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An efficient approach for spin–angular integrations in atomic structure calculations

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Abstract. A general method is described for finding algebraic expressions for matrix elements of any one- and two-particle operator for an arbitrary number of subshells in an atomic configuration, requiring neither coefficients of fractional parentage nor unit tensors. It is based on the combination of second quantization in the coupled tensorial form, angular momentum theory in three spaces (orbital, spin and quasispin), and a generalized graphical technique. The latter allows us to graphically calculate the irreducible tensorial products of the second-quantization operators and their commutators, and to formulate additional rules for operations with diagrams. The additional rules allow us to graphically find the normal form of the complicated tensorial products of the operators. All matrix elements (diagonal and non-diagonal with respect to configurations) differ only by the values of the projections of the quasispin momenta of separate shells and are expressed in terms of completely reduced matrix elements (in all three spaces) of the second-quantization operators. As a result, it allows us to use standard quantities uniformly for both diagonal and off-diagonal matrix elements.

1. Introduction

In order to obtain accurate values of atomic quantities it is necessary to account for relativistic and correlation effects. Relativistic effects may be taken into account as Breit–Pauli corrections or, in a fully relativistic approach, by starting with the Dirac–Coulomb Hamiltonian and wavefunctions defined in terms of four-component one-electron orbitals. In both cases, correlation effects may be considered either variationally or perturbatively. For complex atoms and ions, a considerable part of the effort must be devoted to coping with integrations over spin–angular variables, occurring in the matrix elements of the operators under consideration.

Many existing codes for integrating the spin–angular parts of matrix elements (Glass 1978, Glass and Hibbert 1978, Grant 1988, Burke *et al* 1994) are based on the computational scheme proposed by Fano (1965). In essence, it consists of evaluating recoupling matrices. Although such an approach uses Racah algebra, it may be necessary to carry out multiple summations over intermediate terms. Due to these summations and the complexity of the recoupling matrix itself, the associated computer codes become rather time consuming. A solution to this problem was found by Burke *et al* (1994). They tabulated separate standard parts of recoupling matrices along with coefficients of fractional parentage at the beginning of a calculation and then used them later to calculate the coefficients needed. Computer codes by Glass (1978), Glass and Hibbert (1978), Grant (1988), Burke *et al* (1994) utilize

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the program NJSYM (Burke 1970) or NJGRAF (Bar-Shalom and Klapisch 1988) for the calculation of recoupling matrices. Both are rather time consuming when calculating matrix elements of complex operators or electronic configurations with many open subshells.

In order to simplify the calculations, Cowan (1981) suggested grouping matrix elements into 'classes' (see Cowan 1981, figures 13–15). Unfortunately, this approach was not generalized to all two-electron operators. Perhaps this is the reason why Cowan's approach is not widely used although the program itself, based on this approach is widely used.

Many approaches for the calculation of spin–angular coefficients (Glass 1978, Glass and Hibbert 1978, Grant 1988, Burke *et al* 1994) are based on the usage of Racah algebra only on the level of coefficients of fractional parentage. A few authors (Jucys and Savukynas 1973, Cowan 1981) utilized the unit tensors, simplifying the calculations in this way, because the tables of unit tensors and selection rules can be used to check whether the spin–angular coefficients are zero prior to computation. Moreover, the recoupling matrices themselves have a simpler form. Unfortunately, these ideas were applied only to diagonal matrix elements with respect to configurations, although Cowan (1981) suggested the usage of unit tensors for non-diagonal ones as well.

All the above-mentioned approaches were applied in the coordinate representation. The second-quantization formalism (Judd 1967, Rudzikas and Kaniauskas 1984, Rudzikas 1991 and Rudzikas 1997) has a number of advantages compared with the coordinate representation. First, it is much easier to find algebraic expressions for complex operators and their matrix elements, when relying on second-quantization formalism. It has contributed significantly to the successful development of perturbation theory (see Lindgren and Morrison 1982, Merkelis *et al* 1985), and orthogonal operators (Uylings 1984), where three-particle operators already occur. Uylings (1992) suggested a fairly simple approach for dealing with separate cases of three-particle operators. Moreover, in the second quantization approach the quasispin formalism was efficiently developed by Rudzikas and Kaniauskas (1984). The main advantage of this approach is that applying the quasispin method for calculating the matrix elements of any operator, we can use the reduced coefficients of fractional parentage whose matrix elements are independent of the occupation number of the shell. All this enabled Merkelis and Gaigalas (1985) to work out a general perturbation theory approach for complex cases of several open shells.

Thus, it seems that it is possible to formulate an efficient and general approach for finding the spin–angular parts of matrix elements of atomic interactions, relying on the combination of the second-quantization approach in the coupled tensorial form, the generalized graphical technique and angular momentum theory in orbital, spin and quasispin spaces as well as the symmetry properties of the quantities considered, which would be free of previous shortcomings. Gaigalas and Rudzikas (1996) suggested such an approach for finding matrix elements of any one- and two-particle atomic operator for the case of two open shells of equivalent electrons. But the situation is different when the matrix elements between more complex configurations are considered.

An approach for the latter case is described in this paper. One of the main ideas proposed here allows one to solve the problems related to the more complex configurations. Namely, we propose applying Wick's theorem (see Lindgren and Morrison 1982) not in its usual general form while calculating the matrix elements, but rather only for groups of operators acting upon distinct shells of equivalent electrons. So, the ordering of operators generally would not be normal.

It is a universal approach for finding algebraic expressions for matrix elements of any one- and two-particle operator in the general case of an arbitrary number of subshells in an atomic configuration, heavily based on the exploitation of the quasispin technique and the Wigner–Eckart theorem in quasispin space. Expressions for matrix elements and recoupling matrices are obtained by first classifying each matrix element into one of four classes, depending on the number of subshells being acted upon. Each class is then further subdivided into cases and explicit expressions derived for each case in terms of triangular conditions, nj-symbols, and reduced matrix elements. From these expressions, efficient procedures can be developed, that apply tests before performing computation.

Tensorial expressions for any two-particle operator are presented in section 2. They are based on the underlying assumption that the second quantization operators (both creation and annihilation), acting on the same open shell, must always be beside one another in a tensorial product and must be coupled into a resultant momentum. Then the second quantization operators, acting on the next shell, must follow, etc. Section 3 deals with the matrix elements between complex configurations. General expressions for recoupling matrices were found (section 4) by using the modified graphical technique of Jucys and Bandzaitis (1977), allowing us to graphically calculate the irreducible tensorial products of the second-quantization operators and their commutators, and to formulate additional rules for operations with diagrams. The additional rules allow us to graphically find the normal form of the complicated tensorial products of the operators. All the graphical transformations we use here are fully described in Gaigalas and Rudzikas (1996).

Exploitation of this new version of Racah algebra based on the angular momentum theory, on a generalized graphical approach, on quasispin approach, and on the use of reduced coefficients of fractional parentage for finding the spin–angular parts of two-particle operators is outlines in sections 5–7. Some details of the calculations are presented in the appendix.

2. Tensorial expressions for any two-particle operators

In order to be able to find the expressions for matrix elements of the operators studied, we have to express these operators in terms of the irreducible tensors or their irreducible products. In this section we will present all the necessary tensorial expressions for any two-particle operator G.

First, we express the operator in second-quantization form (Gaigalas and Rudzikas 1996) as

$$G = \sum_{n_il_i,n_jl_j,n_i'l_i',n_j'l_j'} \hat{G}(n_il_in_jl_jn_i'l_i'n_j'l_j') = \frac{1}{2}\sum_{i,j,i',j'} a_ia_ja_{j'}^{\dagger}a_{i'}^{\dagger}(i,j|g|i',j') \tag{1}$$

where, as is customary, the creation operators a_ia_j appear to the left of the annihilation operators $a_{j'}^{\dagger}a_{i'}^{\dagger}$ before defining the shells upon which the second-quantization operators are acting. After defining the shells explicitly, the second-quantization operators are transformed using their commutation relations so that all operators with the same $n\lambda(\lambda \equiv l, s)$ are beside one another. For example, in the case where the electron creation operator a_i, and electron annihilation operators $a_{i'}^{\dagger}$ (where $i \equiv n_il_ism_{l_i}m_{s_i}$) and $a_{j'}^{\dagger}$ act upon the same shell α, and operator a_j acts upon another shell β, we have:

$$\hat{G}(\alpha\beta\alpha\alpha) = \frac{1}{2}\sum_{m_{l_\alpha}m_{s_\alpha}m_{l_\beta}m_{s_\beta}m_{l_\alpha}'m_{s_\alpha}'m_{l_\alpha}''m_{s_\alpha}''} a_{m_{l_\alpha}m_{s_\alpha}}^{(l_\alpha s_\alpha)} a_{m_{l_\alpha}''m_{s_\alpha}''}^{\dagger(l_\alpha s_\alpha)} a_{m_{l_\alpha}'m_{s_\alpha}'}^{\dagger(l_\alpha s_\alpha)} a_{m_{l_\beta}m_{s_\beta}}^{(l_\beta s_\beta)} \times(n_\alpha\lambda_\alpha m_{l_\alpha}m_{s_\alpha}n_\beta\lambda_\beta m_{l_\beta}m_{s_\beta}|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}|n_\alpha\lambda_\alpha m_{l_\alpha}'m_{s_\alpha}'n_\alpha\lambda_\alpha m_{l_\alpha}''m_{s_\alpha}''). \tag{2}$$

Here we imply that a tensorial structure indexed by $(\kappa_1\kappa_2k, \sigma_1\sigma_2k)$ at g has rank κ_1 for electron 1, rank κ_2 for electron 2, and a resulting rank k in the l space, and corresponding ranks $\sigma_1\sigma_2k$ in the s space.

Now, applying the graphical approach of angular momentum theory (Gaigalas *et al* 1985), we can get an expression, namely

$$\hat{G}(\alpha\beta\alpha\alpha) = \frac{1}{2}\sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}}\sum_{p}(-1)^{\kappa_{12}+\sigma_{12}-\kappa'_{12}-\sigma'_{12}-k-p}(n_\alpha\lambda_\alpha n_\beta\lambda_\beta\|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\|n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha)$$
$$\times[\kappa_{12},\sigma_{12}][\kappa'_{12},\sigma'_{12}]^{1/2}\begin{Bmatrix} l_\alpha & l_\alpha & \kappa'_{12} \\ \kappa_1 & \kappa_2 & k \\ l_\alpha & l_\beta & \kappa_{12}\end{Bmatrix}\begin{Bmatrix} s & s & \sigma'_{12} \\ \sigma_1 & \sigma_2 & k \\ s & s & \sigma_{12}\end{Bmatrix}$$
$$\times\sum_{K_lK_s}[K_l,K_s]^{1/2}\begin{Bmatrix} l_\beta & l_\alpha & \kappa_{12} \\ \kappa'_{12} & k & K_l\end{Bmatrix}\begin{Bmatrix} s & s & \sigma_{12} \\ \sigma'_{12} & k & K_s\end{Bmatrix}$$
$$\times[a^{(l_\beta s)}\times[a^{(l_\alpha s)}\times[\tilde{a}^{(l_\alpha s)}\times\tilde{a}^{(l_\alpha s)}]^{(\kappa'_{12}\sigma'_{12})}]^{(K_lK_s)}]^{(kk)}_{p,-p} \qquad (3)$$

where $[a,b] = (2a+1)(2b+1)$, $(n_\alpha\lambda_\alpha n_\beta\lambda_\beta\|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\|n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha)$ is the two-electron submatrix (reduced matrix) element of operator $\hat{G}$ and $\tilde{a}^{(l_\alpha s)}$ is defined as (Judd 1967)

$$\tilde{a}^{(l_\alpha s)}_{m_{l_\alpha}m_s} = (-1)^{l_\alpha+s-m_{l_\alpha}-m_s}a^{\dagger(l_\alpha s)}_{-m_{l_\alpha}-m_s}. \qquad (4)$$

Expression (3) has summations over intermediate ranks κ'_{12}, σ'_{12}, K_l, K_s in tensorial product. The angular momentum projection of (kk) is $p, -p$.

In order to calculate the spin–angular part of a two-particle operator matrix element with an arbitrary number of open shells, it is necessary to consider all possible distributions of subshells, upon which the second-quantization operators are acting. These are presented in table 1. We point out that for distributions 2–5 and 19–42 the shells' sequence numbers α, β, γ, δ (in bra and ket functions of a submatrix element) satisfy the condition $\alpha < \beta < \gamma < \delta$, while for distributions 6–18 no conditions upon α, β, γ, δ are imposed.

Let Ξ be an array of intermediate coupling parameters in tensorial form, including κ_{12}, σ_{12}, κ'_{12}, σ'_{12} and also possibly others. Then the tensorial expressions for all these distributions can be grouped into four classes, where in each class, the two-particle operator $\hat{G}$, operating on specific shells (see equation (1)), has one of the following four forms.

(1) All the second-quantization operators act upon the same shell (distribution 1) and

$$\hat{G}(I) \sim \sum_{\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12}}\sum_{p}\Theta(n\lambda,\Xi)A^{(kk)}_{p,-p}(n\lambda,\Xi). \qquad (5)$$

(2) The second-quantization operators act upon the two different shells (distributions 2–10) and

$$\hat{G}(II) \sim \sum_{\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12}}\sum_{p}\Theta(n_\alpha\lambda_\alpha,n_\beta\lambda_\beta,\Xi)[B^{(\kappa_{12}\sigma_{12})}(n_\alpha\lambda_\alpha,\Xi)\times C^{(\kappa'_{12}\sigma'_{12})}(n_\beta\lambda_\beta,\Xi)]^{(kk)}_{p,-p}. \qquad (6)$$

(3) The second-quantization operators act upon three shells (distributions 11–18)

$$\hat{G}(III) \sim \sum_{\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12}}\sum_{p}\Theta(n_\alpha\lambda_\alpha,n_\beta\lambda_\beta,n_\gamma\lambda_\gamma,\Xi)$$
$$\times[[D^{(l_\alpha s)}\times D^{(l_\beta s)}]^{(\kappa_{12}\sigma_{12})}\times E^{(\kappa'_{12}\sigma'_{12})}(n_\gamma\lambda_\gamma,\Xi)]^{(kk)}_{p,-p}. \qquad (7)$$

(4) The second-quantization operators act upon four shells (distributions 19–42) and

$$\hat{G}(IV) \sim \sum_{\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12}}\sum_{p}\Theta(n_\alpha\lambda_\alpha,n_\beta\lambda_\beta,n_\gamma\lambda_\gamma,n_\delta\lambda_\delta,\Xi)$$
$$\times[[D^{(l_\alpha s)}\times D^{(l_\beta s)}]^{(\kappa_{12}\sigma_{12})}\times[D^{(l_\gamma s)}\times D^{(l_\delta s)}]^{(\kappa'_{12}\sigma'_{12})}]^{(kk)}_{p,-p}. \qquad (8)$$

Table 1. Distributions of subshells, upon which the second-quantization operators are acting, that appear in the submatrix elements of any two-particle operator, when bra and ket functions have u open subshells.

No	a_i	a_j	$a_{i'}^{\dagger}$	$a_{j'}^{\dagger}$	Submatrix element
1	α	α	α	α	$(\ldots n_\alpha l_\alpha^{N_\alpha} \ldots \Vert \hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j') \Vert \ldots n_\alpha l_\alpha^{N_\alpha} \ldots)$
2	α	β	α	β	
3	β	α	β	α	$(\ldots n_\alpha l_\alpha^{N_\alpha} \ldots n_\beta l_\beta^{N_\beta} \ldots \Vert$
4	α	β	β	α	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
5	β	α	α	β	$\Vert \ldots n_\alpha l_\alpha^{N_\alpha} \ldots n_\beta l_\beta^{N_\beta} \ldots)$
6	α	α	β	β	$(\ldots n_\alpha l_\alpha^{N_\alpha} \ldots n_\beta l_\beta^{N_\beta} \ldots \Vert \hat{G} \Vert \ldots n_\alpha l_\alpha^{N_\alpha-2} \ldots n_\beta l_\beta^{N_\beta+2} \ldots)$
7	β	α	α	α	
8	α	β	α	α	$(\ldots n_\alpha l_\alpha^{N_\alpha} \ldots n_\beta l_\beta^{N_\beta} \ldots \Vert$
9	β	β	β	α	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
10	β	β	α	β	$\Vert \ldots n_\alpha l_\alpha^{N_\alpha+1} \ldots n_\beta l_\beta^{N_\beta-1} \ldots)$
11	β	γ	α	γ	
12	γ	β	γ	α	$(\ldots n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} \ldots \Vert$
13	γ	β	α	γ	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
14	β	γ	γ	α	$\Vert \ldots n_\alpha l_\alpha^{N_\alpha+1} n_\beta l_\beta^{N_\beta-1} n_\gamma l_\gamma^{N_\gamma} \ldots)$
15	γ	γ	α	β	$(\ldots n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} \ldots \Vert \hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
16	γ	γ	β	α	$\Vert \ldots n_\alpha l_\alpha^{N_\alpha+1} n_\beta l_\beta^{N_\beta+1} n_\gamma l_\gamma^{N_\gamma-2} \ldots)$
17	α	β	γ	γ	$(\ldots n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} \ldots \Vert \hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
18	β	α	γ	γ	$\Vert \ldots n_\alpha l_\alpha^{N_\alpha-1} n_\beta l_\beta^{N_\beta-1} n_\gamma l_\gamma^{N_\gamma-2} \ldots)$
19	α	β	γ	δ	
20	β	α	γ	δ	$(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \Vert$
21	α	β	δ	γ	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
22	β	α	δ	γ	$\Vert n_\alpha l_\alpha^{N_\alpha-1} n_\beta l_\beta^{N_\beta-1} n_\gamma l_\gamma^{N_\gamma+1} n_\delta l_\delta^{N_\delta+1})$
23	γ	δ	α	β	
24	γ	δ	β	α	$(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \Vert$
25	δ	γ	α	β	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
26	δ	γ	β	α	$\Vert n_\alpha l_\alpha^{N_\alpha+1} n_\beta l_\beta^{N_\beta+1} n_\gamma l_\gamma^{N_\gamma-1} n_\delta l_\delta^{N_\delta-1})$
27	α	γ	β	δ	
28	α	γ	δ	β	$(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \Vert$
29	γ	α	δ	β	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
30	γ	α	β	δ	$\Vert n_\alpha l_\alpha^{N_\alpha-1} n_\beta l_\beta^{N_\beta+1} n_\gamma l_\gamma^{N_\gamma-1} n_\delta l_\delta^{N_\delta+1})$
31	β	δ	α	γ	
32	δ	β	γ	α	$(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \Vert$
33	β	δ	γ	α	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
34	δ	β	α	γ	$\Vert n_\alpha l_\alpha^{N_\alpha+1} n_\beta l_\beta^{N_\beta-1} n_\gamma l_\gamma^{N_\gamma+1} n_\delta l_\delta^{N_\delta-1})$

Table 1. (Continued)

No	a_i	a_j	$a_{i'}^{\dagger}$	$a_{j'}^{\dagger}$	Submatrix element
35	α	δ	β	γ	
36	δ	α	γ	β	$(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \|$
37	α	δ	γ	β	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
38	δ	α	β	γ	$\| n_\alpha l_\alpha^{N_\alpha - 1} n_\beta l_\beta^{N_\beta + 1} n_\gamma l_\gamma^{N_\gamma + 1} n_\delta l_\delta^{N_\delta - 1})$
39	β	γ	α	δ	
40	γ	β	δ	α	$(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \|$
41	β	γ	δ	α	$\hat{G}(n_i l_i n_j l_j n_i' l_i' n_j' l_j')$
42	γ	β	α	δ	$\| n_\alpha l_\alpha^{N_\alpha + 1} n_\beta l_\beta^{N_\beta - 1} n_\gamma l_\gamma^{N_\gamma - 1} n_\delta l_\delta^{N_\delta + 1})$

In (5)–(8), $\Theta(n\lambda, \Xi), \ldots, \Theta(n_\alpha\lambda_\alpha, n_\beta\lambda_\beta, n_\gamma\lambda_\gamma, n_\delta\lambda_\delta\Xi)$ are proportional to the radial part of the operator $\hat{G}$, and $A^{(kk)}(n\lambda, \Xi), \ldots, E^{(kk')}(n\lambda, \Xi)$ denote tensorial products of irreducible tensors. Parameter Ξ implies the array of coupling parameters that connect Θ to the tensorial part. The explicit tensorial expressions are presented in the appendix, using the graphical approach of Gaigalas *et al* (1985). Graphical methods make it possible to reduce the number of expressions from 42 to 6 for all distributions presented in table 1. Such a joining up of several distributions is possible by graphical means, because in the graphical technique of Jucys and Bandzaitis (1977), as in the tensorial products of operators of second quantization, the main elements are the Clebsch–Gordan coefficients. Therefore we may join up all the distributions having essentially the same algebraic structure, although with different tensorial products. The latter are represented by diagrams in which all the peculiarities of a tensorial product are seen, and the differences of particular distributions are easily noticed. The use of other graphical methods (see e.g. Yutsis *et al* 1962 or Lindgren and Morrison 1982) in joining up the distributions is complicated, since there the Wigner coefficients play the main role, and these are not fully compatible with the graphical transformations of the operators of second quantization in coupled form. Having classified the operators, we will now consider matrix elements of these operators for arbitrary configurations.

3. Matrix elements between complex configurations

Now, having the irreducible tensorial form of the operator being considered, we are in a position to find their matrix elements and recoupling matrices. Suppose that we have a bra function with u shells in LS-coupling:

$$\begin{aligned}\psi_u^{\mathrm{bra}}(LSM_LM_S) \equiv (&n_1l_1n_2l_2\ldots n_ul_u\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}\\ &\ldots\alpha_uL_uS_uQ_uM_{Q_u}\mathcal{A}LSM_LM_S|\end{aligned} \tag{9}$$

and a ket function:

$$\begin{aligned}\psi_u^{\mathrm{ket}}(L'S'M_L'M_S') \equiv |&n_1l_1n_2l_2\ldots n_ul_u\alpha_1'L_1'S_1'Q_1'M_{Q_1}'\alpha_2'L_2'S_2'Q_2'M_{Q_2}'\\ &\ldots\alpha_u'L_u'S_u'Q_u'M_{Q_u}'\mathcal{A}'L'S'M_L'M_S')\end{aligned} \tag{10}$$

where $\mathcal{A}$ stands for all intermediate quantum numbers, depending on the order of coupling of momenta L_iS_i. Label Q_i is the quasispin momentum of the shell $n_il_i^{N_i}$, which is related to the seniority quantum number ν_i, namely, $Q_i = (2l_i + 1 - \nu_i)/2$, and its projection,

$M_{Q_i} = (N_i - 2l_i - 1)/2$. In (9) and (10), α_i denotes all additional quantum numbers needed for the classification of the energy levels of the relevant shell.

Using the Wigner–Eckart theorem in LS space we shift from the matrix element of any two-particle operator G between functions (9) and (10) to the submatrix element $(\psi_u^{\rm bra}(LS)\|G\|\psi_u^{\rm ket}(L'S'))$ of this operator.

A general expression for the submatrix element of any two-particle operator between functions (9) and (10) with u open shells can be written as

$$(\psi_u^{\rm bra}(LS)\|G\|\psi_u^{\rm ket}(L'S')) = \sum_{n_il_i,n_jl_j,n_i'l_i',n_j'l_j'} \sum_{\kappa_{12},\sigma_{12},\kappa_{12}',\sigma_{12}'} \sum (-1)^{\Delta}\Theta'(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Xi)$$
$$\times T(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Xi, \Gamma) \times R(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Gamma) \tag{11}$$

where $\Lambda^{\rm bra} \equiv (L_iS_i, L_jS_j, L_i'S_i', L_j'S_j')^{\rm bra}$ is the array for the bra function shells' terms, and similarly for $\Lambda^{\rm ket}$. This expression is similar to equation (136) of Grant (1988) used in his derivation. So, to calculate the spin–angular part of a submatrix element, one has to compute the following.

(1) The recoupling matrix $R(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Gamma)$. This recoupling matrix accounts for the change in going from matrix element $(\psi_u^{\rm bra}(LS)\|G\|\psi_u^{\rm ket}(L'S'))$, which has u open shells in the bra and ket functions, to the submatrix element $T(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Xi, \Gamma)$, which has only the shells being acted upon by the two-particle operator in its bra and ket functions.

(2) The submatrix element $T(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Xi, \Gamma)$, which denotes the submatrix elements of operators of the types $A^{(kk')}(n\lambda, \Xi)$, $B^{(kk')}(n\lambda, \Xi)$, $C^{(kk')}(n\lambda, \Xi)$, $D^{(ls)}$, $E^{(kk')}(n\lambda, \Xi)$ (see (5)–(8)). Here Γ refers to the array of coupling parameters connecting the recoupling matrix $R(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Gamma)$ to the submatrix element.

(3) Phase factor Δ.

(4) $\Theta'(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Xi)$, which is proportional to the radial part and corresponds to one of $\Theta(n\lambda, \Xi), \ldots, \Theta(n_\alpha\lambda_\alpha, n_\beta\lambda_\beta, n_\gamma\lambda_\gamma, n_\delta\lambda_\delta, \Xi)$. It consists of a submatrix element $(n_i\lambda_in_j\lambda_j\|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\|n_i'\lambda_i'n_j'\lambda_j')$, and in some cases of simple factors and $3nj$-coefficients. For instance, for the distributions $\alpha\alpha\beta\beta$, $\gamma\gamma\alpha\beta$, $\gamma\gamma\beta\alpha$, $\alpha\beta\gamma\gamma$, $\beta\alpha\gamma\gamma$, $\alpha\beta\gamma\delta$, $\beta\alpha\delta\gamma$, $\alpha\beta\delta\gamma$, $\beta\alpha\gamma\delta$, $\gamma\delta\alpha\beta$, $\delta\gamma\beta\alpha$, $\gamma\delta\beta\alpha$, $\delta\gamma\alpha\beta$ (see expressions (52), (53) and notes on Θ' and $\tilde{\Theta}$ in the appendix) it is:

$$\begin{aligned}\Theta'(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Xi) &= (-1)^t\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j'\Xi)\\ &= \tfrac{1}{2}(-1)^{k-p+t+1}(n_i\lambda_in_j\lambda_j\|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\|n_i'\lambda_i'n_j'\lambda_j')\\ &\quad\times[\kappa_{12}, \sigma_{12}, \kappa_{12}', \sigma_{12}']^{1/2}\begin{Bmatrix} l_i & l_i' & \kappa_1\\ l_j & l_j' & \kappa_2\\ \kappa_{12} & \kappa_{12}' & k\end{Bmatrix}\begin{Bmatrix} s & s & \sigma_1\\ s & s & \sigma_2\\ \sigma_{12} & \sigma_{12}' & k\end{Bmatrix},\end{aligned} \tag{12}$$

where the integer t determining the phase depends upon the configuration states involved. Rules for its determination are given in the appendix.

The calculation of $\Theta'(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Xi)$ is straightforward (from an angular momentum point of view) and depends on the radial form of the operator. In the next sections we will describe expressions for the recoupling matrix, the submatrix elements, and the phase factor, respectively.

4. Recoupling matrices

In this section we present the expressions for the recoupling matrices

$$R(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{\text{bra}}, \Lambda^{\text{ket}}, \Gamma).$$

These matrices may be treated in the orbital l and spin s spaces separately. That is,

$$R(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{\text{bra}}, \Lambda^{\text{ket}}, \Gamma) = R(l_i, l_j, l_i', l_j', \Lambda_l^{\text{bra}}, \Lambda_l^{\text{ket}}, \Gamma_l) R(s, s, s, s, \Lambda_s^{\text{bra}}, \Lambda_s^{\text{ket}}, \Gamma_s) \tag{13}$$

where $\lambda_l^{\text{bra}} \equiv (L_i, L_j, L_i', L_j')^{\text{bra}}$ and $\Lambda_s^{\text{bra}} \equiv (S_i, S_j, S_i', S_j')^{\text{bra}}$. Therefore, for simplicity we present only the expressions in l space. The recoupling matrices in s space are easily obtained from analogous expressions in l space by making corresponding substitutions $l_1, l_2, \ldots, l_u \to s$; $L_1 \to S_1$, $L_2 \to S_2$; $\ldots$; $L_{12} \to S_{12}, \ldots, L_{123..u-1} \to S_{123...u-1}$; $L \to S$, $L' \to S'$. Also, the analytical expressions for recoupling matrices presented in this section are valid in the case of jj-coupling.

As we have mentioned earlier, there are four classes as defined by equations (5)–(8), we will consider each class separately. All the expressions presented below are obtained by using the approach of angular momentum theory described by Jucys and Bandzaitis (1977).

4.1. One interacting shell

Let us assume that the operators of second quantization act upon shell a as in distribution 1 of table 1, where $a \equiv \alpha$. Then the recoupling matrix has the expression:

$$R(l_a, L_a, k) = [L_a]^{-1/2} \delta(L_1, L_1') \ldots \delta(L_{a-1}, L_{a-1}') \delta(L_{a+1}, L_{a+1}') \ldots \delta(L_u, L_u') \\ \times \begin{cases} \delta(L_1, L_1', k); & \text{for } u = 1 \\ C_1; & \text{for } u = 2 \\ C_1 C_2(k, a+1, u-1) C_3; & \text{for } a < 3, u > 2 \\ \delta(L_{12}, L_{12}') \ldots \delta(L_{12...a-1}, L_{12...a-1}') & \\ \quad \times C_1 C_2(k, a+1, u-1) C_3; & \text{for } a > 3, a \neq u, u > 2 \\ \delta(L_{12}, L_{12}') \ldots \delta(L_{12...a-1}, L_{12...a-1}') C_3; & \text{for } a = u, u > 2. \end{cases} \tag{14}$$

In the above, the notation $\delta(L_1, L_1', k)$ means the triangular condition $|L_1 - L_1'| \leqslant k \leqslant L_1 + L_1'$ and

$$C_1 = (-1)^{\varphi} [L_a, T']^{1/2} \begin{Bmatrix} k & L_a' & L_a \\ J & T & T' \end{Bmatrix}, \tag{15}$$

where the values of parameters φ, J, T and T' present in expression (15) are given in table 2. The remaining two coefficients are

$$C_2(k, k_{\min}, k_{\max}) = \prod_{i=k_{\min}}^{k_{\max}} (-1)^{k+L_i+L_{12...i-1}+L_{12...i}'} [L_{12...i-1}, L_{12...i}']^{1/2} \\ \times \begin{Bmatrix} k & L_{12...i-1}' & L_{12...i-1} \\ L_i & L_{12...i} & L_{12...i}' \end{Bmatrix}; \tag{16}$$

and

$$C_3 = (-1)^{\varphi} [J, T']^{1/2} \begin{Bmatrix} k & J' & J \\ j & T & T' \end{Bmatrix}; \tag{17}$$

where the parameters φ, j, J, J', T and T' are given in table 3.

Table 2. Parameters for equation (15).

u	a	φ	J	T	T'
2	1	$L_1+2L_1'-L_2-L'+k$	L_2	L	L'
2	2	$L_1+L+L_2'+k$	L_1	L	L'
$u\neq 2$	1	$L_1+2L_1'-L_2-L_{12}'+k$	L_2	L_{12}	L_{12}'
$u\neq 2$	2	$L_1+L_{12}+L_2'+k$	L_1	L_{12}	L_{12}'
$u\neq 2$	$a>2$	$L_{12\ldots a-1}+L_{12\ldots a}+L_a'+k$	$L_{12\ldots a-1}$	$L_{12\ldots a}$	$L_{12\ldots a}'$

Table 3. Parameters for equation (17).

u	φ	j	J	J'	T	T'
$u\neq a$	$k+L_u+L_{12\ldots u-1}+L'$	L_u	$L_{12\ldots u-1}$	$L_{12\ldots u-1}'$	L	L'
a	$k-L_{12\ldots u-1}+2L_u+L_u'-L$	$L_{12\ldots u-1}$	L_u	L_u'	L	L'

When the total rank $k=0$, the recoupling matrix becomes simply

$$\begin{aligned}R(l_a,L_a,0)=\;&\delta(L_1,L_1')\delta(L_2,L_2')\delta(L_{12},L_{12}')\ldots\delta(L_{a-1},L_{a-1}')\\&\times\delta(L_{12\ldots a-1},L_{12\ldots a-1}')\delta(L_a,L_a')\delta(L_{12\ldots a},L_{12\ldots a}')\delta(L_{a+1},L_{a+1}')\\&\times\delta(L_{12\ldots a+1},L_{12\ldots a+1}')\ldots\delta(L_u,L_u')\delta(L,L')\end{aligned}\tag{18}$$

expression (18) is equivalent to (13.60) of Cowan (1981).

4.2. Two interacting shells

In this case let us assume that the operators of second quantization act upon the shells a and b (distributions 2–10 in table 1, where for distributions 2–5 $a\equiv\alpha$, $b\equiv\beta$ and for others (6–10) $a=\min\{\alpha,\beta\}$, $b=\max\{\alpha,\beta\}$). Then

$$\begin{aligned}R(l_a,L_a,l_b,L_b,\kappa_{12},\kappa_{12}',k)=\;&(-1)^{\zeta}[L_a,L_b]^{-1/2}\delta(L_1,L_1')\ldots\delta(L_{a-1},L_{a-1}')\\&\times\delta(L_{a+1},L_{a+1}')\ldots\delta(L_{b-1},L_{b-1}')\delta(L_{b+1},L_{b+1}')\ldots\delta(L_u,L_u')\end{aligned}$$
$$\times\begin{cases}C_4(K_{12},K_{12}',k,1)C_2(k,3,u-1)C_3; & \text{for } a=1,\ b=2\\ C_1C_2(K_{12},a+1,b-1)C_4(K_{12},K_{12}',k,1) & \\ \quad\times C_2(k,b+1,u-1)C_3; & \text{for } a<3,\ b>2,\ b\neq u\\ C_1C_2(K_{12},a+1,b-1)C_4(K_{12},K_{12}',k,1); & \text{for } a<3,\ b=u\\ \delta(L_{12},L_{12}')\ldots\delta(L_{12\ldots a-1},L_{12\ldots a-1}')C_1 & \\ \quad\times C_2(K_{12},a+1,b-1)C_4(K_{12},K_{12}',k,1) & \\ \quad\times C_2(k,b+1,u-1)C_3; & \text{for } a\geqslant 3,\ b>2,\ b\neq u\\ \delta(L_{12},L_{12}')\ldots\delta(L_{12\ldots a-1},L_{12\ldots a-1}')C_1 & \\ \quad\times C_2(K_{12},a+1,b-1)C_4(K_{12},K_{12}',k,1); & \text{for } a\geqslant 3,\ b=u\end{cases}\tag{19}$$

where

$$\zeta=\begin{cases}0 & \text{for } \alpha<\beta\\ \kappa_{12}+\kappa_{12}'-k & \text{for } \alpha>\beta,\end{cases}\tag{20}$$

Table 4. Parameters for equation (21).

P	a	b	u	J_1	J_1'	J_2	J_2'	J_3	J_3'
1	1	2	$u \neq b$	L_1	L_1'	L_2	L_2'	L_{12}	L_{12}
1	1	2	b	L_1	L_1'	L_2	L_2'	L	L
1	$a \neq 1$	$b \neq 2$	b	$L_{1\ldots u-1}$	$L'_{1\ldots u-1}$	L_u	L_u'	L	L'
1	in all other cases			$L_{1\ldots b-1}$	$L'_{1\ldots b-1}$	L_b	L_b'	$L_{1\ldots b}$	$L'_{1\ldots b}$
2	in all cases			$L_{1\ldots c-1}$	$L'_{1\ldots c-1}$	L_c	L_c'	$L_{1\ldots c}$	$L'_{1\ldots c}$

Table 5. Parameters for equation (23).

P	Case	J_1	J_1'	J_2
1	$a = 1$ and $b = 2$	L_a	L_a'	$L_{12\ldots b}$
1	$b \neq u$	$L_{1\ldots b-1}$	$L'_{1\ldots b-1}$	$L_{12\ldots b}$
1	$b = u$	$L_{1\ldots b-1}$	$L'_{1\ldots b-1}$	L
2	$c \neq u$	$L_{1\ldots c-1}$	$L'_{1\ldots c-1}$	$L_{12\ldots c}$
2	$c = u$	$L_{1\ldots c-1}$	$L'_{1\ldots c-1}$	L
3	$d \neq u$	$L_{1\ldots d-1}$	$L'_{1\ldots d-1}$	$L_{12\ldots d}$
3	$d = u$	$L_{1\ldots d-1}$	$L'_{1\ldots d-1}$	L

and

$$C_4(k_1, k_2, k, P) = [J_1, J_2, J_3', k]^{1/2} \left\{ \begin{matrix} J_1' & k_1 & J_1 \\ J_2' & k_2 & J_2 \\ J_3' & k & J_3 \end{matrix} \right\}. \tag{21}$$

The values of parameters J_1, J_1', J_2, J_2', J_3 and J_3' present in expression (21) must be taken from table 4. For the case $\alpha < \beta$ in equation (19) $K_{12} = \kappa_{12}$, $K_{12}' = \kappa_{12}'$ and when $\alpha > \beta$, then $K_{12} = \kappa_{12}'$, $K_{12}' = \kappa_{12}$.

When the total rank $k = 0$, and $\kappa_{12} = \kappa_{12}' = k$, the recoupling matrix has the form:

$$\begin{aligned} R(l_a, L_a, l_b, L_b, k, k, 0) &= [L_a, L_b', k]^{-1/2} \delta(L_1, L_1') \ldots \delta(L_{a-1}, L_{a-1}') \\ &\times \delta(L_{a+1}, L_{a+1}') \ldots \delta(L_{b-1}, L_{b-1}') \delta(L_{b+1}, L_{b+1}') \ldots \delta(L_u, L_u') \\ &\times \delta(L_{12}, L_{12}') \ldots \delta(L_{12\ldots a-1}, L_{12\ldots a-1}') \delta(L_{12\ldots b}, L_{12\ldots b}') \ldots \delta(L, L') \\ &\times \begin{cases} C_5(1); & \text{for } a = 1,\ b = 2 \\ C_1 C_2(k, a+1, b-1) C_5(1); & \text{for } a < 3 \\ \delta(L_{12}, L_{12}') \ldots \delta(L_{12\ldots a-1}, L_{12\ldots a-1}') & \\ \quad \times C_1 C_2(k, a+1, b-1) C_5(1); & \text{for } a \geqslant 3, \end{cases} \end{aligned} \tag{22}$$

where

$$C_5(P) = (-1)^{k + L_b + J_1' + J_2} [J_1, L_b']^{1/2} \left\{ \begin{matrix} k & L_b' & L_b \\ J_2 & J_1 & J_1' \end{matrix} \right\}. \tag{23}$$

The values of parameters J_1, J_1' and J_2 present in expression (23) must be taken from table 5.

Formula (22) has no analogue in Cowan (1981). Our expressions for the recoupling matrix do not depend on coefficients of fractional parentage and have no intermediate summations. Therefore they will be very convenient for practical calculations.

Table 6. Parameters for equation (24).

Case	a	b	c	ζ	K_1	K_2	K_3	C_6
$\alpha < \beta < \gamma$	α	β	γ	0	k_1	k_2	κ_{12}'	$\delta(j_{12}, \kappa_{12})$
$\beta < \alpha < \gamma$	β	α	γ	$k_1 + k_2 - \kappa_{12}$	k_2	k_1	κ_{12}'	$\delta(j_{12}, \kappa_{12})$
$\beta < \gamma < \alpha$	β	γ	α	0	k_2	κ_{12}'	k_1	$C_6'(\kappa_{12}', k_2, j_{12}, k_1, k, \kappa_{12})$
$\alpha < \gamma < \beta$	α	γ	β	$k_1 + k_2 - \kappa_{12}$	k_1	κ_{12}'	k_2	$C_6'(\kappa_{12}', k_1, j_{12}, k_2, k, \kappa_{12})$
$\gamma < \alpha < \beta$	γ	α	β	$2k_1 + k_2 - \kappa_{12} + \kappa_{12}' - j_{12}$	κ_{12}'	k_1	k_2	$C_6'(\kappa_{12}', k_1, j_{12}, k_2, k, \kappa_{12})$
$\gamma < \beta < \alpha$	γ	β	α	$k_1 + k_2 - \kappa_{12}$	κ_{12}'	k_2	k_1	$C_6'(\kappa_{12}', k_2, j_{12}, k_1, k, \kappa_{12})$

4.3. Three interacting shells

When the operators of second quantization act upon three shells a, b and c (distributions 11–18 in table 1), we have:

$$
\begin{aligned}
R(l_a, L_a, l_b, L_b, l_c, L_c, k_1, k_2, \kappa_{12}, \kappa_{12}', k) &= [L_a, L_b, L_c]^{-1/2}\delta(L_1, L_1') \ldots \delta(L_{a-1}, L_{a-1}') \\
&\times \delta(L_{a+1}, L_{a+1}') \ldots \delta(L_{b-1}, L_{b-1}')\delta(L_{b+1}, L_{b+1}') \ldots \delta(L_{c-1}, L_{c-1}') \\
&\times \delta(L_{c+1}, L_{c+1}') \ldots \delta(L_u, L_u') \sum_{j_{12}} (-1)^{\zeta} C_6 \\
&\times \begin{cases}
C_4(K_1, K_2, j_{12}, 1)C_2(j_{12}, 3, c-1) & \\
\quad \times C_4(j_{12}, K_3, k, 2)C_2(k, c+1, u-1)C_3; & \text{for } a = 1,\ b = 2 \\
C_1 C_2(K_1, a+1, b-1)C_4(K_1, K_2, j_{12}, 1) & \\
\quad \times C_2(j_{12}, b+1, c-1)C_4(j_{12}, K_3, k, 2) & \\
\quad \times C_2(k, c+1, u-1)C_3; & \text{for } a < 3 \\
\delta(L_{12}, L_{12}') \ldots \delta(L_{12\ldots a-1}, L_{12\ldots a-1}')C_1 & \\
\quad \times C_2(K_1, a+1, b-1)C_4(K_1, K_2, j_{12}, 1) & \\
\quad \times C_2(j_{12}, b+1, c-1)C_4(j_{12}, K_3, k, 2) & \\
\quad \times C_2(k, c+1, u-1)C_3; & \text{for } a \geqslant 3,
\end{cases}
\end{aligned} \tag{24}
$$

where parameters a, b, c, ζ, K_1, K_2, K_3 and coefficient C_6 are given in table 6. The coefficient $C_6'(k_1, k_2, k_3, k_4, k_5, k_6)$ is

$$
C_6'(k_1, k_2, k_3, k_4, k_5, k_6) = (-1)^{k_1+k_2-k_3+2k_5}[k_3, k_6]^{1/2} \begin{Bmatrix} k_1 & k_2 & k_3 \\ k_4 & k_5 & k_6 \end{Bmatrix}. \tag{25}
$$

From (7) we have that in expressions (24) and (25) the ranks $k_1 = l_\alpha$, $k_2 = l_\beta$.

When the total rank $k = 0$, and $\kappa_{12} = \kappa_{12}' = k$, the recoupling matrix has the form:

$$
\begin{aligned}
R(l_a, L_a, l_b, L_b, l_c, L_c, k_1, k_2, k, k, 0) &= (-1)^{\zeta}[L_a, L_b, L_c', K_3]^{-1/2} \\
&\times \delta(L_1, L_1') \ldots \delta(L_{a-1}, L_{a-1}')\delta(L_{a+1}, L_{a+1}') \ldots \delta(L_{b-1}, L_{b-1}') \\
&\times \delta(L_{b+1}, L_{b+1}') \ldots \delta(L_{c-1}, L_{c-1}')\delta(L_{c+1}, L_{c+1}') \ldots \delta(L_u, L_u') \\
&\times \delta(L_{12}, L_{12}') \ldots \delta(L_{12\ldots a-1}, L_{12\ldots a-1}')\delta(L_{12\ldots c}, L_{12\ldots c}') \ldots \delta(L, L')
\end{aligned}
$$

Table 7. Parameters for equation (26).

Case	ζ	K_1	K_2	K_3
$\alpha < \beta < \gamma$	0	k_1	k_2	k
$\beta < \alpha < \gamma$	$k_1 + k_2 - k$	k_2	k_1	k
$\beta < \gamma < \alpha$	$2k_1$	k_2	k	k_1
$\alpha < \gamma < \beta$	$k_1 - k_2 - k$	k_1	k	k_2
$\gamma < \alpha < \beta$	$2k$	k	k_1	k_2
$\gamma < \beta < \alpha$	$k_1 + k_2 + k$	k	k_2	k_1

$$
\times \begin{cases} C_4(K_1, K_2, K_3, 1)C_2(K_3, b+1, c-1)C_5(2); & \text{for } a = 1,\ b = 2 \\ C_1C_2(K_1, a+1, b-1)C_4(K_1, K_2, K_3, 1) & \\ \quad \times C_2(K_3, b+1, c-1)C_5(2); & \text{for } a < 3 \\ \delta(L_{12}, L'_{12}) \ldots \delta(L_{12\ldots a-1}, L'_{12\ldots a-1})C_1 & \\ \quad \times C_2(K_1, a+1, b-1)C_4(K_1, K_2, K_3, 1) & \\ \quad \times C_2(K_3, b+1, c-1)C_5(2); & \text{for } a \geqslant 3 \end{cases} \tag{26}
$$

where the parameters ζ, K_1, K_2, K_3 values are given in table 7.

The recoupling matrix for three interacting shells (26) has the same advantages as the equivalent quantity, equation (22), for two shells.

4.4. Four interacting shells

When the operators of second quantization act upon four shells, a, b, c and d (distributions 19–42 in table 1), we have:

$$
\begin{aligned}
R(l_a, L_a, l_b, L_b, l_c, L_c, l_d, L_d, k_1, k_2, \kappa_{12}, k_3, k_4, \kappa'_{12}, k) \\
&= [L_a, L_b, L_c, L_d]^{-1/2}\delta(L_1, L'_1) \ldots \delta(L_{a-1}, L'_{a-1}) \\
&\quad \times \delta(L_{a+1}, L'_{a+1}) \ldots \delta(L_{b-1}, L'_{b-1})\delta(L_{b+1}, L'_{b+1}) \ldots \delta(L_{c-1}, L'_{c-1}) \\
&\quad \times \delta(L_{c+1}, L'_{c+1}) \ldots \delta(L_{d-1}, L'_{d-1})\delta(L_{d+1}, L'_{d+1}) \ldots \delta(L_u, L'_u) \\
&\quad \times \begin{cases} C_4(k_1, k_2, \kappa_{12}, 1)C_2(\kappa_{12}, 3, c-1)C_7(c, d) & \\ \quad \times C_2(k, d+1, u-1)C_3; & \text{for } a = 1,\ b = 2 \\ C_1C_2(k_1, a+1, b-1)C_4(k_1, k_2, \kappa_{12}, 1) & \\ \quad \times C_2(\kappa_{12}, b+1, c-1)C_7(c, d) & \\ \quad \times C_2(k, d+1, u-1)C_3; & \text{for } a < 3 \\ \delta(L_{12}, L'_{12}) \ldots \delta(L_{12\ldots a-1}, L'_{12\ldots a-1})C_1 & \\ \quad \times C_2(k_1, a+1, b-1)C_4(k_1, k_2, \kappa_{12}, 1) & \\ \quad \times C_2(\kappa_{12}, b+1, c-1)C_7(c, d) & \\ \quad \times C_2(k, d+1, u-1)C_3; & \text{for } a \geqslant 3, \end{cases}
\end{aligned} \tag{27}
$$

where

$$C_7(k_{\min}, k_{\max}) = \begin{cases} \sum_I C_8(I)C_{10}(I), & \text{for } k_{\max} - k_{\min} = 1 \\ \sum_{I_1}\sum_{I_2} C_8(I_1)C_9(I_1, I_2, k_{\min}+1)C_{10}(I_2), & \text{for } k_{\max} - k_{\min} = 2 \\ \sum_{I_1}\sum_{I_2} C_8(I_1)C_{11}(I_1, I_2)C_{10}(I_2); & \text{for } k_{\max} - k_{\min} < 2 \end{cases} \tag{28}$$

$$C_8(I) = (-1)^{\kappa_{12}+L'_{12\ldots c}-I}[L_c, I, L_{12\ldots c-1}, L'_{12\ldots c}]^{1/2} \times \begin{Bmatrix} k_3 & L'_c & L_c \\ L_{12\ldots c-1} & L_{12\ldots c} & I \end{Bmatrix} \begin{Bmatrix} L'_{12\ldots c-1} & \kappa_{12} & L_{12\ldots c-1} \\ I & L'_c & L'_{12\ldots c} \end{Bmatrix}, \tag{29}$$

$$C_9(I_1, I_2, i) = (-1)^{2(I_1+L_i)+L_{12\ldots i}+L'_{12\ldots i}+k_3+\kappa_{12}}[L_{12\ldots i-1}, I_1, I_2, L'_{12\ldots i}]^{1/2} \times \begin{Bmatrix} L_{12\ldots i-1} & I_1 & k_3 \\ I_2 & L_{12\ldots i} & L_i \end{Bmatrix} \begin{Bmatrix} L'_{12\ldots i-1} & I_1 & \kappa_{12} \\ I_2 & L'_{12\ldots i} & L_i \end{Bmatrix}, \tag{30}$$

$$\begin{aligned} C_{10}(I) = {} & (-1)^{2(I+k_3)+k_4+\kappa_{12}+\kappa'_{12}+k+L_{12\ldots d}+L'_{12\ldots d}+L_d+L'_d+L'_{12\ldots d-1}} \\ & \times[\kappa_{12}, \kappa'_{12}, L_d, I, L'_{12\ldots d}, L_{12\ldots d-1}]^{1/2} \sum_x (-1)^x [x] \\ & \times \begin{Bmatrix} I & \kappa'_{12} & x \\ k & L'_{12\ldots d-1} & \kappa_{12} \end{Bmatrix} \begin{Bmatrix} I & \kappa'_{12} & x \\ k_4 & L_{12\ldots d-1} & k_3 \end{Bmatrix} \\ & \times \begin{Bmatrix} L_{12\ldots d-1} & k_4 & x \\ L'_d & L_{12\ldots d} & L_d \end{Bmatrix} \begin{Bmatrix} L'_{12\ldots d-1} & k & x \\ L_{12\ldots d} & L'_d & L'_{12\ldots d} \end{Bmatrix}. \end{aligned} \tag{31}$$

$$C_{11}(I_1, I_2) = (-1)^{I_1-I_2+L'_{12\ldots c}-L'_{12\ldots d-1}}[I_1, I_2]^{1/2} \sum_x [x] C_2(x, c+1, d-1) \times \begin{Bmatrix} k_3 & \kappa_{12} & x \\ L'_{12\ldots c} & L_{12\ldots c} & I_1 \end{Bmatrix} \begin{Bmatrix} k_3 & \kappa_{12} & x \\ L'_{12\ldots d-1} & L_{12\ldots d-1} & I_2 \end{Bmatrix}. \tag{32}$$

From (8) we have that in expressions (27) and (30)–(32) the ranks $k_1 = l_\alpha$, $k_2 = l_\beta$, $k_3 = l_\gamma$, $k_4 = l_\delta$.

When the total rank $k = 0$ and $\kappa_{12} = \kappa'_{12} = k$, the recoupling matrix has the form:

$$\begin{aligned} & R(l_a, L_a, l_b, L_b, l_c, L_c, l_d, L_d, k_1, k_2, k, k_3, k_4, k, 0) \\ & \quad = [L_a, L_b, L_c, L'_d, k]^{-1/2}\delta(L_1, L'_1)\ldots\delta(L_{a-1}, L'_{a-1}) \\ & \qquad \times\delta(L_{a+1}, L'_{a+1})\ldots\delta(L_{b-1}, L'_{b-1})\delta(L_{b+1}, L'_{b+1})\ldots \\ & \qquad \times\ldots\delta(L_{c-1}, L'_{c-1})\delta(L_{c+1}, L'_{c+1})\ldots\delta(L_{d-1}, L'_{d-1}) \\ & \qquad \times\delta(L_{d+1}, L'_{d+1})\ldots\delta(L_u, L'_u) \\ & \qquad \times\delta(L_{12}, L'_{12})\ldots\delta(L_{12\ldots a-1}, L'_{12\ldots a-1})\delta(L_{12\ldots d}, L'_{12\ldots d})\ldots\delta(L, L') \end{aligned}$$

$$\times\begin{cases} C_4(k_1,k_2,k,1)C_2(k,b+1,c-1) & \\ \quad\times C_4(k,k_3,k_4,1)C_2(k_4,c+1,d-1) & \\ \quad\times C_5(3); & \text{for } a=1, b=2 \\ C_1C_2(k,a+1,b-1)C_4(k_1,k_2,k,1) & \\ \quad\times C_2(k,b+1,c-1)C_4(k,k_3,k_4,2) & \\ \quad\times C_2(k_4,c+1,d-1)C_5(3); & \text{for } a<3 \\ \delta(L_{12},L'_{12})\ldots\delta(L_{12\ldots a-1},L'_{12\ldots a-1})C_1 & \\ \quad\times C_2(k,a+1,b-1)C_4(k_1,k_2,k,1) & \\ \quad\times C_2(k,b+1,c-1)C_4(k,k_3,k_4,2) & \\ \quad\times C_2(k_4,c+1,d-1)C_5(3) & \text{for } a\geqslant 3. \end{cases} \tag{33}$$

Expression (33) also has no analogue in Cowan (1981).

Thus, we have studied all possible cases of matrix elements of arbitrary two-electron operators. The expressions for recoupling matrices ((22), (26) and (33)) obtained in this section are simpler and, thus, more convenient for practical applications, than those of Cowan (1981), except for the simplest case $k=0$ of an operator acting on one shell (18), where they are equivalent.

5. Calculation of tensorial quantities

In this section we will consider the submatrix elements

$$T(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Lambda^{\text{bra}}, \Lambda^{\text{ket}}, \Xi, \Gamma)$$

appearing in (11). Taking into account the fact that operators $a^{(\lambda)}_{m_\lambda}$ and $\tilde{a}^{(\lambda)}_{m_\lambda}$ are components of the tensor $a^{(q\lambda)}_{m_q m_\lambda}$, having in quasispin space the rank $q=\frac{1}{2}$ and projections $m_q=\pm\frac{1}{2}$, i.e. $a^{(q\lambda)}_{\frac{1}{2}m_\lambda}=a^{(ls)}_{m_l m_s}$ and $a^{(q\lambda)}_{-\frac{1}{2}m_\lambda}=\tilde{a}^{(ls)}_{m_l m_s}$ the operators $A^{(kk')}(n\lambda,\Xi)$, $B^{(kk')}(n\lambda,\Xi)$, $C^{(kk')}(n\lambda,\Xi)$, $D^{(ls)}$, $E^{(kk')}(n\lambda,\Xi)$ (see (5)–(8)) in our case correspond, respectively, to the following five expressions:

$$a^{(q\lambda)}_{m_q}, \tag{34}$$

$$[a^{(q\lambda)}_{m_{q1}}\times a^{(q\lambda)}_{m_{q2}}]^{(\kappa_1\sigma_1)}, \tag{35}$$

$$[a^{(q\lambda)}_{m_{q1}}\times [a^{(q\lambda)}_{m_{q2}}\times a^{(q\lambda)}_{m_{q3}}]^{(\kappa_1\sigma_1)}]^{(\kappa_2\sigma_2)}, \tag{36}$$

$$[[a^{(q\lambda)}_{m_{q1}}\times a^{(q\lambda)}_{m_{q2}}]^{(\kappa_1\sigma_1)}\times a^{(q\lambda)}_{m_{q3}}]^{(\kappa_2\sigma_2)}, \tag{37}$$

$$[[a^{(q\lambda)}_{m_{q1}}\times a^{(q\lambda)}_{m_{q2}}]^{(\kappa_1\sigma_1)}\times [a^{(q\lambda)}_{m_{q3}}\times a^{(q\lambda)}_{m_{q4}}]^{(\kappa_2\sigma_2)}]^{(kk)}. \tag{38}$$

We will discuss the derivation of submatrix elements of these operators, and present the expressions for these quantities. It is worth noting that these tensorial quantities all act upon the *same* shell. So, all the advantages of tensor algebra and the quasispin formalism may be exploited efficiently.

We obtain the submatrix elements of operator (34) by straightforwardly using the Wigner–Eckart theorem in quasispin space:

$$(l^N\alpha QLS\|a^{(qls)}_{m_q}\|l^{N'}\alpha' Q'L'S') = -[Q]^{-1/2}\begin{bmatrix} Q' & 1/2 & Q \\ M'_Q & m_q & M_Q \end{bmatrix}(l\alpha QLS|||a^{(qls)}|||l\alpha' Q'L'S'), \tag{39}$$

where the last multiplier in (39) is the so-called completely reduced (reduced in the quasispin, orbital and spin spaces) matrix element. The coefficient

$$\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix}$$

is a Clebsch–Gordan coefficient. Different notations for it appear, for example, $A^{jj_1j_2}_{mm_1m_2}$ in Eckart (1930), $S^{j_1j_2}_{jm_1m_2}$ in Wigner (1931), $(j_1j_2m_1m_2|j_1j_2jm)$ in Condon and Shortley (1935) and Judd (1967).

The value of the submatrix element of operator (35) is obtained by basing our development on (33), (34) of Gaigalas and Rudzikas (1996). In the other three cases (36)–(38) we obtain them by using (2.28) of Jucys and Savukynas (1973):

$$\begin{aligned}(nl^N\alpha QLS\|[F^{(\kappa_1\sigma_1)}(n\lambda)\times G^{(\kappa_2\sigma_2)}(n\lambda)]^{(kk)}\|nl^{N'}\alpha' Q'L'S') = (-1)^{L+S+L'+S'+2k}[k] \\ \times \sum_{\alpha'' Q'' L'' S''}(nl^N\alpha QLS\|F^{(\kappa_1\sigma_1)}(n\lambda)\|nl^{N''}\alpha'' Q''L''S'') \\ \times(nl^{N''}\alpha'' Q''L''S''\|G^{(\kappa_2\sigma_2)}(n\lambda)\|nl^{N'}\alpha' Q'L'S') \\ \times\begin{Bmatrix} \kappa_1 & \kappa_2 & k \\ L' & L & L'' \end{Bmatrix}\begin{Bmatrix} \sigma_1 & \sigma_2 & k \\ S' & S & S'' \end{Bmatrix},\end{aligned} \tag{40}$$

where $F^{(\kappa_1\sigma_1)}(n\lambda)$, $G^{(\kappa_2\sigma_2)}(n\lambda)$ is one of (34) or (35) and the submatrix elements correspondingly are defined by (39) and (33), (34) of Gaigalas and Rudzikas (1996). N'' is defined by the second-quantization operators occurring in $F^{(\kappa_1\sigma_1)}(n\lambda)$ and $G^{(\kappa_2\sigma_2)}(n\lambda)$.

As is seen, by using this approach, the calculation of the angular parts of matrix elements between functions with u open shells is reduced to requiring the submatrix elements of tensors (34) and (35) within one shell of equivalent electrons. As these completely reduced submatrix elements do not depend on the occupation number of the shell, the tables for these quantities are considerably reduced in size in comparison with the tables of analogous submatrix elements of tensorial quantities U^k, $V^{k_1k_2}$ (Jucys and Savukynas 1973) and the tables of fractional parentage coefficients.

6. Phase factor

In this section we present the phase factors Δ in (11), which appear for submatrix elements of operators in equations (5)–(8).

For distributions 1–6 (table 1):

$$\Delta = 0. \tag{41}$$

For distributions 7–18 (table 1):

$$\Delta = 1 + \sum_{k=i}^{j-1} N_k, \tag{42}$$

where if $\alpha < \beta$, then $i = \alpha$, $j = \beta$, and if $\alpha > \beta$, then $i = \beta$, $j = \alpha$; N_k is the occupation number of a shell of equivalent electrons having the label k. For distributions 19–42 (table 1):

$$\Delta = \sum_{k=\alpha}^{\beta-1} N_k + \sum_{k=\gamma}^{\delta-1} N_k. \tag{43}$$

7. Spin–angular part of any two-particle operator

In the previous sections, all the expressions required calculating the spin–angular part of any two-particle operator given. For convenience, the structure of the expressions (the numbers of the corresponding formulae) are summarized in table 8 for each distribution given in table 1. The classification numbers of the distributions are presented in the first column of table 8. The equation number of the tensorial expression of the two-particle operator $\hat{G}$ is given in the second column, and the equation number of the tensorial class of the two-particle operator, denoted by $\hat{G}(T)$, in the third column.

The next four columns give the numbers of the formulae of the tensors, which act inside the shell. A tensor acting upon the α shell is given in the α column, and in the columns β, γ, δ—upon the β, γ, δ shells, respectively. Consequently, if we want to find submatrix element, $T(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Lambda^{\mathrm{bra}}, \Lambda^{\mathrm{ket}}, \Xi, \Gamma)$, first we have to calculate the submatrix element of the tensor from column α between functions, consisting only of the α shell, and then to look for the submatrix element of the tensor from column β between functions, consisting only of the β shell, etc. Thus, we need to calculate only submatrix elements of the tensors acting upon a certain shell. The details of the calculation of these submatrix elements were discussed in section 5.

The coefficients $\tilde{\Theta}$ are given in the $\tilde{\Theta}$ column. The numbers of expressions for the recoupling matrix $R(\lambda_i, \lambda_j, \lambda'_i, \lambda'_j, \Lambda^{\mathrm{bra}}, \Lambda^{\mathrm{ket}}, \Gamma)$ and phase factor Δ are given in the last two columns. From this table it is easy to derive the general formulae for spin–angular parts of matrix elements of any two-particle operator.

8. Conclusions

The approach to matrix element evaluations that we present, is based on the combination of the angular momentum theory as described in Jucys and Bandzaitis (1977), on the concept of irreducible tensorial sets (Judd 1967, Rudzikas and Kaniauskas 1984), on a generalized graphical approach (Gaigalas *et al* 1985), on the quasispin approach (Rudzikas and Kaniauskas 1984), and on the use of reduced coefficients of fractional parentage (Rudzikas 1991, Rudzikas 1997, Judd 1996). All this, in its entirety, introduces a number of new features, in comparison with the following traditional approaches.

(1) The tensorial expressions of a two-particle operator, presented in section 2, allow one to exploit all the advantages of a new version of Racah algebra based on quasispin formalism when the latter is applied within each particular shell only. In particular, this is not only a reformulation of spin–angular calculations in terms of standard quantities, but also the determination beforehand from symmetry properties, of which matrix elements are equal to zero without performing further explicit calculations. That is determined from the submatrix elements $T(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Lambda^{\mathrm{bra}}, \Lambda^{\mathrm{ket}}, \Xi, \Gamma)$.

(2) It enables one to use the Wigner–Eckart theorem in quasispin space. This provides an opportunity to use tables of reduced coefficients of fractional parentage and tables of other standard quantities (section 5), which do not depend on the occupation number of a shell of equivalent electrons. Thus, the volume of tables of standard quantities is reduced considerably in comparison with the analogous tables of submatrix elements of tensorial operators U^k, V^{k1} and the tables of fractional parentage coefficients. This undoubtedly makes the inclusion of shells of equivalent f electrons with arbitrary occupation numbers considerably easier, and the process of selecting the standard quantities from the tables becomes simpler.

(3) The tensorial form of any operator presented in section 2 allows one to obtain

Table 8. Scheme of the expressions for matrix elements of any two-particle operator.

No.	$\hat{G}$	$\hat{G}(T)$	α	β	γ	δ	$\tilde{\Theta}$	R	Δ
1	(44)	(5)	(38)	—	—	—	(45)	(14), (18)	(41)
	(47)	(5)	(38)	—	—	—	(48), (49)	(14), (18)	(41)
2	(50)	(6)	(35)	(35)	—	—	(51)	(19), (22)	(41)
3	(50)	(6)	(35)	(35)	—	—	(51)	(19), (22)	(41)
4	(54)	(6)	(35)	(35)	—	—	(55)	(19), (22)	(41)
5	(54)	(6)	(35)	(35)	—	—	(55)	(19), (22)	(41)
6	(52)	(6)	(35)	(35)	—	—	(53)	(19), (22)	(41)
7	(56)	(6)	(36)	(34)	—	—	(58)	(19), (22)	(42)
8	(56)	(6)	(36)	(34)	—	—	(59)	(19), (22)	(42)
9	(60)	(6)	(34)	(37)	—	—	(62)	(19), (22)	(42)
10	(60)	(6)	(34)	(37)	—	—	(63)	(19), (22)	(42)
11	(50)	(7)	(34)	(34)	(35)	—	(51)	(24), (26)	(42)
12	(50)	(7)	(34)	(34)	(35)	—	(51)	(24), (26)	(42)
13	(54)	(7)	(34)	(34)	(35)	—	(55)	(24), (26)	(42)
14	(54)	(7)	(34)	(34)	(35)	—	(55)	(24), (26)	(42)
15	(52)	(7)	(34)	(34)	(35)	—	(53)	(24), (26)	(42)
16	(52)	(7)	(34)	(34)	(35)	—	(53)	(24), (26)	(42)
17	(52)	(7)	(34)	(34)	(35)	—	(53)	(24), (26)	(42)
18	(52)	(7)	(34)	(34)	(35)	—	(53)	(24), (26)	(42)
19	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
20	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
21	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
22	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
23	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
24	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
25	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
26	(52)	(8)	(34)	(34)	(34)	(34)	(53)	(27), (33)	(43)
27	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
28	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)
29	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
30	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)
31	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
32	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
33	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)
34	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)
35	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
36	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
37	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)
38	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)
39	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
40	(50)	(8)	(34)	(34)	(34)	(34)	(51)	(27), (33)	(43)
41	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)
42	(54)	(8)	(34)	(34)	(34)	(34)	(55)	(27), (33)	(43)

simple expressions for the recoupling matrices (section 4). Hence, the computer code based on this approach would immediately use the analytical formulae for recoupling matrices $R(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Gamma)$. This feature also saves computing time, because (i) complex calculations leading finally to simple analytical expressions (Bar-Shalom and Klapisch 1988) are avoided, and (ii) a number of momenta triads (triangular conditions) can be checked before the explicit calculation of a recoupling matrix leading to a zero value. These triangular conditions may be determined not only for the terms of shells that the operators of second quantization act upon, as is the case for the submatrix elements $T(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{\rm bra}, \Lambda^{\rm ket}, \Xi\Gamma)$ (see conclusion 1), but also for the rest of the shells and resulting terms.

In this approach both diagonal and non-diagonal matrix elements, with respect to configurations, are considered in a uniform way, and are expressed in terms of the same quantities. The difference is only in the values of the projections of the quasispin momenta of separate shells.

In this paper all the expressions needed in the spin–angular parts of matrix elements of two-particle operators calculation are presented. This approach is also applicable to one-particle operators. While calculating the spin–angular parts of the latter, all the expressions needed are included in the cases discussed for the two-particle operator. For instance, in the recoupling matrix calculation two of the four cases discussed above appear, namely, when all the second-quantization operators act upon the same shell (section 4.1) and when they act upon two different shells of equivalent electrons (section 4.2). Thus, this approach is applicable to any one- and two-particle operator. Practical usage shows that a series of difficulties persisting in the traditional approach to the calculation of angular parts of matrix elements based on the usage of coefficients of fractional parentage and unit tensors can be avoided and high efficiency may be achieved. Indeed, preliminary calculations show that computer programs based on our approach on average are 4–6 times faster than the other well known codes (Gaigalas *et al* 1995). This methodology can easily be generalized to cover the case of relativistic operators and relativistic wavefunctions.

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Appendix

Here algebraic expressions are presented for the two-particle operator (1) in the irreducible tensorial form for all the distributions from table 8. Although there are quite a few distributions, the structure of their algebraic formulae is similar, and therefore on the basis of a graphical approach (Gaigalas *et al* 1985) the expressions may be written in a compact form, where one general formula includes all the cases having the same structure. Each particular formula is obtained from these by performing elementary graphical transformations according to the rules explained below. The general expressions are as follows.

(1) Distribution $\alpha\alpha\alpha\alpha$ (case 1 from table 8).

For this distribution the analytical expressions (7), (8) in Gaigalas and Rudzikas (1996)

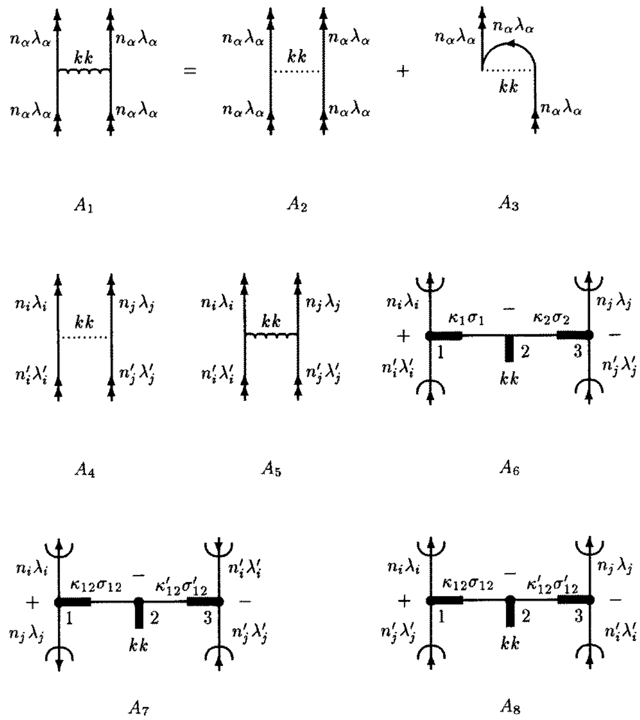

Figure A1. Diagrams for an arbitrary two-particle operator. Diagrams A_1, A_2 and A_3 represent two-particle operators when this operator has distribution $\alpha\alpha\alpha\alpha$. Diagrams A_4 and A_5 represent two-particle operators for all other distributions. Diagrams A_1, A_2, A_3, A_4 and A_5 are similar to the usual Feynman–Goldstone diagrams. Diagrams A_6, A_7 and A_8 represent tensorial products of second quantization operators (A_6 for the second group, A_7 for the third, and A_8 for the fourth).

are used, in which the quantum numbers $n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j$ acquire particular values of a shell α. For the first form (figure A1, A_1), we have

$$A_1 = \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} \tilde{\Theta}_I(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi)$$
$$\times [[a^{(l_\alpha s)} \times a^{(l_\alpha s)}]^{(\kappa_{12}\sigma_{12})} \times [\tilde{a}^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)}]^{(\kappa'_{12}\sigma'_{12})}]^{(kk)}_{p,-p}, \tag{44}$$

where

$$\tilde{\Theta}_I(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi) \equiv \Theta'(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi)$$
$$\equiv \Theta(n_\alpha\lambda_\alpha, \Xi) \tag{45}$$

and

$$\tilde{\Theta}_I(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi) = \tfrac{1}{2}(-1)^{k-p+1}[\kappa_{12}, \sigma_{12}, \kappa'_{12}, \sigma'_{12}]^{1/2}$$
$$\times (n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha)$$
$$\times \begin{Bmatrix} l_\alpha & l_\alpha & \kappa_1 \\ l_\alpha & l_\alpha & \kappa_2 \\ \kappa_{12} & \kappa'_{12} & k \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_1 \\ s & s & \sigma_2 \\ \sigma_{12} & \sigma'_{12} & k \end{Bmatrix}. \tag{46}$$

In an equivalent second form (figure A1, $A_2 + A_3$), we have

$$A_2 + A_3 = \tilde{\Theta}_{IIa}(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi)$$

$$\times[[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)}]^{(\kappa_1\sigma_1)} \times [\tilde{a}^{(l_\alpha s)} \times a^{(l_\alpha s)}]^{(\kappa_2\sigma_2)}]^{(kk)}_{p,-p}$$
$$+\tilde{\Theta}_{IIb}(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi)[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)}]^{(kk)}_{p,-p}, \tag{47}$$

where

$$\tilde{\Theta}_{IIa}(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi) = \tfrac{1}{2}(-1)^{k-p}[\kappa_1, \sigma_1, \kappa_2, \sigma_2]^{-1/2}$$
$$\times(n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha) \tag{48}$$

and

$$\tilde{\Theta}_{IIb}(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi) = (-1)^{k-p+1}(n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha)$$
$$\times \begin{Bmatrix} \kappa_1 & \kappa_2 & k \\ l_\alpha & l_\alpha & l_\alpha \end{Bmatrix} \begin{Bmatrix} \sigma_1 & \sigma_2 & k \\ s & s & s \end{Bmatrix}. \tag{49}$$

Both factors $\tilde{\Theta}_{IIa}(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi)$ and $\tilde{\Theta}_{IIb}(n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, n_\alpha\lambda_\alpha, \Xi)$ have properties analogous to those of $\tilde{\Theta}_I$ as stated in (45).

(2) Distributions $\alpha\beta\alpha\beta$, $\beta\alpha\beta\alpha$, $\beta\gamma\alpha\gamma$, $\gamma\beta\gamma\alpha$, $\alpha\gamma\beta\delta$, $\gamma\alpha\delta\beta$, $\beta\delta\alpha\gamma$, $\delta\beta\gamma\alpha$, $\alpha\delta\beta\gamma$, $\delta\alpha\gamma\beta$, $\beta\gamma\alpha\delta$, $\gamma\beta\delta\alpha$ (cases 2, 3, 11, 12, 27, 29, 31, 32, 35, 36, 39, 40 from table 8) (figure A1, A_4, A_6):

$$A_4 = \tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi)A_6, \tag{50}$$

where

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) = \tfrac{1}{2}(-1)^{k-p}[\kappa_1, \sigma_1, \kappa_2, \sigma_2]^{-1/2}$$
$$\times(n_i\lambda_i n_j\lambda_j \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n'_i\lambda'_i n'_j\lambda'_j). \tag{51}$$

Diagram A_6 corresponds to tensorial products of the operators of second quantization for a two-particle operator (for details see Gaigalas and Rudzikas (1996)).

(3) Distributions $\alpha\alpha\beta\beta$, $\gamma\gamma\alpha\beta$, $\gamma\gamma\beta\alpha$, $\alpha\beta\gamma\gamma$, $\beta\alpha\gamma\gamma$, $\alpha\beta\gamma\delta$, $\beta\alpha\delta\gamma$, $\alpha\beta\delta\gamma$, $\beta\alpha\gamma\delta$, $\gamma\delta\alpha\beta$, $\delta\gamma\beta\alpha$, $\gamma\delta\beta\alpha$, $\delta\gamma\alpha\beta$ (cases 6, 15–26 from table 8) (figure A1, A_5, A_7):

$$A_5 = \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} \tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi)A_7, \tag{52}$$

where

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) = \tfrac{1}{2}(-1)^{k-p+1}[\kappa_{12}, \sigma_{12}, \kappa'_{12}, \sigma'_{12}]^{1/2}$$
$$\times(n_i\lambda_i n_j\lambda_j \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n'_i\lambda'_i n'_j\lambda'_j)$$
$$\times \begin{Bmatrix} l_i & l'_i & \kappa_1 \\ l_j & l'_j & \kappa_2 \\ \kappa_{12} & \kappa'_{12} & k \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_1 \\ s & s & \sigma_2 \\ \sigma_{12} & \sigma'_{12} & k \end{Bmatrix}. \tag{53}$$

(4) Distributions $\alpha\beta\beta\alpha$, $\beta\alpha\alpha\beta$, $\gamma\beta\alpha\gamma$, $\beta\gamma\gamma\alpha$, $\alpha\gamma\delta\beta$, $\gamma\alpha\beta\delta$, $\beta\delta\gamma\alpha$, $\delta\beta\alpha\gamma$, $\alpha\delta\gamma\beta$, $\delta\alpha\beta\gamma$, $\beta\gamma\delta\alpha$, $\gamma\beta\alpha\delta$ (cases 4, 5, 13, 14, 28, 30, 33, 34, 37, 38, 41, 42 from table 8) (figure A1, A_4, A_8):

$$A_4 = \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} \tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi)A_8, \tag{54}$$

where

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) = \tfrac{1}{2}(-1)^{k-p+1+l'_i+l'_j+\kappa_2+\sigma_2+\kappa_{12}+\sigma_{12}}$$
$$\times[\kappa_{12}, \sigma_{12}, \kappa'_{12}, \sigma'_{12}]^{1/2}(n_i\lambda_i n_j\lambda_j \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n'_i\lambda'_i n'_j\lambda'_j)$$
$$\times \begin{Bmatrix} l_i & l'_i & \kappa_1 \\ l'_j & l_j & \kappa_2 \\ \kappa_{12} & \kappa'_{12} & k \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_1 \\ s & s & \sigma_2 \\ \sigma_{12} & \sigma'_{12} & k \end{Bmatrix}. \tag{55}$$

(5) Distributions $\beta\alpha\alpha\alpha$, $\alpha\beta\alpha\alpha$ (cases 7, 8 from table 8) figure A1, A_5):

$$A_5 = \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} \tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi)$$
$$\times [a^{(l_\beta s)} \times [a^{(l_\alpha s)} \times [\tilde{a}^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)}]^{(\kappa'_{12}\sigma'_{12})}]^{(K_l K_s)}]^{(kk)}_{p,-p}, \tag{56}$$

where

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) \equiv \Theta'(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi)$$
$$\equiv \Theta(n_\alpha\lambda_\alpha, n_\beta\lambda_\beta, \Xi). \tag{57}$$

When $\hat{G}(T) = \hat{G}(\beta\alpha\alpha\alpha)$, then

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) = \tfrac{1}{2}(-1)^{k-p+\kappa'_{12}+\sigma'_{12}+l_\alpha+l_\beta}[\kappa_{12}, \sigma_{12}]$$
$$\times [\kappa'_{12}, \sigma'_{12}]^{1/2}(n_\beta\lambda_\beta n_\alpha\lambda_\alpha \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha)$$
$$\times \begin{Bmatrix} l_\alpha & l_\alpha & \kappa'_{12} \\ \kappa_1 & \kappa_2 & k \\ l_\beta & l_\alpha & \kappa_{12} \end{Bmatrix} \begin{Bmatrix} s & s & \sigma'_{12} \\ \sigma_1 & \sigma_2 & k \\ s & s & \sigma_{12} \end{Bmatrix}$$
$$\times \sum_{K_l K_s} [K_l, K_s]^{1/2} \begin{Bmatrix} l_\beta & l_\alpha & \kappa_{12} \\ \kappa'_{12} & k & K_l \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_{12} \\ \sigma'_{12} & k & K_s \end{Bmatrix}, \tag{58}$$

and when $\hat{G}(T) = \hat{G}(\alpha\beta\alpha\alpha)$, then

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) = \tfrac{1}{2}(-1)^{k-p+\kappa'_{12}+\sigma'_{12}+\kappa_{12}+\sigma_{12}}[\kappa_{12}, \sigma_{12}]$$
$$\times [\kappa'_{12}, \sigma'_{12}]^{1/2}(n_\alpha\lambda_\alpha n_\beta\lambda_\beta \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha$$
$$\times \begin{Bmatrix} l_\alpha & l_\alpha & \kappa'_{12} \\ \kappa_1 & \kappa_2 & k \\ l_\alpha & l_\beta & \kappa_{12} \end{Bmatrix} \begin{Bmatrix} s & s & \sigma'_{12} \\ \sigma_1 & \sigma_2 & k \\ s & s & \sigma_{12} \end{Bmatrix}$$
$$\times \sum_{K_l K_s} [K_l, K_s]^{1/2} \begin{Bmatrix} l_\beta & l_\alpha & \kappa_{12} \\ \kappa'_{12} & k & K_l \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_{12} \\ \sigma'_{12} & k & K_s \end{Bmatrix}. \tag{59}$$

(6) Distributions $\beta\beta\beta\alpha$, $\beta\beta\alpha\beta$ (cases 9, 10 from table 8) (figure A1, A_5):

$$A_5 = \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} \tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi)$$
$$\times [[[a^{(l_\beta s)} \times a^{(l_\beta s)}]^{(\kappa_{12}\sigma_{12})} \times \tilde{a}^{(l_\beta s)}]^{(K_l K_s)} \times \tilde{a}^{(l_\alpha s)}]^{(kk)}_{p,-p}, \tag{60}$$

where

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) \equiv \Theta'(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi)$$
$$\equiv \Theta(n_\alpha\lambda_\alpha, n_\beta\lambda_\beta, \Xi). \tag{61}$$

When $\hat{G}(T) = \hat{G}(\beta\beta\beta\alpha)$:

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n'_i\lambda'_i, n'_j\lambda'_j, \Xi) = \tfrac{1}{2}(-1)^{k-p+\kappa'_{12}+\sigma'_{12}+l_\alpha+l_\beta}[\kappa'_{12}, \sigma'_{12}]$$
$$\times [\kappa_{12}, \sigma_{12}]^{1/2}(n_\beta\lambda_\beta n_\beta\lambda_\beta \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_\beta\lambda_\beta n_\alpha\lambda_\alpha)$$
$$\times \begin{Bmatrix} l_\beta & l_\alpha & \kappa'_{12} \\ \kappa_1 & \kappa_2 & k \\ l_\beta & l_\beta & \kappa_{12} \end{Bmatrix} \begin{Bmatrix} s & s & \sigma'_{12} \\ \sigma_1 & \sigma_2 & k \\ s & s & \sigma_{12} \end{Bmatrix}$$
$$\times \sum_{K_l K_s} [K_l, K_s]^{1/2} \begin{Bmatrix} l_\alpha & l_\beta & \kappa'_{12} \\ \kappa_{12} & k & K_l \end{Bmatrix} \begin{Bmatrix} s & s & \sigma'_{12} \\ \sigma_{12} & k & K_s \end{Bmatrix}, \tag{62}$$

and when $\hat{G}(T) = \hat{G}(\beta\beta\alpha\beta)$:

$$\tilde{\Theta}(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Xi) = \frac{1}{2}(-1)^{k-p+\kappa_{12}'+\sigma_{12}'+\kappa_{12}+\sigma_{12}}[\kappa_{12}', \sigma_{12}'] \times [\kappa_{12}, \sigma_{12}]^{1/2}(n_\beta\lambda_\beta n_\beta\lambda_\beta \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_\alpha\lambda_\alpha n_\beta\lambda_\beta) \times \begin{Bmatrix} l_\alpha & l_\beta & \kappa_{12}' \\ \kappa_1 & \kappa_2 & k \\ l_\beta & l_\beta & \kappa_{12} \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_{12}' \\ \sigma_1 & \sigma_2 & k \\ s & s & \sigma_{12} \end{Bmatrix} \times \sum_{K_l K_s} [K_l, K_s]^{1/2} \begin{Bmatrix} l_\alpha & l_\beta & \kappa_{12}' \\ \kappa_{12} & k & K_l \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_{12}' \\ \sigma_{12} & k & K_s \end{Bmatrix}. \tag{63}$$

The final analytical expressions for diagram A_6 appearing in (50), diagram A_7 in (52) and diagram A_8 in (54), are obtained after the following graphical transformations.

(i) The second quantization operators are interchanged, until (from left to right) first come the operators acting upon shell α, then correspondingly upon β, γ, δ.

(ii) The generalized Clebsch–Gordan coefficient is transformed to match the order of operators. This is performed by changing the order of angular momenta coupling at some of the nodes 1, 2, 3 (figure A1, A_6, A_7 and A_8).

We immediately write down the algebraic expressions for diagrams A_6, A_7 and A_8 (of figure A1) after transforms (i) and (ii) by applying usual generalized graphical technique (see Gaigalas *et al* 1985). Also we have to notice that Θ' is equal to $\tilde{\Theta}$ with a phase factor, which is found by transforming the diagram of the tensorial structure according to the rules (i) and (ii). Only in cases 1 and 7–10 (see table 8) does $\Theta' \equiv \tilde{\Theta}$, because there is no need to transform the tensorial structure.

As an example, let us consider in particular the case where the operator a_j acts upon the first shell $n_1\lambda_1$, operator a_i acts upon the second shell $n_2\lambda_2$, and operators $a_{i'}^{\dagger}$, $a_{j'}^{\dagger}$, act upon the third shell $n_3\lambda_3$ (see equation (1)). This is distribution 18 in table 8. We obtain the algebraic expression for distribution $\beta\alpha\gamma\gamma$ from (52). The two-particle operator for this distribution can be represented by diagram B_1 which is proportional to its tensorial part (diagram B_2) as (figure A2 B_1, B_2):

$$B_1 = \sum_{\kappa_{12}\sigma_{12}\kappa_{12}'\sigma_{12}'} \tilde{\Theta}(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) B_2, \tag{64}$$

where

$$\tilde{\Theta}(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) = \frac{1}{2}(-1)^{k-p+1}[\kappa_{12}, \sigma_{12}, \kappa_{12}', \sigma_{12}']^{1/2} \times (n_2\lambda_2 n_1\lambda_1 \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_3\lambda_3 n_3\lambda_3) \times \begin{Bmatrix} l_2 & l_3 & \kappa_1 \\ l_1 & l_3 & \kappa_2 \\ \kappa_{12} & \kappa_{12}' & k \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_1 \\ s & s & \sigma_2 \\ \sigma_{12} & \sigma_{12}' & k \end{Bmatrix}. \tag{65}$$

We use (i) for diagram B_2 (figure A2, B_2) then as in expression (64) the order of second-quantization operators is $a^{(l_2 s)} a^{(l_1 s)} \tilde{a}^{(l_3 s)} \tilde{a}^{(l_3 s)}$, so we change it according to (i) and obtain (figure A2 B_1, B_3):

$$B_1 = -\sum_{\kappa_{12}\sigma_{12}\kappa_{12}'\sigma_{12}'} \tilde{\Theta}(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) B_3. \tag{66}$$

We use (ii) for diagram B_3 then change the sign at the node 1 to finally obtain (figure A2 B_1, B_4):

$$B_1 = \sum_{\kappa_{12}\sigma_{12}\kappa_{12}'\sigma_{12}'} (-1)^{l_1+l_2+2s-\kappa_{12}-\sigma_{12}+1} \tilde{\Theta}(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) B_4$$

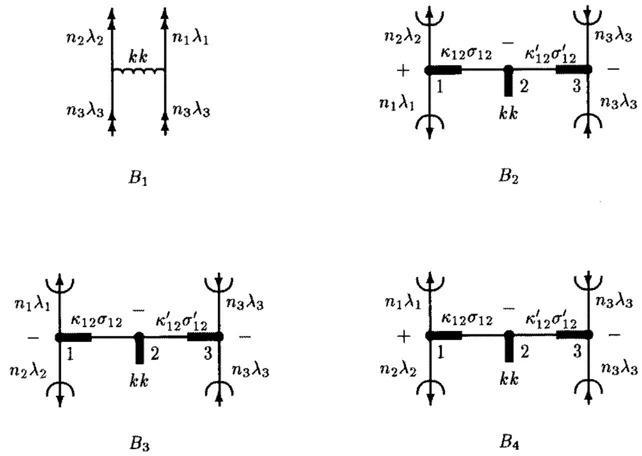

Figure A2. Diagrams for distribution $a^{(l_2s)}a^{(l_1s)}\tilde{a}^{(l_3s)}\tilde{a}^{(l_3s)}$. Diagram B_1 represents a two-particle operator G. Diagrams B_2, B_3 and B_4 represent graphical transformations. Diagram B_2 represents the tensorial part of the two-particle operator B_1 before transformations, diagram B_3 represents this tensorial part after transformation (i), and diagram B_4 represents it after transformation (ii).

$$
\begin{aligned}
&= \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} \Theta'(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) B_4 \\
&= \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} \Theta'(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) \\
&\quad \times [[a^{(l_1s)} \times a^{(l_2s)}]^{(\kappa_{12}\sigma_{12})} \times [\tilde{a}^{(l_3s)} \times \tilde{a}^{(l_3s)}]^{(\kappa'_{12}\sigma'_{12})}]^{(kk)}_{p,-p},
\end{aligned} \tag{67}
$$

where

$$
\begin{aligned}
\Theta'(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) &= \Theta(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) \\
&= (-1)^{l_1+l_2+2s-\kappa_{12}-\sigma_{12}+1} \tilde{\Theta}(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) \\
&= \frac{1}{2} \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} (-1)^{k-p+l_1+l_2-\kappa_{12}-\sigma_{12}+1} [\kappa_{12}, \sigma_{12}, \kappa'_{12}, \sigma'_{12}]^{1/2} \\
&\quad \times (n_2\lambda_2 n_1\lambda_1 \| g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)} \| n_3\lambda_3 n_3\lambda_3) \\
&\quad \times \begin{Bmatrix} l_2 & l_3 & \kappa_1 \\ l_1 & l_3 & \kappa_2 \\ \kappa_{12} & \kappa'_{12} & k \end{Bmatrix} \begin{Bmatrix} s & s & \sigma_1 \\ s & s & \sigma_2 \\ \sigma_{12} & \sigma'_{12} & k \end{Bmatrix}.
\end{aligned} \tag{68}
$$

All the graphical transformations are made and the correspondence between angular momentum diagrams B_2, B_3 and B_4 in figure A2 and algebraic expressions is defined according to the graphical approach of Gaigalas *et al* (1985).

Now, using (67) and (68) we can write down the irreducible tensorial form for the Coulomb operator with tensorial structure $\kappa_1 = \kappa_2 = k$, $\sigma_1 = \sigma_2 = 0$, $k = 0$ and the two-electron submatrix element:

$$
(n_2\lambda_2 n_1\lambda_1 \| g^{(kk0,000)}_{\text{Coulomb}} \| n_3\lambda_3 n_3\lambda_3) = 2[k]^{1/2} (l_2 \| C^{(k)} \| l_3)(l_1 \| C^{(k)} \| l_3) R_k(n_2l_2n_3l_3, n_1l_1n_3l_3). \tag{69}
$$

From (68) we have:

$$
\Theta'_{\text{Coulomb}}(n_2\lambda_2, n_1\lambda_1, n_3\lambda_3, n_3\lambda_3, \Xi) = \frac{1}{2} \sum_{\kappa_{12}\sigma_{12}\kappa'_{12}\sigma'_{12}} (-1)^{l_1+l_2-\kappa_{12}-\sigma_{12}+1} [\kappa_{12}, \sigma_{12}, \kappa'_{12}, \sigma'_{12}]^{1/2}
$$

$$
\begin{aligned}
&\times 2[k]^{1/2}(l_2\|C^{(k)}\|l_3)(l_1\|C^{(k)}\|l_3)R_k(n_2l_2n_3l_3, n_1l_1n_3l_3)\\
&\times\left\{\begin{matrix} l_2 & l_3 & k\\ l_1 & l_3 & k\\ \kappa_{12} & \kappa'_{12} & 0\end{matrix}\right\}\left\{\begin{matrix} s & s & 0\\ s & s & 0\\ \sigma_{12} & \sigma'_{12} & 0\end{matrix}\right\}\\
= &-\tfrac{1}{2}\sum_{\kappa_{12}\sigma_{12}}(-1)^{l_2+l_3-\sigma_{12}+k}[\kappa_{12},\sigma_{12}]^{1/2}(l_2\|C^{(k)}\|l_3)(l_1\|C^{(k)}\|l_3)\\
&\times R_k(n_2l_2n_3l_3, n_1l_1n_3l_3)\left\{\begin{matrix} l_2 & l_3 & k\\ l_3 & l_1 & \kappa_{12}\end{matrix}\right\}.
\end{aligned}
\tag{70}
$$

From (67), by (70), we finally obtain the following expression, in second-quantized form, for the Coulomb operator for the case $\alpha = 1$, $\beta = 2$ and $\gamma = 3$:

$$
\begin{aligned}
B_{1(\mathrm{Coulomb})} = &-\tfrac{1}{2}(-1)^{l_2+l_3+k}(l_2\|C^{(k)}\|l_3)(l_1\|C^{(k)}\|l_3)R_k(n_2l_2n_3l_3, n_1l_1n_3l_3)\\
&\times\sum_{\kappa_{12}\sigma_{12}}(-1)^{\sigma_{12}}[\kappa_{12},\sigma_{12}]^{1/2}\left\{\begin{matrix} l_2 & l_3 & k\\ l_3 & l_1 & \kappa_{12}\end{matrix}\right\}\\
&\times[[a^{(\lambda_1)}\times a^{(\lambda_2)}]^{(\kappa_{12}\sigma_{12})}\times[\tilde{a}^{(\lambda_3)}\times\tilde{a}^{(\lambda_3)}]^{(\kappa_{12}\sigma_{12})}]^{(00)}.
\end{aligned}
\tag{71}
$$

This kind of operator needs to be calculated when we are considering, for example, the matrix element

$$(3\mathrm{s}^2 3\mathrm{d}^2 L_1S_1Q_1L_2S_2Q_2LS\|H_{\mathrm{Coulomb}}\|3\mathrm{s}3\mathrm{d}3\mathrm{p}^2 L'_1S'_1Q'_1L'_2S'_2Q'_2L'_{12}S'_{12}L'_3S'_3Q'_3L'S').$$

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