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Vector-coupling approach to orbital and spin-dependent tableau matrix elements in the theory of complex spectra

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Vector-coupling approach to orbital and spin-dependent tableau matrix elements in the theory of complex spectra*

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The power of the Young tableau scheme for labeling a complete spin-adapted basis set in the theory of complex spectra lies in one's ability to evaluate matrix elements of irreducible tensor operators directly in terms of the tableau labels and shapes. We show that the matrix-element rules stated by Harter for one-body operators can be easily derived from simple vector-coupling considerations. The graphical method of angular momentum analysis is used to derive closed-form expressions for the matrix elements of two-body operators. This study yields several interesting new relationships between spin-dependent operators and purely orbital operators.

I. INTRODUCTION

In a recent series of papers, Harter and Patterson[1-3] and Drake *et al.*[4] have developed simplified rules for the application of the Young tableaux representation of Gelfand basis states to problems involving many equivalent fermions. Paldus[5-8] has obtained equivalent rules for the evaluation of matrix elements directly in terms of the Gelfand array labeling scheme. The $U(n)$ group theoretical basis of these methods has been extensively discussed by several authors,[9-12] and will not be repeated here.

The purpose of this paper is threefold. We first point out that the entire scheme, in particular Harter's so-called jawbone and assembly formulas, can be built up in a very transparent way from elementary angular-momentum coupling theory and a few simple notions from group representation theory.[13] Secondly, our approach makes explicit the relationship between the rules for evaluating Young tableau matrix elements, and the corresponding rules derived in the second-quantization scheme by Gouyet, Schranner, and Seligman.[12] Thirdly, we extend their results to obtain closed-form expressions for the matrix elements of two-body operators. This study yields several interesting new relationships between spin-dependent operators and purely orbital operators.

We first review in Sec. II the tableau labeling scheme, and then show that the Harter-Patterson assembly formula follows from simple vector-coupling considerations. The matrix elements of one- and two-body orbital operators are discussed in Secs. III and IV. Finally, the relationship between spin-dependent and purely orbital operators is discussed in Sec. V.

II. CONSTRUCTION OF BASIS SETS

As is well known, a completely antisymmetric N-electron state can be represented by the product of a two-column Young tableau with boxes labeling the one-electron orbital quantum numbers of the electrons, and the conjugate two-row tableau with boxes labeling the corresponding one-electron spin quantum numbers. Each such product represents a state of definite M_L, S, and M_S. In the papers of Harter and Paldus, the two-column orbital tableaux are used to label an irreducible representation of $U(n)$, and the matrix representatives of spin-independent operators in this basis set are derived from the commutation relations

$$[E_{ij}, E_{kl}] = \delta_{jk}E_{il} - \delta_{il}E_{kj} , \tag{1}$$

for the generators E_{ij} of $U(n)$, together with the Hermitian property

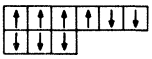
$$E^{\dagger}_{ij} = E_{ji} . \tag{2}$$

The explicit formulas of Gelfand and Zetlin[9] and Baird and Biedenharn[10] for the one-step operators $E_{i-1,i}$ have been greatly simplified by Harter[1,2] and Paldus[7,8] for the special case of spin-$\frac{1}{2}$ N-electron problems (i.e., partitions $\{2^{N/2-S}1^{2S}\}$ of N). Although this approach has a compelling group-theoretical significance, there are several difficulties. First, it is very laborious to obtain simple closed-form expressions directly from the commutation relation (1) for the general multi-step operator $E_{i,j}$, or for products of such operators. Second, there is no obvious way of treating spin-dependent operators at all within this scheme. Third, the physical significance of the tableau states is not at all apparent.

The crucial point of departure in our approach,

which is contained implicitly in the papers of Harter and Paldus but not exploited, is that the conjugate spin tableaux label a basis set for an irreducible representation $D^{(j)}$ of SU(2), with $j=2S+1$, in addition to an irreducible representation of the symmetric group $S(N)$. For example, the tableau

$$|S_9 M_9\rangle = \tag{3}$$



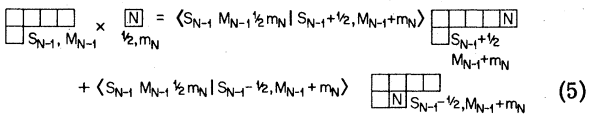
corresponds to a nine-electron spin state with $S_9 = \frac{3}{2}$, $M_9 = \frac{1}{2}$. The notation ↑ (↓) denotes an electron with $m_s = +\frac{1}{2}$ $(-\frac{1}{2})$. In general, $2S_N$ is the number of unpaired boxes in the top row, and

$$M_N = \sum_{i=1}^{N} m_{s,i} \ .$$

It is not necessary to insert the arrows explicitly since they are uniquely determined by the S_N, M_N labels. When an extra electron $|\frac{1}{2}, m_N\rangle$ is added to an $(N-1)$-electron spin state $|S_{N-1}, M_{N-1}\rangle$, the rule for expressing the reducible representation $|S_{N-1} M_{N-1}\rangle\,|\frac{1}{2}, m_N\rangle$ in terms of irreducible representations of SU(2) [and simultaneously of S(N)] is the well-known Clebsch-Gordan formula

$$|S_N, M_N\rangle = \sum_{M_{N-1}, m_N} \langle S_{N-1} M_{N-1}\, \tfrac{1}{2} m_N | S_N M_N\rangle \times |S_{N-1}, M_{N-1}\rangle\,|\tfrac{1}{2}, m_N\rangle \ . \tag{4}$$

In tableau notation, the inverse transformation to Eq. (4) is



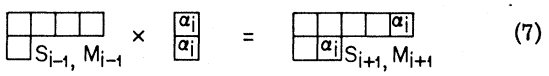
$$+ \langle S_{N-1}\, M_{N-1}\, \tfrac{1}{2} m_N | S_{N-1} - \tfrac{1}{2}, M_{N-1} + m_N\rangle \tag{5}$$

By repeated application of Eq. (4), one can build up N-electron spin states in terms of simple products of one-electron states according to

$$|S_N, M_N\rangle = \sum_{\substack{\text{all } M_i, m_i \\ M_N \text{ fixed}}} \prod_{i=1}^{N} \langle S_{i-1} M_{i-1}\, \tfrac{1}{2} m_i | S_i M_i\rangle\,|\tfrac{1}{2}, m_i\rangle \tag{6}$$

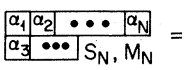
starting with $S_0 = 0$.

There still is a large amount of ambiguity in the state labeling because a given final S_N can be achieved by many different spin-coupling chains $S_i = S_{i-1} \pm \frac{1}{2}$. This ambiguity is resolved by numbering the boxes sequentially as they are added as shown in Eq. (5). One can choose any other convenient labeling scheme α_i to label uniquely the order in which the boxes are added. In particular, α_i can denote the orbital quantum numbers l, m_l of the one-electron states, together with any other necessary labels. Once repeated labels $\alpha_i = \alpha_{i+1}$ (doubly occupied or paired orbitals) must also be considered, but since these spin-orbitals must first be coupled separately to form an antisymmetric singlet state according to the Pauli principle, they do not enter the spin-coupling chain, i.e., $S_{i+1} = S_{i-1}$, $M_{i+1} = M_{i-1}$ and



(7)

The fully labeled states of definite spin permutation symmetry are thus



$$= \sum_{\substack{\text{all } M_i, m_i \\ M_N \text{ fixed}}} \left[\prod_{\substack{i=1; \\ \text{no pairs}}}^{N} \langle S_{i-1} M_{i-1}\, \tfrac{1}{2} m_i | S_i M_i\rangle\right] \left[\prod_{\substack{i=1; \\ \text{pairs}}}^{N} \frac{1}{\sqrt{2}} \begin{pmatrix} \frac{1}{2} \\ m_{i+1} \end{pmatrix} \begin{pmatrix} \\ m_i \end{pmatrix}\right] \left(\prod_{i=1}^{N} |\alpha_i, m_i\rangle\right), \tag{8}$$

where $(_{\alpha}{}^{a}{}_{\beta}) = \delta_{\alpha,-\beta}(-1)^{a+\alpha}$ is the antisymmetric symbol and the product over pairs contains one such factor for each $\alpha_{i+1} = \alpha_i$ pair. The product over "no pair" states omits all factors for which $\alpha_i = \alpha_{i\pm1}$. The spin-coupling chain is now uniquely specified by the way in which the α_i's alternate between rows 1 and 2. As shown in Eq. (7), paired states are simply skipped over without interrupting the chain.

As a final step, the totally antisymmetric states denoted by $|\alpha_1^{\pm}, \alpha_2^{\pm}, \ldots, \alpha_N^{\pm}; S_N M_N\rangle$ are obtained from Eq. (8) by explicitly antisymmetrizing the right-hand side, i.e., by replacing the simple spin-orbital product $\prod_{i=1}^{N} |\alpha_i, m_i\rangle$ by the corresponding Slater determinant. The notation α_i^+ and α_i^- denotes whether α_i appears in the upper or lower row, respectively, and thereby specifies the spin-coupling chain. The resulting functions are

$$|\alpha_1^{\pm}, \ldots, \alpha_N^{\pm}; S_N M_N\rangle = \sum_{\substack{M_i, m_i; \\ M_N \text{ fixed}}} \left[\prod_{\substack{i=1; \\ \text{no pairs}}}^{N} \langle S_{i-1} M_{i-1}\, \tfrac{1}{2} m_i | S_i M_i\rangle\right] \left[\prod_{i=1; \text{pairs}}^{N} \frac{1}{2} \begin{pmatrix} \frac{1}{2} \\ m_{i+1} \end{pmatrix} \begin{pmatrix} \\ m \end{pmatrix}\right] \frac{1}{\sqrt{N!}} \sum_{P} (-1)^P \prod_{i=1}^{N} |\alpha_i, m_i\rangle \tag{9}$$

where the sum over P denotes the $N!$ permutations of the electronic coordinates in the product of spin-orbitals and $(-1)^P$ is positive or negative depending on whether the permutation is even or odd.

The relationship between the states defined by Eq. (9) and Harter's tableau states is easily seen from the standard vector coupling formulas

$$|\cdots\alpha_{N-1}^{\pm},\alpha_N^{+};S_NM_N\rangle=\mathcal{A}\sum_{M_{N-1},m_N}\langle S_N-\tfrac{1}{2},M_{N-1}\tfrac{1}{2}m_N|S_NM_N\rangle\,|\cdots\alpha_{N-1}^{\pm};S_N-\tfrac{1}{2},M_{N-1}\rangle\,|\alpha_N,m_N\rangle\quad(\alpha_{N-1}\neq\alpha_N)\tag{10}$$

and

$$|\cdots\alpha_{N-1}^{\pm},\alpha_N^{-};S_NM_N\rangle=\mathcal{A}\sum_{M_{N-1},m_N}\langle S_N+\tfrac{1}{2},M_{N-1}\tfrac{1}{2}m_N|S_NM_N\rangle\,|\cdots\alpha_{n-1}^{\pm};S_N+\tfrac{1}{2},M_{N-1}\rangle\,|\alpha_N,m_N\rangle\tag{11}$$

where $\mathcal{A}$ antisymmetrizes the electronic coordinates in $|\alpha_n,m_n\rangle$ with all the rest. Equations (10) and (11) are the same as Harter and Patterson's[2] "assembly" formula to within an arbitrary phase. In fact, replacing $\mu_1-\mu_2$ in their Fig. 5 by $\frac{1}{2}S_N$ shows that their cases A and B (Ref. 2) are identical to Eq. (10). For example in case A,

$$\langle S_N-\tfrac{1}{2},M_N+\tfrac{1}{2},\tfrac{1}{2},-\tfrac{1}{2}|S_NM_N\rangle=\left(\frac{S_N-M_N}{2S_N}\right)^{1/2}=\left(\frac{\mu_1-(\text{no. of spin }\uparrow)}{\mu_1-\mu_2}\right)^{1/2}\tag{12}$$

The phase differences in their cases C, D, and E are discussed in the following section.

The identification of Harter and Patterson's assembly formula with the standard vector coupling coefficients contributes so greatly to one's understanding of the tableau formalism for fermions that it should be stressed.

Instead of writing the fully antisymmetrized state Eq. (9) in the usual way as the product of conjugate orbital and spin tableaux, one can simplify the notation by omitting the spin tableau and adding one additional label M_N to specify uniquely the spin part. Subsequent references to the removal of boxes refer to this type of notation. Explicitly, a tableau state such as

specifies the same linear combination of Slater determinants as Eq. (9).

III. EVALUATION OF ONE-BODY OPERATORS

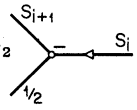
The power of the tableau formalism lies in one's ability to find simple expressions for matrix elements directly in terms of the tableau labels, rather than breaking them down first into linear combinations of Slater determinants via Eq. (9). The matrix element of an N-particle spin-independent multipole operator $V_q^k=\sum_{i=1}^N v_q^k(i)$ is written in the form

$$\langle(\alpha');S_NM_N|V_q^k|(\alpha);S_NM_N\rangle=\sum_{j,i}^{N}(-1)^{l_j'-m_j'}\begin{pmatrix}l_j' & k & l_i\\ -m_j' & q & m_i\end{pmatrix}\langle\alpha_j'\|v^k\|\alpha_i\rangle\,\langle(\alpha');S_NM_N|E(\alpha_j',\alpha_i)|(\alpha);S_NM_N\rangle\tag{13}$$

where (α) denotes the complete set of labels $\alpha_1^{\pm},\alpha_2^{\pm},\ldots,\alpha_N^{\pm}$ and l_i and m_i are the orbital labels specified by α_i. $E(\alpha_j',\alpha_i)$ is the elementary one-body operator which destroys the state α_i and creates the state α_j' when acting to the right. The angular analysis part of the problem is therefore solved once the matrix elements of the elementary operators $E(\alpha_j',\alpha_i)$ are known.

General results are easily obtained by means of the graphical technique of angular-momentum analysis[14] as described by Brink and Satchler.[15] It is convenient to reverse the direction of counting so that S_0 is the spin before any boxes are removed, S_1 is the residual spin after the first box α_1 is removed, etc. If a node with three lines denotes a 3-j symbol (as in Brink and Satchler), then the vector coupling coefficients in Eq. (9) are

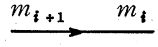
$$\langle S_{i+1}M_{i+1}\tfrac{1}{2}m_i|S_iM_i\rangle=-(2S_i+1)^{1/2}$$



(14)

and the antisymmetric symbols are

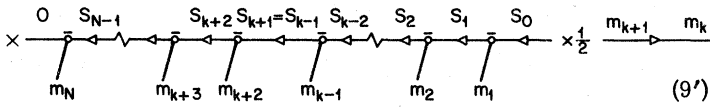
$$\begin{pmatrix}\frac{1}{2}\\ m_i & m_{i+1}\end{pmatrix}=$$



(15)

The graphical representation of Eq. (9) is then

$$|\alpha_N^{\pm},\ldots,\alpha_1^{\pm};S_0M_0\rangle = \sum_{\text{all } m} \mathcal{C} \prod_{i=1}^{N} |\alpha_i, m_i\rangle \prod_{\substack{i=1 \\ \text{no pairs}}}^{N} (2S_{i-1}+1)^{1/2}(-1)^N$$



(9′)

for each paired state $\alpha_k=\alpha_{k+1}$, and each undefined spin S_k is set equal to zero. If we agree on a common lexical ordering for the one-electron states labeled by (α) and (α'), then the matrix element of $E(\alpha_p',\alpha_q)$ $(p\geq q)$ in Eq. (13) vanishes in the absence of paired states unless $\alpha_1'=\alpha_1$, $\alpha_2'=\alpha_2,\ldots,\alpha_{q-1}'=\alpha_{q-1}$, $\alpha_q'=\alpha_{q+1},\ldots,\alpha_{p-1}'=\alpha_p$, $\alpha_p'=\alpha_q$, $\alpha_{p+1}'=\alpha_{p+1},\ldots,\alpha_N'=\alpha_N$ as shown for example in Fig. 1. The multiplicity of contributing linkages for paired states always cancels the factors of $\frac{1}{2}$ in Eq. (9′). Drawing the corresponding diagram for the state $\langle\alpha_N'^{\pm},\ldots,\alpha_1'^{\pm},S_0M_0|$ and mapping the set (m') into (m) in the same way as (α') maps into (α) yields

$$\langle(\alpha');S_0M_0|E(\alpha_p',\alpha_q)|(\alpha);S_0M_0\rangle$$

$$=(-1)^{p-q}\prod_{i=0}^{N}[(2S_i+1)(2S_i'+1)]^{1/2}\times G^{(1)}(p,q) \tag{16}$$

where $G^{(1)}(p,q)$ is the graph shown in Fig. 2. Block B is obtained from A by rotation about the horizontal axis, i.e., the arrows remain unchanged while the signs of the nodes reverse. All unlabeled lines correspond to $j=\frac{1}{2}$ in this and subsequent graphs. As shown in Eq. (9′) paired states are to be skipped over unless they occur inside one of the blocks A,B. The factor $(-1)^{p-q}$ comes from the number of interchanges required to bring the α's into alignment as shown in Fig. 1. Using rules (7.33) and (7.34) of Brink and Satchler, $G^{(1)}(p,q)$ decomposes immediately into

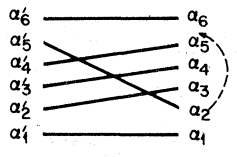
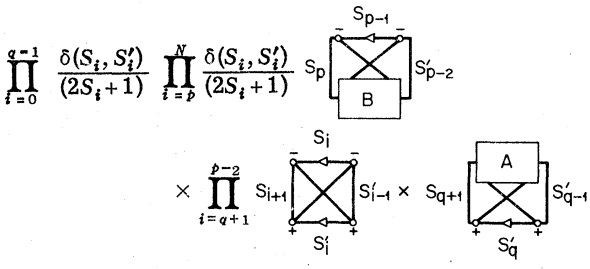


FIG. 1. Diagram showing how the set (α') must map into (α) to obtain a nonzero result for $E(\alpha_5',\alpha_2)$. Three interchanges are required to bring the labels into alignment as shown by the dashed arrow.

$$\prod_{i=0}^{q-1}\frac{\delta(S_i,S_i')}{(2S_i+1)}\prod_{i=p}^{N}\frac{\delta(S_i,S_i')}{(2S_i+1)}$$



(17)

Since the ith square in the above product can be written in terms of a 6-j symbol as

$$(-1)^{S_i+S_i'+1}\begin{Bmatrix}\frac{1}{2} & S_{i-1}' & S_i\\ \frac{1}{2} & S_{i+1} & S_i'\end{Bmatrix},$$

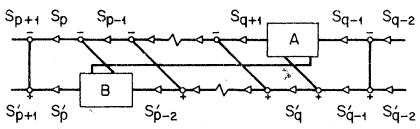
the final result is $(p>q)$

$$\langle(\alpha');S_0M_0|E(\alpha_p',\alpha_q)|(\alpha);S_0M_0\rangle$$

$$=\prod_{i=0}^{q-1}\delta(S_i,S_i')\prod_{i=p}^{N}\delta(S_i,S_i')A_qB_p\prod_{\substack{i=q+1\\ \text{no pairs}}}^{p-2}T(i) \tag{18}$$

where

$$T(i)=[(2S_i+1)(2S_i'+1)]^{1/2}(-1)^{S_i+S_i'+1}\begin{Bmatrix}\frac{1}{2} & S_{i-1}' & S_i\\ \frac{1}{2} & S_{i+1} & S_i'\end{Bmatrix},$$



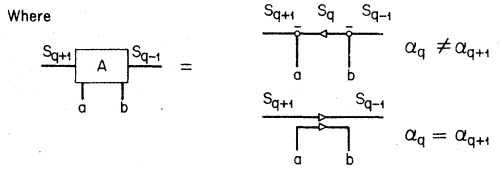


FIG. 2. Angular-momentum coupling graph for one-body operators [see Eq. (16)]. The definition of the blocks depends on whether or not the state in question is paired. All unlabeled lines correspond to $j=\frac{1}{2}$.

$$A_q = \begin{cases} T(q), & \alpha_q \neq \alpha_{q+1} \\ (-1)^{S'_{q-1}-S'_q-1/2}\left(\dfrac{2S'_q+1}{2S_{q+1}+1}\right)^{1/2}, & \alpha_q=\alpha_{q+1} \end{cases}$$

and

$$B_p = \begin{cases} T(p-1), & \alpha'_p \neq \alpha'_{p-1} \\ (-1)^{S_p-S_{p-1}-1/2}\left(\dfrac{2S_{p-1}+1}{2S'_{p-2}+1}\right)^{1/2}, & \alpha'_p=\alpha'_{p-1}, \end{cases}$$

The only nonvanishing 6-j symbols of the above type are[16]

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ \frac{1}{2} & j_3-\frac{1}{2} & j_2+\frac{1}{2} \end{Bmatrix} = (-1)^{j_1+j_2+j_3}\left(\frac{(j_1+j_3-j_2)(j_1+j_2-j_3+1)}{(2j_2+1)(2j_2+2)2j_3(2j_3+1)}\right)^{1/2} \tag{19}$$

and

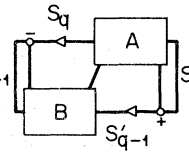
$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ \frac{1}{2} & j_3-\frac{1}{2} & j_2-\frac{1}{2} \end{Bmatrix} = (-1)^{j_1+j_2+j_3}\left(\frac{(j_1+j_2+j_3+1)(j_2+j_3-j_1)}{2j_2(2j_2+1)2j_3(2j_3+1)}\right)^{1/2}. \tag{20}$$

For computational purposes, these results can be considerably simplified by removing explicitly factors which cancel.

Due to our inverted counting, the case $p>q$ corresponds to an elementary lowering operator. The corresponding raising operator $E(\alpha'_q, \alpha_p)$ $(p>q)$ can be obtained by Hermitian conjugation [see Eq. (2)], or by replacing A, B, T in Eq. (18) by A', B', T', which are obtained from A, B, T by priming all unprimed S's and unpriming all primed S's.

The case $p=q$ deserves special consideration because it establishes the phase relationship with the Gelfand-Zetlin phase convention of Harter and Paldus in which all such matrix elements are positive. The matrix element is

$$\langle(\alpha');S_0M_0|E(\alpha'_q,\alpha_q)|(\alpha);S_0M_0\rangle = \prod_{i=0}^{q-2}\delta(S_i,S'_i)\prod_{i=q+1}^{N}\delta(S_i,S'_i)\prod_{\substack{i=q-1;\\ \text{no pairs}}}^{q}[(2S_i+1)(2S'_i+1)]^{1/2}$$



(21)

There are four distinct cases depending on whether or not the initial and final states are paired. They are

$$\langle(\alpha');S_0M_0|E(\alpha'_q,\alpha_q)|(\alpha);S_0M_0\rangle = \prod_{i=0}^{q-2}\delta(S_i,S'_i)\prod_{i=q+1}^{N}\delta(S_i,S'_i)E, \tag{22}$$

where

$$E = \begin{cases} \delta(S_q,S'_q)\delta(S_{q-1},S'_{q-1}), & \text{if } \alpha_q\neq\alpha_{q-1},\ \alpha'_q\neq\alpha_{q+1} \\ \delta(S_q,S'_q)\delta(S_q,S'_{q-2})(-1)^{S'_q-S'_{q-1}+1/2}\left(\dfrac{2S'_{q-1}+1}{2S_q+1}\right)^{1/2}, & \text{if } \alpha_q=\alpha_{q-1},\ \alpha'_q\neq\alpha'_{q+1} \\ \delta(S_{q+1},S'_{q-1})\delta(S_{q-1},S'_{q-1})(-1)^{S_{q-1}-S_q+1/2}\left(\dfrac{2S_q+1}{2S'_{q-1}+1}\right)^{1/2}, & \text{if } \alpha_q\neq\alpha_{q-1},\ \alpha'_q=\alpha'_{q+1} \\ -\delta(S_{q+1},S'_{q-1})\delta(S_q,S'_{q-2}), & \text{if } \alpha_q=\alpha_{q-1},\ \alpha'_q=\alpha'_{q+1}. \end{cases} \tag{23}$$

Remembering that S_q is the intermediate spin *after* the box α_q is removed, it is not difficult to verify that all signs can be made positive if one multiplies by $(-1)^{2S_{q-1}}$ or $(-1)^{2S'_{q-1}}$ each time a box α_q^- or $\alpha_q^{-\prime}$ is removed (i.e., a box from column two), or a pair of boxes with $\alpha_q=\alpha_{q+1}$ or $\alpha'_q=\alpha'_{q+1}$ is removed. This is also precisely the phase difference between our Eqs. (7) and (11), and Harter's assembly formula rules C, D, and E. Therefore, all formulas can be brought into correspondence if the above phase change is made, although there is no advantage in doing so. In particular, our Eq. (21) with the phase change is identical to Harter and Patterson's "jawbone" formulas (a)–(h) (their Fig. 3). This constitutes a proof of the rules stated in Refs. 1 and 2. However, our phases as they stand are the commonly used ones in atomic physics as defined by the Clebsch-Gordan coefficients.

In summary, to evaluate the matrix element of an arbitrary one-body elementary operator, $E(\alpha'_j,\alpha_i)$, one simply makes a list of the residual spins S_i and S'_i as the boxes are removed in sequential order, and then substitutes the lists into Eq. (18). These results, which are essentially equivalent to those of Gouyet, Schranner and

Seligman,[12] are used in the following sections to discuss two-body operators and their relation to spin-dependent operators.

IV. EVALUATION OF TWO-BODY OPERATORS

Products of one-body operators such as $E(\alpha'_q, \alpha_p)E(\alpha'_r, \alpha_t)$ occur in the evaluation of two-body operators such as $1/r_{12}$. The matrix elements can be evaluated by multiplication of the matrix representatives of the one-body operators, but for calculations involving truncated basis sets, it is essential to have a direct closed-form expression. It is convenient to distinguish between unlinked products, for which the intervals $[q,p]$ and $[r,t]$ do not overlap, and linked products for which the intervals do overlap. Unlinked products are simply evaluated by applying separately to each interval the formulas of Sec. III for one-body operators. For linked products, we consider explicitly only the case of a lowering operator with a raising operator. The results for two lowering operators or two raising operators are slightly different in form, but can be obtained by the same techniques.

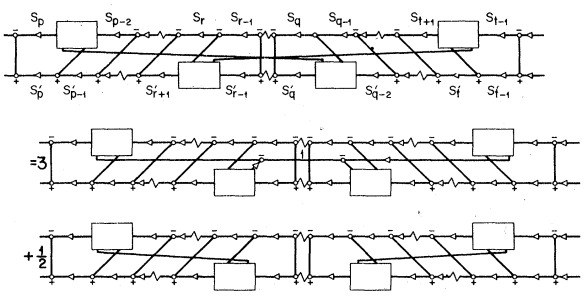


FIG. 3. Graphical transformation of a two-body operator matrix element into a sum of reducible parts [Eq. (24)].

As a concrete example, assume that $p>r>q>t$. A straightforward extension of the results of Sec. III yields for the matrix element

$$\langle(\alpha');S_0M_0|E(\alpha'_q,\alpha_p)E(\alpha'_r,\alpha_t)|(\alpha);S_0M_0\rangle=(-1)^{p+q+r+t+1}\prod_{i=0;\ \text{no pairs}}^{N}[(2S_i+1)(2S'_i+1)]^{1/2}\times G^{(2)}\ , \tag{24}$$

where $G^{(2)}$ is the graph drawn in Fig. 3 and obvious products of Kronecker δ's have been omitted. Although the central part of $G^{(2)}$ is irreducible, it can be expressed as the sum of two reducible parts as shown in Fig. 3 by application of rule (7.11) of Brink and Satchler to the two cross-linking lines. The second part is clearly proportional to an unlinked product of a lowering operator and a raising operator. The matrix element can therefore be written in the form

$$\langle(\alpha');S_0M_0|E(\alpha'_q,\alpha_p)E(\alpha'_r,\alpha_t)|(\alpha);S_0M_0\rangle=3X^{q,p}_{r,t}-\tfrac{1}{2}\langle(\alpha');S_0M_0|E(\alpha'_r,\alpha_p)E(\alpha_q',\alpha_t)|(\alpha);S_0M_0\rangle\ , \tag{25}$$

where $X^{q,p}_{r,t}$ contains the middle graph in Fig. 3. For any combination of a raising operator and a lowering operator, $X^{q,p}_{r,t}$ is always reducible, and one of the two operator products is unlinked. The second term on the right-hand side of Eq. (25) is multiplied by -1 because the number of interchanges required to bring the α's into alignment for an unlinked product (see Fig. 1) is always one less than the number for the corresponding linked product. The decomposition of the graph for $X^{q,r}_{r,t}$ into 6-j symbols yields

$$X^{q,p}_{r,t}=(-1)^{p+q+r+t}A_tB'_p\prod_{\substack{i=t+1\\ \text{no pairs}}}^{q-2}T(i)\prod_{\substack{i=r+1\\ \text{no pairs}}}^{p-2}T'(i)X_{\text{core}}\ , \tag{26}$$

$$X_{\text{core}}=(-1)^{S'_{r-1}-S_{r-1}}\tilde{A}'_r\tilde{B}_q[(2S_{r-1}+1)(2S'_q+1)]^{1/2}\prod_{\substack{i=q\\ \text{no pairs}}}^{r-2}M(i)\ , \tag{27}$$

where

$$M(i)=(-1)^{S_i+S'_{i+1}-1/2}[(2S_i+1)(2S'_{i+1}+1)]^{1/2}\begin{Bmatrix}1 & S'_i & S_i\\ \frac{1}{2} & S_{i+1} & S'_{i+1}\end{Bmatrix}\ , \tag{28}$$

$$\tilde{A}_r=\begin{cases}T(r)(-1)^{S_r+S'_{r-1}-1/2}\begin{Bmatrix}S'_{r-1} & S_{r-1} & 1\\ \frac{1}{2} & \frac{1}{2} & S_r\end{Bmatrix}, & (\alpha_r\neq\alpha_{r+1})\\ \left(\dfrac{2S'_r+1}{2S_{r-1}+1}\right)^{1/2}(-1)^{S_{r-1}+S'_{r-1}}\begin{Bmatrix}S'_{r-1} & S_{r-1} & 1\\ \frac{1}{2} & \frac{1}{2} & S'_r\end{Bmatrix}, & (\alpha_r=\alpha_{r+1})\end{cases} \tag{29}$$

$$\tilde{B}_q=\begin{cases} T(q-1)(-1)^{S_q+S'_{q-1}-1/2}\begin{Bmatrix} S'_q & S_q & 1 \\ \frac{1}{2} & \frac{1}{2} & S'_{q-1}\end{Bmatrix}, & (\alpha'_q\neq\alpha'_{q-1}) \\ \left(\frac{2S_{q-1}+1}{2S'_q+1}\right)^{1/2}(-1)^{S_q+S'_q}\begin{Bmatrix} S'_q & S_q & 1 \\ \frac{1}{2} & \frac{1}{2} & S_{q-1}\end{Bmatrix}, & (\alpha'_q=\alpha'_{q-1})\end{cases} \tag{30}$$

$T(i)$, A_t, and B'_p are defined in Eq. (18) and $\tilde{A}'_r$ is obtained from $\tilde{A}_r$ above by priming the unprimed S's and α's, and unpriming the primed S's. $T'(i)$ is similarly obtained from $T(i)$. X_{core} comes from the part of Fig. 3 between and including the two middle blocks, and the other factors in Eq. (26) (aside from the overall phase factor) come from the wings.

The other distinct case, again assuming that $p>r>q>t$, is

$$\langle(\alpha');S_0M_0|E(\alpha'_q,\alpha_r)E(\alpha'_p,\alpha_t)|(\alpha);S_0M_0\rangle=3X^{q,r}_{p,t}-\tfrac{1}{2}\langle(\alpha');S_0M_0|E(\alpha'_p,\alpha_r)E(\alpha'_q,\alpha_t)|(\alpha);S_0M_0\rangle \tag{31}$$

In this example, the range of the raising operator $E(\alpha'_q,\alpha_r)$ lies entirely inside the range of the lowering operator $E(\alpha'_p,\alpha_t)$ so that, unlike the previous example, the term on the right is an unlinked product of two *lowering* operators. The graphs are a minor variation on Fig. 3, which decompose in a similar way to yield

$$X^{q,r}_{p,t}=(-1)^{p+q+r+t}A_tB_p\prod_{\substack{i=t+1\\ \text{no pairs}}}^{q-2}T(i)\prod_{\substack{i=r+1\\ \text{no pairs}}}^{p-2}T(i)X_{\text{core}}\,, \tag{32}$$

$$X_{\text{core}}=\tilde{A}_r\tilde{B}_q[(2S_{r-1}+1)(2S'_q+1)]^{1/2}\prod_{\substack{i=q\\ \text{no pairs}}}^{r-2}M(i)\,. \tag{33}$$

The other two possible combinations of a lowering and a raising operator are $E(\alpha'_p,\alpha_q)E(\alpha'_t,\alpha_r)$, which is obtainable from the Hermitian conjugate of Eq. (25), and $E(\alpha'_r,\alpha_p)E(\alpha'_q,\alpha_t)$, which is obtainable from the Hermitian conjugate of Eq. (31).

The quantity $X^{a,b}_{c,d}$ above has a deeper significance in terms of spin-dependent operators as shown in the following section. The matrix elements of the complete electron-electron interaction are discussed in the Appendix.

V. EVALUATION OF SPIN-DEPENDENT OPERATORS

In discussing spin-dependent operators, it is convenient to introduce a unit double tensor operator $\Sigma_\gamma(\alpha'_q,\alpha_p)$ which behaves like $E(\alpha'_q,\alpha_p)$ when acting on orbital labels and like the one-electron unit spin operator $s_\gamma/\langle\frac{1}{2}\|s\|\frac{1}{2}\rangle=s_\gamma\sqrt{\frac{2}{3}}$ $(\gamma=\pm1,0)$ when acting on spin labels. The one-electron matrix elements are thus

$$\langle\alpha'_im'_i|\Sigma_\gamma(\alpha'_q,\alpha_p)|\alpha_jm_j\rangle=\delta(\alpha'_i,\alpha'_q)\delta(\alpha_p,\alpha_j)(-1)^{1/2-m'_i}\times\begin{pmatrix}\frac{1}{2} & 1 & \frac{1}{2}\\ -m'_i & \gamma & m_j\end{pmatrix}. \tag{34}$$

As a first example, we show that the quantity $X^{a,b}_{c,d}$ of the previous section can be written in terms of spin-dependent operators. Consider the scalar product

$$\vec{\Sigma}(\alpha'_r,\alpha_p)\cdot\vec{\Sigma}(\alpha'_q,\alpha_t)=-\sum_{\gamma,\delta,m,m'}\begin{pmatrix}\frac{1}{2} & 1 & \frac{1}{2}\\ m' & \gamma & m_p\end{pmatrix}\begin{pmatrix}\frac{1}{2} & 1 & \frac{1}{2}\\ m & \delta & m_t\end{pmatrix}\begin{pmatrix}\frac{1}{2} & \\ m' & m'_r\end{pmatrix}\times\begin{pmatrix}\frac{1}{2} & \\ m & m'_q\end{pmatrix}\begin{pmatrix}1 & \\ \gamma & \delta\end{pmatrix}E(\alpha'_r,\alpha_p)E(\alpha'_q,\alpha_t)\,. \tag{35}$$

The angular momentum coupling graph for the matrix element of Eq. (35) is identical to that for $X^{q,p}_{r,t}$ (the middle graph in Fig. 3). It follows that

$$X^{q,p}_{r,t}=-\langle(\alpha');S_0M_0|\vec{\Sigma}(\alpha'_r,\alpha_p)\cdot\vec{\Sigma}(\alpha'_q,\alpha_t)|(\alpha);S_0M_0\rangle \tag{36}$$

and similarly for $X^{q,r}_{p,t}$ in Eq. (31).

Substituting Eq. (36) into Eq. (25) yields the interesting operator identity

$$\vec{\Sigma}(\alpha'_r,\alpha_p)\cdot\vec{\Sigma}(\alpha'_q,\alpha_t)=-\tfrac{1}{3}[\tfrac{1}{2}E(\alpha'_r,\alpha_p)E(\alpha'_q,\alpha_t)+E(\alpha'_q,\alpha_p)E(\alpha'_r,\alpha_t)] \tag{37}$$

valid for any combination of raising and lowering operators. Thus the scalar product of spin-dependent operators can always be calculated in terms of two-body orbital operators alone.

A word of clarification is necessary concerning the use of Eq. (37) for pure spin-spin type operators such as

$$O_{ss}=\sum_{i>j}^{N}\vec{s}_i\cdot\vec{s}_j\,.$$

The one-electron orbital labels α_i for paired states should be taken as distinct, even though they label the same orbital. Then

$$O_{ss}=\frac{3}{2}\sum_{i>j}^{N}\vec{\Sigma}(\alpha'_j,\alpha_j)\cdot\vec{\Sigma}(\alpha'_i,\alpha_i)\,, \tag{38}$$

and the results from Eq. (37) for the simplest

case of two-electron states are

$$\left\langle \boxed{\alpha_1'}\boxed{\alpha_2'} \,\middle|\, O_{ss} \,\middle|\, \boxed{\alpha_1}\boxed{\alpha_2} \right\rangle = -\tfrac{3}{4} \tag{39}$$

and

$$\left\langle \begin{matrix}\boxed{\alpha_1'}\\ \boxed{\alpha_2'}\end{matrix} \,\middle|\, O_{ss} \,\middle|\, \begin{matrix}\boxed{\alpha_1}\\ \boxed{\alpha_2}\end{matrix} \right\rangle = \tfrac{1}{4} \tag{40}$$

The same results of course also follow from the relation

$$O_{ss} = \frac{1}{2}\left(S^2 - \sum_{i=1}^{N} s_i^2\right). \tag{41}$$

with $N=2$, $s_1^2 = s_2^2 = \frac{3}{4}$ and $S^2 = 0, 2$. For the general case of N-particle tableaux, each two-box row contributes $-\frac{3}{4}$ and each of the $2S(2S-1)/2$ combinations of two unpaired column boxes contributes $\frac{1}{4}$ for a total which agrees with the result obtained from Eq. (41). All other contributions to Eq. (38) vanish. The purpose of the foregoing example is to emphasize that spin-dependent operators can be obtained from orbital operators alone.

As a second example, the spin-orbit operator

$$\sum_i \vec{l}_i \cdot \vec{s}_i = \sum_{i,\gamma} (-1)^{\gamma} l_{i,\gamma} s_{i,-\gamma}$$

can be written in terms of $\Sigma_\gamma(\alpha_\tau', \alpha_\rho)$. In general, the tableaux can differ in shape by the displacement of one box (i.e., $S_0' = S_0 \pm 1$), and only a single value of γ can give a nonvanishing matrix element for a given pair of tableaux. The general matrix element factors according to

$$\langle (\alpha');\ S_0' M_0' \,|\, \Sigma_\gamma(\alpha_\tau', \alpha_\rho) \,|\, (\alpha);\ S_0 M_0 \rangle = (-1)^{S_0' - M_0'} \begin{pmatrix} S_0' & 1 & S_0 \\ -M_0' & \gamma & M_0 \end{pmatrix} \times \langle (\alpha');\ S_0' \,\|\Sigma(\alpha_\tau', \alpha_\rho)\|\, (\alpha);\ S_0 \rangle \tag{42}$$

so that only the reduced matrix element need be evaluated. It is given by

$$\langle (\alpha');\ S_0' \,\|\Sigma(\alpha_\tau', \alpha_\rho)\|\, (\alpha);\ S_0 \rangle = (-1)^{\rho+\tau} \prod_{\substack{i=0 \\ \text{no pairs}}}^{N} [(2S_i+1)(2S_i'+1)]^{1/2} \times G(\vec{l} \cdot \vec{s}), \tag{43}$$

where $G(\vec{l} \cdot \vec{s})$ is the graph shown in Fig. 4. The graph can be brought into coincidence with the middle graph in Fig. 3 by multiplying and dividing by one more 6-j symbol as shown. This corresponds to enlarging both tableaux in the matrix element by one more box, labeled α_0 and α_0', respectively, in such a way that the shapes are brought into agreement if they differ, i.e., $S_{-1} = (S_0 + S_0')/2 = S_{-1}'$ if $S_0' = S_0 \pm 1$. Using Eq. (25), the result can be summarized by the general operator equation

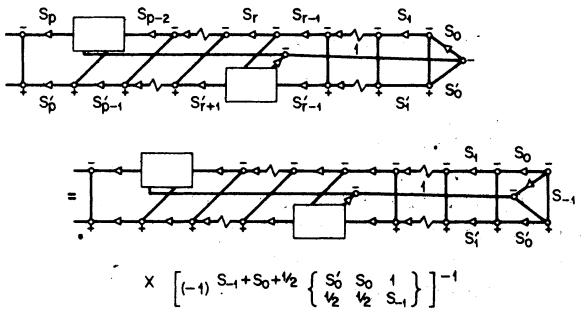


FIG. 4. Graphical transformation of a spin-orbit matrix element into an equivalent two-body spin-independent matrix element.

$$\|\Sigma(\alpha_\tau', \alpha_\rho)\|_N = \frac{(-1)^{S_{-1}+S_0-1/2}}{3} \begin{Bmatrix} S_0' & S_0 & 1 \\ \frac{1}{2} & \frac{1}{2} & S_{-1} \end{Bmatrix}^{-1} \times [E(\alpha_0', \alpha_\rho)E(\alpha_\tau', \alpha_0) + \tfrac{1}{2}E(\alpha_\tau', \alpha_\rho)]_{N+1}, \tag{44}$$

where the subscripts N and $N+1$ mean that the matrix element is to be evaluated in the N and $N+1$ electron systems, respectively. It follows that the computer algorithms developed for example by Paldus[7] for two-body orbital operators can be used directly for the evaluation of spin-orbit matrix elements. All of these results can be re-expressed in the Gelfand-Zetlin phase convention by application of the phase change described at the end of Sec. 3.

V. DISCUSSION

Perhaps the most significant aspect of this paper is the development of formulas relating spin-dependent operators to purely orbital operators, thereby largely removing a long-standing difficulty with the tableau formalism. Spin-orbit type matrix elements are completely expressible in terms of Eq. (44). However, further development along the lines of Eq. (37) is still necessary before the spin-spin interaction can be handled without resorting to the inefficient technique of first breaking down the tableaux into linear combinations of Slater determinants.[2] This problem, which is not insurmountable, will be discussed in a future publication. The operator relationships we have found undoubtedly have a deeper group-theoretical significance which has yet to be explored.

From a computational point of view, the direct formulas for the one- and two-body operators may be less efficient than the recursion relations used by Paldus.[7] The latter allow the simultaneous evaluation of all the nonvanishing matrix elements in a given row of the matrix representative of a one-body operator. However, in calculations involving large basis sets, the direct for-

mulas for two-body operators, together with the results in the Appendix, avoid the multiplication of large matrices. This approach is essential in calculations involving truncated basis sets. From a formal point of view, the direct formulas appear to be necessary to establish the connection between orbital and spin-dependent operators. However, a more abstract derivation of equations such as Eq. (44) may be possible since the purely orbital tableaux already contain all the spin information necessary to evaluate the reduced matrix elements of spin-dependent operators.

APPENDIX: MATRIX ELEMENTS OF THE ELECTRON-ELECTRON INTERACTION

We consider in this Appendix the diagonal and off-diagonal matrix elements of the electron-electron interaction in a tableau basis set. The results are a generalization of the rules given by Slater[17] for the same matrix elements with respect to ordinary Slater determinants.

Consider a two-body operator

$$O_2 = \sum_{j>i} g_{ij}, \tag{A1}$$

such as $g_{ij} = 1/r_{ij}$. The diagonal matrix element can be written as the sum of a direct part and an exchange part. Since the tableau states are orthonormal linear combinations of Slater determinants with the same orbital labels, but different spin labels [see Eq. (9)], the direct part is the same as for a single Slater determinant matrix element. The angular momentum coupling graph for the exchange part is similar to Fig. 3 with the upper boxes shifted horizontally to lie directly above the lower boxes. The final result is

$$\langle(\alpha); S_0 M_0 | O_2 | (\alpha); S_0 M_0\rangle = \Delta_0^N \sum_{j>i}^{N} \langle\alpha_i\alpha_j | g | \alpha_i\alpha_j\rangle - \sum_{j>i;\,\alpha_i\neq\alpha_j}{}' C_{ij}\langle\alpha_i\alpha_j | g | \alpha_j\alpha_i\rangle, \tag{A2}$$

where

$$C_{i,j} = \begin{cases} \Delta_0^N, & \alpha_i \text{ or } \alpha_j \text{ repeated} \\ \tfrac{1}{2}\Delta_0^N - 3\Delta_0^{i-1}\Delta_j^N A_e B_e \prod_{k=i;\,\text{no pairs}}^{j-2} M(k), & \\ \text{otherwise} & \end{cases}$$

$$\Delta_a^b = \prod_{k=a}^{b} \delta(S_k, S_k')$$

$$A_e = (2S_{j-1}+1)^{1/2}(-1)^{S'_{j-1}+S_j-1/2} \begin{Bmatrix} S'_{j-1} & S_{j-1} & 1 \\ \frac{1}{2} & \frac{1}{2} & S_j \end{Bmatrix}$$

$$B_e = (2S'_i+1)^{1/2}(-1)^{S_i+S'_{i-1}-1/2} \begin{Bmatrix} S'_i & S_i & 1 \\ \frac{1}{2} & \frac{1}{2} & S_{i-1} \end{Bmatrix}$$

and the prime on the second summation in (A2) means that repeated labels are to be counted only once. $M(k)$ is defined by Eq. (28). The product over $M(k)$ is to be omitted for terms with $j = i+1$. Equation (A2) also applies to those off-diagonal elements where the tableaux differ only by a rearrangement of the labels in the boxes.

The off-diagonal matrix element for tableaux which differ by two labels $(\alpha_p, \alpha_t) \to (\alpha'_r, \alpha'_q)$ with $\alpha_p \neq \alpha_t$ and $\alpha'_r \neq \alpha'_q$ is

$$\langle(\alpha'); S_0 M_0 | O_2 | (\alpha); S_0 M_0\rangle = \langle(\alpha'); S_0 M_0 | E(\alpha'_r, \alpha_p)E(\alpha'_q, \alpha_t) | (\alpha); S_0 M_0\rangle \langle\alpha'_r\alpha'_q | g | \alpha_p\alpha_t\rangle + \langle(\alpha'); S_0 M_0 | E(\alpha'_q, \alpha_p)E(\alpha'_r, \alpha_t) | (\alpha); S_0 M_0\rangle \langle\alpha'_q\alpha'_r | g | \alpha_p\alpha_t\rangle \tag{A3}$$

where

$$\langle\alpha'_r\alpha'_q | g | \alpha_p\alpha_t\rangle = \int \alpha'^*_r(1)\alpha'^*_q(2) g_{12} \alpha_p(1)\alpha_t(2) d\vec{r}_1 d\vec{r}_2$$

and the matrix elements of the products of E operators are calculated as described in Sec. IV. For the special case $\alpha'_r = \alpha'_q$, only one of the two identical terms in (A3) is to be counted. If we arbitrarily choose $r = q+1$, then it can be shown by separating the angular momentum coupling graph at the lines S_q and $S'_{q\pm1}$ that for $p > q \geq t$ and $\alpha'_{q+1} = \alpha'_q$,

$$E(\alpha'_{q+1}, \alpha_p)E(\alpha'_q, \alpha_t) = (-1)^{S'_{q-1}-S_q+1/2}\left(\frac{2S_q+1}{2S'_{q-1}+1}\right)^{1/2} \times [E(\alpha'_{q+1}, \alpha_p)E(\alpha'_q, \alpha_t)]_{\text{unlinked}}, \tag{A4}$$

where the unlinked product is to be evaluated as if $\alpha'_{q+1} \neq \alpha'_q$ and $S'_q = S_q$, i.e., by applying twice the one-body operator equations in Sec. III.

Using the above formulas, one can immediately write down the examples

$$\langle {}^1_2\,{}^2 | O_2 | {}^1_2\,{}^2\rangle = \langle 22 | g | 22\rangle + 2\langle 12 | g | 12\rangle - \langle 12 | g | 21\rangle,$$
$$\langle {}^1_3\,{}^1 | O_2 | {}^1_3\,{}^1\rangle = \langle 11 | g | 11\rangle + 2\langle 13 | g | 13\rangle - \langle 13 | g | 31\rangle,$$
$$\langle {}^1_2\,{}^2 | O_2 | {}^1_3\,{}^1\rangle = -\langle 22 | g | 13\rangle. \tag{A5}$$

These are the same results as obtained by Harter and Patterson [Ref. 2, Eq. (25)] when their spurious self-interaction contribution is subtracted. (The sign in the last case is different due to the different phase convention.) The self-interaction is automatically excluded in our approach, and it is not necessary to generate the complete matrix of all possible one-body operators.

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