Spin-dependent operators in the unitary-group approach

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(Received 30 July 1993; revised manuscript received 28 February 1994)

We discuss the evaluation of matrix elements of spin-dependent operators expressed in terms of products of up to four U(n) generators. Such operators arise in connection with spin-orbit, spin–other-orbit, and spin-spin interaction operators in the Pauli-Breit Hamiltonian discussed recently by Gould and Battle [J. Chem. Phys. **98**, 8843 (1993); **99**, 5983 (1993)]. Those authors point out the need for closed-form expressions suitable for numeric calculations. In this work we enumerate the many factors which arise in molecular configuration interaction and complex-atom electronic-structure calculations. We also present numerical examples to illustrate the use of the methods.

PACS number(s): 31.15.+q, 03.65.Fd, 02.20.−a

I. INTRODUCTION

In the past two decades the *unitary-group approach* (UGA) has emerged as a powerful tool for analysis and computation of properties of many-electron systems in atomic and molecular physics and quantum chemistry [1–10]. Large-scale electronic structure calculations have been for the most part limited to the treatment of spin-independent Hamiltonians, however [11,12].

With regard to spin-dependent Hamiltonians, the essential issues regarding at least spin-orbit and scalar spin-spin interactions have been worked out by Drake and Schlesinger and co-workers [4,8] in 1977 using spin-graphical methods [13] adapted from the vector-coupling paradigm. Gould and Chandler [14] achieved partial, similar results for U($2n$). A more complete analysis of spin-dependent interactions was carried out by Kent and Schlesinger [15] in the context of the S_N and SU(2) UGA formalism. Further results on spin-orbit and tensor spin-spin interactions were obtained by Kent, Schlesinger, and Shavitt [16] for application to U($2n$)-based UGA in the context of molecular configuration-interaction (CI) type calculations treated using the COLUMBUS suite of programs [11]. It should be pointed out that such calculations are of relevance for fine and hyperfine spectroscopy.

Techniques for treating spin-dependent interactions in the UGA involve adapting the relevant operators to the spin-orbital basis using the generators of the spin-orbital group U($2n$). Operators are represented in terms of products of two, three, or four generators. An immediate advantage, in the UGA basis, is that operator matrix elements are expressed as products of U(i):U($i-1$) segment factors. In turn, these are expressed in terms of fundamental, easily evaluated Racah-Wigner coefficients.

In recent papers, Gould and Paldus and co-workers [17,18] and Gould and Battle [19,20] have treated spin-dependent interactions, including spin-orbit and spin-spin terms, within the context of the U($2n$) spin-orbital basis applied to the Pauli-Breit Hamiltonian. They have referred to their approach as the *spin-dependent unitary-group approach.*

An outstanding issue in the Gould and Battle approach involves the evaluation of matrix elements of U(n) generator products. Products of three generators arise in connection with spin-other-orbit interaction operators while spin-spin-type operators are characterized by products of four generators. Gould and Battle state the need to obtain appropriate matrix element formulas suitable for efficient computer implementation.

In this paper, we apply the techniques of Refs. [15] and [16] to obtain a complete delineation of operator matrix element expressions suitable for use in the U($2n$) spin-dependent unitary-group approach. In Sec. II we present a brief review of relevant aspects of the unitary-group approach. In Sec. III we state closed-form factorized expressions for the matrix elements of spin-other-orbit operators involving products of three U(n) generators. In Sec. IV we state the analogous expressions for spin-spin operators expressed in terms of products of four generators. In Sec. V we show how the methods apply in several illustrative numerical examples.

II. REVIEW OF BASIC PRINCIPLES

A. Representation of U(n) bases

We assume at the outset $2n$ orthonormal atomic or molecular spin orbitals labeled

$$|i\mu\rangle=\psi_{i\mu}(\mathbf{r},\xi)=\phi_i(\mathbf{r})\chi_\mu(\xi)\quad(1\le i\le n;\mu=1,2)\,,$$

where $(\mathbf{r},\xi)$ denote the spatial and spin coordinates and it is assumed that the spin orbitals factor into orbital and spin parts. Within the second quantized formalism [1,2] we introduce fermion creation (annihilation) operators $a^\dagger_{i\mu}$ ($a_{i\mu}$) satisfying anticommutation relations $\{a^\dagger_{i\mu},a_{j\nu}\}=\delta_{i,j}\delta_{\mu,\nu}$ with the remaining anticommutators all vanishing.

In the usual manner N-electron wave functions are formed from the outer direct product of orbit and spin Young-symmetrized Nth-order products of fermion creation operators acting on the vacuum state,

$$|(\mathbf{p})_n;SM_S\rangle = Y^R_{(\mathbf{p})_n}\otimes Y^S_{(\tilde{\mathbf{p}})_2}\left[\prod_{k=1}^{N} a^\dagger_{i_k\mu_k}\right]|0\rangle$$
$$= |(\mathbf{p})_n;S\rangle\otimes|(\tilde{\mathbf{p}})_2;SM_S\rangle \ . \tag{2.1}$$

Labels S and M_S denote the total spin and magnetic quantum numbers while the Young symmetrizers Y^R and Y^S act on orbital and spin labels, respectively. The notation $(\mathbf{p})$ is adapted from conventional Gel'fand [2] tableau nomenclature and refers to a list, say, of Yamanouchi S_N-partition labels $[\mathbf{p}_i]$ $(i=1,\ldots,n)$ which denote an N_i-electron irreducible representation (irrep) of S_{N_i}. Alternatively, for molecular-CI applications, the Paldus $[abc]$-tabeau representation [3] is particularly useful. In this notation $[\mathbf{p}_n]=\{2^a l^b 0^c\}_n=[a_n b_n c_n]$, where $a_n+b_n+c_n=n$, $b_n=2S_n$, and $2a_n+b_n=N_n$. The U(2) conjugate irrep $[\tilde{\mathbf{p}}_2]$ is denoted by the Yamanouchi labels $\{(a+b)^\alpha a^\beta\}=[\alpha\beta]_{\{ab\}}$, where $\alpha+\beta=2$. Finally, we define the orbital occupancy ω_i; for orbital i the value of ω_i is 0 for no electrons, 1 for single-electron states, and 2 for paired states with the same orbital quantum number forming a *singlet*. The spin values associated with these orbital occupancies are 0, $\frac{1}{2}$, and 0, respectively.

Alternatively and equivalently, Drake and Schlesinger [4] constructed symmetric group S_N defined states adapted to total spin using vector coupling; applied recursively,

$$\left|\begin{bmatrix}[\mathbf{p}_{N_i}]\\(\mathbf{p})_{N_i-\omega_i}\end{bmatrix};S_{N_i}M_{N_i}\right\rangle$$
$$= \sum_{\substack{M_{n_i-\omega_i'}\\ \tilde{m}_{N_i}}} \langle S_{N_i-\omega_i}\tilde{s}_{\omega_i}M_{N_i-\omega_i}\tilde{m}_{\omega_i}|S_{N_i}M_{N_i}\rangle$$
$$\times|(\mathbf{p})_{N_i-\omega_i};S_{N_i-\omega_t}M_{N_i-\omega_i}\rangle\otimes|\omega_i;\tilde{s}_{\omega_t}\tilde{m}_{\omega_i}\rangle \ . \tag{2.2}$$

The recursion is carried out in order for orbitals i from 1 to n. Once the spins are coupled an antisymmetrizing operation is carried out on the orbital labels. This procedure is equivalent to the application of Young operators. The ordering of vector coupling by orbital labels ensures that a standard Young tableau is constructed. The S_N-based approach is made equivalent to the U(n) approach by including in (2.2) hole states for which ω_i is 0 (and orbital spin is 0).

The U($2n$) infinitesimal generators are written

$$E^{i\mu}_{j\nu}=a^\dagger_{i\mu}a_{j\nu} \tag{2.3}$$

$(1\le i,j\le n;1\le\mu,\nu\le 2)$ from which one defines orbital and spin group generators, respectively,

$$E^i_j=\sum_{\mu=1}^{2}E^{i\mu}_{j\mu};\quad E^\mu_\nu=\sum_{i=1}^{n}E^{i\mu}_{i\nu} \tag{2.4}$$

and their associated products,

$$E^{ik}_{jl}=E^i_jE^k_l-\delta^k_jE^i_l \ , \tag{2.5a}$$

$$E^{\mu\alpha}_{\nu\beta}=E^\mu_\nu E^\alpha_\beta-\delta^\alpha_\nu E^\mu_\beta \ . \tag{2.5b}$$

The evaluation of matrix elements of the generators and their products (2.5) has been discussed by a number of authors. Results have been presented for all cases of single generators and products of two generators [4,7,9]. We [15,16,21] have also presented several special cases of 3 and 4 generator products [for SU(m) in general] and shown that these are all expressible in terms of fundamental Racah (and higher order; 6-j,9-j) coefficients. These methods demonstrate that the matrix elements of an arbitrary product of generators can be written as a product of segment factors (matrices) each of which is computed based only on the irrep labels of linked U(i):U($i-1$) subgroups. Our aim in this work is to identify the appropriate factors and phases which arise.

B. Spin operators

The spin-vector operator is defined, using vector coupling,

$$\mathbf{S}(i,j)=\sum_{q=-1}^{1}(-1)^qS_q(i,j)\hat{\mathbf{e}}_{-q} \ , \tag{2.6a}$$

$$S_q(i,j)=\sum_{\mu,\nu=1}^{2}\sqrt{\tfrac{3}{2}}(-1)^{(1/2)-m_\mu}\begin{pmatrix}\frac{1}{2}&1&\frac{1}{2}\\ m_\mu&q&-m_\nu\end{pmatrix}E^{i\mu}_{j\nu} \ , \tag{2.6b}$$

where $\{\hat{\mathbf{e}}_0=\hat{\mathbf{e}}_z,\hat{\mathbf{e}}_{\pm1}=\hat{\mathbf{e}}_x\pm i\hat{\mathbf{e}}_y\}$ is a triad of basis vectors in $\mathbf{R}^3$ and $m_1=-m_2=\frac{1}{2}$.

For $q=1$, -1, and 0 Eq. (2.6) is equivalent to

$$\mathbf{S}(i,j)=\tfrac{1}{2}\sigma^\nu_\mu E^{i\mu}_{j\nu};\quad 1\le\mu,\nu\le 2 \tag{2.7}$$

from which it follows, with $S_\pm=\frac{1}{2}(S_x\pm iS_y)$,

$$S_+(i,j)=\sqrt{\tfrac{1}{2}}E^{i1}_{j2},\quad S_-(i,j)=\sqrt{\tfrac{1}{2}}E^{i2}_{j1} \ ,$$
$$S_z(i,j)=\tfrac{1}{2}(E^{i1}_{j1}-E^{i2}_{j2}) \ . \tag{2.8}$$

We note that the definition of $S_\pm$ (chosen for symmetry of normalization) differs by a factor of $1/\sqrt{2}$ from that of Gould and Battle [19], hence the difference between (2.8) and their expression (20).

The spin operator defined by (2.6) or (2.8) is expressed in terms of single spin orbitals, $|i\mu\rangle$, through the generators as in (2.3). In order to express $\mathbf{S}(i,j)$ in the many-electron irrep basis $|(\mathbf{p})_n;SM\rangle$ defined in (2.1) we utilize the Wigner-Eckart theorem and obtain

$$S_q(i,j)=\sum_{S,M,S',M'}\langle S'\|S_q(i,j)\|S\rangle$$
$$\times(-1)^{S-M+q}\begin{pmatrix}S&1&S'\\ M&q&M'\end{pmatrix}$$
$$\times|S'M'\rangle\langle SM| \ . \tag{2.9}$$

We note that the operator couples states of the same spin as well as states for which bra and ket spins differ by one.

Drake and Schlesinger [4] treated the reduced matrix element in (2.9) introducing two *reference* orbitals $\{|n'\mu\rangle,\langle n'\nu|\}$ which are coupled to bra and ket spins such that the resultant spins are identical, $S'_{n'}=S_{n'}=\frac{1}{2}(S'_n+S_n)$. By recoupling the n', i, and j orbital creation and annihilation operators they obtained the result that the $\mathbf{S}(i,j)$ operator is expressible purely in terms of the orbital generators of the symmetric group S_{N+1} (see expressions (42)–(44) and Fig. 4 of Ref. [4]). The orbital label n' is arbitrary except to the extent that the Pauli principle must hold (therefore, choose $n'=n+1$). In this context the reduced matrix element in (2.9) is expressed in terms of the U($n+1$) orbital generators,

$$\langle S'_n\|S_q(i,j)\|S_n\rangle=\langle S_{n+1}|E^i_{n+1}E^{n+1}_j+\tfrac{1}{2}E^{n+1}_{n+1}E^i_j|S_{n+1}\rangle \times(-1)^{S_{n+1}+S-(1/2)}\begin{Bmatrix} S' & S & 1\\ \frac{1}{2} & \frac{1}{2} & S_{n+1}\end{Bmatrix}^{-1}. \tag{2.10}$$

The process of embedding S_N in S_{N+1} or U(n) in U($n+1$) is particularly convenient due to the fact that in those higher rank groups reduced matrix elements (2.10) can be evaluated in terms of orbital generator products whose matrix elements are diagonal in the spin S_{n+1}.

The construction of the rank-2 tensor spin operators adapted to UGA proceeds in a manner analogous to the rank-1 vector operators,

$$S^{(2)}_Q(s_1,s_2)=\sum_{i,j,k,l=1}^{n} S^{(2)}_Q(i,j,k,l)\ , \tag{2.11a}$$

$$S^{(2)}_Q(i,j,k,l)=-\sqrt{5}\sum_{\substack{q_1,q_2;\\ q_1+q_2=-Q}}(-1)^Q\begin{bmatrix}1 & 2 & 1\\ q_1 & Q & q_2\end{bmatrix}\times S_{q_1}(i,j)S_{q_2}(k,l)\ . \tag{2.11b}$$

Operators (2.11) transform two-electron states $|jl\rangle$ to $|ik\rangle$. Clearly, such operators connect many-electron states of the same total spin as well as states whose total spins differ by 1 or 2.

As shown previously [14] the rank-2 operators can be composed in terms of linear combinations of products of four generators. The result obtained in Ref. [14] was specialized, however, to cases where $i=j$ and $k=l$, that is, when two spin states are flipped within the same orbitals. The general expression is

$$S^{(2)}_Q(i,j,k,l)_{n+2}=\sum_{\substack{S'_n,M',S_n,M\\ S'_{n+1},S_{n+1},S_{n+2}}}\frac{(-1)^{S_n+S_{n+2}+2S'_n}}{45}\begin{bmatrix}S'_n & 2 & S_n\\ -M' & Q & M\end{bmatrix}\times\prod_{t=n}^{n+1}[(2S'_t+1(2S_t+1]^{-1/2}\begin{Bmatrix}S'_{n+1} & \frac{1}{2} & S_{n+1}\\ \frac{1}{2} & S_{n+1} & 1\end{Bmatrix}\begin{Bmatrix}S'_n & 2 & S_n\\ \frac{1}{2} & 1 & \frac{1}{2}\\ S'_{n+1} & 1 & S_{n+1}\end{Bmatrix}^{-1}$$
$$\times\Big[E^i_{n+1}E^{n+1}_jE^k_{n+2}E^{n+2}_l-\tfrac{1}{2}E^i_jE^{n+1}_{n+1}E^k_{n+2}E^{n+2}_l -\tfrac{1}{2}E^i_{n+1}E^{n+1}_jE^k_lE^{n+2}_{n+2}+\tfrac{1}{4}E^i_jE^k_lE^{n+1}_{n+1}E^{n+2}_{n+2} -\tfrac{1}{9}(E^i_lE^k_j-\tfrac{1}{2}E^i_jE^k_l)(E^{n+2}_{n+1}E^{n+1}_{n+2}-\tfrac{1}{2}E^{n+1}_{n+1}E^{n+2}_{n+2})\Big]\ . \tag{2.12}$$

In order to establish the relationship between operators as in (2.11) and the generators, it is necessary to consider the group U($n+2$) used to describe an ($N+2$)-electron system. The addition of two extra *reference* orbitals at levels $n+1$ and $n+2$ is required to establish the result (2.12). In order to evaluate operator matrix elements, however, we do not require the generators [4,14] as will be seen in Secs. III and IV.

C. Spin-dependent operators

Gould and Battle [19] treat the spin-dependent Pauli-Breit Hamiltonian for an N-electron, M-ion system,

$$H=H_O+H_S+H_{SO}+H_{SS}\ . \tag{2.13}$$

In (2.13) H_O is a spin-independent operator containing the kinematic terms, Coulomb interactions (between electrons and nuclei as well as between electrons), relativistic mass corrections, and first and second order Darwin corrections. Remaining terms in (2.13) refer to spin-own-orbit (H_S), spin-other-orbit (H_{SO}), and spin-spin (H_{SS}) operators.

Ignoring higher-order multipole interactions the H_O operator can be split into one- and two-electron interaction operators, H_1 and H_2, expressible as bilinear forms involving only the orbital U(n) generators, E^i_j, and products, E^{ik}_{jl}, respectively. Matrix elements of these generators have been worked out previously [4,7,9]. Additionally, the matrix elements of the H_S operator were obtained

by Drake and Schlesinger [4] and the present authors [8]. An important feature is that the matrix element expressions are factorizable into products of terms which depend only on $U(i):U(i-1)$ segment labels.

The spin-other-orbit interaction is expressed

$$H_{SO}=\xi_0\sum_{i<j}^{N}\frac{(\mathbf{S}_i+\mathbf{S}_j)}{|\mathbf{r}_i-\mathbf{r}_j|^3}\cdot[(\mathbf{r}_i-\mathbf{r}_j)\times(\nabla_j-\nabla_i)]\ , \tag{2.14}$$

with $\xi_0=e^2\hbar/m_e^2c^2$, while the spin-spin interaction is written

$$H_{SS}=\hbar\xi_0\sum_{i<j}^{N}\left\{\frac{-1}{|\mathbf{r}_i-\mathbf{r}_j|^3}\times\mathbf{S}_i\cdot\left[\frac{3(\mathbf{r}_i-\mathbf{r}_j)(\mathbf{r}_i-\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|^2}-I\right]\cdot\mathbf{S}_j-\frac{8\pi}{3}\delta(\mathbf{r}_i-\mathbf{r}_j)\mathbf{S}_i\cdot\mathbf{S}_j\right\}\ . \tag{2.15}$$

It is important to note that the operators in (2.14) and (2.15) are stated using single-particle vector spin operators and are not suitable, therefore, for direct implementation within the spin-dependent UGA.

Kent and Schlesinger [15] and Gould and Battle [19] determined alternative forms for the spin-orbit-type interactions expressing them directly in terms of spin operators defined below, themselves written in terms of $U(2n)$ generators. Equation (2.14) is restated,

$$H_{SO}=\tfrac{1}{2}\sum_{i,j,k,l=1}^{n}\langle ik|\mathbf{h}_{SO}|jl\rangle\times[\mathbf{S}(i,j)E_l^k+E_j^i\mathbf{S}(k,l)-2\delta_j^k\mathbf{S}(i,l)] \tag{2.16}$$

where the two-electron orbit operator $\mathbf{h}_{SO}$ is defined

$$\mathbf{h}_{SO}=\frac{\xi_0}{|\mathbf{r}_1-\mathbf{r}_2|^3}(\mathbf{r}_1-\mathbf{r}_2)\times(\nabla_2-\nabla_1)\ . \tag{2.17}$$

The spin-spin operator (2.15) is restated in the form

$$H_{SS}=-\hbar\xi_0\sum_{\substack{i,j,\\k,l=1}}^{n}\left\{\sum_{Q=-2}^{2}\frac{15}{r_{ik,jl}^5}(-1)^Q\times S_Q^{(2)}(i,j,k,l)T_{-Q}^{(2)}(i,j,k,l)+\sum_{q=-1}^{1}\frac{8\pi}{3}\delta(\mathbf{r}_{ikjl})(-1)^q\times S_q(i,j)S_{-q}(k,l)\right\}\ , \tag{2.18}$$

where the factor $T^{(2)}(i,j,k,l)$ is a second-rank orbital tensor which expresses the radial vector dyadic in (2.15); this tensor is expressible also using spherical harmonic tensors,

$$T^{(2)}(\mathbf{r}_{ij},\mathbf{r}_{ij})=\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|^3}\left[3\frac{(\mathbf{r}_i-\mathbf{r}_j)(\mathbf{r}_i-\mathbf{r}_j)}{|\mathbf{r}_i-\mathbf{r}_j|^2}-I\right]=\sqrt{\tfrac{2}{3}}r_{ij}^2C^{(2)}(\theta_{ij},\phi_{ij})\ . \tag{2.19}$$

The second term in (2.18) is the Fermi contact term. This scalar spin-spin interaction component was treated by Drake and Schlesinger [4].

The above presentation can be considered a general outline of the UGA methods relating to spin-dependent operators.

III. SPIN ORBIT: THREE GENERATOR PRODUCTS

Matrix element formulas for spin–own-orbit interaction were first presented in the S_N basis by Drake and Schlesinger [4,8]. For completeness we include their main result herein. Their reduced matrix element of the rank-1 spin-vector operator $\mathbf{S}(i,j)$ can be expressed in $U(n)$,

$$\langle(\mathbf{p}');S_n'\|\mathbf{S}(i,j)\|(\mathbf{p});S_n\rangle=(-1)^{S-S_n+2S_n'+(1/2)}\begin{Bmatrix}S_n' & \frac{1}{2} & S\\ \frac{1}{2} & S_n & 1\end{Bmatrix}^{-1}\prod_{t=1}^{i-1}\delta(S_t,S_t')\times\mathbf{A}_i\prod_{t=i+1}^{j-1}T_t\,\mathbf{A}_j^{(2)}\prod_{t=j+1}^{n}T_t^{(2)}\mathbf{B}_{n+1}^{(2)}\ , \tag{3.1}$$

where $S=(S_n+S_n')/2$. The scalar factors A_i, T_t, $A_j^{(2)}$, and $B_{n+1}^{(2)}$ are all defined in Appendix A.

We note that the factor $B_{n+1}^{(2)}$ in (3.1) [see (A7)] is precisely cancelled by the Racah (6-j) coefficient and phase. The inclusion of these cancelling factors, though formally necessary for calculating the matrix element, still is useful for two reasons. The first is to express the spin operator in terms of the orbital generators directly. The second is that the inclusion of the coefficient allows for immediate use of the formulas in established procedures in CI calculations [11]. These methods rely on the expression of operators in terms of the generators to achieve computational efficiency. Also, for the same reason, those calculations require that matrix elements be represented by *closed-loop* subgraphs in the Shavitt distinct row-table graphical unitary group approach (DRT-GUGA) scheme. In the absence of the factor $\mathbf{B}_{n+1}^{(2)}$ at segment level $U(n+1):U(n)$ the spin-dependent operator matrix element subgraphs are *not* closed between irreps of differing spin.

Matrix elements of the spin-other-orbit operator (2.16) involve products of three $U(n+1)$ generators upon expansion of the spin $\mathbf{S}(i,j)$ operator, following (2.10). Matrix elements of these products can be calculated directly as linear combinations of products of factors for each level $U(m):U(m-1)$. To illustrate the formulas obtained we list below expressions assuming generator indices with relative values $i<j<k<l$ only. To facilitate the presentation of results we have placed definitions in Appendix A for the various factors which arise below.

The evaluation of $\mathbf{S}(i,j)E_l^k$ and $E_j^i\mathbf{S}(k,l)$ products in (2.9) proceeds in similar ways. Applying the Wigner-Eckart theorem we obtain the formulas for the reduced matrix elements,

$$\langle(\mathbf{p}')\|\mathbf{S}(i,j)E_l^k\|(\mathbf{p})\rangle=(-1)^{S-S_n+(1/2)+2S_n'}\begin{Bmatrix}S_n' & \frac{1}{2} & S\\ \frac{1}{2} & S_n & 1\end{Bmatrix}^{-1}\prod_{t=1}^{i-1}\delta(S_t,S_t')$$
$$\times\mathbf{A}_i\prod_{t=i+1}^{j-1}T_t\,\mathbf{A}_j^{(2)}\prod_{t=j+1}^{k-1}T_t^{(2)}\mathbf{A}_k^{(3)}\prod_{t=k+1}^{l-1}T_t^{(3)}\mathbf{B}_l^{(3)}\prod_{t=l+1}^{n}T_t^{(2)}\mathbf{B}_{n+1}^{(2)}\,. \tag{3.2}$$

Reversing the order of operators, we obtain

$$\langle(\mathbf{p}')\|E_j^i\mathbf{S}(k,l)\|(\mathbf{p})\rangle=(-1)^{S-S_n+(1/2)+2S_n'}\begin{Bmatrix}S_n' & \frac{1}{2} & S\\ \frac{1}{2} & S_n & 1\end{Bmatrix}^{-1}\prod_{t=1}^{i-1}\delta(S_t,S_t')$$
$$\times\mathbf{A}_i\prod_{t=i+1}^{j-1}T_tB_j\prod_{t=j+1}^{k-1}\delta(S_t,S_t')\,\mathbf{A}_k\prod_{t=k+1}^{l-1}T_t\,\mathbf{A}_l^{(2)}\prod_{t=l+1}^{n}T_t^{(2)}\mathbf{B}_{n+1}^{(2)}\,. \tag{3.3}$$

Continuing with remaining cases, we obtain

$$\langle(\mathbf{p}')\|\mathbf{S}(j,l)E_k^i\|(\mathbf{p})\rangle=(-1)^{S-S_n+(1/2)+2S_n'}\begin{Bmatrix}S_n' & \frac{1}{2} & S\\ \frac{1}{2} & S_n & 1\end{Bmatrix}^{-1}\prod_{t=1}^{i-1}\delta(S_t,S_t')$$
$$\times A_i\prod_{t=i+1}^{j-1}T_t\,\mathbf{A}_j^{(2)}\prod_{t=j+1}^{k-1}T_t^{(2)}\mathbf{B}_k^{(2)}\prod_{t=k+1}^{l-1}T_t\,\mathbf{A}_l^{(2)}\prod_{t=l+1}^{n}T_t^{(2)}\mathbf{B}_{n+1}^{(2)} \tag{3.4}$$

and

$$\langle(\mathbf{p}')\|\mathbf{S}(i,k)E_l^j\|(\mathbf{p})\rangle=(-1)^{S-S_n+(1/2)+2S_n'}\begin{Bmatrix}S_n' & \frac{1}{2} & S\\ \frac{1}{2} & S_n & 1\end{Bmatrix}^{-1}\prod_{t=1}^{i-1}\delta(S_t,S_t')$$
$$\times A_i\prod_{t=i+1}^{j-1}T_t\,\mathbf{A}_j^{(2)}\prod_{t=j+1}^{k-1}\mathbf{T}_t^{(2)}C_k^{(3)}\prod_{t=k+1}^{l-1}\mathbf{T}_t^{(3)}\mathbf{B}_t^{(3)}\prod_{t=l+1}^{n}T_t^{(2)}\mathbf{B}_{n+1}^{(2)}\,. \tag{3.5}$$

Equations (3.2)–(3.5) serve merely to illustrate the nature of expressions which arise in the context of spin-other-orbit interaction operator matrix elements. Since such operators involve products of three generators the number of special cases enumerated by correlating the generator indices is large. In all cases, however, the matrix element expressions are factorizable into scalar and matrix terms depending only on the spins, or equivalently the Paldus labels [*abc*], at segment levels U(i):U($i-1$). By utilizing the techniques of vector and tensor coupling and the Wigner-Eckart theorem an alternative means of obtaining these results is also realized.

IV. SPIN-SPIN: MATRIX ELEMENTS OF FOUR GENERATORS

In this section we present formulas for matrix element cases involving products of four U(n) generators arising in the context of rank-2 tensor spin-spin interaction operators as in (2.11). We state the basic formula for each segment factor in Appendix B.

Matrix elements of the spin tensor are written

$$\langle(p')\|S^{(2)}(i,j,k,l)\|(\mathbf{p})\rangle=\prod_{t=1}^{i-1}\delta(S_t,S_t')G_{ijkl}((p'),(p))\,, \tag{4.1}$$

where the factor $G_{ijkl}((p'),(p))$ can be decomposed into a product of (matrix) factors each of which depends only on the intermediate partition indices, $[\mathbf{p}_t']$ and $[\mathbf{p}_t]$ and certain other intermediate-coupling spin values. This decomposition can be expressed schematically in the form

$$G_{ijkl}((p'),(p))=\prod_{t=\min(i,j,k,l)}^{n}\mathbf{W}_t^{(\rho_t)}([\mathbf{p}_{t-1}'],[\mathbf{p}_t'],[\mathbf{p}_{t-1}],[\mathbf{p}_t];\{K_t\})\,. \tag{4.2}$$

Here, the $\mathbf{W}_t^{(\rho_t)}$ factors are scalars or matrices which depend explicitly on the U(t) and U($t-1$) irrep indices, ρ_t is the number of generators whose ranges overlap at level t, and $\{K_t\}$ represent intermediate-coupling spin values which arise at the head or tail of intersecting generator ranges. Alternatively, $\{K_t\}$ labels the irreps of

$$\mathrm{SU}(2)\otimes\mathrm{SU}(2)\otimes\cdots\otimes\mathrm{SU}(2)\supset\bigoplus_{[p]\in S_\rho}\mathrm{SU}_{[p]}(2)\,.$$

The use of matrices requires that factors be strictly ordered by increasing t. The advantage of this decomposition form (4.2) is that all the matrix factor components can be calculated simultaneously from the same sets of irrep indices.

The indices i, j, k, and l provide a convenient means for categorizing the subcases and factors. We enumerate these cases below according to the relative index values.

$i<j<k<l$: For this case both ket orbital indices j and l are increased. We refer to these as *raising-raising* (RR) cases

$$G_{ijkl}=A_i\prod_{t=i+1}^{j-1}T_t A_t^{(2)}\prod_{t=j+1}^{k-1}T_t^{(2)}\times \mathbf{A}_k^{(3)}\prod_{t=k+1}^{l-1}\mathbf{T}_t^{(3)}\mathbf{A}_l^{(4)}\prod_{t=l+1}^{n}T_t^{(4)}. \tag{4.3}$$

The superscript (3) indicates three-generator intermediate spin couplings of $K=\frac{1}{2}$ (doublet) or $\frac{3}{2}$ (quartet) terms starting in orbital k proceeding to $l-1$. The superscript (4) denotes four-generator intermediate spin couplings of $K=2$ only for the rank-2 tensor spin operator.

$i<j<l<k$: This case is closely related to the previous one and, since orbital index k is now being decreased to l, is referred to as *raising-lowering* (RL).

$i<j<k=l$: For this case we have single occupancy in the k orbital. The spin operator causes a spin flip on that orbital. It follows

$$G_{ijkk}=\mathbf{A}_i\prod_{t=i+1}^{j-1}T_t\mathbf{A}_j^{(2)}\prod_{t=j+1}^{k-1}T_t^{(2)}C_k^{(4)}\prod_{t=k+1}^{n}T_t^{(4)}. \tag{4.4}$$

$i=j<k<l$: Spin-flip now occurs on orbital i,

$$G_{iikl}=\mathbf{A}_i^{(2)}\prod_{t=i+1}^{k-1}T_t^{(2)}\mathbf{A}_k^{(3)}\prod_{t=k+1}^{l-1}\mathbf{T}_t^{(3)}\mathbf{A}_t^{(4)}\prod_{t=l+1}^{n}T_t^{(4)}. \tag{4.5}$$

$i<k<j<l$: In this case the spin operator index subranges $[i,j]$ and $[k,l]$ overlap leading to the expression

$$G_{ijkl}=A_i\prod_{t=i+1}^{k-1}T_t\mathbf{A}_k^{(2)}\prod_{t=k+1}^{j-1}\mathbf{T}_t^{(2)}\times\mathbf{A}_j^{(3)}\prod_{t=j+1}^{l-1}\mathbf{T}_t^{(3)}\mathbf{D}_l^{(4)}\prod_{t=l+1}^{n}T_t^{(4)}, \tag{4.6}$$

where we note the doublet and quartet coupling in the $[j,l]$ overlap subrange resulting from the overlap of three generators.

$i<j=k<l$: This case once again involves a spin flip of the singly occupied orbital k. We obtain

$$G_{ikkl}=A_i\prod_{t=i+1}^{k-1}T_t\mathbf{F}_k^{(3)}\prod_{t=k+1}^{l-1}\mathbf{T}_t^{(3)}\mathbf{A}_k^{(4)}\prod_{t=l+1}^{n}T_t^{(4)}. \tag{4.7}$$

$i<k<l<j$:

$$G_{ijkl}=A_i\prod_{t=i+1}^{k-1}T_t\mathbf{A}_k^{(2)}\prod_{t=k+1}^{l-1}\mathbf{T}_t^{(2)}\times\mathbf{H}_l^{(3)}\prod_{t=l+1}^{j-1}\mathbf{T}_t^{(3)}\mathbf{A}_j^{(4)}\prod_{t=j+1}^{n}T_t^{(4)}. \tag{4.8}$$

$i=j<k=l$: Spin flips now occur for both orbitals i and k,

$$G_{iikk}=A_i^{(2)}\prod_{t=i+1}^{k-1}T_t^{(2)}C_k^{(4)}\prod_{t=k+1}^{n}T_t^{(4)}. \tag{4.9}$$

$i<k<j<l$:

$$G_{ijkl}=A_i\prod_{t=i+1}^{k-1}T_t\mathbf{A}_k^{(2)}\prod_{t=k+1}^{j-1}\mathbf{T}_t^{(2)}\times\mathbf{A}_j^{(3)}\prod_{t=j+1}^{l-1}T_t^{(3)}\mathbf{A}_l^{(4)}\prod_{t=l+1}^{n}T_t^{(4)}. \tag{4.10}$$

$i=k<j=l$: Spin flips occur for $[i,k]$ and $[j,l]$ orbital pairs

$$G_{iijj}=\mathbf{A}_i^{(2)}\prod_{t=i+1}^{j-1}\mathbf{T}_t^{(2)}\mathbf{A}_j^{(4)}\prod_{t=j+1}^{n}T_t^{(4)}. \tag{4.11}$$

The cases treated in this section, while they do not cover every unique situation, are comprehensive in that other cases which do arise can be related to those above by interchanging labels and/or performing conjugation.

V. NUMERICAL EXAMPLES

In this section we consider a numerical example involving five electrons in seven orbitals. This could describe, for instance, either f electrons or a mixture of atomic or molecular orbitals in singlet, triplet, or quintet spin irreps. Our purpose is to apply the formulas from Secs. III and IV to calculate particular spin components of the spin–other-orbit interaction matrix elements.

The S_5 adapted U(7) irreps to be considered are, in Paldus *abc* notation, [052] and [133] (total spin $\frac{5}{2}$ and $\frac{3}{2}$, respectively). We consider the states, expressed in terms of both Weyl-Young and Gel'fand-Paldus tableaus,

$$|a\rangle=\left|\begin{matrix}1\\2\\3\\4\\5\end{matrix}\right\rangle=\begin{bmatrix}052\\051\\050\\040\\030\\020\\010\end{bmatrix};\quad |b\rangle=\left|\begin{matrix}1&3\\2\\4\\5\end{matrix}\right\rangle=\begin{bmatrix}133\\132\\131\\121\\111\\020\\010\end{bmatrix}. \tag{5.1}$$

For the states a and b defined in (5.1) we obtain, using (3.2) and Appendix A, the matrix elements of spin–other-orbit operator terms, $\mathbf{S}(i,j)E_k^l$,

$$\left\langle a\|\mathbf{S}(3,5)E_5^3\|a\right\rangle=(-\sqrt{\tfrac{10}{9}}\quad 1)\begin{pmatrix}\sqrt{\frac{9}{8}}&0\\0&1\end{pmatrix}\begin{pmatrix}\sqrt{\frac{7}{9}}\\-\sqrt{\frac{7}{5}}\end{pmatrix}=-\tfrac{11}{6}\sqrt{\tfrac{7}{5}} \tag{5.2}$$

and

$$\langle a\|\mathbf{S}(3,5)E_5^3\|b\rangle=(-\sqrt{\tfrac{8}{9}}\quad 0)\begin{pmatrix}-\sqrt{\frac{5}{4}}&0\\0&0\end{pmatrix}\begin{pmatrix}-\sqrt{\frac{1}{6}}\\0\end{pmatrix}=-\tfrac{1}{3}\sqrt{\tfrac{5}{3}}. \tag{5.3}$$

The different matrix terms as well as the diagonal nature of the 2×2 matrix derives immediately from the triplet-singlet coupling of the spin-vector operator to the U(n) generator. For off-diagonal matrix elements it is often the case (but not necessary) that the singlet factors accumulate to zero; the selection criteria provided by the state labels handle this situation rapidly.

In Ref. [14] we presented numerical examples of spin-spin matrix elements in irreps obtained from four atomic d electrons. All examples shown in that reference involved matrix elements of the type treated by Eq. (4.9). The same case also serves to illustrate the more general

case of four electrons in five molecular orbitals.

The previous examples serve to illustrate the application of the formulas stated in Secs. III and IV. Those formulas are equally applicable to both S_N and U(n)-based UGA, particularly the latter approach. With the outstanding issues of matrix element evaluation resolved it would be of interest to see the effect on large-scale Pauli-Breit calculations suggested by Gould and Battle [19] or the density matrix formalism of Gould and Paldus and co-workers [17,18].

A computational issue worth mentioning concerns the evaluation of segment factor matrix components, and consequent accumulation of factor products. The speed of this process could be greatly increased through introduction of hardware which, upon accessing the segment labels, simultaneously derives the case logic, evaluates matrix components, and accumulates products. The last process also requires simplification if integer arithmetic is used (complete precision can be assured in this case). Since matrix and pipelined hardware is used widely in computers specific adaptation to cases of present interest is appealing.

VI. CONCLUSIONS

We have expanded and clarified the treatment of spin-dependent operators first presented by Drake and Schlesinger [4] and ourselves [8,15,16] in the context of the S_N and SU(2)-based unitary-group approach. The results obtained by Gould and Battle [19,20], for matrix elements of spin-orbit-type operators were shown to be equivalent to those obtained previously in Refs. [4] and [8]. The treatment of spin-spin interaction operators and their matrix elements by Gould and Battle [19] is equivalent to results obtained in Refs. [15] and [16].

We have presented results which solve an outstanding issue concerning the Gould and Battle [19,20] approach, namely, determining the matrix elements of products of three and four U(n) (orbital) generators which arise in their formalism.

Our results complete the evaluation of spin-dependent operators up to rank-2 tensor spin-spin operators. The determination of matrix element expressions is greatly facilitated in the spin-orbital basis of the unitary-group approach. In all cases the expressions factor into U(n):U($n-1$) segment products each of which is a scalar or at most a 2×2 diagonal matrix. The importance of segment product factorization was first realized in molecular CI calculations by Shavitt [11] using his DRT formalism.

Significant advances have been made recently in the size of CI expansions [22] (up to 10^8 configurations have been treated using massively parallel computers). Vector- and parallel-based computing strategies by themselves are incomplete, however, so far as dealing with both the storage and time of calculation issues which arise in large-scale electronic systems. The time taken to perform the product calculations appearing in matrix element expressions should be greatly reduced through the use of pipelining, a hardware-based technique where an entire matrix at each subgroup level is calculated in parallel and accumulated at each segment level. Since the evaluation of each factor depends on determining the appropriate formula subcase to use, which requires tests of the occupancy of each level and other parameters, an unnecessary redundancy can be removed. Other aspects of the multiplication are also accelerated using the pipeline technique.

ACKNOWLEDGMENT

We gratefully acknowledge the support of the Natural Sciences and Engineering Research Council (NSERC) of Canada.

APPENDIX A

We present in this Appendix the definitions of U(m):U($m-1$) factors which were introduced in Sec. III. All our phases adhere to the Baird-Biedenharn-Condon-Shortley convention. The individual factors were arrived at by representing the reduced matrix elements of spin-orbit and spin–other-orbit interactions using U(n) spin graphs [4,6,7]. These matrix elements are represented by coupled angular-momentum lines. The resulting graphs are then decomposed to obtain the individual factors appearing below.

We state three types of factors. The A-type or *tail* factors represent the lower terminal points at levels U(i):U($i-1$), where one or more generators decouple from a product of ρ_i generators leaving a product of ρ_{i-1} generators [16]. Stated differently, shifts to the partition labels $[\mathbf{p}_i]$ are affected by the action of ρ_i generators whereas shifts to labels $[\mathbf{p}_{i-1}]$ are affected by the action of ρ_{i-1} generators. Similarly, B-type or *head* factors represent terminal points at levels U($i+1$):U(i) where one or more generators decouple from a product of ρ_i generators leaving a product of ρ_{i+1} generators [16]. For *intermediate* levels where ρ_i generators are acting the T-type factors are operative.

There are three types of tail factors which arise. The A factor corresponds to the tail of a single generator,

$$A_i=\sqrt{(2S_i+1)(2S_i'+1)}(-1)^{2S_i+S_{i-1}+2\rho_i+\rho_i'-S_i'+1} \times \begin{Bmatrix} S_i & \rho_i & S_{i-1} \\ \rho_i' & S_i' & \frac{1}{2} \end{Bmatrix}. \tag{A1}$$

The $A^{(2)}$ factor represents the tail for a two-generator segment,

$$A_i^{(2)}=3\sqrt{(2S_i+1)(2S_i'+1)} \begin{Bmatrix} S_{i-1}' & \rho_i' & S_i' \\ S_{i-1} & \rho_i & S_i \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix}. \tag{A2}$$

Actually, this factor represents only one of two possible terms which arise due to different couplings. For a simple product of two orbital generators the overlap range can be decomposed into *singlet-* and *triplet*-coupled terms. The factor in (A2) represents the triplet term. The singlet term is determined by replacing the 1 in the lower right position of the 9-j symbol by 0. This case

reduces to the B factor defined below. We define the 1×2 row matrix $\mathbf{A}_i^{(2)}$,

$$\mathbf{A}_{i,1}^{(2)}=-\tfrac{1}{2}\delta(S_i,S_i')B_i;\quad \mathbf{A}_{i,2}^{(2)}=A_i^{(2)}\ . \tag{A3}$$

Finally, the $\mathbf{A}^{(3)}$ factor comes about due to the action of three generators and is represented as a row (1×2) matrix. There are two allowed spin couplings, namely, *doublet* and *quartet*. A third type corresponding to the completely antisymmetric coupling of three spin-$\frac{1}{2}$ particles in S_3 is not allowed due to the Pauli principle [that is, no more than two rows can exist in a U(2) tableau]. The matrix formulation of this factor expedites simultaneous evaluation of the two coupling terms at a given U(i):U($i-1$) segment level. The factors are defined

$$A_{i,r}^{(3)}=\sqrt{(2S_i+1)(2S_i'+1)}\times(-1)^{S_i+S_{i-1}+S_i'+S_{i-1}'+2\rho_i+2\rho_i'+K_r}\times\sqrt{2K_r+1}\begin{Bmatrix} S_i' & S_i & K_r\\ \rho_i' & \rho_i & \tfrac{1}{2}\\ S_{i-1}' & S_{i-1} & 1\end{Bmatrix};\quad 2K_r=2r-1\ ,$$
$$r=1,2\ . \tag{A4}$$

There are also three types of head factors. The B factor is defined

$$B_i=(-1)^{2S_{i-1}+2S_{i-1}'+\rho_i+\rho_i'+(1/2)}\begin{Bmatrix} S_{i-1}' & \rho_i' & S_i\\ \rho_i & S_{i-1} & \tfrac{1}{2}\end{Bmatrix}. \tag{A5}$$

The $B_i^{(2)}$ factor represents the head for a two-generator segment corresponding to triplet spin coupling. Combining singlet and triplet components in a 2×1 column matrix $\mathbf{B}_i^{(2)}$,

$$B_{i,1}^{(2)}=\delta(S_i,S_i')A_i \tag{A6a}$$

$$\mathbf{B}_{i,2}^{(2)}=B_i^{(2)}=\sqrt{(2S_i+1)(2S_i'+1)}\times(-1)^{S_{i-1}'+S_{i-1}+S_i+S_i'+\rho_i'-\rho_i}\times\begin{Bmatrix} S_{i-1}' & \rho_i' & S_i'\\ S_{i-1} & \rho_i & S_i\\ \tfrac{1}{2} & \tfrac{1}{2} & 1\end{Bmatrix}. \tag{A6b}$$

The singlet-coupled term corresponds to the A_i factor (A6a). For the special case at level U($n+1$):U(n) where the total spins of the bra and ket irreps either agree or differ by one ($S_n'=S_n\pm 1$), $B^{(2)}$ takes the special form

$$B_{n+1}^{(2)}=(-1)^{S-S_n+S_n'+(1/2)}\begin{Bmatrix} S_n' & \tfrac{1}{2} & S\\ \tfrac{1}{2} & S_n & 1\end{Bmatrix}. \tag{A7}$$

Finally, analogous to the $\mathbf{A}^{(3)}$ factor, the $\mathbf{B}^{(3)}$ factor is expressed as a column (2×1) matrix with *doublet* and *quartet* terms defined

$$B_{i,r}^{(3)}=\sqrt{(2S_i+1)(2S_i'+1)}\times(-1)^{S_i'+S_{i-1}'+\rho_i'+S_i+S_{i-1}+\rho_i+(3/2)-K_r}\times\sqrt{2K_r+1}\begin{Bmatrix} S_{i-1}' & K_r & S_{i-1}\\ \rho_i' & \tfrac{1}{2} & \rho_i\\ S_i & 1 & S_i\end{Bmatrix};\quad 2K_r=2r-1\ ,$$
$$r=1,2\ . \tag{A8}$$

Intermediate terms representing segment factors in the regions where generators overlap have the following three forms. For single generators,

$$T_t=\sqrt{(2S_t+1)(2S_t'+1)}\times(-1)^{S_t+S_{t-1}'+\rho_t+(1/2)}\begin{Bmatrix} S_t' & S_t & \tfrac{1}{2}\\ S_{t-1} & S_{t-1}' & \rho_t\end{Bmatrix}, \tag{A9}$$

while for two overlapping generators, we use the diagonal 2×2 matrix form,

$$T_{t,11}^{(2)}=\delta(S_t,S_t');\quad T_{t,12}^{(2)}=T_{t,21}^{(2)}=0 \tag{A10a}$$

$$T_{t,22}^{(2)}=\sqrt{(2S_t+1)(2S_t'+1)}\times(-1)^{S_t+S_{t-1}'+\rho_t+1}\begin{Bmatrix} S_t' & S_t & 1\\ S_{t-1} & S_{t-1}' & \rho_t\end{Bmatrix}. \tag{A10b}$$

Cases of three overlapping generators are also treated using a diagonal 2×2 matrix whose elements are

$$T_{t,11}^{(3)}=T_t;\quad T_{t,12}^{(3)}=T_{t,21}^{(3)}=0\ , \tag{A11a}$$

$$T_{t,22}^{(3)}=\sqrt{(2S_t+1)(2S_t'+1)}(-1)^{S_t+S_t'+\rho_t+(3/2)}\times\begin{Bmatrix} S_t' & S_t & \tfrac{3}{2}\\ S_{t-1} & S_{t-1}' & \rho_t\end{Bmatrix}. \tag{A11b}$$

As seen from (A11a) the (1,1) element is just a T factor. That this is so derived from the isomorphism between the U(2) irreps $\{(a+b)^1a^1\}$ and $\{b^1\}$ [removal of all paired boxes from the Weyl-Young spin-SU(2) tableau]. However, there are qualitative differences, especially in the treatment of orbital labels, thus it is useful to retain the distinction.

The final factor is $\mathbf{C}_i^{(3)}$ in Eq. (3.5). Such factors are present when the generator index range partly overlaps the range of the spin operator indices extended to n [e.g., $i<j<k<l<n$ for products like $E_l^j\mathbf{S}(i,k)$]. The factor is represented in diagonal 2×2 matrix form with the (1,2) element equal to zero. The remaining elements are

$$C_{i,11}^{(3)}=\tfrac{1}{2}\delta(S_{i-1},S_{i-1}')\left[\frac{(2S_i+1)(2S_i'+1)}{2(2S_{i-1}-1)}\right]^{1/2}\times(-1)^{2S_i-S_i'-S_{i-1}+2\rho_i+\rho_i'+1}\begin{Bmatrix} S_i & \rho_i & S_{i-1}\\ \rho_i' & S_i' & \tfrac{1}{2}\end{Bmatrix} \tag{A12a}$$

and

$$C^{(3)}_{i,2r}=\sqrt{2K_r+1}(-1)^{2K_r+S'_i-S_i+S_{i-1}+\rho_i+\rho'_i}\sum_{\sigma_1,\sigma_2}(-1)^{2\sigma_2+\sigma_1-(1/2)}\begin{Bmatrix}S_i & 1 & \sigma_2\\ \frac{1}{2} & S'_{i-1} & K_r\end{Bmatrix}\begin{Bmatrix}S'_{i-1} & \frac{1}{2} & \sigma_1\\ \frac{1}{2} & S_{i-1} & 1\end{Bmatrix}$$
$$\times\begin{Bmatrix}\sigma_2 & \sigma_1 & \rho'_i\\ S'_{i-1} & S'_i & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}\sigma_1 & \frac{1}{2} & S_{i-1}\\ \rho'_i & \frac{1}{2} & \rho_i\\ \sigma_2 & 1 & S_i\end{Bmatrix};\quad 2K_r=2r-1,\quad r=1,2\ . \tag{A12b}$$

APPENDIX B

We present in this Appendix the definitions of U(m):U($m-1$) factors which appear in connection with spin-spin operators in Sec. IV. These operators are expressed in terms of products of four generators.

From (4.3) we define the 2×1 matrix $\mathbf{A}^{(4)}_t$ with components

$$A^{(4)}_{t,K+(1/2)}=\sqrt{\tfrac{1}{2}(2K+1)(2S'_t+1)}\sum_{S=S_{t-1}\pm(1/2)}(2S+1)(-1)^{S_t+S'_t+K+S_{t-1}}$$
$$\times\begin{Bmatrix}S'_{t-1} & \frac{1}{2} & S\\ 1 & S_t & K\end{Bmatrix}\begin{Bmatrix}S_t & 1 & S\\ 1 & S'_t & 2\end{Bmatrix}\begin{Bmatrix}S & \frac{1}{2} & S'_{t-1}\\ \frac{1}{2} & S'_t & 1\end{Bmatrix};\quad \Delta N_t=0,2\ , \tag{B1}$$

where the intermediate spin $K=\frac{1}{2}$ (doublet) or $\frac{3}{2}$ (quartet). We also define the scalar,

$$T^{(4)}_t=\sqrt{(2S'_t+1)(2S_t+1)}(-1)^{S_t+S'_{t-1}+\sigma_t}\begin{Bmatrix}S_t & S_{t-1} & \sigma_t\\ S'_{t-1} & S'_t & 2\end{Bmatrix}. \tag{B2}$$

Note in (B1) that the bra state is singly occupied and the ket either unoccupied or doubly occupied with $\Delta N_t=0,2$.

From (4.4) we define the scalar factor,

$$C^{(4)}_t=\sqrt{(2S_t+1)(2S'_t+1)}(-1)^{S_t+S'_t+S_{t-1}+S'_{t-1}}\begin{Bmatrix}S_{t-1} & 1 & S_{t-1}\\ \frac{1}{2} & 1 & \frac{1}{2}\\ S'_t & 2 & S_t\end{Bmatrix}. \tag{B3}$$

The 9-j symbol in (B3) is of a type discussed in Refs. [15] and [13] (see pp. 144 and 145).

From (4.5) we define the 1×2 matrix factor $\mathbf{D}^{(3)}_t$, for $K=\frac{1}{2}$ and $\frac{3}{2}$,

$$D^{(3)}_{t,K+(1/2)}=\sqrt{\tfrac{1}{2}(2K+1)(2S'_t+1)}\sum_{S=S'_{t-1}\pm(1/2)}\sqrt{2S+1}(-1)^{S_t+S'_t+S'_{t-1}+K}$$
$$\times\begin{Bmatrix}S'_{t-1} & \frac{1}{2} & S\\ \frac{1}{2} & S_t & 1\end{Bmatrix}\begin{Bmatrix}S & \frac{1}{2} & S'_{t-1}\\ \frac{1}{2} & S'_t & 1\end{Bmatrix}\begin{Bmatrix}S'_t & K & S_t\\ \frac{1}{2} & S & 1\end{Bmatrix};\quad \Delta N_t=0,2\ . \tag{B4}$$

Here we have considered the case where the bra orbital is unoccupied or doubly occupied and the ket orbital is singly occupied. The reverse situation is handled by replacing primes by no primes, and vice versa, on the spins. This factor is similar to $\mathbf{A}^{(3)}_t$ defined in Eq. (A4).

From (4.6) we define, for $K=\frac{1}{2}$ and $\frac{3}{2}$,

$$F_{t,K+(1/2)}=\tfrac{1}{2}\sqrt{(2K+1)(2S_t+1)(2S'_t+1)}(-1)^{S_t+S'_t+S_{t-1}+S'_{t-1}+K}\begin{Bmatrix}S'_{t-1} & 1 & S_t\\ \frac{1}{2} & S_{t-1} & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}S_t & 1 & S'_{t-1}\\ \frac{1}{2} & S'_t & K\end{Bmatrix}. \tag{B5}$$

From (4.7) we define the 2×2 matrix $\mathbf{H}^{(3)}_t$, for $K=\frac{1}{2}$ and $\frac{3}{2}$ and $L=0$ and 1,

$$H^{(3)}_{t;L+1,K+(1/2)} = \sqrt{\tfrac{1}{2}(2L+1)(2K+1)(2S'_t+1)} \times \sum_{S=S_t\pm(1/2)} \sqrt{2S+1} \times (-1)^{S_t+S'_t+S_{t-1}+S'_{t-1}+K+L} \begin{Bmatrix} S'_{t-1} & \frac{1}{2} & S \\ \frac{1}{2} & S_t & L \end{Bmatrix} \begin{Bmatrix} S & \frac{1}{2} & S'_{t-1} \\ \frac{1}{2} & S'_t & 1 \end{Bmatrix} \begin{Bmatrix} S'_t & K & S_t \\ \frac{1}{2} & S & 1 \end{Bmatrix}; \quad \Delta N_{t=0,2} \cdot \tag{B6}$$

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