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On the secondly quantized theory of the many-electron atom

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Abstract. The traditional theory of many-electron atoms and ions is based on the coefficients of fractional parentage and matrix elements of tensorial operators, composed of unit tensors. The calculation of spin-angular coefficients of radial integrals appearing in the expressions of matrix elements of arbitrary physical operators of atomic quantities has two main disadvantages: (i) the numerical codes for the calculation of spin-angular coefficients are usually very time consuming; (ii) f-shells are often omitted from programs for matrix element calculations since the tables for their coefficients of fractional parentage are very extensive.

The authors assume that a series of difficulties persisting in the traditional approach to the calculation of spin-angular parts of matrix elements can be avoided by using this secondly quantized methodology, based on angular momentum theory, on the concept of the irreducible tensorial sets, on a generalized graphical method, on quasispin and on the reduced coefficients of fractional parentage.

1. Introduction

Modern atomic spectroscopy studies the structure and properties of practically any atom of the periodic table as well as of ions of any degree of ionization. Particular attention is paid to their energy spectra. For the investigations of many-electron atoms and ions, it is of great importance to combine experimental and theoretical methods. Nowadays the possibilities of theoretical spectroscopy are much enlarged thanks to the widespread usage of powerful computers. The theoretical methods utilized must be fairly universal and must ensure reasonably accurate values of the physical quantities studied.

The many-electron atom is usually considered as a many-body problem and is described by the wavefunction constructed from the wavefunctions of one electron, moving in the central nuclear charge field and in the screening field of the remaining electrons. Then the wavefunction of this electron may be represented as a product of radial and spin-angular parts. The radial part is usually found by solving various modifications of the Hartree–Fock equations and can be represented in a numerical or analytical form (Froese Fischer 1977) whereas the angular part is expressed in terms of spherical functions. Then the wavefunction of the whole atom can be constructed in some standard way (Cowan 1981, Jucys and Savukynas 1973, Nikitin and Rudzikas 1983) starting with these one-electron functions and may later be used for the calculations of any matrix elements representing physical quantities.

During the last two decades a number of new versions of the technique (so-called Racah algebra) to cope with spin-angular parts of the wavefunctions and matrix elements have been suggested (Rudzikas 1991). Among them the second quantization and quasispin techniques

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turned out to be of particular efficiency (Judd 1967, Rudzikas and Kaniauskas 1984). The usage of graphical methods (Jucys and Bandzaitis 1977) allowed one to find general expressions even for rather complex cases of matrix elements. All this enabled one to formulate a fairly consistent and general non-relativistic and relativistic theory of the many-electron atom and the processes of its interaction with electromagnetic radiation (Rudzikas 1996). The above-mentioned methods are applicable for both the variational and perturbative approaches for various coupling schemes of spin and orbital momenta.

Practically, we have to solve the so-called eigenvalue problem

$$H\Psi = E\Psi \tag{1}$$

where Ψ is the wavefunction of the system under investigation and H is its Hamiltonian. In various versions of perturbation theory such an equation usually serves as the starting point for further refinements. It turned out that for a very large variety of atoms and their ionization degrees, the so-called Hartree–Fock–Pauli Hamiltonian leads to highly accurate energy values (Nikitin and Rudzikas 1983, Rudzikas 1996) which is why it is widely used in many methods and computer codes.

In order to calculate the energy spectrum of an atom or ion we have to find expressions for the matrix elements of all terms of the Hamiltonian considered. For complex electronic configurations, having several open shells, this is a far from trivial task. For the optimization of their expressions one has to combine the methods of the angular momentum theory, irreducible tensorial sets, tensorial products in a coupled form, coefficients of fractional parentage with the utilization of the graphical (diagrammatic) methods, second quantization and accounting for the symmetry properties of the system under consideration in the additional spaces, for example, quasispin space. This paper describes one such possibility.

Unfortunately, practical calculations show that all realistic atomic Hamiltonians do not lead straightforwardly to an eigenvalue problem (1). Actually we have to calculate all non-zero matrix elements of the Hamiltonian considered including those non-diagonal with respect to electronic configurations, then to form an energy matrix, to diagonalize it, obtaining in this way the values of the energy levels as well as the eigenfunctions (the wavefunctions in the intermediate coupling scheme). The latter may then be used to calculate electronic transitions as well as the other properties and processes. Such a necessity raises special requirements for the theory.

The total matrix element of each term of the energy operator in the case of a complex electronic configuration will consist of matrix elements, describing the interaction inside each shell (each subshell in the relativistic case) of equivalent electrons as well as between these shells. Going beyond the single-configuration approximation we have to be able to take into account in the same way non-diagonal, with respect to configurations, matrix elements. Starting at the very beginning with the second quantization and quasispin methods we are in a position to fulfil all these requirements. Below we shall describe the approach suggested in more detail.

2. Tensorial form of the operators

According to the method of second quantization (Judd 1967, Rudzikas and Kaniauskas 1984) any one-particle operator

$$F = \sum_{i,j} a_i a_j^+ \, (i|f|j) \tag{2}$$

can be expressed in the following tensorial form:

$$F = \sum_{n_i l_i, n_j l_j} F(i,j) = \sum_{n_i l_i, n_j l_j} [\kappa,\sigma]^{-1/2} \left(n_i\lambda_i||f^{(\kappa\sigma)}||n_j\lambda_j\right)\left[a^{(\lambda_i)} \times \tilde{a}^{(\lambda_j)}\right]^{(\kappa\sigma)\Gamma}_{m_\Gamma} \tag{3}$$

where $i \equiv n_i l_i s m_{l_i} m_{s_i}$, $\lambda \equiv ls$, $[\kappa,\sigma] \equiv (2\kappa+1)(2\sigma+1)$, $\left(n_i\lambda_i||f^{(\kappa\sigma)}||n_j\lambda_j\right)$ is the one-electron submatrix (reduced matrix) element of operator F and $a^{(\lambda_i)}$ is the electron creation operator. The tensor $\tilde{a}^{(\lambda_j)}$ is defined as

$$\tilde{a}^{(\lambda)}_{m_\lambda} = (-1)^{\lambda - m_\lambda} a^{(\lambda)+}_{-m_\lambda} \tag{4}$$

where $a^{(\lambda)+}_{-m_\lambda}$ is the electron annihilation operator. From a tensorial point of view it is better to consider tensor $\tilde{a}^{(\lambda_j)}$ as an electron annihilation operator (see section 4). The product of tensors $\left[a^{(\lambda_i)} \times \tilde{a}^{(\lambda_j)}\right]^{(\kappa\sigma)\Gamma}_{m_\Gamma}$ denotes the tensorial part of operator F. Here the rank κ of the orbital space is coupled to the spin-space rank σ to form a tensorial product of total spin-angular rank Γ. As we shall see, this expression is very effective for the calculation of spin-angular coefficients for any one-particle operator. This expression is a general one and the tensorial form of any one-particle physical operator may be obtained from it. For example, the spin–orbit interaction operator has the tensorial structure $\kappa = 1, \sigma = 1, \Gamma = 0$ and its submatrix element is

$$\left(n_i\lambda_i||f^{(11)}_{\text{s-o}}||n_j\lambda_j\right) = -z\alpha^2\left(\tfrac{3}{8} l_i\,(l_i+1)\,(2l_i+1)\right)^{1/2}\left(n_i l_i|1/r^3|n_j l_j\right)\delta\left(l_i, l_j\right). \tag{5}$$

Any two-particle tensorial operator

$$G = \tfrac{1}{2}\sum_{i,j,i',j'} a_i a_j a^+_{j'} a^+_{i'} (i,j|g|i',j') \tag{6}$$

can be expressed in two well known forms (Rudzikas and Kaniauskas 1984). In the first form the operators of the second quantization follow in the normal order:

$$\begin{aligned} G_{\text{I}} = &\sum_{n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j} G_{\text{I}}(iji'j') \\ &= -\tfrac{1}{2}\sum_{n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j}\ \sum_{\kappa_{12}\kappa'_{12}\sigma_{12}\sigma'_{12}}\ \sum_p (-1)^{k-p}\left[\kappa_{12},\kappa'_{12},\sigma_{12},\sigma'_{12}\right]^{1/2} \\ &\times \left(n_i\lambda_i n_j\lambda_j||g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}||n'_i\lambda'_i n'_j\lambda'_j\right) \\ &\times \begin{Bmatrix} l'_i & l'_j & \kappa'_{12} \\ \kappa_1 & \kappa_2 & k \\ l_i & l_j & \kappa_{12} \end{Bmatrix} \begin{Bmatrix} s & s & \sigma'_{12} \\ \sigma_1 & \sigma_2 & k \\ s & s & \sigma_{12} \end{Bmatrix} \\ &\times \left[\left[a^{(\lambda_i)} \times a^{(\lambda_j)}\right]^{(\kappa_{12}\sigma_{12})}\left[\tilde{a}^{(\lambda'_i)} \times \tilde{a}^{(\lambda'_j)}\right]^{(\kappa'_{12}\sigma'_{12})}\right]^{(kk)}_{\text{p-p}} \end{aligned} \tag{7}$$

where $\left(n_i\lambda_i n_j\lambda_j||g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}||n'_i\lambda'_i n'_j\lambda'_j\right)$ is the two-electron submatrix element of operator G.

In another form the second quantization operators are coupled by pairs consisting of electron creation and annihilation operators. In tensorial form:

$$\begin{aligned} G_{\text{II}} = &\sum_{n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j} G_{\text{II}}(iji'j') \\ &= \tfrac{1}{2}\sum_{n_i l_i, n_j l_j, n'_i l'_i, n'_j l'_j}\ \sum_p (-1)^{k-p}\left(n_i\lambda_i n_j\lambda_j||g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}||n'_i\lambda'_i n'_j\lambda'_j\right) \end{aligned}$$

$$\times\Big\{[\kappa_1,\kappa_2,\sigma_1,\sigma_2]^{-1/2}\Big[\Big[a^{(\lambda_i)}\times\tilde{a}^{(\lambda_i')}\Big]^{(\kappa_1\sigma_1)}\Big[a^{(\lambda_j)}\times\tilde{a}^{(\lambda_j')}\Big]^{(\kappa_2\sigma_2)}\Big]^{(kk)}_{\mathrm{p-p}}$$
$$-(-1)^{l_i+l_j'}\begin{Bmatrix}\kappa_1 & \kappa_2 & k\\ l_j' & l_i & l_j\end{Bmatrix}\begin{Bmatrix}\sigma_1 & \sigma_2 & k\\ s & s & s\end{Bmatrix}\Big[a^{(\lambda_i)}\times\tilde{a}^{(\lambda_j')}\Big]^{(kk)}_{\mathrm{p-p}}\delta(n_jl_j,n_i'l_i')\Big\}. \tag{8}$$

The expression (7) consists of only one tensorial product whereas (8) has two, but the summation in the first formula is also over intermediate ranks κ_{12}, σ_{12}, κ_{12}' and σ_{12}', and in this way complicates the calculations. The advantages or disadvantages of these alternative forms of arbitrary two-electron operator may be revealed in practical applications.

In these forms the product of the second quantization operators denotes the tensorial part of operator G. For instance, the tensorial structure of the electrostatic (Coulomb) electron interaction operator is the same as that of orbit–orbit interaction, $\kappa_1=\kappa_2=k,\sigma_1=\sigma_2=0$ (Jucys and Savukynas 1973), and only the two-electron submatrix elements $\big(n_i\lambda_in_j\lambda_j||g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}||n_i'\lambda_i'n_j'\lambda_j'\big)$ of these operators are different. In the case of electrostatic interaction:

$$\big(n_i\lambda_in_j\lambda_j||g^{(kk0,000)}_{\mathrm{Coulomb}}||n_i'\lambda_i'n_j'\lambda_j'\big)$$
$$=2\,[k]^{1/2}\big(l_i||C^{(k)}||l_i'\big)\big(l_j||C^{(k)}||l_j'\big)\,R_k\big(n_il_in_i'l_i',n_jl_jn_j'l_j'\big). \tag{9}$$

From equation (9), using (7) and (8), we finally obtain the following two secondly quantized expressions for the Coulomb operator:

$$V_{\mathrm{I}}=-\tfrac{1}{2}\sum_{n_il_in_jl_jn_i'l_i'n_j'l_j'}\sum_{\kappa_{12}\sigma_{12}k}(-1)^{l_j+l_i'+k+\kappa_{12}}\,[\kappa_{12},\sigma_{12}]^{1/2}\big(l_i||C^{(k)}||l_i'\big)$$
$$\times\big(l_j||C^{(k)}||l_j'\big)\,R_k\big(n_il_in_i'l_i',n_jl_jn_j'l_j'\big)\begin{Bmatrix}l_i & l_i' & k\\ l_j' & l_j & \kappa_{12}\end{Bmatrix}$$
$$\times\Big[\Big[a^{(\lambda_i)}\times a^{(\lambda_j)}\Big]^{(\kappa_{12}\sigma_{12})}\times\Big[\tilde{a}^{(\lambda_i')}\times\tilde{a}^{(\lambda_j')}\Big]^{(\kappa_{12}\sigma_{12})}\Big]^{(00)} \tag{10}$$

$$V_{\mathrm{II}}=\sum_{n_il_in_jl_jn_i'l_i'n_j'l_j'}\sum_{k}\big(l_i||C^{(k)}||l_i'\big)\big(l_j||C^{(k)}||l_j'\big)\,R_k\big(n_il_in_i'l_i',n_jl_jn_j'l_j'\big)$$
$$\times\Big\{[k]^{-1/2}\Big[\Big[a^{(\lambda_i)}\times\tilde{a}^{(\lambda_i')}\Big]^{(k0)}\times\Big[a^{(\lambda_j)}\times\tilde{a}^{(\lambda_j')}\Big]^{(k0)}\Big]^{(00)}$$
$$+(2[l_i])^{-1/2}\Big[a^{(\lambda_i)}\times\tilde{a}^{(\lambda_j')}\Big]^{(00)}\delta(n_jl_j,n_i'l_i')\Big\}. \tag{11}$$

The tensorial expressions for orbit–orbit and other physical operators in second quantization form may be obtained in the same manner.

It is worth mentioning that the expressions (10) and (11) embrace, already in an operator form, the interaction terms both the diagonal ones, relative to configurations, and the non-diagonal ones. Non-diagonal terms define the interaction between all the possible electron distributions over the configurations considered, differing by quantum numbers for not more than two electrons.

The merits of representing operators in one form or another (10) or (11) are mostly determined by the technique used to find their matrix elements and the quantities in terms of which they are expressed.

3. Generalized graphical method

In this section we shall sketch the generalized version of the graphical technique, in which not only one- and two-particle operators are presented in tensorial form (such graphs are

analogous to Feynman–Goldstone diagrams but they do not depend on magnetic quantum numbers (Merkelis *et al* 1986a, b)), but which also allows us to represent graphically any tensorial product of the second quantization operators and to perform graphically the operations with the secondly quantized operators as well as with their tensorial products (Gaigalas *et al* 1985, Gaigalas 1985, Gaigalas and Merkelis 1987). Such a graphical technique is most suitable for representing any one- and two-particle operator already presented in tensorial form and to find general expressions for their matrix elements.

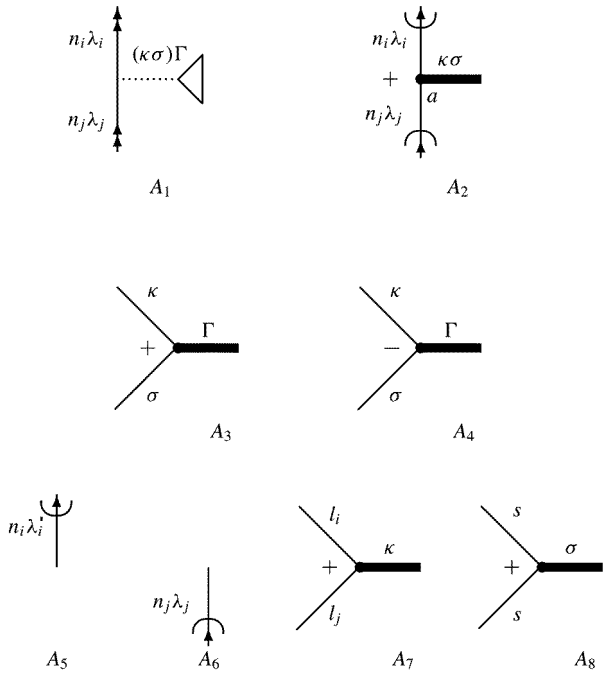

Figure 1. Diagrams for one-particle operators.

In this methodology the item under the summation sign of the one-particle operator (3) has the following graphical form:

$$F(i,j) = A_1 = [\kappa,\sigma]^{-1/2}\left(n_i\lambda_i||f^{(\kappa\sigma)}||n_j\lambda_j\right)A_2A_3 \tag{12}$$

where the diagrams A_1, A_2 and A_3 are presented in figure 1. As we see, the diagram of the operator itself, namely A_1, is similar to the usual Feynman–Goldstone diagram (Lindgren and Morrison 1982), although here the summation over magnetic quantum numbers m_λ is performed. The product of the diagrams A_2, A_3 represents the tensorial structure of the operator:

$$A_2A_3 = \left[a^{(\lambda_i)} \times \tilde{a}^{(\lambda_j)}\right]^{(\kappa\sigma)\Gamma}_{m_\Gamma} = \sum_{m_\kappa,m_\sigma}\left[a^{(\lambda_i)} \times \tilde{a}^{(\lambda_j)}\right]^{(\kappa\sigma)}_{m_\kappa m_\sigma}\begin{bmatrix}\kappa & \sigma & \Gamma\\ m_\kappa & m_\sigma & m_\Gamma\end{bmatrix} \tag{13}$$

where A_2 equals

$$A_2 = \left[a^{(\lambda_i)} \times \tilde{a}^{(\lambda_j)}\right]^{(\kappa\sigma)}_{m_\kappa m_\sigma} \tag{14}$$

whereas A_3, by Jucys and Bandzaitis (1977), is equal to

$$A_3 = \begin{bmatrix}\kappa & \sigma & \Gamma\\ m_\kappa & m_\sigma & m_\Gamma\end{bmatrix}. \tag{15}$$

The heavy line in diagram A_3 represents the resultant momentum Γ whereas the plus sign of the vertex means that the momenta κ and σ are coupled into the resultant Γ in a counterclockwise direction. From the symmetry properties of the Clebsch–Gordan coefficients the equality follows:

$$A_3 = (-1)^{\kappa+\sigma-\Gamma} A_4 \,. \tag{16}$$

Then we can conclude that, if we change the sign of any vertex, then the phase multiplier of the form $(-1)^{\kappa+\sigma-\Gamma}$ occurs.

The electron creation operator $a^{(\lambda_i)}$ has the following graphical form (figure 1, A_5):

$$a^{(\lambda_i)} = A_5 \tag{17}$$

whereas $\tilde{a}^{(\lambda_j)}$

$$\tilde{a}^{(\lambda_j)} = A_6 \,. \tag{18}$$

Thus, it is obvious that the diagram A_2 consists of the second quantization operators $a^{(\lambda_i)}$ and $\tilde{a}^{(\lambda_j)}$ as well as of the Clebsch–Gordan coefficients

$$A_7 = \begin{bmatrix} l_i & l_j & \kappa \\ m_{l_i} & m_{l_j} & m_\kappa \end{bmatrix} \qquad A_8 = \begin{bmatrix} s & s & \sigma \\ m_s & m_s & m_\sigma \end{bmatrix} \tag{19}$$

which couple these operators into a tensorial product and which may be obtained from the diagram A_2 if to omit the graphical symbols of the second quantization operators. It is necessary to bear in mind that, while writing down the algebraic expression from the diagram A_2, in the tensorial product the first element must always be the second quantization operator, which is above the vertex 'a', whereas the second place must be occupied by the operator, which is below the vertex 'a' in diagram A_2. The scheme of their coupling into the tensorial product is defined by the sign of the vertex.

The first form (7) of the two-particle operator $G_1(iji'j')$ is represented by the following

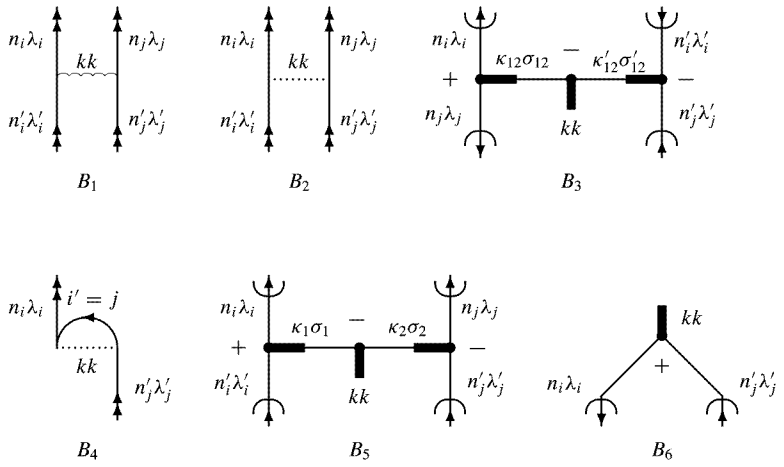

Figure 2. Diagrams for two-particle operators.

diagram (figure 2, B_1):

$$G_{\rm I}(iji'j') = B_1 = -\tfrac{1}{2}\sum_{\kappa_{12}\kappa'_{12}\sigma_{12}\sigma'_{12}}\sum_{p}(-1)^{k-p}\,[\kappa_1,\kappa_2,\sigma_1,\sigma_2]^{1/2}$$
$$\times\left(n_i\lambda_i n_j\lambda_j||g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}||n'_i\lambda'_i n'_j\lambda'_j\right)\begin{Bmatrix} l'_i & l'_j & \kappa'_{12}\\ \kappa_1 & \kappa_2 & k\\ l_i & l_j & \kappa_{12}\end{Bmatrix}$$
$$\times\begin{Bmatrix} s & s & \sigma'_{12}\\ \sigma_1 & \sigma_2 & k\\ s & s & \sigma_{12}\end{Bmatrix}B_3 \tag{20}$$

whereas the second (8):

$$G_{\rm II}(iji'j') = B_2 + B_4$$
$$= \tfrac{1}{2}\sum_{p}(-1)^{k-p}\left(n_i\lambda_i n_j\lambda_j||g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}||n'_i\lambda'_i n'_j\lambda'_j\right)$$
$$\times\left\{[\kappa_1,\kappa_2,\sigma_1,\sigma_2]^{-1/2}\,B_5 - (-1)^{l_i+l'_j}\begin{Bmatrix}\kappa_1 & \kappa_2 & k\\ l'_j & l_i & l_j\end{Bmatrix}\right.$$
$$\left.\times\begin{Bmatrix}\sigma_1 & \sigma_2 & k\\ s & s & s\end{Bmatrix}\delta\left(n_j l_j, n'_i l'_i\right)B_6\right\}. \tag{21}$$

We emphasize here that the winding line of interaction in the Feynman–Goldstone diagram corresponds to the operators of second quantization in the normal order (figure 2, B_1), whereas the dotted interaction line indicates that the second quantization operators are ordered as pairs of creation–annihilation operators. In the latter case first is the pair on the left-hand side of a Feynman–Goldstone diagram (figure 2, B_2). Such a notation of two kinds for an interaction line is meaningful only for two-particle (or more) operators, since for any one-particle operator both the winding and dotted lines correspond to the same order of creation and annihilation operators.

From expressions (20) and (21) we see that the two-particle operator in the first form is represented by one Feynman–Goldstone diagram B_1, whereas in the second it is represented by two diagrams B_2 and B_4. The diagrams, corresponding to the tensorial product, have the following algebraic expressions:

$$B_3 = \left[\left[a^{(\lambda_i)}\times a^{(\lambda_j)}\right]^{(\kappa_{12}\sigma_{12})}\times\left[\tilde{a}^{(\lambda'_i)}\times\tilde{a}^{(\lambda'_j)}\right]^{(\kappa'_{12}\sigma'_{12})}\right]^{(kk)}_{\rm p-p} \tag{22}$$

$$B_5 = \left[\left[a^{(\lambda_i)}\times\tilde{a}^{(\lambda'_i)}\right]^{(\kappa_1\sigma_1)}\times\left[a^{(\lambda_j)}\times\tilde{a}^{(\lambda'_j)}\right]^{(\kappa_2\sigma_2)}\right]^{(kk)}_{\rm p-p} \tag{23}$$

$$B_6 = \left[a^{(\lambda_i)}\times\tilde{a}^{(\lambda'_j)}\right]^{(kk)}_{\rm p-p}. \tag{24}$$

Thus, the method of obtaining algebraic expressions from the diagrams B_3, B_5 and B_6 is similar to the case of diagram A_2. The positions of the second quantization operators in the diagram define their order in the tensorial product: the first place in the tensorial product occupies the upper right second quantization operator, the second place occupies the lower right operator, after them the upper left and lower left operators follow. The angular momenta diagram defines their coupling scheme into a tensorial product.

Thus, obeying these rules it is possible to easily find the algebraic counterparts of the diagrams, not forgetting that the arrangement of the operators must not contradict their coupling order, i.e. only neighbouring second quantization operators are coupled into a tensorial product and their disposition order corresponds to the coupling scheme. Otherwise some graphical operations are necessary. Let us present the simplest of them below as the

example for the case when we have to change the disposition of the second quantization operators and the coupling scheme in the tensorial product.

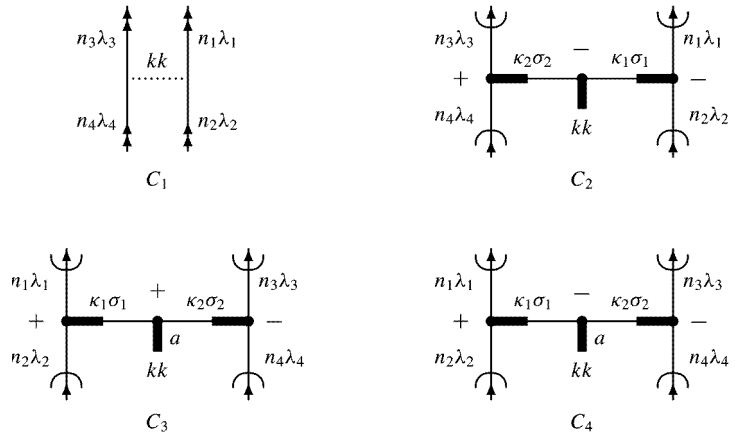

Figure 3. Diagrams for graphical transformations.

Suppose, we have the following correspondence between diagrams (figure 3):

$$C_1 \longrightarrow C_2 \tag{25}$$

in which the second quantization operators are in the order $a^{(\lambda_3)}\,\tilde{a}^{(\lambda_4)}\,a^{(\lambda_1)}\,\tilde{a}^{(\lambda_2)}$. Our goal is to obtain the diagram corresponding to the order $a^{(\lambda_1)}\,\tilde{a}^{(\lambda_2)}\,a^{(\lambda_3)}\,\tilde{a}^{(\lambda_4)}$. Bearing in mind that the second quantization operators anticommute with each other and they all act on different electronic shells and we are not changing the order of their coupling into a tensorial product, we arrive at

$$C_1 \longrightarrow (-1)^4 C_3 = C_3\,. \tag{26}$$

Let us also discuss another situation: we have defined the disposition of the operators and we want to couple them into a certain tensorial product. Suppose that we want to represent graphically the following tensorial product:

$$\left[\left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_1\sigma_1)} \times \left[a^{(\lambda_3)} \times \tilde{a}^{(\lambda_4)}\right]^{(\kappa_2\sigma_2)}\right]^{(\kappa\sigma)}. \tag{27}$$

For this purpose we have to rearrange the generalized Clebsch–Gordan coefficient, which is defining the scheme of coupling of the operators into the tensorial product. It is easy to notice that this coefficient will properly define the tensorial product, if we change the sign of the vertex 'a' in diagram C_3. Making use of (16) we find

$$C_1 \longrightarrow (-1)^{\kappa_1+\kappa_2-\kappa+\sigma_1+\sigma_2-\sigma} C_4\,. \tag{28}$$

The procedures described are fairly simple, however they are sufficient for the majority of cases. The more complete description of this generalized graphical approach may be found in Gaigalas *et al* (1985), Gaigalas (1985) and Gaigalas and Merkelis (1987).

4. Quasispin formalism

A wavefunction with u shells in LS coupling may be denoted in the form

$$\psi_u\,(LSM_LM_S) \equiv |n_1 l_1^{N_1} n_2 l_2^{N_2} \ldots n_u l_u^{N_u} \alpha_1 L_1 S_1 \alpha_2 L_2 S_2 \ldots \alpha_u L_u S_u A L S M_L M_S) \tag{29}$$

where A stands for all intermediate quantum numbers, depending on the order of coupling of momenta $\alpha_i L_i S_i$.

As we shall see later on, it is very convenient for the calculations of matrix elements to use quasispin formalism. Then $a^{(\lambda)}_{m_\lambda}$ and $\tilde{a}^{(\lambda)}_{m_\lambda}$ are components of the tensor $a^{(q\lambda)}_{m_q m_\lambda}$, having in additional 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 $a^{(q\lambda)}_{-\frac{1}{2}m_\lambda} = \tilde{a}^{(ls)}_{m_l m_s}$.

In the quasispin representation, for a wavefunction of the shell of equivalent electrons $|nl^N \alpha LS)$ a label Q (quasispin momentum of the shell) is introduced, which is related to the seniority quantum number ν, namely, $Q = (2l + 1 - \nu)/2$, and its projection, $M_Q = (N - 2l - 1)/2$. Here α denotes all additional quantum numbers needed for the one-to-one classification of the energy levels. Then, we can rewrite the wavefunction (29) as

$$\psi_u (LSM_L M_S) \equiv |n_1 l_1 n_2 l_2 \ldots n_u l_u \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} \ldots \times \alpha_u L_u S_u Q_u M_{Q_u} A L S M_L M_S) . \tag{30}$$

Making use of the Wigner–Eckart theorem in quasispin space of a shell l^N,

$$\left(l\ \alpha Q L S M_Q || T^{(qls)}_{m_q} || l\ \alpha' Q' L' S' M'_Q\right) = (-1)^{2q} [Q]^{-1/2} \times \begin{bmatrix} Q' & q & Q \\ M'_Q & m_q & M_Q \end{bmatrix} \left(l\ \alpha Q L S || T^{(qls)} || l\ \alpha' Q' L' S'\right) \tag{31}$$

it is possible to define the notions of a completely reduced matrix element $(l\ \alpha Q L S || T^{(qls)} || l\ \alpha' Q' L' S')$ and subcoefficient of fractional parentage (reduced coefficient of fractional parentage) $(l\ \alpha Q L S || a^{(qls)} || l\ \alpha' Q' L' S')$. In equation (31) $T^{(qls)}_{m_q}$ is any tensor with rank q and its projection m_q in quasispin space and on the right-hand side of this equation only the Clebsch–Gordan coefficient $\begin{bmatrix} Q' & q & Q \\ M'_Q & m_q & M_Q \end{bmatrix}$ depends on the number N of equivalent electrons.

According to Rudzikas and Kaniauskas (1984) we have the following relation between the coefficients of fractional parentage and completely reduced matrix elements $(l\ \alpha Q L S || a^{(qls)} || l\ \alpha' Q' L' S')$ of the operator of second quantization $a^{(qls)}$:

$$\left(l^N\ \alpha Q L S || l^{N-1}\ \left(\alpha' Q' L' S'\right) l\right) = (-1)^{N-1} \left(N [Q, L, S]\right)^{-1/2} \times \begin{bmatrix} Q' & \frac{1}{2} & Q \\ M'_Q & \frac{1}{2} & M_Q \end{bmatrix} (l\ \alpha Q L S || a^{(qls)} || l\ \alpha' Q' L' S') . \tag{32}$$

Tables of numerical values of $(l\ \alpha Q L S || a^{(qls)} || l\ \alpha Q' L' S')$ are presented in Rudzikas and Kaniauskas (1984) when $l = 0, 1, 2$. For the tensorial product of two one-electron operators, the submatrix element equals

$$\left(nl^N\ \alpha Q L S || \left[a^{(q\lambda)}_{m_{q1}} \times a^{(q\lambda)}_{m_{q2}}\right]^{(k_1 k_2)} || nl^{N'}\ \alpha' Q' L' S'\right) = \sum_{\epsilon, m_\epsilon} [Q]^{-1/2} \begin{bmatrix} q & q & \epsilon \\ m_{q1} & m_{q2} & m_\epsilon \end{bmatrix} \begin{bmatrix} Q' & \epsilon & Q \\ M'_Q & m_\epsilon & M_Q \end{bmatrix} \times \left(nl\ \alpha Q L S || W^{(\epsilon k_1 k_2)} || nl\ \alpha' Q' L' S'\right) . \tag{33}$$

On the right-hand side of equations (32) and (33) only the Clebsch–Gordan coefficient $\begin{bmatrix} Q' & \epsilon & Q \\ M'_Q & m_\epsilon & M_Q \end{bmatrix}$ depends on the number N of equivalent electrons.

$\left(nl\ \alpha Q L S || W^{(\epsilon k_1 k_2)} || nl\ \alpha' Q' L' S'\right)$ denotes a reduced (in quasispin space) submatrix element (completely reduced matrix element) of the triple tensor $W^{(\epsilon k_1 k_2)}(nl, nl) = \left[a^{(qls)} \times\right.$

$a^{(qls)}\big]^{(\epsilon k_1 k_2)}$. It is related to the completely reduced coefficients (subcoefficients) of fractional parentage in the following way:

$$\begin{aligned}\big(nl\ \alpha QLS|||W^{(\epsilon k_1 k_2)}|||nl\ \alpha' Q' L' S'\big) &= (-1)^{Q+L+S+Q'+L'+S'+\epsilon+k_1+k_2}\,[\epsilon, k_1, k_2]^{1/2} \\ &\times \sum_{\alpha'' Q'' L'' S''} \big(l\ \alpha QLS|||a^{(qls)}|||l\ \alpha'' Q'' L'' S''\big) \\ &\times \big(l\ \alpha'' Q'' L'' S''|||a^{(qls)}|||l\ \alpha' Q' L' S'\big) \\ &\times \begin{Bmatrix} q & q & \epsilon \\ Q' & Q & Q'' \end{Bmatrix} \begin{Bmatrix} l & l & k_1 \\ L' & L & L'' \end{Bmatrix} \begin{Bmatrix} s & s & k_2 \\ S' & S & S'' \end{Bmatrix}. \end{aligned} \tag{34}$$

So, by applying the quasispin method for calculating the matrix elements of any operator, we can use the reduced coefficients of fractional parentage or the tensors (for example, $W^{(\epsilon k_1 k_2)}\,(nl, nl)$), which are independent of the occupation number of the shell for a given ν. The main advantage of this approach is that the standard data tables in such a case will be much smaller in comparison with tables of the usual coefficients and, therefore, many summations will be less time consuming. Also one can see that in such an approach the submatrix elements of standard tensors and subcoefficients of fractional parentage can actually be treated in a uniform way as they are all completely reduced matrix elements of the second quantization operators. Hence, the methodology of calculation of matrix elements will be much more universal in comparison with the traditional one.

5. Matrix elements in the case of two open shells of equivalent electrons

The aim of this section is to illustrate the usage of the above-mentioned methodology to obtain the expressions for matrix elements of a two-particle operator, when the wavefunction (30) has two open shells $n_1 l_1^{N_1}$ and $n_2 l_2^{N_2}$. Then it may be written as

$$\psi_2\,(LSM_L M_S) \equiv |n_1 l_1 n_2 l_2 \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LSM_L M_S)\,. \tag{35}$$

To find the numerical value of the physical quantity of a two-electron operator one ought to have the expressions for its matrix elements within each shell of equivalent electrons and between each pair of shells, including non-diagonal, with respect to configurations, matrix elements.

While calculating the diagonal matrix elements between functions (35), the quantum numbers $n_i\lambda_i, n_i'\lambda_i', n_j\lambda_j, n_j'\lambda_j'$ in two alternative expressions (7), (8) acquire the following values:

(i) $n_i\lambda_i = n_i'\lambda_i' = n_j\lambda_j = n_j'\lambda_j' = n_1 l_1 s$. (All the operators of the second quantization act upon the first shell.)

(ii) $n_i\lambda_i = n_i'\lambda_i' = n_j\lambda_j = n_j'\lambda_j' = n_2 l_2 s$. (All the operators of the second quantization act upon the second shell.)

(iii) $n_i\lambda_i = n_i'\lambda_i' = n_1 l_1 s,\ n_j\lambda_j = n_j'\lambda_j' = n_2 l_2 s$.

(iv) $n_j\lambda_j = n_j'\lambda_j' = n_1 l_1 s,\ n_i\lambda_i = n_i'\lambda_i' = n_2 l_2 s$.

(v) $n_i\lambda_i = n_j'\lambda_j' = n_1 l_1 s,\ n_i'\lambda_i' = n_j\lambda_j = n_2 l_2 s$.

(vi) $n_i'\lambda_i' = n_j\lambda_j = n_1 l_1 s,\ n_i\lambda_i = n_j'\lambda_j' = n_2 l_2 s$.

In the first case the matrix elements of the operator in the first (using (7)) and the second (using (8)) forms are equal, respectively,

$$\begin{aligned}\big(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LSM_L M_S|G_1(1111) \\ \times |n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1' L_1' S_1' Q_1' M_{Q_1} \alpha_2' L_2' S_2' Q_2' M_{Q_2} L'S'M_L'M_S'\big)\end{aligned}$$

$$
\begin{aligned}
&= -\tfrac{1}{2}\sum_{\kappa_{12}\kappa'_{12}\sigma_{12}\sigma'_{12}}\sum_{p}(-1)^{k-p}\,[\kappa_1,\kappa_2,\sigma_1,\sigma_2]^{1/2}\\
&\quad\times\left(n_1\lambda_1 n_1\lambda_1||g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}||n_1\lambda_1 n_1\lambda_1\right)\\
&\quad\times\left\{\begin{array}{ccc} l_1 & l_1 & \kappa'_{12}\\ \kappa_1 & \kappa_2 & k\\ l_1 & l_1 & \kappa_{12}\end{array}\right\}\left\{\begin{array}{ccc} s & s & \sigma'_{12}\\ \sigma_1 & \sigma_2 & k\\ s & s & \sigma_{12}\end{array}\right\}\\
&\quad\times(n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha_1 L_1 S_1 Q_1 M_{Q_1}\alpha_2 L_2 S_2 Q_2 M_{Q_2} L S M_L M_S|\\
&\quad\times\left[\left[a^{(\lambda_1)}\times a^{(\lambda_1)}\right]^{(\kappa_{12}\sigma_{12})}\times\left[\tilde{a}^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\right]^{(\kappa'_{12}\sigma'_{12})}\right]^{(kk)}_{\mathrm{p-p}}\\
&\quad\times|n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1}\alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L' S' M'_L M'_S) \qquad (36)
\end{aligned}
$$

$$
\begin{aligned}
&(n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha_1 L_1 S_1 Q_1 M_{Q_1}\alpha_2 L_2 S_2 Q_2 M_{Q_2} L S M_L M_S|G_{\mathrm{II}}(1111)\\
&\quad\times|n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1}\alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L' S' M'_L M'_S)\\
&= \tfrac{1}{2}\sum_{p}(-1)^{k-p}\left(n_1\lambda_1 n_1\lambda_1||g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}||n_1\lambda_1 n_1\lambda_1\right)\\
&\quad\times\Bigg\{[\kappa_1,\kappa_2,\sigma_1,\sigma_2]^{-1/2}\\
&\quad\times(n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha_1 L_1 S_1 Q_1 M_{Q_1}\alpha_2 L_2 S_2 Q_2 M_{Q_2} L S M_L M_S|\\
&\quad\times\left[\left[a^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\right]^{(\kappa_1\sigma_1)}\times\left[a^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\right]^{(\kappa_2\sigma_2)}\right]^{(kk)}_{\mathrm{p-p}}\\
&\quad\times|n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1}\alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L' S' M'_L M'_S)\\
&\quad-\left\{\begin{array}{ccc} \kappa_1 & \kappa_2 & k\\ l_1 & l_1 & l_1\end{array}\right\}\left\{\begin{array}{ccc} \sigma_1 & \sigma_2 & k\\ s & s & s\end{array}\right\}\\
&\quad\times(n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha_1 L_1 S_1 Q_1 M_{Q_1}\alpha_2 L_2 S_2 Q_2 M_{Q_2} L S M_L M_S|\\
&\quad\times\left[a^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\right]^{(kk)}_{\mathrm{p-p}}\\
&\quad\times|n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1}\alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L' S' M'_L M'_S)\Bigg\}. \qquad (37)
\end{aligned}
$$

Schematically these expressions may be written down as

$$
\begin{aligned}
&(n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha_1 L_1 S_1 Q_1 M_{Q_1}\alpha_2 L_2 S_2 Q_2 M_{Q_2} L S M_L M_S|G(1111)\\
&\quad\times|n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1}\alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L' S' M'_L M'_S)\\
&= \sum_{\kappa_{12},\sigma_{12},\kappa'_{12}\sigma'_{12}}\Theta\left(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1\right)\\
&\quad\times(n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha_1 L_1 S_1 Q_1 M_{Q_1}\alpha_2 L_2 S_2 Q_2 M_{Q_2} L S M_L M_S|\\
&\quad\times A^{(kk)}_{\mathrm{p-p}}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)\\
&\quad\times|n_1 l_1^{N_1} n_2 l_2^{N_2}\alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1}\alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L' S' M'_L M'_S) \qquad (38)
\end{aligned}
$$

where $\Theta(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)$ is proportional to the radial part of an operator and $A^{(kk)}_{\mathrm{p-p}}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)$ to the spin-angular part of it. In the first form

$$
\begin{aligned}
&A^{(kk)}_{\mathrm{p-p}}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)\\
&\quad=\left[\left[a^{(\lambda_1)}\times a^{(\lambda_1)}\right]^{(\kappa_{12}\sigma_{12})}\times\left[\tilde{a}^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\right]^{(\kappa'_{12}\sigma'_{12})}\right]^{(kk)}_{\mathrm{p-p}} \qquad (39)
\end{aligned}
$$

whereas in the second form ($\kappa_{12}=\kappa_1, \sigma_{12}=\sigma_1, \kappa'_{12}=\kappa_2, \sigma'_{12}=\sigma_2$)

$$A^{(kk)}_{\mathrm{p-p}}(\kappa_1,\sigma_1,\kappa_2,\sigma_2,n_1,\lambda_1)=\Bigg\{[\kappa_1,\kappa_2,\sigma_1,\sigma_2]^{-1/2} \times\Big[\Big[a^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\Big]^{(\kappa_1\sigma_1)}\times\Big[a^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\Big]^{(\kappa_2\sigma_2)}\Big]^{(kk)}_{\mathrm{p-p}} -\begin{Bmatrix}\kappa_1&\kappa_2&k\\ l_1&l_1&l_1\end{Bmatrix}\begin{Bmatrix}\sigma_1&\sigma_2&k\\ s&s&s\end{Bmatrix}\Big[a^{(\lambda_1)}\times\tilde{a}^{(\lambda_1)}\Big]^{(kk)}_{\mathrm{p-p}}\Bigg\}. \tag{40}$$

So, in order to calculate the spin-angular parts of matrix elements of operators (7), (8), we have to obtain first the matrix elements of operators $A^{(kk)}_{\mathrm{p-p}}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)$. By using the Wigner–Eckart theorem, we find

$$\begin{aligned}(n_1l_1^{N_1}n_2l_2^{N_2}\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LSM_LM_S|&\\ \times A^{(kk)}_{\mathrm{p-p}}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)&\\ \times|n_1l_1^{N_1}n_2l_2^{N_2}\alpha'_1L'_1S'_1Q'_1M_{Q_1}\alpha'_2L'_2S'_2Q'_2M_{Q_2}L'S'M'_LM'_S)&\\ =[L,S]^{-1/2}\begin{bmatrix}L'&k&L\\ M_{L'}&p&M_L\end{bmatrix}\begin{bmatrix}S'&k&S\\ M_{S'}&-p&M_S\end{bmatrix}&\\ \times(n_1l_1^{N_1}n_2l_2^{N_2}\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LS||&\\ \times A^{(kk)}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)&\\ \times||n_1l_1^{N_1}n_2l_2^{N_2}\alpha'_1L'_1S'_1Q'_1M_{Q_1}\alpha'_2L'_2S'_2Q'_2M_{Q_2}L'S')\,.&\end{aligned} \tag{41}$$

Then we proceed with analysing the submatrix elements. As the operator $A^{(kk)}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)$ acts here upon the first shell only, then, using the expression (4.7) from Jucys and Savukynas (1973), namely,

$$\begin{aligned}(\alpha_1j_1\alpha_2j_2j||A^{(k)}_1||\alpha_1j_1\alpha_2j_2j)&=\delta\left(\alpha_2j_2,\alpha'_2j'_2\right)(-1)^{j_1+j_2+j'+k}\\ &\times[j,j']^{1/2}(\alpha_1j_1||A^{(k)}_1||\alpha_1j_1)\begin{Bmatrix}j_1&j&j_2\\ j'&j'_1&k\end{Bmatrix}\end{aligned} \tag{42}$$

we obtain

$$\begin{aligned}(n_1l_1^{N_1}n_2l_2^{N_2}\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LS||&\\ \times A^{(kk)}\left(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1\right)&\\ \times||n_1l_1^{N_1}n_2l_2^{N_2}\alpha'_1L'_1S'_1Q'_1M_{Q_1}\alpha'_2L'_2S'_2Q'_2M_{Q_2}L'S')&\\ =(-1)^{L_1+S_1+L_2+S_2+L'+S'+2k}[L,S,L',S']^{1/2}&\\ \times\begin{Bmatrix}L_1&L&L_2\\ L'&L'_1&k\end{Bmatrix}\begin{Bmatrix}S_1&S&S_2\\ S'&S'_1&k\end{Bmatrix}&\\ \times(n_1l_1^{N_1}\,\alpha_1Q_1L_1S_1||A^{(kk)}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)&\\ \times||n_1l_1^{N_1}\,\alpha'_1Q'_1L'_1S'_1)\,.&\end{aligned} \tag{43}$$

Then there remains only to obtain the formulae for the following submatrix elements:

$$(nl^N\,\alpha QLS||\left[a^{(\lambda)}\times\tilde{a}^{(\lambda)}\right]^{(kk)}||nl^N\,\alpha'Q'L'S') \tag{44}$$

$$(nl^N\,\alpha QLS||\Big[\Big[a^{(\lambda)}\times\tilde{a}^{(\lambda)}\Big]^{(\kappa_1\sigma_1)}\times\Big[a^{(\lambda)}\times\tilde{a}^{(\lambda)}\Big]^{(\kappa_2\sigma_2)}\Big]^{(kk)}||nl^N\,\alpha'Q'L'S') \tag{45}$$

$$\begin{aligned}(nl^N\,\alpha QLS||\Big[\Big[a^{(\lambda)}\times a^{(\lambda)}\Big]^{(\kappa_{12}\sigma_{12})}\times\Big[\tilde{a}^{(\lambda)}\times\tilde{a}^{(\lambda)}\Big]^{(\kappa'_{12}\sigma'_{12})}\Big]^{(kk)}&\\ \times||nl^N\,\alpha'Q'L'S')\,.&\end{aligned} \tag{46}$$

Using the expressions (33) and (34), we straightforwardly find the value of a submatrix element (44). The values of submatrix elements (45), (46) follow directly from the expression (2.28) of Jucys and Savukynas (1973),

$$(\alpha j||\left[A^{(k_1)}\times B^{(k_2)}\right]^{(k)}||\alpha' j') = (-1)^{j+j'+k}\,[k]^{1/2} \times\sum_{\alpha'' j''}(\alpha j||A^{(k_1)}||\alpha'' j'')(\alpha'' j''||B^{(k_2)}||\alpha' j')\left\{\begin{array}{ccc} k_1 & k_2 & k \\ j' & j & j''\end{array}\right\}. \tag{47}$$

So we have

$$\begin{aligned}(nl^N\,\alpha QLS||&\left[\left[a^{(q\lambda)}_{m_{q1}}\times a^{(q\lambda)}_{m_{q2}}\right]^{(\kappa_1\sigma_1)}\times\left[a^{(q\lambda)}_{m_{q3}}\times a^{(q\lambda)}_{m_{q4}}\right]^{(\kappa_2\sigma_2)}\right]^{(kk)}\\ &\times||nl^{N'}\,\alpha' Q'L'S') = (-1)^{L+S+L'+S'+2k}[k]\\ &\times\sum_{\alpha'' Q''L''S''}\left\{\begin{array}{ccc}\kappa_1 & \kappa_2 & k\\ L' & L & L''\end{array}\right\}\left\{\begin{array}{ccc}\sigma_1 & \sigma_2 & k\\ S' & S & S''\end{array}\right\}\\ &\times(nl^N\,\alpha QLS||\left[a^{(q\lambda)}_{m_{q1}}\times a^{(q\lambda)}_{m_{q2}}\right]^{(\kappa_1\sigma_1)}||nl^{N''}\,\alpha'' Q''L''S'')\\ &\times(nl^{N''}\,\alpha'' Q''L''S''||\left[a^{(q\lambda)}_{m_{q3}}\times a^{(q\lambda)}_{m_{q4}}\right]^{(\kappa_2\sigma_2)}||nl^{N'}\,\alpha' Q'L'S').\end{aligned} \tag{48}$$

Schematically we can express the matrix element in the second case, when the operators of second quantization act upon the second shell, as follows:

$$\begin{aligned}(n_1l_1^{N_1}n_2l_2^{N_2}&\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LSM_LM_S|G(2222)\\ &\times|n_1l_1^{N_1}n_2l_2^{N_2}\alpha'_1L'_1S'_1Q'_1M_{Q_1}\alpha'_2L'_2S'_2Q'_2M_{Q_2}L'S'M'_LM'_S)\\ =&\sum_{\kappa_{12},\sigma_{12},\kappa'_{12}\sigma'_{12}}\Theta(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_2,\lambda_2)\\ &\times(n_1l_1^{N_1}n_2l_2^{N_2}\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LSM_LM_S|\\ &\times A^{(kk)}_{\text{p–p}}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_2,\lambda_2)\\ &\times|n_1l_1^{N_1}n_2l_2^{N_2}\alpha'_1L'_1S'_1Q'_1M_{Q_1}\alpha'_2L'_2S'_2Q'_2M_{Q_2}L'S'M'_LM'_S)\end{aligned} \tag{49}$$

and find its value by using the Wigner–Eckart theorem, expressions (4.9), (2.28) from Jucys and Savukynas (1973) as well as (33) and (34).

Differently from the first and the second cases, in the third ($n_i\lambda_i = n'_i\lambda'_i = n_1l_1s,\ n_j\lambda_j = n'_j\lambda'_j = n_2l_2s$) and the fourth ($n_i\lambda_i = n'_i\lambda'_i = n_2l_2s,\ n_j\lambda_j = n'_j\lambda'_j = n_1l_1s$) cases the first tensorial form (7) is not convenient for calculating the matrix elements. This is related to the fact that the spin-angular parts of matrix elements do not have the shape of any expression below:

$$\begin{aligned}(n_1l_1^{N_1}n_2l_2^{N_2}&\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LS||\\ &\times A^{(kk)}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_1,\lambda_1)\\ &\times||n_1l_1^{N_1}n_2l_2^{N_2}\alpha'_1L'_1S'_1Q'_1M_{Q_1}\alpha'_2L'_2S'_2Q'_2M_{Q_2}L'S')\end{aligned} \tag{50}$$

$$\begin{aligned}(n_1l_1^{N_1}n_2l_2^{N_2}&\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LS||\\ &\times A^{(kk)}(\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12},n_2,\lambda_2)\\ &\times||n_1l_1^{N_1}n_2l_2^{N_2}\alpha'_1L'_1S'_1Q'_1M_{Q_1}\alpha'_2L'_2S'_2Q'_2M_{Q_2}L'S')\end{aligned} \tag{51}$$

$$\begin{aligned}(n_1l_1^{N_1}n_2l_2^{N_2}&\alpha_1L_1S_1Q_1M_{Q_1}\alpha_2L_2S_2Q_2M_{Q_2}LS||\\ &\times\left[A^{(\kappa_{12}\sigma_{12})}(n_1\lambda_1)\times B^{(\kappa'_{12}\sigma'_{12})}(n_2\lambda_2)\right]^{(kk)}\\ &\times||n_1l_1^{N'_1}n_2l_2^{N'_2}\alpha'_1L'_1S'_1Q'_1M'_{Q_1}\alpha'_2L'_2S'_2Q'_2M'_{Q_2}L'S')\end{aligned} \tag{52}$$

$$(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LS||$$
$$\times\left[A^{(\kappa_{12}\sigma_{12})}(n_2\lambda_2) \times B^{(\kappa'_{12}\sigma'_{12})}(n_1\lambda_1)\right]^{(kk)}$$
$$\times||n_1 l_1^{N'_1} n_2 l_2^{N'_2} \alpha'_1 L'_1 S'_1 Q'_1 M'_{Q_1} \alpha'_2 L'_2 S'_2 Q'_2 M'_{Q_2} L'S') \,. \tag{53}$$

Here $A^{(\kappa_{12}\sigma_{12})}(n\lambda)$ and $B^{(\kappa'_{12}\sigma'_{12})}(n\lambda)$ represent any tensorial operator.

Only these shapes (50)–(53), in the case of two open shells, guarantee the effective use of Racah algebra. This includes the determination of zero matrix elements from triangular conditions (for example in (52) $\delta(L_1, L'_1, \kappa_{12})$, $\delta(S_1, S'_1, \sigma_{12})$, $\delta(L_2, L'_2, \kappa'_{12})$, $\delta(S_2, S'_2, \sigma'_{12})$) without explicit calculation, the use of tables of standard quantities, and the use of quasispin (see section 4) at last.

Meanwhile the second form (8) allows one to exploit the Racah algebra to its full extent, as the matrix elements for the third case

$$(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LSM_L M_S|G_{\rm II}(1212)$$
$$\times|n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1} \alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L'S' M'_L M'_S)$$
$$= \tfrac{1}{2}\sum_p (-1)^{k-p} [\kappa_1, \kappa_2, \sigma_1, \sigma_2]^{-1/2}$$
$$\times \left(n_1\lambda_1 n_2\lambda_2||g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)}||n_1\lambda_1 n_2\lambda_2\right)$$
$$\times(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LSM_L M_S|$$
$$\times\left[\left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_1)}\right]^{(\kappa_1\sigma_1)} \times \left[a^{(\lambda_2)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_2\sigma_2)}\right]^{(kk)}_{\rm p-p}$$
$$\times|n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1} \alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L'S' M'_L M'_S) \tag{54}$$

and the fourth case

$$(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LSM_L M_S|G_{\rm II}(2121)$$
$$\times|n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1} \alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L'S' M'_L M'_S)$$
$$= \tfrac{1}{2}\sum_p (-1)^{k-p} [\kappa_1, \kappa_2, \sigma_1, \sigma_2]^{-1/2}$$
$$\times \left(n_2\lambda_2 n_1\lambda_1||g^{(\kappa_1\kappa_2 k, \sigma_1\sigma_2 k)}||n_2\lambda_2 n_1\lambda_1\right)$$
$$\times(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LSM_L M_S|$$
$$\times\left[\left[a^{(\lambda_2)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_1\sigma_1)} \times \left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_1)}\right]^{(\kappa_2\sigma_2)}\right]^{(kk)}_{\rm p-p}$$
$$\times|n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1} \alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L'S' M'_L M'_S) \tag{55}$$

are schematically written down in the following as (52) and (53), by using expression (4.3) from Jucys and Savukynas (1973),

$$(\alpha_1 j_1 \alpha_2 j_2 j||\left[A_1^{(k_1)} \times A_2^{(k_2)}\right]^{(k)}||\alpha'_1 j'_1 \alpha'_2 j'_2 j') = \left[j, j', k\right]^{1/2}$$
$$\times(\alpha_1 j_1||A_1^{(k_1)}||\alpha'_1 j'_1)(\alpha_2 j_2||A_2^{(k_2)}||\alpha'_2 j'_2) \begin{Bmatrix} j_1 & j_2 & j \\ j'_1 & j'_2 & j' \\ k_1 & k_2 & k \end{Bmatrix} \tag{56}$$

and in the fourth case, after reversing the order of shells and altering the coupling of their momenta for bra and ket functions we obtain

$$(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} LS||$$
$$\times\left[\left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_1)}\right]^{(\kappa_1\sigma_1)} \times \left[a^{(\lambda_2)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_2\sigma_2)}\right]^{(kk)}$$
$$\times||n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1} \alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L'S')$$

$$= [k]\left[L, S, L', S'\right]^{1/2} \begin{Bmatrix} L_1 & L_2 & L \\ L'_1 & L'_2 & L' \\ \kappa_1 & \kappa_2 & k \end{Bmatrix} \begin{Bmatrix} S_1 & S_2 & S \\ S'_1 & S'_2 & S' \\ \sigma_1 & \sigma_2 & k \end{Bmatrix}$$
$$\times (n_1 l_1^{N_1}\ \alpha_1 Q_1 L_1 S_1 || \left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_1)}\right]^{(\kappa_1\sigma_1)} || n_1 l_1^{N_1}\ \alpha'_1 Q'_1 L'_1 S'_1)$$
$$\times (n_2 l_2^{N_2}\ \alpha_2 Q_2 L_2 S_2 || \left[a^{(\lambda_2)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_2\sigma_2)} || n_2 l_2^{N_2}\ \alpha'_2 Q'_2 L'_2 S'_2) \tag{57}$$

$$(n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha_1 L_1 S_1 Q_1 M_{Q_1} \alpha_2 L_2 S_2 Q_2 M_{Q_2} L S ||$$
$$\times \left[\left[a^{(\lambda_2)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_1\sigma_1)} \times \left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_1)}\right]^{(\kappa_2\sigma_2)} \right]^{(kk)}$$
$$\times || n_1 l_1^{N_1} n_2 l_2^{N_2} \alpha'_1 L'_1 S'_1 Q'_1 M_{Q_1} \alpha'_2 L'_2 S'_2 Q'_2 M_{Q_2} L' S')$$
$$= [k]\left[L, S, L', S'\right]^{1/2} \begin{Bmatrix} L_2 & L_1 & L \\ L'_2 & L'_1 & L' \\ \kappa_1 & \kappa_2 & k \end{Bmatrix} \begin{Bmatrix} S_2 & S_1 & S \\ S'_2 & S'_1 & S' \\ \sigma_1 & \sigma_2 & k \end{Bmatrix}$$
$$\times (n_2 l_2^{N_2}\ \alpha_2 Q_2 L_2 S_2 || \left[a^{(\lambda_2)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_1\sigma_1)} || n_2 l_2^{N_2}\ \alpha'_2 Q'_2 L'_2 S'_2)$$
$$\times (n_1 l_1^{N_1}\ \alpha_1 Q_1 L_1 S_1 || \left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_1)}\right]^{(\kappa_2\sigma_2)} || n_1 l_1^{N_1}\ \alpha'_1 Q'_1 L'_1 S'_1)\,. \tag{58}$$

From this we conclude that in the third and fourth cases the usage of the tensorial expressions of only a two-particle operator (8) allows us to successfully exploit all the advantages of Racah algebra and quasispin formalism in calculating the spin-angular parts of any two-particle operator matrix element. This, in our opinion, not only simplifies the calculations considerably, by allowing the use of the tables of irreducible tensors that are independent of shell occupation numbers, but also allows one to establish the zero matrix elements without performing explicit calculations.

Meanwhile the situation is different when the last two cases are considered, or the matrix elements between more complex configurations are to be established. This is related to the fact that using first (7) or second (8) tensorial forms the spin-angular part of matrix elements for these cases do not have the shape of any expression (50)–(53).

In the next paper we shall present a methodology that allows one to use the Racah algebra and quasispin formalism efficiently in a general case, too.

6. Conclusion

Preliminary usage of the generalized graphical method, irreducible tensorial form of the second quantization operators as well as of a quasispin technique, while calculating the spin-angular parts of matrix elements of the energy operator, has demonstrated high efficiency in obtaining in a uniform way the general expressions for the operators of physical quantities as well as for their matrix elements, covering both diagonal and non-diagonal cases with respect to quantum numbers of electronic configurations. Therefore it is fairly promising to formulate this methodology in a complete and consistent way for an arbitrary number of electronic shells with its successive implementation in the universal computer codes.

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