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Spin−Orbit Configuration Interaction Using the Graphical Unitary Group Approach and Relativistic Core Potential and Spin−Orbit Operators

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Spin−orbit configuration interaction (CI) is formulated in terms of the graphical unitary group approach (GUGA) in combination with relativistic core potential and spin−orbit operators, thus providing an efficient general method for treating the electronic structure of molecules containing heavy atoms. The development of the spin-orbit matrix elements and the implementation of these methods in the COLUMBUS suite of programs are described.

1. Introduction

Relativistic effects can be put into molecular electronic calculations in a variety of ways. Pyykkö reviewed thirteen such methods for relativistic quantum chemical calculations in 1988 ranging from full four-component wave function methods to semiempirical methods.[1] There have been a number of other reviews of aspects of this field since then.[2−9] The most extensively used method so far though has proven to be the relativistic effective core potential (RECP) method. The reason for the success of RECPs is two-fold. First, the effects of the inner-shell electrons (which are the fastest moving electrons) whose major relativistic changes in orbital sizes and energies are propagated out to the valence region, are included in the core potentials, so only the valence electrons need to be treated explicitly. Second, many existing nonrelativistic algorithms can be adapted to relativistic calculations using RECPs. The major additional complication is the need to include the spin−orbit interaction for the valence electrons, which can be quite large even if the electron speeds are not large.

Including RECPs and valence spin−orbit operators in configuration-interaction (CI) calculations is the simplest way to proceed.[2−9] S. Y.[10−13] added the spin−orbit interaction to an (unreleased) early version of the COLUMBUS CI programs,[14,15] which are one of several popular and efficient ab initio quantum chemical computational packages available and portable to most major computers. The graphical unitary group approach (GUGA)[14,15] was used for the direct CI programs[16,21] in this package; this work started in the 1980s,[22] and has continued with many enhancements.[14] In this paper we describe the implementation of the spin−orbit interaction in an impending release of the COLUMBUS programs (version 5.5). Direct spin−orbit CI programs have also been written based on Slater determinants.[23,24]

2. Relativistic Core Potential and Spin−Orbit Operator Method

The RECP method is an extension of the nonrelativistic effective core potential approach,[25] which has been reviewed by Krauss and Stevens.[26] RECPs are obtained by several algorithms, particularly from wave functions from relativistic atomic calculations[27−29] and from fitting the energy results from all-electron atomic calculations.[8] Corresponding spin−orbit operators are obtained as part of the same process,[8,28] or by a separate process.[30]

In the procedure of Christiansen and co-workers[28] a Dirac−Fock atomic wave function is used as the starting point. For each pair of l, j indices, the large-component radial function is used[27] to determine the pseudoorbital by the shape-consistent method;[31] they are defined to be equal to the valence radial function in the valence region and to decrease smoothly and nodelessly through the core region to the value of zero at the nucleus. The pseudoorbital is then used to define the potential for that pair of l, j indices. The electron repulsion interaction among valence electrons is removed from these potentials.

There is no need to include terms for direct relativistic effects, such as the dependence of mass on velocity, which are important only in the core region, in the valence-electron Hamiltonian. Thus the Hamiltonian for the valence electrons is composed of the nonrelativistic Hamiltonian for the valence electrons plus the RECPs, which include the effects of the core electrons as well as the relativistic effects on the valence electrons in the core region.[32] The RECPs thus represent, for the valence electrons, the repulsion of the core electrons, the spin−orbit interaction with the nucleus, the spin−orbit interaction with the core electrons, and an approximation to the spin−orbit interaction between the valence electrons,[33] which has usually been found to be quite small, especially for heavier element systems.[34−36]

The potentials obtained have the form

$$U^{\mathrm{REP}} = \sum_{l=0}^{\infty} \sum_{j=|l-\frac{1}{2}|}^{l+\frac{1}{2}} U_{lj}^{\mathrm{REP}}(r)\hat{O}_{lj} \tag{1}$$

$$\hat{O}_{lj} = \sum_{m=-j}^{j} |ljm\rangle\,\langle ljm| \tag{2}$$

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This form of core potential, with the spin-dependent projection operator $\hat{O}_{lj}$, is suitable for atomic calculations with $j-j$ coupled basis sets, but is awkward with other basis sets, such as those used in molecular work. The REP operators can be expressed in a more readily usable form in terms of the spin-independent projection operators $\hat{O}_l$

$$\hat{O}_l = \sum_{m=-l}^{l} |lm\rangle\langle lm| = \sum_j \hat{O}_{lj} \tag{3}$$

$$\begin{aligned} U^{\text{REP}} &= \sum_{l=0}^{\infty} U_l^{\text{AREP}}(r)\,\hat{O}_l + \sum_{l=1}^{\infty} \xi_l(r)\,\vec{l}\cdot\vec{s}\,\hat{O}_l \\ &= U^{\text{AREP}} + h^{\text{so}} \end{aligned} \tag{4}$$

as the sum of core potentials and spin−orbit operators.[37,38] It is found[27] that the $U_l^{\text{AREP}}(r)$ are approximately independent of l when $l \geq L$, where L is one larger than the largest l value of the core electrons. Then U^{AREP} and h^{so} can be reduced to

$$U^{\text{AREP}} = U_L^{\text{AREP}}(r) + \sum_{l=0}^{L-1} (U_l^{\text{AREP}}(r) - U_L^{\text{AREP}}(r))\hat{O}_l \tag{5}$$

$$h^{\text{so}} = \sum_{l=1}^{L} \xi_l(r)\,\vec{l}\cdot\vec{s}\,\hat{O}_l \tag{6}$$

With core potentials and spin-orbit operators given in the forms of eqs 5 and 6, existing programs for nonrelativistic calculations can be adapted to include relativistic effects. The additional integrals of U^{AREP} and h^{so} are included in those evaluated by the ARGOS program[37,39] in the COLUMBUS programs. The spin−orbit interaction can be included in the correlation step. Such methodology was adopted in a (nondirect) spin−orbit CI program, CIDBG.[38]

For molecules containing heavy elements, the presence of d and f valence shells with possibly large numbers of open-shell electrons will give rise to a large number of closely spaced configurations, so multireference CI calculations are expected in general. In addition, the coupling of electrons in heavy-element systems is likely to be intermediate between $\Lambda-S$ and $\omega-\omega$, thus requiring multireference calculations. States that are of different symmetries in spin−orbit-free calculations may be mixed by the spin-orbit interaction in spin−orbit CI calculations. As a result, the reference space should in general also include, besides the near-degenerate configurations in a spin−orbit-free description, all the configurations that strongly interact through spin−orbit effects. For multireference calculations, CI is the simplest correlation method to use in a general way. As a consequence of the large number of references, the spin−orbit CI spaces for systems containing heavy elements may easily be an order of magnitude larger than those for systems containing only lighter elements.

Since the spin−orbit interaction is a one-electron operator in the present formulation, its largest effects are determined by its matrix elements between pairs of reference configurations and between reference configurations and singly excited configurations. In comparison, the electron repulsion interaction, as a two-electron operator, has major matrix elements between pairs of reference configurations and between reference configurations and doubly excited configurations. Thus, in high-accuracy calculations, the electron repulsion interaction has slower convergence properties than the spin−orbit interaction, so an important criterion for any method is that the electron repulsion aspect of the calculation be handled efficiently.

One limitation to the CIDBG program is that it calculates and stores the whole Hamiltonian matrix, so the calculations are limited to matrices of order 500 000 on today's mainstream workstations. It is, however, flexible in designating which configurations are to be included and efficient in obtaining a large number of energy eigenvalues. Nevertheless, much more efficient programs are needed for high-accuracy calculations.

3. Spin−Orbit Configuration Interaction in the Graphical Unitary Group Approach

The GUGA CI programs in the COLUMBUS system are for multireference singles and doubles CI calculations. We will not attempt to review their formulation here; rather, we will discuss only those parts of the GUGA CI method needed to include spin−orbit matrix elements in the overall formalism and computational procedure.[10−13]

Including the spin−orbit interaction in the RECP approximation, the total Hamiltonian is

$$H_{\text{total}} = H_0 + H_{\text{so}} \tag{7}$$

where the spin−orbit-free Hamiltonian H_0 is given by

$$H_0 = \sum_{\mu=1}^{N} h(\mu) + \frac{1}{2}\sum_{\mu\neq\nu} v(\mu,\nu) \tag{8}$$

and H_{so} is given by

$$H_{\text{so}} = \sum_{\mu=1}^{N} h^{\text{so}}(\mu) \tag{9}$$

where

$$\begin{aligned} h^{\text{so}}(\mu) &= \vec{q}(\mu)\cdot\vec{s}(\mu) \\ &= \sum_{\gamma} (-1)^{\gamma} q_{-\gamma}(\mu) s_{\gamma}(\mu) \end{aligned} \tag{10}$$

where the γ summation here and in succeeding equations is over the 0, ±1 component values of a vector in spherical tensor form. Generalized from eq 6, $\vec{q}$ is given by

$$\vec{q} = \sum_A \sum_{l_A=1}^{L_A} \xi_{Al_A}(r_A)\,\vec{l}_A \hat{O}_{l_A} \tag{11}$$

where A denotes the nuclei.

In second-quantized form, H_0 can be written as

$$H_0 = \sum_{i,j}\sum_{\sigma} h_{ij} X_{i\sigma}^{+} X_{j\sigma} + \frac{1}{2}\sum_{i,j,k,l}\sum_{\sigma,\tau} [ij;kl] X_{i\sigma}^{+} X_{k\tau}^{+} X_{l\tau} X_{j\sigma} \tag{12}$$

and H_{so} can be written as

$$H_{\text{so}} = \sum_{i,j}\sum_{\sigma,\tau} h_{i\sigma,j\tau}^{\text{so}} X_{i\sigma}^{+} X_{j\tau} \tag{13}$$

where the operators $X_{i\sigma}^{+}$ and $X_{i\sigma}$ are the fermion creation and annihilation operators respectively for an electron in spatial orbital i ($i = 1, 2, ..., n$ denoting a basis of real spatial orbitals) with spin σ. The coefficients h_{ij} are the total of the kinetic energy (T_e), nuclear attraction (V_{ne}), and core potential (U^{AREP} from eq 5) integrals; the $[ij;kl]$ are electron repulsion integrals; and the $h_{i\sigma,j\tau}^{\text{so}}$ are the spin−orbit integrals over the spatial orbitals (and spin functions in the spin−orbit case):

$$h_{ij} = \langle i|T_{\mathrm{e}} + V_{\mathrm{ne}} + U^{\mathrm{AREP}}|j\rangle \tag{14}$$

$$[ij;kl] = \langle i(1)k(2)|v(1,2)|j(1)l(2)\rangle \tag{15}$$

$$h^{\mathrm{so}}_{i\sigma,j\tau} = \langle i\sigma|h^{\mathrm{so}}|j\tau\rangle \tag{16}$$

$$= \sum_{\gamma}(-1)^{\gamma}\langle i\sigma|q_{-\gamma}s_{\gamma}|j\tau\rangle \tag{17}$$

$$= \sum_{\gamma}(-1)^{\gamma}\langle i|q_{-\gamma}|j\rangle\langle\sigma|s_{\gamma}|\tau\rangle \tag{18}$$

One-body and two-body operators are defined[16] by

$$E_{i\sigma,j\tau} = X^{+}_{i\sigma}X_{j\tau} \tag{19}$$

$$E_{ij} = \sum_{\sigma} X^{+}_{i\sigma}X_{j\sigma} = \sum_{\sigma} E_{i\sigma,j\sigma} \tag{20}$$

$$e_{ij,kl} = E_{ij}E_{kl} - \delta_{kj}E_{il} \tag{21}$$

and satisfy the commutation relation

$$\begin{aligned}[E_{ij}, E_{kl}] &= E_{ij}E_{kl} - E_{kl}E_{ij} \\ &= \delta_{kj}E_{il} - \delta_{il}E_{kj}\end{aligned} \tag{22}$$

The Hamiltonian can be written in terms of these operators

$$H_{\mathrm{total}} = \sum_{i,j} h_{ij}E_{ij} + \frac{1}{2}\sum_{i,j,k,l}[ij;kl]e_{ij,kl} + \sum_{ij}\sum_{\sigma\tau}h^{\mathrm{so}}_{i\sigma,j\tau}E_{i\sigma,j\tau} \tag{23}$$

Once the values of these integrals are available, the evaluation of the matrix elements of H_{total} over a chosen orbital (and spin) space is reduced to the calculation of the matrix elements of the unitary-group operators $E_{i\sigma,j\tau}$, E_{ij}, and operator products $e_{ij,kl}$ in the same space(s).

The N-electron Hilbert space is usually constructed from the antisymmetric component of the Nth rank tensor product of the one-electron Hilbert space which exhibits the unitary symmetry $U(2n)$, and the wave function can be expanded in terms of a suitable basis for this irreducible presentation (irrep). We can choose a spin-adapted basis by considering the following subgroup chain:

$$U(2n) \supset U(n) \otimes U(2) \tag{24}$$

In this representation, a basis function of the $U(2n)$ irrep is the direct product of a basis function of an irrep Γ of $U(n)$, defined by an orthonormal set of n spatial orbitals and spin quantum number S, and a basis function of the irrep of $U(2)$ conjugate to Γ, defined by the standard one-electron spin functions and spin quantum numbers S and M. The $U(n)$ basis can be labeled[17] by the following subgroup chain:

$$U(n) \supset U(n-1) \supset \cdots \supset U(2) \supset U(1) \tag{25}$$

Such a basis is known as the Gel'fand−Tsetlin basis and the individual basis functions are referred to as Gel'fand states.

The Shavitt distinct row graph[19] is an elegant scheme of representing this basis graphically. The irrep of $U(n)$ can be specified by the spin quantum number $S_n = S$ and the total number of electrons $N_n = N$. Then, for each subgroup $U(j)$, S_j and N_j may similarly be specified. The complete set of S_j and N_j values for $0 \leq j \leq n$ uniquely specifies a Gel'fand−Tsetlin basis. Equivalently, the complete set of changes $\Delta S_j = S_j - S_{j-1}$ and $\Delta N_j = N_j - N_{j-1}$, collectively called the step numbers d_j (Table 1), also uniquely specifies the basis. The cases of d_j = 0, 1, 2, and 3 correspond to the addition of zero electrons, one electron such that $\Delta S_j = +1/2$, one electron such that $\Delta S_j = -1/2$, and two electrons, respectively, to the intermediate state formed from the first $j - 1$ spatial orbitals.

TABLE 1: Step Numbers for the Distinct Row Graph

d_j	ΔS_j	ΔN_j
0	0	0
1	$1/2$	1
2	$-1/2$	1
3	0	2

The step vector formed from the step numbers,

$$d = (d_n, d_{n-1}, ..., d_1) \tag{26}$$

then provides a unique labeling of the Gel'fand states corresponding to the subgroup chain of eq 25 and can be represented compactly as a graph. The four step-number values are distinguished by the different arc slopes.

Once this graphical representation is defined,[19] it can be shown[16,21] that the matrix elements of the operators in eqs 20 and 21 can be derived entirely graphically. Knowing the values of these matrix elements and the values of the one- and two-electron integrals, the nonzero matrix elements of the Hamiltonian H_0 can be identified and calculated. With this compact representation of the Hilbert space as a graph, the structure of the calculations can easily be visualized and very efficient algorithms based on the Shavitt graph can be designed and implemented.[22,40−46]

The above basis functions of the $U(2n)$ irrep, with step numbers d and spin quantum numbers S and M, can be written as

$$|(d)SM\rangle \tag{27}$$

The advantage of using such a basis is that the solution of the spin−orbit problem can be carried out in the same framework as the spin−orbit-free problem. To do so we need the matrix elements of H_{so} over this basis.

As has been shown by a number of authors,[47−55] matrix elements of spin-dependent operators can be expressed in terms of those of spin-independent operators. The simplest way to do this is to make use of vector-coupling (Racah) algebra, but wave functions constructed by this method differ by a phase factor from the corresponding wave functions constructed by GUGA.[47] We will proceed to derive the matrix elements of the spin−orbit interaction term in eq 23 using the vector-coupling method, and then we will insert the phase factors into the final matrix elements expressions in order to have them correspond to GUGA wave functions:

$$\begin{aligned}\langle(d')S'M'|H_{\mathrm{so}}|(d)SM\rangle &= \sum_{i,j}\sum_{\sigma,\tau}\sum_{\gamma}\langle i\sigma|(-1)^{\gamma}q_{-\gamma}s_{\gamma}|j\tau\rangle\langle(d')S'M'|E_{i\sigma,j\tau}|(d)SM\rangle \\ &= \sum_{i,j}\sum_{\gamma}(-1)^{\gamma}\langle i|q_{-\gamma}|j\rangle\langle(d')S'M'|Z_{\gamma}(i,j)|(d)SM\rangle\end{aligned} \tag{28}$$

where

$$\mathrm{Z}_{\gamma}(i,j) = \sum_{\sigma,\tau}\langle\sigma|s_{\gamma}|\tau\rangle E_{i\sigma,j\tau} \tag{29}$$

behaves like a rank-one tensor operator when applied to the spin space. Then by the Wigner−Eckart theorem,

$$\langle (d')S'M'|Z_\gamma(i,j)|(d)SM\rangle = (-1)^{S'-M'}\begin{pmatrix} S' & 1 & S \\ -M' & \gamma & M \end{pmatrix}\langle (d')S'||Z(i,j)||(d)S\rangle \quad (30)$$

For the matrix element $\langle (d')S'M'|H_{\mathrm{so}}|(d)SM\rangle$ to be nonzero (when the spatial orbitals are real), d' and d must differ by exactly one orbital, i.e. d' must be obtainable from d by substituting orbital i for orbital j in state d, and γ must satisfy $\gamma = M' - M$. Thus, only one term in the summation in eq 28, of specific i, j and γ, contributes to the spin-orbit matrix element between given states $|(d')S'M'\rangle$ and $|(d)SM\rangle$. So eq 28 can be further simplified to

$$\begin{aligned}\langle (d')S'M'|H_{\mathrm{so}}|(d)SM\rangle &= (-1)^\gamma \langle i|q_{-\gamma}|j\rangle\langle (d')S'M'|Z_\gamma(i,j)|(d)SM\rangle \\ &= (-1)^{S'-M}\langle i|q_{-\gamma}|j\rangle \begin{pmatrix} S' & 1 & S \\ -M' & \gamma & M \end{pmatrix}\langle (d')S'||Z(i,j)||(d)S\rangle \end{aligned} \quad (31)$$

This reduced matrix element $\langle (d')S'||Z(i,j)||(d)S\rangle$ can be evaluated in terms of the $U(n+1)$ group operators (for example, see ref 47)):

$$\langle (d')S'||Z(i,j)||(d)\mathrm{S}\rangle = (-1)^{S_{N+1}+S-1/2}\,\frac{1}{\sqrt{6}}\begin{Bmatrix} S' & S & 1 \\ \frac{1}{2} & \frac{1}{2} & S_{N+1} \end{Bmatrix}^{-1} \left\langle (d')_{N+1}S_{N+1}M_{N+1}\middle|E_{n+1,j}E_{i,n+1} + \frac{1}{2}E_{ij}\middle|(d)_{N+1}S_{N+1}M_{N+1}\right\rangle \quad (32)$$

where d_{N+1} denotes the step vector in an $(N + 1)$-electron system with $n + 1$ orbitals and S_{N+1} and M_{N+1} are the corresponding total spin and spin projection quantum numbers in the $N + 1$ electron system. For the reduced matrix elements to be nonzero, S' and S in eq 32 must satisfy

$$S' - S = 0, \pm 1 \qquad \text{(but not } S' = S = 0) \quad (33)$$

in accordance with the selection rule. Correspondingly, the quantum number S_{N+1} for the $(N + 1)$-electron system must satisfy

$$S_{N+1} = \begin{cases} S + \frac{1}{2}, & S' = S, \quad (a) \\ S - \frac{1}{2}, & S' = S, \quad (b) \\ S + \frac{1}{2}, & S' = S + 1, \quad (c) \\ S - \frac{1}{2}, & S' = S - 1, \quad (d) \end{cases} \quad (34)$$

Case (d) can be obtained from case (c) by interchanging S and S', so we will not carry it further. The corresponding step numbers, at the $(n + 1)$th level, are $d'_{n+1} = d_{n+1} = 1$, $d'_{n+1} = d_{n+1} = 2$, and $d'_{n+1} = 2$, $d_{n+1} = 1$ respectively, for cases (a), (b), and (c), and are illustrated graphically in Figure 1.

Expressing the 6−j symbols in eq 32 explicitly in terms of S gives:

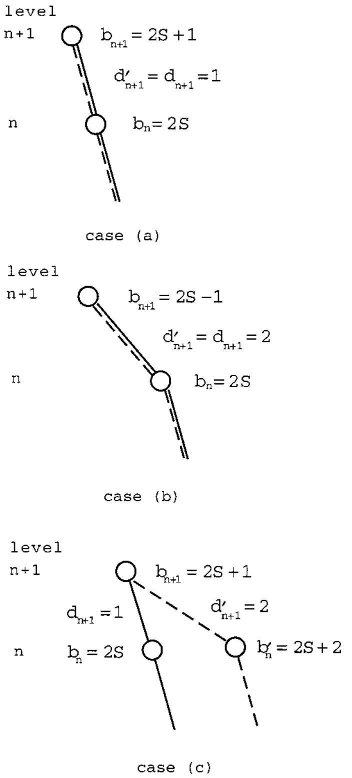

Figure 1. Graphical representation of spin−orbit coupling; according to ref 47, an additional electron is placed in the level $n + 1$ to embed the $U(n)$ basis in $U(n + 1)$ and to close the loop head.

$$\langle (d')S'||Z(i,j)||(d)S\rangle = (F_{ij})_{(N+1)} \times \begin{cases} -\sqrt{\dfrac{(S+1)(2S+1)}{S}} & (a) \\ \sqrt{\dfrac{S(2S+1)}{S+1}} & (b) \\ \sqrt{(S+1)} & (c) \end{cases} \quad (35)$$

where we have defined

$$(F_{ij})_{(N+1)} = \left\langle (d')_{N+1}S_{N+1}M_{N+1}\middle|E_{n+1,j}E_{i,n+1} + \frac{1}{2}E_{ij}\middle|(d)_{N+1}S_{N+1}M_{N+1}\right\rangle \quad (36)$$

Using the eq 22 commutation relation and the eq 21 definition, this can be reexpressed as

$$(F_{ij})_{(N+1)} = \left\langle (d')_{N+1}S_{N+1}M_{N+1}\middle|e_{i,n+1;n+1,j} + \frac{1}{2}E_{ij}\middle|(d)_{N+1}S_{N+1}M_{N+1}\right\rangle \quad (37)$$

The first part of the above matrix elements for $e_{i,n+1;n+1,j}$ is represented by the 8b type of loop defined by Shavitt,[16] as shown in Figure 2 for $i < j$ (In the following we will assume $i < j$; the $i > j$ case can be proved in a similar manner.)

The corresponding value is given by

$$\langle (d')_{N+1}S_{N+1}M_{N+1}|e_{i,n+1;n+1,j}|(d)_{N+1}S_{N+1}M_{N+1}\rangle = W_{\underline{R}}(i)[\prod_{r=i+1}^{j-1} W_R(r)]\{W^{(0)}_{R\underline{L}}(j)[\prod_{r=j+1}^{n} W^{(0)}_{RL}(r)]W^{(0)}_{\overline{RL}}(n+1) + W^{(1)}_{R\underline{L}}(j)[\prod_{r=j+1}^{n} W^{(1)}_{RL}(r)]W^{(1)}_{\overline{RL}}(n+1)\} \quad (38)$$

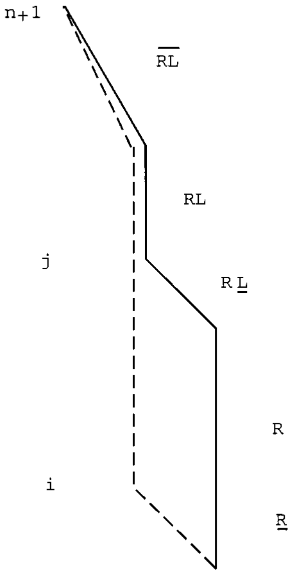

Figure 2. Loop of type 8b from ref 16 representing the matrix elements for $e_{i,n+1;n+1,j}$.

where the *W*'s are the one- and two-body segment values and the superscripts (0) and (1) denote the direct and exchange contributions of the loop, respectively.[16] The direct contribution is identically zero unless the bra and ket coincide above the level *j* and so is the contribution from $^1/_2E_{ij}$. So we need consider the direct contribution only when the bra and ket are the same above the level *j*,

$$W^{(0)}_{R\underline{L}}(j)[\prod_{r=j+1}^{n} W^{(0)}_{RL}(r)]W^{(0)}_{\overline{RL}}(n+1) = -\frac{1}{\sqrt{2}}W_{\bar{R}}(j)[\prod_{r=j+1}^{n} 1]\frac{1}{\sqrt{2}}$$

$$= -\frac{1}{2}W_{\bar{R}}(j) \qquad (39)$$

Then the first term of eq 38 becomes

$$-\frac{1}{2}W_{\underline{R}}(i)[\prod_{r=i+1}^{j-1} W_R(r)]W_{\bar{R}}(j) \qquad (40)$$

exactly cancelling the contribution from $^1/_2E_{ij}$. Thus $(F_{ij})_{(N+1)}$ in the reduced matrix element in eq 35 is entirely given by the following exchange contribution of $e_{i,n+1;n+1,j}$:

$$(F_{ij})_{(N+1)} = W_{\underline{R}}(i)[\prod_{r=i+1}^{j-1} W_R(\mathrm{r})]W^{(1)}_{R\underline{L}}(j)[\prod_{r=j+1}^{n} W^{(1)}_{RL}(r)]W^{(1)}_{\overline{RL}}(n+1) \qquad (41)$$

For cases (a−c) in eqs 34, the segment values $W^{(1)}_{\overline{RL}}(n+1)$ are given by[16]

$$W^{(1)}_{\overline{RL}}(n+1) = \begin{cases} -\frac{1}{\sqrt{2}}A(-1,1) \;=\; -\sqrt{\frac{S}{2(S+1)}} & \text{(a)} \\ \frac{1}{\sqrt{2}}A(3,1) \;=\; \sqrt{\frac{S+1}{2S}} & \text{(b)} \\ 1 & \text{(c)} \end{cases} \qquad (42)$$

Combining eqs 35, 41, and 42, we obtain for the reduced matrix elements

$$\langle(d')S'|Z(i,j)||(d)S\rangle = \sqrt{(S'+S+1)/2}(F_{ij})^N \qquad (43)$$

The value $(F_{ij})_N$ denotes the product of exchange segment values of the 8b type loop for the two-body operator $e_{i,n+1;n+1,j}$ up to the *n*th level:

$$(F_{ij})_N = \begin{cases} W_{\underline{R}}(i)[\prod_{r=i+1}^{j-1} W_R(r)]W^{(1)}_{R\underline{L}}(j)[\prod_{r=j+1}^{n} W^{(1)}_{RL}(r)] & i < j \\ W_{\underline{L}}(j)[\prod_{r=j+1}^{i-1} W_L(r)]W^{(1)}_{\underline{R}L}(i)[\prod_{r=i+1}^{n} W^{(1)}_{RL}(r)] & i > j \end{cases} \qquad (44)$$

With the reduced matrix elements given by eq 43, the spin−orbit matrix element in eq 31 becomes

$$\langle(d')S'M'|H_{\mathrm{so}}|(d)SM\rangle = (-1)^{S'-M}\langle i|q_{M-M'}|j\rangle \begin{pmatrix} S' & 1 & S \\ -M' & M'-M & M \end{pmatrix}\sqrt{\frac{S'+S+1}{2}}(F_{ij})_N \qquad (45)$$

To further simplify the expression for the spin−orbit matrix elements, we need to discuss the choice of the spin functions $|SM\rangle$. The spherical form of the spin functions $|SM\rangle$ is not symmetry adapted to the point group irreps and the spin−orbit matrix elements are complex in general. To have an efficient algorithm for solving the many-electron problem, it is essential to choose a symmetry-adapted many-electron basis and to use a real Hamiltonian matrix. For this purpose, the following "real spherical" form of spin functions can be chosen:[11,12]

$$|SM-\rangle = \iota^S\frac{l}{\sqrt{2}}[|S,-M\rangle - (-1)^M|S,M\rangle], \quad M = 1 \text{ to } S \qquad (46)$$

$$|SM+\rangle = \iota^S\frac{1}{\sqrt{2+2\delta_{M,0}}}[|S,-\mathrm{M}\rangle + (-1)^M|S,M\rangle], \quad M = 0 \text{ to } S \qquad (47)$$

In this transformation, the factor of ι^S is to make matrix elements real for $S' \neq S$. The rest of the transformation is the standard one to change the usual (complex) spherical harmonics into real spherical harmonics.

As will be discussed later, the odd number of electrons case can be adapted to the formalism for the even number of electrons case, so the following discussion will be concentrated on systems with even numbers of electrons. The point groups used in the COLUMBUS programs are the D_{2h} group and its subgroups, so our discussion will be confined to the D_{2h} group also, even though some conclusions are not specific to this requirement. The use of groups of higher than D_{2h} symmetry offers additional reduction of computational expense, but their non-Abelian property would require considerable modification both of the GUGA formalism and algorithms and of the integral-evaluation program.

Under the D'_{2h} (double) group, the Cartesian components of the angular momentum (R_x, R_y, and R_z) transform as B_{3g}, B_{2g}, and B_{1g}, respectively, and the many-electron spin functions of a system with an even number of electrons transform according to $A_g + B_{1g} + B_{2g} + B_{3g}$[38] (The $S = 0$ spin function transforms as A_g). For groups with lower than D_2 or C_{2v} symmetry (in our case, the C_2, C_s, C_i, and C_1 groups), as well as for C_{2h} symmetry, more than one component of the angular momentum transforms according to the same irrep, so we classify the irreps by the transformation properties of the components of the angular momentum. Thus for a system with an even number of electrons, the many-electron spin functions transform as

$$A + R_x + R_y + R_z \tag{48}$$

For integral values of total spin S, it can be shown, by examining the effect of the D_2 group operators C_{2x}, C_{2y}, and C_{2z}, that the spin functions in eqs 46 and 47 are already symmetry-adapted to the irreps, as listed in Table 2.

Using the Cartesian form of the spin−orbit integrals over real orbitals, $\langle i|\vec{q}|j\rangle$, we can show that the spin−orbit matrix elements are purely real and that only one of the Cartesian components, $q_x s_x$, $q_y s_y$, or $q_z s_z$ will contribute to a given matrix element if the spin functions in eqs 46 and 47 are used. First, notice that, by the selection rule, we expect that $q_z s_z$ can couple states with the same M values and $q_x s_x$ or $q_y s_y$ can only couple states with M values that differ exactly by 1.

To put the matrix elements in eq 45 in final, completely real, form, (1) we use the operator $\vec{\Lambda} = -\imath\vec{q}$, which is real but antihermitian (antisymmetric with real spatial orbitals i and j),

$$\langle i|\vec{\Lambda}|j\rangle = -\imath\langle i|\vec{q}|j\rangle = -\langle j|\vec{\Lambda}|i\rangle \tag{49}$$

(2) we drop the d' and d indices for simplicity, (3) we substitute the expressions for the 3-j symbols, (4) we transform to "real spherical" spin functions, (5) we simplify them to $M \geq 0$, and (6) we include the phase factor to convert to GUGA wave functions, which is $(-1)^{S'-S}$ for the single-substitution cases here:[47]

$$\langle S, M+1, \mp|H_{\rm so}|S, M, \pm\rangle = -\langle S, M, \pm|H_{\rm so}|S, M+1, \mp\rangle = \pm\sqrt{\frac{(1 \pm \delta_{M,0})(S-M)(S+M+1)}{8S(S+1)}}\langle i|\Lambda_x|j\rangle(F_{ij})_N \tag{50}$$

$$\langle S, M+1, \mp|H_{\rm so}|S, M, \mp\rangle = -\langle S, M, \mp|H_{\rm so}|S, M+1, \mp\rangle = -\sqrt{\frac{(1 \mp \delta_{M,0})(S-M)(S+M+1)}{8S(S+1)}}\langle i|\Lambda_y|j\rangle(F_{ij})_N \tag{51}$$

$$\langle S, M, \pm|H_{\rm so}|S, M, \mp\rangle = \pm\frac{M}{\sqrt{2S(S+1)}}\langle i|\Lambda_z|j\rangle(F_{ij})_N \tag{52}$$

$$\langle S, M+1, \mp|H_{\rm so}|S+1, M, \mp\rangle = -\sqrt{\frac{(1 \mp \delta_{M,0})(S-M)(S-M+1)}{4(2S+1)(2S+3)}}\langle i|\Lambda_x|j\rangle(F_{ij})_N \tag{53}$$

$$\langle S, M, \mp|H_{\rm so}|S+1, M+1, \mp\rangle = \sqrt{\frac{(1 \mp \delta_{M,0})(S+M+1)(S+M+2)}{4(2S+1)(2S+3)}}\langle i|\Lambda_x|j\rangle(F_{ij})_N \tag{54}$$

$$\langle S, M+1, \mp|H_{\rm so}|S+1, M, \pm\rangle = \mp\sqrt{\frac{(1 \pm \delta_{M,0})(S-M)(S-M+1)}{4(2S+1)(2S+3)}}\langle i|\Lambda_y|j\rangle(F_{ij})_N \tag{55}$$

$$\langle S, M, \mp|H_{\rm so}|S+1, M+1, \pm\rangle = \mp\sqrt{\frac{(1 \mp \delta_{M,0})(S+M+1)(S+M+2)}{4(2S+1)(2S+3)}}\langle i|\Lambda_y|j\rangle(F_{ij})_N \tag{56}$$

TABLE 2: Symmetry Properties of "Real Spherical" Spin Functions

	S even		S odd	
M	spin function	symmetry	spin function	symmetry
0	$\|S0\rangle$	A_g	$\|S0\rangle$	R_z
1,3,5...	$\|SM-\rangle$	R_x	$\|SM-\rangle$	R_y
	$\|SM+\rangle$	R_y	$\|SM+\rangle$	R_x
2,4,6...	$\|SM-\rangle$	R_z	$\|SM-\rangle$	A_g
	$\|SM+\rangle$	A_g	$\|SM+\rangle$	R_z

$$\langle S, M, \mp|H_{\rm so}|S+1, M, \mp\rangle = \sqrt{\frac{(1 \mp \delta_{M,0})(S+M+1)(S-M+1)}{(1+\delta_{M,0})(2S+1)(2S+3)}}\langle i|\Lambda_z|j\rangle(F_{ij})_N \tag{57}$$

Thus these matrix elements are shown to be purely real and have contributions from only one component $q_x s_x$, $q_y s_y$, or $q_z s_z$. Simple symmetry arguments can be used to reach the same conclusion in cases where R_x, R_y, and R_z transform as different species.[38] Notice that the above arguments are independent of the symmetry group used for the system, so implementations based on this formalism can handle cases with symmetry groups lower than D_2 or C_{2v}.

4. Spin−Orbit GUGA CI: Implementation and Performance

Before we discuss the implementation of the spin−orbit formalism in the GUGA CI program units, a brief review of the algorithms of the nonrelativistic GUGA CI is in order. This discussion will be mostly based on ref 20. The multireference CI space is generated by exciting one or two electrons from a set of reference configurations. The orbital space is then divided into internal and external spaces where the internal space consists of all the singly and doubly occupied orbitals in the set of reference configurations and the rest of the orbitals constitute the external space and are placed at the bottom of the graph. The internal space can be further divided into inactive and active orbital spaces. The inactive orbitals are all doubly occupied and are usually placed at the top of the graph. The active orbitals have variable occupation numbers from zero to two (in the reference configurations), and can be placed either below or above the inactive orbitals. This partition results in a simple structure of the distinct row graph as illustrated in Figure 3 for the internal part only. There are at most four vertices at each level in the external part of the graph with singles and doubles excitations. The four boundary vertices between the internal part and external part of the graph are named,[16,22] going from right to left, *Z* vertex (no electrons), *Y* vertex (one electron), *X* vertex (two electrons with triplet coupling), and *W* vertex (two electrons with singlet coupling) according to the number and coupling of electrons in the external space. A walk representing a Gel'fand state then is divided into an internal path and an external path lying within the internal and external parts of the graph, respectively. The ordinal index of a CSF is thus first determined by the ordering of the internal path and then by the ordering of its external path among all the external paths sharing that same internal path. The internal paths are grouped by the boundary vertices from right to left and each group is ordered by reverse lexical ordering. Two vectors, the index vector and the symmetry vector, are used to represent the internal paths and their combined symmetry. There is one entry for each of the internal paths in these two vectors. An entry in the index vector represents the ordinal number of the first Gel'fand state that shares that internal path and any internal path that is to be excluded is represented by the value −1. The

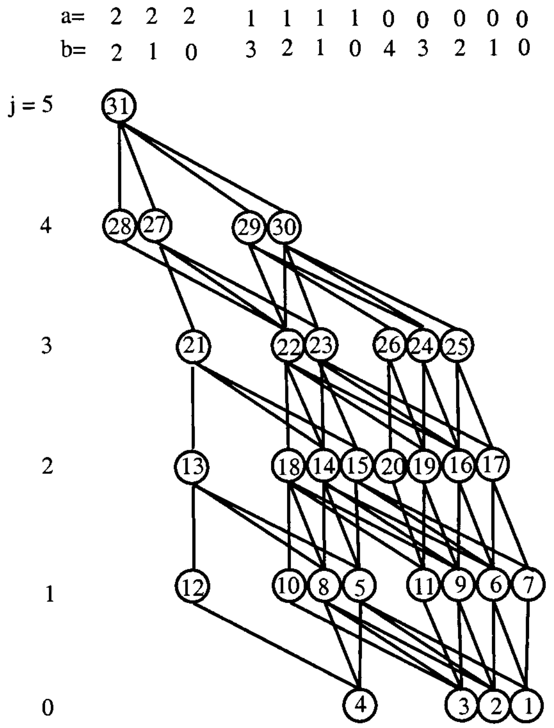

Figure 3. Internal part of a sample distinct row graph.[16]

symmetry of a walk is obtained as the direct product of the internal walk symmetry, given in the symmetry vector, and the external walk symmetry, calculated on the fly.

With the partitioning of the orbital space into internal and external spaces, the calculation of the loop values required for the evaluation of the matrix elements can be confined to the internal space only and the contribution of the part of the loop in the external space can be combined easily due to the simple structure of the external part of the distinct row graph.[22] As the one- or two-body operators in the Hamiltonian can couple configuration state functions (CSFs) that differ by at most two orbital indices, the corresponding loops may have zero, one, two, three, or all four orbital indices in the external space and the calculation is structured accordingly. The integrals are sorted into groups with zero external, one external, two external, three external, and four external orbital indices and so are the corresponding loop values.

The post-Hartree−Fock CI part of the COLUMBUS programs consists of four separate program units, CIDRT, CISRT, CIUFT, and CIUDG. The CIDRT program generates and stores the information about the Shavitt graph for later uses. The other programs are organized according to the number of external orbitals in the outer space and then the loop types, 1a, 1b, etc., as defined in ref 16. For each given set of internal-orbital indices, the internal part of all the valid loops of each type are generated in turn in CIUFT for later use in CIUDG. In this way the integrals naturally fall into categories, so they are sorted accordingly in the CISRT program. A similar approach was later adopted and called “shape-driven” by Brooks et al. in their implementation of GUGA.[41] Finally, the CIUDG program diagonalizes the Hamiltonian matrix by computing successive matrix−vector products without ever forming the matrix explicitly.

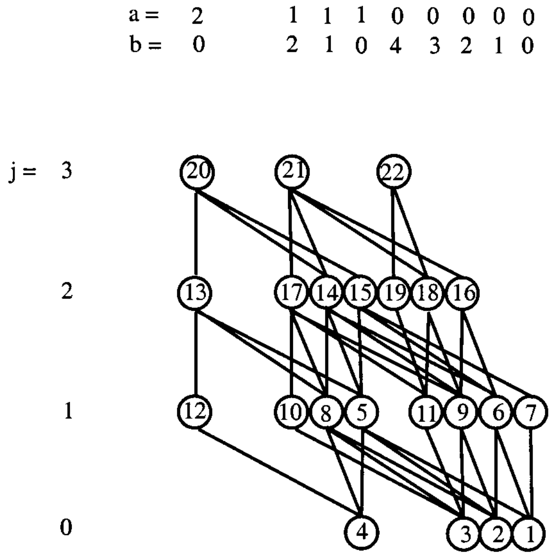

Figure 4. Spin−orbit distinct row graph for four electrons and three internal orbitals.[10,16]

We now proceed to discuss the modification required for the spin−orbit interaction. Without the spin−orbit interaction, the wave function is an eigenfunction of the S^2 operator with fixed value of total spin quantum number S and the CI space spans the irrep specified by the top distinct row so the resulting distinct row graph has a single head. The spin−orbit interaction, however, will couple CSFs with different total spin values S. In general, the appropriate CI space spans the totally antisymmetric irrep of $U(2n)$. A suitable basis then is that adapted to the group chain of eq 24. So we need to consider all the irrep spaces of the $U(n)$ with different total spin values S in the reduction of the totally antisymmetric irrep of $U(2n)$. With the restriction to single- and double-excitations from the reference space, the allowed spin quantum values in the above reduction are determined by the number of singly occupied orbitals, i.e., the possible number of unpaired electrons. The CIDRT program is generalized to accommodate the generation of distinct row tables which are no longer restricted to a single top row of specific S since there will be multiple such top rows consistent with the number of unpaired electrons. Such a graph for four electrons and three internal orbitals is shown in Figure 4.

Consistent with the use of $U(n) \otimes U(2)$, each walk in the distinct row graph, representing the spatial part of the CSF, must be combined with the spin functions as defined in eqs 46 and 47. So the internal path of a CSF will be defined to be the internal part of the walk representing the spatial part of the CSF and the spin function associated with it. Accordingly, instead of a vertex weight of one, each top level vertex is assigned a weight equal to the spin multiplicity of that particular vertex and the vertex weights are calculated similarly. The index vector then will have one entry for each internal path of a CSF and the symmetry vector contains the internal path symmetry, which is the direct product of the symmetry of the internal part of the walk and that of the spin function as given in Table 2.

The CISRT program is modified to sort the spin−orbit integrals in addition to the ordinary integrals. Since we are using a one-body spin-orbit interaction and real spatial orbitals, exactly one orbital index must be different in any two given CSFs for the spin−orbit matrix element between them to be nonzero, so we need to consider only the zero-external, one-external, and two-external cases in which zero, one, and two of the differing orbitals are in the external space, respectively. Each set of q_x, q_y, and q_z type of spin−orbit integrals is sorted into groups of zero-external, one-external, and two-external integrals similar to the other one-electron integrals in CISRT.

Three subroutines are added to the CIUFT program to calculate the spin-orbit loop values F_{ij}, $(i, j = 1...n)$ in eqs 50−57. These are directly adapted from the zero-external, one-external, and two-external subroutines for the spin−orbit-free case. Only the exchange contributions of the 8b type of loops (Figure 2) need be considered in the spin−orbit case and the loops for $e_{i(n+1),(n+1)j}$ are only evaluated up to level n since the contribution of the $(n + 1)$ th level is explicitly folded into eq 42 and the loop may be open-ended at the nth level. The quantities stored in the formula tape file for each spin−orbit loop are the weights of the internal part of the ket and bra walks and the internal loop values, as in the spin−orbit-free case. All the CSFs with the same spatial ket and bra walks and different spin functions share the same loop value. Instead of the weight of the loop head in the spin−orbit-free case, the spin values corresponding to the ket and bra walks are saved.

Similarly three subroutines adapted from zero-external, one-external, and two-external subroutines for the spin−orbit-free case are added to the diagonalization program CIUDG. In this program, the contributions of each integral to the matrix elements of all the CSFs that share the same loop are considered during each iteration. For each pair of ket and bra walks specified for a given loop, the possible spin functions need to be considered also. The contribution of the spin functions to the spin−orbit matrix elements, i.e., the factors other than the spin−orbit integrals and the spin−orbit loop values in eqs 50−57, are stored in an array, and array look-up is used to speed up the calculation.

As already shown in detail, the Hamiltonian matrix for an even number of electrons can always be made to be real symmetric by choosing the spin functions judiciously and including factors of $\imath$ in some of the spin functions. This result can also be obtained without using spin eigenfunctions by considering 2-fold rotation operators working only in spin space, analogous to the D_2 point group (or rotation and reflection operators analogous to C_{2v}) and showing that, for the two-open-shell-electron case, the spin functions $\alpha\beta - \beta\alpha, \imath(\alpha\alpha - \beta\beta)$, $\alpha\alpha + \beta\beta$, and $\imath(\alpha\beta + \beta\alpha)$ used with Slater determinants lead to a real Hamiltonian matrix. Generalizing this result leads to sums and differences of Slater determinants with their spin-reversed counterparts (including some factors of $\imath$) sufficing to insure a real symmetric Hamiltonian matrix. This same result has been derived using the time-reversal operator.[24]

It has also been shown[38] that D_2 or C_{2v} spatial symmetry suffice to make the Hamiltonian matrix real for both even and odd numbers of electrons. This leaves odd-electron systems with less than this level of spatial symmetry giving complex Hermitian Hamiltonian matrices. For odd-electron systems there are in fact three distinct types of behavior for different amounts of spatial symmetry as analyzed including the time-reversal operator,[56−58] of which the third one is the one described above. Some reductions in size for the complex Hermitian cases are possible, but somewhat complicated.[59,60]

A method which makes the Hamiltonian matrix real symmetric in all odd-electron cases involves adding an additional noninteracting electron. It was proposed and implemented by S. Y.,[13] and has the advantage that it uses the even-electron formalism already developed. For the complex Hermitian cases, the replacement real symmetric matrix has twice the dimension. Since the principal computational process in a direct CI calculation is matrix-vector products, and complex multiplications are equivalent to several real multiplications, the two procedures are approximately equivalent computationally. For the D_2 or C_{2v} or higher symmetry cases, there is no change in the size of the matrix.

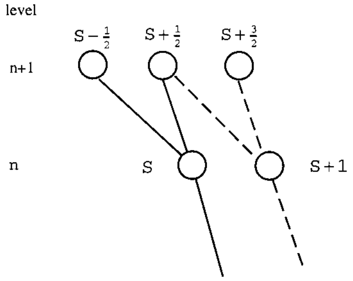

Figure 5. Graphical representation of spin−orbit coupling for a system with an odd number of electrons: an additional noninteracting electron is added to make the system have an even number of electrons.[16]

TABLE 3: Timing Data for Example CI Calculations

size of CI(million)	wall-clock time(hours)
9.16	5.74
4.16	2.00
1.77	0.76
0.25	0.083

This extra-electron implementation for the case of systems with an odd number of electrons is used in the COLUMBUS programs. With one extra electron added, we are considering an $(N + 1)$-electron, $(n + 1)$-orbital problem. The extra electron always occupies the $(n + 1)$st orbital, either with spin up or with spin down, as schematically illustrated in Figure 5. The Hamiltonian is then the same as in eq 23 except that the summation over the orbital indices i, j goes to n instead of $n + 1$. Equivalently only the loops and integrals with orbital indices less than or equal to n are needed in the implementation. Only one of the $(N + 1)$-electron irreps need be chosen in carrying out calculations unless a center of inversion is present in which case two irreps of opposite parity must be used.

In Table 3 we list the timing data (diagonalization step only; other steps require negligible time) for several calculations on the uranyl ion (UO_2^{2+}). All were performed on a Sun Ultra 1 Model 200E Workstation. In all cases only one root was converged and the convergence criterion was approximately 10^{-8} E_h. Other examples are given in the documentation for the COLUMBUS programs.[15]

To date the preliminary versions of the program have been used in studies of iodine compounds,[12,61−69] lanthanide systems,[70−72] actinide systems,[73−77] and for comparison purposes.[78]

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