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SPIN–ANGULAR INTEGRATION FOR STUDIES OF MANY–ELECTRON ATOMS AND IONS

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Contents

1 INTRODUCTION

The urgency of the subject.

The modern theoretical atomic physics faces more and more new tasks. First of all it is important to get theoretically very precise characteristics of atoms and ions applying the *ab initio* methods, where the precision could compete with the experimental results. For example, there has been a renewed interest in intercombination lines which are of great importance as diagnostics for different astrophysical sources. In the spectra of light elements these lines are accessible for observation from both the International Ultraviolet Explorer (IUE) and the Goddard High Resolution Spectrograph (GHRS) aboard the Hubble space telescope. The modern technologies also enable one to find new superheavy atoms, such as Ununnilium (Uun Z=110), Unununium (Uuu Z=111), Ununbium (Uub Z=112). Their lifetimes are very short, therefore it is almost impossible to study those atoms experimentally, not even their basic state, potential of their ionization or the other characteristics, that are of great importance not only to atomic physics, but also to quantum chemistry. In addition, the development of other subjects of theoretical physics requires further progress of atomic theory. Quantum chemistry or solid state physics might serve as an example, the methods of which require very accurate wave functions of the heavy elements, which may be obtained applying the methods of theoretical atomic physics.

Many–electron atom usually is considered as many–body problem and is described by the wave function constructed from the wave functions of one electron, moving in the central nuclear charge field and in the screening field of the remaining electrons. Then the wave function 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 or Dirac–Hartree–Fock equations and can be represented in a numerical or analytical forms (Froese Fischer [1]) whereas the spin–angular part is expressed in terms of spherical functions. Then the wave function of the whole atom can be constructed in some standard way (Cowan [2], Jucys and Savukynas [3], Rudzikas [4]) starting with these one–electron functions and may be used further on for the calculations of any matrix elements representing physical quantities.

For obtaining the values of atomic quantities it is necessary to solve the so–called eigenvalue problem. Unfortunately, practical calculations show that all realistic atomic Hamiltonians do not lead straightforwardly to solving this problem. 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 energy matrix, to diagonalize it, obtaining in this way the values of the energy levels as well as the eigenfunctions (the wave functions in the intermediate coupling scheme). The latter may be used then to calculate electronic transitions as well as the other properties and processes. Such a necessity raises special requirements to the theory.

The matrix element of each term of the energy operator in the case of complex electronic configurations will consist of matrix elements, describing the interaction inside each shell of equivalent electrons as well as between these shells. Going beyond the single–configuration approximation we must be able to take into account in the same way non–diagonal matrix elements, with respect to configurations.

To find the expressions for the matrix elements of all terms of the Hamiltonian considered for complex electronic configurations with several open shells, is a task very far from the trivial one. 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. This habilitation work presents the general methodology, leading to optimal expressions for operators and matrix elements.

The papers of Racach [5, 6, 7, 8] gave a great impulse to the modern atomic physics. While introducing one–electron and two–electron coefficients of fractional parentage [7] as well as the unit tensors [6] into atomic physics, he formed the basis of tensorial algebra applied to the theory of complex atomic spectra. Anyway, almost all modern methods of calculation of spin–angular coefficients are based on these ideas.

One of the most widely–used computational schemes is from Fano [9, 10]. It has been implemented in a number of powerful programs [10, 11, 12, 13, 14, 15, 16] since that time. This methodology is based on having the total wave function of an atom built from the antisymmetrized wave functions of separate shells, and this antisymmetrization is done via coefficients of fractional parentage (CFP). The shells are coupled one to another via their angular momenta. So, the finding of matrix elements amounts to finding the so–called recoupling matrices and CFP.

Suppose that we have a *bra* function with u shells in LS–coupling:

$$\left(\psi_u\left(LSM_LM_S\right)\right| \equiv \left(n_1\lambda_1^{N_1}n_2\lambda_2^{N_2}...n_u\lambda_u^{N_u}\alpha_1L_1S_1\alpha_2L_2S_2...\alpha_uL_uS_u\mathcal{A}LSM_LM_S\right| \tag{1}$$

and a *ket* function:

$$\left|\psi_u\left(L'S'M_L'M_S'\right)\right) \equiv \left|n_1\lambda_1^{N_1}n_2\lambda_2^{N_2}...n_u\lambda_u^{N_u}\alpha_1'L_1'S_1'\alpha_2'L_2'S_2'...\alpha_u'L_u'S_u'\mathcal{A}'L'S'M_L'M_S'\right), \tag{2}$$

where $\mathcal{A}$ stands for all intermediate quantum numbers, depending on the order of coupling of momenta L_iS_i, $\lambda \equiv l, s$ and 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 $\widehat{G}$ between functions (1) and (2) to the submatrix (reduced matrix) element $\left(\psi_u\left(LS\right)\left\|\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\right\|\psi_u\left(L'S'\right)\right)$ of this operator. When the two–particle operator acts upon four distinct shells, then the finding the general expressions of matrix elements, according to methodology by Fano [9], is based upon the formula

$$\begin{aligned}
&\left(\psi_u\left(LS\right)\left\|\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\right\|\psi_u\left(L'S'\right)\right) \\
&\quad\sim \sum_{n_i\lambda_i,n_j\lambda_j,n_{i'}\lambda_{i'},n_{j'}\lambda_{j'}} (-1)^{\Delta}\left[N_i\left(N_j-\delta(i,j)\right)N_{i'}'\left(N_{j'}'-\delta(i',j')\right)\right]^{1/2} \\
&\quad\times\left(l_i^{N_i}\ \alpha_iL_iS_i\left\|l_i^{N_i-1}\ \left(\alpha_i'L_i'S_i'\right),l_i\right)\right.\left(l_j^{N_j}\ \alpha_jL_jS_j\left\|l_j^{N_j-1}\ \left(\alpha_j'L_j'S_j'\right),l_j\right)\right. \\
&\quad\times\left(l_{i'}^{N_{i'}}\ \alpha_{i'}L_{i'}S_{i'}\left\|l_{i'}^{N_{i'}-1}\ \left(\alpha_{i'}'L_{i'}'S_{i'}'\right),l_{i'}\right)\right.\left(l_{j'}^{N_{j'}}\ \alpha_{j'}L_{j'}S_{j'}\left\|l_{j'}^{N_{j'}-1}\ \left(\alpha_{j'}'L_{j'}'S_{j'}'\right),l_{j'}\right)\right. \\
&\quad\times\left\{R_d\left(\lambda_i,\lambda_j,\lambda_i',\lambda_j',\kappa_1,\kappa_2,\kappa,\sigma_1,\sigma_2,\sigma,\Lambda^{bra},\Lambda^{ket}\right)\right. \\
&\quad\times\left(1+\delta(i,j)\delta(i',j')\right)^{-1}\left(n_i\lambda_in_j\lambda_j\left\|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\right\|n_i'\lambda_i'n_j'\lambda_j'\right) \\
&\quad-R_e\left(\lambda_i,\lambda_j,\lambda_i',\lambda_j',\kappa_1,\kappa_2,\kappa,\sigma_1,\sigma_2,\sigma,\Lambda^{bra},\Lambda^{ket}\right) \\
&\quad\times\left.\left(1+\delta(i,j)\right)\left(1-\delta(i',j')\right)\left(n_i\lambda_in_j\lambda_j\left\|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\right\|n_j'\lambda_j'n_i'\lambda_i'\right)\right\},
\end{aligned} \tag{3}$$

where Δ is a phase factor, (see, e.g., in [10]), $\Lambda^{bra} \equiv \left(L_iS_i, L_jS_j, L_i'S_i', L_j'S_j'\right)^{bra}$ is the array for the *bra* function shells' terms, and similarly for Λ^{ket}. The coefficient

$\left(l^N\ \alpha LS \left\| l^{N-1}\ (\alpha' L' S'), l\right.\right)$ is a CFP, and coefficients

$R_d\left(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \kappa_1, \kappa_2, \kappa, \sigma_1, \sigma_2, \sigma, \Lambda^{bra}, \Lambda^{ket}\right)$ and

$R_e\left(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \kappa_1, \kappa_2, \kappa, \sigma_1, \sigma_2, \sigma, \Lambda^{bra}, \Lambda^{ket}\right)$ are the recoupling matrices in $l-$ and $s-$ spaces of direct and exchange terms, respectively. For more details on recoupling matrices see in Grant [10], Burke *et al.* [13]. The summation in expression (3) implies that the quantum numbers n, λ of all participating shells are included. There are four such pairs of n, λ in the sum.

During the last decades, this procedure was applied both to $LS-$ and jj–coupling. As we see, the Fano's procedure [9] is based on the CFP. Several tabulations of these quantities can be found in the literature. For example, tables of CFPs were presented by Racah [7], Nielson and Koster [17], Karazija *et al.* [18] for LS–coupling or de–Shalit and Talmi [19], Sivcev *et al.* [20] for jj–coupling. There are algebraic expressions for the CFPs for LS–coupling when the seniority quantum number ν is sufficient for the one–to–one classification of the terms, i.e. for p^N, d^N (all N values) and f^N ($0 < N \leq 4$, $10 \leq N \leq 14$) Kaniauskas *et al.* [21]. The corresponding algebraic expressions for j^N ($j \leq 7/2$) are found by Kaniauskas and Rudzikas [22]. But these expressions are rather complicated and, therefore, of little use.

In essence, the Fano calculation scheme consists of evaluating recoupling matrices. Although such an approach uses classical Racah algebra [5, 6, 7, 8] on the level of CFP, 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. So, by using the CFP as the basic quantities, Fano's procedure does not exploit the full power of Racah's algebra.

Jucys and Vizbaraitė [23] proposed to use the two–particle CFP instead of ordinary ones, in matrix elements' calculations for complex electron configurations. The tables of these CFP were presented by Vizbaraitė *et al.* [24] and Donlan [25] in LS–coupling and Slepcov *et al.* [26] in subshells with $j = 3/2$, $5/2$, and $7/2$ in jj–coupling. But even that did not solve the abovementioned problems.

A solution to this problem was found by Burke *et al.* [13]. They tabulated separate standard parts of recoupling matrices along with coefficients of fractional parentage at the beginning of a calculation and used them further on to calculate the needed coefficients. Computer codes by Grant [10], Glass [11], Glass and Hibbert [12], Burke *et al.* [13] use the program NJSYM (Burke [27]) or NJGRAF (Bar–Shalom and Klapisch [28]) for the calculation of recoupling matrices. Both are rather time consuming when calculating the matrix elements of complex operators or electronic configurations with many open shells.

In order to simplify the calculations, Cowan [2] suggested that matrix elements be grouped into "Classes" (see Cowan [2] Figure 13–5). Unfortunately, this approach was not generalized to all two–electron operators. Perhaps for this reason Cowan's approach is not very popular although the program itself, based on this approach, is widely used.

A few authors (Jucys, Savukynas [3], Rudzikas [4] and Racah [6]) utilize the unit tensors U^k, V^k in LS–coupling (Cowan [2], Jucys *et al.* [29], Karazija [30]), or T^k in jj–coupling (Kičkin and Rudzikas [31], Kičkin *et al.* [32], Sivcev *et al.* [33] and Nikitin and Rudzikas [34]) for spin–angular integration.

It allows to benifit from the advantages of tensorial algebra for the finding of matrix elements for one and two shells of equivalent electrons. The tables of submatrix elements of tensors composed of unit tensors and selection rules for them can be used prior to computation to check whether the spin–angular coefficients are zero or not, too. Moreover, the recoupling matrices themselves have a simpler form. A number of tabulations of these quantities are found in the literature. Numerical values for the matrix elements of $U^{(k)}$ and $V^{(1k)}$, for example, are tabulated by Racah [7], Nielson and Koster [17], Karazija *et al.* [18], Tuszynski [35] for LS–coupling and for the $T^{(k)}$ by Slepcov *et al.* [36] for subshells with $j = 5/2$, $7/2$ and $9/2$ in jj–coupling. But so far, unit tensors have been applied only for evaluating the diagonal, with respect to configurations, matrix elments while all non–diagonal matrix elements still have to be evaluated by using the CFP [4, 34].

All the above mentioned approaches were applied in the coordinate representation. The second quantization formalism (Rudzikas [4], Judd [37, 38] and Rudzikas and Kaniauskas [39]) has a number of advantages compared to coordinate representation. First of all, 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 [40], Merkelis *et al.* [41]), and orthogonal operators (Uylings [42]), where three–particle operators already occur. Uylings [43] 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 [39], Innes [44], Špakauskas *et al.* [45, 46], Fano and Rau [47]. The main advantage of this approach is that applying the quasispin method for calculating the matrix elements of any operator, we can use all advantages of the new version of Racah algebra (see Rudzikas [4]) for integration of spin–angular parts of any one– and two–particle operator. For example, the reduced coefficients of fractional parentage (RCFP) or reduced matrix elements of unit tensors are independent of the occupation number of the shell (see Rudzikas and Kaniauskas [39], Gaigalas *et al.* [M10]). The tables of all these quantities are presented for the p– and d– shells in LS–coupling by Rudzikas and Kaniauskas [39], Špakauskas *et al.* [46] and RCFP in jj–coupling by Savičius *et al.* [48]. All this enabled Merkelis and Gaigalas [49] to work out a general perturbation theory approach for complex cases of several open shells. In the paper by Merkelis [50] a detailed review of a version of graphical methodology is presented that allows one to represent the operators graphically and to find the matrix elements of these operators using diagrammatic technique.

As we see from the above, the majority of methods and computer codes for finding spin–angular coefficients are faced with a number of problems. Those which more or less do not have them are not general enough. Therefore, for obtaining theoretical results of very high accuracy one needs to essentially improve the existing approaches for spin–angular integration.

In this habilitation work an efficient and general approach is suggested 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 [39], the generalized graphical technique [51, 52] and angular momentum theory [3] in orbital, spin and quasispin spaces [4] as well as on the symetry properties of the quantities considered. This approach is free of previous shortcomings. The habilitation work based on the methods developed and programs written as well as on concrete practical applications demonstrates the effectiveness of the approach suggested.

Aim of this work.

The majority of methods of finding spin–angular coefficients were faced with a number of problems, especially when atoms with many open shells are treated, and the operators are not trivial. So, for getting theoretical results of very high accuracy in large scale atomic calculations one needs to essentially improve the existing approaches and computer codes. The aim of this habilitation work is to create the general methodology, leading to optimal expressions for operators and matrix elements, which is free of previous shortcomings, to work out the relevant computer programs using this methodology and to demonstrate their efficiency.

Main tasks of the research.

While setting the tasks of the research, many programs dedicated to the calculation of atomic quantities were analyzed. It was found that the majority of methods and computer codes for computing the spin–angular coefficients were faced with a number of problems, the main of these being:

- The demand for CPU time in calculating the spin–angular parts of matrix elements even on the modern computer is high. Moreover, the atomic structure programs for large scale calculations usually have problems with the computer hard disk. Therefore, the high accuracy of characteristics of atomic quantities sometimes is even unattainable.

- The methods practrically used in large scale *ab initio* calculations are being applied mostly for the comparatively simple systems. This is because in the programs based on classical Racah algebra the treatment of recoupling matrices is rather complicated, especially when finding the matrix elements of Breit–Pauli operators between complex configurations.

- The configurations with open f–shells (non–relativistic approach) must often be included into theoretical calculations. This causes problems in a number of methodologies, because the complete account of f–shells implies the usage of a large number of coefficients of fractional parentage[1].
- The configurations with open $j = 9/2$ subshell (relativistic approach) must be included for investigation and prediction of chemical and physical properties (see, e.g., Fricke [53]) of superheavy atoms.

So, for obtaining theoretical results of very high accuracy one needs to improve the existing approaches for spin–angular integration. Taking into consideration the above, the following tasks of the research were formulated:

- To choose an optimal number of distributions, which is necessary to evaluate any two–electron operator in general way.
- To express any physical operator in such a tensorial form which allows us to exploit all the advantages of new versions of Racah algebra (quasispin space included).
- To develop the graphic representation of the theory of angular momentum, in order to easily graphically group the products of the operators of the secondary quantization with the same tensorial structure.
- To obtain the analytical expressions for recoupling matrices.
- To formulate the new 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 on the symmetry properties of the quantities considered.

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[1] The Cowan [2] code supports the configurations with open f–shells only for calculation of matrix elements of Coulomb operator.

- To find the expressions of Breit–Pauli Hamiltonian, that would be most optimized to the new methods of calculation of spin–angular coefficients.

- To acquire the values of all standard quantities, both for LS–coupling and for jj–coupling, necessary for the new methods of finding the spin–angular coefficients. To create complete electronic tables of these quantities.

- To create software based on the new methods.

- To define the guidelines, that would give an opportunity to perform the spin–angular integration symbolically.

- To perform the theoretical studies of a number of spectral characteristics of atoms and ions, demonstrating in such a way the effectiveness of the methods created.

Main statements to be defended.

1. The method that is based on the second quantization in coupled tensorial form, on the angular momentum theory in three spaces (orbital, spin and quasispin), on the Wick's theorem and on the generalized graphical technique of angular momentum, gives the possibility to efficiently calculate the matrix elements of energy operators in general case and allows one to exploit all the advantages of tensorial algebra in both non–relativistic and relativistic approachs for diagonal and off–diagonal (with respect to configurations) matrix elements.

2. The tensorial expressions (7) and (74) allow us to efficiently use the simplifications for any two–particle operator in general way, as, e.g., for spin–other–orbit (see, e.g., formulas (52), (56) and (57)) and orbit–orbit interactions (see, e.g., formulas (69) and (70)) because the expresions are always in irreducible tensorial form and the simplifications are provided in newly defining the tensorial structure of operator and two–electron matrix elements.

3. The tensorial expressions (7) and (74) of any one– and two–particle operator allow one to find simple analytical expressions (75), (79), (80), (83), (85), (87), (88) and

(94) for the recoupling matrices for both diagonal and off–diagonal matrix elements with any number of open shells in both non–relativistic and relativistic approaches.

4. The computer programs based on the approach presented in the habilitation work are much faster compared to standard ones (3–8 times in jj–coupling (see Table 10) and 5–12 times in LS–coupling (see Table 11)) and allow for the computers of various types and classes to use i) the new program organization for large scale calculations, that allows to fully exploit the possessed resources of both supercomputers and personal computers; ii) to effectively apply both parallel and symbolic programming; iii) to investigate any configurations involving f – (or j=9/2) shells.
5. *Ab initio* calculations performed indicate that the methods developed as well as the programs written constitute the prerequisites for obtaining the energies, wavelengths of electronic transitions, oscillator strengths, transition probabilities, lifetimes of excited levels, electron affinities of negative ions, isotope shifts, hyperfine structure as well as the other atomic properties with a high accuracy. For example, the *ab initio* calculations of the Gd ionization energy led us to conclude that correlation effects for Gd are larger than it was obtained before by others.

The novelty and originality of the work.

The developed spin–angular integration approach connects and integrates into the whole the modern mathematical methods of tensorial algebra. Based on these methods there were written a number of programs, which use the advantages of the modern fast developing computer technique, first of all the parallel and symbolic programming. This widens essentially the range of the applicability of the atom theory, both regarding the accuracy and the variety of atoms and ions.

Practical significance of the work.

The approach and programs developed in this work are applicable for obtaining the accurate values of atomic quantities in a number of different universal theoretical approximations: multiconfiguration Hartree–Fock, Dirac–Hartree–Fock or configuration interaction approaches, many–body perturbation theory, orthogonal operators as well as for various versions of semi–empirical methods. This provides a possibility to perform theoretical research on practically any atom and ion.

Implementation of the results. The software created in this work is used at University of Oxford (United Kingdom), Vanderbilt University (Computer Science Department, USA), Universite Libre de Bruxelles (Laboratoire de Chimie Physique Moléculaire, Belgium), Universität Kassel (Fachbereich Physik, Germany), Institute of Theoretical Physics and Astronomy (Department of the Theory of an Atom, Lithuania), Vilnius Pedagogical Universtity (General Physics Department, Vilnius), Vilnius Technical University (Computer center, Vilnius). All software created is based on the methods developed in the habilitation work.

The publications and the personal contribution. The habilitation work is based on 21 main articles and one conference abstract; a special list of these publications [M1–M22] (containing the titles of the publications) preceedes the general list of references. The publications include 3 articles by G. Gaigalas as a single author and 18 papers with co–authors.

The author used his own material while preparing this work. The methods developed were published in [M3, M6, M8, M9, M10, M14, M16, M17]. The author wrote a number of programs [M4, M18, M19, M20, M21] and performed the calculations with them [M1, M2, M5, M7, M11, M12, M13, M15, M22]. The main part of the investigations was performed at the Institute of Theoretical Physics and Astronomy. The part of the work related to the writing and testing of some programs was performed by the habilitant at the University of Oxford (United Kingdom), Vanderbilt University (Compiuter Science Department, USA), Universite Libre de Bruxelles (Laboratoire de Chimie Physique Moléculaire, Belgium), Universität Kassel (Fachbereich Physik, Germany).

Contributions of the other co–authors were as follows:

Prof. Ian P. Grant provided with his written program, participated in the discussions of the results and presentation of the publications.

Prof. Ch. Froese Fischer provided with her written programs, consulted on the issues of their application, there were discussions with her while preparing some new program modifications, adopting the calculation technique and performing some calculations.

Prof. Z. Rudzikas proposed some ideas, consulted on the issues of second quantization as well as quasispin application, participated in the analysis of the results.

Prof. M. Godefroid assisted in extending the possibilities of the search of spin–angular coefficients in LS-coupling, and proposed some ideas on the testing of programs, when the calculations were done with the open f–shell. There was a possibility to use the computers at the University of Brussels.

Hab. Dr. S. Fritzsche participated in formulating the task for searching the spin–angular coefficients in jj–coupling, proposed to create electronic tables in the programming languages both FORTRAN 90 and MAPLE. There was a possibility to use the computers and to make some calculations in Kassel.

Other co–authors participated in the formulation of some particular problems, discussions of the results and presentation of the publications.

The author participated in a number of other investigations (other publications related to the habilitation work) [M23*–M35*] developing the relevent methods as software.

Approbation of the work. The results of the habilitation work have been presented at the 3rd International Colloquium on Atomic Spectra and Oscillator Strengths for Astrophysics and Fusion (Amsterdam, Netherlands 1990), XXII EGAS Conference (Uppsala, Sweden, 1990), XIII EGAS Conference (Torun, Poland, 1991), 4th EPS Europhysics Conference (Riga, Latvia, 1992), IAU Symposium No. 155 (Innsbruck, Austria, 1992), XXV EGAS Conference (Caen, France, 1993), XXVI EGAS Conference (1994, Barcelona, Spain, 1994), 7th International Conference on the Physics of Highly Charged Ions HCI–94 (Vienna, Austria, 1994), 5th EPS Conference on Atomic and Molecular Physics (Edinburgh, UK, 1995), XXVIII EGAS Conference (Graz, Austria, 1996), 8th International Conference on the Physics of Highly Charged Ions HCI–96 (Omiya, Saitama, JAPAN, 1996), PECAM II Second Europhysics Study Conference on Photon and Electron Collisions with Atomis and Molecules (Belfast, UK, 1996), XXIX EGAS Conference (Berlin, Germany, 1997), Conference on Atomic and Molecular Data and Their Applications (Gaithersburg, MD, USA, 1997), 6th EPS Conference on Atomic and Molecular Physics (Siena, Italy, 1998), 6th International Colloquium on Atomic Spectra and Oscillator Strengths (Victoria, Canada, 1998), 9th International Conference on the Physics of Highly Charged Ions HCI–98 (Bensheim, Germany, 1998), XXXI EGAS Conference (Marseille, France, 1999), Deutschen Physikalischen Gesellschaft (Bonn, Germany, 2000), 7 Kolloquium des Schwerpunktes ”Relativische Effekte in der Chemie und physik Schwerer elemente” (Kloster Banz, Germany, 2000), International Conference on Atomic and Molecular Data and Their Applications (Oxford, UK, 2000), ICAP XVII International Conference on Atomic Physics (Florence, Italy, 2000), XXXIII EGAS Conference (Vilnius, Lithuania, 2000), ECAMP VII The Seventh European Conference on Atomic and Molecular Physics (Berlin, Germany, 2001).

In addition, the author has presented many results included in this habilitation work at the scientific seminars of the following institutions: Institute of Theoretical Physics and Astronomy (Vilnius), Institute of Physics (Vilnius), Vilnius Pedagogical University (General Physics Department, Vilnius), University of Oxford (Mathematical Institute, United Kingdom), Vanderbilt University (Compiuter Science Department, USA), Universite Libre De Bruxelles (Laboratoire de Chimie Physique Moléculaire, Belgium), Universität Kassel (Fachbereich Physik, Germany).

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2 THEORETICAL OUTLINE [M3, M6, M8, M9, M10, M13, M14, M16, M17, M21]

2.1 Efficient tensorial form of any two–particle operator [M3, M6, M8, M9, M14, M17]

2.1.1 Tensorial expressions for two–particle operator

It is well known in the literature that a scalar two–particle operator may be presented in the following form (see Jucys and Savukynas [3], Glass [11]):

$$\widehat{G}^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)} = \sum_{i>j} g\left(r_i, r_j\right) \sum_p \left(-1\right)^{k-p} \left[\widehat{g}_i^{(\kappa_1\sigma_1)} \times \widehat{g}_j^{(\kappa_2\sigma_2)}\right]^{(k\ k)}_{p,-p}, \tag{4}$$

where $g\left(r_i, r_j\right)$ is the radial part of operator, $\widehat{g}_i^{(\kappa_1\sigma_1)}$ is a tensor acting upon the orbital and spin variables of the i–th function, κ_1, κ_2 are the ranks of operator acting in orbital space, and σ_1, σ_2 are the ranks of operator acting in spin space.

All the above mentioned approaches were usually applied in the coordinate representation. Now we will investigate the second quantization formalism, which is broadly applied in atomic physics as well.

A two–particle operator in second quantization method is written as follows:

$$G^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)} = \sum_{n_i l_i, n_j l_j, n_{i'} l_{i'}, n_{j'} l_{j'}} \widehat{G}(ij, i'j') = \frac{1}{2} \sum_{i,j,i',j'} a_i a_j a_{j'}^{\dagger} a_{i'}^{\dagger} \left(i, j \left| g \right| i', j'\right), \tag{5}$$

where $i \equiv n_i l_i s m_{l_i} m_{s_i}$, $(i, j|g|i', j')$ is the two–electron matrix element of operator

$G^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}$, and a_i is the electron creation and $a_j^{\dagger}$ electron annihilation operators. Meanwhile two tensorial forms are well known in second quantization [54]. In the first form the two–electron operator has tensorial product $\left[\left[a^{(\lambda_i)} \times a^{(\lambda_j)}\right]^{(\kappa_{12}\sigma_{12})} \times \left[\tilde{a}^{(\lambda_i')} \times \tilde{a}^{(\lambda_j')}\right]^{\left(\kappa_{12}'\sigma_{12}'\right)}\right]^{(kk)}_{p,-p}$. The tensor $\tilde{a}^{(\lambda)}_{m_\lambda}$ is defined as

$$\tilde{a}^{(\lambda)}_{m_\lambda} = \left(-1\right)^{\lambda - m_\lambda} a^{\dagger(\lambda)}_{-m_\lambda}, \tag{6}$$

where $\lambda \equiv l, s$ in non–relativistic theory and $\lambda \equiv j$ in relativistic theory.

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

In the paper Gaigalas and Rudzikas [M3] it was shown that these tensorial forms do not take full advantage of tensor algebra. The most characteristic examples are when configurations considered have many open shells, or when the non–diagonal with respect to configurations matrix elements are seeked.

In the paper Gaigalas *et al.* [M6] the following general expression of two–particle operator is proposed, which allows one to make the most of the advantages of Racah algebra (see Racah [5, 6, 7, 8]).

$$
\begin{aligned}
\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)} = & \sum_{\alpha} \sum_{\kappa_{12},\sigma_{12},\kappa'_{12},\sigma'_{12}} \Theta\left(\Xi\right) \Big\{ A^{(kk)}_{p,-p}\left(n_\alpha\lambda_\alpha,\Xi\right)\delta\left(u,1\right) \\
& + \sum_{\beta} \left[B^{(\kappa_{12}\sigma_{12})}\left(n_\alpha\lambda_\alpha,\Xi\right) \times C^{\left(\kappa'_{12}\sigma'_{12}\right)}\left(n_\beta\lambda_\beta,\Xi\right)\right]^{(kk)}_{p,-p}\delta\left(u,2\right) \\
& + \sum_{\beta\gamma} \left[\left[D^{(l_\alpha s)} \times D^{\left(l_\beta s\right)}\right]^{(\kappa_{12}\sigma_{12})} \times E^{\left(\kappa'_{12}\sigma'_{12}\right)}\left(n_\gamma\lambda_\gamma,\Xi\right)\right]^{(kk)}_{p,-p}\delta\left(u,3\right) \\
& + \sum_{\beta\gamma\delta} \left[\left[D^{(l_\alpha s)} \times D^{\left(l_\beta s\right)}\right]^{(\kappa_{12}\sigma_{12})} \times \left[D^{(l_\gamma s)} \times D^{(l_\delta s)}\right]^{\left(\kappa'_{12}\sigma'_{12}\right)}\right]^{(kk)}_{p,-p}\delta\left(u,4\right)\Big\}, \qquad (7)
\end{aligned}
$$

In the expression (7) u is the overall number of shells acted upon by a given tensorial product of creation/annihilation operators. Parameter Ξ implies the whole array of parameters (and sometimes an internal summation over some of these is implied, as well) that connects the amplitudes Θ of tensorial products of creation/annihilation operators in the expression (7) to these tensorial products (see Gaigalas *et al.* [M6]). Also, attention must be paid to the fact that the ranks κ_1, κ_2, κ, σ_1, σ_2 and σ are also included into the parameter Ξ.

Whereas in traditional expressions, e. g. (5), the summation runs over the principle and the orbital quantum numbers of open shells without detailing these, in the expression written above the first term represents the case of a two–particle operator acting upon the same shell $n_\alpha\lambda_\alpha$, the second term corresponds to operator $\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}$ acting upon two different shells $n_\alpha\lambda_\alpha$, $n_\beta\lambda_\beta$. When operator $\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}$ acts upon three shells the third term in (7) must be considered and when it acts upon four – the fourth one. We define in this expression the shells $n_\alpha\lambda_\alpha$, $n_\beta\lambda_\beta$, $n_\gamma\lambda_\gamma$, $n_\delta\lambda_\delta$ to be different. Thus, the expression (7) describe the most general use of the operator, suitable to account even for the matrix elements of non–diagonal with respect to configuration.

The tensorial part of a two–particle operator is expressed in terms of operators of the type $A^{(kk)}(n\lambda,\Xi)$, $B^{(kk)}(n\lambda,\Xi)$, $C^{(kk)}(n\lambda,\Xi)$, $D^{(ls)}$, $E^{(kk)}(n\lambda,\Xi)$ (for more details see [M6]). They correspond to one of the forms:

$$a_{m_q}^{(q\lambda)}, \tag{8}$$

$$\left[a_{m_{q1}}^{(q\lambda)} \times a_{m_{q2}}^{(q\lambda)}\right]^{(\kappa_1\sigma_1)}, \tag{9}$$

$$\left[a_{m_{q1}}^{(q\lambda)} \times \left[a_{m_{q2}}^{(q\lambda)} \times a_{m_{q3}}^{(q\lambda)}\right]^{(\kappa_1\sigma_1)}\right]^{(\kappa_2\sigma_2)}, \tag{10}$$

$$\left[\left[a_{m_{q1}}^{(q\lambda)} \times a_{m_{q2}}^{(q\lambda)}\right]^{(\kappa_1\sigma_1)} \times a_{m_{q3}}^{(q\lambda)}\right]^{(\kappa_2\sigma_2)}, \tag{11}$$

$$\left[\left[a_{m_{q1}}^{(q\lambda)} \times a_{m_{q2}}^{(q\lambda)}\right]^{(\kappa_1\sigma_1)} \times \left[a_{m_{q3}}^{(q\lambda)} \times a_{m_{q4}}^{(q\lambda)}\right]^{(\kappa_2\sigma_2)}\right]^{(kk)}. \tag{12}$$

For example, if we take a two–particle operator acting upon two shells, then we see from expression (7) that the spin–angular part of two–particle operator is expressed via operators $B^{(\kappa_{12}\sigma_{12})}(n_\alpha\lambda_\alpha,\Xi)$ and $C^{\left(\kappa'_{12}\sigma'_{12}\right)}(n_\beta\lambda_\beta,\Xi)$. In the case when the operator $\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}$ acts in such a manner that two operators of second quantization act upon one shell and two act upon another, the $B^{(\kappa_{12}\sigma_{12})}(n_\alpha\lambda_\alpha,\Xi)$ and $C^{\left(\kappa'_{12}\sigma'_{12}\right)}(n_\beta\lambda_\beta,\Xi)$ are expressed as (9). But in the case when three operators of second quantization act upon one shell and one acts upon another, then $B^{(\kappa_{12}\sigma_{12})}(n_\alpha\lambda_\alpha,\Xi)$ and $C^{\left(\kappa'_{12}\sigma'_{12}\right)}(n_\beta\lambda_\beta,\Xi)$ are expressed either as (8) and (10) or (8) and (11).

In writing down the expressions (8)–(12) the quasispin formalism was used, where $a_{m_\lambda}^{(\lambda)}$ and $\tilde{a}_{m_\lambda}^{(\lambda)}$ are components of the tensor $a_{m_q m_\lambda}^{(q\lambda)}$, having in additional quasispin space the rank $q=\frac{1}{2}$ and projections $m_q=\pm\frac{1}{2}$, i.e.

$$a_{\frac{1}{2}m_\lambda}^{(q\lambda)} = a_{m_l m_s}^{(ls)} \tag{13}$$

and

$$a^{(q\lambda)}_{-\frac{1}{2}m_\lambda} = \tilde{a}^{(ls)}_{m_l m_s} \, . \tag{14}$$

The amplitudes $\Theta\left(\Xi\right)$ are all proportional to the two–electron submatrix element of a two–particle operator g,

$$\Theta\left(\Xi\right) \sim \left(n_i\lambda_i n_j\lambda_j \left\|g\right\| n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right). \tag{15}$$

To obtain the expression of a concrete physical operator, analogous to expression (7), the tensorial structure of the operator and the two–particle matrix elements (15) must be known. We shall investigate this now, for example, in non–relativistic atomic theory.

The *electrostatic (Coulomb) electron interaction* operator $H^{Coulomb}$ itself contains the tensorial structure

$$H^{Coulomb} \equiv \sum_k H^{(kk0,000)}_{Coulomb} \tag{16}$$

and its submatrix element is

$$\begin{aligned}&\left(n_i\lambda_i n_j\lambda_j \left\|H^{(kk0,000)}_{Coulomb}\right\| n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right)\\ &\quad = 2[k]^{1/2}\left(l_i \left\|C^{(k)}\right\| l_{i'}\right)\left(l_j \left\|C^{(k)}\right\| l_{j'}\right) R_k\left(n_i l_i n_{i'} l_{i'}, n_j l_j n_{j'} l_{j'}\right),\end{aligned} \tag{17}$$

where we have used the conventional shorthand notation $(2k+1)\cdot ... \equiv [k, ...]$.

The *spin–spin* operator H^{ss} itself contains tensorial structure of two different types, summed over k (Gaigalas and Rudzikas [M9]),

$$H^{ss} \equiv \sum_k \left[H^{(k+1k-12,112)}_{ss} + H^{(k-1k+12,112)}_{ss}\right]. \tag{18}$$

Their submatrix elements are (Jucys and Savukynas [3])

$$\begin{aligned}&\left(n_i\lambda_i n_j\lambda_j \left\|H^{(k+1k-12,112)}_{ss}\right\| n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right)\\ &\quad = \frac{3}{\sqrt{5}}\sqrt{(2k+3)^{(5)}}\left(l_i \left\|C^{(k+1)}\right\| l_{i'}\right)\left(l_j \left\|C^{(k-1)}\right\| l_{j'}\right) N^{k-1}\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right),\end{aligned} \tag{19}$$

$$\begin{aligned}&\left(n_i\lambda_i n_j\lambda_j \left\|H^{(k-1k+12,112)}_{ss}\right\| n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right)\\ &\quad = \frac{3}{\sqrt{5}}\sqrt{(2k+3)^{(5)}}\left(l_i \left\|C^{(k-1)}\right\| l_{i'}\right)\left(l_j \left\|C^{(k+1)}\right\| l_{j'}\right) N^{k-1}\left(n_j l_j n_i l_i, n_{j'} l_{j'} n_{i'} l_{i'}\right),\end{aligned} \tag{20}$$

where we use a shorthand notation

$(2k+3)^{(5)} \equiv (2k+3)(2k+2)(2k+1)(2k)(2k-1)$ and radial integral (19), (20) is defined as in Glass and Hibbert [12]:

$$N^{k}\left(n_{i}l_{i}n_{j}l_{j},n_{i'}l_{i'}n_{j'}l_{j'}\right)$$
$$=\frac{\alpha^{2}}{4}\int\limits_{0}^{\infty}\int\limits_{0}^{\infty}P_{i}\left(r_{1}\right)P_{j}\left(r_{2}\right)\frac{r_{2}^{k}}{r_{1}^{k+3}}\epsilon(r_{1}-r_{2})P_{i'}\left(r_{1}\right)P_{j'}\left(r_{2}\right)dr_{1}dr_{2}, \tag{21}$$

where $\epsilon(x)$ is a Heaviside step–function,

$$\epsilon(x)=\begin{cases}1; & \text{for } x>0,\\ 0; & \text{for } x\leq 0.\end{cases} \tag{22}$$

The *spin–other–orbit* operator H^{soo} (see Godefroid [55]) itself contains tensorial structure of six different types, summed over k (Gaigalas *et al.* [M8]):

$$H^{sso}\equiv\sum_{k}\left[H_{sso}^{(k-1k1,101)}+H_{sso}^{(k-1k1,011)}+H_{sso}^{(kk1,101)}\right.$$
$$\left.+H_{sso}^{(kk1,011)}+H_{sso}^{(k+1k1,101)}+H_{sso}^{(k+1k1,011)}\right]. \tag{23}$$

Their submatrix elements are:

$$\left(n_{i}\lambda_{i}n_{j}\lambda_{j}\left\|H_{soo}^{(k-1k1,\sigma_{1}\sigma_{2}1)}\right\|n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right)$$
$$=2\cdot 2^{\sigma_{2}}\left(k\right)^{-1/2}\left\{\left(2k-1\right)\left(2k+1\right)\left(l_{i}+l_{i'}-k+1\right)\left(k-l_{i}+l_{i'}\right)\left(k+l_{i}-l_{i'}\right)\right.$$
$$\left.\times\left(k+l_{i}+l_{i'}+1\right)\right\}^{1/2}\left(l_{i}\left\|C^{(k)}\right\|l_{i'}\right)\left(l_{j}\left\|C^{(k)}\right\|l_{j'}\right)N^{k-2}\left(n_{j}l_{j}n_{i}l_{i},n_{j'}l_{j'}n_{i'}l_{i'}\right), \tag{24}$$

$$\left(n_{i}\lambda_{i}n_{j}\lambda_{j}\left\|H_{soo}^{(kk1,\sigma_{1}\sigma_{2}1)}\right\|n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right)$$
$$=-2\cdot 2^{\sigma_{2}}\left(2k+1\right)^{1/2}\left(l_{i}\left\|C^{(k)}\right\|l_{i'}\right)\left(l_{j}\left\|C^{(k)}\right\|l_{j'}\right)\left\{\left(k\left(k+1\right)\right)^{-1/2}\right.$$
$$\times\left(l_{i}\left(l_{i}+1\right)-k\left(k+1\right)-l_{i'}\left(l_{i'}+1\right)\right)\left\{\left(k+1\right)N^{k-2}\left(n_{j}l_{j}n_{i}l_{i},n_{j'}l_{j'}n_{i'}l_{i'}\right)\right.$$
$$\left.\left.-kN^{k}\left(n_{i}l_{i}n_{j}l_{j},n_{i'}l_{i'}n_{j'}l_{j'}\right)\right\}-2\left(k\left(k+1\right)\right)^{1/2}V^{k-1}\left(n_{i}l_{i}n_{j}l_{j},n_{i'}l_{i'}n_{j'}l_{j'}\right)\right\}, \tag{25}$$

$$\left(n_{i}\lambda_{i}n_{j}\lambda_{j}\left\|H_{soo}^{(k+1k1,\sigma_{1}\sigma_{2}1)}\right\|n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right)$$
$$=2\cdot 2^{\sigma_{2}}\left(k+1\right)^{-1/2}\left\{\left(2k+1\right)\left(2k+3\right)\left(l_{i}+l_{i'}-k\right)\left(k-l_{i}+l_{i'}+1\right)\left(k+l_{i}-l_{i'}+1\right)\right.$$
$$\left.\times\left(k+l_{i}+l_{i'}+2\right)\right\}^{1/2}\left(l_{i}\left\|C^{(k)}\right\|l_{i'}\right)\left(l_{j}\left\|C^{(k)}\right\|l_{j'}\right)N^{k}\left(n_{i}l_{i}n_{j}l_{j},n_{i'}l_{i'}n_{j'}l_{j'}\right). \tag{26}$$

The radial integrals in (24)–(26) are (see Glass and Hibbert [12]):

$$\begin{aligned} &V^{k}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right) \\ &\quad = \frac{\alpha^{2}}{4} \int_{0}^{\infty}\int_{0}^{\infty} P_{i}\left(r_{1}\right) P_{j}\left(r_{2}\right) \frac{r_{<}^{k-1}}{r_{>}^{k+2}} r_{2} \frac{\partial}{\partial r_{1}} P_{i'}\left(r_{1}\right) P_{j'}\left(r_{2}\right) dr_{1}dr_{2}. \end{aligned} \tag{27}$$

The tensorial form of *orbit–orbit* operator is (see Eissner *et al.* [56])

$$H^{oo} = \sum_{k} \left(H_{oo1}^{(kk0,000)} + H_{oo2}^{(kk0,000)} + H_{oo3}^{(kk0,000)} + H_{oo4}^{(kk0,00)}\right). \tag{28}$$

The sum of submatrix elements of three terms $H_{oo1}^{(kk0,000)}$, $H_{oo2}^{(kk0,000)}$ and $H_{oo4}^{(kk0,000)}$ is equal to (see Badnell [57]):

$$\begin{aligned} &\left(n_{i}\lambda_{i}n_{j}\lambda_{j} \left\| H_{oo1}^{(kk0,000)} + H_{oo2}^{(kk0,000)} + H_{oo4}^{(kk0,000)} \right\| n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right) \\ &\quad = -2[k]^{1/2} \left(l_{i} \left\| C^{(k)} \right\| l_{i'}\right) \left(l_{j} \left\| C^{(k)} \right\| l_{j'}\right) \left(1 - \delta\left(k,0\right)\right) Z_{k}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right), \end{aligned} \tag{29}$$

where

$$\begin{aligned} &Z_{k}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right) \\ &\quad = 2k\left(k+1\right)\left(T^{k+1}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right) - T^{k-1}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right)\right) \\ &\quad + \left(l_{i}\left(l_{i}+1\right) - k\left(k+1\right) - l_{i'}\left(l_{i'}+1\right)\right)\left(U^{k+1}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right) - U^{k-1}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right)\right) \\ &\quad + \left(l_{j}\left(l_{j}+1\right) - k\left(k+1\right) - l_{j'}\left(l_{j'}+1\right)\right)\left(U^{k+1}\left(n_{j}l_{j}n_{i}l_{i}, n_{j'}l_{j'}n_{i'}l_{i'}\right) - U^{k-1}\left(n_{j}l_{j}n_{i}l_{i}, n_{j'}l_{j'}n_{i'}l_{i'}\right)\right) \\ &\quad + \frac{1}{2}\left(l_{i}\left(l_{i}+1\right) - k\left(k+1\right) - l_{i'}\left(l_{i'}+1\right)\right)\left(l_{j}\left(l_{j}+1\right) - k\left(k+1\right) - l_{j'}\left(l_{j'}+1\right)\right) \\ &\quad \times \left[\frac{k-2}{k\left(2k-1\right)}\left(N^{k-2}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right) + N^{k-2}\left(n_{j}l_{j}n_{i}l_{i}, n_{j'}l_{j'}n_{i'}l_{i'}\right)\right)\right. \\ &\quad \left. - \frac{k+3}{\left(k+1\right)\left(2k+3\right)}\left(N^{k}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right) + N^{k}\left(n_{j}l_{j}n_{i}l_{i}, n_{j'}l_{j'}n_{i'}l_{i'}\right)\right)\right]. \end{aligned} \tag{30}$$

The radial integrals are defined as

$$\begin{aligned} &T^{k}\left(n_{i}l_{i}n_{j}l_{j}, n_{i'}l_{i'}n_{j'}l_{j'}\right) = \frac{\alpha^{2}}{4\left(2k+1\right)} \\ &\quad \times \int_{0}^{\infty}\int_{0}^{\infty} P_{i}\left(r_{1}\right) P_{j}\left(r_{2}\right) \frac{r_{<}^{k}}{r_{>}^{k+1}} \left(\frac{\partial}{\partial r_{1}} + \frac{1}{r_{1}}\right) P_{i'}\left(r_{1}\right) \left(\frac{\partial}{\partial r_{2}} + \frac{1}{r_{2}}\right) P_{j'}\left(r_{2}\right) dr_{1}dr_{2}, \end{aligned} \tag{31}$$

$$U^{k}\left(n_{i}l_{i}n_{j}l_{j},n_{i'}l_{i'}n_{j'}l_{j'}\right)=\frac{\alpha^{2}}{4\left(2k+1\right)}$$

$$\times\int_{0}^{\infty}\int_{0}^{\infty}P_{i}\left(r_{1}\right)P_{j}\left(r_{2}\right)\left(\left(k-1\right)\frac{r_{2}^{k}}{r_{1}^{k+2}}\epsilon(r_{1}-r_{2})-\left(k+2\right)\frac{r_{1}^{k-1}}{r_{2}^{k+1}}\epsilon(r_{2}-r_{1})\right)$$

$$\times P_{i'}\left(r_{1}\right)\left(\frac{\partial}{\partial r_{2}}+\frac{1}{r_{2}}\right)P_{j'}\left(r_{2}\right)dr_{1}dr_{2}. \tag{32}$$

The submatrix element of remaining term $H_{oo3}^{(kk0,000)}$ is:

$$\left(n_{i}\lambda_{i}n_{j}\lambda_{j}\left\|H_{oo3}^{(kk0,000)}\right\|n_{i'}\lambda_{i'}n_{j'}\lambda_{j'}\right)$$

$$=2\sqrt{2k+1}\frac{1}{k(k+1)}\left(l_{i}\left\|C^{(k+1)}\right\|l_{i'}\right)\left(l_{j}\left\|C^{(k+1)}\right\|l_{j'}\right)$$

$$\times\left(\left(l_{i}+l_{i'}+k+2\right)\left(l_{i}+l_{i'}-k\right)\left(l_{i}-l_{i'}+k+1\right)\left(l_{i'}-l_{i}+k+1\right)\right.$$

$$\left.\times\left(l_{j}+l_{j'}+k+2\right)\times\left(l_{j}+l_{j'}-k\right)\left(l_{j}-l_{j'}+k+1\right)\left(l_{j'}-l_{j}+k+1\right)\right)^{1/2}$$

$$\times\left(N^{k-1}\left(n_{i}l_{i}n_{j}l_{j},n_{i'}l_{i'}n_{j'}l_{j'}\right)+N^{k-1}\left(n_{j}l_{j}n_{i}l_{i},n_{j'}l_{j'}n_{i'}l_{i'}\right)\right). \tag{33}$$

The rest of two–particle Breit–Pauli operators that we did not investigate so far are the two–body Darwin and spin–spin–contact terms. They do not bring any additional difficulties into the investigation of Hamiltonian, but for the sake of completeness of presentation we will discuss them briefly.

The *two–body Darwin* operator H_{D2} (see for more detail Nikitin and Rudzikas [34]), as well as the *spin–spin–contact* operator H_{SSC} (see Shalit and Talmi [19] and Feneuille [58]), both have the following tensorial structure:

$$H\equiv\sum_{k}H^{(kk0,000)}. \tag{34}$$

These two terms are included into calculation by adding to the radial integral

$R_{k}\left(n_{i}l_{i}n_{i'}l_{i'},n_{j}l_{j}n_{j'}l_{j'}\right)$ a term

$$\left(2k+1\right)X\left(n_{i}l_{i}n_{i'}l_{i'},n_{j}l_{j}n_{j'}l_{j'}\right),$$

where

$$X\left(n_{i}l_{i}n_{j}l_{j},n_{i'}l_{i'}n_{j'}l_{j'}\right)$$

$$=\frac{\alpha^{2}}{4}\int_{0}^{\infty}\int_{0}^{\infty}P_{i}\left(r_{1}\right)P_{j}\left(r_{2}\right)\frac{1}{r_{1}^{2}}\delta\left(r_{1}-r_{2}\right)P_{i'}\left(r_{1}\right)P_{j'}\left(r_{2}\right)dr_{1}dr_{2}. \tag{35}$$

The expression (7) has a series of terms, and, thus, at first glance seems to be difficult to apply. For this purpose in the next sections we shall discuss in more detail about:

- the Wick's theorem and it application to the study of any two–particle operator;
- the compact written form of all terms, using the extended graphical technique;
- obtaining the values of recoupling matrix and of standard quantities. We shall also compare the existing methodologies of finding spin–angular parts, showing their advantages and shortcomings.

This methodology is fully applicable also to the one–particle operator (see Gaigalas and Rudzikas [M3], Gaigalas *et al.* [M6]). As this operator does not cause big problems in the atomic physics, we will not stop for details.

2.1.2 Wick's theorem

Wick's theorem in the second quantization formalism is formulated as follows (see Wick [59]; Bogoliubov and Shirkov [60]): If A is a product of creation and annihilation operators, then

$$A = \{A\} + \left\{\overline{A}\right\}, \tag{36}$$

where $\{A\}$ represents the normal form of A and $\left\{\overline{A}\right\}$ represents the sum of the normal–ordered terms obtained by making all possible single, double, ... contractions within A. Based on Bogoliubov and Shirkov [60], the operator is presented in normal form when all of the operators of annihilation included in it are transferred to the right of the creation operators.

Usually, Wick's theorem is applied when treating complex operators that are represented by a large number of second quantization operators in a non–normal product form. In atomic physics such operators are used in perturbation theory (see Lindgren and Morrison [40], Merkelis *et al.* [41] and Fetter and Walečka [61]) and in the orthogonal operator method (see Uylings [42]). Most often the Wick's theorem is applied to the products of second quantization operators that are not tensorially coupled (see Lindgren and Morrison [40]). While applying the perturbation theory in an extended model space, two different groups of second quantization operators are defined (see for details in Lindgren and Morrison [40]). The second quantization operators acting upon core states belong to one group, whereas the operators acting upon open and excited shells belong to another one. These two groups are very different in applying Wick's theorem to them.

In the first group, the creation operators are re–named to annihilation operators and are called the hole absorption operators, while the annihilation operators are re–named to creation operators and are called the hole creation operators. The creation operators of the second group are called the particle creation operators, while annihilation ones are called the particle absorption operators. Such a division of second quantization operators into two groups is called the particle–hole formalism.

Merkelis *et al.* [41] have proposed to use the so–called graphical analogue of Wick's theorem in perturbation theory (see Gaigalas *et al.* [52], Gaigalas [62]). It is an efficient tool for obtaining the normal products of second quantization operators in a coupled tensorial form. Before applying this theorem, particular second quantization terms are in a normal product in coupled form. In addition, this theorem is applied in the particle–hole formalism, too [41, 63].

In all the cases mentioned above, the Wick's theorem is applied for the most general case of operators, i.e. when that are acted upon are not detailed. But in the case of the extended model space (see Lindgren and Morrison [40]), the group that the second quantization operators belong to, depending on the electronic structure of atom or ion under investigation, is defined.

Gaigalas *et al.* [M6] proposed to apply the Wick's theorem for obtaining the optimal tensorial expression of any two–particle operator. The peculiarity of Wick's theorem application in this case lies in applying it only when the shells that are acted upon by the secondary quantization operators are known, i.e. it is applied for each particular term $\widehat{G}(ij,i'j')$ separately. Such an interpretation of Wick's theorem bears similarity with the particle–hole formalism and was before used, for example, by Karazija [64], too. The only difference is that in this case the second quantization operators are differentiated formally not on the basis of structure of atom under investigation, but on the basis of shells acted upon.

This is done in the following way. The second quantization operators acting upon a shell with a lowest index are attributed to the first group. Those acting upon a shell with a next–lowest index are attributed to the second group, etc. In the most general case we have four distinct groups. Assuming that all the operators from first group are the creation ones, and the rest are annihilation operators, we apply the Wick's theorem. After that, we apply Wick's theorem assuming that the operators from the first and the second groups are creation ones, and the rest of them are annihilation operators. If in the product that we investigate there are operators of second quantization acting upon four distinct shells, then we apply Wick's theorem once again, assuming that operators from the first, second and third groups are creation ones, and from the fourth group – annihilation ones. In this case the Wick's theorem is applied to the second quantization operators in uncoupled form.

From (5) we see that in second quantization approach a two–electron operator is written as a sum, where parameters i, j, i', j' run over all possible arrays of quantum numbers. So, the greater the number of open shells in *bra* and *ket* functions, the greater the number of terms $\widehat{G}(ij, i'j')$ in the expression of two–electron operator. It is obvious that all these terms must be systematized in order to obtain in general case the most efficient tensorial expression of a two–electron operator, in the way described above.

In the work by Gaigalas *et al.* [M6] there is chosen an optimal number of distributions, which is necessary to obtain the matrix elements of any two–electron operator, when the *bra* and *ket* functions consist of arbitrary number of shells. This is 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. This permits to reduce the number of distributions. For distributions 19–42 this condition is imposed only for obtaining simple analytical expressions for the recoupling matrices $R\left(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Gamma\right)$. This will be discussed in more detail in the section 2.3.2.

So, in the way that is described earlier, the Wick's theorem is applied, assuming that

Table 1: Distributions of shells, 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 shells (see Gaigalas *et al.* [M6]).

No.	a_i	a_j	$a^\dagger_{i'}$	$a^\dagger_{j'}$	**submatrix element**
1.	α	α	α	α	$\left(...n_\alpha l_\alpha^{N_\alpha}... \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert ...n_\alpha l_\alpha^{N_\alpha}...\right)$
2.	α	β	α	β	$\left(...n_\alpha l_\alpha^{N_\alpha}...n_\beta l_\beta^{N_\beta}... \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert ...n_\alpha l_\alpha^{N_\alpha}...n_\beta l_\beta^{N_\beta}...\right)$
3.	β	α	β	α	
4.	α	β	β	α	
5.	β	α	α	β	
6.	α	α	β	β	$\left(...n_\alpha l_\alpha^{N_\alpha}...n_\beta l_\beta^{N_\beta}... \Vert \widehat{G} \Vert ...n_\alpha l_\alpha^{N_\alpha-2}...n_\beta l_\beta^{N_\beta+2}...\right)$
7.	β	α	α	α	$\left(...n_\alpha l_\alpha^{N_\alpha}...n_\beta l_\beta^{N_\beta}... \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert ...n_\alpha l_\alpha^{N_\alpha+1}...n_\beta l_\beta^{N_\beta-1}...\right)$
8.	α	β	α	α	
9.	β	β	β	α	
10.	β	β	α	β	
11.	β	γ	α	γ	$\left(...n_\alpha l_\alpha^{N_\alpha}n_\beta l_\beta^{N_\beta}n_\gamma l_\gamma^{N_\gamma}... \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert ...n_\alpha l_\alpha^{N_\alpha+1}n_\beta l_\beta^{N_\beta-1}n_\gamma l_\gamma^{N_\gamma}...\right)$
12.	γ	β	γ	α	
13.	γ	β	α	γ	
14.	β	γ	γ	α	
15.	γ	γ	α	β	$\left(...n_\alpha l_\alpha^{N_\alpha}n_\beta l_\beta^{N_\beta}n_\gamma l_\gamma^{N_\gamma}... \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert ...n_\alpha l_\alpha^{N_\alpha+1}n_\beta l_\beta^{N_\beta+1}n_\gamma l_\gamma^{N_\gamma-2}...\right)$
16.	γ	γ	β	α	
17.	α	β	γ	γ	$\left(...n_\alpha l_\alpha^{N_\alpha}n_\beta l_\beta^{N_\beta}n_\gamma l_\gamma^{N_\gamma}... \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert ...n_\alpha l_\alpha^{N_\alpha-1}n_\beta l_\beta^{N_\beta-1}n_\gamma l_\gamma^{N_\gamma+2}...\right)$
18.	β	α	γ	γ	
19.	α	β	γ	δ	$\left(n_\alpha l_\alpha^{N_\alpha}n_\beta l_\beta^{N_\beta}n_\gamma l_\gamma^{N_\gamma}n_\delta l_\delta^{N_\delta} \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert n_\alpha l_\alpha^{N_\alpha-1}n_\beta l_\beta^{N_\beta-1}n_\gamma l_\gamma^{N_\gamma+1}n_\delta l_\delta^{N_\delta+1}\right)$
20.	β	α	γ	δ	
21.	α	β	δ	γ	
22.	β	α	δ	γ	
23.	γ	δ	α	β	$\left(n_\alpha l_\alpha^{N_\alpha}n_\beta l_\beta^{N_\beta}n_\gamma l_\gamma^{N_\gamma}n_\delta l_\delta^{N_\delta} \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert n_\alpha l_\alpha^{N_\alpha+1}n_\beta l_\beta^{N_\beta+1}n_\gamma l_\gamma^{N_\gamma-1}n_\delta l_\delta^{N_\delta-1}\right)$
24.	γ	δ	β	α	
25.	δ	γ	α	β	
26.	δ	γ	β	α	
27.	α	γ	β	δ	$\left(n_\alpha l_\alpha^{N_\alpha}n_\beta l_\beta^{N_\beta}n_\gamma l_\gamma^{N_\gamma}n_\delta l_\delta^{N_\delta} \Vert \widehat{G}(n_il_in_jl_jn'_il'_in'_jl'_j) \Vert n_\alpha l_\alpha^{N_\alpha-1}n_\beta l_\beta^{N_\beta+1}n_\gamma l_\gamma^{N_\gamma-1}n_\delta l_\delta^{N_\delta+1}\right)$
28.	α	γ	δ	β	
29.	γ	α	δ	β	
30.	γ	α	β	δ	

Table 1: (continued).

No.	a_i	a_j	$a^\dagger_{i'}$	$a^\dagger_{j'}$	**submatrix element**
31.	β	δ	α	γ	$\left(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \Vert \widehat{G}(n_i l_i n_j l_j n'_i l'_i n'_j l'_j) \Vert n_\alpha l_\alpha^{N_\alpha+1} n_\beta l_\beta^{N_\beta-1} n_\gamma l_\gamma^{N_\gamma+1} n_\delta l_\delta^{N_\delta-1}\right)$
32.	δ	β	γ	α	
33.	β	δ	γ	α	
34.	δ	β	α	γ	
35.	α	δ	β	γ	$\left(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \Vert \widehat{G}(n_i l_i n_j l_j n'_i l'_i n'_j l'_j) \Vert n_\alpha l_\alpha^{N_\alpha-1} n_\beta l_\beta^{N_\beta+1} n_\gamma l_\gamma^{N_\gamma+1} n_\delta l_\delta^{N_\delta-1}\right)$
36.	δ	α	γ	β	
37.	α	δ	γ	β	
38.	δ	α	β	γ	
39.	β	γ	α	δ	$\left(n_\alpha l_\alpha^{N_\alpha} n_\beta l_\beta^{N_\beta} n_\gamma l_\gamma^{N_\gamma} n_\delta l_\delta^{N_\delta} \Vert \widehat{G}(n_i l_i n_j l_j n'_i l'_i n'_j l'_j) \Vert n_\alpha l_\alpha^{N_\alpha+1} n_\beta l_\beta^{N_\beta-1} n_\gamma l_\gamma^{N_\gamma-1} n_\delta l_\delta^{N_\delta+1}\right)$
40.	γ	β	δ	α	
41.	β	γ	δ	α	
42.	γ	β	α	δ	

the second quantization operators acting upon shells α, β, γ and δ belong to different groups.

In the next section we shall discuss the way to obtain irreducible tensorial form of these distributions. In addition, the arguments will be given in evidence of superiority of the obtained tensorial expressions against other expressions known in the literature.

The methodology presented in this section demonstrates the way to obtain optimal arrangement of the second quantization operators, for any two–electron operator. It can be applied without restrictions for obtaining the optimal tensorial form of any–electron terms of orthogonal operators and of perturbation theory operators, too.

2.1.3 Graphical methods for two–electron operator

The graphical technique of angular momentum is widely used in the atomic physics: see Jucys *et al.* [65], Jucys and Bandzaitis [51], Brink and Satcher [66], El–Baz [67]. It is applied efficiently both in the coordinate representation (see, e.g., Jucys and Bandzaitis [51]), and in the second quantization formalism (Gaigalas *et al.* [68]). The use of it allows one to obtain the analytical expressions for the recoupling matrices conveniently (see, e.g., Kaniauskas and Rudzikas [69]), to investigate the tensorial products of operators (see, e.g., Jucys *et al.* [70]), and to seek for the matrix elements of operators (see, e.g., Huang and Starace [71]). Gaigalas and Merkelis [68] have proposed a graphical way to obtain the values of matrix elements when the operator is a many–particle (one–, two–, three–, etc.) one and has irreducible tensorial form. The matrix elements in this methodology are expressed not only in terms of CFP or RCFP, but in terms of standard quantities $U^{(k)}$ and $V^{(k1)}$, too. Gaigalas *et al.* [M6] have proposed to calculate the matrix elements by using the tensorial expressions for such two–particle operator, that take full advantage of Racah algebra. In this case the tensorial form of operator depends on the shells that the operator acts upon (distributions 1–42 from Table 1). This is the difference of this methodology from others. It is most convenient to obtain the tensorial expressions for 42 distributions graphically, using the generalized graphical technique by Gaigalas *et al.* [68]. In such a case not only the similarities between different distributions are easily seen, but also the compact graphical representation of the obtained expressions is possible. We will stop for details on this in the present section.

A two–particle operator may be represented graphically by a Feynman–Goldstone diagram D_1 from Figure 1 (Lindgren and Morrison [40]). As it is shown in the paper Bolotin *et al.* [72], the Feynman–Goldstone diagrams are topologically equivalent to the angular momentum graphs. Due to that, an irreducible tensorial form for every Feynman–Goldstone diagram may be obtained (see Merkelis *et al.* [63]). The graph D_2 is the angular momentum graph corresponding to the diagram D_1. So the two–particle operator will be written down as follows:

$$\widehat{G}(ij,i'j') = D_1 = -\frac{1}{2}\sum_{m_{\lambda_i} m_{\lambda_j} m_{\lambda'_i} m_{\lambda'_j}} \sum_{p} [\kappa_1,\kappa_2,\sigma_1,\sigma_2]^{-1/2}$$

$$\times \left(n_i\lambda_i n_j\lambda_j \left\| g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)} \right\| n'_i\lambda'_i n'_j\lambda'_j \right)\ D_2\ \ a^{(\lambda_i)}_{m_{\lambda_i}} a^{(\lambda_j)}_{m_{\lambda_j}}\ \tilde{a}^{(\lambda'_i)}_{m_{\lambda'_i}} \tilde{a}^{(\lambda'_j)}_{m_{\lambda'_j}}, \tag{37}$$

It must be noted that in expression (37) the projection m_{λ_i} of $a^{(\lambda_i)}_{m_{\lambda_i}}$, as well as that of the momentum line λ_i in graph D_2 are the same. This is also to be said about the remaining operators of second quantization and the three open lines af graph D_2.

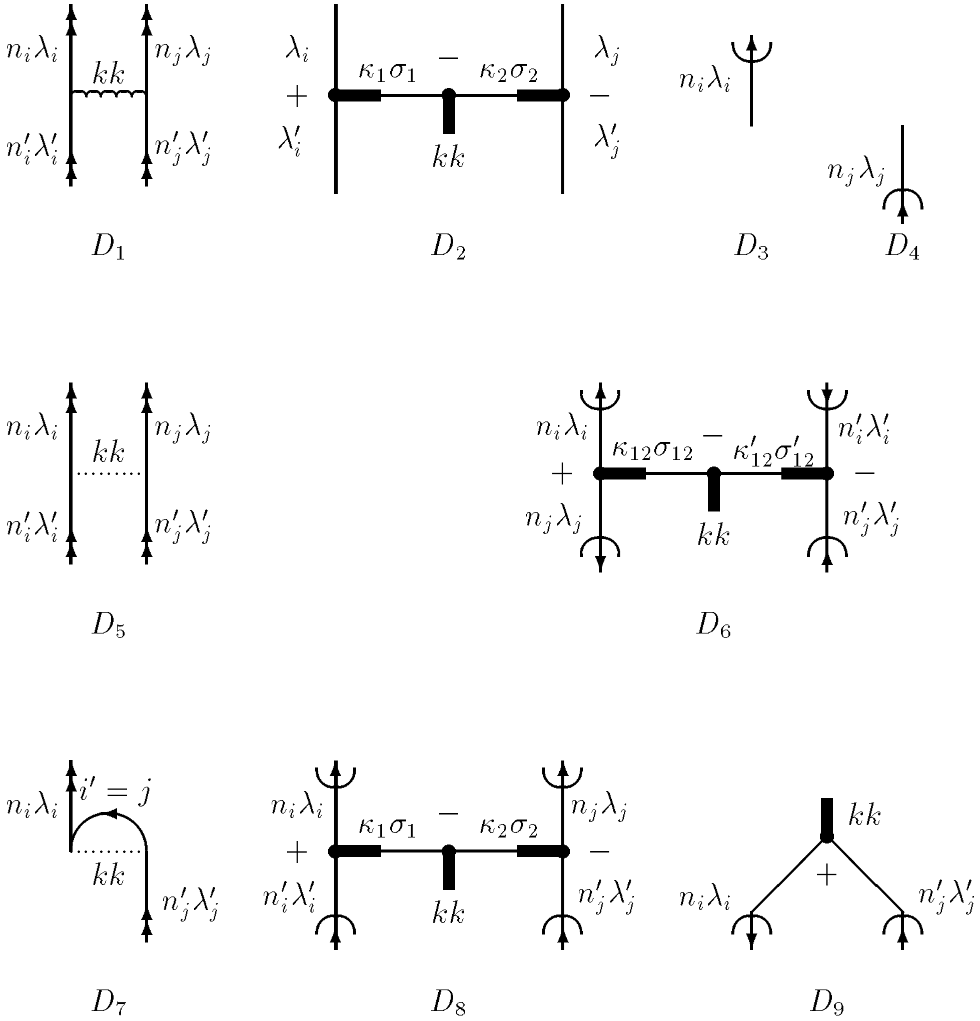


Figure 1: Diagrams for two–particle operators.

As it has been mentiond in section 2.1.1, this operator has two tensorial forms. These may be represented graphically, since the creation operator $a^{(\lambda_i)}$, as well as operator $\tilde{a}^{(\lambda'_j)}$ respectivelly, are graphically denoted by diagrams D_3 and D_4.

The first form of two–particle operator $G_I(ij,i'j')$ is represented as:

$$G_I(ij,i'j') = D_1 = -\frac{1}{2}\sum_{\kappa_{12}\kappa'_{12}\sigma_{12}\sigma'_{12}}\sum_{p}(-1)^{k-p}\left[\kappa_1,\kappa_2,\sigma_1,\sigma_2\right]^{1/2}$$

$$\times\left(n_i\lambda_i n_j\lambda_j\left\|g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}\right\|n'_i\lambda'_i n'_j\lambda'_j\right)\left\{\begin{array}{ccc} l'_i & l'_j & \kappa'_{12}\\ \kappa_1 & \kappa_2 & k\\ l_i & l_j & \kappa_{12}\end{array}\right\}\left\{\begin{array}{ccc} s & s & \sigma'_{12}\\ \sigma_1 & \sigma_2 & k\\ s & s & \sigma_{12}\end{array}\right\}D_6 \quad (38)$$

whereas the second one:

$$\begin{aligned} &G_{II}(ij,i'j')\\ &= D_5 + D_7 = \frac{1}{2}\sum_{p}(-1)^{k-p}\left(n_i\lambda_i n_j\lambda_j\left\|g^{(\kappa_1\kappa_2 k,\sigma_1\sigma_2 k)}\right\|n'_i\lambda'_i n'_j\lambda'_j\right)\\ &\times\left\{\left[\kappa_1,\kappa_2,\sigma_1,\sigma_2\right]^{-1/2}D_8 - (-1)^{l_i+l'_j}\left\{\begin{array}{ccc}\kappa_1 & \kappa_2 & k\\ l'_j & l_i & l_j\end{array}\right\}\right.\\ &\times\left.\left\{\begin{array}{ccc}\sigma_1 & \sigma_2 & k\\ s & s & s\end{array}\right\}\delta\left(n_j l_j, n'_i l'_i\right)D_9\right\}. \qquad (39)\end{aligned}$$

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 1, D_1). Whereas the dotted interaction line indicates that the second quantization operators are ordered in pairs of creation–annihilation operators. In the latter case first comes the pair on the left side of a Feynman–Goldstone diagram (Figure 1, D_5). 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 (38), (39) we see that the two–particle operator in the first form is represented by one Feynman–Goldstone diagram D_1, whereas in the second – by two diagrams D_5 and D_7. The diagrams, corresponding to tensorial product, have the following algebraic expressions:

$$D_6 = \left[\left[a^{(\lambda_i)} \times a^{(\lambda_j)} \right]^{(\kappa_{12}\sigma_{12})} \times \left[\tilde{a}^{(\lambda_i')} \times \tilde{a}^{(\lambda_j')} \right]^{(\kappa_{12}'\sigma_{12}')} \right]^{(kk)}_{p,-p}, \tag{40}$$

$$D_8 = \left[\left[a^{(\lambda_i)} \times \tilde{a}^{(\lambda_i')} \right]^{(\kappa_1\sigma_1)} \times \left[a^{(\lambda_j)} \times \tilde{a}^{(\lambda_j')} \right]^{(\kappa_2\sigma_2)} \right]^{(kk)}_{p,-p}, \tag{41}$$

$$D_9 = \left[a^{(\lambda_i)} \times \tilde{a}^{(\lambda_j')} \right]^{(kk)}_{p,-p}. \tag{42}$$

The positions of the second quantization operators in the diagrams D_6, D_8 and D_9 define their order in tensorial products: the first place in tensorial product occupies the upper right second quantization operator, the second – lower right, after them the upper left and lower left operators follow. The angular momenta diagram defines their coupling scheme into tensorial product. For more details see Gaigalas and Rudzikas [M3].

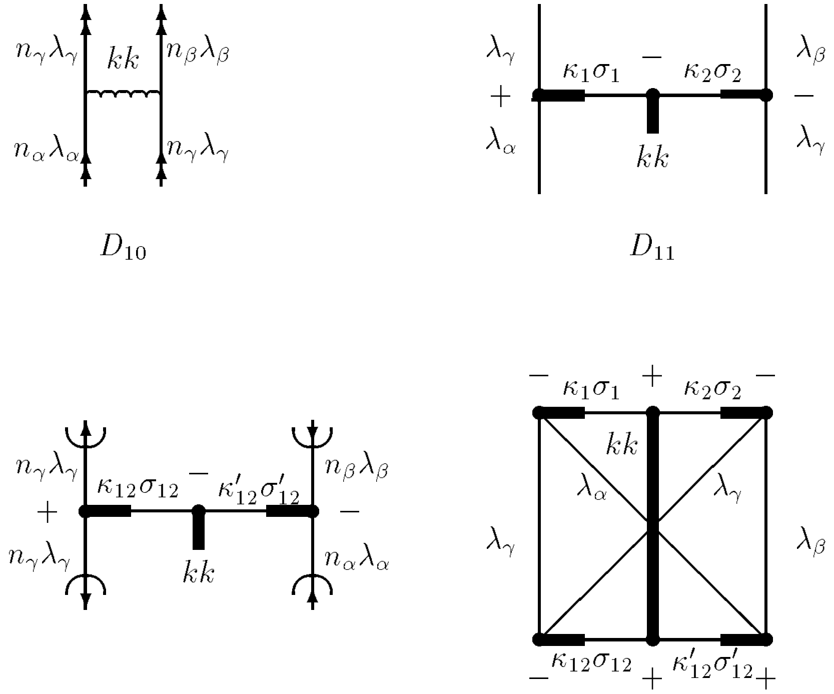
As it has been mentioned earlier, these two forms do not always take full advantage of the Racah algebra (see Gaigalas and Rudzikas [M3]). The expression (7) has no such shortcomings. Now we will demonstrate the way to obtain graphically a tensorial expressions for particular distributions 1–42 from Table 1.

We take the distribution γ, β, α, γ (13 form Table 1) as an example for investigation. Then the Feynman–Goldstone diagram of operator $\widehat{G}(\gamma\beta, \alpha\gamma)$ is D_{10}, the angular momentum graph is D_{11}, and the second quantization operators are in the following order:

$$a_\gamma a_\beta a_\alpha^\dagger a_\gamma^\dagger. \tag{43}$$

Applying the Wick's theorem as described in Section 2.1.2, and assuming that the operators acting upon shell γ belong to the first group, the once acting upon β belong to the second, and the ones acting upon α belong to the third group, we obtain the following order of operators:

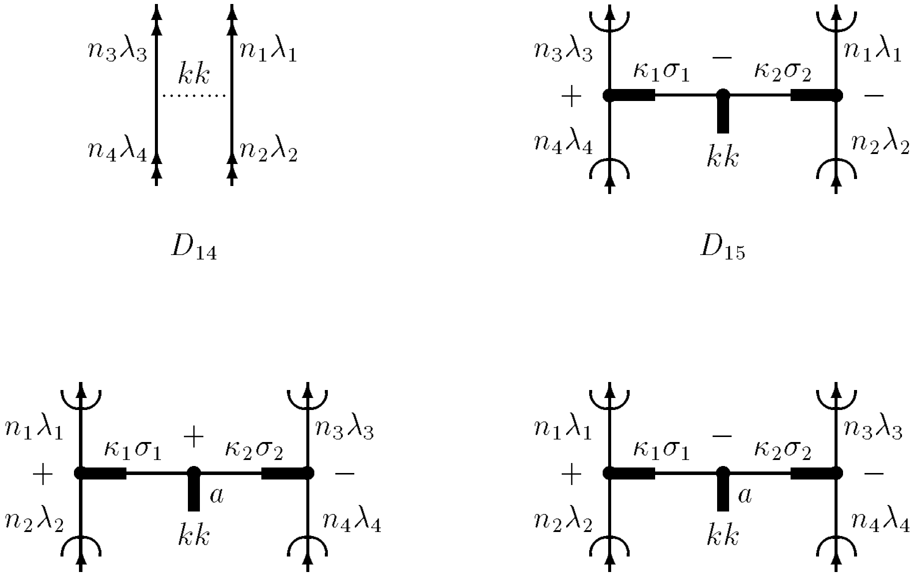
$$a_\gamma a_\gamma^\dagger a_\beta a_\alpha^\dagger. \tag{44}$$



D_{10} D_{11}

D_{12} D_{13}

Figure 2: Diagrams for distribution γ, β, α, γ.



D_{14} D_{15}

D_{16} D_{17}

Figure 3: Diagrams for graphical transformations.

Using the generalized graphical technique of angular momentum by Gaigalas *et al.* [52], we couple the operators of second quantization into tensorial product D_{12} (see Figure 2):

$$D_{12} = \left[\left[a^{(\lambda_\gamma)} \times a^{(\lambda_\gamma)} \right]^{(\kappa_{12}\sigma_{12})} \times \left[\tilde{a}^{(\lambda_\beta)} \times \tilde{a}^{(\lambda_\alpha)} \right]^{(\kappa'_{12}\sigma'_{12})} \right]^{(kk)}_{p,-p} . \tag{45}$$

In the course of obtaining D_{12} graphically, a recoupling matrix D_{13} appears, whose analytical expression is readily obtained by using the graphical technique of Jucys and Bandzaitis [51]. All the needed expressions are obtained in the same way.

In obtaining these expressions, as well as in representing them graphically, it is very convenient to use the rule of changing the sign of a node, existing in the graphical technique of angular momentum (see Jucys and Bandzaitis [51]). Therefore now we will treat an example of using such a rule.

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

$$D_{14} \longrightarrow D_{15}, \tag{46}$$

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 tensorial product, we arrive at

$$D_{14} \longrightarrow (-1)^4 D_{16} = D_{16}. \tag{47}$$

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

$$\left[\left[a^{(\lambda_1)} \times \tilde{a}^{(\lambda_2)}\right]^{(\kappa_1\sigma_1)} \times \left[a^{(\lambda_3)} \times \tilde{a}^{(\lambda_4)}\right]^{(\kappa_2\sigma_2)}\right]^{(\kappa\sigma)}. \tag{48}$$

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 D_{16}:

$$D_{14} \longrightarrow (-1)^{\kappa_1+\kappa_2-\kappa+\sigma_1+\sigma_2-\sigma} D_{17}. \tag{49}$$

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.* [52], Gaigalas [62], Gaigalas and Merkelis [68].

All the analytical expressions for distributions 1–42 from Table 1 are presented in the paper Gaigalas *et al.* [M6]. They are written down using the generalized graphical methodology of angular momentum, and the vortex sign change rule, which was discussed in this section. As a consequence of that, the analytical expressions for 42 terms may be written down via 6 different expressions. This, undoubtedly, facilitates a lot the implementation of methodology proposed in Gaigalas *et al.* [M6].

This graphical method is useful for getting analytical expressions in the other areas of atomic theory, too. See, e.g., Bogdanovich *et al.* [73, 74].

2.2 New simplifications for Breit–Pauli Hamiltonian [M8, M17]

The general tensorial form of any two–particle operator proposed in subsection 2.1.1 (Eq. (7)) is sutable for evaluation of diagonal and non–diagonal matrix elements in a uniform way. It allows one to make the most of the advantages of Racah algebra (see Racah [5, 6, 7, 8]). So further we will investigate two–particle operator in the framework of this formalism.

In this section we will discuss some special cases of distributions from Table 1 for spin–other–orbit [M8] and orbit–orbit [M17] interaction operators. In these cases of coincidence some of the submatrix elements vanish, and therefore can be omitted in spin–angular integrations, thus simplifying the calculations of matrix elements.

2.2.1 Spin–other–orbit interaction operator

For the distribution $\alpha\alpha\alpha\alpha$, on the basis of definition of submatrix elements (25) and the relation for radial integrals

$$\begin{aligned} & V^{k-1}\left(n_il_in_jl_j, n_{i'}l_{i'}n_{j'}l_{j'}\right) + V^{k-1}\left(n_{i'}l_{i'}n_{j'}l_{j'}, n_il_in_jl_j\right) \\ & \quad = kN^{k}\left(n_il_in_jl_j, n_{i'}l_{i'}n_{j'}l_{j'}\right) - (k+1)\,N^{k-2}\left(n_jl_jn_il_i, n_{j'}l_{j'}n_{i'}l_{i'}\right) \end{aligned} \tag{50}$$

we easily see that those integrals compensate each other in tensorial structures $(kk1, 101)$ and $(kk1, 011)$ [M8]:

$$\begin{aligned} & \left(n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha \left\| H_{soo}^{(kk1,\sigma_1\sigma_2 1)} \right\| n_\alpha\lambda_\alpha n_\alpha\lambda_\alpha\right) \\ & \quad = -2\cdot 2^{\sigma_2}\,(2k+1)^{1/2}\left(l_\alpha \left\| C^{(k)} \right\| l_\alpha\right)^2 \Big\{ (k\,(k+1))^{-1/2}\left(l_\alpha\,(l_\alpha+1) - k\,(k+1) - l_\alpha\,(l_\alpha+1)\right) \\ & \quad \times \Big\{ (k+1)\,N^{k-2}\left(n_\alpha l_\alpha n_\alpha l_\alpha, n_\alpha l_\alpha n_\alpha l_\alpha\right) - kN^{k}\left(n_\alpha l_\alpha n_\alpha l_\alpha, n_\alpha l_\alpha n_\alpha l_\alpha\right) \Big\} \\ & \quad -2\,(k\,(k+1))^{1/2}\,V^{k-1}\left(n_\alpha l_\alpha n_\alpha l_\alpha, n_\alpha l_\alpha n_\alpha l_\alpha\right) \Big\} = 0. \end{aligned} \tag{51}$$

Then from expressions (47), (48) and (49) of [M6], and using expression (25) for H_{12}^{soo}, we obtain the final tensorial form of spin–other–orbit interaction operator acting within a particular shell of electrons α:

$$\widehat{H}_{12}^{soo}(\alpha\alpha\alpha\alpha)$$

$$
\begin{aligned}
&= \sum_k \sum_p (-1)^{1-p} \Big\{ \left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k-1k1,101)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \\
&\times [k-1,k,1]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k-11)} \times \left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k0)} \right]^{(11)}_{p,-p} \\
&+ \left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k-1k1,011)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \\
&\times [k-1,k,1]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k-10)} \times \left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k1)} \right]^{(11)}_{p,-p} \\
&+ \left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k+1k1,101)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \\
&\times [k+1,k,1]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k+11)} \times \left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k0)} \right]^{(11)}_{p,-p} \\
&+ \left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k+1k1,011)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \\
&\times [k+1,k,1]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k+10)} \times \left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k1)} \right]^{(11)}_{p,-p} \\
&- \Big\{ \left(k(2l_\alpha - k + 1)(2l_\alpha + k + 1) \right)^{1/2} [k-1]^{-1/2} \\
&\times \left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k-1k1,101)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \\
&- \left((k+1)(2l_\alpha - k)(2l_\alpha + k + 2) \right)^{1/2} [k+1]^{-1/2} \\
&\times \left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k+1k1,101)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \Big\} \\
&\times \frac{1}{2} \sqrt{\frac{3}{2}} (-1)^k \left(l_\alpha (l_\alpha + 1) [l_\alpha, k] \right)^{-1/2} \left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(11)}_{p,-p} \Big\}. \qquad (52)
\end{aligned}
$$

We also have from (24) and (26):

$$
\begin{aligned}
&\left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k-1k1,\sigma_1 \sigma_2 1)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \\
&\quad = 2 \cdot 2^{\sigma_2} \left((2k-1)\, k\, (2k+1)\, (2l_\alpha - k + 1)\, (2l_\alpha + k + 1) \right)^{1/2} \\
&\quad \times \left(l_\alpha \left\| C^{(k)} \right\| l_\alpha \right)^2 N^{k-2} \left(n_\alpha l_\alpha n_\alpha l_\alpha, n_\alpha l_\alpha n_\alpha l_\alpha \right) \qquad (53)
\end{aligned}
$$

$$
\begin{aligned}
&\left(n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \left\| H_{soo}^{(k+1k1,\sigma_1 \sigma_2 1)} \right\| n_\alpha \lambda_\alpha n_\alpha \lambda_\alpha \right) \\
&\quad = 2 \cdot 2^{\sigma_2} \left((2k+1)\, (k+1)\, (2k+3)\, (2l_\alpha - k)\, (2l_\alpha + k + 2) \right)^{1/2} \\
&\quad \times \left(l_\alpha \left\| C^{(k)} \right\| l_\alpha \right)^2 N^{k} \left(n_\alpha l_\alpha n_\alpha l_\alpha, n_\alpha l_\alpha n_\alpha l_\alpha \right). \qquad (54)
\end{aligned}
$$

An expression equivalent to (52) (with (53) and (54)) was already presented in the monograph Jucys and Savukynas [3], formulae (13.23) and (13.24), where a matrix element of spin–other–orbit interaction within a single shell of equivalent electrons is defined. The differences are that they use the coordinate representation, and the Marvin notation of radial integrals (see Marvin [75]), where

$$M_k\left(n_il_i, n_jl_j\right) = N^k\left(n_il_in_jl_j, n_il_in_jl_j\right). \tag{55}$$

Thus, there are four terms $H_{soo}^{(k-1k1,101)}$, $H_{soo}^{(k-1k1,011)}$, $H_{soo}^{(k+1k1,101)}$ and $H_{soo}^{(k+1k1,011)}$ having different tensorial structure for this distribution instead of six (see expression (23)). All of them are general in the sense that they may be applied to obtain matrix elements of spin–other–orbit interaction operator for distribution $\alpha\alpha\alpha\alpha$ between functions with any number of open electronic shells (see [M6]).

For the distributions $\alpha\beta\alpha\beta$ and $\beta\alpha\beta\alpha$ we also have that the submatrix elements $\left(n_\alpha\lambda_\alpha n_\beta\lambda_\beta \left\| H_{soo}^{(kk1,\sigma_1\sigma_2 1)} \right\| n_\alpha\lambda_\alpha n_\beta\lambda_\beta\right)$ and $\left(n_\beta\lambda_\beta n_\alpha\lambda_\alpha \left\| H_{soo}^{(kk1,\sigma_1\sigma_2 1)} \right\| n_\beta\lambda_\beta n_\alpha\lambda_\alpha\right)$ vanish, on the basis of the same relation (50). Then from expressions (50) and (51) of [M6], we obtain the final tensorial form of the spin–other–orbit interaction operator for the distribution $\alpha\beta\alpha\beta$:

$$\begin{aligned}
&\widehat{H}_{12}^{soo}(\alpha\beta\alpha\beta) \\
&= \sum_k\sum_p (-1)^{1-p}\left\{\left(n_\alpha\lambda_\alpha n_\beta\lambda_\beta \left\| H_{soo}^{(k-1k1,101)} \right\| n_\alpha\lambda_\alpha n_\beta\lambda_\beta\right)\right. \\
&\times[k-1,k,1]^{-1/2}\left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)}\right]^{(k-11)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)}\right]^{(k0)}\right]^{(11)}_{p,-p} \\
&+ \left(n_\alpha\lambda_\alpha n_\beta\lambda_\beta \left\| H_{soo}^{(k-1k1,011)} \right\| n_\alpha\lambda_\alpha n_\beta\lambda_\beta\right) \\
&\times[k-1,k,1]^{-1/2}\left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)}\right]^{(k-10)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)}\right]^{(k1)}\right]^{(11)}_{p,-p} \\
&+ \left(n_\alpha\lambda_\alpha n_\beta\lambda_\beta \left\| H_{soo}^{(k+1k1,101)} \right\| n_\alpha\lambda_\alpha n_\beta\lambda_\beta\right) \\
&\times[k+1,k,1]^{-1/2}\left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)}\right]^{(k+11)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)}\right]^{(k0)}\right]^{(11)}_{p,-p} \\
&+ \left(n_\alpha\lambda_\alpha n_\beta\lambda_\beta \left\| H_{soo}^{(k+1k1,011)} \right\| n_\alpha\lambda_\alpha n_\beta\lambda_\beta\right)
\end{aligned}$$

$$\times \left[k+1,k,1\right]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k+10)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)} \right]^{(k1)} \right]^{(11)}_{p,-p} \Bigg\} \tag{56}$$

and for the distribution $\beta\alpha\beta\alpha$:

$$\begin{aligned}
&\widehat{H}^{soo}_{12}(\beta\alpha\beta\alpha) \\
&= \sum_k \sum_p (-1)^{1-p} \Big\{ \Big(n_\beta \lambda_\beta n_\alpha \lambda_\alpha \left\| H^{(k-1k1,101)}_{soo} \right\| n_\beta \lambda_\beta n_\alpha \lambda_\alpha \Big) \\
&\times \left[k-1,k,1\right]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k0)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)} \right]^{(k-11)} \right]^{(11)}_{p,-p} \\
&+ \Big(n_\beta \lambda_\beta n_\alpha \lambda_\alpha \left\| H^{(k-1k1,011)}_{soo} \right\| n_\beta \lambda_\beta n_\alpha \lambda_\alpha \Big) \\
&\times \left[k-1,k,1\right]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k1)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)} \right]^{(k-10)} \right]^{(11)}_{p,-p} \\
&+ \Big(n_\beta \lambda_\beta n_\alpha \lambda_\alpha \left\| H^{(k+1k1,101)}_{soo} \right\| n_\beta \lambda_\beta n_\alpha \lambda_\alpha \Big) \\
&\times \left[k+1,k,1\right]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k0)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)} \right]^{(k+11)} \right]^{(11)}_{p,-p} \\
&+ \Big(n_\beta \lambda_\beta n_\alpha \lambda_\alpha \left\| H^{(k+1k1,011)}_{soo} \right\| n_\beta \lambda_\beta n_\alpha \lambda_\alpha \Big) \\
&\times \left[k+1,k,1\right]^{-1/2} \left[\left[a^{(l_\alpha s)} \times \tilde{a}^{(l_\alpha s)} \right]^{(k1)} \times \left[a^{(l_\beta s)} \times \tilde{a}^{(l_\beta s)} \right]^{(k+10)} \right]^{(11)}_{p,-p} \Bigg\}.
\end{aligned} \tag{57}$$

The expression (57) can be obtained from (56) by interchange $\alpha \rightleftharpoons \beta$ and anticommutation of the second quantization operators. We present it here because according to the approach of [M6] the condition $\alpha < \beta$ is imposed upon α, β, so the distributions $\alpha\beta\alpha\beta$ and $\beta\alpha\beta\alpha$ are different.

We obtain the submatrix elements appearing in (56) and (57) from (24) and (26). In these two cases the tensorial form of the spin–other–orbit [M8] interaction operator also contains the radial integrals of only one type, as in (52), i.e. $N^k\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right)$. These tensorial forms (56) and (57) are general in the sense that they may be applied to obtain matrix elements for given distributions between functions with any number of open electronic shells, as stated already in subsection 2.1.1. Then the case of just two open electronic shells would be a special one, and it was treated by [3]. Those authors had obtained expressions for matrix elements of direct interaction terms diagonal with respect to configuration, containing one type of radial integrals, (see formulae (27.2)–(27.4) there), and our expressions (56) and (57) are equivalent to the operators they used (except that we have used second quantization). Jucys and Savukynas [3] had also presented matrix elements of exchange terms for two open shells case in their (27.7)–(27.9). Their operators for these cases correspond to our operators for distributions $\alpha\beta\beta\alpha$ and $\beta\alpha\alpha\beta$. For these distributions there are no vanishing tensorial structures in the spin–other–orbit interaction operator, so the simplification mentioned above is no longer possible. Then we directly use a general approach as described in subsection 2.1.1.

2.2.2 Orbit–orbit interaction operator

In this subsection we will discuss some special cases for the orbit–orbit interaction operator [M17].

Let us at first consider the distribution $\alpha\beta\alpha\beta$. Using the (29) we express the coefficient Z_k as

$$Z_k\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) = Z_k^{\prime}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) + Z_k^{\prime\prime}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right), \tag{58}$$

where

$$\begin{aligned} & Z_k^{\prime}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) \\ & \quad = k\left(k+1\right)\Big[\, 2T^{k+1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) \\ & \quad - U^{k+1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) - U^{k+1}\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right) \\ & \quad - \frac{k\left(k+1\right)\left(k+3\right)}{2\left(k+1\right)\left(2k+3\right)}\Big(N^k\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) + N^k\left(n_\beta l_\beta n_\alpha l_\alpha n_\beta l_\beta n_\alpha l_\alpha\right)\Big)\Big], \end{aligned} \tag{59}$$

$$\begin{aligned} & Z_k^{\prime\prime}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) \\ & \quad = -k\left(k+1\right)\Big[\, 2T^{k-1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) \\ & \quad - U^{k-1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) - U^{k-1}\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right) - \frac{k\left(k+1\right)\left(k-2\right)}{2k\left(2k-1\right)} \\ & \quad \times\Big(N^{k-2}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) + N^{k-2}\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right)\Big)\Big]. \end{aligned} \tag{60}$$

Let us start to evaluate the expression (59). We can rewrite the $T^{k+1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right)$ using the relation

$$T^k\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right) + T^k\left(n_{i'} l_{i'} n_j l_j, n_i l_i n_{j'} l_{j'}\right) = U^k\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right), \tag{61}$$

from [76] as

$$\begin{aligned} &2T^{k+1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) \\ &\quad = \left[T^{k+1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) + T^{k+1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right)\right] \\ &\quad = U^{k+1}\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right). \end{aligned} \tag{62}$$

With the help of equation

$$\begin{aligned} &U^k\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right) + U^k\left(n_{i'} l_{i'} n_{j'} l_{j'}, n_i l_i n_j l_j\right) \\ &\quad = -\frac{(k-1)(k+2)}{2k+1}\left\{N^{k-1}\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right) + N^{k-1}\left(n_j l_j n_i l_i, n_{j'} l_{j'} n_{i'} l_{i'}\right)\right\} \\ &\quad +A\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right), \end{aligned} \tag{63}$$

where

$$A\left(n_i l_i n_j l_j, n_{i'} l_{i'} n_{j'} l_{j'}\right) = \frac{\alpha^2}{4}\int_0^\infty R_i(r)\, R_j(r)\, R_{i'}(r)\, R_{j'}(r)\, r^2 dr. \tag{64}$$

we are rewriting the $U^{k+1}\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right)$ as

$$\begin{aligned} &U^{k+1}\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right) \\ &\quad = \frac{1}{2}\left[U^{k+1}\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right) + U^{k+1}\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right)\right] \\ &\quad = -\frac{k(k+3)}{2(2k+3)}\left[N^k\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right) + N^k\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right)\right] \\ &\quad +\frac{1}{2}A\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right). \end{aligned} \tag{65}$$

So, inserting equations (62) and (65) in the (59) we have:

$$Z'_k\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) = -\frac{k(k+1)}{2}A\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right). \tag{66}$$

After similar rearrangements of the expression (60) we have [M17]:

$$Z''_k\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) = \frac{k(k+1)}{2}A\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right). \tag{67}$$

So, finally

$$Z_k\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) = 0 \tag{68}$$

or

$$\left(n_\alpha \lambda_\alpha n_\beta \lambda_\beta \left\| H_{oo1}^{(kk0,000)} + H_{oo2}^{(kk0,000)} + H_{oo4}^{(kk0,000)} \right\| n_\alpha \lambda_\alpha n_\beta \lambda_\beta\right) = 0. \tag{69}$$

It means that for distributions $\alpha\beta\alpha\beta$ we do not need to calculate matrix elements of the terms $H_{oo1}^{(kk0,000)}$, $H_{oo2}^{(kk0,000)}$ and $H_{oo4}^{(kk0,000)}$ at all. In a similar way it is possible to prove that

$$\begin{aligned}
&Z_k\left(n_\alpha l_\alpha n_\alpha l_\alpha, n_\alpha l_\alpha n_\alpha l_\alpha\right) = Z_k\left(n_\beta l_\beta n_\alpha l_\alpha, n_\beta l_\beta n_\alpha l_\alpha\right) = Z_k\left(n_\beta l_\beta n_\alpha l_\alpha, n_\alpha l_\alpha n_\alpha l_\alpha\right) \\
&\quad = Z_k\left(n_\alpha l_\alpha n_\beta l_\beta, n_\alpha l_\alpha n_\alpha l_\alpha\right) = Z_k\left(n_\beta l_\beta n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) = Z_k\left(n_\beta l_\beta n_\beta l_\beta, n_\alpha l_\alpha n_\beta l_\beta\right) \\
&\quad = Z_k\left(n_\beta l_\beta n_\gamma l_\gamma, n_\alpha l_\alpha n_\gamma l_\gamma\right) = Z_k\left(n_\beta l_\beta n_\gamma l_\gamma, n_\alpha l_\alpha n_\gamma l_\gamma\right) = 0.
\end{aligned} \tag{70}$$

So, for the distributions $\alpha\alpha\alpha\alpha$, $\alpha\beta\alpha\beta$, $\beta\alpha\beta\alpha$, $\beta\alpha\alpha\alpha$, $\alpha\beta\alpha\alpha$, $\beta\beta\beta\alpha$, $\beta\beta\alpha\beta$, $\beta\gamma\alpha\gamma$, $\gamma\beta\gamma\alpha$ we do not need to calculate matrix elements of $H_{oo1}^{(kk0,000)}$, $H_{oo2}^{(kk0,000)}$ and $H_{oo4}^{(kk0,000)}$ terms, too. In these cases the orbit–orbit interaction operator contains the term $H_{oo3}^{(kk0,000)}$ only. The matrix element of this term has the radial integral of only one type, i.e. $N^{k-1}\left(n_j l_j n_i l_i, n_{j'} l_{j'} n_{i'} l_{i'}\right)$.

It is well known in the literature [3] that the matrix elements of the orbit–orbit operator $\mathcal{H}_{OO}$, $\left(ns^2\ {}^1S\left\|\mathcal{H}_{OO}\right\| ns^2\ {}^1S\right)$ and $\left(ns\ n's\ {}^1S\left\|\mathcal{H}_{OO}\right\| ns\ n's\ {}^1S\right)$, are zeroes. It is possible to generalize these statements using the results of the habilitation work. We see that for direct part of any diagonal matrix elements or the off–diagonal matrix elements of the type

$\left(...nl^N...n'l'^{N'}...\ LS\left\|\mathcal{H}_{OO}\right\|...nl^{N\pm1}...n'l'^{N'\mp1}...\ L'S'\right)$ we need to calculate the matrix element of $H_{oo3}^{(kk0,000)}$ operator only. Using the fact that $\left(0\left\|C^{(1)}\right\|0\right) = 0$, we strightforwardly from (33) find values of these matrix elements in the case $l, l' = 0$. These values and values of exchange part of diagonal matrix elements are equal to zero in this case. This is valid for matrix elements between functions with any number of open electron shells.

Remaining 33 distributions from Table 1 have all terms $H_{oo1}^{(kk0,000)}$, $H_{oo2}^{(kk0,000)}$, $H_{oo3}^{(kk0,000)}$ and $H_{oo4}^{(kk0,000)}$. For calculation of matrix elements of these distributions we need to find the values of $T^{k\pm1}\left(n_jl_jn_il_i, n_{j'}l_{j'}n_{i'}l_{i'}\right)$, $U^{k\pm1}\left(n_jl_jn_il_i, n_{j'}l_{j'}n_{i'}l_{i'}\right)$,

$N^{k-1}\left(n_jl_jn_il_i, n_{j'}l_{j'}n_{i'}l_{i'}\right)$, $N^{k-2}\left(n_jl_jn_il_i, n_{j'}l_{j'}n_{i'}l_{i'}\right)$ and $N^{k}\left(n_jl_jn_il_i, n_{j'}l_{j'}n_{i'}l_{i'}\right)$ integrals (see (30) and (33)).

2.3 Matrix elements in non–relativistic theory [M3, M6, M9, M10, M13, M14, M16]

2.3.1 Matrix elements between complex configurations

In this section we will discuss in more detail several ways to obtain matrix elements of a two–particle operator in non–relativistic atomic theory. As it was mentioned earlier in the Introduction, up to now the Fano calculation scheme [9] is the most popular one. Its general expression when a two–particle operator acts upon different shells is presented in (3).

The general expression for a matrix element in other cases is similar to (3). For example, when the operator acts only upon one shell, we have

$$
\begin{aligned}
&\left(\psi_u\left(LS\right)\left\|\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\right\|\psi_u\left(L'S'\right)\right)\\
&\quad\sim\sum_{n_i\lambda_i}\left(-1\right)^{\Delta}N_i\left(N_i-1\right)\left(n_i\lambda_in_i\lambda_i\left\|g^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\right\|n_i\lambda_in_i\lambda_i\right)\\
&\quad\times\sum_{\{T\}}\left(l_i^{N_i}\;\alpha_iL_iS_i\left\|l_i^{N_i-1}\;\left(\alpha_i''L_i''S_i''\right),l_i\right)\right.\left(l_i^{N_i-1}\;\alpha_i''L_i''S_i''\left\|l_j^{N_i-2}\;\left(\alpha_i'''L_i'''S_i'''\right),l_i\right)\right.\\
&\quad\times\left(l_i^{N_i'}\;\alpha_i'''L_i'''S_i'''\left\|l_i^{N_i'-1}\;\left(\alpha_i'^{V}L_i'^{V}S_i'^{V}\right),l_i\right)\right.\left(l_i^{N_i'-1}\;\alpha_i'^{V}L_i'^{V}S_i'^{V}\left\|l_i^{N_i'-2}\;\left(\alpha_i'L_i'S_i'\right),l_i\right)\right.\\
&\quad\times R_d\left(\lambda_i,\lambda_i,\lambda_i,\lambda_i,\kappa_1,\kappa_2,\kappa,\sigma_1,\sigma_2,\sigma,\Lambda^{bra},\Lambda^{ket}\right). \qquad (71)
\end{aligned}
$$

As we see here, in contrast to (3), the summation is performed only over one array n, λ of quantum numbers, because the operator acts only upon one shell. But here a summation over $\{T\}$ occurs, though, which indicates the summation over arrays of intermediate terms $\alpha_i''L_i''S_i''$, $\alpha_i'''L_i'''S_i'''$, $\alpha_i'^{V}L_i'^{V}S_i'^{V}$.

Remembering the relationship between a CFP and a reduced matrix element of a second quantization operator (see Špakauskas *et al.* [46], Rudzikas and Kaniauskas [39]):

$$\begin{aligned}&\left(l^N \ \alpha LS \left\| a^{(ls)} \right\| l^{N-1} \ \alpha' L' S'\right) \\ &\quad = (-1)^{N+(N+1)\varphi(N)} \sqrt{N[L,S]} \left(l^N \ \alpha LS \left\| l^{N-1} \ (\alpha' L' S'), l\right.\right)\end{aligned} \tag{72}$$

we see that the Racah algebra in expressions (3) and (71) is used only on the level of CFP. In separate cases, e.g., when the two–particle operator acts upon one or two shells, it is possible to use expressions which exploit the Racah algebra at a higher level, i.e. to take more advantage of the tensor algebra (see Judd [77], Jucys and Savukynas [3]). For example, let us investigate the case when a matrix element is calculated for *bra* and *ket* functions having one shell only. The tensorial forms (38) and (39) are of value here. Taking the second one of these, we have

$$\begin{aligned}&\left(nl^N \alpha LS \left\| \widehat{G}_{II} \right\| nl^N \alpha' L' S'\right) \\ &\quad = \frac{1}{2} \left(n\lambda n\lambda \left\| g^{(\kappa_1 \kappa_2 k, \sigma_1 \sigma_2 k)} \right\| n\lambda n\lambda\right) \left\{ [\kappa_1, \kappa_2, \sigma_1, \sigma_2]^{-1/2} \right. \\ &\quad \times \left(nl^N \alpha LS \left\| \left[\left[a^{(\lambda)} \times \tilde{a}^{(\lambda)} \right]^{(\kappa_1 \sigma_1)} \times \left[a^{(\lambda)} \times \tilde{a}^{(\lambda)} \right]^{(\kappa_2 \sigma_2)} \right]^{(kk)} \right\| nl^N \alpha' L' S'\right) \\ &\quad \left. - \left\{ \begin{array}{ccc} \kappa_1 & \kappa_2 & k \\ l & l & l \end{array} \right\} \left\{ \begin{array}{ccc} \sigma_1 & \sigma_2 & k \\ s & s & s \end{array} \right\} \left(nl^N \alpha LS \left\| \left[a^{(\lambda)} \times \tilde{a}^{(\lambda)} \right]^{(kk)} \right\| nl^N \alpha L' S'\right) \right\}. \end{aligned} \tag{73}$$

Using the relationships between the tensorial product of creation and annihilation operators and the tensorial quantities $U^{(k)}$ and $V^{(k1)}$ (see Rudzikas and Kaniauskas [39]), the expression (73) for matrix elements can be writen down in terms of $U^{(k)}$ and $V^{(k1)}$. In comparing (71) to (73) we see that the summation over intermediate terms $\alpha_i'' L_i'' S_i''$, $\alpha_i''' L_i''' S_i'''$, $\alpha_i^{IV} L_i^{IV} S_i^{IV}$ is already performed in expression (73). So, in this case the Racah algebra is exploited at the level of standard quantities $U^{(k)}$ ir $V^{(k1)}$. This simplifies calculations a lot:

- For zero matrix elements are easily tracked down from triangular conditions even before the actual calculation is performed. In case (73) only the triangular conditions $\delta(L, k, L')$ and $\delta(S, k, S')$ are present, but their number may be greater in other cases.

(In the above, the notation $\delta(L,k,L')$ means the triangular condition $\mid L-L' \mid \leq k \leq L+L'$.)

- The tables of standard quantities (see Nielson and Koster [17], Karazija *et al.* [18], Cowan [2], Gaigalas [M10, M16]) may be used.

- The recoupling matrix is simpler in this case, and it has an analitical expression.

So, the expressions exploiting the Racah algebra at the level of $U^{(k)}$ and $V^{(k1)}$ are much more advantageous than (3). Such expressions are obtained for all two–particle operators. For example, the expressions for spin–other–orbit operator are presented in papers Horie [78], Karazija *et al.* [79] and Vizbaraitė *et al.* [80], the ones for spin–spin operator – in papers Horie [78] and Karazija *et al.* [81], and the ones for orbit–orbit operator in the monograph Jucys and Savukynas [3]. The shortcoming of the expressions of this type is that the Racah algebra is exploited to its full extent in separate cases only. This is discussed in detail in paper by Gaigalas *et al.* [M3].

Gaigalas *et al.* [M6] on the basis of two–partical operator tensorial form (7) have proposed a methodology which allows one to take all the advantages of the Racah algebra in the most general case. According to the approach by Gaigalas *et al.* [M6], a general expression of submatrix element for any two–particle operator between functions with u open shells can be written down as follows:

$$\begin{aligned}
&\left(\psi_u\left(LS\right)\left\|\widehat{G}^{(\kappa_1\kappa_2k,\sigma_1\sigma_2k)}\right\|\psi_u\left(L'S'\right)\right)\\
&\quad=\sum_{n_il_i,n_jl_j,n_i'l_i',n_j'l_j'}\left(\psi_u\left(LS\right)\left\|\widehat{G}\left(n_il_i,n_jl_j,n_i'l_i',n_j'l_j'\right)\right\|\psi_u\left(L'S'\right)\right)\\
&\quad=\sum_{n_il_i,n_jl_j,n_i'l_i',n_j'l_j'}\sum_{\kappa_{12},\sigma_{12},\kappa_{12}',\sigma_{12}'}\sum_{K_l,K_s}(-1)^{\Delta}\,\Theta'\left(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Xi\right)\\
&\quad\times T\left(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Lambda^{bra},\Lambda^{ket},\Xi,\Gamma\right)R\left(\lambda_i,\lambda_j,\lambda_i',\lambda_j',\Lambda^{bra},\Lambda^{ket},\Gamma\right),\qquad(74)
\end{aligned}$$

where Γ refers to the array of coupling parameters connecting the recoupling matrix $R\left(\lambda_i,\lambda_j,\lambda_i',\lambda_j',\Lambda^{bra},\Lambda^{ket},\Gamma\right)$ to the submatrix element

$T\left(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Lambda^{bra},\Lambda^{ket},\Xi,\Gamma\right)$. The exprssion (74) has summations over intermediate ranks κ_{12}, σ_{12}, κ_{12}', σ_{12}', K_l, K_s in $T\left(n_i\lambda_i,n_j\lambda_j,n_i'\lambda_i',n_j'\lambda_j',\Lambda^{bra},\Lambda^{ket},\Xi,\Gamma\right)$.

In calculating the spin–angular part of a submatrix element using (74), one has to compute the following quantities (for more details see Gaigalas [M6]):

1. The recoupling matrix $R\left(\lambda_i,\lambda_j,\lambda'_i,\lambda'_j,\Lambda^{bra},\Lambda^{ket},\Gamma\right)$. This recoupling matrix accounts for the change in going from matrix element $\left(\psi_u\left(LS\right)\left\|\widehat{G}\left(n_il_i,n_jl_j,n'_il'_i,n'_jl'_j\right)\right\|\psi_u\left(L'S'\right)\right)$, which has u open shells in the *bra* and *ket* functions, to the submatrix element $T\left(n_i\lambda_i,n_j\lambda_j,n'_i\lambda'_i,n'_j\lambda'_j,\Lambda^{bra},\Lambda^{ket},\Xi,\Gamma\right)$, which has only the shells being acted upon by the two–particle operator in its *bra* and *ket* functions.

2. The submatrix element $T\left(n_i\lambda_i,n_j\lambda_j,n'_i\lambda'_i,n'_j\lambda'_j,\Lambda^{bra},\Lambda^{ket},\Xi,\Gamma\right)$, which denotes the submatrix elements of operators (8)–(12). Here Γ refers to the array of coupling parameters connecting the recoupling matrix $R\left(\lambda_i,\lambda_j,\lambda'_i,\lambda'_j,\Lambda^{bra},\Lambda^{ket},\Gamma\right)$ to the submatrix element.

3. Phase factor Δ (for more details see Gaigalas [M6]).

4. $\Theta'\left(n_i\lambda_i,n_j\lambda_j,n'_i\lambda'_i,n'_j\lambda'_j,\Xi\right)$, which is proportional to the radial part and corresponds to one of $\Theta\left(n\lambda,\Xi\right)$,...,$\Theta\left(n_\alpha\lambda_\alpha,n_\beta\lambda_\beta,n_\gamma\lambda_\gamma,n_\delta\lambda_\delta,\Xi\right)$. It consists of a submatrix element $\left(n_i\lambda_in_j\lambda_j\left\|g^{\left(\kappa_1\kappa_2k,\sigma_1\sigma_2k\right)}\right\|n'_i\lambda'_in'_j\lambda'_j\right)$, and in some cases of simple factors and $3nj$–coefficients (for more details see Gaigalas [M6]).

In the next sections we shall discuss the finding of these quantities.

2.3.2 Recoupling matrix

While seeking the matrix elements of one– or two–particle operators, it is necessary to obtain the values of a recoupling matrix $R\left(\lambda_i,\lambda_j,\lambda'_i,\lambda'_j,\Lambda^{bra},\Lambda^{ket},\Gamma\right)$, if we use the methodology by Gaigalas *et al.* [M6] (see expresion (74)), or the recoupling matrices

$R_d\left(\lambda_i,\lambda_j,\lambda'_i,\lambda'_j,\kappa_1,\kappa_2,\kappa,\sigma_1,\sigma_2,\sigma,\Lambda^{bra},\Lambda^{ket}\right)$ and

$R_e\left(\lambda_i,\lambda_j,\lambda'_i,\lambda'_j,\kappa_1,\kappa_2,\kappa,\sigma_1,\sigma_2,\sigma,\Lambda^{bra},\Lambda^{ket}\right)$, if we use the methodology by Fano [9] (see expresion (3)).

Meanwhile, for the more complex configurations, i.e. the ones having many open shells, the recoupling matrices are much more complicated. Beside that, the complexity of a two–particle operator adds to this. When the tensorial structure of an operator is complex, the recoupling matrix is rather complex, too, e.g., the spin–other–orbit operator (see Gaigalas [M8]). While attempting to calculate the spin–angular part of matrix elements in all the mentioned cases, a general methodology for calculating the recoupling matrices is necessary. It has to be efficient, too, because the speed of calculation of spin–angular parts of matrix elements depends on that.

The majority of methodologies to obtain spin–angular parts are based on the Fano [9] calculation scheme (see, e.g., Glass [11], Glass and Hibbert [12], Grant [10]). In finding the matrix elements using this, one of the tasks is to obtain the recoupling matrices for direct and exchange terms.

The first program to calculate the recoupling matrices of this type, NJSYM, was written by Burke [27]. It performs the calculations in two stages: 1) the recoupling matrix is expressed as a sum of products of the $6j$–coefficients; 2) this expression is used in calculation.

Tutlys [82] wrote a program to calculate spin–angular parts of matrix elements, ANGULA, which expressed the recoupling matrix in terms of Clebsch–Gordan coefficients before the actual calculations. While finding the recoupling matrix by the Clebsch–Gordan coefficient summation, this program eliminates trivial coefficients from the expression.

Bar–Shalom and Klapisch [28] developed a new program NJGRAF. This program calculates the recoupling matrix in several stages. On the basis of graphical methodology by Jucys, Levinson and Vanagas [65], the recoupling matrix is analysed graphically and an optimal expression is found. Afterwards, the value of recoupling matrix itself is calculated. An analogous program RECOUP was written by Lima [83], and a program NEWGRAPH was written by Fack *et al.* [84]. All these (NJGRAF, RECOUP and NEWGRAPH) are based on the same principle. An optimal analytical expression for the recoupling matrix is obtained by graphical method, and then the calculations are carried out according to it. But the optimal expressions they find are different quite often, and are not really optimal.

As it was mentioned above, the methodology of spin–angular calculation based on the Fano calculation scheme has a shortcoming that the intermediate sums appear in complex recoupling matrices. 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.* [13]. They tabulated separate standard parts of recoupling matrices along with CFP at the beginning of a calculation and then used them later on to calculate the coefficients needed.

As was mentioned in introduction of this work a computer codes by Glass [11], Glass and Hibbert [12], Burke *et al.* [13], Froese Fischer [85], Fischer [14] and Dyall *et al.* [15] use the program NJSYM (Burke [27]) or NJGRAF (Bar–Shalom and Klapisch [28]) for the calculation of recoupling matrices. Both are rather time consuming when calculating matrix elements of complex operators or electronic configurations with many open shells. In order to simplify the calculations, Cowan [2] suggested grouping matrix elements into 'classes' (see Cowan [2], Figure 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 well known.

Gaigalas *et al.* [M6] proposed a methodology where the analytical expressions for recoupling matrices are obtained for the most general case. In this methodology, analogically as in Cowan [2], the matrix elements are attributed to four different groups. The operators acting upon only one shell belong to the first group (distribution 1 from Table 1), the ones acting upon two – to the second (distributions 2–10 from Table 1), upon three – to the third (distributions 11–18 from Table 1), and upon four – to the fourth group (distributions 19–42 from Table 1) respectively. Each group has a different recoupling matrix.

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:

$$R\left(l_a, L_a, k\right)$$

$$= \left[L_a\right]^{-1/2} \delta\left(L_1, L_1'\right) ... \delta\left(L_{a-1}, L_{a-1}'\right) \delta\left(L_{a+1}, L_{a+1}'\right) ... \delta\left(L_u, L_u'\right)$$

Table 2: Parameters for equation (76).

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}
$u \neq 2$	$a > 2$	$L_{12\ldots a-1} + L_{12\ldots a} + L'_a + k$	$L_{12\ldots a-1}$	$L_{12\ldots a}$	$L'_{12\ldots a}$

$$\times \begin{cases} \delta\left(L_1, L'_1, k\right); & \text{for } u = 1 \\ C_1; & \text{for } u = 2 \\ C_1 C_2\left(k, a+1, u-1\right) C_3; & \text{for } a < 3, u > 2 \\ \begin{array}{l} \delta\left(L_{12}, L'_{12}\right) \ldots \delta\left(L_{12\ldots a-1}, L'_{12\ldots a-1}\right) \\ \quad \times C_1 C_2\left(k, a+1, u-1\right) C_3; \end{array} & \text{for } a > 3, a \neq u, u > 2 \\ \delta\left(L_{12}, L'_{12}\right) \ldots \delta\left(L_{12\ldots a-1}, L'_{12\ldots a-1}\right) C_3; & \text{for } a = u, u > 2, \end{cases} , \tag{75}$$

where

$$C_1 = (-1)^{\varphi}\left[L_a, T'\right]^{1/2} \begin{Bmatrix} k & L'_a & L_a \\ J & T & T' \end{Bmatrix} \tag{76}$$

and the values of parameters φ, J, T and T' present in expression (76) are given in Table 2. The remaining two coefficients are

$$C_2\left(k, k_{\min}, k_{\max}\right) = \prod_{i=k_{\min}}^{k_{\max}} (-1)^{k+L_i+L_{12\ldots i-1}+L'_{12\ldots i}} \left[L_{12\ldots i-1}, L'_{12\ldots i}\right]^{1/2} \begin{Bmatrix} k & L'_{12\ldots i-1} & L_{12\ldots i-1} \\ L_i & L_{12\ldots i} & L'_{12\ldots i} \end{Bmatrix} \tag{77}$$

and

$$C_3 = (-1)^{\varphi}\left[J, T'\right]^{1/2} \begin{Bmatrix} k & J' & J \\ j & T & T' \end{Bmatrix}, \tag{78}$$

Table 3: Parameters for equation (78).

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

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

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

$$\begin{aligned} & R\left(l_a, L_a, 0\right) \\ & \quad = \delta\left(L_1, L_1'\right)\delta\left(L_2, L_2'\right)\delta\left(L_{12}, L_{12}'\right)...\delta\left(L_{a-1}, L_{a-1}'\right)\delta\left(L_{12...a-1}, L_{12...a-1}'\right)\delta\left(L_a, L_a'\right) \\ & \quad \times\delta\left(L_{12...a}, L_{12...a}'\right)\delta\left(L_{a+1}, L_{a+1}'\right)\delta\left(L_{12...a+1}, L_{12...a+1}'\right)...\delta\left(L_u, L_u'\right)\delta\left(L, L'\right). \qquad (79) \end{aligned}$$

Expression (79) is equivalent to (13.60) of Cowan [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

$$\begin{aligned} & R\left(l_a, L_a, l_b, L_b, \kappa_{12}, \kappa_{12}', k\right) \\ & \quad = (-1)^{\zeta}\left[L_a, L_b\right]^{-1/2}\delta\left(L_1, L_1'\right)...\delta\left(L_{a-1}, L_{a-1}'\right)\delta\left(L_{a+1}, L_{a+1}'\right)...\delta\left(L_{b-1}, L_{b-1}'\right) \\ & \quad \times\delta\left(L_{b+1}, L_{b+1}'\right)...\delta\left(L_u, L_u'\right) \end{aligned}$$

$$\times\begin{cases} C_4\left(K_{12},K'_{12},k,1\right)C_2\left(k,3,u-1\right)C_3; & \text{for } a=1,b=2 \\[2em] \begin{array}{l} C_1C_2\left(K_{12},a+1,b-1\right)C_4\left(K_{12},K'_{12},k,1\right) \\ \quad\times C_2\left(k,b+1,u-1\right)C_3; \end{array} & \text{for } a<3,b>2,b\neq u \\[2em] C_1C_2\left(K_{12},a+1,b-1\right)C_4\left(K_{12},K'_{12},k,1\right); & \text{for } a<3,b=u \\[2em] \begin{array}{l} \delta\left(L_{12},L'_{12}\right)...\delta\left(L_{12...a-1},L'_{12...a-1}\right)C_1 \\ \quad\times C_2\left(K_{12},a+1,b-1\right)C_4\left(K_{12},K'_{12},k,1\right) \\ \quad\times C_2\left(k,b+1,u-1\right)C_3; \end{array} & \text{for } a\geq 3,b>2,b\neq u \\[2em] \begin{array}{l} \delta\left(L_{12},L'_{12}\right)...\delta\left(L_{12...a-1},L'_{12...a-1}\right)C_1 \\ \quad\times C_2\left(K_{12},a+1,b-1\right)C_4\left(K_{12},K'_{12},k,1\right); \end{array} & \text{for } a\geq 3,b=u \end{cases} \tag{80}$$

where

$$\zeta=\begin{cases} 0 & \text{for } \alpha<\beta, \\ \kappa_{12}+\kappa'_{12}-k & \text{for } \alpha>\beta, \end{cases} \tag{81}$$

and

$$C_4\left(k_1,k_2,k,P\right)=\left[J_1,J_2,J'_3,k\right]^{1/2}\left\{\begin{array}{ccc} J'_1 & k_1 & J_1 \\ J'_2 & k_2 & J_2 \\ J'_3 & k & J_3 \end{array}\right\}. \tag{82}$$

The values of parameters J_1, J'_1, J_2, J'_2, J_3 and J'_3 present in the expression (82) must be taken from Table 4. For the case $\alpha<\beta$ in Eq. (80) $K_{12}=\kappa_{12}$, $K'_{12}=\kappa'_{12}$ 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:

$$\begin{aligned} &R\left(l_a,L_a,l_b,L_b,k,k,0\right) \\ &\quad=\left[L_a,L'_b,k\right]^{-1/2}\delta\left(L_1,L'_1\right)...\delta\left(L_{a-1},L'_{a-1}\right)\delta\left(L_{a+1},L'_{a+1}\right)...\delta\left(L_{b-1},L'_{b-1}\right) \\ &\quad\times\delta\left(L_{b+1},L'_{b+1}\right)...\delta\left(L_u,L'_u\right)\delta\left(L_{12},L'_{12}\right)...\delta\left(L_{12...a-1},L'_{12...a-1}\right)\delta\left(L_{12...b},L'_{12...b}\right)...\delta\left(L,L'\right) \end{aligned}$$

Table 4: Parameters for equation (82).

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 (84).

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

$$\times \left\{ \begin{array}{ll} C_5(1); & \text{for } a = 1, b = 2 \\ & \\ C_1C_2(k, a+1, b-1)\, C_5(1); & \text{for } a < 3 \\ & \\ \delta(L_{12}, L_{12}') \ldots \delta\left(L_{12\ldots a-1}, L_{12\ldots a-1}'\right) & \\ \quad \times C_1C_2(k, a+1, b-1)\, C_5(1); & \text{for } a \geq 3 \end{array} \right. , \tag{83}$$

where

$$C_5(P) = (-1)^{k+L_b+J_1'+J_2} [J_1, L_b']^{1/2} \left\{ \begin{array}{ccc} k & L_b' & L_b \\ J_2 & J_1 & J_1' \end{array} \right\}. \tag{84}$$

The values of parameters J_1, J_1' and J_2 present in the expression (84) must be taken from Table 5.

Formula (83) has no analogue in Cowan [2]. Our expressions for the recoupling matrix do not depend on CFP and have no intermediate summations. Therefore they will be very convenient for practical calculations.

Three interacting shells

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

$$
\begin{aligned}
&R\left(l_a, L_a, l_b, L_b, l_c, L_c, k_1, k_2, \kappa_{12}, \kappa'_{12}, k\right)\\
&\quad= \left[L_a, L_b, L_c\right]^{-1/2} \delta\left(L_1, L'_1\right) ... \delta\left(L_{a-1}, L'_{a-1}\right) \delta\left(L_{a+1}, L'_{a+1}\right) ... \delta\left(L_{b-1}, L'_{b-1}\right)\\
&\quad\times \delta\left(L_{b+1}, L'_{b+1}\right) ... \delta\left(L_{c-1}, L'_{c-1}\right) \delta\left(L_{c+1}, L'_{c+1}\right) ... \delta\left(L_u, L'_u\right) \sum_{j_{12}} (-1)^{\zeta} C_6\\
&\quad\times \begin{cases}
\begin{array}{l} C_4\left(K_1, K_2, j_{12}, 1\right) C_2\left(j_{12}, 3, c-1\right) \\ \quad \times C_4\left(j_{12}, K_3, k, 2\right) C_2\left(k, c+1, u-1\right) C_3; \end{array} & \text{for } a=1, b=2 \\[2ex]
\begin{array}{l} C_1 C_2\left(K_1, a+1, b-1\right) C_4\left(K_1, K_2, j_{12}, 1\right) \\ \quad \times C_2\left(j_{12}, b+1, c-1\right) C_4\left(j_{12}, K_3, k, 2\right) \\ \quad \times C_2\left(k, c+1, u-1\right) C_3; \end{array} & \text{for } a<3 \\[2ex]
\begin{array}{l} \delta\left(L_{12}, L'_{12}\right) ... \delta\left(L_{12...a-1}, L'_{12...a-1}\right) C_1 \\ \quad \times C_2\left(K_1, a+1, b-1\right) C_4\left(K_1, K_2, j_{12}, 1\right) \\ \quad \times C_2\left(j_{12}, b+1, c-1\right) C_4\left(j_{12}, K_3, k, 2\right) \\ \quad \times C_2\left(k, c+1, u-1\right) C_3; \end{array} & \text{for } a \geq 3, \end{cases} ,
\end{aligned}
\tag{85}
$$

where parameters a, b, c, ζ, K_1, K_2, K_3 and coefficient C_6 are given in Table 6. The coefficient $C'_6\left(k_1, k_2, k_3, k_4, k_5, k_6\right)$ is

$$
C'_6\left(k_1, k_2, k_3, k_4, k_5, k_6\right) = (-1)^{k_1+k_2-k_3+2k_5} \left[k_3, k_6\right]^{1/2} \begin{Bmatrix} k_1 & k_2 & k_3 \\ k_4 & k_5 & k_6 \end{Bmatrix}. \tag{86}
$$

From (7) we have that in expressions (85) and (86) 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:

$$R\left(l_a, L_a, l_b, L_b, l_c, L_c, k_1, k_2, k, k, 0\right)$$

Table 6: Parameters for equation (85).

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}	$\delta\left(j_{12}, \kappa_{12}\right)$
$\beta < \alpha < \gamma$	β	α	γ	$k_1 + k_2 - \kappa_{12}$	k_2	k_1	κ'_{12}	$\delta\left(j_{12}, \kappa_{12}\right)$
$\beta < \gamma < \alpha$	β	γ	α	0	k_2	κ'_{12}	k_1	$C'_6\left(\kappa'_{12}, k_2, j_{12}, k_1, k, \kappa_{12}\right)$
$\alpha < \gamma < \beta$	α	γ	β	$k_1 + k_2 - \kappa_{12}$	k_1	κ'_{12}	k_2	$C'_6\left(\kappa'_{12}, k_1, j_{12}, k_2, k, \kappa_{12}\right)$
$\gamma < \alpha < \beta$	γ	α	β	$2k_1 + k_2 - \kappa_{12} + {}$ $+\kappa'_{12} - j_{12}$	κ'_{12}	k_1	k_2	$C'_6\left(\kappa'_{12}, k_1, j_{12}, k_2, k, \kappa_{12}\right)$
$\gamma < \beta < \alpha$	γ	β	α	$k_1 + k_2 - \kappa_{12}$	κ'_{12}	k_2	k_1	$C'_6\left(\kappa'_{12}, k_2, j_{12}, k_1, k, \kappa_{12}\right)$

$$= (-1)^{\zeta}\left[L_a, L_b, L'_c, K_3\right]^{-1/2} \delta\left(L_1, L'_1\right) ... \delta\left(L_{a-1}, L'_{a-1}\right) \delta\left(L_{a+1}, L'_{a+1}\right) ... \delta\left(L_{b-1}, L'_{b-1}\right)$$

$$\times \delta\left(L_{b+1}, L'_{b+1}\right) ... \delta\left(L_{c-1}, L'_{c-1}\right) \delta\left(L_{c+1}, L'_{c+1}\right) ... \delta\left(L_u, L'_u\right)$$

$$\times \delta\left(L_{12}, L'_{12}\right) ... \delta\left(L_{12...a-1}, L'_{12...a-1}\right) \delta\left(L_{12...c}, L'_{12...c}\right) ... \delta\left(L, L'\right)$$

$$\times \begin{cases} C_4\left(K_1, K_2, K_3, 1\right) C_2\left(K_3, b+1, c-1\right) C_5(2)\,; & \text{for } a = 1, b = 2 \\ \\ C_1 C_2\left(K_1, a+1, b-1\right) C_4\left(K_1, K_2, K_3, 1\right) & \\ \quad \times C_2\left(K_3, b+1, c-1\right) C_5(2)\,; & \text{for } a < 3 \\ \\ \delta\left(L_{12}, L'_{12}\right) ... \delta\left(L_{12...a-1}, L'_{12...a-1}\right) C_1 & \\ \quad \times C_2\left(K_1, a+1, b-1\right) C_4\left(K_1, K_2, K_3, 1\right) & \text{for } a \geq 3 \\ \quad \times C_2\left(K_3, b+1, c-1\right) C_5(2)\,; & \end{cases}, \qquad (87)$$

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

The recoupling matrix for three interacting shells (87) has the same advantages as the equivalent quantity, Eq. (83), for two shells.

Four interacting shells

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

$$R\left(l_a, L_a, l_b, L_b, l_c, L_c, l_d, L_d, k_1, k_2, \kappa_{12}, k_3, k_4, \kappa'_{12}, k\right)$$

$$= \left[L_a, L_b, L_c, L_d\right]^{-1/2} \delta\left(L_1, L'_1\right) ... \delta\left(L_{a-1}, L'_{a-1}\right) \delta\left(L_{a+1}, L'_{a+1}\right) ... \delta\left(L_{b-1}, L'_{b-1}\right)$$

Table 7: Parameters for equation (87).

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

$$\times\delta\left(L_{b+1}, L'_{b+1}\right)...\delta\left(L_{c-1}, L'_{c-1}\right)\delta\left(L_{c+1}, L'_{c+1}\right)...\delta\left(L_{d-1}, L'_{d-1}\right)$$

$$\times\delta\left(L_{d+1}, L'_{d+1}\right)...\delta\left(L_u, L'_u\right)$$

$$\times\begin{cases} \begin{array}{l} C_4\left(k_1, k_2, \kappa_{12}, 1\right)C_2\left(\kappa_{12}, 3, c-1\right)C_7\left(c, d\right) \\ \quad\times C_2\left(k, d+1, u-1\right)C_3; \end{array} & \text{for } a = 1, b = 2 \\ \\ \begin{array}{l} C_1C_2\left(k_1, a+1, b-1\right)C_4\left(k_1, k_2, \kappa_{12}, 1\right) \\ \quad\times C_2\left(\kappa_{12}, b+1, c-1\right)C_7\left(c, d\right) \\ \quad\times C_2\left(k, d+1, u-1\right)C_3; \end{array} & \text{for } a < 3 \\ \\ \begin{array}{l} \delta\left(L_{12}, L'_{12}\right)...\delta\left(L_{12...a-1}, L'_{12...a-1}\right)C_1 \\ \quad\times C_2\left(k_1, a+1, b-1\right)C_4\left(k_1, k_2, \kappa_{12}, 1\right) \\ \quad\times C_2\left(\kappa_{12}, b+1, c-1\right)C_7\left(c, d\right) \\ \quad\times C_2\left(k, d+1, u-1\right)C_3; \end{array} & \text{for } a \geq 3 \end{cases}, \qquad (88)$$

where

$$C_7\left(k_{\min}, k_{\max}\right)$$

$$= \begin{cases} \sum_{I} C_8\left(I\right) C_{10}\left(I\right), & \text{for } k_{\max} - k_{\min} = 1 \\ \sum_{I_1}\sum_{I_2} C_8\left(I_1\right) C_9\left(I_1, I_2, k_{\min}+1\right) C_{10}\left(I_2\right), & \text{for } k_{\max} - k_{\min} = 2 \\ \sum_{I_1}\sum_{I_2} C_8\left(I_1\right) C_{11}\left(I_1, I_2\right) C_{10}\left(I_2\right); & \text{for } k_{\max} - k_{\min} < 2 \end{cases}, \qquad (89)$$

$$\begin{aligned} & C_8\left(I\right) \\ & \quad = \left(-1\right)^{\kappa_{12}+L'_{12\ldots c}-I} \left[L_c, I, L_{12\ldots c-1}, L'_{12\ldots c}\right]^{1/2} \\ & \quad \times \begin{Bmatrix} k_3 & L'_c & L_c \\ L_{12\ldots c-1} & L_{12\ldots c} & I \end{Bmatrix} \begin{Bmatrix} L'_{12\ldots c-1} & \kappa_{12} & L_{12\ldots c-1} \\ I & L'_c & L'_{12\ldots c} \end{Bmatrix}, \end{aligned} \qquad (90)$$

$$\begin{aligned} & C_9\left(I_1, I_2, i\right) \\ & \quad = \left(-1\right)^{2\left(I_1+L_i\right)+L_{12\ldots i}+L'_{12\ldots i}+k_3+\kappa_{12}} \left[L_{12\ldots i-1}, I_1, I_2, L'_{12\ldots i}\right]^{1/2} \\ & \quad \times \begin{Bmatrix} L_{12\ldots i-1} & I_1 & k_3 \\ I_2 & L_{12\ldots i} & L_i \end{Bmatrix} \begin{Bmatrix} L'_{12\ldots i-1} & I_1 & \kappa_{12} \\ I_2 & L'_{12\ldots i} & L_i \end{Bmatrix}, \end{aligned} \qquad (91)$$

$$\begin{aligned} & C_{10}\left(I\right) \\ & \quad = \left(-1\right)^{2\left(I+k_3\right)+k_4+\kappa_{12}+\kappa'_{12}+k+L_{12\ldots d}+L'_{12\ldots d}+L_d+L'_d+L'_{12\ldots d-1}} \\ & \quad \times \left[\kappa_{12}, \kappa'_{12}, L_d, I, L'_{12\ldots d}, L_{12\ldots d-1}\right]^{1/2} \sum_{x} \left(-1\right)^{x} \left[x\right] \begin{Bmatrix} I & \kappa'_{12} & x \\ k & L'_{12\ldots d-1} & \kappa_{12} \end{Bmatrix} \\ & \quad \times \begin{Bmatrix} I & \kappa'_{12} & x \\ k_4 & L_{12\ldots d-1} & k_3 \end{Bmatrix} \begin{Bmatrix} L_{12\ldots d-1} & k_4 & x \\ L'_d & L_{12\ldots d} & L_d \end{Bmatrix} \begin{Bmatrix} L'_{12\ldots d-1} & k & x \\ L_{12\ldots d} & L'_d & L'_{12\ldots d} \end{Bmatrix}, \end{aligned} \qquad (92)$$

$$\begin{aligned} & C_{11}\left(I_1, I_2\right) \\ & \quad = \left(-1\right)^{I_1-I_2+L'_{12\ldots c}-L'_{12\ldots d-1}} \left[I_1, I_2\right]^{1/2} \sum_{x} \left[x\right] C_2\left(x, c+1, d-1\right) \end{aligned}$$

$$\times\left\{\begin{array}{ccc} k_3 & \kappa_{12} & x \\ L'_{12\ldots c} & L_{12\ldots c} & I_1 \end{array}\right\}\left\{\begin{array}{ccc} k_3 & \kappa_{12} & x \\ L'_{12\ldots d-1} & L_{12\ldots d-1} & I_2 \end{array}\right\}. \tag{93}$$

From (7) we have that in the expressions (88), (91), (92) and (93) 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:

$$\begin{aligned}
&R\left(l_a, L_a, l_b, L_b, l_c, L_c, l_d, L_d, k_1, k_2, k, k_3, k_4, k, 0\right) \\
&\quad = \left[L_a, L_b, L_c, L'_d, k\right]^{-1/2} \delta\left(L_1, L'_1\right) \ldots \delta\left(L_{a-1}, L'_{a-1}\right) \delta\left(L_{a+1}, L'_{a+1}\right) \ldots \delta\left(L_{b-1}, L'_{b-1}\right) \\
&\quad \times \delta\left(L_{b+1}, L'_{b+1}\right) \ldots \delta\left(L_{c-1}, L'_{c-1}\right) \delta\left(L_{c+1}, L'_{c+1}\right) \ldots \delta\left(L_{d-1}, L'_{d-1}\right) \\
&\quad \times \delta\left(L_{d+1}, L'_{d+1}\right) \ldots \delta\left(L_u, L'_u\right) \delta\left(L_{12}, L'_{12}\right) \ldots \delta\left(L_{12\ldots a-1}, L'_{12\ldots a-1}\right) \\
&\quad \times \delta\left(L_{12\ldots d}, L'_{12\ldots d}\right) \ldots \delta\left(L, L'\right) \\
&\quad \times \begin{cases}
\begin{array}{l} C_4\left(k_1, k_2, k, 1\right) C_2\left(k, b+1, c-1\right) \\ \quad \times C_4\left(k, k_3, k_4, 1\right) C_2\left(k_4, c+1, d-1\right) C_5\left(3\right); \end{array} & \text{for } a = 1, b = 2 \\
\\
\begin{array}{l} C_1 C_2\left(k, a+1, b-1\right) C_4\left(k_1, k_2, k, 1\right) \\ \quad \times C_2\left(k, b+1, c-1\right) C_4\left(k, k_3, k_4, 2\right) \\ \quad \times C_2\left(k_4, c+1, d-1\right) C_5\left(3\right); \end{array} & \text{for } a < 3 \\
\\
\begin{array}{l} \delta\left(L_{12}, L'_{12}\right) \ldots \delta\left(L_{12\ldots a-1}, L'_{12\ldots a-1}\right) C_1 \\ \quad \times C_2\left(k, a+1, b-1\right) C_4\left(k_1, k_2, k, 1\right) \\ \quad \times C_2\left(k, b+1, c-1\right) C_4\left(k, k_3, k_4, 2\right) \\ \quad \times C_2\left(k_4, c+1, d-1\right) C_5\left(3\right) \end{array} & \text{for } a \geq 3
\end{cases} .
\end{aligned} \tag{94}$$

Expression (94) has also no analogue in Cowan [2].

Thus, we have studied all possible cases of matrix elements of arbitrary two–electron operators. The expressions for recoupling matrices ((83), (87) and (94)) obtained in this subsection are simpler and, thus, more convenient for practical applications, than those of Cowan [2], except for the simplest case $k = 0$ of an operator acting on one shell (79), where they are equivalent.

2.3.3 Calculation of tensorial quantities

In this subsection we will consider the submatrix elements

$T\left(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma\right)$ appearing in (74). As the spin–angular part of expression (74) contains the tensors (8)–(12), so we will discuss the derivation of submatrix elements of these operators, and will 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 (8) by straightforwardly using the Wigner–Eckart theorem in quasispin space (see Rudzikas [4]):

$$\left(l^N\;\alpha QLS\left\|a_{m_q}^{(qls)}\right\|l^{N'}\;\alpha'Q'L'S'\right)$$
$$= -\left[Q\right]^{-1/2}\begin{bmatrix} Q' & 1/2 & Q \\ M_Q' & m_q & M_Q \end{bmatrix}\left(l\;\alpha QLS\left\|a^{(qls)}\right\|l\;\alpha'Q'L'S'\right), \tag{95}$$

where the last multiplier in (95) is the so–called completely reduced (reduced in the quasispin, orbital and spin spaces) matrix element.

The value of the submatrix element of operator (9) is obtained by

$$\left(nl^N\;\alpha QLS\left\|\left[a_{m_{q1}}^{(q\lambda)}\times a_{m_{q2}}^{(q\lambda)}\right]^{(k_lk_s)}\right\|nl^{N'}\;\alpha'Q'L'S'\right)$$
$$= \sum_{k_q,m_q}\left[Q\right]^{-1/2}\begin{bmatrix} q & q & k_q \\ m_{q1} & m_{q2} & m_q \end{bmatrix}\begin{bmatrix} Q' & k_q & Q \\ M_Q' & m_q & M_Q \end{bmatrix}$$
$$\times\left(nl\;\alpha QLS\left\|W^{(k_qk_lk_s)}\right\|nl\;\alpha'Q'L'S'\right). \tag{96}$$

On the right–hand side of equations (95) and (96) only the Clebsch–Gordan coefficient $\begin{bmatrix} Q' & k_q & Q \\ M_Q' & m_q & M_Q \end{bmatrix}$ depends on the number N of equivalent electrons. Different notations for it occur, e.g., $A^{QQ'k_q}_{M_QM_{Q'}m_q}$ in Eckart [86], $S^{Q'k_q}_{QM_Q'm_q}$ in Wigner [87], $(Q'k_qM_Q'm_q|Q'k_qQM_Q)$ in Condon and Shortley [88] or Judd [37].

$\left(nl\;\alpha QLS\left\|W^{(k_qk_lk_s)}\right\|nl\;\alpha'Q'L'S'\right)$ denotes reduced in quasispin space submatrix element (completely reduced matrix element) of the triple tensor

$W^{(k_q k_l k_s)}(nl, nl) = \left[a^{(qls)} \times a^{(qls)}\right]^{(k_q k_l k_s)}$. It is related to the RCFP in a following way:

$$
\begin{aligned}
&\left(nl\ \alpha QLS \left\| W^{(k_q k_l k_s)} \right\| nl\ \alpha' Q' L' S'\right) \\
&\quad = (-1)^{Q+L+S+Q'+L'+S'+k_q+k_l+k_s} \left[k_q, k_l, k_s\right]^{1/2} \\
&\quad \times \sum_{\alpha'' Q'' L'' S''} \left(l\ \alpha QLS \left\| a^{(qls)} \right\| l\ \alpha'' Q'' L'' S''\right) \left(l\ \alpha'' Q'' L'' S'' \left\| a^{(qls)} \right\| l\ \alpha' Q' L' S'\right) \\
&\quad \times \left\{ \begin{array}{ccc} q & q & k_q \\ Q' & Q & Q'' \end{array} \right\} \left\{ \begin{array}{ccc} l & l & k_l \\ L' & L & L'' \end{array} \right\} \left\{ \begin{array}{ccc} s & s & k_s \\ S' & S & S'' \end{array} \right\}.
\end{aligned}
\tag{97}
$$

In the other three cases (10), (11), (12) we obtain the submatrix elements of these operators by using (2.28) of Jucys and Savukynas [3]:

$$
\begin{aligned}
&(nl^N\ \alpha QLS \left\| \left[F^{(\kappa_1\sigma_1)}(n\lambda) \times G^{(\kappa_2\sigma_2)}(n\lambda)\right]^{(kk)} \right\| nl^{N'}\ \alpha' Q' L' S') \\
&\quad = (-1)^{L+S+L'+S'+2k} [k] \sum_{\alpha'' Q'' L'' S''} (nl^N\ \alpha QLS \left\| F^{(\kappa_1\sigma_1)}(n\lambda) \right\| nl^{N''}\ \alpha'' Q'' L'' S'') \\
&\quad \times (nl^{N''}\ \alpha'' Q'' L'' S'' \left\| G^{(\kappa_2\sigma_2)}(n\lambda) \right\| nl^{N'}\ \alpha' Q' L' S') \\
&\quad \times \left\{ \begin{array}{ccc} \kappa_1 & \kappa_2 & k \\ L' & L & L'' \end{array} \right\} \left\{ \begin{array}{ccc} \sigma_1 & \sigma_2 & k \\ S' & S & S'' \end{array} \right\},
\end{aligned}
\tag{98}
$$

where $F^{(\kappa_1\sigma_1)}(n\lambda)$, $G^{(\kappa_2\sigma_2)}(n\lambda)$ are one of (8) or (9) and the submatrix elements are defined correspondingly by (95), (96) and (97). 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 the approach Gaigalas *et al.* [M10], the calculation of the spin–angular parts of matrix elements between functions with u open shells is reduced to requiring the RCFP or the tensors (for example $W^{(k_q k_l k_s)}(nl, nl)$), which are independent of the occupation number of the shell and are acting on one shell of equivalent electrons.

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 $U^{(k)}$, $V^{(k_1 k_2)}$ (see Jucys and Savukynas [3]) 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 RCFP actually can be treated in a uniform way as they all are the completely reduced matrix elements of the second quantization operators. Hence, all methodology of calculation of matrix elements will be much more universal in comparison with the traditional one (see Cowan [2], Jucys and Savukynas [3], Wybourne [89]).

The moste complete tables of standard quantities were presented by Gaigalas *et al.* [M10] for LS–coupling and by Gaigalas *et al.* [M16] for jj–coupling. They are general and should be used for all spin–angular integration schemes. The tabulation was performed for all f–shells (LS–coupling) and for all shells with $j \leq 9/2$ (jj–coupling). These tabulations have been encouraged in particular by systematic MCDF studies on open $d-$ and $f-$shell elements [90, 91] and [M15] where correlation effects force to include single, double, and (sometimes even) triple excitations within large active spaces. Additional motivation arise from the recent experiments and the discovery of heavy and superheavy elements ($Z > 95$) for which excitations into $j = 9/2$ subshells are inevitable.

Other scientific area for which it is very important to know the values of standard quantities is related with the problem of the coupling scheme optimization [92], [M13]. In order to obtain consistent results for the jj–LS transformation coefficients (see, e.g, [93, 94, 95]), it was found by Dyall and Grant [96] that it is necessary to adopt the quasispin phase conventions for CFP. This is the same convention as applied by Gaigalas *et al.* [M10, M16] for the RCFP for LS–coupling and jj–coupling. Thus, the transformation matrix from $jj-$ to $LS-$coupling can now be easily obtained by using the tables [M10, M16].

2.4 Matrix elements in relativistic theory [M6, M14, M21]

2.4.1 One–particle operator

In relativistic atomic theory, each electron shell nl (apart from ns) is split into two subshells with $j = l \pm 1/2 = l_{\pm}$. Instead of the configuration state function $\left|l^N \alpha LSJ\right)$, we then have to deal with $|nl{j_1}^{N_1}{j_2}^{N_2}\alpha_1 J_1 \alpha_2 J_2 J\rangle$[2]. In this notation, the *orbital angular momentum* l is left to denote the parity of the configuration. A closed subshell contains

---

[2] The matrix elements of the operators with respect to the relativistic wave functions are denoted as $\langle \quad || \, || \quad \rangle$ to distinguish them clearly from the case of non–relativistic functions, when we use simple brackets $(\quad || \, || \quad)$.

$2j+1$ electrons. A separation of an electron configuration nl^N into ($jj-$coupled) subshells is unique only for closed shells and for shells with a single vacancy. In general, several jj–coupled configurations with different distributions of the electrons can be found for each single non–relativistic configuration.

The matrix elements of a one–particle scalar operator $\widehat{F}^{(0)}$ between configuration state functions with u open shells can be expressed as a sum over one–electron contributions

$$\langle \psi_u(J) \left\| \widehat{F}^{(0)} \right\| \psi_u(J') \rangle = \sum_{n_i\kappa_i, n_j\kappa_j} \langle \psi_u(J) \left\| \widehat{F}(n_i\kappa_i, n_j\kappa_j) \right\| \psi_u(J') \rangle, \tag{99}$$

where

$$\begin{aligned} &\langle \psi_u(J) \left\| \widehat{F}(n_i\kappa_i, n_j\kappa_j) \right\| \psi_u(J') \rangle \\ &\quad = (-1)^{\Delta+1} \sqrt{2j_i+1}\; R\left(j_i, j_j, \Lambda^{bra}, \Lambda^{ket}\right)\; \delta(\kappa_i, \kappa_j)\; \left(n_i\kappa_i \left\| f^{(0)} \right\| n_j\kappa_j \right) \\ &\quad \times \left\{ \delta(n_i, n_j) \left(j_i^{N_i}\; \alpha_i Q_i J_i \left\| \left[a_{1/2}^{(q\;j_i)} \times a_{-1/2}^{(q\;j_i)} \right]^{(0)} \right\| j_i^{N_i}\; \alpha_i' Q_i' J_i' \right) \right. \\ &\quad + (1 - \delta(n_i, n_j)) \left(j_i^{N_i}\, \alpha_i Q_i J_i \left\| a_{1/2}^{(q\,j_i)} \right\| j_i^{N_i'}\, \alpha_i' Q_i' J_i' \right) \\ &\quad \times \left. \left(j_j^{N_j}\; \alpha_j Q_j J_j \left\| a_{-1/2}^{(q\,j_j)} \right\| j_j^{N_j'}\; \alpha_j' Q_j' J_j' \right) \right\}. \end{aligned} \tag{100}$$

All states are defined in jj–coupling. $\langle \psi_u(J) \|$ and $\| \psi_u(J') \rangle$ are respectively *bra* and *ket* functions with u open subshells, $\kappa \equiv (2j+1)(l-j)$, $\left(n_i\kappa_i \left\| f^{(0)} \right\| n_j\kappa_j \right)$ is the one–electron reduced matrix element of the operator $\widehat{F}^{(0)}$, $\Lambda^{bra} \equiv (J_i, J_j, J_{i'}, J_{j'})^{bra}$ and $\Lambda^{ket} \equiv (J_i, J_j, J_{i'}, J_{j'})^{ket}$ denote the respective sets of active subshell angular momenta. The operators $a_{m_q}^{(q\,j)}$ are second quantization operators in quasispin space of rank $q = 1/2$. The operator $a_{1/2\,m_j}^{(q\,j)} = a_{m_j}^{(j)}$ creates electrons with angular momentum quantum numbers j, m_j and its conjugate $a_{-1/2\,m_j}^{(q\,j)} = \tilde{a}_{m_j}^{(j)} = (-1)^{j-m_j} a_{-m_j}^{\dagger(j)}$ annihilates electrons with the same quantum numbers j, m_j in a given subshell.

The general expression (99) can be used for any scalar one–particle physical operator. It only remains to define the one–electron submatrix element

$$\left(n_i l_i j_i \left\| f^{(0)} \right\| n_j l_j j_j \right)$$

in (99). The only operator required in this implementation is the matrix element of the

Dirac operator, a tensor operator of rank zero,

$$\left(n_i l_i j_i \left\| \widehat{H}_D \right\| n_j l_j j_j\right) = I(n_i l_i j_i, n_i l_i j_i)\delta(\kappa_i, \kappa_j), \tag{101}$$

where $I(n_i l_i j_i, n_i l_i j_i)$ is defined by [10, Eq. (22)]. The Dirac kinetic energy operator, denoted by T in [16, Eq. (3.13)], can be obtained from this by setting the nuclear charge $Z = 0$.

The value of pure spin–angular coefficients[3] for one–particle scalar operator we will get with the help of (99) and keeping in mind that the one–electron submatrix element is equal to one

$$\left(n_i l_i j_i \left\| f^{(0)} \right\| n_j l_j j_j\right) = 1. \tag{102}$$

The recoupling matrix $R\left(j_i, j_j, \Lambda^{bra}, \Lambda^{ket}\right)$ in (99) is particularly simple. It is either a product of delta functions (see (79)) when $n_i\kappa_i = n_j\kappa_j$ or a combination of delta functions and $6j-$coefficients (see (83)) when $n_i\kappa_i \neq n_j\kappa_j$.

By applying the Wigner–Eckart theorem in quasispin space we obtain the submatrix elements of operators of type $a^{(qj)}_{m_q}$ in the form [M3]

$$\begin{aligned} &\left(j^N \alpha Q J \left\| a^{(q\,j)}_{m_q} \right\| j^{N'} \alpha' Q' J'\right) \\ &\quad = -[Q]^{-1/2} \begin{bmatrix} Q' & 1/2 & Q \\ M'_Q & m_q & M_Q \end{bmatrix} \left(j\,\alpha Q J \left\| a^{(q\,j)} \right\| j\,\alpha' Q' J'\right), \end{aligned} \tag{103}$$

where the last factor is RCFP. The submatrix elements of the simplest compound tensor operator of type $\left[a^{(q\,j)}_{m_{q2}} \times a^{(q\,j)}_{m_{q2}}\right]^{(k_j)}$ uses

$$\begin{aligned} &\left(nj^N \alpha Q J \left\| \left[a^{(q\,j)}_{m_{q1}} \times a^{(q\,j)}_{m_{q2}}\right]^{(k_j)} \right\| nj^{N'} \alpha' Q' J'\right) \\ &\quad = \sum_{k_q, m_q} [Q]^{-1/2} \begin{bmatrix} q & q & k_q \\ m_{q1} & m_{q2} & m_q \end{bmatrix} \begin{bmatrix} Q' & k_q & Q \\ M'_Q & m_q & M_Q \end{bmatrix} \\ &\quad \times \left(nj\;\alpha Q J \left\| W^{(k_q k_j)} \right\| nj\;\alpha' Q' J'\right), \end{aligned} \tag{104}$$

---

[3] The pure spin–angular coefficients of one– or two–particle operator are defined as the spin–angular coefficients divided by a one– or two–electron submatrix elements of that operator, respectively.

where $\left(nj\ \alpha QJ\left\|W^{(k_qk_j)}\right\|nj\ \alpha'Q'J'\right)$ denotes the reduced matrix element of the tensor operator $W^{(k_qk_j)}(nj,nj)=\left[a^{(qj)}\times a^{(qj)}\right]^{(k_qk_j)}$ in quasispin space. In terms of the fully RCFP $\left(j\ \alpha QJ\left\|a^{(qj)}\right\|j\ \alpha'Q'J'\right)$, we find

$$\begin{aligned}&\left(nj\ \alpha QJ\left\|W^{(k_qk_j)}\right\|nj\ \alpha'Q'J'\right)\\&\quad=(-1)^{Q+J+Q'+J'+k_q+k_j}\left[k_q,k_j\right]^{1/2}\sum_{\alpha''Q''J''}\left\{\begin{array}{ccc}q&q&k_q\\Q'&Q&Q''\end{array}\right\}\left\{\begin{array}{ccc}j&j&k_j\\J'&J&J''\end{array}\right\}\\&\qquad\times\left(j\ \alpha QJ\left\|a^{(qj)}\right\|j\ \alpha''Q''J''\right)\left(j\ \alpha''Q''J''\left\|a^{(qj)}\right\|j\ \alpha'Q'J'\right).\end{aligned} \quad (105)$$

This construction has the advantage that the completely reduced matrix elements on the right–hand side of (103) and (104) are independent of the occupation number of the shell, and so it reduces requirements of storage in comparison with earlier work.

The phase factor Δ arises from the reordering needed to match the recoupled creation and annihilation operators in the *bra* and *ket* vectors. We have

$$\Delta=0. \quad (106)$$

when $n_i\kappa_i=n_j\kappa_j$; otherwise

$$\Delta=1+\sum_{r=a}^{b-1}N_r, \quad (107)$$

where N_r is the occupation number of subshell r, $a=\min\{i,j\}$, and $b=\max\{i,j\}$.

2.4.2 Two–particle operator

According to (74), the matrix element of any two–particle scalar operator $\widehat{G}^{(kk0)}$ between configuration state functions with u open shells can be written

$$\begin{aligned}&\langle\psi_u(J)\left\|\widehat{G}^{(kk0)}\right\|\psi_u(J')\rangle\\&\quad=\sum_{n_i\kappa_i,n_j\kappa_j,n_{i'}\kappa_{i'},n_{j'}\kappa_{j'}}\langle\psi_u(J)\left\|\widehat{G}(n_i\kappa_i,n_j\kappa_j,n_{i'}\kappa_{i'},n_{j'}\kappa_{j'})\right\|\psi_u(J')\rangle,\end{aligned} \quad (108)$$

where

$$\begin{aligned}&\langle\psi_u\left(J\right)\left\|\widehat{G}\left(n_i\kappa_i,n_j\kappa_j,n_{i'}\kappa_{i'},n_{j'}\kappa_{j'}\right)\right\|\psi_u\left(J'\right)\rangle\\&\quad=\sum_{k_{12}}(-1)^{\Delta}\Theta'(n_il_ij_i,n_jl_jj_j,n_{i'}l_{i'}j_{i'},n_{j'}l_{j'}j_{j'},\Xi)\\&\quad\times T\left(n_ij_i,n_jj_j,n_{i'}j_{i'},n_{j'}j_{j'},\Lambda^{bra},\Lambda^{ket},\Xi,\Gamma\right)R\left(j_i,j_j,j_{i'},j_{j'},\Lambda^{bra},\Lambda^{ket},\Gamma\right),\end{aligned} \quad (109)$$

Γ specifies the recoupling scheme required for each matrix element and Ξ, when required, specifies the coupling scheme of the tensor operators defining each matrix element. The operator $\widehat{G}^{(kk0)}$ couples tensor operators of rank k for each electron to give an overall scalar operator.

From (109) we see that the matrix element of any two–particle operator can be written as a sum over all possible sets of active shell quantum numbers $n_i\kappa_i$, $n_j\kappa_j$, $n_{i'}\kappa_{i'}$, $n_{j'}\kappa_{j'}$. The systematic analysis of [M6] aims to minimize the computation needed in this expansion. The parameter distributions are presented in Table 8. Note that for distributions 2–5 and 19–42 the subshell labels are ordered so that $\alpha < \beta < \gamma < \delta$, while for distributions 6–18 no conditions upon the ordering are imposed. We discuss these structures in more detail below.

The recoupling coefficients defined in [97, 98, 99] did not reduce the recoupling coefficients to their simplest forms but relied on the analysis module of the NJSYM package (later NJGRAF) to perform the reduction mechanically. The analysis [M6] leads to simpler forms denoted by $R\left(j_i, j_j, j_{i'}, j_{j'}, \Lambda^{bra}, \Lambda^{ket}, \Gamma\right)$ in (109). In the case of one interacting shell $R\left(j_i, j_j, j_{i'}, j_{j'}, \Lambda^{bra}, \Lambda^{ket}, \Gamma\right)$ reduces to delta functions (see (79)). For two, three and four interacting shells, the recoupling coefficients are given by (83), (87) and (94), replacing l, L by j, J respectively. The recoupling parameters Γ for each distribution can be found in Table 8.

The expressions $T\left(n_ij_i, n_jj_j, n_{i'}j_{i'}, n_{j'}j_{j'}, \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma\right)$ in (109) are matrix elements of standard subshell creation/annihilation operators

$$a = a^{(qj)}_{m_q}, \tag{110}$$

$$W = \left[a^{(qj)}_{m_{q1}} \times a^{(qj)}_{m_{q2}}\right]^{(k_{12})}, \tag{111}$$

$$aW = \left[a^{(qj)}_{m_{q1}} \times \left[a^{(qj)}_{m_{q2}} \times a^{(qj)}_{m_{q3}}\right]^{(k_{12})}\right]^{(k_2)}, \tag{112}$$

$$Wa = \left[\left[a^{(qj)}_{m_{q1}} \times a^{(qj)}_{m_{q2}}\right]^{(k_{12})} \times a^{(qj)}_{m_{q3}}\right]^{(k_2)}, \tag{113}$$

$$WW = \left[\left[a^{(qj)}_{m_{q1}} \times a^{(qj)}_{m_{q2}}\right]^{(k)} \times \left[a^{(qj)}_{m_{q3}} \times a^{(qj)}_{m_{q4}}\right]^{(k)}\right]^{(0)}. \tag{114}$$

The creation and annihilation operators in (110)–(114) refer to a single subshell. The

Table 8: Scheme of the definitions for matrix elements of any two–particle operator. *The operators a, W, aW and Wa defined in (110)–(114) act on the indicated subshells.*

No.	i	j	i'	j'	Γ	Ξ	α	β	γ	δ	φ
1.	α	α	α	α	–	j_α, k	WW	–	–	–	–
					–	j_α	W	–	–	–	–
2.	α	β	α	β	k	j_α, j_β	W	W	–	–	0
3.	β	α	β	α	k	j_α, j_β	W	W	–	–	0
4.	α	β	β	α	k_{12}	j_α, j_β	W	W	–	–	0
5.	β	α	α	β	k_{12}	j_α, j_β	W	W	–	–	0
6.	α	α	β	β	k_{12}	j_α, j_β	W	W	–	–	$j_\alpha + j_\beta + k_{12}$
7.	β	α	α	α	j_β	j_α, k_{12}	aW	a	–	–	$k + k_{12}$
8.	α	β	α	α	j_β	j_α, k_{12}	aW	a	–	–	k
9.	β	β	β	α	j_α	j_β, k_{12}	a	Wa	–	–	$k + k_{12}$
10.	β	β	α	β	j_α	j_β, k_{12}	a	Wa	–	–	k
11.	β	γ	α	γ	j_α, j_β, k	–	a	a	W	–	$1 + j_\alpha + j_\beta - k$
12.	γ	β	γ	α	j_α, j_β, k	–	a	a	W	–	$1 + j_\alpha + j_\beta - k$
13.	γ	β	α	γ	$j_\alpha, j_\beta, k_{12}$	–	a	a	W	–	$1 + j_\alpha + j_\beta - k_{12}$
14.	β	γ	γ	α	$j_\alpha, j_\beta, k_{12}$	–	a	a	W	–	$1 + j_\alpha + j_\beta - k_{12}$
15.	γ	γ	α	β	$j_\alpha, j_\beta, k_{12}$	–	a	a	W	–	$j_\alpha + j_\gamma + k_{12}$
16.	γ	γ	β	α	$j_\alpha, j_\beta, k_{12}$	–	a	a	W	–	$j_\alpha + j_\gamma$
17.	α	β	γ	γ	$j_\alpha, j_\beta, k_{12}$	–	a	a	W	–	$j_\alpha + j_\beta + k_{12}$
18.	β	α	γ	γ	$j_\alpha, j_\beta, k_{12}$	–	a	a	W	–	$j_\beta + j_\gamma$
19.	α	β	γ	δ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\beta + k_{12}$
20.	β	α	γ	δ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\beta + j_\gamma + k_{12}$
21.	α	β	δ	γ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\beta + j_\gamma$
22.	β	α	δ	γ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\beta + j_\gamma$
23.	γ	δ	α	β	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\delta + k_{12}$
24.	γ	δ	β	α	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\delta + k_{12}$
25.	δ	γ	α	β	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\delta$
26.	δ	γ	β	α	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\delta$
27.	α	γ	β	δ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	0
28.	α	γ	δ	β	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	0
29.	γ	α	δ	β	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	0
30.	γ	α	β	δ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	0

Table 8: (continued).

No.	i	j	i'	j'	Γ	Ξ	α	β	γ	δ	φ
31.	β	δ	α	γ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\beta + j_\gamma + j_\delta$
32.	δ	β	γ	α	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\beta + j_\gamma + j_\delta$
33.	β	δ	γ	α	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\beta + j_\gamma + j_\delta$
34.	δ	β	α	γ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$j_\alpha + j_\beta + j_\gamma + j_\delta$
35.	α	δ	β	γ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\gamma + j_\delta - k$
36.	δ	α	γ	β	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\gamma + j_\delta - k$
37.	α	δ	γ	β	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\gamma + j_\delta - k_{12}$
38.	δ	α	β	γ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\gamma + j_\delta - k_{12}$
39.	β	γ	α	δ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\alpha + j_\beta - k$
40.	γ	β	δ	α	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\alpha + j_\beta - k$
41.	β	γ	δ	α	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\alpha + j_\beta - k_{12}$
42.	γ	β	α	δ	$j_\alpha, j_\beta, j_\gamma, j_\delta$	–	a	a	a	a	$1 + j_\alpha + j_\beta - k_{12}$

evaluation of the submatrix elements of operator of type a (110) and the simplest compound tensor operator of type W (111) was explained in Subsection 2.4.1. For types (112)–(114), we use the formula

$$\begin{aligned}
&\left(nj^N\,\alpha QJ\left\|\left[U^{(k_1)}(nj)\times V^{(k_2)}(nj)\right]^{(k)}\right\|nj^{N'}\,\alpha'Q'J'\right) \qquad (115)\\
&\quad= (-1)^{J+J'+k}[k]^{1/2}\sum_{\alpha''Q''J''}\begin{Bmatrix} k_1 & k_2 & k\\ J' & J & J''\end{Bmatrix}\\
&\quad\times\left(nj^N\,\alpha QJ\left\|U^{(k_1)}(nj)\right\|nj^{N''}\,\alpha''Q''J''\right)\left(nj^{N''}\,\alpha''Q''J''\left\|V^{(k_2)}(nj)\right\|nj^{N'}\,\alpha'Q'J'\right),
\end{aligned}$$

where $U^{(k_1)}(nj)$, $V^{(k_2)}(nj)$ are either of type (110) or type (111). The occupation number N'' is defined by second quantization operators occurring in $U^{(k_1)}(nj)$ and $V^{(k_2)}(nj)$.

The phase factors Δ in (109) arise from the reordering necessary to match the recoupled creation and annihilation operators in *bra* and *ket* vectors contributing to the matrix element. For each of the cases considered in Table 8 we find

Cases 1–6:

$$\Delta = 0. \qquad (116)$$

Cases 7–18:

$$\Delta = 1 + \sum_{r=i}^{j-1} N_r, \tag{117}$$

where N_r is the occupation number of subshell r. If $\alpha < \beta$, then $i = \alpha$, $j = \beta$, and if $\alpha > \beta$, then $i = \beta$, $j = \alpha$.

Cases 19–42:

$$\Delta = \sum_{k=\alpha}^{\beta-1} N_k + \sum_{k=\gamma}^{\delta-1} N_k. \tag{118}$$

The coefficients $\Theta'\left(n_i l_i j_i, n_j l_j j_j, n_{i'} l_{i'} j_{i'}, n_{j'} l_{j'} j_{j'}, \Xi\right)$ for the different cases tabulated in Table 8 have different muliplicative factors defined as follows:

Case 1: Single subshell ($\alpha\alpha\alpha\alpha$)

$$\begin{aligned}&\Theta'_{IIa}\left(n_\alpha l_\alpha j_\alpha, n_\alpha l_\alpha j_\alpha, n_\alpha l_\alpha j_\alpha, n_\alpha l_\alpha j_\alpha, \Xi\right)\\ &\quad = \frac{1}{2}[k]^{-1/2}\left(n_\alpha l_\alpha j_\alpha n_\alpha l_\alpha j_\alpha \left\| g^{(kk)} \right\| n_\alpha l_\alpha j_\alpha n_\alpha l_\alpha j_\alpha\right)\delta\left(k_{12}, k\right)\end{aligned} \tag{119}$$

and

$$\begin{aligned}&\Theta'_{IIb}\left(n_\alpha l_\alpha j_\alpha, n_\alpha l_\alpha j_\alpha, n_\alpha l_\alpha j_\alpha, n_\alpha l_\alpha j_\alpha, \Xi\right)\\ &\quad = (-1)^k\left[j_\alpha\right]^{-1/2}\left(n_\alpha l_\alpha j_\alpha n_\alpha l_\alpha j_\alpha \left\| g^{(kk)} \right\| n_\alpha l_\alpha j_\alpha n_\alpha l_\alpha j_\alpha\right)\delta\left(k_{12}, 0\right).\end{aligned} \tag{120}$$

Cases 2, 3, 11, 12, 27, 29, 31, 32, 35, 36, 39, 40: Subshell assignments $\alpha\beta\alpha\beta, \beta\alpha\beta\alpha$, $\beta\gamma\alpha\gamma$, $\gamma\beta\gamma\alpha$, $\alpha\gamma\beta\delta$, $\gamma\alpha\delta\beta$, $\beta\delta\alpha\gamma$, $\delta\beta\gamma\alpha$, $\alpha\delta\beta\gamma$, $\delta\alpha\gamma\beta$, $\beta\gamma\alpha\delta$, $\gamma\beta\delta\alpha$

$$\begin{aligned}&\Theta'\left(n_i l_i j_i, n_j l_j j_j, n_{i'} l_{i'} j_{i'}, n_{j'} l_{j'} j_{j'}, \Xi\right)\\ &\quad = \ (-1)^{\varphi}\frac{1}{2}[k]^{-1/2}\left(n_i l_i j_i n_j l_j j_j \left\| g^{(kk)} \right\| n_{i'} l_{i'} j_{i'} n_{j'} l_{j'} j_{j'}\right)\delta\left(k_{12}, k\right).\end{aligned} \tag{121}$$

Cases 6, 15–26: Subshell assignments $\alpha\alpha\beta\beta$, $\gamma\gamma\alpha\beta$, $\gamma\gamma\beta\alpha$, $\alpha\beta\gamma\gamma$, $\beta\alpha\gamma\gamma$, $\alpha\beta\gamma\delta$, $\beta\alpha\delta\gamma$, $\alpha\beta\delta\gamma$, $\beta\alpha\gamma\delta$, $\gamma\delta\alpha\beta$, $\delta\gamma\beta\alpha$, $\gamma\delta\beta\alpha$, $\delta\gamma\alpha\beta$

$$\begin{aligned}&\Theta'\left(n_i l_i j_i, n_j l_j j_j, n_{i'} l_{i'} j_{i'}, n_{j'} l_{j'} j_{j'}, \Xi\right)\\ &\quad = (-1)^{1+k+\varphi}\frac{1}{2}\left[k_{12}\right]^{1/2}\begin{Bmatrix} j_i & j_{i'} & k \\ j_{j'} & j_j & k_{12}\end{Bmatrix}\left(n_i l_i j_i n_j l_j j_j \left\| g^{(kk)} \right\| n_{i'} l_{i'} j_{i'} n_{j'} l_{j'} j_{j'}\right).\end{aligned} \tag{122}$$

Cases 4, 5, 7, 8, 9, 10, 13, 14, 28, 30, 33, 34, 37, 38, 41, 42: Subshell arrangements $\alpha\beta\beta\alpha$, $\beta\alpha\alpha\beta$, $\beta\alpha\alpha\alpha$, $\alpha\beta\alpha\alpha$, $\beta\beta\beta\alpha$, $\beta\beta\alpha\beta$, $\gamma\beta\alpha\gamma$, $\beta\gamma\gamma\alpha$, $\alpha\gamma\delta\beta$, $\gamma\alpha\beta\delta$, $\beta\delta\gamma\alpha$, $\delta\beta\alpha\gamma$, $\alpha\delta\gamma\beta$, $\delta\alpha\beta\gamma$, $\beta\gamma\delta\alpha$, $\gamma\beta\alpha\delta$

$$\Theta'\left(n_il_ij_i, n_jl_jj_j, n_{i'}l_{i'}j_{i'}, n_{j'}l_{j'}j_{j'}, \Xi\right)$$
$$= (-1)^{\varphi}\frac{1}{2}\left[k_{12}\right]^{1/2}\left\{\begin{matrix} j_i & j_{i'} & k \\ j_j & j_{j'} & k_{12}\end{matrix}\right\}\left(n_il_ij_in_jl_jj_j\left\|g^{(kk)}\right\|n_{i'}l_{i'}j_{i'}n_{j'}l_{j'}j_{j'}\right). \quad (123)$$

The phase factors φ in expressions (121)–(123) are defined in column φ of Table 8. This construction exploits the common tensorial structure of the Coulomb, Breit and Gaunt interactions [10] and exploits this similarity to simplify the calculation of spin–angular coefficients. The relativistic jj–coupling expressions for the two–electron submatrix element of the Coulomb interaction [10, 100] is

$$\left(n_il_ij_in_jl_jj_j\left\|g^{(kk)}\right\|n_{i'}l_{i'}j_{i'}n_{j'}l_{j'}j_{j'}\right) = (-1)^{(l_i+l_j-l_{i'}-l_{j'})/2}$$
$$\times\langle n_il_ij_i\|C^{(k)}\|n_{i'}l_{i'}j_{i'}\rangle\langle n_jl_jj_j\|C^{(k)}\|n_{j'}l_{j'}j_{j'}\rangle R^k(n_il_ij_in_jl_jj_jn_{i'}l_{i'}j_{i'}n_{j'}l_{j'}j_{j'}). \quad (124)$$

The same construction can be used for the Gaunt interaction (the leading part of the magnetic Breit interaction) [10, Eq. (91)] and for the full transverse Breit interaction [10, Eq. (101)], although the selection rules and the two–electron submatrix elements corresponding to (123) are, of course, different.

The value of pure spin–angular coefficients for two–particle operator we will get if we take into account that the two–electron submatrix element is equal to one

$$\left(n_il_ij_in_jl_jj_j\left\|g^{(kk)}\right\|n_{i'}l_{i'}j_{i'}n_{j'}l_{j'}j_{j'}\right) = 1 \quad (125)$$

in Θ'. So the pure spin–angular coefficient for operators with the same tensorial structure have the same value.

* * *

The approach to matrix element evaluation, presented in this section, is based on the combination of the angular momentum theory as described in Jucys and Bandzaitis [51], on the concept of irreducible tensorial sets (Judd [37], Rudzikas and Kaniauskas [39]), on a generalized graphical approach (Gaigalas *et al.* [52]), on the second quantization in coupled tensorial form (Rudzikas and Kaniauskas [39]), on the quasispin approach (Rudzikas [4]), and on the use of reduced coefficients of fractional parentage (Rudzikas [4], Rudzikas [101], Judd [37]). All this, in its entity, introduces a number of new features, in comparison with traditional approaches:

- It is possible to use the algebraic expressions for the recoupling matrices,
- Before the calculations, it is possible to check triangular conditions of both non-interacting and interacting shells;
- To apply Tables of standard quantities;
- Easily to move from the common definition of the two–particle operator to the expression of the concrete operator, as well as in general case to include in it simplifications of the operator analyzed.

All that may be applied to both diagonal and non–diagonal, with respect to configurations, matrix elements.

3 SOFTWARE FOR SPIN–ANGULAR INTEGRATION [M4, M18, M19, M20, M21]

In this section there will be discussed the software created in this work. All these programs are based on the approach of spin–angular integration developed in this habilitation work. The program for evaluating the expressions from the theory of angular momentum is presented in subsection 3.1. The program to calculate pure spin–angular coefficients in jj–coupling is described in 3.2. The library for integration over spin–angular variables in LS–coupling is reported in 3.3.

3.1 Program for evaluating the expressions from the theory of angular momentum [M20]

3.1.1 The program Racah III

During recent years, the Racah program [102, 103] has been found useful for evaluating expressions from the theory of angular momentum [104, 105]. The interactive and modular design of this package does not only support numerical computations of standard expressions (as other libraries do) but also facilitate current research work which is based on the techniques of Racah's algebra [5, 6, 7, 8]. The Racah program is particularly helpful for such (complex) expressions for which the known algebraic and gaphical methods start to become tedious and prone to making errors.

Beside of further applications, atomic structure theory is one of the main areas which, tradiationaly, makes use of the rotational symetry of free atoms. In this theory, the efficient evaluation of many–electron matrix elements for different one– and two–particle operators plays a very crucial role. These oparators can be a part of the atomic Hamiltonian, or they describe the interaction of the electrons with other particles and fields. By exploiting the techniques of Racah's algebra in atomic structure [2], the evaluation of these matrix elements may often be considerably simplified by carrying out the integration over the spin–angular coordinates analytically.

Different computational schemes have been developed to evaluate many–electron matrix elements, including those for open–shell structure [9, 10, 4] and [M6]. They deal with different couplings of the individual angular momenta as well as different notations for classifying the subshell states of equivalent electrons for open–shell configurations. One of the most popular scheme ist due to Fano [9] which is based on the CFP. Each computation method exploits a set of *standard quantities* to decompose the many–electron matrix elements. Quantities which occur frequently are i) CFP, ii) RCFP, iii) the reduced matrix elements of the unit tensors $U^{(k)}$ and $V^{(k1)}$ in $LS-$coupling or of $T^{(k)}$ in $jj-$coupling, respectively, and iv) the completely reduced matric elements of the single–particle operator $W^{(k_q k_l k_s)}$ ($LS-$coupling) or $W^{(k_q k_j)}$ ($jj-$coupling). Of course, details in the final evaluation depend on the underlying coupling scheme, phase coventions, and on quite a number of different notations which are found in the literature. For all these quantities is common, however, that they are closely related to angular momentum theory.

Among these standard entities, the RCFPs play a central role in that most of the other quantities above can be represented in terms of these coefficients. The well–known CFPs, for example, can be expressed as a product of Wigner $3j-$ and corresponding RCFPs which are independent of the occupation number N of the subshell states. Similarly, the (completely) reduced matrix element of the unit tensor can be written as a weighted sum of products of Wigner $6j$–coefficients and RCFPs where the summation is always finite owing to triangular conditions for the quantum numbers.

In practice, however, the handling and the application of such standard entities in the evaluation of open–shell matrix elements is not always that simple and often requires considerable effort to bring new implementations into work. Compilations of various coefficients and matrix elements can be found (in printed form) in the literature, but their arrangement and notation is often not very suitable for numerical studies. Therefore, in order to facilitate the usage of these (reduced) coefficients and matrix elements, was developed by Gaigalas *et al.* [M20] the RACAH III which provides the user with a fast and interactive access to these quantities. The program is written in MAPLE [106]. In the following subsections there will be presented the main commands of RACAH III and we will present several examples of using this program.

Table 9: **Additional commands of the Racah package.**

Racah_cfp()	Computes a CFP in either $LS-$ or jj–coupling.
Racah_rcfp()	Return a RCFP in either $LS-$ or jj–coupling.[a]
Racah_reduced_T()	Calculates a reduced matrix element of standard operator $T^{(k)}$ in jj–coupling.
Racah_reduced_U()	Calculates a reduced matrix element of the standard operator $U^{(k)}$ in LS–coupling.[b]
Racah_reduced_V()	Calculates a reduced matrix element of the standard operator $V^{(k1)}$ in LS–coupling.
Racah_reduced_W()	Calculates a completely reduced matrix element either of the standard operators $W^{(k_q k_l k_s)}$ in LS–coupling or of the $W^{(k_q k_j)}$ in jj–coupling.
Racah_set_coupling_scheme()	Set the correct framework for evaluating CFP and RCFP as well as reduced matrix elements.

[a] The RCFP is taken from [M10, M16].

[b] In the present program the submatrix elements of $U^{(k)}$ are defined as in [4, 18].

3.1.2 Commands of Racah III

The RACAH package [102, 103] has been designed originally for simplifying expressions from the theory of angular momentum [107, 108]. Emphasis was paid to developing an interactive and user–friendly tool which does not require detailed knowlegde neither about the group–theoretical background [109, 110] which leads to these expressions nor about techniques for their simplification. Previous set of RACAH procedures concerned both, numerical computations as well as the simplification of complex expressions due to the use of graphical and sum rules where a *simplification* means to reduce the number of summation variables, integrals, and/or Wigner $nj-$ symbols. Here, there is extented these features of the RACAH program by adding the knowledge about important standard quantities in the evaluation of matrix elements.

These reduced coefficients and matrix elements of spherical tensorial operators are closely related to the theory of angular momentum. This stimulate the present extension which creates a fast access to these quantities in different classification and coupling schemes. We currently support the computation of the RCFP's and the completely reduced matrix elements of $W^{(k_q k_j)}$ and $W^{(k_q k_l k_s)}$ as well as the CFP's and the reduced matrix elements of $T^{(k)}$, $U^{(k)}$ and $V^{(k1)}$. Table 9 gives a brief overview of the additional procedures which are relevant to the user; these procedures are based on developments [102, 103]. In total, 18 new procedures have been added to the RACAH program in the present work. Since all coefficients are evaluated directly to their numerical values, no additional data structures had to be defined for the present work.

One procedure, namely Racah_set_coupling_scheme(), differs from previous work in that it "assigns" a (string) value to the global variable Racah_save_coupling_scheme() which specifies the currently coupling scheme and the choice of quantum numbers to classify the individual subshells states. The 'valu' of this variable also specifies how the quantum numbers for the reduced coefficients and matrix elements are to be *interpreted* to ensure a large flexibility of the program. The command Racah_set_coupling_scheme() must therefore be invoked before any other quantity can be evaluated. It is supported in the present version the classification schemes *LS_quasispin*, *LS_seniority*, *jj_quasispin*, *jj_seniority*.

3.1.3 Example

To illustrate the usage of the present extension, we 'prove' the relation

$$\left(j^N \, \alpha Q J \right\| j^{N-1} \, \left(\alpha' Q' J'\right), j\Big)$$

$$= \frac{(-1)^{N+Q-M_Q}}{\sqrt{N\,[J]}} \begin{pmatrix} Q & 1/2 & Q' \\ -M_Q & 1/2 & M_Q' \end{pmatrix} \left(j \; \alpha Q J \left\| a^{(qj)} \right\| j \; \alpha' Q' J'\right) . \qquad (126)$$

For this, we consider the left– and right–hand side of Eq. (126) separately for $j = 7/2$, $N = 4$, $\nu = 2$, $J = 2$, $\nu' = 1$, and $J' = 7/2$. Again, we use seniority notation for the CFP $\left(j^N \, \alpha \nu Q J \right\| j^{N-1} \, \left(\alpha' \nu' Q' J'\right), j\Big)$ on the lhs

```
> Racah_set_coupling_scheme(jj_seniority);
> left := Racah_cfp(7/2,4,2,2,1,7/2,algebraic);
```

$$\text{left} := 1/3 \,\sqrt{3} \,.$$

To obtain the value from the rhs

$$\frac{(-1)^{N+Q-M_Q}}{\sqrt{N\,[J]}} \begin{pmatrix} Q & 1/2 & Q' \\ -M_Q & 1/2 & M'_Q \end{pmatrix} \left(j\ \alpha Q J \left\| a^{(qj)} \right\| j\ \alpha' Q' J' \right) \tag{127}$$

we have, in addition, the quantum numbers $Q = (\frac{(2j+1)}{2} - \nu)/2 = 1$, $M_Q = (N - \frac{(2j+1)}{2})/2 = 0$, $Q' = 3/2$, $M'_Q = -1/2$

```
> right := Racah_rcfp(7/2,2,2,1,7/2,algebraic);
> w3jr := Racah_set(w3j,1,1/2,3/2,0,1/2,-1/2);
> right := right * Racah_compute(w3jr,algebraic);
> right := right * (-1)^ (4+1+0) / sqrt(4*(2*2+1));
```

$$\mathrm{right} := 1/30\ \sqrt{10 \times 6 \times 5}\ .$$

This is a very simple example to establish (new) 'relations' among the standard quantities in the evaluation of matrix elements for open–shell configurations. Although, of course, such a numerical treatment will not *prove* any analytic relation it may help to obtain further hints on such symmetries. We therefore hope that our present tool will help to point towards *new* relations wich have not yet been found by other, group–theoretical studies.

Racah program may influence also the work in neighboured fields like nuclear structure and the scattering of particles and light at composite systems. In these fields, numerical studies are often based on similar entities which could be incorporated as well in the framework of the Racah package.

3.2 Program to calculate pure spin–angular coefficients in relativistic atomic physics [M18, M21]

3.2.1 Program organization

The program `ANCO` [M18, M21] constructs the pure spin–angular coefficients for one– (Eqs. (99) and (102)) and two–electron (Eqs. (108) and (125)) operators contributing to matrix elements of the Dirac–Coulomb–Breit Hamiltonian. The coefficients $T_{rs}(ab)$

(Eqs. (99) and (101)) and $V_{rs}^{k}(abcd)$ (Eqs. (108) and (124)) used in `GRASP92` [16] and in earlier version of the system are available as an option. The new format generates what we have called pure spin–angular momentum coefficients which can be used unchanged with any one–particle tensor operator of rank 0, and any two–particle interaction. The Coulomb and Breit interactions use different subsets of the complete set of the two–particle pure spin–angular coefficients, which are selected automatically when multiplying by the relevant two–electron submatrix elements to complete the matrix element calculation. The `MCP` and `MCBP` modules of `GRASP92` calculated the full matrix elements for each of these subsets, so that the new formulation reduced the computational overheads and the memory requirements, which renders `ANCO` more suitable for large scale problems.

`ANCO` is written in Fortran 90/95 [111] and is designed as an addition to the `RATIP` package [112]. There are three new modules `rabs_rcfp` [M18], `rabs_recoupling` and `rabs_anco` [21] for extracting spin–angular coefficients relating to formula (108). The program `rabs_rcfp` supports the computation of the CFP, the RCFP, the completely reduced matrix elements of the operator $W^{(k_q k_j)}$ as well as the matrix elements of the unit tensor $T^{(k)}$. The module `rabs_recoupling` evaluates recoupling coefficients $R\left(j_i, j_j, \Lambda^{bra}, \Lambda^{ket}\right)$ (Eqs. (79) and (83)) and $R\left(j_i, j_j, j_{i'}, j_{j'}, \Lambda^{bra}, \Lambda^{ket}, \Gamma\right)$ (Eqs. (79), (83), (87) and (94)) as described in [M6], module `rabs_rcfp` [M18] evaluates the

$T\left(n_i j_i, n_j j_j, n_{i'} j_{i'}, n_{j'} j_{j'}, \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma\right)$ (the main equations are (103), (104), (105) and (115)) whilst `rabs_anco` evaluates all the contributions to (108) for both scalar one– and two–particle operators.

3.2.2 Timing of `ANCO`

Tests and timing studies using the Dirac–Coulomb Hamiltonian only were performed for the $3s^2 3p^6\ {}^1S$ state of Ar I with the common closed shells $1s^2 2s^2 2p^6$ for different values of final orbital momentum J. The wave function expansions used were:

1. 3SD: Singles and doubles excitations from $3s^2 3p^6$ to the active set $\{3s, 3p, 3d\}$ contains 14 configuration state functions (CSF) for $J = 0$ and 34 CSF (the maximum) for $J = 2$.

Table 10: Timing Comparison for `GRASP92` and `ANCO` codes. *Times are given in hours, minutes, seconds.*

ASF	**Number of**				**Running time of**		**Speed**
expan.	**CSF**	$T^k_{rs}(ab)$ **or** $t^k_{rs}(ab)$	$V^k_{rs}(abcd)$	$v^k_{rs}(abcd)$	`GRASP92`	`ANCO`	**-up**
4SDT (J=0)	2 149	3 606	756 023	1 530 086	00:08:11	00:03:01	2.7 (5.4)
4SDT (J=1)	5 786	14 017	4 070 156	8 188 130	00:59:01	00:15:19	3.9 (7.8)
4SDT (J=2)	8 016	21 356	7 018 885	14 077 044	01:42:47	00:26:28	3.9 (7.8)
4SDT (J=3)	8 378	21 342	7 634 136	15 290 955	01:53:55	00:30:37	3.7 (7.4)
4SDT (J=4)	7 284	15 971	6 111 074	12 260 139	01:33:17	00:23:01	4.1 (8.2)
4SDT (J=5)	5 349	9 435	3 810 165	7 656 054	00:50:27	00:14:18	3.6 (7.2)
4SDT (J=6)	3 370	4 556	1 836 602	3 706 544	00:21:52	00:06:40	3.3 (6.6)
4SDT (J=7)	1 788	1 789	693 761	1 412 443	00:07:26	00:02:29	3.0 (6.0)
5SD (J=0)	468	621	75 192	150 455	00:00:32	00:00:17	1.9 (3.8)
5SD (J=1)	1 134	2 324	395 450	792 560	00:03:10	00:01:29	2.1 (4.2)
5SD (J=2)	1 609	3 704	697 651	1 395 839	00:06:27	00:02:44	2.4 (4.8)
5SD (J=3)	1 584	3 441	721 907	1 444 095	00:06:43	00:02:59	2.3 (4.6)
5SD (J=4)	1 361	2 500	558 223	1 117 681	00:05:15	00:02:17	2.3 (4.6)
5SD (J=5)	920	1 361	314 909	632 306	00:02:30	00:01:22	1.8 (3.6)
5SD (J=6)	559	644	141 328	284 102	00:01:02	00:00:36	1.7 (3.4)
5SD (J=7)	259	226	44 137	89 398	00:00:15	00:00:12	1.3 (2.6)

2. 3SDT: Singles, doubles and triples excitations from $3s^2 3p^6$ to the active set $\{3s, 3p, 3d\}$. The maximum number of CSF is 145 for $J = 2$.
3. 4SD: Singles and doubles excitations from $3s^2 3p^6$ to the active set $\{3s, 3p, 3d, 4s, 4p, 4d, 4f\}$. The maximum number of CSF is 465 for $J = 2$.
4. 4SDT: Singles, doubles and triples excitations from $3s^2 3p^6$ to the active set $\{3s, 3p, 3d, 4s, 4p, 4d, 4f\}$.
5. 5SD; Singles and doubles excitations from $3s^2 3p^6$ to the active set $\{3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, 5g\}$.

We first considered simple cases with a small number of CSF (3SD, 3SDT, 4SD with $J = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9$). Although `ANCO` generates the full set of pure spin–angular coefficients for both one– and two–particle operators, the calculation runs 1.4–2.3 times faster than an equivalent calculation with `GRASP92` because of the lower computational overheads. Table 10 demonstrates similar enhanced performance for the much larger 4SDT and 5SD examples, showing the improvement expected for large scale calculations.

From the results presented in the Table 10 we conclude that the new program is not much faster in simple cases, but does better in more complicated cases. The fact that `ANCO` calculates approximately twice the number of angular coefficients as `GRASP92` reduces the effective cost per coefficient by a further factor of two (the values in brackets).

3.3 The library for integration over spin–angular variables in non–relativistic atomic physics [M4, M19]

3.3.1 Program organization

In order to obtain accurate values of atomic quantities it is necessary to account for relativistic and correlation effects (see, e.g., Froese Fischer *et al.* [113, 14]). Relativistic effects may be taken into account as Breit–Pauli corrections or in a fully relativistic approach. In both cases for complex atoms and ions, a considerable part of the effort must be devoted to integrations over spin–angular variables, occurring in the matrix elements of the operators under consideration.

Many existing codes for integrating are based on scheme first proposed by Fano [9]. In this approach, the integrations over spin–angular variables constitute a considerable part of the computation, especially when atoms with many open shells are treated, and the operators are non–trivial. Over the last decade, an efficient approach for finding matrix elements of any one– and two–particle atomic operator between complex configurations has been developed [M3, M6, M8, M9, M10, M14, M17]. It is free of the shortcomings of previous approaches [M14]. This method is introduced in the library `SAI` presented in this subsection. This library was incorporated in other codes, for example, in `BREIT` from `MCHF_ASP` [113, 14] (see [114]). It extends the capabilities of these programs and has resulted in faster execution of spin–angular integrations.

The library `SAI` presented in this subsection aimed at the spin–angular integration for any one– and two–paricle operator in LS–coupling. It is a separate unit. It can be easily adapted to the old programs as, for example, `MCHF_ASP` [113, 14] or can easily be used to create a new one. It contains five modules – `sai_recls`, `sai_sqlsf1`, `sai_sqlsf2`, `sai_nore` and `sai_dudu`. They are classified according to the methodology presented in papers [M3, M6, M8, M9, M10, M14, M16, M17], and adhere to the principles of modular programming (although FORTRAN 77 [115] does not fully support this).

This library `sai_recls` contains 20 routines for calculation of recoupling matrices

$$\begin{aligned} & R\left(\lambda_i, \lambda_j, \lambda_i', \lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Gamma\right) \\ & \quad = R\left(l_i, l_j, l_i', l_j', \Lambda_l^{bra}, \Lambda_l^{ket}, \Gamma_l\right) R\left(s, s, s, s, \Lambda_s^{bra}, \Lambda_s^{ket}, \Gamma_s\right), \end{aligned} \tag{128}$$

which are defined in subsection 2.3.2 (Eqs. (75), (79), (80), (83), (85), (87), (88) and (94)). Most of the subroutines from this module use common blocks CONSTS and MEDEFN from `MCHF_ASP` [113, 14].

The section `sai_sqlsf1` [M19], (standard quantities in LS–coupling, part one) is a collection of utilities used by the modules `sai_recls` `sai_nore` and `sai_dudu`. They compiute the submatrix element $T\left(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma\right)$ for s–, p– and d–subshells in Eq. (74). But most of the subroutines are independent and may be useful for other programs. 67 subroutines are contained in this library (the main equations are (95), (96), (97) and (98)).

The library `sai_sqlsf2` [M19] is the second part of standard quantities in LS–coupling. Everything in it is related to the f–shells. The tables of CFP for f–shell (see [M10]) and the term characteristics are in this library. This library can be used in other programs to its full extent, by employing programs from `sai_sqlsf1` library. These are the subroutines SLS, RWLS, W1, AWP1LS, WAP1LS, WWLS1, WWPLS1. The remaining two subroutines may also be used independently.

The library `sai_nore` is for calculating the spin–angular parts of matrix elements for a scalar two–particle operator. It contains 18 subroutines. Most of the subroutines from this module use common blocks CONSTS and MEDEFN from `MCHF_ASP` [14, 113]. The calculations are performed according to (74). The special case of this library is realized in the program `HF96` [M4]. It allows the calculation of term dependent Hartree–Fock orbitals and energies in LS–coupling for configurations with no more than two open subshells, including f–subshells.

The library `sai_dudu` is meant for the calculation of matrix elements of any one– or two– particle operator. It contains 44 subroutines. Most of the subroutines from this module use common blocks CONSTS and MEDEFN from `MCHF_ASP` [14, 113]. Similarly as the `sai_nore` library, it uses the methodology described in subsection 2.3.1. Therefore the arrangement of library `sai_dudu` is analogous to that of library `sai_nore`.

3.3.2 Timing of new angular code for `MCHF_ASP`

Tests and timing studies of library `SAI` were performed for the $3d^5 4s^2\ ^4G$ state of Fe II with the common closed shells $1s^2 2s^2 2p^6 3s^2 3p^6$. The wave function expansions used were:

1. 4SD: Singles and doubles excitations from $3d^5 4s^2$ to the active set $\{3d, 4s, 4p, 4d, 4f\}$ contains 467 configuration state functions (CSF).
2. 5SD: Singles and doubles excitations from $3d^5 4s^2$ to the active set $\{3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f\}$ contains 1963 CSF.
3. 6SD: Singles and doubles excitations from $3d^5 4s^2$ to the active set $\{3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d, 5f, 6s, 6p, 6d, 6f\}$ contains 4492 CSF.
4. 4SDT: Singles, doubles and triples excitations from $3d^5 4s^2$ to the active set $\{3d, 4s, 4p, 4d, 4f\}$ contains 2548 CSF.

Table 11 demonstrate the problem size, times of the old (`BREIT`) and new (`GBREIT` [114]) codes, the ration $\Delta t_{BREIT}/\Delta t_{GBREIT}$.

In the first case, the calculations included only electrostatic electron interaction operator $H^{Coulomb}$. In the second case there was the analysis of both Coulomb operator and Breit–Pauli operators. As it is indicated in the Table 11, based on the methods created in the work, the written program `GBREIT` calculates 5–12 times faster, compared to Fano scheme written program.

Table 11: Comparison of time for old and new code. *The time in hours, minutes, seconds is given as hh:mm:ss.*

Expansion	1)	2)	3)	4)
Size	467	1963	4492	2548
		Case i)		
`BREIT`	00:19:00	02:35:00	09:35:00	06:40:00
`GBREIT`	00:01:32	00:29:35	01:55:00	01:21:00
Speed-up	7.5	5.7	5.0	5.0
		Case ii)		
`BREIT`	4:05:06	29:49:08		
`GBREIT`	0:20:14	05:00:09		
Speed-up	12.11	6		

In the cases when in the analyzed configurations there are f^N, with $N > 2$ shells, there was no analysis of time characteristics of programs performed. This is due to the fact that the old program `BREIT` cannot perform such calculations.

* * *

The three independent programs (`Racah III`, `ANCO` and `SAI`) are considered in this section. The programs `ANCO` and `SAI` not only support large scale computations of open–shell atoms in atomic theory but may be applied widely in the quantum chemistry as well as in the theory of the solid state physics. The program `Racah III` may influence the work in neighboured fields like nuclear structure and the scattering of particles.

4 PRACTICAL APPLICATIONS OF THE METHODOLOGY AND SOFTWARE DEVELOPED TO ATOMIC THEORY [M1, M2, M5, M7, M11, M12, M13, M15, M22]

This section provides the results got with the help of the methods developed in the habilitation work as well as of the software written for calculation of the spin–angular coefficients. The codes support large scale computations of open–shell atoms using multiconfiguration Hartree–Fock, multiconfiguration Dirac–Hartree–Fock or configuration interaction approaches. It also may help to develope codes for calculating the spin–angular parts of effective operators from many–body perturbation theory [116, 117] and orthogonal operators or for evaluating Hamiltonian in $LS-$ and $jj-$coupling as well as for various versions of semi–empirical methods.

The codes not only support large scale compiutations of open–shell atoms but may also help for correct and optimal calssification of the energy spectra measured. The best way to achieve this is by calculations of energy spectra in one coupling scheme (usually LS) and subsequent transformation of the weights of the wave functions, obtained after diagonalization of the energy matrix, to the other coupling schemes [4]. A few examples of such a procedure are presented for a number of ions in Gaigalas *et al.* [M13].

The codes are also intented for approaches and/or calculations presented in [64, 118, 119, 120, 121]. Some very accurate calculations were performed using these codes (see, e.g., [122, 123, 124] and [M12, M15, M22]). The programs created in the work may be applied widely in the quantum chemistry as well as in the theory of the solid state physics, where the exact wave functions of an atom are required [125, 126]. They may be of use in the analysis of the derivatives of the molecules and crystals, formed by heavy atoms.

Further section provides some calculations that further illustrate the possibilities and efficiency of the methods and programs.

4.1 The $2s^2\ ^1S_0$–$2s2p\ ^3P_1$ intercombination line of B II and C III [M7]

The $2s^2\ ^1S_0$–$2s2p\ ^3P_1$ intercombination line of C III is a case of particular interest in astrophysics [127] and has become somewhat of a test case, both for theory [128, 129, 130] and experiment [131, 132]. The earlier multi–configuration Hartree–Fock (MCHF) calculations for this transition in C III [129] and also for B II [133] used a program which, under certain situations, produced an error in the spin–other–orbit interaction, an error found while implementing ideas for the evaluation of matrix elements based on the approach from Subsection 2.1. As was discussed in paper by Froese Fischer and Gaigalas [M7], the effect of this error becomes less important for more highly ionized members of the series, but does affect the B II and C III values at the level of accuracy that is now our goal.

In addition, a detailed study of this transition in C III using the multi–configuration Dirac–Fock (MCDF) approach [134] has suggested an adjustment or "normalization" process that differs slightly from the procedure advocated by Fleming *et al.* [128, 135]. The computed normalized results are extremely stable with respect to changes in the computational model once core–polarization has been included, and allow us to predict reliable values with smaller uncertainty estimates.

For B II, the wave functions obtained by the process described in [133] were used in the Breit–Pauli calculations as before and transition rates obtained with the help of the biorthogonal transformation methods [136] which applied the spin–angular integration from Subsection 2.1, too. In the case of C III, earlier wave functions were used for valence and core–valence calculations, but new calculations including some correlation in the core were performed and followed closely the procedure used in MCDF calculations [134]. That is, calculations for initial and final states were performed completely independently; each started with a complete active space calculation for an active set of orbitals followed by single and double substitutions with at most electron coming from the $1s^2$ core. Details may be found in earlier papers [129, 133, 134].

In the Fleming *et al.* [128, 135] papers, a "fine–tuning" method was used that modified the computed transition rate for three factors: the rations of experimental and computed transition energies, singlet and triplet term separation, and fine structure splitting defined as $E(^3P_2)$–$E(^3P_0)$. The adjustment for observed transition energy is clearly appropriate, by definition. In effect, a transition calculation is a calculation for the transition matrix element. In the present transition, the Breit–Pauli mixing of terms is almost entirely the singlet–triplet mixing in the final state: the $2s^2\ ^1S_0$ and $2p^2\ ^3P_0$ mixing in the initial state is a rather small correction. Thus, the 2×2 model for the final state is an accurate model and adjusting for the singlet–triplet separation will improve the predicted transition rate. Adjusting for the fine structure splitting, which is only indirectly related to the $^3P_1$ state, is a somewhat different matter. Indeed, it improves the valence correlation results since both the splitting and the transition rate are too small. However, once an accurate ratio of the experimental and computed splitting cannot be related directly to an incorrect mixing of the singlet and triplet terms. At best it is an indication of the quality of the wave function for the $J = 2$, 0 state and, indirectly by association, also an indication of $J = 1$ in the absence of mixing. For C III, where a splitting of 80.05 cm^{-1} is observed [137], an MCDF [134] estimate of QED effects [138, 139] would reduced that value by 0.19 cm^{-1} to 79.86 cm^{-1} whereas the Zhu and Chung [140] estimate was a reduction of 0.23 cm^{-1}. Thus, we "normalize" for the first two factors and use the fine structure splitting as a parameter for comparison and for the estimation of uncertainty. The Table 12 shows the results for the revised B II calculations. In a sense, many of the spectrum parameters of the core–valence (CV) calculation are in better agreement with observed one than for the more difficult calculation that also includes some correlation in the core. This is seen in the smaller normalization correction. However, as we will see from C III where more reliable comparisons can be made with other theories, there is a small core–correlation effect. In B II, there are no accurate fine structure splitting observations and we propose a transition rate of 10.27 ± 0.20 s^{-1}where the uncertainty was selected somewhat arbitrarily to include the CV value.

The Table 13 shows similar, though somewhat more detailed results for C III. Valence correlation predicts transition rates that are too small as is the fine structure splitting; inclusion of core–valence greatly improves the transition energy and the term separation,

Table 12: Breit–Pauli transition data for the $2s^2\ ^1S_0 - 2s2p\ ^3P_1$ in B II. *The transition energy (ΔE) and level separations are in cm^{-1}. The $^3P_0 - ^1S_0$ separation refers to the term separation of $2p^2\ ^3P_0$ and $2s^2\ ^1S_0$. Both calculated and normalized transition rates are reported. Calculations for all models used orbital set with principal quantum number $n \leq 7$ optimized on the primary (^1S and $^3P^o$, respectively) and with an extra layer optimized on the secondary ($2p^2\ ^3P$ and $2s2p\ ^1P^o$) term, respectively.*

					$A_{ki}(s^{-1})$	
Calc'n	ΔE	$^1P^o_1 - ^3P^o_1$	$^3P^o_2 - ^3P^o_0$	$^3P_0 - ^1S_0$	Calc.	Norm.
(i) Valence correlation						
n=7	37 562	36 528	20.97	99 817	9.06	9.14
(ii) Core–valence						
n=7	37 453	36 528	20.97	99 308	10.45	10.41
(iii) Partial core correlation and core–valence						
n=7	37 303	36 225	22.19	98 902	10.14	10.27
Other theory [140]	37 345	36 065	22.2			
Exp't [141]	37 340	36 057	22.8	98 910		
Exp't [142]	37 340	36 057	21.6 ± 0.8[a]	98 910		

[a] Uncertainties determined from quoted uncertainity of the measured wavelength.

Table 13: Breit–Pauli transition data for the $2s^2\ {}^1S_0 - 2s2p\ {}^3P_1$ transition in C III. *The transition energy (ΔE) and level separations are in cm^{-1}. The ${}^3P_0 - {}^1S_0$ separation refers to the term separation of $2p^2\ {}^3P_0$ and $2s^2\ {}^1S_0$. Normalized values are scaled to the observed singlet–triplet energy separation. The oscillator strength for the allowed transition is also reported. Calculations are now based on orbital set of differing sizes as indicated by n, but with $n \leq 6$.*

					$A_{ki}({}^1S_0 - {}^3P_1^o)(s^{-1})$		
Calc'n	ΔE	${}^1P_1^o - {}^3P_1^o$	${}^3P_2^o - {}^3P_0^o$	${}^3P_0 - {}^1S_0$	Calc.	Norm.	$gf({}^1S_0 - {}^1P_1^o)$
(i) Valence correlation							
n=7	52 728	50 673	70.10	138 740	95.2	96.1	
(ii) Core–polarization							
n=6	52 513	50 100	80.24	137 811	103.81	103.66	
(iii) CAS (n=3) + SD (core–valence)							
n=7	52 374	50 138	79.62	137 504	102.22	103.04	0.7565
n=8	52 376	50 129	79.66	137 514	102.28	103.06	0.7568
n=8[a]	52 374	50 105	79.65	137 496	102.33	103.10	0.7570
n=8[b]	52 374	50 087	79.65	137 488	102.45	103.07	0.7570
n=9	52 379	50 123	79.67	137 520	102.40	103.08	0.7568
(iv) CAS (n=4) + SD (core–valence)							
n=7	52 269	50 125	79.67	137 636	101.69	103.08	0.7561
n=8	52 267	50 116	79.72	137 645	101.67	103.03	0.7563
n=9	52 357	50 112	79.72	137 404	102.23	103.05	0.7563
Exp't [131, 141]	52 391	49 961	80.05	137 426	120.9		

[a] Core valence with some triplet substitutions.

[b] Triple substitutions and secondary terms ($2p^2\ {}^3P, 2s2p\ {}^1P^o$) with two layers of extra orbitals.

but overestimates the fine structure splitting and also the transition rate. Indeed, the fine–tuned result for this calculation (103.17 s^{-1}) is in better agreement with the value ultimately recommend than the normalized value included in the table. It is the final two sets of calculations that start with a complete active space calculation (the first with all possible configurations states from orbitals with principal quantum number $n \leq 3$; the second with $n \leq 4$), and then add the single and double substitutions for outer correlation and core–valence that show the stability of the normalized values as parameters of the calculation are changed. Though the calculated values range from 101.69–102.45 s^{-1}, the normalized values are essentially constant, ranging only from 103.03–103.10 s^{-1}. Even so, there is still a discrepancy in the computed fine structure splitting. This can be a basis for an estimate of uncerainty. Using the smaller QED estimate of 0.19 cm^{-1} which leads to a larger discrepancy, adjusting by the factor $[(80.05–0.19)/79.72]^2$, and correcting for the fact that the Breit–Pauli gf value for the allowed transition differs from the best MCDF prediction by 0.2% we can estimate the uncertainty and obtain the value of 103.0 ± 0.4 s^{-1}, a value to be compared with 102.9 ± 1.5 s^{-1} for the more difficult MCDF calculations [134].

The latter are both in excellent agreement with the recently proposed value of 102.94 ± 0.14 s^{-1} obtained by Doerefert *et al.* [132] from an extremely accurate storage ring experiment, but differs significantly form the value of 120.9 ± 7 s^{-1} obtained from an ion trap experiment by Kwong *et al.* [131].

4.2 The $2s^2\ ^1S_0 - 2s3p\ ^3P_1^o$ intercombination line in the Be–like sequence [M5]

The $2s^2\ ^1S_0 - 2s2p\ ^3P_1^o$ intercombination line in the Be–like sequence has been studied extensively theoretically (Froese Fischer [129], Fleming *et al.* [128, 135], Ynnerman and Froese Fischer [133, 130]). In the Breit–Pauli scheme, it provides a critical test of the wave function in that not only the transition energy needs to be predicted accurately but also the mixing of LS terms and fine structure splitting (Fleming, *et al.* [135]). By using these properties, along with systematic methods, an estimate of the uncertainty in the computed transition rate can be obtained. In C III and N IV the uncertainty in the computed result is in the order of 2–3%. In a fully relativistic Dirac approach, there is extensive cancellation in the transition matrix element and Breit corrections are extremely important, particularly for lower nuclear charges. Using the accurate theoretical results from C III and N VI, Curtis and Ellis [143] performed semi–empirical studies to predict the $2s^2 - 2s2p$ resonance and intercombination transitions in the Be isoelectronic sequence.

The $2s^2\ {}^1S_0 - 2s3p\ {}^3P_1^o$ transition has not been investigated theoretically nearly as extensively to the same level of accuracy. Curtis *et al.* [144] have analysed also the $2s^2 - 2s3p$ transitions through the isoelectronic sequence, obtaining the transition rate for the intercombination line from the difference in lifetimes of the $J = 1$ and the $J = 2, 0$ levels. Some new experimental data were also presented. Their semi–empirical method was applied and transition data were predicted both for the allowed transition and the intercombination line.

From a theoretical point of view, the $\Delta n = 1$ transitions differ from $\Delta n = 0$ transitions in that now wave functions are required for an excited state, not lowest of its symmetry. Also important is the fact that the electron cloud of the initial state is compact, whereas the final state has an orbital that is much more diffuse. The recently developed non–orthogonal methodology (Olsen *et al.* [136]) can be used to advantage in such cases. Recently we reported results for the allowed $2s^2\ {}^1S_0 - 2s3p\ {}^1P_1^o$ transition for the elements with $Z = 4 - 10$ (Froese Fischer *et al.* [145]) using the non–relativistic MCHF approach for which the Breit–Pauli correction was small. Though there was cancellation in the calculation of the line strength in Be I, for higher Z the cancellation decreased and an agreement in length and velocity (see Rudzikas *et al.* [146]) was reached of 1 part in 4,000 for Ne VII. To obtain this excellent agreement it was essential to include the effect of core–polarization. Inclusion of some correlation in the core continued to improve agreement in length and velocity form of the oscillator strength, but by C III the core–core effect on the gf–value already was less than 5 in 2,400. In a final step, Breit–Pauli calculations were performed to capture small relativistic corrections.

In this Subsection, we report some systematic studies for determining the transition rate for the spin–forbidden transition $2s^2\ ^1S_0 - 2s3p\ ^3P_1^o$ of the Be–like sequence that may provide insight into how transition probability calculations may be performed for more complex systems [M5]. Calculations are reported for the range of $Z = 4 - 10$.

Table 14 reports the transition data for these calculations. Unlike the allowed transitions where length and velocity forms of the line strength (or oscillator strength) can be used as a test for accuracy, Breit–Pauli calculations must rely on other related factors. Included in this table are:

1. the $^3P_1^o -\ ^1P_1^o$ energy separation which, in a first–order theory, would influence the strength of the mixing;
2. the $^3P_1^o -\ ^3P_0^o$ energy separation which checks the effect of the mixing on the fine structure, though in light elements this separation is not significantly affected by singlet/triplet mixing;
3. the $^3P_2^o -\ ^3P_0^o$ energy separation which is not affected by the dominant singlet/triplet mixing, but checks the adequacy of the Breit–Pauli approximation;
4. the $^3P_1^o -\ ^1S_0$ transition energy;
5. the $^1P_1^o -\ ^1S_0$ transition energy;
6. the transition rate A($^1P_1^o$) determined from the previous calculation (Froese Fischer *et al.* [145]) where the orbitals were optimized for the $^1P^o$ term.

All these are "accuracy indicators" for the transition rate, A($^3P_1^o$), for decay from $2s3p\ ^3P_1^o$ to the $2s^2\ ^1S_0$ ground state. The experimental value are mostly from Bashkin and Stoner [147] and Kelly [137]. For F II, the values reported by Engström [148] are included. With this exception, the experimental value listed is the value closest to the highly accurate theoretical energy level determined by Zhu and Chung [140] (who tabulate a complete comparison).

The Table 14 shows that $^3P_1^o$ is lower than $^1P_1^o$, only in Be I and B II, that thereafter, in the range of Z considered here, $^3P_1^o$ is the higher state, although the separation is never very large. There is an indication that the extra orbitals used in the expansion

Table 14: Transition data for the $2s^2\ {}^1S_0 - 2s3p\ {}^3P_1^o$ transition of Be I–Ne VII. *All energies are in cm^{-1} and transition rates in s^{-1}. The notation x.xx(nn) denotes* x.xx$\times 10^{nn}$.

n	${}^3P_1^o - {}^1P_1^o$	${}^3P_1^o - {}^3P_0^o$	${}^3P_2^o - {}^3P_0^o$	ΔE (${}^3P_1^o - {}^1S_0$)	A(${}^3P_1^o$)	ΔE (${}^1P_1^o - {}^1S_0$)	A(${}^1P_1^o$)
	Be I						
Valence Correlation							
$n = 4$	−1395	0.08	0.39	58774	0.287	60169	1.159(7)
$n = 5$	−1370	0.08	0.40	58785	0.330	60155	1.073(7)
$n = 6$	−1363	0.07	0.39	58789	0.334	60152	1.038(7)
Core-valence and Valence Correlation							
$n = 6$	−1323	0.10	0.46	58947	0.534	60270	8.564(6)
$n = 7$	−1308	0.09	0.46	58943	0.568	60252	7.853(6)
$n = 8$	−1306	0.09	0.46	58943	0.572	60249	7.772(6)
Experimental energy and $A({}^1P_1^o)$ from theory (see text)							
	−1285	0.091	0.374	58909		60187	7.12(6)
	B II						
Valence Correlation							
$n = 4$	−218	1.16	4.33	143845	6.652(4)	144063	4.465(8)
$n = 5$	−217	1.17	4.36	143856	6.743(4)	144073	4.661(8)
$n = 6$	−215	1.17	4.36	143862	6.864(4)	144077	4.676(8)
Core-valence and Valence Correlation							
$n = 6$	−102	1.21	4.67	144076	3.622(5)	144178	5.011(8)
$n = 7$	−119	1.23	4.67	144064	2.640(5)	144183	5.014(8)
$n = 8$	−126	1.24	4.68	144063	2.406(5)	144189	5.020(8)
Experimental energy and $A({}^1P_1^o)$ from theory (see text)							
	−113	1.30	4.74	143990		144103	5.042(8)
	C III						
Valence Correlation							
$n = 4$	611	5.42	17.98	259582	5.644(5)	258891	3.458(9)
$n = 5$	684	5.46	18.05	259592	5.782(5)	258908	3.466(9)
$n = 6$	684	5.47	18.06	259600	5.803(5)	258916	3.478(9)
Core-valence and Valence Correlation							
$n = 6$	798	5.66	18.80	259829	4.725(5)	259031	3.572(9)
$n = 7$	778	5.67	18.81	259820	4.980(5)	259042	3.571(9)
$n = 8$	769	5.67	18.82	259818	5.144(5)	259049	3.589(9)
Experimental energy and $A({}^1P_1^o)$ from theory (see text)							
	780	5.67	18.75	259711		258931	3.598(9)

Table 14: (continued).

n	${}^3P^o_1 - {}^1P^o_1$	${}^3P^o_1 - {}^3P^o_0$	${}^3P^o_2 - {}^3P^o_0$	ΔE (${}^3P^o_1 - {}^1S_0$)	A(${}^3P^o_1$)	ΔE (${}^1P^o_1 - {}^1S_0$)	A(${}^1P^o_1$)
	N IV						
Valence Correlation							
$n = 4$	1382	15.66	50.04	405878	3.319(6)	404496	1.048(10)
$n = 5$	1376	15.72	50.18	405890	3.357(6)	404514	1.186(10)
$n = 6$	1373	15.74	50.18	405899	3.380(6)	404526	1.190(10)
Core-valence and Valence Correlation							
$n = 6$	1483	16.10	51.54	406143	3.106(6)	404659	1.207(10)
$n = 7$	1461	16.16	51.60	406137	3.209(6)	404676	1.206(10)
$n = 8$	1451	16.12	51.59	406131	3.273(6)	404680	1.213(10)
Experimental energy and $A({}^1P^o_1)$ from theory (see text)							
	1465	15.83	51.2	405988		404522	1.214(10)
	O V						
Valence Correlation							
$n = 4$	1940	36.06	111.75	582757	1.986(7)	580817	2.951(10)
$n = 5$	1932	36.15	111.97	582767	2.001(7)	580836	2.950(10)
$n = 6$	1931	36.22	112.09	582781	2.013(7)	580850	2.959(10)
Core-valence and Valence Correlation							
$n = 6$	2037	36.78	114.25	583048	1.902(7)	581011	2.988(10)
$n = 7$	2011	36.81	114.28	583048	1.954(7)	581037	2.984(10)
$n = 8$	2002	36.88	114.34	583041	1.985(7)	581039	2.998(10)
Experimental energy and $A({}^1P^o_1)$ from theory (see text)							
	2015	36.7	113.9	582840		580825	3.000(10)
	F VI						
Valence Correlation							
$n = 4$	2402	72.13	217.00	790265	9.866(7)	787863	6.130(10)
$n = 5$	2399	72.38	217.44	790280	9.924(7)	787887	6.115(10)
$n = 6$	2393	72.50	217.63	790296	9.985(7)	787903	6.138(10)
Core-valence and Valence Correlation							
$n = 6$	2498	73.32	220.88	790609	9.526(7)	788111	6.184(10)
$n = 7$	2467	73.44	220.94	790621	9.771(7)	788154	6.172(10)
$n = 8$	2457	73.50	221.06	790610	9.908(7)	788153	6.197(10)
Experimental energy and $A({}^1P^o_1)$ from theory (see text)							
	2482	73.	221.	790326		787844	6.200(10)

Table 14: (continued).

n	${}^3P_1^o - {}^1P_1^o$	${}^3P_1^o - {}^3P_0^o$	${}^3P_2^o - {}^3P_0^o$	ΔE (${}^3P_1^o - {}^1S_0$)	A(${}^3P_1^o$)	ΔE (${}^1P_1^o - {}^1S_0$)	A(${}^1P_1^o$)
	Ne VII						
Valence Correlation							
$n = 4$	2791	131.56	382.37	1028461	4.012(8)	1025670	1.130(11)
$n = 5$	2779	131.88	382.94	1028486	4.142(8)	1025707	1.124(11)
$n = 6$	2780	132.13	383.44	1028503	4.172(8)	1025723	1.130(11)
Core-valence and Valence Correlation							
$n = 6$	2886	133.25	388.00	1028897	3.994(8)	1026011	1.137(11)
$n = 7$	2848	133.44	388.19	1028932	4.102(8)	1026084	1.134(11)
$n = 8$	2838	133.62	388.37	1028917	4.156(8)	1026079	1.138(11)
Experimental energy and $A({}^1P_1^o)$ from theory (see text)							
	2809	132.8	388.2	1028499		1025690	1.138(11)

of the ${}^1P_1^o$ to compensate for the fact that all other orbitals were optimized on the ${}^3P$ state, were not sufficient to determine the energy of ${}^1P_1^o$ relative to ${}^3P_1^o$ to the desired accuracy, except for Ne VII. In all cases but the latter, the energy of ${}^1P_1^o$ is too high and the separation too small. However, it should be mentioned that the Breit–Pauli interaction *reduces* the separation, at least for the higher members of the sequence, and in F IV, for example, it reduced a separation of 2581 cm^{-1} to 2457 cm^{-1}, over–correcting by 11 cm^{-1}. This over–correcting might be related to the ${}^3P_2^o - {}^3P_0^o$ separation being too large. The inclusion of core–polarization improves the fine structure splitting and the term energy separation, even in B II which is hardly typical since the singlet and triplet states are almost degenerate. In all cases except Be I where there is extensive cancellation in the transition matrix element, the rate of decay of $2s3p$ ${}^1P_1^o$ to the ground state in this calculation is in excellent agreement with the values obtained when optimizing orbitals on the $2s3p$ ${}^1P_1^o$ state (Froese Fischer *et al.* [145]).

In Table 15, the present transition energies are compared with other theory and experiment. The Z–expansion results of Ralchenko and Vainshtein [149] are based on perturbation theory along with an adjustable parameter. The GRASP results were obtained using a fully relativistic Dirac–Coulomb Hamiltonian with Breit corrections (Fritzsche and Grant [150]). Only valence correlation was considered and the same orbitals were used to

Table 15: Comparison of $2s^2\ ^1S_0 - 2s3p\ ^3P_1^o$ transition energies (in cm^{-1}).

Z	Z-exp.[a]	GRASP[b]	FCPC[c]	MCHF[d]	Exp.[e]
6	259 613	–	259 713	259 818	259 711
7	405 960	406 040	405 992	406 131	405 988
8	582 871	582 770	582 839	583 041	582 840
9	790 395	790 470	790 331	790 610	790 326
10	1 028 591	1 028 680	1 028 505	1 028 917	1 028 499

[a] Ralchenko and Vainshtein [149]
[b] Fritzsche and Grant [150]
[c] Zhu and Chung [140]
[d] present work
[e] Bashkin and Stoner [147]; Kelly [137]

describe both the initial and final states. The full–core plus–correlation (FCPC) method of Zhu and Chung [140] starts with an accurate description of the $1s^2$ core common to both states, and then adds correlation corrections determined from restricted variational calculations. These are extrapolated and corrected for a number of small effects to yield the total non–relativistic energy. To these are added relativistic, mass–polarization, and QED corrections [151, 152]. Clearly, of these energies, the FCPC energies are the most accurate whereas the present MCHF energies are 100 – 400 cm^{-1} too high. In the study of the allowed transition (Froese Fischer *et al.* [145]), the main effect of core correlation was to reduce the transition energy. Thus we attribute the present discrepancy to this source. In this table we have included the Bashkin and Stoner [147] value from the transition energy since the Engström [148] value of 790 312 cm^{-1} deviates by 19 cm^{-1} from the FCPC values, a deviation much larger than for other members of the sequence.

The fine structure splitting from the present calculation is compared in Table 16 with values from FCPC (Zhu and Chung [140]) and experiment. For F VI and Ne VII, there is disagreement among the reported experimental values, in which case we included those given by Bashkin and Stoner [147], consistenly in better agreement with our theory in Table 15. For comparison we also include the Engström [148] value for F VI. Ne VII is the first ion where the singlet/triplet coupling shifts the energy of the $^3P_1^o$ significantly.

Table 16: Comparison of the $^3P_J -^3 P_0$ fine structure splitting (in cm^{-1}) with other theory and experiment.

	B II	C III	N IV	O V	F VI	Ne VII
	i) $^3P_1^o -^3 P_0^o$					
MCHF[a]	1.24	5.67	16.12	36.88	73.50	133.62
FCPC[b]	1.20	5.58	16.1	36.7	72.8	132.1
Exp.[c]	1.30	5.67	15.83	36.7	73.	132.8
Exp.[d]					72.	
	ii) $^3P_2^o -^3 P_0^o$					
MCHF[a]	4.68	18.82	51.59	114.34	221.06	388.37
FCPC[b]	4.60	18.61	51.3	113.7	219.6	385.5
Exp.[c]	4.74	18.75	51.2	113.9	221.	388.2
Exp.[d]					220.	

[a] present work
[b] Zhu and Chung [140]
[c] Bashkin and Stoner [147]; Kelly [137]
[d] Engström [148]

In the FCPC results, this was computed using first–order perturbation theory yielding an increase in energy of 10.1 cm^{-1} whereas the corresponding MCHF shift from direct diagonalization of the Breit–Pauli interaction matrix, both with and without single/triplet mixing, was 10.25 cm^{-1}. The $J = 2 - 0$ separation is independent of the singlet/triplet mixing and our result here is in good agreement with experiment.

Transition rates are tabulated in Table 17 for valence correlation (v) and also for core–valence (cv) calculations. Both have been adjusted for the fact that the energy level data are not in accurate agreement with observation. To first order, the transition rate would be proportional to

$$\left(\Delta E(^3P_1^o -^1 S_0)\right)^3 \left(\frac{\Delta E(^3P_2^o -^3 P_0^o)}{\Delta E(^3P_1^o -^1 P_1^o)}\right)^2 ,$$

where $\Delta E(^3P_2^o -^3 P_0^o)$ is assumed to be a measure of the Breit–Pauli interaction. As shown in Fleming *et al.* [135], adjusting computed transition rates by correction factors derived from the above relation, improves the accuracy of computed values. Thus, in Table 17, the adjusted values for valence correlation, v(adj), and core–valence, cv(adj),

Table 17: Breit–Pauli transition rates ($10^6 s^{-1}$) for the $2s^2\ ^1S_0$–$2s3p\ ^3P^o_1$ transition from valence correlation (v) and core–valence (cv) calculations, as computed and when adjusted to the observed fine structure splitting and transition energy. *A recommended value (rv) is also given along with an uncertainty (in parentheses).*

Z	v	v(adj)	cv	cv(adj)	rv
5	0.069	0.294	0.241	0.306	0.27(6)
6	0.580	0.482	0.514	0.496	0.50(2)
7	3.38	3.09	3.27	3.16	3.2(1)
8	20.13	19.05	19.85	19.42	19.6(4)
9	99.85	97.4	99.08	98.7	98.9(9)
10	417.20	410.	415.6	414.4	415.(4)

are also reported. It is remarkable to note the agreement in the adjusted values for B II, when the computed values differ by a factor of three. Of course, such adjustments rely on accurate experimental value. The especially large deviation of our term energy separation in F VI from experiment, suggests that these experimental energy levels have not been determined to sufficient accuracy. Instead, for adjustment purposes, we use a slightly larger separation of 2 460.8 cm^{-1} by Zhu and Chung [140], consistent with other deviations. In all cases, the adjustment process changes the core–valence result the least, but in Ne VII, valence correlation was less affected. In fact, as Z increases, the transition energy from valence correlation alone, is in better agreement with experiment than the core–valence calculation. From this data, a recommended transition rate was determined from the average of the core–valence and its adjusted value, the uncertainty being roughly equal to the size of the adjustment. In contrast to the allowed transition, the addition of core–valence correlation, which accounts for the polarization of the core by the presence of the valence electrons, has a decreasing effect on the transition rate for the six ions considered.

In Table 18, the present recommended value is compared with other theory and experiment. For higher members of the isoelectronic sequence, the agreement with the trend predicted by Curtis *et al.* [144] from a semi–empirical study of experimental data is ex-

Table 18: Comparison of present Breit–Pauli transition rates ($10^6 s^{-1}$) for the $2s^2\ ^1S_0 - 2s3p\ ^3P^o_1$ transition with other theory, experiment, and semi–empirical values predicted by Curtis *et al.* [144]. *Numbers in parentheses represent the uncertainty.*

Z	MCHF[a]	GRASP[b]	CIV3[c]	Z-exp[d]	Curtis *et al.*	
					Exp.	Pred.
5	0.27(6)					0.1
6	0.50(2)		0.520			0.4
7	3.2(1)	1.40	3.07	4.97	3.3(20)[f]	2.8
8	19.6(4)	16.4	18.3	22.2	22.6(4)	19.
9	98.9(9)	85.5	88.6	95.9	102(9)	100.
10	415.(4)	385.	275.	370.	430(60)	418.

[a] present work
[b] Fritzsche and Grant [150]
[c] Hibbert [154]
[d] Ralchenko and Vainshtein [149]
[f] Engström *et al.* [153]

ceptional. For N IV, agreement is better with experiment (Engström *et al.* [153]), though the error bar for the experiment is large. For C III, our value differs only slightly from the value obtained by Hibbert [154] but is somewhat larger than what is predicted by Curtis *et al.* [144]. Since the latter include B II in their trend, we have included it in Tables 17 and 18 as well. Because the order of $2s3p\ ^3P_1^o$ and $2s3p\ ^1P_1^o$ levels changes in going from C III to B II, an irregular behaviour can be expected. Though this computed transition rate is likely to be affected by core correlation more than others, a value larger than predicted by Curtis *et al.* [144] semi–empirical model is plausible. Of the other theoretical results, both GRASP (Fritzsche and Grant [150]) and the Z–expansion results (Ralchenko and Vainshtein [149]) show improving trends as Z increases, as expected from the theory. CIV3 (Hibbert [154]) however is the reverse, with low–Z being the more reliable.

So, finaly we can made some conclusions. The theoretical computation of the transition rate for the $\Delta n = 1$, $2s^2\ ^1S_0 - 2s3p\ ^3P_1^o$ intercombination line is considerably more difficult from that for the $\Delta n = 0$ intercombination line for the Be–like sequence. The final state is now an excited state, and the contribution from the spin–orbit contribution of the outer $3p$ is considerably less than that of the $2p$. Thus, two–body operators of the Breit–Pauli Hamiltonian play a more important role. Recently, Fritzsche and Froese Fischer [155] have performed a non–orthogonal GRASP calculation for F VI where orbitals were independently optimized for the initial and final states. The valence correlation transition energy was 790342 cm^{-1} (compared with 790326 cm^{-1} for experiment) and the transition rate was 100.18 $\times 10^6$ and 100.76×10^6 for the Coulomb and Babushkin gauges, respectively. No systematic studies were reported and agreement in the gauges could be accidental. It is possible that a more extensive multiconfiguration Dirac–Fock calculation, including also the effect of polarization of the core, can resolve some of the uncertainties. On the whole, the present agreement with the semi–empirical trend predicted by Curtis *et al.* [144] is encouraging.

4.3 Breit–Pauli energies, transition probabilities, and lifetimes for $2s$, $2p$, $3s$, $3p$, $3d$, $4s$ ^2L levels of the lithium sequence [M11]

With the aid of powerful workstations and systematic methods, a considerable improvement in accuracy has been achieved in the calculation of non–relativistic transition data for light atoms using the MCHF method (see [156] for a review). Accuracy criteria for such calculations are agreement in length and velocity form of the line strength or oscillator strength along with a simultaneous close agreement with the observed transition energy. For the $2s^22p\ ^2P^o - 2s2p^2\ ^2D$ transition in B I, for example, the length and velocity gf–values differed by less than 0.4% when the non–relativistic transition energy differed from the observed by about 0.1% [157]. Besides neglecting the finite nuclear mass and relativistic effects, most of these calculations have been benchmark calculations of isolated resonance transitions.

In this Subsection we report results of Breit–Pauli calculations for a portion of a spectrum of lithium and lithium–like ions with nuclear charge $Z \leq 8$. Included are the energies of all J–levels of the six lowest $2s$, $2p$, $3s$, $3p$, $3d$, $4s$ ^2L terms and all allowed transitions between the levels of these terms. From the latter, the lifetime of each level can be computed, the quantity measured in experimental techniques relying on the analysis of decay curves. For some transitions, lifetimes immediately provide transition rates, but for excited states a knowledge of branching ratios is needed before measured lifetimes can yield transition rates. Thus, theoretical calculations for excited states play a valuable role in spectroscopy.

This work was undertaken to test the accuracy of our codes for the Breit–Pauli approximation as well as the application of our techniques to excited states. The computational method follows standard procedures [113]. For more datails see [M11].

The configuration states included in the expansions of the different terms were obtained by including all possible CSFs of a given LS symmetry that could be constructed from orbitals with $n \leq 10$, $l \leq 7$ (k orbitals), and with at least one orbital in the configuration with $n \leq 4$. The largest expansion for this rule–based scheme was for ^2D where the interaction matrix size was 15,606. A distributed version of the Breit–Pauli code using a message passing interface was used to generate the interaction matrix and obtain selected eigenvalues and eigenvectors. Once the eigenvectors were determined, a non–orthogonal version of the transition code was used to compute transition data [136].

Table 19 shows the energy levels in cm^{-1} relative to the ground state for part of the lithium sequence with $Z \leq 8$, comparing observed and computed energies, and their difference, observed minus computed. If we assume the observed energy levels are accurate, this difference represents the error in our approximation. For lithium, the observed energy levels were from the very accurate tabulations reported by Radziemski *et al.* [158], for beryllium from [159], for boron from [160], for carbon from [161] and all others from the NIST tabulations [162]. The differences with observed energies range from a few cm^{-1} for lithium to as many as 84 cm^{-1} in oxygen ($Z = 8$). Not included in this work were the QED effects which are particularly important for the $2s\ ^2S$ ground states. In the case of O^{+5}, Chung [163] reports a QED correction which would add 29.5 cm^{-1} to the differences between observed and computed, reducing the error by about a factor of two, except in the case of $3d\ ^2D$. The results reported here are entirely *ab initio:* there has been no extrapolation with respect to the basis or the angular quantum number in the non–relativistic wave function. The errors reported in Table 19 represent an imbalance in the correlation included in the individual calculations (particularly the correlation in the core), and an incomplete representation of the relativistic shift and other Breit–Pauli operators computed from a basis optimized for the non–relativistic Hamiltonian. For the $^2P^o$ and ^2D states the difference in the errors for the two J–levels is the discrepancy between theory and observation in the fine structure splitting.

Table 20 analyzes the fines tructure splitting more carefully. For the $2p\ ^2P^o_{1/2,3/2}$ state, a very accurate calculation has been reported by Yan and Drake [164] in perfect agreement with experiment for lithium. We also compare the present results with FCPC results obtained by Wang *et al.* [165] that include a small QED correction, increasing the splitting. Thus, our uncorrected results should be smaller than the observed ones which is not the case for N V ($Z = 7$). For $3p$ of B^{+2}, our splitting is too large by 0.025 cm^{-1} or 0.25%. The fine structure splitting for $3d$ is also reported. Differences with observation are now

Table 19: Comparison of observed and computed Breit–Pauli excitation energies in cm^{-1} as a function of Z, along with the difference, observed–computed. *For lithium, observed values are from [158], for beryllium from [159], for boron from [160], for carbon from [161], and all others from the NIST publication [162].*

Level \ $Z =$		3	4	5	6	7	8
$2p$	$^2P^o_{1/2}$						
	Exp.	14903.6481	31928.76	48358.40	64483.8	80463.2	96375.0
	MCHF	14904.1089	31932.27	48367.61	64503.2	80500.2	96441.0
	Diff.	-0.4608	-3.51	-9.21	-19.4	-37.0	-66.0
$2p$	$^2P^o_{3/2}$						
	Exp.	14903.9835	31935.34	48392.50	64591.0	80721.9	96907.5
	MCHF	14904.4423	31938.82	48401.64	64610.3	80759.1	96972.8
	Diff	-0.4588	-3.48	-9.14	-19.3	-37.2	-65.3
$3s$	$^2S_{1/2}$						
	Exp.	27206.0952	88231.91	180202.09	302847.8	456126.6	640039.8
	MCHF	27203.9689	88230.45	180203.33	302861.4	456165.5	640126.5
	Diff.	2.1263	1.46	-1.24	-13.6	-38.9	-86.7
$3p$	$^2P^o_{1/2}$						
	Exp.	30925.5530	96495.36	192951.40	320048.9	477765.7	666113.2
	MCHF	30924.0285	96494.71	192952.65	320061.6	477792.3	666169.4
	Diff.	1.5245	0.65	-1.25	-12.7	-26.6	-56.2
$3p$	$^2P^o_{3/2}$						
	Exp.	30925.6494	96497.28	192961.42	320080.4	477842.0	666269.8
	MCHF	30924.1241	96496.64	192962.69	320093.1	477867.6	666324.5
	Diff.	1.5253	0.64	-1.27	-12.7	-25.6	-54.7
$3d$	$^2D_{3/2}$						
	Exp.	31283.0505	98054.57	196068.89	324878.5	484404.3	674625.7
	MCHF	31280.5311	98052.61	196067.89	324882.3	484407.0	674632.9
	Diff.	2.5194	1.96	1.00	-3.8	-2.7	-7.2
$3d$	$^2D_{5/2}$						
	Exp.	31283.0866	98055.12	196071.81	324887.7	484426.3	674676.8
	MCHF	31280.5671	98053.19	196070.81	324891.5	484429.5	674679.5
	Diff.	2.5195	1.93	1.00	-3.8	-3.2	-2.7
$4s$	$^2S_{1/2}$						
	Exp.	35011.5432	115464.40	237698.45	401346.6	606348.8	852696.
	MCHF	35009.2270	115461.45	237695.60	401352.1	606363.3	852736.8
	Diff.	2.3162	2.95	2.85	-5.5	-14.5	-40.8

Table 20: Comparison of the fine structure separation (in cm^{-1}) with other theory (FCPC [165], HR [165]) and experiment. *For lithium, observed values are from [158], for beryllium from [159], for boron from [160], and all others from the NIST publication [162].*

Term	Method \ $Z =$	3	4	5	6	7	8
$2p\ ^2P$	MCHF	0.3334	6.5542	34.032	107.085	259.919	531.76
	FCPC	0.3333	6.5569	34.038	107.06	258.74	530.94
	HR	0.335273					
	Exp.	0.3353	6.58	34.10	107.2	258.7	532.5
$3p\ ^2P$	MCHF	0.0957	1.9280	10.045	31.529	75.275	155.07
	FCPC	0.0954	1.9263	10.019	31.519	76.180	156.37
	Exp.	0.0964	1.92	10.02	31.5	76.3	156.6
$3d\ ^2D$	MCHF	0.0360	0.5759	2.913	9.206	22.480	46.629
	Exp.	0.0361	0.55	2.92	10.5	22.0	51.1

more variable and may be due to uncertainty in the experimental value.

The $2s-2p$ transition in lithium has been determined to high precision by Yan and Drake [166], whose paper contains an extensive review of the literature for this transition. Using a Hylleraas expansion, correlation and finite nuclear mass are treated to high accuracy. When a small relativistic correction is included, their results are in excellent agreement with the most accurate experiment by McAlexander *et al.* [167]. Recently their work has been extended to the iso–electronic sequence [168] and compared with earlier work by Chung [169]. Agreement between the two theories is excellent (within a few units in the last place reported by Chung) though the Yan *et al.* [168] non–relativistic f–values have been determined to about nine significant digits. In order to correct these for relativistic effects, they rely on relativistic many–body perturbation theory (RMBPT) tabulations [170] believed not to be sufficiently accurate for low Z because of an incomplete treatment of correlation. In Table 21 we compare the present Breit–Pauli transition or decay rates for the $2p\ ^2P^o_{1/2}$ and $2p\ ^2P^o_{3/2}$ levels.

The accuracy of the present methodology can be assessed from this extensively studied transition. In Table 21, six digits are quoted in order to show the difference between our

Table 21: Comparison of present decay rates for $2p$ $^2P^o$ states of the lithium sequence (in units of 10^8 s^{-1}) with HR [168] and RMBPT [170] values. *(MCHF^a normalized to the obseved transition energy).*

Method \ $Z =$	3	4	5	6	7	8
	$2p$ $^2P^o_{1/2}$ $-$ $2s$ $^2S_{1/2}$					
MCHF	0.368960	1.12958	1.89069	2.63205	3.36234	4.08832
MCHF^a	0.368926	1.12923	1.88961	2.62970	3.35771	4.07993
HR	0.36894	1.1289(1)	1.8886(1)	2.6281(1)	3.3556(2)	4.0764(2)
RMBPT	0.3690	1.129	1.889	2.630	3.357	4.078
	$2p$ $^2P^o_{3/2}$ $-$ $2s$ $^2S_{1/2}$					
MCHF	0.368986	1.13032	1.89494	2.64592	3.39648	4.15928
MCHF^a	0.368952	1.12998	1.89387	2.64364	3.39179	4.15088
HR	0.36896(2)	1.1297(1)	1.8932(1)	2.6425(1)	3.3905(2)	4.1487(2)
RMBPT	0.3690	1.130	1.894	2.644	3.392	4.150

results and those of the Hylleraas result (HR) and RMBPT. For low Z, given the nature of the three methods, it is difficult to say with certainty which is the definitive value. The experimental measurement [167], for $2p$ $^2P^o_{1/2}$, converted to a decay rate, is 0.368976(95) 10^8 s^{-1}, a result in agreement with all three methodologies. For higher Z, the present decay rates are affected by the neglect of QED corrections [171]. Because the rate depends on the ΔE^3, any error in the theoretical transition energy is magnified. Transition energies can often be measured accurately. In such cases, theoretical results can be *normalized* to the observed transition energy, yielding the most reliable transition rates. Such normalized values are also shown in Table 21 and agree closely with RMBPT values (which likewise had been normalized to observed transition energies). Included with the HR values is an estimate of uncertainty: from the agreement between the MCHF normalized results and RMBPT, it would appear that some of these estimates are no the low side. As shown in Table 22, the present decay rates from $3s$ $^2S_{1/2}$ to the $2p$ $^2P^o_{1/2}$ and $2p$ $^2P^o_{3/2}$ levels also are in excellent agreement with the similar quantities reported by Johnson *et al.* [170].

The accuracy of computed transition data depends on both the accuracy of the transition energy and the accuracy of the line strength. The accuracy of the former is best

Table 22: Comparison of present decay rates for $3s\ ^2S$ to $2p\ ^2P^o$ states of the lithium sequence (in units of 10^9 s^{-1}) with RMBPT [170] values.

Method \ $Z =$	3	4	5	6	7	8
	$3s\ ^2S_{1/2}$	$-\ 2p\ ^2P^o_{1/2}$				
MCHF	0.011154	0.13609	0.53744	1.4188	3.0354	5.6952
RMBPT	0.01114	0.1359	0.5367	1.418	3.032	5.680
	$3s\ ^2S_{1/2}$	$-\ 2p\ ^2P^o_{3/2}$				
MCHF	0.022306	0.27212	1.0745	2.8365	6.0679	11.386
RMBPT	0.02228	0.2719	1.074	2.840	6.073	11.39

determined from experiment, where often (though not always!) more reliable values can be obtained. The sensitivity of the line strength to cancellations in the calculation of the one–electron radial dipole matrix element and correlation can be assessed through a comparison of the deviation from unity of the ratio of the length (independent of transition energy) and velocity (dependent on transition energy) matrix elements in the non–relativistic limit. The most stable line strength is for the $2p - 3d$ transition where both radial functions have the same sign so that there is no cancellation in the one–electron dipole matrix element. At the same time, the transition energy is sufficiently large that it can be computed to a relatively high accuracy fairly readily. On the other hand, the $3s - 3p$ one–electron radial dipole matrix element is sensitive to cancellation and the transition energy, being small, cannot be computed to a high accuracy, manifesting itself in a relatively large discrepancy in the length (S_l) and velocity (S_v) form of the line strength obtained from non–relativistic wave functions. Thus, we propose to use the deviation from unity of S_l/S_v as a measure of the uncertainty in the strength. To this needs to be added some uncertainty due to relativistic corrections. In this particular study, the relativistic effects on the line strength are small, in fact less than 2% for the highest ion, O^{+5}. Assuming that these effects themselves are captured accurately to within 2% in our methodology, the result is an uncertainty of 0.4 parts per thousand for $Z = 8$.

In the paper [M11] we present similar data for the six terms and dipole transitions between these terms, for $Z = 3$ to $Z = 8$. Table I from [M11] contains energy level information, the fine structure splitting, and the lifetimes computed from the allowed E1 transitions. These values are similar to the non–relativistic values reported by Chung [169], but show the relativistic effect. Table II reports the transition energy, line strength (in length from), oscillator strength, and transition rate.

4.4 The negative ion of boron [M1, M2]

Ab initio calculations of electron affinities for even small systems have been a challenge for many atomic and molecular codes. Quantum chemical calculations strive for "chemical accuracy" of 1 kcal/mol (about 40meV), but in experimental atomic physics an accuracy of a few meV is desirable. Though the electron affinity of carbon has been measured to an accuracy of 0.3 meV [172], the experimental uncertainty in the electron affinity of boron is 10 meV [172].

Many calculations for electron affinities have been performed for the first row elements, including boron. Most are quantum chemical basis–set methods [173, 174] where basis–set truncation errors are present as well as errors arising from an unbalanced treatment of correlation in the atom and anion. Some very acurate valence correlation results have been reported by Noro *et al.* [175] using multireference configuration interaction calculation. The best results were obtained when the weight of the reference states was the same in both systems. In boron the quadrupole correction appeared not to be needed since it changed their value of 278 meV to 273 meV. The former compared well with the experimental value of 277(10) meV [172] but, in fact, both are within experimental uncertainty. For carbon, their corrected value of 1.264 eV was the more accurate when compared with the most recent electron affinity of 1.2629(3) eV [172]. In this subsection there is presented the study of the electron affinity of ground state [M1] and the excited $2s2p^2\ {}^4P$ state [M2]. The Table 23 compares the present results with other theories and experiment of the electron affinity of ground state.

Most theoretical results are for valence correlation. Let us consider this limit first, omitting the relativistic correction.

Because of the greater complexity of correlation in the anion, some correlation can

Table 23: A comparition of the present non–relativistic electron affinities (in meV) from different theories.

Reference	Valence corr.	With core polarization	Experiment
Hotop and Lineberger [172]			277(10)
Present	273.2(2)	279.5(20)	
Sundholm and Olsen [178]	286.6(17)	267.8(20)	
Noro *et al.* (with correction) [175]	273		
Kendell *et al.* [173]	263		
Raghavachari [174]	269		
Kancerevičius [176]	32		

easily be lost and most of the theories have predicted electron affinities that are too small. Raghavachari [174] used a perturbation scheme with which it is difficult to compare other than the final value. Kancerevičius [176] used multiconfiguration approximation only for the outer shells. Kendell *et al.* [173] and Noro *et al.* [175] both used a multireference single and double configuration interaction scheme but with different bases. The latter recognized the importance of computing energy differences from calculations where the weight to the reference configurations was the same in both states. They also used the Davidson correction [177] for estimating the remaining quadrupole corrections. Plots of the energies as a function of the weight of the reference state were flatter and easier to extrapolate. For boron, their estimate of the electron affinity was 273 meV, though their uncorected value of 278 meV appeared to be more accurate in that the agreement with experiment was better. However, we believe this limit is 273.2 meV, in agreement with their corrected value.

In many respects, the present calculations are most like those of Sundholm and Olsen [178]. In fact, for valence correlation up to $n = 5$ our total energies are in perfect agreement. However, thereafter, Sundholm and Olsen estimate effects in a differential manner from which they determine the valence correlation limit to be 269.6(17) meV. It would appear that the different effects are enhanced when they are all considered together. Again, the effect of core–valence correlation was estimated from a small expansion including only s and p orbitals in the basis. A reduction in the electron affinity was predicted by this process whereas in our calculation a small increase was predicted from core–valence together with core rearrangement. Buth of us agree on the reduction of the electron affinity by the relativistic effect though our estimate of -1.1 meV was obtained from the $n = 9$ valance correlation calculation using the non–fine–structure contributions of the Breit–Pauli Hamiltonian (omitting the orbit–orbit interaction).

4.5 Atomic properties of lithium–like ions [M12]

The multiconfiguration Hartree–Fock method (MCHF) is used for calculating the non–relativistic limit of electric dipole transition probabilities, isotope shifts and hyperfine structure parameters involving the terms $3s\ ^2S$, $3p\ ^2P^o$, $3d\ ^2D$, $4s\ ^2S$, and $4p\ ^2P^o$ of the stable isotopes of ions Li I, Be II, B III, C IV, N V and O VI. Comparison with the most recent observations and other theoretical calculations is done for selected examples.

4.5.1 Oscillator strengths

The length and velocity oscillator strengths of the resonance line $2s - 2p$ are compared in Table 24 with the non–relativistic full–core–plus correlation (FCPC) results of Chung [169] and with the Hylleraas–type variational (HV) results of Yan *et al.* [168], corresponding to the infinite nuclear mass limit (f_∞). The present MCHF approach cannot compete with this exceptional accuracy, but as it can be seen from this table, is of the same quality as the FCPC method.

4.5.2 Isotope shifts

As an illustration of the accuracy of the present results, we compare the present results with observation and other theories for neutral lithium. The isotope shifts of a series of lines have been measured for the isotope pair ^{6,7}Li using Fourier–transform spectroscopy by Radziemski *et al.* [158] and, for the resonance line, isotope shifts have been derived from Doppler–free frequency–modulation spectroscopy (Sansonetti *et al.* [179]). The transition isotope shifts (in cm^{-1}) are reported in Table 25 for the eight E1 transitions considered and are compared with observation. The agreement is very nice, even in cases for which

Table 24: Comparison between theoretical non–relativistic oscillator strengths in lithiumlike ions

	MCHF		FCPC		HV
	f_l	f_v	f_l	f_v	f_∞
			$2s\ ^2S - 2p\ ^2P^o$		
Li I	0.74704	0.74690	0.74704	0.74704	0.746 956 939 6(98)
Be II	0.49812	0.49807	0.49813	0.49820	0.498 067 381(25)
B III	0.36327	0.36325	0.36329	0.36340	0.363 243 128 5(92)
C IV	0.28423	0.28421	0.28429	0.28429	0.284 204 795 2(30)
N V	0.23299	0.23298	0.23299	0.23300	0.232 970 178 3(15)
O VI	0.19724	0.19724	0.19725	0.19725	0.197 228 627 94(79)

strong cancellation occurs between normal mass shift (NMS) and specific mass shift (SMS) contributions.

4.5.3 Hyperfine structures

The purpose of our study is to evaluate the accuracy of the hyperfine parameters calculated with the MCHF method using large configuration expansions. The most recent theoretical work on hyperfine structures in lithium–like ions is due to Guan and Wang [180] who studied the convergence of the non–relativistic parameters using "full core plus correlation" (FCPC) wave functions for the low–lying states $1s^2ns\ ^2$ and $1s^2np\ ^2P^o (n \leq 5)$. Table 26 collects the MCHF results for some levels of ^{7}Li I for which experimental data are available. In the same table, a second set of theoretical results labelled MCHF$_c$ is presented, corresponding to the MCHF values corrected for both relativistic effects and finite nuclear mass. The finite nuclear mass effect has been introduced by multiplying the MCHF result by the appropriate mass scaling factor $(\mu/m)^3$. The relativistic effects are taken into account by using the Dirac–Fock/Hartree–Fock ratio of the hyperfine parameters obtained in the one–configuration approximation. For $2s$ and $3s$, Hylleraas–type variational (HV) calculations are also available (Yan *et al.* [181]) for comparison.

The significant discrepancy for $3s\ ^2S$ of ^{7}Li I between theory and experiment, pointed out by Yan *et al.* [181], is confirmed by the MCHF study. A similar problem appears for

Table 25: Comparison between theoretical non–relativistic and experimental isotope shifts

Transition	MCHF (this work)			Obs.(FS)
	NMS	SMS	total	
$2s\,^2S - 2p\,^2P^o$	0.1940	0.1573	0.3512	0.3511(5)
$2s\,^2S - 3p\,^2P^o$	0.4025	0.0740	0.4765	0.48(2)
$2p\,^2P^o - 3s\,^2S$	0.1601	-0.1293	0.0308	0.0311(10)
$2p\,^2P^o - 3d\,^2D$	0.2132	-0.1204	0.0927	0.0932(15)
$2p\,^2P^o - 4s\,^2S$	0.2617	-0.1239	0.1378	0.1383(10)
$3s\,^2S - 3p\,^2P^o$	0.0484	0.0461	0.0945	0.0943(10)
$3p\,^2P^o - 3d\,^2D$	0.0047	-0.0372	-0.0325	–
$3p\,^2P^o - 4s\,^2S$	0.0532	-0.0406	0.0125	0.0127(10)

Table 26: Comparison between theoretical non–relativistic and experimental hyperfine parameters

		Theory		Experiment	
Ion	Level	A(MHz)	Method	A(MHz)	ref.
^{7}Li I	$2s\,^2S_{1/2}$	401.714	HV	401.7520433(5)	Beckmann *et al.* [182]
		401.352	FCPC		
		401.63	MCHF (this work)		
		401.76	MCHF$_c$ (this work)		
	$3s\,^2S_{1/2}$	93.251	FCPC	94.68(22)	Stevens *et al.* [183]
		93.09	HV		
		93.055	MCHF (this work)		
		93.084	MCHF$_c$ (this work)		
	$4s\,^2S_{1/2}$	35.068	FCPC	36.4(4)	Kowalski *et al.* [184]
		35.08	MCHF (this work)		
		35.09	MCHF$_c$ (this work)		
	$3d\,^2D_{3/2}$	838.6 kHz	MCHF (this work)	843(41) kHz	Burghardt *et al.* [185]
		838.4	MCHF$_c$ (this work)		
	$3d\,^2D_{5/2}$	343.2 kHz	MCHF (this work)	343.6(1.0) kHz	Burghardt *et al.* [185]
		343.1	MCHF$_c$ (this work)		

the more excited state $4s\ ^2S$ for which both the FCPC and MCHF values fall outside the experimental uncertainty. For ^{7}Li $3d\ ^2D_{3/2,5/2}$, the hyperfine interaction constants A have been determined using two–photon Doppler–free laser spectroscopy. To the knowledge of the authors, our work provides the first theoretical evaluation of these and the agreement between theory and observation is very satisfactory.

4.6 *Ab initio* studies on energies and lifetimes for $[Ar]3d^8 4p\ ^{2S+1}L$ levels of Ni II [M15]

Nickel is known to be an essential component in the manufacturing of stainless steel and other corrosion–resistant alloys. In combination with titanium and chromium, various nickel alloys occur inside of magnetic fusion devices as a first–wall material. Therefore, knowing the spectral data of nickel at different stages of ionization is important both for plasma diagnostics and for a better understanding of the influence of impurities on the temporal behaviour of fusion plasmas. Moreover, reliable data for the highly abundant iron–group elements not only are helpful in fusion research but are also needed for the interpretation of astronomical observations since the iron–group elements often dominate the photospheric spectra of many stellar objects. For a reliable spectral synthesis, for example, one not only requires information about a few individual lines but also often needs the (theoretical) knowledge of the line intensities for a whole spectral range in order to be able to substract away the dominant parts of some spectrum, thereby opening up access to much weaker lines of other, lower–abundance elements.

For the low–lying levels of Ni II, the need for accurate transition data has led to several compilations in the past which list wavelengths and transition probabilities in the optical and near–ultraviolet region [186, 187]. A critical and very useful review on the available transition data of nickel atoms and ions (at different stages of ionization) was carried out, in particular, by Wiese and Musgrove [188], who provide wavelengths and transition rates for several prominent lines as well as for less intense ones. However, as pointed out by Wiese and Musgrove, some of the transition probabilities are (presumably) not very accurate and provide just a first approximation to these spectra. Also, the overall amount of available data remains small and much work needs to be done before these spectra are fully understood. Apart from earlier measurements on Ni II in the past, Ferreroem et al. [189] recently determined branching rations for several strong lines from which they derived absolute transition probabilities by applying semiempirical computations of lifetimes that they compared with the lifetime measurements of Lawler and Salih [190].

The rather small amount of the presently available data for Ni II is related to the lack of accurate structure calculations on spectra with open d shells. For a long time, such computations have not been feasible due to the complexity of this open–shell structure. To demonstrate recent progress in the field of atomic structure calculations and to facilitate the identification of further lines of the (low–lying) Ni II spectrum, we reported the energy and lifetimes calculations for Ni II in the paper [M15]. These calculations were performed using multiconfiguration Dirac–Fock method. The Table 27 lists the excitation energies of the 18 even–parity levels (from the $3d^9$ and $3d^84s$) and the 45 odd–parity levels. The liftimes of odd–parity levels included in it as well.

All energies in Table 27 are given with respect to the ${}^2D_{5/2}$ ground state. Even though differences of up to 2000 cm^{-1} occur for a few of the higher levels, the levels ordering is well reproduced with only a very few "crossings" for levels with different symmetries. Somewhat larger deviations arise for the two highest levels ($3d^74s4p\ {}^6F_{3/2}$ and $3d^74s4p\ {}^6F_{1/2}$), which, in fact, belong to the $3d^74s4p$ configuration. These two levels are described only very approximately in the present computation.

4.7 Studies of Gd ionization energy from $[Xe]4f^75d6s^2\ {}^9D$ to $[Xe]4f^75d6s\ {}^{10}D$ [M22]

There is considerable current interest in understanding lanthanide chemistry and physics, for example, in the field of catalysis (Jeske *et al.* [191] and high–temperature superconductors (Rao and Raveau [192]). The ground configurations of those chemical elements have one open $4f$–shell. This fact brings major difficulties for their theoretical study and is the main reason of the sparseness of theoretical data on lanthanides. The aim of the work Gaigalas *et al.* [M22] was to apply the MCHF approach to evaluate Gd ionization

Table 27: Excitation energies and liftimes for Ni II.

Ni II Levels	Energy (cm^{-1})		Lifetimes (ns)	
	Cal.	Exp. [193]	Length	Velocity
even-parity				
$3d^9\ {}^2D_{5/2}$	0.00	0.00		
$3d^9\ {}^2D_{3/2}$	1503.40	1506.94		
$3d^84s\ {}^4F_{9/2}$	6607.36	8393.90		
$3d^84s\ {}^4F_{7/2}$	7922.01	9330.04		
$3d^84s\ {}^4F_{5/2}$	8878.02	10115.66		
$3d^84s\ {}^4F_{3/2}$	9295.52	10663.89		
$3d^84s\ {}^2F_{7/2}$	12140.31	13550.39		
$3d^84s\ {}^2F_{5/2}$	13890.34	14995.57		
$3d^84s\ {}^4P_{5/2}$	23581.05	23108.28		
$3d^84s\ {}^2D_{3/2}$	24345.30	23796.18		
$3d^84s\ {}^4P_{3/2}$	25738.96	24788.20		
$3d^84s\ {}^4P_{1/2}$	25662.15	24835.93		
$3d^84s\ {}^2D_{5/2}$	25904.63	25036.38		
$3d^84s\ {}^2P_{3/2}$	30053.83	29070.93		
$3d^84s\ {}^2P_{1/2}$	30681.53	29593.46		
$3d^84s\ {}^2G_{9/2}$	33760.76	32499.53		
$3d^84s\ {}^2G_{7/2}$	33841.97	32523.54		
$3d^84s\ {}^2S_{1/2}$	64649.62	68709.76		
odd-parity				
$3d^84p\ {}^4D_{7/2}$	49367.60	51557.85	2.62	2.37
$3d^84p\ {}^4D_{5/2}$	50833.69	52738.45	2.58	2.36
$3d^84p\ {}^4G_{9/2}$	51046.58	53365.17	2.54	3.18
$3d^84p\ {}^4G_{11/2}$	50914.90	53496.49	2.30	2.96
$3d^84p\ {}^4D_{3/2}$	50876.20	53634.62	2.63	2.39
$3d^84p\ {}^4D_{1/2}$	52326.12	54176.26	2.63	2.41
$3d^84p\ {}^4G_{7/2}$	52262.47	54262.63	2.41	2.97
$3d^84p\ {}^4F_{9/2}$	52308.56	54557.05	2.35	2.61
$3d^84p\ {}^4G_{5/2}$	52929.67	55018.71	2.39	3.04
$3d^84p\ {}^2G_{9/2}$	53438.86	55299.65	2.52	4.01
$3d^84p\ {}^4F_{7/2}$	53441.05	55417.84	2.28	2.52
$3d^84p\ {}^4F_{5/2}$	54296.04	56075.26	2.29	2.46
$3d^84p\ {}^2G_{7/2}$	54384.79	56371.41	2.84	3.28

Table 27: (continued).

Ni II Levels	Energy (cm^{-1})		Lifetimes (ns)	
	Cal.	Exp. [193]	Length	Velocity
$3d^8 4p\ ^4F_{3/2}$	54523.06	56424.49	2.32	2.52
$3d^8 4p\ ^2F_{7/2}$	55166.12	57080.55	1.12	1.20
$3d^8 4p\ ^2D_{5/2}$	55440.46	57420.16	1.83	1.57
$3d^8 4p\ ^2F_{5/2}$	56610.26	58493.21	2.10	1.93
$3d^8 4p\ ^2D_{3/2}$	56970.20	58705.95	1.80	1.25
$3d^8 4p\ ^4P_{5/2}$	66418.58	66571.34	2.40	2.40
$3d^8 4p\ ^4P_{3/2}$	66512.96	66579.71	2.54	2.51
$3d^8 4p\ ^4P_{1/2}$	67092.37	67031.02	2.68	2.73
$3d^8 4p\ ^2F_{5/2}$	67480.84	67694.64	2.38	2.69
$3d^8 4p\ ^2F_{7/2}$	67853.95	68131.21	2.26	2.63
$3d^8 4p\ ^2D_{3/2}$	68163.41	68154.31	2.12	2.05
$3d^8 4p\ ^2P_{1/2}$	68382.88	68281.62	2.69	2.64
$3d^8 4p\ ^2D_{5/2}$	68848.17	68735.98	2.08	2.03
$3d^8 4p\ ^2P_{3/2}$	69034.72	68965.65	2.50	2.46
$3d^8 4p\ ^4D_{5/2}$	70992.44	70635.46	2.23	2.56
$3d^8 4p\ ^4D_{3/2}$	71075.84	70706.77	2.26	2.67
$3d^8 4p\ ^4D_{1/2}$	70891.95	70748.70	2.27	2.67
$3d^8 4p\ ^4D_{7/2}$	71067.06	70778.12	2.18	2.55
$3d^8 4p\ ^2D_{5/2}$	72085.42	71770.83	2.41	2.59
$3d^8 4p\ ^2D_{3/2}$	72577.04	72375.42	2.06	2.12
$3d^8 4p\ ^2P_{3/2}$	73015.99	72985.65	1.26	1.25
$3d^8 4p\ ^2P_{1/2}$	74181.40	73903.25	1.27	1.25
$3d^8 4p\ ^2S_{1/2}$	74820.07	74283.33	2.09	2.14
$3d^8 4p\ ^4S_{3/2}$	74921.03	74300.93	1.91	2.12
$3d^8 4p\ ^2H_{9/2}$	75783.57	75149.48	2.66	3.59
$3d^8 4p\ ^2H_{11/2}$	76172.04	75721.68	2.60	3.40
$3d^8 4p\ ^2F_{7/2}$	76648.30	75917.63	1.69	1.48
$3d^8 4p\ ^2F_{5/2}$	77104.81	76402.03	1.63	1.45
$3d^8 4p\ ^2G_{7/2}$	80796.37	79823.03	0.64	0.51
$3d^8 4p\ ^2G_{9/2}$	80901.72	79923.88	2.12	2.36
$3d^7 4s4p\ ^6F_{3/2}$	109084.45	88582.01		
$3d^7 4s4p\ ^6F_{1/2}$	108456.76	88881.59		

energy. The methodology (see Subsection 2.1) and developments (see Subsection 3.3) implemented in the ATSP_MCHF code [14, 113] allow to study the configurations with open f–shells without any restrictions.

4.7.1 Restricted active space construction

In a MCHF approach, the wave function is expressed as a liner combination of configuration state functions which are antisymmetrized products of one–electron spin–orbitals. A set of orbitals, or active set (AS), determines the set of all possible CSFs or the complete active space (CAS) for a multiconfiguration Hartree–Fock (MCHF) calculations. The size of the latter grows rapidly with the number of electrons and also the size of the active set. Most MCHF expansions are therefore limited to a restricted active space (RAS).

Model I. It follows already from the single configuration Hartree–Fock calculation that $4f$ function (mean distance $< r >$ is 0.78897 a.u.) is closer to the nucleus than $5s$, $5p$, $5d$, $6s$ (mean distances $< r > =$ 1.45141, 1.61997, 2.46260 and 4.57121 a.u. respectively). Therefore it is quite reasonable to assume that ionization energy from $4f^7 5d^1 6s^2\ {}^9D$ to $4f^7 5d^1 6s^1\ {}^{10}D$ can be evaluated by using the wave functions of

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^7 \equiv [Xe]4f^7$$

obtained solving the single configuration Hartree–Fock equations. When solving the MCHF equations, these shells are frozen and only the remaining shells from the active set are allowed to vary. In other terms it is assumed that both the Gd atom and Gd$^+$ ion in the ground state have the same core $[Xe]4f^7\ {}^8_7S$ and that correlation effects *within* the core compensate each other between the neutral atom and the ion.

In order to check this assumption, two sets of RAS where chosen for neutral Gd and singly ionized Gd$^+$. In the first expansion the single and double excitations $\{4f, 5d, 6s\}$ to the active set $\{5f, 5g, 6p, 6d\}$ were chosen (see column I_a from Table 28). For $[Xe]4f^7 5d^1 6s^2$ RAS expansion contains 2045 configurations and for $[Xe]4f^7 5d^1 6s^1$, the RAS function contains 305 configurations. In the second expansion (see column I_b from Table 28), SD from $\{4f, 5d, 6s\}$ to the active set $\{5f, 5g, 6p, 6d, 6f, 6g, 6h, 7s, 7p, 7d\}$ were included. The number of CSFs becomes 10074 and 1445 for Gd and Gd$^+$ respectively. Our MCHF results

Table 28: Comparison of ionization energies (IE) in different approaches in eV. *NCSF is the number of configuration state functions.*

	I_a	I_b	II_a	II_b	HF	CI [194]	Expt. [195, 196]
NCSF (^9D)	2045	10074	75	321			
NCSF (^{10}D)	305	1445	6	24			
IE	5.08	5.21	5.50	5.57	4.525	5.249	6.150

are close to the large scale non–relativistic configuration–interaction (CI) calculations performed by Sekiya *et al.* [194].

Model II. Let us assume as above that both the Gd atom and the Gd$^+$ ion have in the ground state the same core $[Xe]4f^7\ {}^8_7S$. As above, excitations from $\{4f, 5d, 6s\}$ are considered but only configurations of the form

$$[Xe]4f^N\ {}^8_7S\ nln'l' \qquad (N = 7, 6)$$

are kept in the RAS expansions.

The results of calculations are presented in Table 28, columns II_a ir II_b. In approach II_a, the RAS expansions were obtained taking single and doubles excitations from $\{4f, 5d, 6s\}$ to the active set $\{5f, 5g, 6p, 6d\}$, producing 75 and 6 CSFs respectively. In approach II_b, SD excitations from $\{4f, 5d, 6s\}$ to the active set $\{5f, 5g, 6p, 6d, 6f, 6g, 6h, 7s, 7p, 7d\}$ were considered with 321 and 24 configurations for Gd and Gd$^+$ respectively.

As we can see, Model II leads to IE values which are closer to experiment than the values resulting from Model I or from the CI non–relativistic calculations of Sekiya *et al.* [194]. We conclude that Model II is more appropriate for the calculation of accurate Gd ionization potentials and that RAS must be constructed on that basis. The size of RAS expansions has been reduced substancially. This gain factor is fairly important because a much larger number of shells can be included for building the CSFs expansions.

Table 29: Comparison of non–relativistic ionization energies in different approaches, in eV.

Cases	NCSF (^9D)	NCSF (^{10}D)	$E(\,^9D)$ a.u.	$E(\,^{10}D)$ a.u.	IP eV
Non-relat. MCHF (S, D)					
I_b	10 074	1445	-10820.8459	-10820.6545	5.208
Non-relat. MCHF (S, D)					
II_a	75	6	-10820.7003	-10820.4983	5.496
II_b	321	24	-10820.7042	-10820.4996	5.568
II_c	804	58	-10820.7046	-10820.4997	5.576
Non-relat. MCHF (S, D, T)					
III_a	125	6	-10820.7010	-10820.4983	5.515
III_b	974	24	-10820.7052	-10820.4996	5.596
III_c	3806	58	-10820.7056	-10820.4997	5.604
Non-relat. HF calculation			-10820.6612	-10820.4949	4.525
Non-relat. CI (see Sekiya *et al.* [194])			-10820.8548		5.249

4.7.2 $6s$ ionization energy

Calculations are performed in the framework of Model II. Table 29 presents IE using non–relativistic MCHF approach. The RAS rules for I$_a$, II$_a$, II$_b$ were discussed above. For II$_c$ the RAS expansion was constructed as for II$_a$ and II$_b$, but considering singles and doubles exitations from $\{4f, 5d, 6s\}$ to a larger set

$$\{5f, 5g, 6p, 6d, 6f, 6g, 6h, 7s, 7p, 7d, 7f, 7g, 7h, 7i, 8s, 8p, 8d\}\ .$$

For III$_a$, III$_b$ and III$_c$ the RAS wave functions were formed as for II$_a$, II$_b$ and II$_c$ but also including the triple excitations. In this way, the RAS expansions for the ground state of the Gd atom contain up to 125, 974 and 3806 configurations for the a, b, c active sets. For the ground state of singly ionized Gd$^+$, the number of configurations remained the same.

As already mentioned, the I$_b$ results are fairly close to the non–relativistic CI calculations of Sekiya *et al.* [194]. One can expect that with the increase of the active space, the result will approach the non–relativistic CI data. However, using RAS expansions built on the basis of Model II, the simplest case (II$_a$) gives results which are much more

Table 30: Comparison of ionization energies in different approaches with relativistic corrections, in eV.

Cases	NCSF(^9D)	NCSF(^{10}D)	E(^9D) a.u.	E(^{10}D) a.u.	IP eV
Relativistic MCHF (S, D)					
I_b	10 074	1445	-11221.68661	-11221.49031	5.341
Relativistic MCHF (S, D)					
II_a	75	6	-11221.52628	-11221.31761	5.678
II_b	321	24	-11221.53826	-11221.32587	5.780
II_c	804	58	-11221.54190	-11221.32853	5.806
Relativistic MCHF (S, D, T)					
III_a	125	6	-11221.52696	-11221.31761	5.697
III_b	974	24	-11221.53932	-11221.32587	5.808
III_c	3806	58	-11221.54305	-11221.32853	5.837
HF with relativistic correction (see Sekiya *et al.* [194])					4.89
Relativistic HF (see [197, 198])					
			-11274.2171	-11274.0259	5.204
CI with Davidson Q correction (see Sekiya *et al.* [194])					
			-10820.8662		5.468
Estimate (see Sekiya *et al.* [194])					5.84
Experiment (see [195, 196])					6.150

accurate than those of Sekiya *et al.* [194], using CI with Davidson Q correction (CI$_{+Q}$) for taking the quadrupols into account (see Table 30). The effect of correlation on *Gd* ionization energy is much more important than it was thought before.

Our final results are presented in Table 30. They are obtained using MCHF method including the relativistic shift corrections and the various RAS expansions decribed above. They are compared with the relativistic HF (see [197, 198]), with the results of Sekiya *et al.* [194] and experimental data [195, 196]. As expected, the best agreement with observation is achieved using Model III$_c$. Our approach gives the most accurate results, compared to CI with Davidson Q correction method used in [197, 198].

Our results are in excellent agreement with the estimated results of Sekiya *et al.* [194] which have been obtained by adding the extra relativistic corrections, estimated from both non–relativistic and relativistic HF calculations, to the CI$_{+Q}$ values.

* * *

So, the software based on improvements presented in habilitation work allows us to efficiently account for correlation efects practically for any atom or ion of periodical table, atoms with open f^N shell included in both non–relativistic and relativistic approximations.

5 CONCLUSIONS

The approach to matrix element evaluation, presented in the habilitation work, is based on the combination of the angular momentum theory as described in Jucys and Bandzaitis [51], on the concept of irreducible tensorial sets (Judd [37], Rudzikas and Kaniauskas [39]), on a generalized graphical approach (Gaigalas *et al.* [52]), on the second quantization in coupled tensorial form (Rudzikas and Kaniauskas [39]), on the quasispin approach (Rudzikas [4]), and on the use of reduced coefficients of fractional parentage (Rudzikas [4], Rudzikas [101], Judd [37]). All this, in its entity, introduces a number of new features, in comparison with traditional approaches. Based on the development of the above–mentioned methods (Section 2) in the habilitation work there is a software created (see Section 3) for theoretical studies of many–electron atoms and ions. These are three independent programs (`Racah III`, `ANCO` and `SAI`). The calculations performed in the work demonstrate the effectiveness of the methods and programs. The following main conclusions may be drawn from the results of the habilitation work:

1. A number of theoretical methods is known in atomic physics that facilitate a lot the treatment of spin–angular parts of matrix elements, among them the theory of angular momentum, its graphical representation, the quasispin, the second quantization in its coupled tensorial form. But while treating the matrix elements of physical operators in general including ones, non–diagonal with respect to configurations, the methods mentioned above are usually applied only partly or inefficiently.

   An idea of unifying all these methods in order to optimize the way to treat the general form of matrix elements of physical operators in atomic spectroscopy is presented and carried out in this work. It allows us to investigate efficiently even the most complex cases of atoms and ions, in the both non–relativistic and relaivistic approaches.

2. In the methodology described, the application of Wick's theorem for the products of second quantization operators from Table 1 and Table 8, where they have the values of quantum numbers already defined, is proposed. This allows one to obtain

immediately the optimal tensorial expressions for any operator, using the methodology of second quantization in coupled tensorial form. Then, in treating the matrix elements of physical operators, the advantages of a new modification of the Racah algebra are exploited to their full extent.

3. The general tensorial expressions of a two–particle operator (see (7) and (74)), presented in this work, allow one to exploit all the advantages of tensorial algebra. 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, which matrix elements are equal to zero without performing further explicit calculations. That is determined from the submatrix elements $T\left(n_i\lambda_i, n_j\lambda_j, n_i'\lambda_i', n_j'\lambda_j', \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma\right)$ (see Subsection 2.3.1).

4. The tensorial form of any operator presented as products of tensors $a^{(q\lambda)}$, $W^{(k_qk_\lambda)}$, $\left[a^{(q\lambda)} \times W^{(k_qk_\lambda)}\right]^{(K_qK_\lambda)}$, $\left[W^{(k_qk_\lambda)} \times a^{(q\lambda)}\right]^{(K_qK_\lambda)}$, $\left[W^{(k_qk_\lambda)} \times W^{(k_q'k_\lambda')}\right]^{(K_qK_\lambda)}$, ($\lambda = ls$ for LS–coupling and $\lambda = j$ for jj–coupling) allows one to exploit all the advantages of a new version of Racah algebra based on quasispin formalism. So, the application of the Wigner–Eckart theorem in quasispin space for (7) and (74) provides an opportunity to use the tables of reduced coefficients of fractional parentage and tables of the other standard quantities (Subsections 2.3.3 and 2.4), 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 $U^{(k)}$, $V^{(k1)}$ (for LS–coupling) or $T^{(k)}$ (for jj–coupling) and the tables of coefficients of fractional parentage. These tables cover all the electronic configurations needed in practice. This undoubtedly makes the inclusion of shells of equivalent f–electrons (for LS–coupling) or $j = 9/2$ (for jj–coupling) with arbitrary occupation numbers considerably easier, and the process of selecting the standard quantities from the tables becomes simpler.

5. The formulas (7) and (74) are suitable to calculate any possible cases of matrix elements, non–diagonal with respect to configurations and acting upon the quantum numbers of up to four different shells included. Tensorial parts of these two–particle

operators are expressed in terms of five types (8)–(12) for LS–coupling and (110)–(114) for jj–coupling of tensorial products of second quantization operators acting in quasispin space. Distribution of shells, upon which the second quantization operators are acting, that appear in the submatrix elements of any two–particle operator when the wave functions have an arbitrary number of open shells is presented in Table 1 for LS–coupling and Table 8 for jj–coupling. All this leads to the most general and efficient tensorial expressions of an arbitrary two–particle operator.

6. The new modification of the diagrammatic technique presented in this work allows us to find graphically in an efficient way the irreducible tensorial expressions for general two–particle operator in all cases of shell's distributions 1–42 from Table 1 and Table 8.

7. The simplifications of some terms of the Breit–Pauli Hamiltonian written in the general irreducible tensorial form and suitable for evaluation of the both diagonal and non–diagonal, with respect to configurations, matrix elements in the case of arbitrary number of open shells (namely, spin–other–orbit (see, e.g., formulas (52), (56) and (57)) and orbit–orbit ((69) and (70))) simplifies their calculation and, thus, increases the efficiency of the methodology and software presented in this work.

8. The tensorial forms of a two–particle operator (see (7) and (74)), allow one to obtain simple expressions for the recoupling matrices (Subsection 2.3.2 e.g., formulas (75), (79), (80), (83), (85), (87), (88) and (94)). Hence, the computer code based on this approach would use immediately the analytical formulas for recoupling matrices $R\left(\lambda_i, \lambda_j, \lambda_i^\prime, \lambda_j^\prime, \Lambda^{bra}, \Lambda^{ket}, \Gamma\right)$. This feature also saves computing time, because i) complex calculations leading finally to simple analytical expressions (Bar–Shalom and Klapisch [28]) 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 of the submatrix elements $T\left(n_i\lambda_i, n_j\lambda_j, n_i^\prime\lambda_i^\prime, n_j^\prime\lambda_j^\prime, \Lambda^{bra}, \Lambda^{ket}, \Xi, \Gamma\right)$, but also for the rest of the shells and resulting terms.

9. In this approach both diagonal and non–diagonal, with respect to configurations, matrix elements are considered in a uniform way, and are expressed in terms of the same quantities, namely, reduced coefficients of fractional parentage or reduced submatrix elements of standard tensors, which are independent of the number of electrons in a shell. The difference is only in the values of the projections of the quasispin momenta of separate shells. The complete numerical tables of these quantities allow practical studies of any atom or ion of periodical table using the both LS– or jj–coupling.

10. The `Racah III` (see Section 3.1) program facilitates the use of standard quantities in the evaluation of many–electron matrix elements in atomic structure theory. It is based on symbolic programming. The program `Racah III` developed in this work is useful for evaluating the expressions from the theory of angular momentum and helpful for such (complex) expressions for which the known algebraic methods start to become tedious and prone to making errors. All basic entities are now easily accessible or can be modified within a few additional lines of code. In the past, such developments were often hampered by the low flexibility in using the reduced coefficients of fractional parentage and reduced matrix elements.

11. The program `ANCO` (see Section 3.2) is designed for large scale atomic structure calculations and its computational cost is less than that of the corresponding angular modules of `GRASP92` [16]. From the results presented in Table 10 we conclude that the new program though not much faster in simple cases, works much better in more complicated cases. The fact that `ANCO` calculates approximately twice the number of spin–angular coefficients as `GRASP92` reduces the effective cost per coefficient by a further factor of two. Therefore, the computer programs based on the approach presented in the habilitation work allow one to use the new program organization for large scale calculation: spin–angular coefficients are calculated when they are needed without using hard disk; therefore the calculation with this program is much faster.

12. The library `SAI` (see Section 3.3) supports large scale computations of open–shell

atoms using multiconfiguration Hartree–Fock or configuration interaction approaches and may be useful for developing codes for calculating the spin–angular parts of effective operators from many–body perturbation theory and orthogonal operators or for evaluating the relativistic Hamiltonian in LS–coupling as well as for various versions of semi–empirical methods.

13. Timing comparison of old and new codes indicates that for complex electronic configurations new programs are much faster, leading to speed–up of 3–8 times (see Table 10) or even 5–12 times (see Table 11).

    Beyond further developments in atomic structure theory, programs presented may influence also the research work in neighbouring fields like nuclear structure and the scattering of particles and light in composite systems. In these fields, quantitave investigations are often based on very similar entities which could be incorporated as well in the framework of the RACAH III package.

14. The methods developed and software based on the improvements presented in the habilitation work allows us to efficiently account for correlation effects practically for any atom or ion of periodical table, atoms with open f^N shell included in both non–relativistic and relativistic approximations.

15. Indeed, *ab initio* calculations performed indicate that the methods developed as well as the programs written enable us to get energies, wavelengths of electronic transitions, oscillator strengths, transition probabilities, lifetimes of excited levels, electron affinities of negative ions, isotope shifts, hyperfine structure as well as the other atomic properties of high accuracy in different approximations and using computer equipment of different capacity and type.

    - Transition rate, computed using MCHF for the $2s^2\ {}^1S_0 - 2s3p\ {}^3P_1^o$ intercombination line, leads to the value of 10.27 ± 0.20 s^{-1} for B II and 103.0 ± 0.4s^{-1} for C III. The latter is in excellent agreement with the value of 102.94 ± 0.14 s^{-1} obtained by Doerfert *et al.* [132] from an extremely accurate storage ring experiment.

- The results from systematic MCHF studies of the $2s^2\ ^1S_0 - 2s3p\ ^3P_1^o$ intercombination line in the Be–like sequence in the rage of $Z = 4 - 10$, reported for valence and core–valence models of correlation, indicate that, the inclusion of core–valence correlation is essential for obtaining good agreement for the fine structure splitting. The most accurate transition rates are in good agreement with the rates predicted from a semi–empirical analysis of experimental data.
- Systematic MCHF procedures, applied to the study of the electron affinity of boron, for a valence correlation calculation give an electron affinity of 273.2(2) meV, which is reduced by 1.1 meV by a relativistic correction. Core polarization and core rearrangement were found to increase the electron affinity to 279.5(20) meV. The latter agrees well with the experimental value of 277(10) meV. An electron affinity of the boron relative to the $2s2p^2\ ^4P$ state is predicted (1.072 eV).
- A complete tabulation of wavelengths and transition probabilities is presented for transitions between the $3d^9 - 3d^84p$ and the $3d^84s - 3d^84p$ configurations of Ni II. For these configurations with an open d shell, we applied extensive MCDF wave functions to compute excitation energies, transition probabilities, and lifetimes. Our *ab initio* data are compared with available measurements and other calculations, where the overall agreement is seen to be satisfactory. Experimental data are still very scarce for these two transition arrays. Therefore, the present data set not only supports the evaluation of the currently available data base, but may also help to identify or calibrate additional (less intense and intercombination) lines in the low–lying spectrum of Ni II.
- The *ab initio* results of Gd ionization energy from $4f^75d6s^2\ ^9D$ to $4f^75d6s\ ^{10}D$ are in excellent agreement with experimental, data thus also demonstrating the efficiency of the approach and software even for very complex electronic configurations and heavy atoms.

16. The created programs were installed in the computers of different capacity in a number of countries (Vanderbilt University (Computer Science Department, USA),

Universite Libre De Bruxelles (Laboratoire de Chimie Physique Moléculaire, Belgium), Universität Kassel (Fachbereich Physik, Germany), Institute of Theoretical Physics and Astronomy (Department of the Theory of an Atom, Lithuania), Vilnius Pedagogical University (General Physics Department, Vilnius), Vilnius Technical University (Computer department, Vilnius)) and they were, are and will be successfully used to get various characteristics of high accuracy of many–electron atoms and ions. The created methods and programs fully enable us to use both the parallel and symbolic programming as well as the existing resources of supercomputers and personal computers.

Main publications by the author reviewed in the habilitation work

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Padėka

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