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Spin recoupling and *n*-electron matrix elements

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Abstract. For *n*-electron systems with well defined total spin antisymmetric states are constructed by successively coupling the spins associated with each orbital. A second quantized scheme is used and the matrix elements of these states are expressed both for spin-independent and spin-dependent interactions in terms of recoupling coefficients of SU(2). The latter are evaluated to give very simple expressions. As a particular case a simple formula for the matrix elements of generators of U(N) for two-column partitions is obtained.

1. Introduction

A large number of methods are available to construct antisymmetric *n*-electron states with good total spin. Here we shall be interested in the orthogonal basis one obtains by successively coupling the spins associated with each orbital. To impose antisymmetry in a simple way we shall use a second quantization formalism. In fact, we use the states defined in Moshinsky and Seligman (1971) which were shown, for N orbitals, to be equal up to a phase, to Gel'fand states of U(N) associated with a two-column Young diagram. These states are isomorphic to those given in Gouyet (1970). We may also mention that in a permutational formulation, these states would correspond to a Kotani–Yamanouchi representation (Kotani *et al* 1963).

We shall proceed to show that it is possible to give simple closed forms for the matrix elements of both spin-independent and spin-dependent operators using the recoupling techniques of SU(2) developed by Yutsis *et al* (1962).

The spin-independent one-body operators are known to be given in terms of the generators of U(N) (Moshinsky 1967) and we could in principle use the result by Gel'fand and Zetlin (1950) for their matrix elements. Yet actually this formula proves rather clumsy to handle for large N and one of the reasons to start this investigation was that association in the permutation group suggests that for the rather trivial case of a two-column partition a solution in SU(2) should be possible. Indeed we find a simple expression for this matrix element that has proved to be adequate for numerical calculations (J F Gouyet, B Huron, M T Prat unpublished program (SPINCIP) for calculation of excited states of polyelectronic systems).

The relation shown in Gouyet and Goychman (unpublished) and Gouyet (1971) between the diagrammatic techniques customary in perturbation theory and those introduced for recoupling problems by Yutsis *et al* (1962) may easily be extended to this approach and allows a very transparent interpretation of the techniques developed for the evaluation of matrix elements.

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2. The second quantization picture

We shall consider a system of N orthonormal orbitals labelled by $\mu = 1 \ldots N$. The two components of the spin of the electrons shall be denoted by $\sigma = \pm\frac{1}{2}$ and we write a spin–orbital as $|\mu\sigma\rangle$.

Then, a creation operator applied to a vacuum state $|0\rangle$ is equivalent to a spin–orbital as

$$b^\dagger_{\mu\sigma}|0\rangle \Leftrightarrow |\mu\sigma\rangle. \tag{2.1}$$

The Hermitian conjugate operators $b^{\mu\sigma}$ are the corresponding annihilation operators yielding zero when applied to the vacuum.

We further require the anticommutation relations

$$\{b^\dagger_{\mu\sigma}, b^\dagger_{\mu'\sigma'}\} = \{b^{\mu\sigma}, b^{\mu'\sigma'}\} = 0: \qquad \{b^\dagger_{\mu\sigma}, b^{\mu'\sigma'}\} = \delta^{\mu'}_{\mu}\delta^{\sigma'}_{\sigma} \tag{2.2}$$

where the δ^α_β are Kronecker symbols.

A monomial in $b^\dagger_{\mu\sigma}$ applied to $|0\rangle$ is equivalent to a Slater determinant of n states $\langle j|\mu_i\sigma_i\rangle$, particle j occupying the spin–orbital $|\mu_i\sigma_i\rangle$:

$$b^\dagger_{\mu_1\sigma_1} \ldots b^\dagger_{\mu_n\sigma_n}|0\rangle \Leftrightarrow \det\|\langle j|\mu_i\sigma_i\rangle\|. \tag{2.3}$$

Using these states the one- and two-body operators

$$\sum_{i=1}^{n} W_i, \tag{2.4a}$$

$$\sum_{i<j=1}^{n} V_{ij} \tag{2.4b}$$

are replaced by the equivalent operators

$$\mathscr{W} = \sum_{\mu\sigma,\mu'\sigma'} \langle\mu\sigma|W_1|\mu'\sigma'\rangle b^\dagger_{\mu\sigma} b^{\mu'\sigma'} \tag{2.5a}$$

$$\mathscr{V} = \tfrac{1}{2} \sum_{\substack{\mu_1\sigma_1,\mu'_1\sigma'_1 \\ \mu_2\sigma_2,\mu'_2\sigma'_2}} \langle\mu_1\sigma_1\mu_2\sigma_2|V_{12}|\mu'_1\sigma'_1\mu'_2\sigma'_2\rangle b^\dagger_{\mu_1\sigma_1} b^\dagger_{\mu_2\sigma_2} b^{\mu'_2\sigma'_2} b^{\mu'_1\sigma'_1} \tag{2.5b}$$

containing the one- and two-body matrix elements, respectively (see eg Moshinsky 1967 pp 6–7).

Thus, the monomials in $b^\dagger_{\mu\sigma}$ correspond to antisymmetric states. But actually in most electron problems we need antisymmetric states with good total spin and we want a basis of independent states for a given total spin. One possibility to obtain such a basis, and indeed an orthogonal one, is given by successively coupling the spins associated with the orbitals. Each orbital may be occupied at most twice and therefore we have the correspondence:

$$(b^\dagger_\mu)^{n_\mu}: \begin{cases} s_\mu = \sigma_\mu = 0 & \text{for } n_\mu = 0 \\ s_\mu = \frac{1}{2}; \sigma_\mu = \pm\frac{1}{2} & \text{for } n_\mu = 1 \\ s_\mu = \sigma_\mu = 0 & \text{for } n_\mu = 2 \end{cases}$$

implying that the total spin in a doubly-occupied orbital is zero and that in a singly-occupied orbital is $s_\mu = \frac{1}{2}$.

Using the usual angular bracket notation to denote vector coupling in SU(2) we obtain the states:

$$|n_1 n_2, \ldots n_N; S_1 \ldots S_{N-1} S M_S\rangle \equiv |\underline{n}; \underline{S} S M_S\rangle$$
$$= [\ldots[(b_1^\dagger)^{n_1}(b_2^\dagger)^{n_2}]_{S_2}\ldots]_{S_{N-1}}(b_N^\dagger)^{n_N}]_{SM_S}|0\rangle. \tag{2.6}$$

Here the S_i imply the intermediate spins, $S_1 = s_1$ denoting the spin of the first shell. $\underline{n}$ and $\underline{S}$ are the shorthand notation for the sets n_μ and S_μ.

These states are identical to the ones of the occupation branching number representation (Gouyet 1970) and have also been shown to be equal up to a phase to Gel'fand states corresponding to a two-column partition characterizing an IR of U(N) (Moshinsky and Seligman 1971).

Now, the problem we have to deal with is from the point of view of SU(2) one of multiple coupling and, regarding matrix elements, one of multiple recoupling. Such problems are discussed extensively by Yutsis *et al* (1962) and we shall adopt their notation by explicitly writing the coupled spins s_μ in the ket

$$|\underline{n}; \underline{S} S M_S\rangle = |\underline{n}(s_1 \ldots s_N)^{A_0} \underline{S} S M_S\rangle. \tag{2.7}$$

Here A_0 stands for the successive order of coupling as

$$A_0 = ((\ldots((\bullet + \bullet) + \bullet) + \ldots) + \bullet)$$

(Yutsis *et al* 1962, equation (2.2.12)).

3. The matrix elements of spin-independent single-particle operators

In this section we shall be concerned with the calculation of matrix elements of the operator:

$$\mathscr{C}_k^N = b_{k+\frac{1}{2}}^\dagger b^{N+\frac{1}{2}} + b_{k-\frac{1}{2}}^\dagger b^{N-\frac{1}{2}} \equiv b_{k\sigma}^\dagger b^{N\sigma} \tag{3.1}$$

between states of the type (2.6). This operator occurs in the one-body operator (2.5a) if the one-body matrix element is diagonal in the spin component and does not depend on it, ie if we have a spin-independent operator. It is important to note that $\mathscr{C}_k^N$ is actually the generator of the group U(N) of unitary transformations in the space spanned by the N orbitals.

First let us calculate the matrix element of $\mathscr{C}_{N-1}^N$. Using expression (2.7) for the states we find:

$$(n_1' \ldots n_N'(s_1' \ldots s_N')^{A_0} \underline{S}' S M_S|\mathscr{C}_{N-1}^N|n_1 \ldots n_N(s_1 \ldots s_N)^{A_0} \underline{S} S M_S)$$
$$= \prod_{\mu=1}^{N-2} \delta_{n_\mu}^{n_\mu'} \delta_{s_\mu}^{s_\mu'} \delta_{S_\mu}^{S_\mu'} (n_{N-1}' n_N'((S_{N-2} s_{N-1}') S_{N-1}' s_N')$$
$$S M_S|\mathscr{C}_{N-1}^N|n_{N-1} n_N((S_{N-2} s_{N-1}) S_{N-1} s_N) S M_S)$$
$$= \prod_{\mu=1}^{N-2} \delta_{n_\mu}^{n_\mu'} \delta_{s_\mu}^{s_\mu'} \delta_{S_\mu}^{S_\mu'} \sum_{\lambda,\lambda'} \langle((S_{N-2} s_{N-1}') S_{N-1} s_N') S|(S_{N-2}(s_{N-1}' s_N')\lambda') S\rangle$$
$$\times (n_{N-1}' n_N'(S_{N-2}(s_{N-1}' s_N')\lambda') S M_S|\mathscr{C}_{N-1}^N|n_{N-1} n_N(S_{N-2}(S_{N-1} s_N)\lambda) S M_S)$$
$$\times \langle(S_{N-2}(S_{N-1} s_N)\lambda) S|((S_{N-2} s_{N-1}) S_{N-1} s_N) S\rangle$$

$$= \prod_{\mu=1}^{N-2} \delta_{n_\mu}^{n'_\mu} \delta_{s_\mu}^{s'_\mu} \delta_{S_\mu}^{S'_\mu} (-1)^{s'_{N-1}+s'_N+s_{N-1}+s_N+2\lambda}$$

$$\times (\lambda)[(S'_{N-1})(S_{N-1})]^{1/2} \begin{Bmatrix} S_{N-2} & s'_{N-1} & S'_{N-1} \\ s'_N & S & \lambda \end{Bmatrix} \begin{Bmatrix} S_{N-2} & s_{N-1} & S_{N-1} \\ s_N & S & \lambda \end{Bmatrix}$$

$$\times (n'_{N-1} n'_N | \mathscr{C}^N_{N-1} | n_{N-1} n_N) \delta_{\lambda, |s_{N-1}-s_N|} \tag{3.2}$$

with $(X) = 2X+1$.

In the first step we use the fact that $\mathscr{C}^N_{N-1}$ only acts in the last two orbitals, then we perform a recoupling of the spins S_{N-2}, s'_{n-1}, s'_N and S_{N-2}, s_{N-1}, s_N, respectively to couple the spins of the orbitals that appear in the operator. In the last step we write the recoupling coefficients in the usual way as 6-j symbols and use the fact that $\mathscr{C}^N_{N-1}$ is a scalar in spin space. Therefore $\lambda = \lambda'$ and we can write a matrix element depending only on the occupation numbers of the last two orbitals. All possible combinations of n'_{N-1}, n'_N, n_{N-1} and n_N leading to a non-vanishing matrix element of $\mathscr{C}^N_{N-1}$ together with the values of s'_{N-1}, s'_N, s_{N-1}, s_N, λ and λ' are shown in table 1. Inspection shows that λ is determined uniquely by the occupation numbers, ie by the spins as $\lambda = |s_{N-1} - s_N|$. In table 2 the remaining matrix elements of $\mathscr{C}^N_{N-1}$ are listed. They may readily be evaluated using the anticommutation relations (2.2). Both in tables 1 and 2 we write k for $N-1$ as this will be useful in the general case.

Table 1. Possible values of occupation numbers and spins.

n_k	n_N	n'_k	n'_N	s_k	s_N	s'_k	s'_N	λ	λ'
0	2	1	1	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0, 1
0	1	1	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$
1	2	2	1	$\frac{1}{2}$	0	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
1	1	2	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0, 1	0

Table 2. Matrix elements of $(n_k\, n'_N | \mathscr{C}^N_k | n_k\, n_N)$.

$(n'_k\, n'_N)$ \ $(n_k\, n_N)$	(0 1)	(1 1)	(0 2)	(1 2)
(1 0)	1	0	0	0
(1 1)	0	0	$\sqrt{2}$	0
(2 0)	0	$\sqrt{2}$	0	0
(2 1)	0	0	0	-1

Considering the possibilities for s'_{N-1}, s'_N, s_{N-1} and s_N according to table 1 we find that at least one of the 6-j symbols always contains a zero and the other is also a particularly simple one.

Later, we shall distinguish the cases that correspond to $s'_{N-1} = 0$ and $s_{N-1} = 0$ introducing the resulting simplifications.

But first, let us reduce the matrix elements of $\mathscr{C}^N_k$ to that of $\mathscr{C}^N_{N-1}$. To do so we apply the cyclic permutation $P^{N-1}_k = (k, N-1, N-2, \ldots, k+1)$ to the orbitals both in bra and ket.

Using equation (2.7) for the states we obtain:

$$
\begin{aligned}
&(n'_1 \ldots n'_N(s'_1 \ldots s'_N)^{A_0}\underset{\sim}{S}' SM_S|\mathscr{E}^N_k|n_1 \ldots n_N(s_1 \ldots s_N)^{A_0}\underset{\sim}{S}SM_S) \\
&\quad = (-1)^{n'_k \sum_{i=k+1}^{N-1} n'_i}(-1)^{n_k \sum_{i=k+1}^{N-1} n_i} \\
&\qquad \times \sum_{\mathcal{T},\mathcal{T}'} \delta^{S_{N-1}}_{T_{N-1}} \langle (s'_1 \ldots s'_N)^{A_0}\underset{\sim}{S}'|(P^{N-1}_k(s'_1 \ldots s'_N))^{A_0}\mathcal{T}'\rangle \\
&\qquad \times (P^{N-1}_k(n'_1 \ldots n'_N)(P^{N-1}_k(s'_1 \ldots s'_N))^{A_0}\mathcal{T}' SM_S|\mathscr{E}^N_k|P^{N-1}_k(n_1 \ldots n_N) \\
&\qquad \times (P^{N-1}_k(s_1 \ldots s_N))^{A_0}\mathcal{T}SM_S)\delta^{T_{N-1}}_{S_{N-1}}\langle (P^{N-1}_k(s_1 \ldots s_N))^{A_0}\mathcal{T}|(s_1 \ldots s_N)^{A_0}\underset{\sim}{S}\rangle. \quad (3.3)
\end{aligned}
$$

The phases appearing stem from the interchanges of the Fermi operators, denoted symbolically by writing the set of occupation numbers as $P^{N-1}_k(n_1 \ldots n_N)$. Further we have two recoupling coefficients of SU(2) for the spins on both sides. $\mathcal{T}'$ and $\mathcal{T}$ denote the sets of new intermediate spins.

The recoupling coefficients in equation (3.3) may be chosen to be real and therefore the two coefficients appearing are of the same type. We now proceed to simplify such a coefficient using the techniques of Yutsis *et al* (1962). We find:

$$
\begin{aligned}
&\langle (P^{N-1}_k(s_1 \ldots s_{N-1}))^{A_0}T_1 \ldots T_{N-2}S_{N-1}|(s_1 \ldots s_{N-1})^{A_0}S_1 \ldots S_{N-2}S_{N-1}\rangle \\
&\quad = \prod_{\mu=1}^{k-1} \delta^{T_\mu}_{S_\mu}\langle (S_{k-1}, s_{k+1} \ldots s_{N-1}s_k)^{A_0}T_k \ldots T_{N-2}S_{N-1}|(S_{k-1}s_k \ldots s_{N-1})^{A_0} \\
&\qquad \times S_k \ldots S_{N-1}\rangle \\
&\qquad \times \prod_{\mu=1}^{k-1}\delta^{T_\mu}_{S_\mu} \prod_{\mu=k}^{N-2}\langle (((T_{\mu-1}s_{\mu+1})T_\mu s_k)S_{\mu+1}|(T_{\mu-1}s_k)S_\mu s_{\mu+1})S_{\mu+1}\rangle. \quad (3.4)
\end{aligned}
$$

In the first step we used the fact that the first $k-1$ spins are not affected by the permutation. Then we factorized the multiple recoupling coefficient into a product of recoupling coefficients of three angular momenta corresponding to a transposition $(k, \mu+1)$ each time.

That the result is a simple product may be seen according to Yutsis *et al* (1962, equation (9.3)). The recoupling coefficients in the last line of equation (3.4) may of course be expressed in terms of 6-*j* symbols as

$$
\begin{aligned}
&\langle (((T_{\mu-1}s_{\mu+1})T_\mu s_k)S_{\mu+1}|(((T_{\mu-1}s_k)S_\mu s_{\mu+1})S_{\mu+1}\rangle \\
&\quad = [(T_\mu)(S_\mu)]^{1/2}(-1)^{T_\mu+S_\mu+s_k+s_{\mu+1}}\begin{Bmatrix} s_k & T_{\mu-1} & S_\mu \\ s_{\mu+1} & S_{\mu+1} & T_\mu \end{Bmatrix}. \quad (3.5)
\end{aligned}
$$

In principle we have now obtained the matrix elements of $\mathscr{E}^N_k$ as we may introduce the result (equation (3.2)) for $\mathscr{E}^N_{N-1}$ into the remaining matrix element in the last line of equation (3.3), replacing $N-1$ by k. Yet we still lack a large amount of simplifications due to the strong restrictions imposed on s'_k, s'_N, s_k and s_N for non-vanishing matrix elements according to table 1. First we note that, as either s'_k or $s_k = 0$, one of the two recoupling coefficients in equation (3.4) is trivial and yields $\mathcal{T} = \underset{\sim}{S}$ or $\mathcal{T}' = \underset{\sim}{S}'$, respectively thus eliminating one of the sums over intermediate couplings. If we also consider the Kronecker $\delta^{T_\mu}_{T_\mu}$ for the intermediate coupling in equation (3.2) the sums over both $\mathcal{T}'$ and $\mathcal{T}$ have to vanish but the coefficient will be different for the two cases $s'_k = 0$ and $s_k = 0$, respectively. The remaining 6-*j* symbols are still very simple and may be given explicitly without summations if one distinguishes the possible cases appropriately.

The final result can now be given as:

$$(n'_1 \ldots n'_N(s'_1 \ldots s'_N)^{A_0} \underset{\sim}{S}' SM_S | \mathscr{C}^N_k | n_1 \ldots n_N (s_1 \ldots s_N)^{A_0} \underset{\sim}{S} SM_S)$$

$$= \prod_{\mu=1}^{k-1} \delta^{n'_\mu}_{n_\mu} \delta^{s'_\mu}_{s_\mu} \delta^{S'_\mu}_{S_\mu} \prod_{\mu=k+1}^{N-1} \delta^{n'_\mu}_{n_\mu} \delta^{s'_\mu}_{s_\mu} (n'_k n'_N | \mathscr{C}^N_k | n_k n_N) \delta_{\lambda, |s_k - s_N|}$$

$$\times \left[\delta_{s'_k,0} (-1)^{n_k \sum_{i=k+1}^{N-1} n_i} (-1)^{2s_k + s_N + S + 2S_{N-1} + S_{N-1}} \left(\frac{(s'_N)}{(s_k)} \frac{(S_{N-1})}{(S)} \right)^{1/2} \prod_{i=k}^{N-2} T(i) \right.$$

$$\left. + \delta_{s_k,0} (-1)^{n'_k \sum_{i=k+1}^{N-1} n'_i} (-1)^{2s'_k + s'_N + S + 2S_{N-1} + S'_{N-1}} \left(\frac{(s_N)}{(s'_k)} \frac{(S'_{N-1})}{(S)} \right)^{1/2} \prod_{i=k}^{N-2} T'(i) \right]. \tag{3.6}$$

The coefficients $T(i)$ are given in table 3 and are obtained directly by evaluating the 6-j symbols in equation (3.5). The $T'(i)$ are obtained by interchanging in table 3 the primed and unprimed quantities.

Table 3. $T(i)$:

$T(i) = \langle (S_i s'_k s'_{i+1})^{A_0} S'_i S'_{i+1} | (S_i s'_{i+1} s'_k)^{A_0} S_{i+1} S'_{i+1} \rangle$

$T'(i) = \langle (S'_i s_k s_{i+1})^{A_0} S_i S_{i+1} | (S'_i s_{i+1} s_k)^{A_0} S'_{i+1} S_{i+1} \rangle$

$S'_i - S_i$	$-\frac{1}{2}$		$+\frac{1}{2}$	
$S'_{i+1} - S_i$	-1	0	0	$+1$
$S_{i+1} - S_i$				
$-\frac{1}{2}$	1	$\frac{1}{(S_i)}$	$\left(\frac{(S'_i)(S_{i+1})}{(S_i)(S_i)} \right)^{1/2}$	0
$+\frac{1}{2}$	0	$\left(\frac{(S'_i)(S_{i+1})}{(S_i)(S_i)} \right)^{1/2}$	$-\frac{1}{(S_i)}$	1

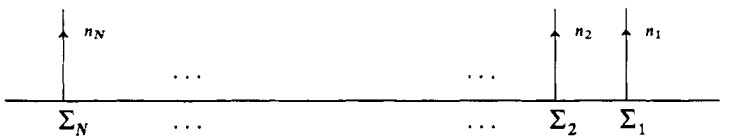
Equation (3.6) gives indeed the result for the most general spin-independent operator. This is the case because if we consider $\mathscr{C}^{k'}_k$ rather than $\mathscr{C}^N_k$ we obtain the result by considering it in a smaller space of k' or k orbitals depending on whether $k' > k$ or $k' < k$. While the first case corresponds to an operator $\mathscr{C}^N_k$ in the smaller space, the second corresponds to $\mathscr{C}^k_N$, related to $\mathscr{C}^N_k$ trivially by Hermitian conjugation. Naturally, we have also found a simplified expression for the generators of U(N) in the special case of two-column partitions in a basis that is up to a phase equal to the usual Gel'fand basis.

4. The diagrammatic formulation

In this section we shall connect the results of § 3 with the diagrammatic approach given in Gouyet (1970, 1971), Gouyet and Goychman (unpublished) and with the graphs of Yutsis for recoupling.

It is important to note that in the occupation branching number representation as formulated in Gouyet (1970) only the singly-occupied orbitals appeared explicitly while we shall include all orbitals in our notation to obtain a more compact form. For actual calculations doubly-occupied and empty orbitals corresponding to spin zero are certainly irrelevant if the operators do not act in these orbitals and they will drop out again.

Thus we may represent the state (2.6) graphically as

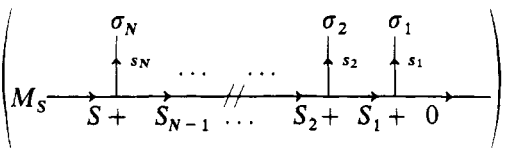


(4.1)

where $n_\mu = 0, 1, 2$ again denotes the occupation number of the μth orbital and $\Sigma_\mu = S_\mu - S_{\mu-1}$ denotes the change in the total spin occurring when coupling the orbital μ. We imply $\Sigma_1 = S_1$ and $\Sigma_N = S - S_{N-1}$ and we denote the set of Σ_μ by $\gamma = (\Sigma_1, \ldots, \Sigma_N)$. This set is of course equivalent to $\{S, S\}$. We recall that $\Sigma_\mu = \pm\frac{1}{2}$ for $n_\mu = 1$ and $\Sigma_\mu = 0$ for $n_\mu = 0, 2$.

The Yutsis diagram corresponding to the state (4.1) is

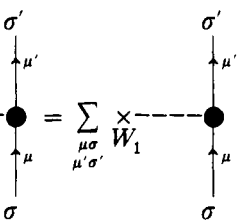
$$\prod_{i=1}^{N-1} (-1)^{S_{i+1}+S_i-s_{i+1}}[(S_{i+1})]^{1/2} \left(\right. \quad (4.2)$$



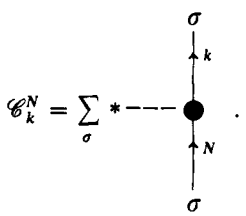
$\left. \right)$

including the factors necessary to change *jm* symbols into Clebsch–Gordan coefficients. Note that equation (4.2) is not sufficient to define the state (4.1) as the occupation numbers are not specified and $s_\mu = 0$ may be associated with $n_\mu = 0$ or 2. Indeed, we shall have to take into account the parts of the state not contained in (4.2) when calculating matrix elements and it is therefore useful to distinguish the diagrams (4.1) and (4.2) while exploiting their similarity. Graphically a mono-electronic operator (2.5*a*) is represented by:

$$\mathscr{W} = \sum_{\mu\sigma,\mu'\sigma'} \langle \mu\sigma | W_1 | \mu'\sigma' \rangle \quad (4.3)$$



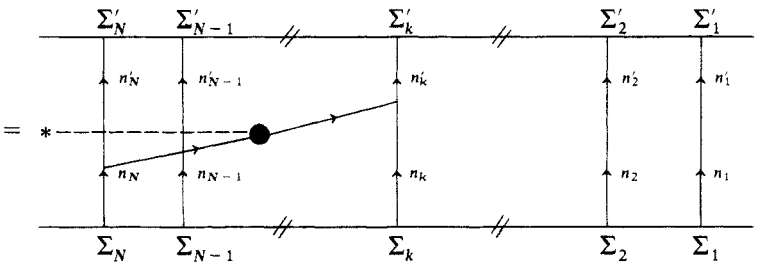
and in particular we obtain for the operator $\mathscr{E}_k^N$



(4.4)

Then the matrix element of $\mathscr{C}_k^N$ (3.3) is

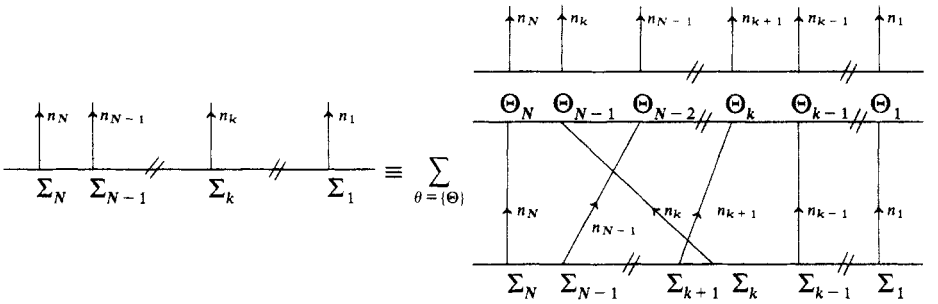
$$(n'_1 \ldots n'_N(s'_1 \ldots s'_N)^{A_0}\mathcal{S}'SM_S|\mathscr{C}_k^N|n_1 \ldots n_N(s_1 \ldots s_N)^{A_0}\mathcal{S}SM_S)$$



(4.5)

We see immediately that $n_\mu = n'_\mu$ if $\mu \neq k$ or N, as well as $n'_k = n_k + 1$, $n'_N = n_N - 1$ and $\Sigma_\mu = \Sigma'_\mu$ if $\mu < k$ must hold.

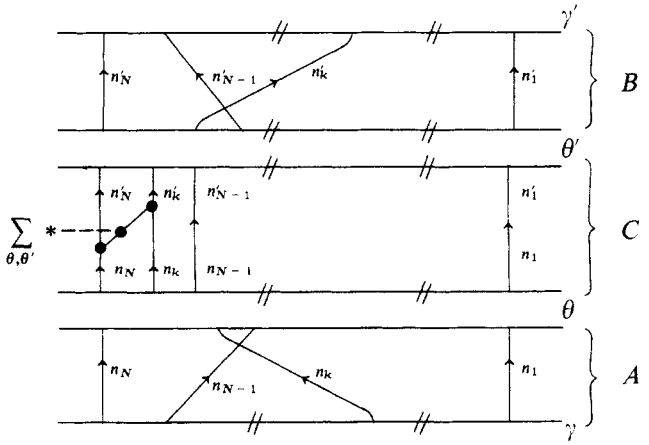
To reduce the calculation of the matrix element of $\mathscr{C}_k^N$ to that of $\mathscr{C}_{N-1}^N$ we have seen that we need the cyclic permutation P_k^{N-1} of the orbitals and thus the expansion



(4.6)

Here $\theta = (\Theta_1, \ldots, \Theta_N)$ plays exactly the role of the intermediate couplings $\boldsymbol{T}$ in equations (3.3) and (3.4). Also we must have $\Sigma_N = \Theta_N$ corresponding to $S_{N-1} = T_{N-1}$ in equation (3.3).

Performing this procedure twice, we may rewrite the matrix element (4.5) as



(4.7)

Here we did not write explicitly all $\Theta_\mu, \Theta'_\mu, \Sigma_\mu, \Sigma'_\mu$. We note that now, because of $n'_k = n_k + 1$ either $n_k = 0$ or $n'_k = 2$. Therefore either the transformation coefficient A is trivial since an empty orbital is permuted or the transformation coefficient B is trivial

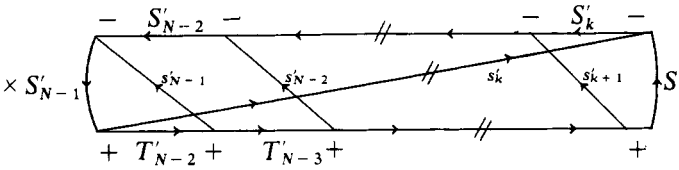
since a doubly-occupied orbital is commuted. In either case the spin associated with this orbital is zero.

Thus in the case $n_k = 0$ we have $\Sigma_k = 0$ and $\Theta_{N-1} = 0$ and

$$A = \delta_{\Sigma_1}^{\Theta_1} \cdots \delta_{\Sigma_{k-1}}^{\Theta_{k-1}} \delta_{\Sigma_{k+1}}^{\Theta_k} \cdots \delta_{\Sigma_{N-1}}^{\Theta_{N-2}} \delta_{\Sigma_N}^{\Theta_N}. \tag{4.8}$$

Then the recoupling factor B may be evaluated by passing to Yutsis diagrams and we find:

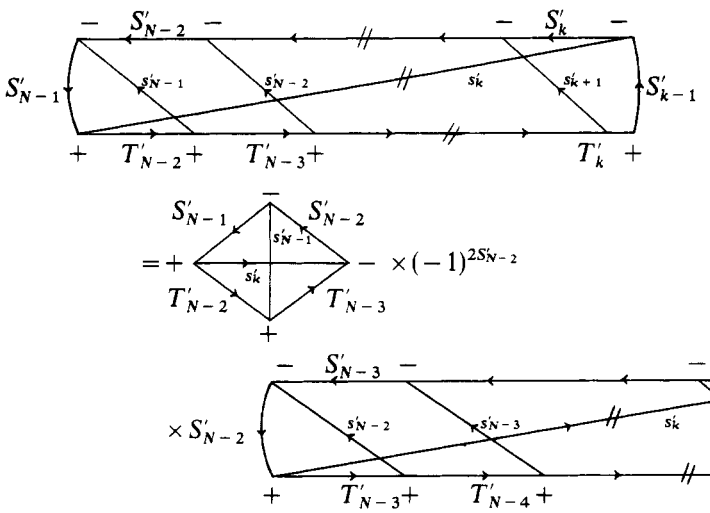
$$B = ((-1)^{nk \sum_{i=k+1}^{N-1} n_i}) \left(\prod_{\mu=k}^{N-2} (-1)^{2S'_\mu} [(S'_\mu)(T'_\mu)]^{1/2} \right) \left(\prod_{\mu=1}^{k-1} \delta_{T'_\mu}^{S'_\mu} \right) \delta_{T_{N-1}}^{S_{N-1}}$$



(4.9)

The first phase factor stems from the permutations of the Fermi operators. The second factor is necessary to pass from a recoupling to an invariant of the $3N$-j type. The δ symbols occur because we have cut those parts of the diagram involving a trivial recoupling. It is immediately possible to decompose the remaining graph into 6-j symbols (Yutsis *et al* 1962, p 47, figure 15.2) and recover equations (3.4) and (3.5). Actually we only obtain contributions from singly-occupied orbitals.

The case $s_k = \frac{1}{2}$ and $s'_k = 0$ is treated in quite the same way. Then the factor B becomes trivial and A is given by an expression similar to equation (4.9). For a numerical calculation where the matrix elements of $\mathscr{C}_k^N$ for all k will be necessary it is useful to take an iterative procedure to evaluate the graph in equation (4.9) as



(4.10)

which is equivalent to using the recursion relation obtained in Gouyet and Goychman (unpublished) and Gouyet (1971) considering the coefficient A as a matrix element of the permutation group S(N). This recursion relation was used in Gouyet *et al* (unpublished).

In this way all necessary coefficients may be calculated step by step without repetitions.

Finally, the remaining factor C in equation (4.7) is exactly the matrix element of $\mathscr{C}^N_{N-1}$ given in (3.2) and the recoupling performed there could also be done graphically. The important point to note is that the $\delta_{\Theta^{\mu'}_{\mu}}$, $\mu = 1, \ldots, N-2$ that may be read off the graph immediately, together with equation (4.8), will cancel all summations in equation (4.7). We thus obtain the result equation (3.7) considering the two possible cases $s'_k = \frac{1}{2}$, $s_k = 0$ and $s'_k = 0, s_k = \frac{1}{2}$.

5. Matrix elements of a spin-dependent single-particle operator

If the mono-electronic operator (2.5*a*) is spin-dependent, it may be expressed in terms of irreducible tensor operators of rank 1 and possibly a scalar part that is omitted here since it may be treated as in §§ 3 or 4.

$$\mathscr{W} = \sum_{\mu\sigma,\mu'\sigma'} \langle \mu\sigma | W_1(K,q) | \mu'\sigma' \rangle b^\dagger_{\mu\sigma} b^{\mu'\sigma'}$$

$$= \sum_{\mu,\mu'} \langle \mu \| W_1(K) \| \mu' \rangle O_q(\mu,\mu') \tag{5.1}$$

$$O^k_q(\mu,\mu') = \sum_{\sigma,\sigma'} (-1)^{1/2-\sigma} \begin{pmatrix} \frac{1}{2} & K & \frac{1}{2} \\ -\sigma & q & \sigma' \end{pmatrix} b^\dagger_{\mu\sigma} b^{\mu'\sigma'}.$$

Therefore we only have to consider matrix elements of vector operators ($k = 1$) as:

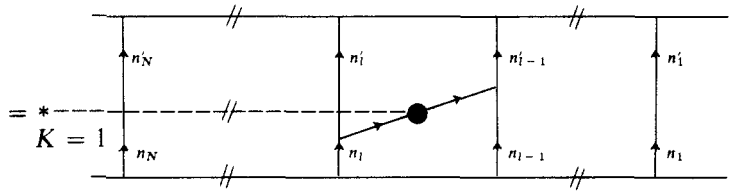
$$(n'_1 \ldots n'_N (s'_1 \ldots s'_N)^{A_0} \mathcal{S} S' M' | O^1_q(\mu,\mu') | n_1 \ldots n_N (s_1 \ldots s_N)^{A_0} \mathcal{S} S M)$$

$$= (-1)^{S'-M'} \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} (n'_1 \ldots n'_N (s'_1 \ldots s'_N)^{A_0} \mathcal{S}' S' \| O^1(\mu,\mu') \|$$

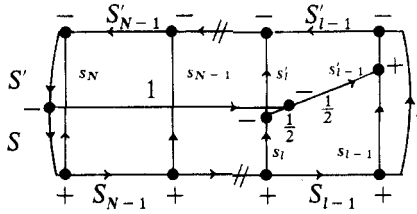
$$\times n_1 \ldots n_N (s_1 \ldots s_N)^{A_0} \mathcal{S} S) \tag{5.2}$$

where we may assume $\mu' > \mu$, as before. As a first step we calculate the matrix element of $O^1(l, l-1)$ which is in graphical representation

$$(n'_1 \ldots n'_N (s'_1 \ldots s'_N)^{A_0} \mathcal{S}' S' M' | O^1(l, l-1) | n_1 \ldots n_N (s_1 \ldots s_N)^{A_0} \mathcal{S} S M)$$



(5.3)



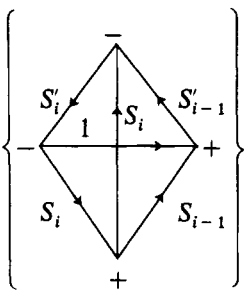
$$S_{l-2} \times \prod_{\substack{i \neq l \\ i \neq l-1 \\ i=1}}^{N} \delta^{n'_i}_{n_i} \delta^{s'_i}_{s_i} \prod_{j=1}^{l-2} \delta^{s'_j}_{s_j} \times \delta_{n_l, n'_l + 1} \delta_{n_{l-1}, n_{l-1} + 1}$$

$$\times \prod_{i=l}^{N} (-1)^{S_i + S_{i-1} - s_i} [(S_i)]^{1/2} (-1)^{S'_i - S'_{i-1} + s'_i} [(S'_i)]^{1/2}.$$

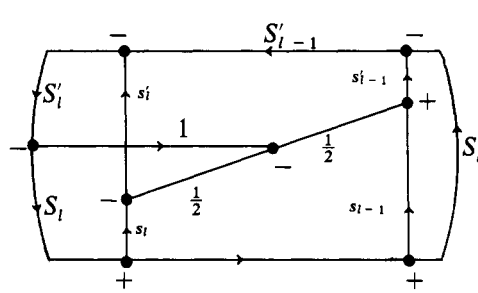
In distinction to equation (4.5) we now have an ($K = 1$) interaction line coupling the spin K of the operator, to the total spin.

But again the diagram is decomposable into a product of 6-j coefficients and a reduced matrix element involving only two orbitals as

$$\prod_{i=l+1}^{N}(-1)^{2S_{i-1}}$$



$\times$



(5.4)

Inserting (5.4) into (5.3) and evaluating the graphs we obtain:

$$\begin{aligned}
&(n'_1 \ldots n'_N(s'_1 \ldots s'_N)^{A^0}\Sigma' S'\|O^1(l,l-1)\|n_1 \ldots n_N(s_1 \ldots s_N)^{A^0}\Sigma S)\\
&\quad=\prod_{\mu=1}^{l-2}\delta_{n_\mu}^{n'_\mu}\delta_{S_\mu}^{S'_\mu}(-1)^{S_{l-2}+S'_l+\lambda_0+1}[(S_l)(S'_l)]^{1/2}\begin{Bmatrix}\lambda'_0 & S'_l & S_{l-2}\\ S_l & \lambda_0 & 1\end{Bmatrix}\\
&\quad\times(-1)^{2S_{l-2}+S_l+S'_l+s'_{l-1}+s'_l+s_{l-1}+s_l}[(S_{l-1})(S'_{l-1})(\lambda_0)(\lambda'_0)]^{1/2}\\
&\quad\times\begin{Bmatrix}S_{l-2} & s'_{l-1} & S'_{l-1}\\ s'_l & S'_l & \lambda'_0\end{Bmatrix}\begin{Bmatrix}S_{l-2} & s_{l-1} & S_{l-1}\\ s_l & S_l & \lambda_0\end{Bmatrix}\\
&\quad\times(n'_{l-1}n'_l(s'_{l-1}s'_l)\lambda'_0\|O^1(l,l-1)\|n_{l-1}n_l(s_{l-1}s_l)\lambda_0)\\
&\quad\times\delta_{\lambda_0,s_{l-1}+s_l}\delta_{\lambda'_0,s'_{l-1}+s'_l}\\
&\quad\times\prod_{i=l+1}^{N}\delta_{n_i}^{n'_i}\delta_{s_i}^{s'_i}[(S_i)(S'_i)]^{1/2}(-1)^{S_i+S'_{i-1}+s_i+1}\begin{Bmatrix}S'_{i-1} & S'_i & s_i\\ S_i & S_{i-1} & 1\end{Bmatrix}
\end{aligned}\tag{5.5}$$

λ_0 and λ'_0 are again uniquely determined by the occupation numbers. The remaining matrix element may be evaluated using the anticommutator relations (2.2).

Now, the matrix elements of the operators $O^1(l_i,k)$, $1 \leqslant k < l \leqslant N$ are easily obtained. Following the arguments of §§ 3 or 4 we have:

$$\begin{aligned}
&(n'_1 \ldots n'_N(s'_1 \ldots s'_N)^{A^0}\Sigma' S'\|O^1(l,k)\|n_1 \ldots n_N(s_1 \ldots s_N)^{A^0}\Sigma S)\\
&\quad=(-1)^{n_k\sum_{i=k+1}^{l}n_i}(-1)^{n'_k\sum_{i=k+1}^{l}n'_i}\\
&\quad\times\sum_{T,T'}\delta_{S'_{l-1}}^{T'_{l-1}}\langle(s'_1 \ldots s'_l)^{A^0}\Sigma'_l|(P_k^{l-1}(s'_1 \ldots s'_l))^{A^0}T'\rangle\\
&\quad\times((P_k^{l-1}(s'_1 \ldots s'_l))^{A^0}T'S'_l\|O^1(l,k)\|(P_k^{l-1}(s_1 \ldots s_l))^{A^0}T,S_l)\\
&\quad\times\delta_{T_{l-1}}^{S_{l-1}}\langle(P_k^{l-1}(s_1 \ldots s_l))^{A^0}T|(s_1 \ldots s_l)^{A^0}\Sigma_l\rangle\\
&\quad\times\prod_{i=l+1}^{N}\delta_{n_i}^{n'_i}[(S_i)(S'_i)]^{1/2}(-1)^{S_i+S'_{i-1}+s_i+1}\begin{Bmatrix}1 & S'_{i-1} & S_{i-1}\\ s_i & S_i & S'_i\end{Bmatrix}\\
&\quad=\prod_{\mu=1}^{k-1}\delta_{n_\mu}^{n'_\mu}\delta_{S_\mu}^{S'_\mu}\prod_{\mu=k+1}^{l-1}\delta_{n_\mu}^{n'_\mu}\prod_{\mu=l+1}^{N}\delta_{n_\mu}^{n'_\mu}V(\mu)\\
&\quad\times(n'_k n'_l;\lambda'_0\|O^1(l,k)\|n_k n_l;\lambda_0)\delta_{\lambda_0,s_k+s_l}\delta_{\lambda'_0,s'_k+s'_l}
\end{aligned}$$

$$\times\left(\delta_{s_k,0}(-1)^{n_k\sum_{i=k+1}^{l-2}n_i}G_1\prod_{i=k}^{l-2}T(i)+\delta_{s_k,0}(-1)^{n_k\sum_{i=k+1}^{l-2}n_i}G_2\prod_{i=k}^{l-2}T'(i)\right)$$

where

$$G_1=(-1)^{2S_{l-1}+S_l+S_l'+2s_l}[(S_l)(S_l')(S_{l-1})(s_l+\tfrac{1}{2})]^{1/2}\begin{Bmatrix}S_{l-1} & s_l & S_l\\ s_{l+\frac{1}{2}} & S_{l-1}' & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}S_{l-1}' & s_l' & S_l'\\ 1 & S_l & s_{l+\frac{1}{2}}\end{Bmatrix}$$

$$G_2=(-1)^{2S_{l-1}+2S_l}[(S_l)(S_l')(S_{l-1}')(s_l'+\tfrac{1}{2})]^{1/2}\begin{Bmatrix}S_{l-1}' & s_l' & S_l'\\ s_{l+\frac{1}{2}}' & S_{l-1} & \frac{1}{2}.\end{Bmatrix}\begin{Bmatrix}S_{l-1} & s_l & S_l\\ 1 & S_l' & s_l'+\frac{1}{2}\end{Bmatrix}$$

and the $V(\mu)$ are defined as

$$V(\mu)=1 \qquad \text{if } s_\mu=0$$

else

$$V(\mu)=(-1)^{S_\mu+S_{\mu-1}'+\frac{1}{2}}[(S_\mu)(S_\mu')]^{1/2}\begin{Bmatrix}1 & S_{\mu-1} & S_{\mu-1}'\\ \frac{1}{2} & S_\mu' & S_\mu\end{Bmatrix}$$

$$(l<\mu\leqslant N).$$

These coefficients are listed in table 4.

6. Conclusion

Starting from states built from successively spin-coupled Fermi operators we were able to give the matrix elements of one-body operators both spin-independent and spin-dependent in terms of two-body matrix elements and simple algebraic expressions involving the dimensions of spin multiplets. We found these expressions using recoupling techniques of SU(2) as well as the corresponding graphical methods of Yutsis *et al* (1962) which proved particularly useful. The connection to the graphical approach Gouyet introduces for perturbation expansions (Gouyet 1970, 1971, Gouyet and Goychman, unpublished) was established, and the results are equivalent to those obtained in Gouyet (1971, 1972), Gouyet and Goychman (unpublished) by different considerations.

The method readily extends to two-body operators. Drawing the graphs for two-body operators we may evaluate them using the same ideas, the main difference being that now no longer will all summations cancel and therefore the results will be somewhat more complicated. (This problem is discussed from a different point of view in Gouyet (1971) and Gouyet and Goychman (unpublished)). For spin-independent operators alternatively the usual second-order polynomial (Moshinsky 1967) in the generators (3.1) can be chosen. Its matrix elements may be evaluated by inserting a complete basis in the second-order term, again giving rise to a summation. The generalization to non-orthogonal orbitals is straightforward if one applies the dual space techniques discussed in Moshinsky and Seligman (1971).

As a final point we wish to emphasize that the expressions obtained are very accessible to numerical calculations because the matrix elements may be generated by iteration starting eg with $\mathscr{C}^N_{N-1}$, $\mathscr{C}^N_{N-2}$ up to $\mathscr{C}^N_1$ always using the previous matrix element and multiplying by one factor of the type (3.7). A program of this type has been elaborated by one of the authors (JFG) for spin-independent one- and two-body operators and for up to eight unpaired electrons, an upper limit for practical calculations.

Table 4. $V(i)$.

$S'_{i-1}-S_{i-1}$	-1		0		$+1$	
S_i-S_{i-1}	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$
S'_i-S_{i-1}						
$-\frac{3}{2}$	$\left(\frac{(S'_i)}{(S'_{i-1})}\right)^{1/2}$	0	0	0	0	0
$-\frac{1}{2}$	$\left(\frac{2}{(S'_{i-1})(S_{i-1})}\right)^{1/2}$	$\left(\frac{(S_i)}{(S_{i-1})}\right)^{1/2}$	$\left(\frac{(S_{i-1}+\frac{1}{2})(S'_i-\frac{1}{2})}{(S'_{i-1})(S_{i-1})}\right)^{1/2}$	$-\left(\frac{2}{(S'_{i-1})(S_{i-1})}\right)^{1/2}$	0	0
$+\frac{1}{2}$	0	0	$\left(\frac{2}{(S'_{i-1})(S_{i-1})}\right)^{1/2}$	$\left(\frac{(S_{i-1}-\frac{1}{2})(S'_i+\frac{1}{2})}{(S'_{i-1})(S_{i-1})}\right)^{1/2}$	$\left(\frac{(S_i)}{(S_{i-1})}\right)^{1/2}$	$-\left(\frac{2}{(S'_{i-1})(S_{i-1})}\right)^{1/2}$
$+\frac{3}{2}$	0	0	0	0	0	$\left(\frac{(S'_i)}{(S'_{i-1})}\right)^{1/2}$

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