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A determinantal approach to spin-orbit configuration interaction

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Abstract. A general configuration interaction (CI) algorithm incorporating one- and two-electron spin-orbit operators is presented. The algorithm is determinant based and enables the use of highly vectorized non-relativistic algorithms in the most operation-intensive part. Excitations between α and β spin orbitals are avoided in the time consuming parts by performing separate S_+ and S_- operations. The relativistic CI expansions are often very large, so the algorithms require only the presence of segments of vectors in memory. Double-group symmetry is fully accounted for and time-reversal symmetry is exploited for both even and odd numbers of electrons.

Key words: Spin-orbit coupling – Determinant configuration interaction – Time-reversal symmetry – Relativistic configuration interaction

1 Introduction

The development of algorithms for accurate and efficient description of relativistic effects has received considerable attention during the last decade [1]. The RECP (Relativistic Effective Core Potentials) methods have been available for a long time [2] and have been applied to a broad spectrum of problems. Lately, however, all-electron methods centred around the Dirac equation have appeared which enable the theorist to approach the problems of relativistic effects in chemistry with greater accuracy. The four-component Dirac-Coulomb method has developed over the last few years and can now be applied to small and medium-size molecules [3]. This method is still relatively resource-demanding and for larger systems more effective approximate one- and two-component methods have been developed.

Calculations using one-component spin-free relativistic operators may be done on a routine basis with practically no extra cost, whereas the inclusion of spin-dependent terms is far more complicated and relatively few programs are available which include these terms. For this reason spin-dependent relativistic effects are often neglected. For ground state properties and highly coordinated (saturated) compounds this is often reasonable but for many compounds, including the third row transition metals, spin-orbit interactions are of the same order as the chemical bond.

The spin-orbit interaction brings about a fundamental change of practice. These changes are a consequence of the *symmetry properties* of the spin-orbit Hamiltonian. Corresponding to a scaler observable, both the electrostatic Hamiltonian and the spin-orbit Hamiltonian ($\mathscr{H}_{so}$) are *scalar operators*. The electrostatic Hamiltonian, including spin-independent relativistic effects, also has *scalar* space and spin parts and will conserve any space or spin symmetry present in the wave function on which it operates. But ($\mathscr{H}_{so}$) is a contraction of two *vector operators* in orbital and spin space and will in general not preserve space or spin symmetry. It shows the same symmetry properties as the Dirac operator and the eigen states will transform according to the corresponding *double-group* symmetry, containing symmetry operations that work both on space and spin coordinates [4]. Accordingly, a new set of programs is required to treat the spin-orbit coupling.

Due to the computational expense, the inclusion of spin-orbit coupling is usually postponed until the last stage of a calculation, and the easiest way to handle the effect is to include it as a *perturbation*. This has been done for the lighter elements since the 1970s using the *Breit-Pauli operator* [5, 6]. However, moving towards the heavier atoms, the perturbation approach becomes questionable, and the effect should be included using some *variational procedure*.

The Breit-Pauli operator, although not bounded from below, may be used in variational valence methods but overestimates spin-orbit splittings for heavy elements. There are, however, other methods available for the treatment of spin-orbit coupling which are not hampered with these difficulties. Most of them employ effective core potential techniques, for instance calibrated to reproduce four-component results [7]. An all-electron method which has gained prominence over

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the last decade is based on the Douglas-Kroll transformation, resulting in a well-behaved spin-orbit operator that can be used in variational calculations on heavy elements [8, 9].

The dominant spin-orbit effects can often be obtained as the spin-orbit interactions of a limited set of close-lying states. The latter states can either be non-relativistic or include the spin-conserving relativistic effects. A very efficient variational solution is then to calculate the spin-orbit matrix over this set of wave functions and diagonalize the resulting matrix. Programs of this type are available [10, 11] and have been applied with success for elements as heavy as platinum [9, 12].

In this approach one has, however, to assume that electron correlation and spin-orbit coupling are additive and that the relativistic wave function can be described as a linear combination of a small number of wave functions of non-relativistic symmetry. None of these assumptions hold in general. The relative weights of the various determinants in the CI expansion are determined solely by the electron repulsion operator, whereas the spin-orbit operator shows completely different properties. For instance, single excitations are relatively unimportant for r_{ij}^{-1}, whereas they are very important contributors to spin-orbit matrix elements. Leaving them out would result in underestimation of the spin-orbit coupling. It is also to be expected that the amount of correlation energy will differ between, for instance, a $p_{1/2}$ and a $p_{3/2}$ shell when the spin-orbit coupling is large, requiring a simultaneous treatment of the two effects.

Probably a less serious drawback is that the method relies on the validity of the approximate spin-orbit selection rules within the *Russel-Saunders* coupling scheme, accounting only for *L-S* states that couple directly through the spin-orbit Hamiltonian.

Within the two-component theory the most through approach would be to develop both two-component self-consistent field (SCF)/multiconfigurational (MC) SCF and CI (or some other correlation method) codes. SCF and CI programs of this category has been developed by the Siegen group [13–16], but no MCSCF/Multi-reference MRCI package is available to our knowledge.

An intermediate approach has been chosen in this work, introducing the spin-orbit operator in the CI step, thus neglecting spin-orbit coupling during the orbital optimization. Conventional CI codes of this type are available [17–20].

An accurate description of electron correlation is still a challenge to quantum chemistry. Dolg and Stoll suggest in a recent review [21] that the bottleneck in performing accurate relativistic calculations is connected to the correlation problem rather than to the actual form of the relativistic operator. The problem at hand is then to find a method, based on a two-component operator, which is able to include an extensive part of the correlation energy, thus treating very long CI expansions in an efficient way.

The spin-orbit CI program presented below is a generalization of a *direct* non-relativistic CI code by Olsen [22–24]. The program uses a restricted active space (RAS) wave function defined by separating the orbital space into three subspaces I, II and III and imposing restrictions on the minimal occupation of space I and maximal occupation of space III. A core of doubly occupied (inactive) orbitals may also be included. The strong point about the RAS concept is that a wide range of CI expansions can be used in an efficient manner.

The algorithms are determinant based and, using the idea of Handy [25], are separated into α and β strings which allows very efficient vectorization of the time-consuming σ algorithms. Another important feature is that the structure of the CI and σ vectors allows subblocks of the vectors to reside in the memory at any one time.

This presentation will concentrate on the problems connected with spin-orbit CI and how they can be solved, while maintaining the original structures and keeping the non-relativistic σ algorithms as the basic *production units* of the program. Section 2 will focus on different aspects of the theory connected to spin-orbit coupling, including *time-reversal* and *double-group symmetry*, whereas Sect. 3 will deal with the realization of the spin-orbit code based on the theory and facilities offered by the non-relativistic code. Concluding remarks are summarized in Sect. 4.

2 Theory

The complications arising from the inclusion of the spin-orbit coupling can be illustrated by considering a one-electron spin-orbit operator [5]

$$\mathscr{H}_{so} = \sum_i \xi(r_i) l_i \cdot s_i \ , \tag{1}$$

where l_i and s_i are the total orbital and spin angular momenta, respectively, and $\xi(r_i)$ is a radial function, being roughly proportional to the square of the nuclear charge [26].

For light atoms, the spin-orbit coupling is much smaller than the electron repulsion and the *LSJ* coupling scheme is appropriate, having zeroth-order wave functions with well-defined quantum numbers *L, S, J* and M_J. The quantum numbers J and M_J correspond to the total angular momentum and its projection. The spin-orbit coupling within a basis of *LSJ* states follows the *selection rules*

$$S + S' \geq 1 \geq |S - S'| \ , \tag{2}$$

$$L + L' \geq 1 \geq |L - L'| \tag{3}$$

and

$$\delta_{JJ'} \ ; \quad \delta_{M_J M_{J'}} \ . \tag{4}$$

The spin-orbit coupling increases with increasing nuclear charge, and at some point the zeroth-order *L-S* picture breaks down and the orbital and spin quantum numbers lose their meaning. The only angular quantum numbers being strictly conserved are then J and M_J, corresponding to the so-called *J-J* coupling scheme. The only valid selection rules are then given by Eq. (4)

For diatomic and typical linear molecules, the projection of the angular momentum M_L, the total spin S and the spin projection M_S are the conserved quantum numbers for a non-relativistic Hamiltonian. Adding spin-orbit coupling reduces the quantum numbers to M_J.

For a typical polyatomic molecule, the symmetry of a state is described by the *irreducible representations* (irreps) of a point group in non-relativistic quantum mechanics, and by the irreps of the corresponding *double group* in relativistic quantum mechanics. The symmetry properties of the spin-orbit Hamiltonian in a molecular environment will be treated below. We will concentrate on D_{2h} and subgroups, which in the following will be termed *binary groups* as introduced by Saue [27].

2.1 The spin-orbit operator

There are a number of different spin-orbit Hamiltonians in use, some of which contain both one- and two-electron terms, whereas others are effective one-electron operators, based on mean-field or ECP (Effective Core Potential) approaches [7, 28].

Whatever the specific form, they show the same symmetry and spin properties and may all be written as

$$\mathscr{H}_{so} = \sum_i A_i \cdot s_i \ , \tag{5}$$

where the sum runs over all electrons i, and A_i and s_i denote the spatial and spin parts of $\mathscr{H}_{so}$, respectively. The operator A_i can contain a sum over electrons, thereby allowing $\mathscr{H}_{so}$ to contain a two-electron operator.

As an illustration consider the Breit-Pauli operator

$$\mathscr{H}_{so} = \frac{\alpha^2}{2}\left(\sum_{A,i} Z_A \frac{(r_{iA} \times p_i) \cdot s_i}{r_{iA}^3} - \sum_{i \neq j} \frac{(r_{ij} \times p_i) \cdot (s_i + 2s_j)}{r_{ij}^3}\right) \tag{6}$$

which can be presented in the form of Eq. (5) by defining

$$A_i = \frac{\alpha^2}{2}\left\{\sum_A \frac{Z_A}{r_{iA}^3}(r_{iA} \times p_i) + \sum_{j \neq i} \frac{r_{ij} \times (2p_j - p_i)}{r_{ij}^3}\right\} \ . \tag{7}$$

It is well known that the Breit-Pauli operator is unbounded from below, suggesting that it is unsuited for unrestricted variational use. In a limited expansion of configurations of moderate energies, there is no room for variational collapse, however, and the Breit-Pauli operator might work well, although it often overestimates the spin-orbit splitting. Forms of spin-orbit operators suited for variational use are available and may be put in the form of Eq. (5).

In a basis of states of well-defined space and spin symmetry, $\mathscr{H}_{so}$ will cause a mixing of previously non-interacting states. It is most convenient to study this with the spin part of the spin-orbit operator in the spherical form and the space part of the operator in the cartesian form, since the spherical components of the angular momentum operator do not transform as irreps of the binary groups. Expanding the scalar products and introducing the spherical components of s

$$s_{+1} = -\frac{(s_x + is_y)}{\sqrt{2}}; \quad s_0 = s_z; \quad s_{-1} = \frac{(s_x - is_y)}{\sqrt{2}} \ , \tag{8}$$

the general spin-orbit operator in Eq. (5) yields

$$\mathscr{H}_{so} = \sum_i \Big\{ A_{ix}[s_{i-1} - s_{i+1}]/\sqrt{2} + iA_{iy}[s_{i-1} + s_{i+1}]/\sqrt{2} + A_{iz}\, s_{i0} \Big\} \ . \tag{9}$$

For the spatial parts we note that A_x, A_y and A_z transform with the components R_x, R_y and R_z of the rotation operator and have a well-defined symmetry with in D_{2h} and the subgroups.

Since the rotation operators commute with the inversion operators

$$[R_x, i] = [R_y, i] = [R_z, i] = 0 \ , \tag{10}$$

it is found that $\mathscr{H}_{so}$ always preserves spatial *inversion symmetry*. The operators R_x, R_y and R_z are, however, not invariant under any C_2 rotation perpendicular to their own rotation axis or with any reflection operation parallel to it. The result is that no other spatial symmetry than inversion is preserved for the binary groups. The point groups for spatial symmetry operations become thus either C_i or C_1, for systems with or without inversion symmetry, respectively. For the matrix element between two determinants ψ_1 and ψ_2 and one spatial component A_μ to be non-zero one must require, using the *matrix element theorem*, that the direct product between the irreps

$$\Gamma(\psi_1) \otimes \Gamma(A_\mu) \otimes \Gamma(\psi_2) \tag{11}$$

contains the totally symmetric representation.

For the spin part we have

$$[\mathscr{H}_{so}, S^2] \neq 0 \ ,$$

$$[\mathscr{H}_{so}, S_z] \neq 0 \tag{12}$$

and spin symmetry is not conserved. It is easily seen from Eq. (9) that a non-zero matrix element requires that the spin part satisfies $\Delta M_s = \pm 1$ for the x and y terms whereas the z term requires $\Delta M_s = 0$.

2.2 Time-reversal symmetry

As suggested above, spin symmetry will not be preserved by the Hamiltonian once the spin-orbit term is introduced. There is, however, another symmetry operation related to spin that commutes with the Hamiltonian in the absence of external magnetic fields, namely the *time-reversal operator* $(\hat{\mathscr{K}})$ [29]. In a two-component theory it may be defined as

$$\hat{\mathscr{K}} = -i\sigma_y \hat{\mathscr{K}}_0 \ , \tag{13}$$

where σ_y is the Pauli-spin matrix and $\hat{\mathscr{K}}_0$ a complex conjugation operator.

The single particle fermion functions are doubly degenerate by *Kramer's theorem* [4], and the two degenerate states are related by time-reversal symmetry. Letting $\hat{\mathscr{K}}$ act on a single α or β spin function yields

$$\hat{\mathscr{K}}\alpha = \beta \ ,$$

$$\hat{\mathscr{K}}\beta = -\alpha \ . \tag{14}$$

The degenerate spin functions α and β are termed *partners* of a *Kramer's pair*, as are all fermion functions related in this way by time-reversal.

Before examining the behaviour of N-electron functions under time reversal, we adopt the convention of writing all α creation operators in front of all β creation operators, in which case a Slater determinant (SD) can be written

$$\begin{aligned} |I,J\rangle &= |\alpha(I)\beta(J)\rangle \\ &= \alpha(I)\beta(J)|vac\rangle \ , \end{aligned} \tag{15}$$

where $\alpha(I)$ is an ordered product of α creation operators and $\beta(J)$ an ordered product of β creation operators; an α and β string, respectively.

Applying the time-reversal operator to a SD containing real orbitals gives

$$\hat{\mathscr{K}}|I,J\rangle = (-1)^{(n_\alpha+1)n_\beta}|J,I\rangle \ , \tag{16}$$

where n_α and n_β are the number of electrons with α and β spin, respectively. So $\hat{\mathscr{K}}$ changes the α string to the corresponding β string and vice versa, together with a possible change of phase, producing a $-M_s$ determinant from a $+M_s$ determinant.

If the system contains an *even number of electrons*, the effect of the Kramer's operator on a determinant $|I,J\rangle$ is given by

$$\hat{\mathscr{K}}|I,J\rangle = |J,I\rangle \tag{17}$$

from Eq. (16).

It is easily seen that the following simple combinations

$$\begin{aligned} |(I,J)^+\rangle &= |I,J\rangle + |J,I\rangle \ , \\ |(I,J)^-\rangle &= |I,J\rangle - |J,I\rangle \ , \end{aligned} \tag{18}$$

are eigenfunctions of the Kramer's operator with an eigenvalue (κ) equal to $+1$ or -1:

$$\begin{aligned} \hat{\mathscr{K}}|(I,J)^+\rangle &= +1|(I,J)^+\rangle \ , \\ \hat{\mathscr{K}}|(I,J)^-\rangle &= -1|(I,J)^-\rangle \ . \end{aligned} \tag{19}$$

Note that the symmetry operation of time-reversal is *not* included in the double groups and may be exploited in addition to double-group symmetry.

2.3 Double-group symmetry

The spin-orbit operator shows the same commutation properties as the Dirac operator, and symmetry operations other than inversion commuting with $\mathscr{H}_{so}$ will have to work both on space and spin coordinates. For functions with half-integer angular momentum, such as the spin functions α and β, the unit operation is a rotation by 4π, whereas a rotation of 2π, corresponding to the unit operation in ordinary groups, leads to a change of sign. The double groups are constructed by introducing an extra element $\bar{E}$ representing a rotation by 2π around an arbitrary axis [4]. The additional (fermion) irreps appearing describe the transformation properties of fermion functions and will have a negative character for $\bar{E}$, whereas the original single group (boson) irreps are invariant under the operation.

The double group C_{2v} is shown in Table 1. The four boson irreps are equivalent to the irreps of the C_{2v} spatial group, and a new two-dimensional irrep E describing the behaviour of fermion functions of the group is shown.

Examples of spin functions spanning the various representations are also shown in Table 1. A Kramer's pair, such as α and β, together span the irrep E. A similar picture is seen for the point groups D_{2h} and D_2, whereas they span different but degenerate one-dimensional irreps for C_s, C_2 and C_{2h}. The groups C_1 and C_i are the most complicated, with the Kramer's partners spanning the same singly degenerate representation.

We further see that the cartesian components s_x, s_y, s_z of a triplet-spin function span the irreps B_2, B_1 and A_2 whereas the singlet-spin function spans the totally symmetric representation. On comparing these symmetry-adapted functions with the Kramer's eigenstates defined in Eq. (18) it can be seen that time-reversal symmetry and double-group symmetry coincide in this case.

The combinations $\alpha\beta - \beta\alpha$ and $\alpha\alpha + \beta\beta$ have a positive κ for $\hat{\mathscr{K}}$ and the combinations of $\alpha\beta + \beta\alpha$ and $\alpha\alpha - \beta\beta$ a negative κ. This might be confusing since, as indicated by Eq. (19), the plus combinations always have $\kappa = +1$ and minus combinations $\kappa = -1$. This is a consequence of the alpha-beta string formalism in which creation operators are permutated, putting all α creation operators first (i.e. $a^+_{i\alpha}a^+_{j\beta} + a^+_{i\beta}a^+_{j\alpha} = a^+_{i\alpha}a^+_{j\beta} = -a^+_{j\alpha}a^+_{i\beta}$).

The relation between double-group and time-reversal symmetry is the same for the groups D_{2h} and D_2. For the lower symmetry groups the Kramer's eigenstates correspond to fixing a phase between equivalent $+M_s$ and $-M_s$ states which is otherwise arbitrary as far as the Hamiltonian is concerned. Here lies potential for making the computation more effective.

2.4 Spin-orbit CI

When the spin-orbit operator is introduced, the structure of CI space alters, exhibiting now the symmetry of a relativistic Hamiltonian. Following the exact selection

Table 1. The $C_{2\mathrm{v}}$ double group

$\bar{D}_2$	E	$\bar{E}$	$C_2(z), C_2(z)\bar{E}$	$\sigma_v(xz), \sigma_v(xz)\bar{E}$	$\sigma_v(yz), \sigma_v(yz)\bar{E}$	
A_1	1	1	1	1	1	$\alpha\beta - \beta\alpha$
A_2	1	1	1	−1	−1	$R_z, \hat{s}_z, \alpha\beta + \beta\alpha$
B_1	1	1	−1	1	−1	$R_y, \hat{s}_y, \alpha\alpha + \beta\beta$
B_2	1	1	−1	−1	1	$R_x, \hat{s}_x, \alpha\alpha - \beta\beta$
E	2	−2	0	0	0	(α, β)

rule analogue of Eq. (4) for molecules, the space must contain all possible N-particle states of a given double-group symmetry. A consequence is that all possible M_s values are included. Note that the dimension of the CI space is therefore the same as that for a four-component CI method.

As an example we consider a system having a reference wave function with one open shell, from which we allow all single and double excitations, corresponding to a maximum of five open shells. In the spin-orbit CI case, this corresponds to including six M_s values in the CI expansion. Furthermore, the CI vector will generally be complex, since the x and z terms of $\mathscr{H}_{so}$ are imaginary. In the absence of spatial symmetry, the number of variational parameters should then be roughly 12 times that of a non-relativistic CI.

A further illustration of the computational demands is made by looking at the spin-orbit operator in the form of Eq. (9). We find five different combinations of space and spin operators, and one of these terms is comparable to the non-relativistic Hamiltonian in complexity if the spin-orbit operator contains two-electron terms. Calculating one element of the σ vector should then take roughly 6 times as long when the spin-orbit operator has been added to the Hamiltonian, and calculating the whole σ vector in the example above should take $12 \times 6 = 72$ times as long as in the non-relativistic case.

In a non-relativistic CI the length of the CI expansion may be reduced considerably by the use of a CSF (Configuration State Function) basis. In the spin-orbit CI however, the numbers of CSFs and SDs are in fact the same, and the simplicity of the determinant basis is clearly favourable compared to the CSF basis, for which the number of coupling coefficients will grow drastically compared to the non-relativistic case.

The advantage of the CSF approach is that one can limit the CI expansion by discarding multiplets which are expected to be unimportant, for instance by enforcing the approximate selection rule $S + S' \geq 1 \geq |S - S'|$. This approach becomes increasingly more effective as the number of open shells increases, but relies of course on the validity of the selection rule.

In a SD basis the selection rule $\Delta M_s = 0, \pm 1$ also determines the first-order interacting subspace. For states of atoms and linear molecules, the proper zero-order wave functions are linear combination of states with different values of M_s, so the restriction on M_s does not lead to a restriction on the interacting spaces. For molecules with non-degenerate spatial symmetry, the $\Delta M_s = 0, \pm 1$ can as a rule be used to advantage.

3 Implementation

As already mentioned an efficient non-relativistic CI code was at our disposal and the idea was to maintain the basic structures and algorithms of the existing program, building the spin-orbit peculiarities around it.

The spin-independent Hamiltonian can be expressed entirely in terms of singlet-spin operators, i.e.

$$S_{ij}(0,0) = \frac{1}{\sqrt{2}} \left(a^{+}_{i\alpha} a_{j\alpha} + a^{+}_{i\beta} a_{j\beta} \right) \ , \tag{20}$$

preserving the number of α and β electrons when acting on a determinant. The spin-orbit operator also contains triplet operators in spin space, given by

$$T_{ij}(1,1) = -a^{+}_{i\alpha} a_{j\beta} \ , \tag{21}$$

$$T_{ij}(1,0) = \frac{1}{\sqrt{2}} \left(a^{+}_{i\alpha} a_{j\alpha} - a^{+}_{i\beta} a_{j\beta} \right) \ , \tag{22}$$

$$T_{ij}(1,-1) = a^{+}_{i\beta} a_{j\alpha} \tag{23}$$

and will not preserve the number of α and β electrons. We can therefore not restrict the CI expansion to a given value of M_s.

The operator $\mathscr{H}_{so}$ is furthermore not, in general, invariant to the symmetry operations of the non-relativistic point group, and one can therefore not associate a single spatial symmetry to a relativistic wave function. Examining $\mathscr{H}_{so}$ in Eq. (6) reveals also that the two-electron term is, in contrast to $1/r_{ij}$, not symmetric in the two-particle indices. Furthermore, an angular momentum operator is anti-symmetric, i.e. $\mathrm{l}_{ij} = -\mathrm{l}_{ji}$, leading to the following permutation rules for one- and two-electron spin-orbit integrals

$$h_{ij} = -h_{ji} \ , \tag{24}$$

$$g_{\hat{i}jkl} = g_{\hat{i}jlk} = -g_{\hat{j}ikl} \neq g_{\hat{k}lij} \ , \tag{25}$$

where $g_{\hat{i}jkl} = (i(1)j(1)|k(2)l(2))$ and the hat indicates that the momentum operator is working on particle 1. The non-relativistic integrals are symmetric with respect to all the permutations of indices shown above.

In extending a non-relativistic program to include the spin-orbit operator, a number of generalizations must thus be introduced. The CI vector must contain several spatial symmetries and spin projections, and general one- and two-electron operators that change spin projection and spatial symmetry must be allowed. A radical approach would be to completely abandon spatial symmetry and spin projection. This would, however, be computationally expensive, since the well-defined symmetry properties of the individual operators would be neglected and lead to states that are difficult to classify. Instead we will use an approach that makes maximal use of the non-relativistic symmetry properties.

Below we will first describe the features of the non-relativistic program that are necessary for further discussion and then focus on how the problems encountered in the generalization of spin-orbit CI are solved. A more detailed presentation of the non-relativistic program is given in Refs. [22–24].

3.1 The framework

The RAS is a simple way of defining restricted CI spaces and may be handled very efficiently in direct CI iterations. The active orbital space is divided into three subspaces RAS1, RAS2 and RAS3, requiring a minimal number of occupied spin orbitals of RAS1 and a maximal number in RAS3.

Splitting the determinants into α and β strings as shown in Eq. (15) the CI vector may be written as

$$|0\rangle = \sum_{I_\alpha, I_\beta} C(I_\alpha, I_\beta)|I_\alpha, I_\beta\rangle \ , \tag{26}$$

where indices I, J have been replaced by I_α, I_β. In the case of a full CI, the CI vector has the form of a matrix in this representation, but all α and β strings are not allowed to be combined for restricted CI spaces, and the structure of the CI vector does not automatically result in a matrix notation.

A *graphical string representation* provides an efficient way of ordering the strings [34], and this may be realized in several ways. Defining separate occupation graphs for different *types*, the latter referring to the number of electrons in RAS1 and RAS3 occupations, allows a simple handling of the RAS1-RAS3 restrictions by restricting which graphs of α and β strings can be combined. A unique index I_α/I_β for each string is obtained by the lexical ordering suggested by Duch [34]. The strings may further be ordered according to symmetry so all strings of the same symmetry and type have contiguous addresses. The CI vector (Eq. 26) will now have the form of a blocked matrix, and each subblock may be treated in the same way as a full CI matrix.

We further need in the direct CI an efficient way of obtaining the effect of a creation or annihilation operator on a string and this information can easily be obtained from the graphs. A table for each string I giving the effect of all possible annihilations and creations

$$\begin{aligned} a_i|I\rangle &= \pm|J\rangle \ , \\ a_j^+|I\rangle &= \pm|K\rangle \ , \end{aligned} \tag{27}$$

can be calculated. This implies that strings not contained in the CI space have to be defined. At most two electrons are annihilated by the excitation operators in $\mathscr{H}$, thus string groups containing n_α to $n_\alpha - 2$ electrons have to be defined for α strings and likewise for β strings, even if only the groups containing n_α and n_β are allowed in the CI expansion. The effect of several creation/annihilation operators may be accessed in the σ routines by repeated table lookups.

The terms *string group*, referring to the number of electrons, was introduced above, and the spin-orbit CI requires that several groups of strings are allowed in the CI expansion. Inspired by the approximate selection rule $\Delta M_s = 0, \pm 1$ we introduce the possibility of restricting the allowed range of M_s values by giving a fundamental or reference M_s and an interval Δ, allowing an expansion over all values from $M_s - \Delta$ to $M_s + \Delta$.

The necessary string information is then simply provided by defining the additional string groups and "relaxing" the restrictions on which graphs can be combined. The strings are now ordered according to group, symmetry and type.

3.2 Relativistic CI expansion

The relativistic CI-vector will have the general form

$$\begin{aligned} |0\rangle = \sum_{M_s, K} \sum_{I_\alpha, I_\beta} {}^{M_s K}C^r(I_\alpha I_\beta)|I_\alpha, I_\beta\rangle \\ + i \sum_{I_\alpha, I_\beta} {}^{M_s K}C^i(I_\alpha, I_\beta)|I_\alpha, I_\beta\rangle \ . \end{aligned} \tag{28}$$

The indices M_s and K refer to the spin projection and spatial symmetry, respectively. The determinants can be divided at a number of different levels. The collection of all the determinants of the CI expansion is called a *CI super space*. The collection of determinants with given spin projection, spatial symmetry, and real/imaginary characters corresponds to a non-relativistic wave function, and is in the following referred to as a *CI space*. A *CI super space* is the sum of *CI spaces*. The CI spaces constitute the basis units of the program and they can be divided into symmetry blocks, where each symmetry block corresponds to the determinants with a given M_s, real/imaginary character and symmetries of the α and β strings. The symmetry blocks can again be divided into symmetry-type blocks where each symmetry-type block corresponds to all determinants with given M_s, real/imaginary character, symmetries of the α and β strings and type of the α and β strings.

In the relativistic CI algorithm we must calculated the σ vector in the CI super space from a CI vector in the CI super space. We will organize this as a sequence of calculations, each only giving the contribution to the σ vector in a given space from a CI vector in a given CI space. The above blocking of CI spaces opens the possibility of working with individual segments of the CI and σ vectors in the memory at any one time, so that the sigma routines calculate the contribution from a given symmetry-type-type block of the CI vector to a given symmetry-type-type block of the σ vector. The two-electron integrals may be sorted by symmetry and type, so that the contributing block is easily accessed in this step. Before describing the relativistic CI routines in greater detail it is advantageous to briefly review the corresponding non-relativistic codes.

3.3 Non-relativistic sigma algorithms

Any spin-independent Hamiltonian may in second quantization form be written as

$$\mathscr{H}_0 = \sum_{ij} h_{ij} E_{ij} + 1/2 \sum_{ijkl} (ij|kl)(E_{ij}E_{kl} - \delta_{jk}E_{il}) \ , \tag{29}$$

where $E_{ij} = a_{i\alpha}^+ a_{j\alpha} + a_{i\beta}^+ a_{j\beta}$. The central task in direct CI schemes is the construction of the σ vector which is defined by

$$\sigma(I_\alpha, I_\beta) = \sum_{J_\alpha, J_\beta} \langle I_\alpha I_\beta | \mathscr{H}_0 | J_\alpha J_\beta \rangle C(J_\alpha, J_\beta) \ , \tag{30}$$

The σ vector has to be generated directly from the orbital representation of the operator and is the most time-consuming step of a direct CI iteration. Several different approaches to the construction of σ have been tried out by Olsen [24]. The most efficient ones are made possible by separating the σ vector into three contributions

$$\sigma = \sigma_{\alpha\alpha} + \sigma_{\alpha\beta} + \sigma_{\beta\beta} \ , \tag{31}$$

with

$$\begin{aligned}
\sigma_{\alpha\alpha}\left(I_\alpha, I_\beta\right) = \sum_{J_\alpha} \Bigg\{ & \sum_{ij} \langle I_\alpha | a^+_{i\alpha} a_{j\alpha} | J_\alpha \rangle h_{ij} \\
& + \sum_{i>k,l>j} \langle I_\alpha | a^+_{i\alpha} a^+_{k\alpha} a_{l\alpha} a_{j\alpha} | J_\alpha \rangle [(ij|kl) \\
& - (il|kj)] \Bigg\} C\left(J_\alpha, I_\beta\right) \\
\sigma_{\alpha\beta}\left(I_\alpha, I_\beta\right) = \sum_{J_\alpha, J_\beta} & \sum_{ijkl} \left\langle I_\beta \middle| a^+_{i\beta} a_{j\beta} \middle| J_\beta \right\rangle \\
& \times \langle I_\alpha | a^+_{k\alpha} a_{l\alpha} | J_\alpha \rangle (ij|kl) C\left(J_\alpha, J_\beta\right) \qquad (32) \\
\sigma_{\beta\beta}\left(I_\alpha, I_\beta\right) = \sum_{J_\beta} \Bigg\{ & \sum_{ij} \left\langle I_\beta \middle| a^+_{i\beta} a_{j\beta} \middle| J_\beta \right\rangle h_{ij} \\
& + \sum_{i>k,l>j} \left\langle I_\beta \middle| a^+_{i\beta} a^+_{k\beta} a_{l\beta} a_{j\beta} \middle| J_\beta \right\rangle [(ij|kl) \\
& - (il|kj)] \Bigg\} C\left(I_\alpha, J_\beta\right) \ .
\end{aligned}$$

The potential for vectorization may be easily comprehended for $\sigma_{\alpha\alpha}$ and $\sigma_{\beta\beta}$ as excitations are only performed on the α and β strings, respectively, and allows vectorization over the string that remains unchanged. We will not discuss further the algorithms used for the construction of the three contributions to σ, but only note that a number of schemes for the efficient evaluation have been proposed.

3.4 Spin-orbit sigma algorithms

In generating the spin-orbit contributions to the σ vector, we intend to apply the non-relativistic σ algorithms. However, as already mentioned above, a number of difficulties have to be overcome, since the spin-orbit operator has a fundamentally different structure. In the second quantization formalism $\mathscr{H}_{so}$ can be written as

$$\mathscr{H}_{so} = \sum_{ij} h_{ij} \cdot s_{ij} + \sum_{ijkl} \left(\tilde{i}j|kl\right) \cdot \left(s_{ij} E_{kl} - \delta_{jk} s_{il}\right) \ . \tag{33}$$

For the *Breit-Pauli operator* the one-electron integrals are of the form

$$h_{ij} = \frac{\alpha^2}{2} \sum_A Z_A \left\langle i(1) \middle| \frac{r_A \times p_1}{r_A^3} \middle| j(1) \right\rangle \tag{34}$$

and the two-electron integrals are defined as

$$\begin{aligned}
\left(\tilde{i}j|kl\right) &= g_{\hat{i}jkl} + 2 g_{ij\hat{k}l}; \\
g_{\hat{i}jkl} &= \frac{\alpha^2}{2} \left\langle i(1)k(2) \middle| \frac{r_{12} \times p_1}{r_{12}^3} \middle| j(1)l(2) \right\rangle \ .
\end{aligned} \tag{35}$$

The excitation operators s_{ij} have cartesian components

$$\begin{aligned}
s^x_{ij} &= 1/2\left(a^+_{i\alpha} a_{j\beta} + a^+_{i\beta} a_{l\alpha}\right) \\
s^y_{ij} &= -i/2\left(a^+_{i\alpha} a_{j\beta} - a^+_{i\beta} a_{l\alpha}\right) \\
s^z_{ij} &= 1/2\left(a^+_{i\alpha} a_{j\alpha} - a^+_{i\beta} a_{j\beta}\right) \ .
\end{aligned} \tag{36}$$

It is clear from Eqs. (33) and (36) that the non-relativistic σ algorithms can not be used directly for the x and y components, since s^x_{ij} and s^y_{ij} contain operators of the form $a^+_{i\alpha} a_{j\beta}$ and $a^+_{i\beta} a_{j\alpha}$, exciting electrons between α and β spin orbitals.

For a CSF-based approach, it is possible to avoid treating these excitation operators by expressing s_{ij} in terms of the components of the triplet tensor operator T_{ij} as given in Eq. (21). In a basis of states having well-defined spin quantum numbers S and M_s, one can avoid treating the $\alpha \leftrightarrow \beta$ excitations directly. The $T_{ij}(1,1)$ and $T_{ij}(1,-1)$ operators in $\mathscr{H}_{so}$ are replaced by the $T_{ij}(1,0)$ component, and matrix elements between states differing in the spin projection may then be calculated by the *Wigner-Eckhart theorem.* Only a few routines for calculating $3J$ coefficients are required in addition to efficient routines for handling the $M_s = 0$ components of triplet operators.

The possibilities of utilizing the tensor properties of the excitation operators are more limited in determinant-based CI, since S is no longer defined. However, as we will show later, it is trivial to generalize a determinant program for singlet operators to treat the $M_s = 0$ components of triplet operators. One can exploit a somewhat less complete formulation of the transformation properties if ITOs (Irreducible Tensor Operators), expressed through the following relations

$$\begin{aligned}
T_{ij}(1,1) \quad &= 1/\sqrt{2}\left[S_+, T_{ij}(1,0)\right] \\
T_{ij}(1,-1) \quad &= 1/\sqrt{2}\left[S_-, T_{ij}(1,0)\right] \ .
\end{aligned} \tag{37}$$

Using this result, one can rewrite $\mathscr{H}_{so}$ entirely in terms of the $m = 0$ component of the triplet operator T_{ij} and the step operators S_+ and S_-.

For simplicity we define an operator

$$\begin{aligned}
\mathscr{O}_\mu \equiv \ & \sum_{ij} h^\mu_{ij} T_{ij}(1,0) + \sum_{ijkl} \left(\tilde{i}j|kl\right)_\mu \\
& \times \ \left[T_{ij}(1,0) E_{kl} - \delta_{jk} T_{il}(1,0)\right] \ .
\end{aligned} \tag{38}$$

Compared with Eq. (29) we see that $\mathscr{O}_\mu$ has a structure which is very similar to the spin-independent Hamiltonian. The operator $T_{ij}(1,0)$ differs from E_{ij} by a minus sign for the $\beta\beta$ part and a factor of $\sqrt{2}$. Substituting x, y, z for μ the spin-orbit operator can be written as

$$\mathscr{H}_{so} = \mathscr{H}^x_{so} + \mathscr{H}^y_{so} + \mathscr{H}^z_{so} \ , \tag{39}$$

with

$$\begin{aligned}
\mathscr{H}^x_{so} &= 2^{-3/2}(-S_+ + S_-)\mathscr{O}_x + 2^{-3/2}\mathscr{O}_x(S_+ - S_-) \\
\mathscr{H}^y_{so} &= 2^{-3/2} i(-S_+ - S_-)\mathscr{O}_y + 2^{-3/2} i\mathscr{O}_y(S_+ + S_-) \\
\mathscr{H}^z_{so} &= 2^{-1/2}\mathscr{O}_z \ .
\end{aligned} \tag{40}$$

For the two-electron part we have applied $[S_+, E_{kl}] = [S_-, E_{kl}] = 0$.

The advantage of this approach is that one can separate the "spin transformation" from the most time-consuming part of the direct CI, using only the $m = 0$ component of the triplet operator inside the σ routines. Instead simple S_+ and S_- operations are performed on the vectors before or after a Hamilton transformation using the type of operator defined in Eq. (38).

Let us now consider the calculation of the σ vector for the operator $\mathcal{O}_\mu$ (38). In accordance with the non-relativistic sigma algorithms, the σ vector is split into three terms as given in Eqs. (31) and (32). The two-electron $\alpha\alpha$ contribution may be rewritten in the following way

$$\begin{aligned}\sigma_{\alpha\alpha}(I_\alpha, I_\beta) &= \sum_{J_\alpha} \left\{ \sum_{ij} \langle I_\alpha | a^+_{i\alpha} a_{j\alpha} | J_\alpha \rangle h^\mu_{ij} \right. \\ &\qquad \left. + \sum_{ijkl} \langle I_\alpha | a^+_{i\alpha} a^+_{k\alpha} a_{l\alpha} a_{j\alpha} | J_\alpha \rangle \left(\tilde{ij}|kl\right)_\mu \right\} C(J_\alpha, I_\beta) \\ &= \sum_{J_\alpha} \left\{ \sum_{ij} \langle I_\alpha | a^+_{i\alpha} a_{j\alpha} | J_\alpha \rangle h^\mu_{ij} \right. \\ &\qquad + \sum_{i>k,l>j} \langle I_\alpha | a^+_{i\alpha} a^+_{k\alpha} a_{l\alpha} a_{j\alpha} | J_\alpha \rangle \\ &\qquad \left. \times \left[(ij|kl)^+_\mu - (il|kj)^+_\mu \right] \right\} C(J_\alpha, I_\beta) \ , \end{aligned} \tag{41}$$

where the summation has been restricted by defining a *symmetric* combination of integrals

$$(ij|kl)^+_\mu = \left(\tilde{ij}|kl\right) + \left(\tilde{kl}|ij\right) = 3\left(g^\mu_{\hat{i}jkl} + g^\mu_{\hat{k}lij} \right) \ . \tag{42}$$

An equivalent expression is obtained for the $\beta\beta$ contribution, the only difference being a minus sign, which originates from the anti-symmetric combination of α and β excitation operators in $T_{ij}(1,0)$. For the $\alpha\beta$ part one can write

$$\begin{aligned}\sigma_{\alpha\beta}(I_\alpha, I_\beta) &= \sum_{J_\alpha, J_\beta} \sum_{ijkl} \Big\langle I_\alpha, I_\beta \Big| a^+_{i\alpha} a_{j\alpha} a^+_{k\beta} a_{l\beta} \\ &\qquad - a^+_{i\beta} a_{j\beta} a^+_{k\alpha} a_{l\alpha} \Big| J_\alpha, J_\beta \Big\rangle C(J_\alpha, J_\beta) \left(\tilde{ij}|kl\right)_\mu \\ &= \sum_{J_\alpha, J_\beta} \sum_{ijkl} \langle I_\alpha | a^+_{i\alpha} a_{j\alpha} | J_\alpha \rangle \\ &\qquad \times \Big\langle I_\beta \Big| a^+_{k\beta} a_{l\beta} \Big| J_\beta \Big\rangle C(J_\alpha, J_\beta) (ij|kl)^-_\mu \ , \end{aligned} \tag{43}$$

where this time an *anti-symmetric* combination of integrals has been defined

$$(ij|kl)^-_\mu = \left(\tilde{ij}|kl\right)_\mu - \left(\tilde{kl}|ij\right)_\mu = g^\mu_{\hat{i}jkl} - g^\mu_{\hat{k}lij} \ . \tag{44}$$

Comparing Eqs. (41) and (43) with Eq. (32), we find that they are almost identical in structure and the existing sigma algorithms can be used with trivial changes for the operators $\mathcal{O}^\mu_{so}$, involving a possible prefactor and a sign change for the $\beta\beta$ contributions. The + and − combination spin-orbit integrals may be generated on the fly.

This result shows that the only thing required in addition to the already existing non-relativistic CI algorithms is a machinery performing S_+ and S_- operations on the c and σ vectors.

The spin-flip operators have the form $S_+ = \Sigma_i a^+_{i\alpha} a_{i\beta}$ and $S_- = \Sigma_i a^+_{i\beta} a_{i\alpha}$. The transformation of the CI vector by S_+ (i.e. $C \rightarrow C_+$) may be written as

$$\begin{aligned} C_+(I_\alpha, I_\beta) &= \sum_{J_\alpha, J_\beta} \sum_i \langle I_\alpha | a^+_{i\alpha} | J_\alpha \rangle \\ &\qquad \times \langle I_\beta | a_{i\beta} | J_\beta \rangle C(J_\alpha, J_\beta) (-1)^{n_\alpha(J_\alpha)} \end{aligned} \tag{45}$$

and this S_- transformation

$$\begin{aligned} C_-(I_\alpha, I_\beta) &= \sum_{J_\alpha, J_\beta} \sum_i \langle I_\alpha | a_{i\alpha} | J_\alpha \rangle \langle I_\beta | a^+_{i\beta} | J_\beta \rangle \\ &\qquad \times C(J_\alpha, J_\beta) (-1)^{n_\alpha(J_\alpha)+1} \ . \end{aligned} \tag{46}$$

The factor $(-1)^{n_\alpha(J_\alpha)}$ appears for S_+ because the β creation operator must be moved through the string of n_α α creation operators in J_α, whereas for S_- there is an additional α operator $a_{i\alpha}$ to the right of $a^+_{i\beta}$, leading to a factor $(-1)^{n_\alpha(J_\alpha)+1}$.

The calculation of C_+ can be realized in the following way.

```
Loop over orbitals $i$.
    Set up arrays $P(I_\alpha) = J_\alpha$ and $pha(I_\alpha)$ where
        $|I_\alpha\rangle = a^+_{i\alpha}|J_\alpha\rangle \ pha(I_\alpha)$ .
    Set up arrays $M(I_\beta) = J_\beta$ and $phb(I_\beta)$ where
        $|I_\beta\rangle = a_{i\beta}|J_\beta\rangle phb(I_\beta)$ .
    Loop over $I_\beta$
        $C_+(I_\alpha, I_\beta) = C_+(I_\alpha, I_\beta) + (-1)^{n_\alpha(J_\alpha)}$
            $pha(I_\alpha) \ phb(I_\beta) \ C(P(I_\alpha), M(I_\beta))$;
        vectorized over $I_\alpha$,
    end loop over $I_\beta$,
end loop over i.
```

The S_- operation may be performed in a similar manner.

The S_+ and S_- operations are easily vectorized but they will inherently be slowed down by the use of indirect addressing in the innermost loop as the operators change both the α and the β string. However, the operation counts of the S_+ and S_- operations are $n_\beta N_{det}$ and $n_\alpha N_{det}$, respectively, where n_α and n_β are the number of α and β electrons and N_{det} is the number of determinants. This is to be compared to the operation count for the two-electron contributions to the σ vector which is a quartic function of the number of electrons and orbitals times the number of determinants. The time required for the calculation of S_+/S_- times a vector is thereby unimportant for the total time required to construct the σ vector.

All the necessary machinery is now available. The Hamiltonian contains a spin-independent operator and a spin-orbit operator

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} \ , \tag{47}$$

where the spin-orbit operator has the form given in Eqs. (39) and (40). It may be viewed as a sum of *six* terms of which $\mathcal{H}_0$ and $\mathcal{H}^z_{so}$ have a simple structure similar to $\mathcal{O}_\mu$, whereas $\mathcal{H}^z_{so}$ and $\mathcal{H}^y_{so}$ each contain two terms having the spin-flip operators to the left and to the right, respectively. The construction of the spin-orbit CI vector may be organized as suggested below:

```
loop over operators in $\mathscr{H}$,
  loop over CI spaces of $\sigma$ ,
      loop over contributing CI spaces of $c$ .
        If the operator is of the type $\mathscr{O}_\mu(S_+ \pm S_-)$ then
          step 1: $c' = (S_+ \pm S_-)c$ ;
          step 2: $\sigma = \sigma + \mathscr{O}_\mu c'$
        If operator is of the type $(S_+ \pm S_-)\mathscr{O}_\mu$, then
          step 1: $\sigma' = \mathscr{O}_\mu c$ ;
          step 2: $\sigma = \sigma + (S_+ \pm S_-)\sigma'$
        or
          $\sigma = \sigma + \mathscr{O}_\mu c$
        End if
      end loop over CI spaces of $c$,
    end loop over CI spaces of $\sigma$,
end loop over operators.
```

Returning to Sect. 2.4, where the time required for calculating one element of σ was estimated to be *six* times that of a non-relativistic operator, we have in our algorithm above six operators, having the same operation count as $\mathscr{H}_0$. Hence, the algorithm should be very efficient.

We decided to use a conservative approach to the complex arithmetic. Instead of declaring the variables as complex and using the complex arithmetic provided by the FORTRAN compiler, we stuck to real variables, and considered complex numbers as pairs of real numbers. A number of simple linear algebraic routines for the manipulation of this form of complex vectors and matrices were written, utilizing the corresponding routines for real numbers. The rationale for this approach is that most compilers have been carefully optimized for real arithmetic, while the corresponding complex operations have received less attention. Furthermore, many of the variables, for example the integrals, are either pure, real or imaginary. This cannot be exploited if we declare all the variables as complex.

The construction of the σ vector is thus realized as a number of computational tasks, each task being the calculation of the action of either S_+/S_- or a triplet operator. These computational tasks are organized as a sequence of calculations of contributions from a given symmetry-type block of the CI vector to a given symmetry-type block of the σ vector. The program can therefore by organized so that only two symmetry-type blocks are required at any given time. This leads to a simple parallel algorithm with limited communication between the computing nodes. The initial version assumes, however, the presence in memory of all the symmetry-type blocks of a given CI space, and no effort to parallel the program has been undertaken.

For more general choices of one-electron functions, were the α- and β-spin functions are mixed, it is not possible to rewrite the σ vector in terms of $M_s = 0$ components of a triplet operator. One must instead use the general form of triplet operators. In Appendix A, we describe direct CI algorithms for these operators.

3.5 Symmetry

Exploitation of double-group and time-reversal symmetry is highly desirable for computational efficiency. We start out by specifying one or more reference CI spaces, giving spin projection and spatial symmetry for each reference space. The program will then identify other CI spaces that may interact with properties of the Hamiltonian described in Sect. 2.1 and set up the CI super space. Thus, we do not obtain the double-group symmetry directly.

For binary groups it is found that whenever a C_2 principal axis is present, the R_x and R_y operators change sign under C_2 rotation, whereas R_z maintains the sign. Therefore, the z term of $\mathscr{H}_{so}$ will only couple determinants which have the same character for C_2 rotation, while x and y will couple determinants which have the opposite character for C_2 rotation. In the C_s case the same is seen for σ_h reflection. In addition the z component will only couple determinants having the same M_s value, whereas the x and y components will couple states satisfying $\Delta M_s = \pm 1$. Defining the two-valued quantity ξ

$$\xi = \begin{cases} (-1)^{|M_s|}\chi(C_2) & N \text{ even} \\ (-1)^{|M_s+1/2|}\chi(C_2) & N \text{ odd} \end{cases} , \tag{48}$$

where $\chi(C_2)$ is the character for C_2 rotation, the CI expansion may be restricted to determinants having $\xi = +1$ or $\xi = -1$ by the considerations above.

As an example we return to the C_{2v} case. It can be shown that for an even number of electrons the observations above correspond to the discovery of two reducible representations, denoted A and B, grouping the boson irreps A_1, A_2, B_1, B_2 into $A = \{A_1, A_2\}$ and $B = \{B_1, B_2\}$. The same applies for the point groups D_{2h} and D_2, with the additional constraint to a single-inversion symmetry, which is conserved by the spin-orbit Hamiltonian. Hence, we still lack some information for the full exploitation of double-group symmetry for these point groups.

For C_s and C_2, on the other hand, double-group symmetry is fully accounted for by the introduction of ξ, whereas inversion symmetry suffices for C_i.

For an odd number of electrons the restriction to one value of ξ corresponds in fact to selecting one partner of a Kramer's pair, thus removing one of the Kramer's partners from the variational space. But the variable ξ is not defined for C_1 and C_i. These point groups are denoted *quaternionic groups* and time-reversal symmetry may only be exploited through quaternion algebra [27] [35].

For a system with an even number of electrons, the eigenfunctions can be chosen so they are eigenfunctions of $\hat{\mathscr{K}}$ as indicated by Eq. (18). Introducing an alternative orthonormal basis

$$|(I,J)^+\rangle = \begin{cases} \frac{1}{\sqrt{2}}(|I,J\rangle + |J,I\rangle) & I > J \\ |I,J\rangle & I = J \end{cases} , \tag{49}$$

$$|(I,J)^-\rangle = \frac{1}{\sqrt{2}}(|I,J\rangle - |J,I\rangle) \quad I > J \tag{50}$$

and choosing a CI wave function with an eigenvalue of $+1$.

$$\hat{\mathscr{K}}|0\rangle = |0\rangle \ , \tag{51}$$

Table 2. ξ and κ values of the boson irreducible representations (irreps) of C_{v2}

Irrep	κ	ξ
A_1	1	1
A_2	-1	1
B_1	1	-1
B_2	-1	-1

we can expand an eigenvector $|0\rangle$ in terms of the combinations as

$$|0\rangle = \sum_{I \geq J} C^r(I,J)|(I,J)^+\rangle + i \sum_{I > J} C^i(I,J)|(I,J)^-\rangle \quad . \tag{52}$$

This explicit use of the Kramer's symmetry reduces the number of independent parameters by about a factor of 2, as can be realized by comparison with Eq. (28) where the sum runs over all I,J. Having a linear vector space with basis functions $|(I,J)^+\rangle, i|(I,J)^-\rangle$, the time-reversal symmetry is preserved if we require a real eigenvector (c_r, c_i) and the CI iterations can be carried out using real algebra.

For C_{2v} in Table 1 it can be shown that restricting the basis to states of eigenvalue $+1$ or -1 for the time-reversal operator corresponds to "resolving" the previously obtained reducible representations A and B into A_1, A_2 and B_1, B_2, respectively. Table 2 shows the values of ξ and κ for the boson irreps of C_{2v} which enables the full exploitation of symmetry for an even number of electrons.

A similar result is obtained for the groups D_{2h} and D_2 whereas for the lower-symmetry groups the use of time-reversal symmetry adds to the savings achieved by double-group symmetry.

When implementing time-reversal symmetry the CI vector is formally expanded in the combination basis Eqs. (49) and (50). Diagonal combinations $|(I,I)^-\rangle$ are not included, but in order to maximize symmetry between the real and imaginary parts it is convenient to formally include these combinations, ensuring that the corresponding coefficients vanish. Letting string indices increase for an increasing number of electrons, the restriction $I \geq J$ implies $n_\alpha \geq n_\beta$. The outer loop for the CI super space thus runs over all CI spaces with $M_s \geq 0$. When performing the direct CI calculation, the contributions to the σ vector are actually calculated in the SD basis; when looping over CI spaces, a CI space with $M_s = 0$ is expanded to the complete form; if it is a CI space with $M_s > 0$ it is first processed as this space, and then transposed and processed as the corresponding $M_s < 0$ space. The saving is still made, as the number of σ coefficients has been reduced by roughly a factor of two.

In this way we have achieved the maximum exploitation of double-group symmetry. Time-reversal symmetry has been fully accounted for except for the point groups C_1 and C_i for cases with an odd number of electrons. As mentioned above a quaternionic scheme would be required in this case to restrict the CI to one of the Kramer's partners. This has not been pursued any further.

3.6 Diagonalization

A good starting point for the diagonalization is to obtain a set of start vectors by performing CI calculations using the spin-independent part of the Hamiltonian. Note that the initial spin-orbit CI iteration will then correspond to the methods in Refs. [9, 10], building a small spin-orbit matrix over a set of CI wave functions which is then diagonalized.

It has proven advantageous to first neglect the active two-electron part of the spin-orbit Hamiltonian, thus merely using an effective one-electron operator, defined by the *inactive Fock matrix*

$$F_{ij} = h_{ij} \sum_c 2g_{\hat{i}jcc} - 3g_{\hat{i}ccj} - 3g_{\hat{c}jic} \quad , \tag{53}$$

where the sum over c runs over all core (inactive) orbitals. The most important contributions to the spin-orbit coupling are in fact accounted for in F and in our experience, only two or three additional iterations including the two-electron spin-orbit part is required if the wave function is first converged using only the inactive Fock matrix contributions. The savings in computational time are substantial.

The complex nature of the CI and σ vectors does not allow the use of a traditional Davidson algorithm [37] which assumes real vectors and matrices. We have therefore written a solver for the iterative construction of selected eigenvalues and eigenvectors of a general complex hermitian matrix. The current routine is a straightforward generalization of the Davidson method. We have found that this algorithm often exhibits poor convergence for relativistic CI wave functions due to the presence of many near degenerate states, and the need to truncate the subspace of trial vectors for very large CI expansions. The inclusion of the so-called inverse iteration correction [23] and the use of more general preconditioners than the diagonal should eliminate the problems of slow convergence.

4 Discussion

We have demonstrated how a determinant based direct CI for non-relativistic Hamiltonians can be generalized to treat the relativistic spin-orbit operator, maintaining the basic structure of the original algorithm in the most time-consuming step. The $\alpha \leftrightarrow \beta$ excitation operators appearing in the spin-orbit Hamiltonian are avoided inside the σ routines by performing separate S_+/S_- operations. The resulting algorithm is efficient, staying close to the minimal operation count of the operator.

The division of the c and σ vectors into blocks, similar to a non-relativistic CI space, opens the possibility of treating very long CI expansions, as one segment of c and σ may be memorized at anyone time, and the memory requirements are not larger than for the corresponding non-relativistic CI calculation. The vectors are further divided into blocks, corresponding to a given RAS1-RAS3 occupation, which opens the possibility of working with even smaller segments at a time.

We suggest a simple way of paralleling the σ algorithm by having six operators in $\mathscr{H}$, six CI spaces in c and σ and having a real and imaginary part. There are $6 \times 12 = 72$ contributions to be calculated which are roughly of the same size, and *packets* corresponding to one operator, one CI space of σ and one CI space of c (real or imaginary part) can be sent to different nodes and calculated independently. A finer subdivision can be obtained by separating the CI spaces into symmetry blocks or symmetry-type blocks and restricting the calculations at each node to the calculation of the contribution of a given operator and symmetry-type block of the CI vector to a given symmetry-type block of the σ vector.

The program has been used for CI expansions with up to 20 million determinants in the CI super space, and we will report the initial calculations separately. The code can, in its current form, be effectively used to produce benchmark numbers for CI expansions containing very highly correlated wave functions. The program is also used to perform multireference single and double calculations. This use of the program is, however, complicated by the very large number of strings that occur for such expansions. Work is in progress to eliminate this bottleneck by generating all the information about the strings and the annihilation/creation of electrons when needed eliminating memory and disk areas. Furthermore, we are studying the use of more general CI expansions then are allowed in the RAS concept.

Appendix A

Algorithms for general triplet operators

In the text we described how the spin-orbit operator in the basis of non-relativistic orbitals can be written in terms of one- and two-body triplet operators with $M_s = 0$. For more general choices of the orbital space, such as the Kramer's paired orbitals obtained by diagonalizing the one-body density matrix of the relativistic wave function, this rewriting of the two-electron operator is not possible. In this case one must develop an algorithm for general one- and two-body triplet operators. This is dealt with in this appendix. Consider as an example the $M_s = 1$ component of a two-body triplet operator which can be written as

$$\mathscr{T}_1 = 1/2 \sum_{ijkl} (ij|kl) \Big(T(1,1)_{ij} E_{kl} - \delta_{jk} T(1,1)_{il} \Big) \tag{54}$$

$$= 1/2 \sum_{ijkl} (ij|kl) \Big(a^\dagger_{i\alpha} a^\dagger_{k\alpha} a_{l\alpha} a_{j\beta} + a^\dagger_{i\alpha} a^\dagger_{k\beta} a_{l\beta} a_{j\beta} \Big) \ . \tag{55}$$

The spin indices α and β do not necessarily correspond to the $m_s = \pm 1/2$ spin functions; they can be a general pair of Kramer's orbitals. The corresponding σ vector can be written as

$$\sigma\big(I_\alpha, I_\beta\big) = \sum_{J_\alpha, J_\beta} \langle I_\alpha I_\beta | \mathscr{T}_1 | J_\alpha J_\beta \rangle C\big(J_\alpha, J_\beta\big) \ , \tag{56}$$

$$= \sigma_{\alpha\alpha\alpha\beta}\big(I_\alpha, I_\beta\big) + \sigma_{\alpha\beta\beta\beta}\big(I_\alpha, I_\beta\big) \ , \tag{57}$$

where

$$\sigma_{\alpha\alpha\alpha\beta}\big(I_\alpha, I_\beta\big) = 1/2 \sum_{ijklJ_\alpha J_\beta} (ij/kl) \Big\langle I_\alpha I_\beta \Big| a^\dagger_{i\alpha} a^\dagger_{k\alpha} a_{l\alpha} a_{j\beta} \Big| J_\alpha J_\beta \Big\rangle \times C\big(J_\alpha, J_\beta\big) \ , \tag{58}$$

$$\sigma_{\alpha\beta\beta\beta}\big(I_\alpha, I_\beta\big) = 1/2 \sum_{ijklJ_\alpha J_\beta} (ij/kl) \Big\langle I_\alpha I_\beta \Big| a^\dagger_{i\alpha} a^\dagger_{k\beta} a_{l\beta} a_{j\beta} \Big| J_\alpha J_\beta \Big\rangle \times C\big(J_\alpha, J_\beta\big) \ , \tag{59}$$

Let us consider one of the terms, say $\sigma_{\alpha\alpha\alpha\beta}$. Separating the α and β operators gives

$$\sigma_{\alpha\alpha\alpha\beta}\big(I_\alpha, I_\beta\big) = \frac{P}{2} \sum_{ijklJ_\alpha J_\beta} (ij/kl) \Big\langle I_\alpha \Big| a^\dagger_{i\alpha} a^\dagger_{k\alpha} a_{l\alpha} \Big| J_\alpha \Big\rangle \times \langle I_\beta | a_{j\beta} | J_\beta \rangle C\big(J_\alpha, J_\beta\big) \ , \tag{60}$$

with

$$P = (-1)^{N_\alpha N_\beta} \ . \tag{61}$$

Using the algorithms of Ref. [22] as an example we can calculate the contributions from a given orbital index j to $\alpha_{\alpha\alpha\alpha\beta}$ in the following steps

$$\big|\beta\big(L\big(K_\beta\big)\big)\big\rangle = s\big(K_\beta\big) a_{j\beta} \big|\beta\big(R\big(K_\beta\big)\big)\big\rangle \ , \tag{62}$$

$$C^j\big(J_\alpha, K_\beta\big) = Ps\big(K_\beta\big) C\big(J_\alpha, R\big(K_\beta\big)\big) \ , \tag{63}$$

$$\sigma^j\big(I_\alpha, K_\beta\big) = 1/2 \sum_{iklJ_\alpha} (ij|kl) \Big\langle I_\alpha \Big| a^\dagger_{i\alpha} a^\dagger_{k\alpha} a_{l\alpha} \Big| J_\alpha \Big\rangle C^j\big(J_\alpha, K_\beta\big) \ , \tag{64}$$

$$\sigma\big(I_\alpha, L\big(K_\beta\big)\big) = \sigma\big(I_\alpha, L\big(K_\beta\big)\big) + \sigma^j\big(I_\alpha, K\big) \ . \tag{65}$$

In the first step, one obtains the strings $\beta(R(K_\beta))$ containing orbital j, the corresponding strings with orbital j annihilated, $\beta(L(K_\beta))$ and the sign array $s(K_\beta)$. In the next step, the C matrix is gathered to obtain a smaller matrix C^j containing only the β strings belonging to $\beta(R(K_\beta))$. In the third and most time-consuming step the non-vanishing excitations in the α space are obtained and the σ vector σ^j is constructed for the non-trivial beta strings. To minimize cache traffic all contributions to a given row of σ^j should be obtained before proceeding to the next row, and vectorization over K_β can be employed. In the final fourth step we scatter the elements of σ^j to the complete σ vector. The other contribution to the σ vector is obtained in a similar way.

The efficiency of the time-consuming third step depends on the number of β strings in the reduced list. If this number of β strings is large, the excitations $\langle I_\alpha | a^\dagger_{i\alpha} a^\dagger_{k\alpha} a_{l\alpha} | J_\alpha \rangle$ are used for a large number for a β-string and the computation of excitation matrix elements will be a small part of the total computation. A large number of β strings also improves the use of vector or superscalar instructions. Conversely, if the number of β strings is small, the calculation in this critical step will be dominated by construction of the α excitations, and the step will become rather inefficient. For typical multireference CI expansions the number of β strings in C^j is large enough to support an efficient realization of this step. One can inquire whether it would be advantageous to use the above construction also for the operators discussed in the text. A detailed analysis of operation counts reveals that the operation count for the direct use of the general triplet operators is about 30% less than the method of rewriting the operators as $M_s = 0$ components. We did not find this sufficient to warrant the additional coding at the present time.

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