elements reduce to

$$\begin{aligned}
&\langle \alpha \Gamma i S M_s | \hat{H}_{so} | \alpha' \Gamma' i' S' M'_s \rangle \\
&= \sum_{q=-1}^1 (S', 1, M'_s, -q | S, M_s) \langle \alpha \Gamma i S | \hat{L}_q \hat{S} | \alpha' \Gamma' i' S' \rangle \\
&\quad \times (-1)^q, \tag{3}
\end{aligned}$$

where α , Γ , and i are the symmetry labels of the CI states and $(S', 1, M'_s, q | S, M_s)$ is a Clebsch–Gordan coefficient, \hat{S} is the reduced spin-operator and \hat{L}_q is an angular momentum operator, whose exact definition is not needed since the symmetry properties are contained in the Clebsch–Gordan coefficient. $\langle \alpha \Gamma i S | \hat{L}_q \hat{S} | \alpha' \Gamma' i' S' \rangle$ is a so-called reduced matrix

element (RME), with the property that $RME(q=1)$ and $RME(q=-1)$ are connected by a simple relation, so that only two need to be explicitly calculated (e.g., $q=0$ and $q=1$). An important consequence of this formula is that for a pair of states (e.g., determinants) only one q in the above sum survives, namely $q=M'_s-M_s$.

The point group selection rules are deduced from the product $\Gamma \times \Gamma_{L_q} \times \Gamma'$ of the irreducible representations, to which bra, angular momentum L_q and ket belong. Matrix elements between two singlets are zero. Provided that the wave function is real, the matrix elements for bra equal to ket are zero.

It is worth keeping in mind that usually the CI states are not pure symmetry-wise, i.e., they belong to several irreducible representations with different weights, so the point group symmetry rules hold only approximately if a state is assumed to belong to only one of them.

Integral index permutational symmetry is discussed below when the integrals are defined for the indirect method.

IV. INDIRECT METHOD

Furlani derived and coded a limited version of this method as a part of his PhD thesis.²⁰ The method itself was derived for singlet and triplet states only. The code was limited to 10 active orbitals and up to d -functions.

Close examination of the derivations reveals that for the general case of arbitrary multiplicities the following holds for $\langle SM_s | \hat{H}_{so} | S' M'_s \rangle$:

- the matrix element is zero if $|S-S'| > 1$ or $|M_s-M'_s| > 1$
- if $M_s=M'_s$, then the formulas for singlet and triplet $M_s=0$ can be used to calculate such a matrix element
- if $M'_s-M_s = \pm 1$, the formulas for singlet and triplet $M_s = \pm 1$ are to be used.

A brief review of the generalized method is now given. Ψ is taken to be a linear combination of CSFs with coefficients q , each of which is a linear combination of Slater determinants Δ with coefficients C .

$$\begin{aligned} & \langle \Psi(S, M_s) | \hat{H}_{so} | \Psi(S', M'_s) \rangle \\ &= \sum_{I=1}^{N_{CSF}} \sum_{J=1}^{N'_{CSF}} q_I q_J \sum_{K=1}^{N_{DET}} \sum_{L=1}^{N'_{DET}} C_K^{M_s} C_L^{M'_s} \langle \Delta_K^{M_s} | \hat{H}_{so} | \Delta_L^{M'_s} \rangle \\ &= \sum_{I=1}^{N_{CSF}} \sum_{J=1}^{N'_{CSF}} q_I q_J \left\{ \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} \Gamma_{ij}^{IJ} \langle \varphi_i^{M_s} | \hat{l}_{\Delta M_s}^{(1)} | \varphi_j^{M'_s} \rangle \right. \\ & \quad \times \prod_{\substack{k \neq i \\ k \neq j}}^{N_e} \langle \varphi_{k(K)}^{M_s} | \varphi_{k(L)}^{M'_s} \rangle \\ & \quad - \sum_{i,j=1}^N \sum_{k,l=1}^N \Gamma_{ijkl}^{IJ} \langle \varphi_i^{M_s} \varphi_j^{M'_s} | \hat{l}_{\Delta M_s}^{(2)} | \varphi_k^{M'_s} \varphi_l^{M'_s} \rangle \\ & \quad \left. \times \prod_{\substack{m \neq i \\ m \neq j}}^{N_e} \langle \varphi_{m(K)}^{M_s} | \varphi_{m(L)}^{M'_s} \rangle \right\} \end{aligned}$$

$$\begin{aligned} &= \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} \Gamma_{ij}^{\Delta M_s} \langle \varphi_i^{M_s} | \hat{l}_{\Delta M_s}^{(1)} | \varphi_j^{M'_s} \rangle \\ & - \sum_{i,j=1}^N \sum_{k,l=1}^{N'} \Gamma_{ijkl}^{\Delta M_s} \langle \varphi_i^{M_s} \varphi_j^{M'_s} | \hat{l}_{\Delta M_s}^{(2)} | \varphi_k^{M'_s} \varphi_l^{M'_s} \rangle, \end{aligned} \quad (4)$$

where \hat{l}_{so} is what is left of the one- and two-electron spin-orbit coupling operators after taking the scalar product over the spin variables as defined below, $k(L)$ denotes an orbital with ordinal number k in a determinant L . N is the total number of doubly occupied core (N_c) and active (N_a) orbitals, $N=2N_c+N_a$, N_e is the number of electrons in the active space, $\Delta M_s = M'_s - M_s$ ($|\Delta M_s| \leq 1$).

The quantities Γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} are known as the one- and two-electron form-factors (FFs) (both are ΔM_s dependent), and $\Gamma_{ij}^{\Delta M_s}$ and $\Gamma_{ijkl}^{\Delta M_s}$ are the one- and two-electron generalized density, respectively

$$\Gamma_{ij}^{\Delta M_s} \equiv \sum_{I=1}^{N_{CSF}} \sum_{J=1}^{N'_{CSF}} q_I q_J \Gamma_{ij}^{IJ}$$

and

$$\Gamma_{ijkl}^{\Delta M_s} \equiv \sum_{I=1}^{N_{CSF}} \sum_{J=1}^{N'_{CSF}} q_I q_J \Gamma_{ijkl}^{IJ}.$$

The FFs are derived from application of the Slater rules to pairs of determinants Δ_K and Δ_L and comparison of the left and right hand sides.

The main properties of the form-factors are:

- (1) Γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} are dependent *only* upon N_e and N_a and are sparse.
- (2) Γ_{ij}^{IJ} are zero unless both i and j are in the active space.
- (3) Γ_{ijkl}^{IJ} are zero unless (i) all indices are in the active space or (ii) two indices are from the core and two from the active space (of which there are four combinations). In the latter case they are independent of the core indices (This is analogous to the direct method: These core-active form-factors correspond to the partial two-electron direct method considered below.) and are proportional to Γ_{ij}^{IJ} .

The MOs φ are taken as linear combination of atomic orbitals (AO) χ , and by using the index permutational symmetry the final result for the matrix element in Eq. (4) is

$$\begin{aligned} & \langle \Psi(S, M_s) | \hat{H}_{so} | \Psi(S', M'_s) \rangle \\ &= \sum_{\gamma=1}^{N_{AO}} \sum_{\rho=1}^{\gamma-1} \sum_{\alpha=1}^{N_{atom}} \langle \chi_\gamma | \hat{l}_{\Delta M_s}^{(1)}(1, \alpha) | \chi_\rho \rangle \hat{D}_{\gamma\rho}^1 \\ & - \sum_{\gamma=1}^{N_{AO}} \sum_{\nu=1}^{N_{AO}} \sum_{\rho=1}^{\gamma-1} \sum_{\mu=1}^{\nu} \langle \chi_\gamma \chi_\nu | \hat{l}_{\Delta M_s}^{(2)} | \chi_\rho \chi_\mu \rangle \hat{D}_{\gamma\nu\rho\mu}^2, \end{aligned} \quad (6)$$

where

$$\begin{aligned} \hat{l}_{\Delta M_s}^{(1)}(i, \alpha) &= Z_\alpha / |\vec{r}_i - \vec{r}_\alpha|^3 [(\vec{r}_i - \vec{r}_\alpha) \times \vec{p}_i]_{\Delta M_s}, \\ \hat{l}_{\Delta M_s}^{(2)}(i, j) &= 1/|\vec{r}_i - \vec{r}_j|^3 [(\vec{r}_i - \vec{r}_j) \times \vec{p}_i]_{\Delta M_s} \end{aligned}$$

TABLE II. The rapidly growing number of FFs.

CAS[m/n] ^a	# singlet CSFs	# triplet CSFs	# 1e FFs	# 2e FFs	FF disk, bytes
[2/2]	3	1	8	16	192
[4/4]	20	15	320	2896	76 800
[6/6]	175	51	3368	78 810	6 693 488
[8/8]	1764	2352	294 370	12 282 038	232 448 352
[10/10]	19 074	29 700	8 214 402	536 127 134	4 656 497 344

^a[m/n] denotes m electrons in n orbitals.

and

$$\hat{l}_q^{(1)}(i) \equiv \sum_{\alpha} \hat{l}_q^{(1)}(i, \alpha), \quad \hat{l}_q^{(1)} \equiv \hat{l}_q^{(1)}(1), \quad \hat{l}_q^{(2)} \equiv \hat{l}_q^{(2)}(1,2), \quad (7)$$

$$\hat{L}_q \equiv \hat{L}_q^{(1)} + \hat{L}_q^{(2)}, \quad \hat{L}_q^{(1)} \equiv \sum_i \hat{l}_q^{(1)}(i), \quad \hat{L}_q^{(2)} \equiv \sum_{i \neq j} \hat{l}_q^{(2)}(i,j).$$

Note that for atoms $\hat{L}_q = \hat{L}_q^{(1)}$, where \hat{L}_q is the total electronic angular momentum.

$$D_{\gamma\rho}^a \equiv \sum_{i,j=1}^{N_a} \Gamma_{ij}^{\Delta M_s} c_{\gamma i}^{M_s} c_{\rho j}^{M'_s}, \quad \hat{D}^1 = D^a - D^{a^\dagger},$$

$$D_{\gamma\rho}^c \equiv \sum_{i,j=1}^{N_c} c_{\gamma i} c_{\rho j},$$

$$B_{\gamma\nu\rho\mu} \equiv \sum_{i,j,k,l=1}^{N_o} \Gamma_{ijkl}^{\Delta M_s} c_{\gamma i}^{M_s} c_{\nu j}^{M_s} c_{\rho k}^{M'_s} c_{\mu l}^{M'_s},$$

$$\begin{aligned} \hat{D}_{\gamma\nu\rho\mu}^2 &= \frac{1}{1 + \delta_{\nu\mu}} [4D_{\nu\mu}^c \hat{D}_{\gamma\rho}^1 + 3D_{\gamma\nu}^c \hat{D}_{\rho\mu}^1 \\ &\quad + 3D_{\nu\rho}^c \hat{D}_{\mu\gamma}^1 + 3D_{\gamma\mu}^c \hat{D}_{\rho\nu}^1 + 3D_{\mu\rho}^c \hat{D}_{\gamma\nu}^1 \\ &\quad + B_{\gamma\nu\rho\mu} + B_{\gamma\mu\rho\nu} - B_{\rho\nu\gamma\mu} - B_{\rho\mu\gamma\nu}] \end{aligned} \quad (8)$$

(following Furlani's convention with a few extra definitions for use below).

The c are MO→AO expansion coefficients for the active orbitals: c without superscript refers to the core orbitals (assumed to be independent of M_s). The superscripts “ c ” and “ a ” refer to core and active, respectively. Rapidly growing computational expenses can be seen in Table II.

It should be noted that the FFs are first generated and then sorted by MO indices. The number of FFs for a given set of MO indices is not known *a priori*, but the code has to allocate space before the generation starts. This can be done in two ways. One is to allocate a sufficiently large amount of space, however, this increases the size of the disk file. Another option is to first generate the form factors and save the number of form factors for each set of indices while not saving the FFs themselves. Then the proper space is allocated and during the second run the FFs are actually generated and sorted. In Table II the last line ([10/10]) shows the disk space associated with the second (disk saving) option: all other lines reflect the fixed space option.

V. DIRECT METHODS

A. Introductory definitions

Similarly to the indirect case [Eq. (4)]

$$\begin{aligned} &\langle \Psi(S, M_s) | \hat{H}_{\text{so}} | \Psi(S', M'_s) \rangle \\ &= \sum_{I=1}^{N_{\text{CSF}}} \sum_{J=1}^{N'_{\text{CSF}}} q_I q'_J \sum_{K=1}^{N_{\text{DET}}} \sum_{L=1}^{N'_{\text{DET}}} C_K C'_L \langle \Delta_K | \hat{H}_{\text{so}} | \Delta'_L \rangle. \end{aligned} \quad (9)$$

The Slater rules are now applied dynamically, for each pair of determinants. While there may be a very large number of them, it has to be recognized that for large CI expansions many products of CSF coefficients will be very small in magnitude. Keeping in mind that these coefficients themselves are obtained with finite precision, one is justified in omitting contributions from such very small coefficients. This is achieved via introduction of a threshold value; the details are given below.

First, consider the basic schematic equation:

$$\langle \Delta | \hat{H}_{\text{so}} | \Delta' \rangle = H_{\text{act-act}}^{1e} + H_{\text{core-act}}^{2e} + H_{\text{act-act}}^{2e} \quad (10)$$

($H_{\text{core-core}}^{1e} + H_{\text{core-act}}^{1e} + H_{\text{core-core}}^{2e}$ is zero as shown below). The three indirect methods can be defined as follows:

One-electron method:

$$\langle \Delta | \hat{H}_{\text{so}} | \Delta' \rangle = H_{\text{act-act}}^{1e}.$$

Partial two-electron method:

$$\langle \Delta | \hat{H}_{\text{so}} | \Delta' \rangle = H_{\text{act-act}}^{1e} + H_{\text{core-act}}^{2e}.$$

Two-electron method:

$$\langle \Delta | \hat{H}_{\text{so}} | \Delta' \rangle = H_{\text{act-act}}^{1e} + H_{\text{core-act}}^{2e} + H_{\text{act-act}}^{2e}.$$

It is shown below that $H_{\text{core-act}}^{2e}$ becomes pseudo-one-electron after summing over the core. The exact algebraic definitions of all of these quantities are given below. The one-electron method is usually implemented by introducing semiempirical parameters (charges), Z_{eff} , in order to make up for the neglect of the two-electron terms. It is shown below that the partial two-electron method provides reasonable accuracy without the need for fitted parameters.

Recall the Slater rules for a pair of determinants. First, the spin-orbitals in the second determinant are reordered in such a way as to put them in the same order as the first determinant, with different (discoincident) orbitals being placed at the end. The number of these discoincident orbitals needs to be less than or equal to the number of coupled

particles in the operator (i.e., one or two), for a matrix element to be nonzero. For the partial two-electron method (P2E) the number of discoincidences should be less than or equal to one, because two discoincidences can only come from two active orbitals and this term is omitted in the P2E method. The cases for 0, 1, and 2 discoincidences are given below (note that only one spin-discoincidence is allowed, as the spin operators couple only one electron):

$$\begin{aligned} \langle \Delta | \hat{H}_{\text{so}} | \Delta \rangle &= \sum_{\mu=1}^{N_e} \langle \psi_{\mu} | \hat{h}_{\text{so}}^1 | \psi'_{\mu} \rangle O_{\mu} \\ &+ \sum_{\mu, \nu=1}^{N_e} [\langle \psi_{\mu} \psi_{\nu} | \hat{h}_{\text{so}}^2 | \psi'_{\mu} \psi'_{\nu} \rangle \\ &+ \langle \psi_{\nu} \psi_{\mu} | \hat{h}_{\text{so}}^2 | \psi'_{\nu} \psi'_{\mu} \rangle - \langle \psi_{\mu} \psi_{\nu} | \hat{h}_{\text{so}}^2 | \psi'_{\nu} \psi'_{\mu} \rangle \\ &- \langle \psi_{\nu} \psi_{\mu} | \hat{h}_{\text{so}}^2 | \psi'_{\mu} \psi'_{\nu} \rangle] O_{\mu\nu}, \\ \langle \Delta^{\nu} | \hat{H}_{\text{so}} | \Delta^{\sigma} \rangle &= \langle \psi_{\nu} | \hat{h}_{\text{so}}^1 | \psi'_{\sigma} \rangle O_{\nu} + \sum_{\mu=1}^{N_e} [\langle \psi_{\mu} \psi_{\nu} | \hat{h}_{\text{so}}^2 | \psi'_{\mu} \psi'_{\sigma} \rangle \\ &+ \langle \psi_{\nu} \psi_{\mu} | \hat{h}_{\text{so}}^2 | \psi'_{\sigma} \psi'_{\mu} \rangle - \langle \psi_{\mu} \psi_{\nu} | \hat{h}_{\text{so}}^2 | \psi'_{\sigma} \psi'_{\mu} \rangle \\ &- \langle \psi_{\nu} \psi_{\mu} | \hat{h}_{\text{so}}^2 | \psi'_{\mu} \psi'_{\sigma} \rangle] O_{\mu\nu}, \quad (11) \\ \langle \Delta^{\mu\nu} | \hat{H}_{\text{so}} | \Delta^{\rho\sigma} \rangle &= [\langle \psi_{\mu} \psi_{\nu} | \hat{h}_{\text{so}}^2 | \psi'_{\rho} \psi'_{\sigma} \rangle + \langle \psi_{\nu} \psi_{\mu} | \hat{h}_{\text{so}}^2 | \psi'_{\sigma} \psi'_{\rho} \rangle \\ &- \langle \psi_{\mu} \psi_{\nu} | \hat{h}_{\text{so}}^2 | \psi'_{\sigma} \psi'_{\rho} \rangle \\ &- \langle \psi_{\nu} \psi_{\mu} | \hat{h}_{\text{so}}^2 | \psi'_{\rho} \psi'_{\sigma} \rangle] O_{\mu\nu}. \end{aligned}$$

Orbital overlaps $O_{\mu} \equiv \prod_{\nu \neq \mu}^{N_a} \langle \psi_{\nu} | \psi'_{\nu} \rangle$ and $O_{\mu\nu} \equiv \prod_{\rho \neq \nu, \mu}^{N_a} \langle \psi_{\rho} | \psi'_{\rho} \rangle$ do not include core overlaps equal to one. By convention, the Greek indices are used for molecular spin-orbitals $\psi = \varphi\sigma$ and Roman indices for molecular orbitals φ . Greek indices are also used for atomic orbitals. Δ^{ν} and Δ^{σ} denote determinants different by one spin-orbital (ν and σ).

It is worth remembering that SOC between two identical states is zero by hermiticity, therefore, in case of orthogonal (rather than biorthogonal) orbitals for bra and ket states the case of zero discoincidence need not be considered, because the contribution vanishes by symmetry.

B. Spin summation

From the symmetry rules it is seen that only one specific q survives from the sum [Eq. (3)], i.e., $\hat{h}_{\text{so}} \rightarrow \hat{l}_{-q} \hat{s}_q$ where $q = M'_s - M_s$ for a matrix element $\langle SM'_s | \hat{H}_{\text{so}} | SM_s \rangle$. Each spin-orbital (with a Greek index) is now written as a product of an orbital times the spin function σ (α or β), and the summation index is changed to Roman to signify this. It is then possible to take scalar products over the spin variables. The equations are simplified considerably especially for the core orbitals.

The following elementary form-factors are introduced as matrix elements of spin-operators in the spin-function basis (σ_i denotes the spin part of i th orbital). These elementary form-factors are similar to the form-factors Γ introduced for

the indirect method except that they effectively connect two determinants rather than CSFs and γ are unsorted.

$$\begin{aligned} \gamma_{ij}^{\Delta M_s} &\equiv \langle \sigma_i | \hat{s}_{-\Delta M_s} | \sigma_j \rangle, \\ \gamma_{ijkl}^{\Delta M_s} &\equiv \langle \sigma_i(1) \sigma_j(2) | \{ \hat{s}(1) + 2\hat{s}(2) \}_{-\Delta M_s} | \sigma_k(1) \sigma_l(2) \rangle \\ &= \langle \sigma_i | \hat{s}_{-\Delta M_s} | \sigma_k \rangle \delta_{jl} + 2 \langle \sigma_j | \hat{s}_{-\Delta M_s} | \sigma_l \rangle \delta_{ik} \\ &= \gamma_{ik}^{\Delta M_s} \delta_{jl} + 2 \gamma_{jl}^{\Delta M_s} \delta_{ik}. \quad (12) \end{aligned}$$

They are straightforward to calculate, e.g.,

$$\begin{aligned} \gamma_{\alpha\alpha}^0 &\equiv \langle \alpha | \hat{s}_z | \alpha \rangle = \frac{1}{2}, \\ \gamma_{\alpha\beta\alpha\alpha}^1 &\equiv \langle \alpha(1) \beta(2) | \hat{s}_-(1) + 2\hat{s}_-(2) | \alpha(1) \alpha(2) \rangle \\ &= \langle \alpha | \hat{s}_- | \alpha \rangle \langle \beta | \alpha \rangle + 2 \langle \alpha | \alpha \rangle \langle \beta | \hat{s}_- | \alpha \rangle = 0 + 2 = 2. \end{aligned}$$

There are only 16 of these for each ΔM_s , for $\Delta M_s = 0$, see Table III.

Consider the one-electron case for zero discoincidence, ΔM_s is 0 in this case, so $\gamma_{\alpha\alpha}^0 = -\gamma_{\beta\beta}^0 = 1/2$ and

$$\begin{aligned} H_{\text{core-core}}^{1e} &= \sum_{\mu=1}^{N_c} \langle \psi_{\mu} | \hat{h}_{\text{so}}^1 | \psi'_{\mu} \rangle O_{\mu} \\ &= \sum_{i=1}^{N_c} [\langle \varphi_j \alpha | \hat{l}_z \hat{s}_z | \varphi'_i \alpha \rangle O_i + \langle \varphi_i \beta | \hat{l}_z \hat{s}_z | \varphi'_i \beta \rangle O_i] \\ &= \sum_{i=1}^{N_c} [\frac{1}{2} \langle \varphi_i | \hat{l}_z | \varphi'_i \rangle O_i - \frac{1}{2} \langle \varphi_i | \hat{l}_z | \varphi'_i \rangle O_i] = 0. \quad (13) \end{aligned}$$

Thus any doubly occupied orbital (including **all** core orbitals) does not contribute to the one-electron spin-orbit coupling term. Similarly, the two-electron core-core contribution vanishes. $H_{\text{core-act}}^{1e} = 0$, because overlaps between core and active orbitals $\langle \varphi_c | \varphi_a \rangle = 0$.

The following integral quantities are introduced:

$$\begin{aligned} A_{ij} &\equiv \langle \varphi_i | \hat{l}_{\Delta M_s}^{(1)} | \varphi'_j \rangle, \quad A_{ijkl} \equiv \langle \varphi_i \varphi_j | \hat{l}_{\Delta M_s}^{(2)} | \varphi'_k \varphi'_l \rangle, \\ A_{ij}^{caca} &\equiv \sum_{c=1}^{N_c} \langle \varphi_c \varphi_i | \hat{l}_{\Delta M_s}^{(2)} | \varphi_c \varphi'_j \rangle, \\ A_{ij}^{acac} &\equiv \sum_{c=1}^{N_c} \langle \varphi_i \varphi_c | \hat{l}_{\Delta M_s}^{(2)} | \varphi'_j \varphi_c \rangle, \quad (14) \\ A_{ij}^{caac} &\equiv \sum_{c=1}^{N_c} \langle \varphi_c \varphi_i | \hat{l}_{\Delta M_s}^{(2)} | \varphi'_j \varphi_c \rangle, \\ A_{ij}^{acca} &\equiv \sum_{c=1}^{N_c} \langle \varphi_i \varphi_c | \hat{l}_{\Delta M_s}^{(2)} | \varphi_c \varphi'_j \rangle. \end{aligned}$$

The superscripts c and a refer to core and active spaces, respectively.

Symmetry properties of the integrals are

$$A_{ij} = -A_{ji}, \quad (15)$$

$$A_{ijkl} = -A_{kjil} \quad \text{and} \quad A_{ijkl} = A_{ilkj}$$

(i.e., antisymmetric and symmetric for the first and second particle, respectively). This property holds for core integrals, too, so $A_{ij}^{caca} \equiv 0$.

$$\begin{aligned} \langle \Delta | \hat{H}_{\text{so}} | \Delta \rangle &= \sum_{i=1}^{N_a} A_{ii} \gamma_{ii}^{\Delta M_s} O_i + 2 \sum_{i=1}^{N_a} \left\{ \begin{aligned} &A_{ii}^{caca} [\gamma_{\alpha i \alpha i}^{\Delta M_s} + \gamma_{\beta i \beta i}^{\Delta M_s}] + A_{ii}^{acac} [\gamma_{i \alpha i \alpha}^{\Delta M_s} + \gamma_{i \beta i \beta}^{\Delta M_s}] \\ &- A_{ii}^{caac} [\gamma_{\alpha i i \alpha}^{\Delta M_s} + \gamma_{\beta i i \beta}^{\Delta M_s}] - A_{ii}^{acca} [\gamma_{i \alpha i \alpha}^{\Delta M_s} + \gamma_{i \beta i \beta}^{\Delta M_s}] \end{aligned} \right\} O_i \\ &+ \sum_{i,j=1}^{N_a} [A_{ijij} \gamma_{ijij}^{\Delta M_s} + A_{jiji} \gamma_{jiji}^{\Delta M_s} - A_{ijji} \gamma_{ijji}^{\Delta M_s} - A_{jiij} \gamma_{jiij}^{\Delta M_s}] O_{ij}, \\ \langle \Delta^j | \hat{H}_{\text{so}} | \Delta^l \rangle &= A_{jl} \gamma_{jl}^{\Delta M_s} O_j + \left\{ \begin{aligned} &A_{jl}^{caca} [\gamma_{\alpha j \alpha l}^{\Delta M_s} + \gamma_{\beta j \beta l}^{\Delta M_s}] + A_{jl}^{acac} [\gamma_{i \alpha l \alpha}^{\Delta M_s} + \gamma_{j \beta l \beta}^{\Delta M_s}] \\ &- A_{jl}^{caac} [\gamma_{\alpha j l \alpha}^{\Delta M_s} + \gamma_{\beta j l \beta}^{\Delta M_s}] - A_{jl}^{acca} [\gamma_{j \alpha l \alpha}^{\Delta M_s} + \gamma_{j \beta l \beta}^{\Delta M_s}] \end{aligned} \right\} O_j \\ &+ \sum_{i=1}^{N_e} [A_{ijil} \gamma_{ijil}^{\Delta M_s} + A_{jili} \gamma_{jili}^{\Delta M_s} - A_{ijli} \gamma_{ijli}^{\Delta M_s} - A_{jiil} \gamma_{jiil}^{\Delta M_s}] O_{il}, \end{aligned} \quad (16)$$

$$\begin{aligned} \langle \Delta^{ij} | \hat{H}_{\text{so}} | \Delta^{kl} \rangle &= [A_{ijkl} \gamma_{ijkl}^{\Delta M_s} + A_{jilk} \gamma_{jilk}^{\Delta M_s} - A_{ijlk} \gamma_{ijlk}^{\Delta M_s} \\ &- A_{jikl} \gamma_{jikl}^{\Delta M_s}] O_{ij}. \end{aligned}$$

Note that a factor of 2 appears because of symmetry in sums:

$$\sum_{i=1}^{N_e} \sum_{j=1}^{N_e} \rightarrow \sum_{i=1}^{N_a} \sum_{j=1}^{N_c} + \sum_{i=1}^{N_c} \sum_{j=1}^{N_a} = 2 \sum_{i=1}^{N_a} \sum_{j=1}^{N_c}.$$

With a little algebra it can be seen that (Table III)

$$\begin{aligned} \gamma_{\alpha i \alpha j}^{\Delta M_s} + \gamma_{\beta i \beta j}^{\Delta M_s} &= 4 \gamma_{ij}^{\Delta M_s}, \\ \gamma_{i \alpha j \alpha}^{\Delta M_s} + \gamma_{i \beta j \beta}^{\Delta M_s} &= 2 \gamma_{ij}^{\Delta M_s}, \\ \gamma_{\alpha i j \alpha}^{\Delta M_s} + \gamma_{\beta i j \beta}^{\Delta M_s} &= 3 \gamma_{ij}^{\Delta M_s}, \\ \gamma_{i \alpha \alpha j}^{\Delta M_s} + \gamma_{i \beta \beta j}^{\Delta M_s} &= 3 \gamma_{ij}^{\Delta M_s}. \end{aligned} \quad (17)$$

Thus the expressions for the matrix elements are simplified to (using $A_{ij}^{caca} \equiv 0$)

$$\begin{aligned} \langle \Delta | \hat{H}_{\text{so}} | \Delta \rangle &= \sum_{i=1}^{N_a} \{ A_{ii} \gamma_{ii}^{\Delta M_s} O_i + 2 (A_{ii}^{acac} 2 \gamma_{ii}^{\Delta M_s} O_i \\ &- A_{ii}^{caac} 3 \gamma_{ii}^{\Delta M_s} O_i - A_{ii}^{acca} 3 \gamma_{ii}^{\Delta M_s} O_i) \} \\ &+ \sum_{i,j=1}^{N_a} [A_{ijij} \gamma_{ijij}^{\Delta M_s} + A_{jiji} \gamma_{jiji}^{\Delta M_s} - A_{ijji} \gamma_{ijji}^{\Delta M_s} \\ &- A_{jiij} \gamma_{jiij}^{\Delta M_s}] O_{ij}, \end{aligned}$$

In the code, \hat{l}_{\pm} operators (defined as in the indirect case) are written as $\mp (\hat{l}_x \pm \hat{l}_y) / \sqrt{2}$, and the program actually calculates matrix elements of $-i\hat{l}_x$, $-i\hat{l}_y$, and $-i\hat{l}_z$ operators (multiplied by imaginary unity i to get real-valued integrals, as $\mathbf{l} = [\mathbf{r} \times \mathbf{p}]$ and $\mathbf{p} = -i$). Note that $-$ is anti-Hermitian, whereas \mathbf{p} is Hermitian). Subsequently, \hat{l}_{\pm} are reconstructed.

It is possible to rewrite the matrix elements as

$$\begin{aligned} \langle \Delta^j | \hat{H}_{\text{so}} | \Delta^l \rangle &= A_{jl} \gamma_{jl}^{\Delta M_s} O_j + A_{jl}^{acac} 2 \gamma_{jl}^{\Delta M_s} O_j \\ &- A_{jl}^{caac} 3 \gamma_{jl}^{\Delta M_s} O_j - A_{jl}^{acca} 3 \gamma_{jl}^{\Delta M_s} O_j \\ &+ \sum_{i=1}^{N_e} [A_{ijil} \gamma_{ijil}^{\Delta M_s} + A_{jili} \gamma_{jili}^{\Delta M_s} - A_{ijli} \gamma_{ijli}^{\Delta M_s} \\ &- A_{jiil} \gamma_{jiil}^{\Delta M_s}] O_{il}, \end{aligned} \quad (18)$$

$$\begin{aligned} \langle \Delta^{ij} | \hat{H}_{\text{so}} | \Delta^{kl} \rangle &= [A_{ijkl} \gamma_{ijkl}^{\Delta M_s} + A_{jilk} \gamma_{jilk}^{\Delta M_s} - A_{ijlk} \gamma_{ijlk}^{\Delta M_s} \\ &- A_{jikl} \gamma_{jikl}^{\Delta M_s}] O_{ij}, \end{aligned}$$

and finally one arrives at the final formulas

$$\begin{aligned} \langle \Delta | \hat{H}_{\text{so}} | \Delta \rangle &= \sum_{i=1}^{N_a} \{ A_{ii} \gamma_{ii}^{\Delta M_s} O_i + 2 A_{ii}^{ca} \gamma_{ii}^{\Delta M_s} O_i \} \\ &+ \sum_{i,j=1}^{N_a} [A_{ijij} \gamma_{ijij}^{\Delta M_s} + A_{jiji} \gamma_{jiji}^{\Delta M_s} - A_{ijji} \gamma_{ijji}^{\Delta M_s} \\ &- A_{jiij} \gamma_{jiij}^{\Delta M_s}] O_{ij}, \\ \langle \Delta^j | \hat{H}_{\text{so}} | \Delta^l \rangle &= A_{jl} \gamma_{jl}^{\Delta M_s} O_j + A_{jl}^{ca} \gamma_{jl}^{\Delta M_s} O_j + \sum_{i=1}^{N_e} [A_{ijil} \gamma_{ijil}^{\Delta M_s} \\ &+ A_{jili} \gamma_{jili}^{\Delta M_s} - A_{ijli} \gamma_{ijli}^{\Delta M_s} - A_{jiil} \gamma_{jiil}^{\Delta M_s}] O_{il}, \\ \langle \Delta^{ij} | \hat{H}_{\text{so}} | \Delta^{kl} \rangle &= [A_{ijkl} \gamma_{ijkl}^{\Delta M_s} + A_{jilk} \gamma_{jilk}^{\Delta M_s} - A_{ijlk} \gamma_{ijlk}^{\Delta M_s} \\ &- A_{jikl} \gamma_{jikl}^{\Delta M_s}] O_{ij}, \end{aligned} \quad (19)$$

where $A_{ij}^{ca} \equiv 2A_{ij}^{acac} - 3A_{ij}^{caac} - 3A_{ij}^{acca}$.

Now it can be seen that the core-active two-electron contribution may be formally expressed in exactly the same fashion as the one-electron active-active term.

$$\begin{aligned}
 H_{\text{act-act}}^{1e} &= \sum_{i=1}^{N_a} A_{ii} \gamma_{ii}^{\Delta M_s} O_i, \\
 H_{\text{core-act}}^{2e} &= 2 \sum_{i=1}^{N_a} A_{ii}^{ca} \gamma_{ii}^{\Delta M_s} O_i, \\
 H_{\text{act-act}}^{2e} &= \sum_{i,j=1}^{N_a} [A_{ijij} \gamma_{ijij}^{\Delta M_s} + A_{jiji} \gamma_{jiji}^{\Delta M_s} - A_{ijji} \gamma_{ijji}^{\Delta M_s} \\
 &\quad - A_{jiii} \gamma_{jiii}^{\Delta M_s}] O_{ij},
 \end{aligned}
 \tag{20}$$

for zero discoincedence and similarly for one and two discoincedences.

C. SOC integrals

The atomic integrals are calculated by the integral code developed by Furlani²⁰ for his form factor method (in the AO basis). The code has been slightly modified to allow up to g-type orbitals in the basis set.

The usage of AO integrals is different between direct and indirect methods. The indirect method is AO-integral based, i.e., each integral is multiplied by the density and added to the matrix element being calculated. The direct methods store the AO integrals on disk: The one-electron integrals are stored as a triangular matrix and the nonzero two-electron integrals are stored as an integral list, with orbital labels.

Transformation into the MO basis is accomplished for active orbitals in the standard way by doing two and four index transformations.

$$\begin{aligned}
 A_{ij} &\equiv \langle \varphi_i | \hat{l}_{\Delta M_s}^{(1)} | \varphi_j' \rangle = \sum_{\mu, \nu=1}^{N_{\text{AO}}} c_{\mu i}^* c'_{\nu j} \langle \chi_i | \hat{l}_{\Delta M_s}^{(1)} | \chi_j \rangle, \\
 A_{ijkl} &= \langle \varphi_i \varphi_j | \hat{l}_{\Delta M_s}^{(2)} | \varphi_k' \varphi_l' \rangle \\
 &= \sum_{\mu \nu \rho \sigma}^{N_{\text{AO}}} c_{\mu i}^* c_{\nu j}^* c'_{\rho k} c'_{\sigma l} \langle \chi_i \chi_j | \hat{l}_{\Delta M_s}^{(2)} | \chi_k \chi_l \rangle,
 \end{aligned}
 \tag{21}$$

where $c_{\mu i}$ are LCAO coefficients. The core-active transformations are reduced from four to two indices by doing the core summation

TABLE III. Complete $\gamma_{\mu\nu\rho\sigma}^0$ table.

	$ \alpha\alpha\rangle$	$ \alpha\beta\rangle$	$ \beta\alpha\rangle$	$ \beta\beta\rangle$
$\langle\alpha\alpha $	3/2	1/2	1	0
$\langle\alpha\beta $	1/2	-1/2	0	-1
$\langle\beta\alpha $	1	0	1/2	-1/2
$\langle\beta\beta $	0	-1	-1/2	-3/2

$$\begin{aligned}
 A_{ij}^{ca} &\equiv 2A_{ij}^{acac} - 3A_{ij}^{caac} - 3A_{ij}^{acca} \\
 &= 2 \sum_{c=1}^{N_c} \langle \varphi_i \varphi_c | \hat{l}_{\Delta M_s}^{(2)} | \varphi_j' \varphi_c \rangle - 3 \sum_{c=1}^{N_c} \langle \varphi_c \varphi_i | \hat{l}_{\Delta M_s}^{(2)} | \varphi_j' \varphi_c \rangle \\
 &\quad - 3 \sum_{c=1}^{N_c} \langle \varphi_i \varphi_c | \hat{l}_{\Delta M_s}^{(2)} | \varphi_c \varphi_j' \rangle \\
 &= \sum_{c=1}^{N_c} \sum_{\mu\nu\rho\sigma}^{N_{\text{AO}}} \{ 2c_{\mu i}^* c_{\nu c}^* c'_{\rho j} c_{\sigma c} - 3c_{\mu c}^* c_{\nu i}^* c'_{\rho j} c_{\sigma c} \\
 &\quad - 3c_{\mu i}^* c_{\nu c}^* c_{\rho c} c'_{\sigma j} \} \langle \chi_{\mu} \chi_{\nu} | \hat{l}_{\Delta M_s}^{(2)} | \chi_{\rho} \chi_{\sigma} \rangle \\
 &= \sum_{\mu\nu\rho\sigma}^{N_{\text{AO}}} \{ 2D_{\nu\sigma}^c c_{\mu i}^* c'_{\rho j} - 3D_{\mu\sigma}^c c_{\nu i}^* c'_{\rho j} - 3D_{\nu\rho}^c c_{\mu i}^* c'_{\sigma j} \} A_{\mu\nu\rho\sigma},
 \end{aligned}
 \tag{22}$$

where the sum over the core yielded the core density, D^c .

$$\begin{aligned}
 A_{ij}^{ca} &= 2 \sum_{\mu\rho}^{N_{\text{AO}}} A_{\mu\rho}^{acac} c_{\mu i}^* c'_{\rho j} - 3 \sum_{\nu\rho}^{N_{\text{AO}}} A_{\nu\rho}^{caac} c_{\nu i}^* c'_{\rho j} \\
 &\quad - 3 \sum_{\mu\sigma}^{N_{\text{AO}}} A_{\mu\sigma}^{acca} c_{\mu i}^* c'_{\sigma j} = \sum_{\kappa\lambda}^{N_{\text{AO}}} c_{\kappa i}^* A_{\kappa\lambda}^{ca} c'_{\lambda j},
 \end{aligned}
 \tag{23}$$

using the following notation:

$$\begin{aligned}
 A_{\mu\rho}^{acac} &\equiv \sum_{\nu\sigma}^{N_{\text{AO}}} D_{\nu\sigma}^c A_{\mu\nu\rho\sigma}, & A_{\nu\rho}^{caac} &\equiv \sum_{\mu\sigma}^{N_{\text{AO}}} D_{\mu\sigma}^c A_{\mu\nu\rho\sigma}, \\
 A_{\mu\sigma}^{acca} &\equiv \sum_{\nu\rho}^{N_{\text{AO}}} D_{\nu\rho}^c A_{\mu\nu\rho\sigma}, & A_{\kappa\lambda}^{ca} &\equiv 2A_{\kappa\lambda}^{acac} - 3A_{\kappa\lambda}^{caac} - 3A_{\kappa\lambda}^{acca}.
 \end{aligned}
 \tag{24}$$

Thus three four-index transformations are converted into three (to contract the core density) plus one (to contract active MO coefficients) two-index transformations, a considerable savings.

D. Effective core potentials (ECP)

In the effective core potential method, the core inner shell orbitals are replaced by a potential. The primary contribution to SOC comes from the one-electron part that *does not* explicitly include core orbitals, since the core-core and core-active one-electron contributions to SOC are zero. However, the shape of the active orbitals in the core region is lost in most ECP implementations, and this decreases the calculated spin-orbit coupling by orders of magnitude for heavier elements if the Pauli-Breit Hamiltonian is used. Several approaches have been developed to cope with this problem:

- (a) Ermler *et al.*²¹ applied a method wherein the SOC operator itself is changed by utilizing relativistic atomic calculations to obtain the effective one-electron spin-orbit coupling operator and, alternatively, a spin-orbit operator to be used with the pseudo-orbitals is derived by Kühle *et al.*²²
- (b) Model potentials (MP)²³ instead of ECPs do retain the proper shape in the core region.

- (c) By using two related basis sets, an all-electron and an ECP set, the integrals calculated for the all electron basis set can be back-transformed for the ECP basis set,²⁴ thus circumventing the core shape problem.
- (d) Koseki *et al.*³ further developed an effective nuclear charge method, originally developed in Ref. 25 wherein the true nuclear charges appearing in the one-electron SOC operator are replaced by empirical parameters.

E. Empirical parameters

There are several reasons why it can be desirable to introduce some empirical parameters into the spin-orbit coupling calculations:

- (1) ECP produces nodeless orbitals.
- (2) The first-order perturbative treatment and the omission of other interactions (spin-spin) can be corrected to some extent.
- (3) In cases for which the two-electron contribution is either fully (1E) or partially (P2E) neglected, these approximations can be partially compensated by the empirical data. The empirical parameters are optimized using the available atomic and molecular spectral data. The parameters for the first through the third rows of the Periodic Table are available for both ECP and an all-electron basis set,³ to be used with the one-electron method.

F. Thresholds

As pointed out above, thresholds avoid the calculation of very small contributions to SOC, thus saving computational time. One parameter controls all thresholds, denoted by ϵ below. This parameter establishes relative errors in the matrix elements; for example, if ϵ is set to 10^{-4} and the matrix element is 100 cm^{-1} then the absolute error introduced by thresholds should be less than 0.01 cm^{-1} . This parameter is used in the following steps:

- CSFs with coefficients smaller than $\epsilon/N_p N_a$ are ignored (N_p is 2 for the 2E method and 1 for the 1E and the P2E methods).
- In the loop over CSF pairs the calculation proceeds only if the product of two CI coefficients is larger than $\epsilon/N_p N_a^2$.
- In the loop over determinant pairs the calculation proceeds only if the product of two CI coefficients times the determinant's coefficients times the overlap, $q_I q_J C_K C_L O$, is larger than $\epsilon/N_p N_a^2 N_o$, where N_o is the number of occupied orbitals in the active space [i.e., N_e for FOCI (first-order configuration interaction) or SOCI (second-order configuration interaction) and N_a for CAS or FCI].

If there are several CI states with a given multiplicity, the maximum value of the CI coefficient product over these states is taken.

A benefit of using thresholds is the indirect use of symmetry. In many cases, the symmetry used by GUGA has to be lowered, e.g., in case of non-Abelian groups or when several states of different symmetry are requested for the same multiplicity. In such cases the threshold filters out the

CSFs with coefficients equal to zero by symmetry (along with the ones allowed by symmetry but simply small in magnitude). The effect of introducing these thresholds can be seen below in the numerical examples.

It is cumbersome to calculate the matrix elements between two CSFs directly, and determinants provide a simpler alternative. The number of CSFs, however, is usually much smaller than the number of determinants so that the use of thresholds as shown above provides a means for substantial savings. And, the smaller size of the Pauli-Breit Hamiltonian matrix in CSF basis can be advantageous; for example, for contraction of the matrix elements in the CSF basis with CI coefficients.

G. Computational algorithm in detail

The current algorithm is shown in schematic form in Fig. 1. In order to reduce the memory demand, drags and passes are introduced. If sufficient memory is available, there is only one pass and only one drag. If the amount of memory is insufficient to store all integrals at once, at first the code tries to break the $2e$ SOC \hat{l}_x , \hat{l}_y , \hat{l}_z integrals not forbidden by symmetry into passes. Passes are used to divide the work for the components of \hat{l} and drags divide the work for each component of \hat{l} . The following decision is made in the order of decreasing memory available:

one pass: all of symmetry allowed \hat{l}_x , \hat{l}_y , \hat{l}_z

two passes: pass 1: \hat{l}_x , \hat{l}_y ; pass 2: \hat{l}_z

three passes: each \hat{l}_i individually in the order x, y, z .

(Note that “forbidden by symmetry” as applied to integrals here refers not to integrals themselves, but to CI states. The meaning is that none of the CI state pairs requested will require these particular \hat{l} integrals.)

If insufficient memory is available for $2e$ integrals at the maximum number of passes (three or less if all CI states do not require some integrals), the minimum number of passes is used, and to reduce the amount of memory the integrals themselves are divided into chunks. During each drag, a fraction of $2e$ MO integrals is kept in memory and zeros are substituted via an index array in place of integrals not in memory).

VI. COMPARISON OF THE INDIRECT METHODS

A. General comments

The one-electron method is the least resource consuming. The partial two-electron method in practice requires little more resources than the one-electron method. This is true for several reasons:

- (1) The number of determinant pairs to be considered is the same as for the one-electron method (at most one discoincidence allowed).
- (2) The four-index integral transformation can be done with the expense of a two-index transformation.
- (3) There is no need to store four-index two-electron integrals in the MO basis **in memory**.

```

calculate AO SOC integrals.
Loop over bra multiplicities.
  Loop over ket multiplicities
    skip this pair of multiplicities if not allowed by symmetrya
  Loop over drags
    Loop over passes
      calculate SOC integrals
      Loop over ket CSFs
        Loop over bra CSFs
          skip this pair of CSFs if zero by symmetryb or small SOCc
          Loop over bra determinants in the bra CSF
            Loop over ket determinants in the ket CSF
              skip this determinant pair if small SOCc
              calculate SOC and properties
            propagate the CSF matrix element for each pair of CI statesd
          propagate CI state matrix elements into all combinations of  $M_i$  valuese.
        output matrix elements
      diagonalise the  $H_{\text{so}}$  matrix and output results.

```

FIG. 1. SOC algorithm.

^a Symmetry here refers to the rules due to spin angular momentum and Hermiticity, as well as to the point group rules applied to all operators (i.e. SOC and properties) and all CI states.

^b Here symmetry refers to point group symmetry for a pair of CSFs and all operators, as well as permutation symmetry (the maximum number of allowed discoincidences). The orbital occupations and the number of singly occupied orbitals as provided by GUGA are compared.

^c Small SOC refers to the threshold values check

^d This refers to $C^{\dagger}AC$ transformation where C and C' are bra and ket CI coefficient matrices (expansion of CI states over CSFs, A is the matrix of an operator \hat{A} in the CSF basis).

^e The calculated values for SOC $\hat{L}_x, \hat{L}_y, \hat{L}_z$ matrix elements are combined to form matrix elements for each pair of M_i values by means described in the symmetry section.

Additional expenses include having to calculate two-electron integrals in the AO basis. They can be stored on disk while being calculated and read while doing the four-index transformation. This does not require a noticeable amount of memory, although if available, larger buffers can be used to speed up the calculation. These expenses (integrals and transformation) are usually insignificant, especially when compared to the expenses of the further matrix element calculation for a large CI.

On the other hand, the full two-electron method requires treating many more determinant pairs as the number of discoincidences can be two, the four-index transformation is not trivial and most importantly the two-electron integrals are to be kept in memory (for an efficient program) and their number is $N_a^4/4$ for orthogonal and N_a^4 for biorthogonal orbitals.

When comparing the methods numerically it is worth remembering that the first-order perturbative SOC treatment and neglect of other interactions (spin-spin etc.) can introduce errors comparable in magnitude to the error of the partial relative to the full two-electron method even for the first row of the Periodic Table.

The partial two-electron method developed here can be compared to the mean-field method.²⁶ The mean-field method is more general in the treatment of the active-active two-electron contribution. In the partial two-electron method, only the CAS core orbitals (spin-orbital occupation of 1) are included in the two-electron contribution. In the mean-field method, all active orbitals are assigned fixed occupation numbers (between 0 and 1). In both methods, the

two-electron part is then summed over the coincident orbitals with these occupation numbers as weight factors. Both methods neglect contributions due to active-active discoincidences. The mean-field method introduces an approximation to the integrals as well (namely, only one-center integrals are computed and the rest are discarded; this is justified as the SOC operator is short-ranged). In the present partial two-electron method, no such approximation is made. The extra degree of freedom of the mean-field method (the freedom to choose occupation numbers) may be useful.

In the numerical examples below no empirical parameters are used (true nuclear charges). For the notation in the tables in this section, consult Table IV. The results are obtained with 0.1% relative error threshold.

B. Introductory numerical examples

1. XH_2 , $X=C, Si, Ge, Sn, Pb$

Spin-orbit coupling between 1A_1 and 3B_1 states has been studied for a series of XH_2 molecules. The geometries are for the minimum energy potential surface crossing, as found in the previous ECP-based study.²⁷ The active space used here is [6/6], i.e., 6 electrons in 6 active orbitals. CASSCF (complete active space self-consistent field) spin-orbit coupling calculations have been performed using biorthogonal orbitals with the core optimized for the singlet. The second order CI (SOC) SOC calculations were performed with singlet orbitals. Two basis sets have been used. The first (Table IV) is the MINI basis set developed by Huzinaga

TABLE IV. "Mini" basis set CAS XH₂ (X=C, Si, Ge, Sn, Pb) results.

	C_{1e}^a cm ⁻¹	C_{P2e}^a cm ⁻¹	C_{2e}^a cm ⁻¹	E_{P2e} % ^b	M_{1e}^c cm ⁻¹	M_{P2e}^c cm ⁻¹	M_{2e}^c cm ⁻¹
CH ₂	26.78	14.89	13.25	12.4	18.937	8.406	9.565
SiH ₂	96.38	74.57	73.73	1.1	68.15	15.42	16.01
GeH ₂	539.9	481.1	480.4	0.2	381.74	41.53	42.09
SnH ₂	1226	1137	1136	0.05	867.26	63.45	63.86
PbH ₂	2149	2046	2046	0.02	1519.40	72.50	72.79

^a C_{1e} , C_{P2e} , C_{2e} denote SOCC for 1E, P2E, and 2E SOC correspondingly.^b E_{P2e} denotes relative error in $C(C_{P2e}$ relative to C_{2e}).^c M_{1e} , M_{P2e} , M_{2e} denote absolute values of 1E, P2E, and 2E matrix elements. The 1e and 2e matrix elements are always opposite in sign.TABLE V. WTBS basis set CAS XH₂ (X=C, Si, Ge, Sn, Pb) results.

	C_{1e} cm ⁻¹	C_{P2e} cm ⁻¹	C_{2e} cm ⁻¹	E_{P2e} %	M_{1e} cm ⁻¹	M_{P2e} cm ⁻¹	M_{2e} cm ⁻¹
CH ₂	24.34	14.12	12.27	14.6	17.213	7.232	8.540
SiH ₂	74.25	57.93	57.11	1.4	52.50	11.54	12.12
GeH ₂	367.7	328.10	327.3	0.2	260.03	28.03	28.57
SnH ₂	813.8	757.0	756.5	0.06	575.47	40.18	40.56
PbH ₂	2092	1999	1999	0.02	1479.22	65.60	65.92

TABLE VI. WTBS basis set SOCI XH₂ (X=C, Si, Ge, Sn, Pb) results.

	C_{1e} cm ⁻¹	C_{P2e} cm ⁻¹	C_{2e} cm ⁻¹	E_{P2e} %	M_{1e} cm ⁻¹	M_{P2e} cm ⁻¹	M_{2e} cm ⁻¹
CH ₂	23.54	13.66	11.92	15.1	16.645	6.989	8.218
SiH ₂	72.31	56.42	55.64	1.4	51.13	11.24	11.79
GeH ₂	374.2	333.4	332.7	0.2	264.58	28.80	29.32
SnH ₂	850.2	789.6	789.1	0.07	601.18	42.85	43.23
PbH ₂	2242	2140	2140	0.02	1585.69	72.06	72.39

TABLE VII. X₂⁺ (X=O, S, Se, Te) CASSCF/split basis results.

	$R_{X-X'}$, Å	C_{1e} cm ⁻¹	C_{P2e} cm ⁻¹	C_{2e} cm ⁻¹	E_{P2e} %	M_{1e} cm ⁻¹	M_{P2e} cm ⁻¹	M_{2e} cm ⁻¹	${}^2P_{3/2}-{}^2P_{1/2}$, ^a cm ⁻¹
O ₂ ⁺	1.267	177.8	117.0	110.2	6.1	125.70	42.98	47.76	155.9
S ₂ ⁺	1.869	416.1	338.7	336.2	0.74	294.22	54.74	56.51	475.4
Se ₂ ⁺	2.150	1470	1317	1315	0.15	1039.36	107.85	109.24	1860
Te ₂ ⁺	2.585	2643	2452	2451	0.05	1869.04	135.16	136.05	3466

^a ${}^2\Pi_{3/2}-{}^2\Pi_{1/2}$ splitting obtained with the full two-electron SOC.TABLE VIII. BH₂ CAS/FOCI/SOCI SOC results.

CI	Orb ^a	${}^2B_2-{}^2A_1$ cm ⁻¹ ^c	C_{1e} cm ⁻¹	C_{P2e} cm ⁻¹	C_{2e} cm ⁻¹	M_{1e} cm ⁻¹	M_{P2e} cm ⁻¹	M_{2e} cm ⁻¹
CAS	2A_1 ^b	300.6	6.85	3.39	3.01	4.8409	2.4446	2.7157
CAS	2B_2 ^c	-544.6	6.86	3.42	3.02	4.8495	2.4341	2.7137
CAS	2A_1	7578.5	7.00	3.47	3.05	4.9494	2.4927	2.7920
CAS	2B_2	-3852.7	7.16	3.56	3.14	5.0642	2.5456	2.8410
CAS	${}^2A_1+{}^2B_2$ ^d	-1058.1	7.02	3.48	3.07	4.9621	2.5046	2.7944
FOCI	2A_1	578.5	6.68	3.32	2.92	4.7255	2.3801	2.6607
FOCI	2B_2	-2962.9	6.75	3.37	2.98	4.7756	2.3940	2.6707
FOCI	${}^2A_1+{}^2B_2$	-2599.8	6.76	3.35	2.97	4.7800	2.4111	2.6804
SOCI	2A_1	701.9	6.79	3.37	3.00	4.7994	2.4176	2.6795
SOCI	2B_2	-1499.7	6.81	3.40	3.02	4.8147	2.4120	2.6797
SOCI	${}^2A_1+{}^2B_2$	-1160.9	6.78	3.37	3.00	4.7966	2.4168	2.6770

^aOrb stands for the sets of molecular orbitals.^b 2A_1 c: two separate MO sets, fully optimized for 2A_1 and 2B_2 optimized with 2A_1 core.^c 2B_2 c: two separate MO sets, 2B_2 fully optimized and 2A_1 with 2B_2 core.^dAll other rows represent single MO, set ${}^2A_1+{}^2B_2$ being two state averaged (50% + 50%) orbital set.^e ${}^2B_2-{}^2A_1$ refers to adiabatic splitting between the two levels.

TABLE IX. AlH₂ CAS/FOCI/SOCI SOC results.

CI	Orb ^{a,d}	² B ₂ - ² A ₁ cm ⁻¹ ^e	C _{1e} cm ⁻¹	C _{p2e} cm ⁻¹	C _{2e} cm ⁻¹	M _{1e} cm ⁻¹	M _{p2e} cm ⁻¹	M _{2e} cm ⁻¹
CAS	² A _{1c} ^b	337.5	23.77	17.90	17.66	16.8093	4.1529	4.3231
CAS	² B _{2c} ^c	177.9	23.12	17.38	17.14	16.3516	4.0595	4.2296
CAS	² A ₁	8373.7	30.99	23.36	23.05	21.9145	5.3947	5.6152
CAS	² B ₂	-5805.3	29.79	22.31	21.99	21.0682	5.2916	5.5197
CAS	² A ₁ + ² B ₂	387.6	31.28	23.56	23.24	22.1195	5.4618	5.6839
FOCI	² A ₁	1322.2	26.31	19.68	19.38	18.6018	4.6854	4.8971
FOCI	² B ₂	-1282.0	26.97	20.18	19.89	19.0731	4.8031	5.0093
FOCI	² A ₁ + ² B ₂	1357.9	28.05	21.04	20.74	19.8357	4.9595	5.1679
SOCI	² A ₁	579.6	27.01	20.22	19.93	19.1014	4.8056	5.0060
SOCI	² B ₂	-411.7	26.45	19.76	19.48	18.7052	4.7330	4.9330
SOCI	² A ₁ + ² B ₂	38.2	27.62	20.69	20.41	19.5293	4.8971	5.0971

^aOrb stands for the sets of molecular orbitals.

^b²A_{1c}: two separate MO sets, fully optimized for ²A₁ and ²B₂ optimized with ²A₁ core.

^c²B_{2c}: two separate MO sets, ²B₂ fully optimized and ²A₁ with ²B₂ core.

^dAll other rows represent single MO set, ²A₁+²B₂ being two state averaged (50% + 50%) orbital set.

^e²B₂-²A₁ refers to adiabatic splitting between the two levels.

*et al.*²⁸ The second is the WTBS minimal basis set for X and cc-ptvz for H, developed by Huzinaga *et al.*²⁹ with two *s* and two *p* functions on each heavy atom uncontracted; in addition, one *d* on Ge, Sn, and Pb and one *f* on Pb are uncontracted. It is possible to study SOC at both CAS and SOCI levels for the second basis set since this is not a minimal basis set. The results obtained using the larger basis are given in Table V and Table VI. A study of relativistic effects without separating scalar and vector contributions for similar species was conducted by Dyall.³⁰

Note that for both basis sets and at both levels of theory (CAS, SOCI), the agreement between P2E and 2E methods is quite reasonable for all Group IV A elements, and the relative error decreases with increasing mass. The use of SOCI has only a small effect relative to the CASSCF results.

2. X₂⁺, X=O, S, Se, Te

For these species, spin-orbit coupling is studied at the CAS level. The basis set is 6-21G³¹ (X=O) or 3-21G³¹ (X=S,Se,Te). The geometry has been optimized at the CAS level. The experimental value for the ²Π_{3/2}-²Π_{1/2} splitting in O₂⁺ is³² 200.2 cm⁻¹ and with a better basis set the theoretical prediction is³² 195.1 cm⁻¹. The results are presented in Table VII.

As for the XH₂ species, the partial two-electron method is seen to provide reasonable accuracy relative to the full 2E method. The first row of the Periodic Table may require full two-electron treatment if high accuracy is sought after.

C. Effect of orbitals and CI level on SOC

Next, consider the recently studied van der Waals structures of BH₂³³ and AlH₂.³⁴ Spin-orbit coupling plays an important role in the chemistry of many high energy species, because it is very important for such materials to exhibit sufficiently high barriers to ensure stability. Such barriers can be greatly lowered due to potential-energy curve crossing caused by diabatic interactions such as spin-orbit coupling. The geometries used represent the minimum energy crossing of the ²A₁ and ²B₂ surfaces at the multireference CI (MRCI) level of theory. The effect of orbitals and CI level on both the splitting between ²A₁ and ²B₂ surfaces and spin-orbit coupling with both full and partial two-electron methods has been studied. All valence electrons are included in the active space ([5/6]). The basis set for BH₂ is aug-cc-pVTZ³⁵ on both B and H, for AlH₂ it is cc-pVTZ³⁶ on Al and aug-cc-pVTZ on H. The results are summarized in Table VIII and Table IX, for BH₂ and AlH₂, respectively.

The results for these molecules demonstrate the general trend that the choice of orbitals and CI level can have a dramatic impact on the splitting between the two adiabatic levels. Because two similar numbers are subtracted, high accuracy in both is required for an accurate difference. At the same time the spin-orbit coupling is not a property obtained as a difference and thus a much smaller effect of both orbitals and CI level is observed. Nonetheless, the SOC constants

TABLE X. Threshold effect on SOC, AlH₂ at CAS level.

ε	# ² A ₁ CSFs	# ² B ₂ CSFs	C _{1e} cm ⁻¹	C _{p2e} cm ⁻¹	C _{2e} cm ⁻¹	M _{1e} cm ⁻¹	M _{p2e} cm ⁻¹	M _{2e} cm ⁻¹	P2E time ^a	2E time ^a
10 ⁻²	56	55	31.29	23.51	23.25	22.1289	5.4522	5.6865	0.95	1.00
10 ⁻³	59	56	31.28	23.55	23.24	22.1194	5.4606	5.6839	0.94	1.01
10 ⁻⁴	59	56	31.28	23.56	23.24	22.1195	5.4618	5.6839	0.94	1.00
10 ⁻⁵	59	56	31.28	23.56	23.24	22.1195	5.4617	5.6839	0.94	1.01
10 ⁻⁶	59	56	31.28	23.56	23.24	22.1195	5.4617	5.6839	0.94	1.00

^aArbitrary units.

TABLE XI. Threshold influence on SOC, AlH_2 at the SOCI level.

ϵ	# 2A_1 CSFs	# 2B_2 CSFs	C_{1e} cm^{-1}	C_{P2e} cm^{-1}	C_{2e} cm^{-1}	M_{1e} cm^{-1}	M_{P2e} cm^{-1}	M_{2e} cm^{-1}	P2E time ^a	2E time ^a
10^{-2}	37055	39826	27.56	20.64	20.37	19.4859	4.8821	5.0854	0.04	0.13
10^{-3}	90586	93769	27.61	20.68	20.40	19.5220	4.8938	5.0951	0.13	0.42
10^{-4}	122268	123589	27.62	20.69	20.41	19.5293	4.8971	5.0971	0.26	1.
10^{-5}	129483	129651	27.62	20.69	20.41	19.5306	4.8976	5.0975	0.33	1.84
10^{-6}	130317	130251	27.62	20.69	20.41	19.5308	4.8977	5.0975	0.37	2.75

^aArbitrary units.

predicted by the P2E method are in good agreement with the much more resource consuming full 2E method.

D. Effect of thresholds on SOC

AlH_2 as described above is chosen as a test of the influence of the threshold value upon SOC. $^2A_1 + ^2B_2$ orbitals are used throughout. Timings for SOC calculations represent the wall-clock time. The timing for the default value of the threshold (10^{-4}) and 2E method is set to one. At the CAS level, there are 59 2A_1 and 56 2B_2 CSFs (in C_{2v}). In this case the calculation of two-electron SOC integrals gives the dominant contribution to the timings. At the SOCI level, there are 130411 2A_1 and 130314 2B_2 CSFs (in C_{2v}). The results are represented in Table X¹⁰ and Table XI, respectively.

At the 10^{-4} threshold, the preceding CI takes 0.32 and the 1E method 0.23 in the units of the 2E method. Thus, the P2E method takes comparable time with the 1E method (0.26 vs 0.23), the difference coming from two-electron integrals and four-index transformation.

The results obtained in this subsection demonstrate that the threshold values are set properly, that is, the relative error in SOC is not greater than the threshold value used. Some feeling for the increase in computational expense (time) as a function of the threshold value is gained as well. It can be seen that the timings for the P2E method is far less dependent upon threshold as compared to the 2E method, at the SOCI level of theory.

E. Comparison with the mean-field method

The PdCl system was investigated with the mean-field method in Ref. 26. The relative error of the mean-field method relative to the full two-electron result (E_{2e} , %) is 0.02. In Table XII the results obtained with the methods described in this work, using the MINI basis set and full valence active space [17/10] are given. The geometry has been optimized for the term of interest, $^2\Delta$.

As expected, the mean-field method works better than P2E, as it has an extra degree of freedom and treats active-

contributions rather than omit them as the partial method does. The neglect of some two-electron integrals in the mean-field method did cancel the error introduced by neglecting the two disincidence case. The partial two-electron method appears to provide sufficient accuracy, although for Ni the full two-electron approach may be desired for highly accurate calculations. A very interesting observation is made here: The two-electron contribution for transition metals (at least for the molecules considered in this subsection) is much larger than that for the main group elements in the analogous rows in the periodic table.

F. Magnitude of SOC

The question of whether the spin-orbit coupling interaction can be expected to be large or small can be addressed in general. The expressions for the SOC [Eqs. (9) and (19)] suggest that the magnitude of the spin-orbit coupling interaction can be traced to the magnitude of spin-orbit coupling integrals in the molecular orbital basis. These integrals (or their atomic orbital counterparts) are undoubtedly dependent upon the local nature of the spin-orbit coupling operator that has a built in r^{-3} dependence. Therefore, it can be seen that one-center integrals are the major contributors to the interaction. Thus, the SOC integrals in the MO basis are expected to be in general larger for bra and ket MOs localized on the same atom. This leads to a suggestion of using localized orbitals for the approximations of neglecting multicenter integrals.

Second, it can be expected that for atoms the magnitude of SOC is expected to be larger in general than for molecules. Interestingly, some molecules are known to exhibit a SOC interaction virtually identical to that of a single atom.²⁶ Still, as the atomic weight increases, the inner shell core orbitals become less and less changed by chemical bonding, hence it is the core orbitals on these heavy elements that provide the major contribution to the SOC regardless of chemically active valence orbitals. It is expected that molecular complexes involving the interaction of atoms in the middle of the periodic table with light element molecules

TABLE XII. SOC in transition metal systems XCl, where X=Ni, Pd, Pt for the $^2\Delta$ term.

	R_{X-C} , Å	C_{1e}	C_{P2e}	C_{2e}	E_{P2e} %	M_{1e}	M_{P2e}	M_{2e}
NiCl	2.119	1236.0	729.9	677.2	7.8	874.049	357.959	395.21
PdCl	2.491	2496.0	1792.0	1780.0	0.7	1764.839	497.506	506.147
PtCl	2.523	7018.0	5764.0	5755.0	0.1	4962.263	886.487	892.539

retain to a large extent their atomic spin-orbit coupling interactions. The magnitude of these spin-orbit couplings is expected to be larger in general than those in molecules where the middle-sized atoms form bonds and lose their atomic character.

Certainly, symmetry plays an important role in determining the magnitude of SOC because large contributions can occur with opposite phases and the value of SOC is then determined by smaller contributions. The effect of orbital shape upon the magnitude of SOC has also been studied.³⁷

VII. DISCUSSION AND SUMMARY

It is found that the two-electron contribution to the spin-orbit coupling grows roughly as a linear function of the nuclear charge. The one-electron part exhibits a more complicated dependence upon the nuclear charge in the range between linear and square. As expected, the partial two-electron method systematically underestimates the two-electron matrix elements, with the relative error systematically decreasing down the Periodic Table. It can be seen that already for the second period the error introduced by the partial two-electron method becomes negligible or at least comparable to other approximations (nonrelativistic unperturbed wave function, first order perturbative treatment, etc.). With a set of reoptimized empirical parameters, a semiempirical partial two-electron method may offer much better performance (for heavier elements) than the one-electron semiempirical method, for the first row of the periodic table. For the second row, the *ab initio* partial two-electron method is expected to deliver sufficient accuracy. There does not seem to be any real necessity to include two-electron terms for the last row.

Various aspects of the dependence of spin-orbit coupling upon various factors are discussed in the above subsections with appropriate numerical examples.

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