Analytical expressions for special cases of $LS$–$jj$ transformation matrices for a shell of equivalent electrons

G. Gaigalas†, T. Žalandauskas, Z. Rudzikas

State Institute of Theoretical Physics and Astronomy
A. Goštauto 12, Vilnius 2600, Lithuania.
† e–mail: gaigalas@itpa.lt

March 31, 2022

Abstract

Transformation matrices of the weights of the atomic wave functions in $jj$ coupling to the relevant weights of $LS$ coupling are considered for a shell of equivalent electrons. Their use allows one to preserve main part of relativistic effects but to classify the energy levels of an atom or an ion considered with the help of a set of quantum numbers of $LS$ coupling scheme. Having in mind that the numerical values of the abovementioned transformation matrix ($LS$–$jj$) may be generally obtained in a very time consuming recurrent way, the analytical expressions of these matrices for a number of special cases of electronic configurations are presented.
1 Introduction

It is impossible to predict, the spectroscopic data on which chemical element (neutral atom or its arbitrary ionization degree) will become one day urgently need. Therefore, the theoretical methods of the studies of the structure and properties of many-electron atoms and ions must be fairly accurate and universal.

When identifying and classifying the energy levels of atom or ion, one has to find and use the optimal coupling scheme of angular momenta in each open electronic shell of equivalent electrons as well as between them. The special difficulties arise in the relativistic treatment of electronic configurations when the non-relativistic shell of equivalent electrons splits into a number of subshells.

Often it is important to preserve a main part of relativistic effects, but to classify the energy levels with the help of a set of quantum numbers of $LS$ coupling. This may be achieved making use of the transformation matrices of the weights of the atomic functions in $jj$ coupling, obtained in relativistic approximation, to the relevant weights of $LS$ coupling. The efficient method, implementing such a procedure, is described in [1, 2]. A number of practical applications is discussed in [3].

Having in mind that numerical values of the transformation matrices from $jj$ to $LS$ coupling needed may be obtained generally in very time consuming recurrent way, the possibilities to find the analytical expressions of such matrices for a number of special cases of electronic configurations are discussed in this paper.

2 General consideration of the $LS$–$jj$ transformation matrices for a shell of equivalent electrons $l^N$

The relativistic analogue of the non-relativistic wave function of a shell of $l^N$ equivalent electrons ($LS$ coupling)

$$|l^N\alpha LS\rangle,$$

where $\alpha$ denotes the additional quantum numbers necessary for the one-to-one classification of the energy levels of that shell, in the $jj$ coupling splits into so-called subshells. It will look as follows:

$$|l_j^{N_1}j_2^{N_2}\nu_1\nu_2J_1J_2J\rangle,$$

where $j_1 = l - \frac{1}{2}$, $j_2 = l + \frac{1}{2}$ and $N_1 + N_2 = N$. For subshells with angular momenta $j_i = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ and $\frac{7}{2}$ (this corresponds to $s^N$, $p^N$, $d^N$ and $f^N$ shells as well as $j = l - \frac{1}{2}$ of $g^N$ shell) two quantum numbers $\nu$ and $J$ are sufficient to unambiguously classify the relevant states.

The following relationship between the weights $c_{ik}$ and $a_{jr}$ of the wave functions of two pure coupling schemes is known [1, 2]:

$$c_{jk} = \sum_r a_{jr}(\phi_k|\psi_r).$$
It may be used to transform the weights of the relativistic wave function in $jj$ coupling to the relevant weights of $LS$ coupling. However, in such a case this equality becomes not completely accurate because of the changes of the character of the wave functions and the Hamiltonian (non-relativistic and relativistic). Actually a part of the relativistic effects is lost after this transformation. Further on we shall discuss the transformation matrix ($\phi_k|\psi_r$) in Eq 3.

The $LS$–$jj$ transformation matrix $(l^N\alpha LSJ|l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2})$ connecting two wave functions of a shell of equivalent electrons, namely $|l^N\alpha LSJ\rangle$ in $LS$ coupling and $|l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle$ in $jj$ coupling is defined as follows:

$$|l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle = \sum_{\alpha LS} |l^N\alpha LSJ\rangle(l^N\alpha LSJ|l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle)$$ \hspace{1cm} (4)

and

$$|l^N\alpha LSJ\rangle = \sum_{\nu_1J_{\nu_2}J_{J2}N_1} |l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle(l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle|l^N\alpha LSJ\rangle).$$ \hspace{1cm} (5)

The phase system of the wave functions is usually chosen in such a way that the coefficients of fractional parentage (CFP) are real numbers. Then the $LS$–$jj$ transformation matrices will be real too. In the case of orthonormal wave functions the transformation matrices will also obey the following orthonormality relations:

$$\sum_{\alpha LS} (l^N\alpha LSJ|l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle)(l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle|l^N\alpha LSJ\rangle) = \delta(N_1'N_2'\nu_1'J_{\nu_2}'J_{J2}',N_1N_2\nu_1J_{\nu_2}J_{J2})$$ \hspace{1cm} (6)

and

$$\sum_{\nu_1J_{\nu_2}J_{J2}N_1} (l^N\alpha' L'S'J|l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle)(l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle|l^N\alpha LSJ\rangle) = \delta(\alpha' L'S',\alpha LS).$$ \hspace{1cm} (7)

Transformation matrices considered may be calculated using the following recurrent relation [2]:

$$|l^N\alpha LSJ|l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle = \sqrt{[L,S]/N} \sum_{\alpha'L'S'} (l^N\alpha LS|l^{N-1}(\alpha'L'S')l\rangle) \sum_{J'} \left[ \begin{array}{c} L' \ L \\ S' \ S \\ J' \ J \end{array} \right] \sum_{\nu_1J_1} \left( \begin{array}{c} J_2 \ J_1' \ J' \\ J_2 \ J_1 \ J \end{array} \right) \times \times (l_{j_1}^{N_1}j_{j_2}^{N_2}\nu_1J_{\nu_2}J_{J2}\rangle(\alpha'L'S')J_2')$$
Therefore it is usually enough to calculate using Eq. (8) only the matrix elements of partially filled shells:

\[ \begin{align*}
&+ \sqrt{N_2[j_2, J_2]} \left\{ \begin{array}{ccc}
L' & l & L \\
S' & s & S \\
J' & j_2 & J
\end{array} \right\} \sum_{\nu_j' \nu_{j_2}'} (-1)^{j_2'+J_1+J_2'+J} \left\{ \begin{array}{ccc}
J_2' & J_1 & J' \\
J & j_2 & J
\end{array} \right\} \\
&\times (j_2^{N-1} (\nu_2' J_2') j_2 || j_2^{N_2} \nu_2 J_2) (l^{N-1} \alpha' L'S' J'|| l_1^{N_1} j_2^{N_2-1} \nu_1 J_1 \nu_2' J_2' J')
\end{align*} \] (8)

starting with

\[ (l^2 L S J | l_{j_1} j_2 J) = \frac{1}{\sqrt{2}} \left( 1 + (-1)^{L+S} \right) \sqrt{[j_1, j_2, L, S]} \left\{ \begin{array}{ccc}
l & l & L \\
s & s & S \\
j_1 & j_2 & J
\end{array} \right\}, \] (9)

and

\[ (l^2 L S J | j^2 J) = \frac{1}{4} \left( 1 + (-1)^{L+S} \right) \left( 1 + (-1)^J \right) \sqrt{[L, S]} \left\{ \begin{array}{ccc}
l & l & L \\
s & s & S \\
j & j & J
\end{array} \right\}. \] (10)

Here \([a,b] = (2a+1)(2b+1)\).

The equation (8) requires the CFP in \(LS\) and \(jj\) couplings, namely \((l^N \alpha LS || l^{N-1} (\alpha' L'S') l)\) and \((j^{N-1} (\nu' J') j || j^N \nu J)\). It is efficient to use the CFP obtained from reduced coefficients of fractional parentage (RCFP) [2]. The complete tables of their numerical values (the \(f^N\) shells included) may be found in [4] [5]. This gives us natural relation between the CFP’s of partially and almost filled shells:

\[ (l^{4l+1-N} (\alpha' \nu' L'S') l || l^{4l+2-N} \alpha \nu LS) = (-1)^{S+S'+L+L'-l-\frac{1}{2}(\nu+\nu'-1)} \]
\[ \times \left( \frac{(N+1)(2L'+1)(2S'+1)}{(4l+2-N)(2L+1)(2S+1)} \right)^{\frac{1}{2}} (l^N (\alpha' \nu' L'S') l || l^{N+1} \alpha \nu LS), \] (11)

\[ (j^{2j-N} (\nu' J') j || j^{2j+1-N} \nu J) \]
\[ = (-1)^{J+J'-j+\frac{1}{2}(\nu+\nu'-1)} \left( \frac{(N+1)(2J'+1)}{(2j+1-N)(2J+1)} \right)^{\frac{1}{2}} (j^N (\nu' J') j || j^{N+1} \nu J). \] (12)

As noticed in [6] the \(LS-jj\) transformation matrices calculated using CFP’s which satisfy the conditions (11) and (12) are related by the following simple symmetry property:

\[ (l^N \alpha \nu LS J | l_1^{N_1} j_2^{N_2} \nu_1 J_1 \nu_2 J_2 J) \]
\[ = (-1)^{\nu-\nu_1-\nu_2}/2 (l^{4l+2-N} \alpha \nu LS J | l_1^{2j_1+1-N_1} j_2^{2j_2+1-N_2} \nu_1 J_1 \nu_2 J_2 J). \] (13)

Therefore it is usually enough to calculate using Eq. (8) only the matrix elements of partially filled \(l^N\) shells.
3 Special cases of transformation matrices

The explicit formulas for such matrices in the case of configurations \( l^N \) and \( l_1^{N_1} l_2^{N_2} \) (including the special case of configurations \( p^{N_1 N_2} \) and \( l_1^{N_1} p^N \)) are considered in [7]. Below let us consider the possibilities to obtain analytical expressions for such transformation matrices.

In [2] there are presented algebraic expressions for a fairly large number of particular cases of CFP. Making use of them we could find similar algebraic formulas for the transformation matrices under consideration. Let us discuss the case of \( l^3 \) as the example. Further on we will investigate the cases when in one of \( jj \) subshells there is 1 electron and in other 2 electrons (we will denote this case as \( N_1 = 1, N_2 = 2 \) or \( N_1 = 2, N_2 = 1 \)) and the case when all three electrons are in one subshell \( (N_1 = 3 \) or \( N_2 = 3 \)).

a) \( N_1 = 1, N_2 = 2 \) or \( N_1 = 2, N_2 = 1 \)

Let us assume that \( j_1 = l - \frac{1}{2} \) and \( j_2 = l + \frac{1}{2} \). Inserting the expressions for transformation matrix of a shell having two electrons, namely \([9],[10]\) and known expressions for CFP (for example, (9.14) from [2]) into (8) we get:

\[
(l^3 \alpha LS|l_j l_j l_j \nu_2 \nu_2 \nu_2 J J J) = \frac{1}{2 \sqrt{3}} (1 + (-1)^{l_2}) [j_2] \sqrt{|L, S, j_1, J_2|} \times \\
\times \sum_{\alpha' L'S'} (l^3 \alpha LS||l^2 (\alpha' L'S') l)|l', S'| (1 + (-1)^{L'+S'}) \times \\
\times \frac{1}{2} \left\{ \begin{array}{ccc} \ l & l & L' \\ \ s & s & S' \\ j_2 & j_2 & J_2 \end{array} \right\} \left\{ \begin{array}{ccc} \ l & L & L' \\ s & S & S' \\ j_1 & J & J_2 \end{array} \right\} + \sum_{J'} [J'] \left\{ \begin{array}{ccc} \ j_2 & J_2 & J' \\ \ j_1 & J & J_2 \end{array} \right\} \left\{ \begin{array}{ccc} \ l & l & L' \\ s & S & S' \\ j_2 & J & J' \end{array} \right\} \left\{ \begin{array}{ccc} \ l & L & L' \\ s & S & S' \\ j_2 & J & J' \end{array} \right\} \right) (14)

Further simplifications are not obvious. Nevertheless we found that

\[
\sum_{\alpha' L'S'} (l^3 \alpha LS||l^2 (\alpha' L'S') l) \sqrt{|L', S'| (1 + (-1)^{L'+S'})} \left\{ \begin{array}{ccc} \ l & l & L' \\ s & s & S' \\ j_2 & j_2 & J_2 \end{array} \right\} \left\{ \begin{array}{ccc} \ l & L & L' \\ s & S & S' \\ j_1 & J & J_2 \end{array} \right\} \\
= \sum_{\alpha' L'S'} (l^3 \alpha LS||l^2 (\alpha' L'S') l) \sqrt{|L', S'| (1 + (-1)^{L'+S'})} \times \sum_{J'} [J'] \left\{ \begin{array}{ccc} \ j_2 & J_2 & J' \\ \ j_1 & J & J_2 \end{array} \right\} \left\{ \begin{array}{ccc} \ l & l & L' \\ s & S & S' \\ j_2 & J & J' \end{array} \right\} \left\{ \begin{array}{ccc} \ l & L & L' \\ s & S & S' \\ j_2 & J & J' \end{array} \right\} \right) (15)

So, using (15) we get the following simplified expression of matrix elements for the case \( N_1 = 1, N_2 = 2 \):
where parameter $J$ found the property

Inserting (18) into (17) we arrive at the expressions similar to (14). Then analogically to (15) we

$sufficient to classify the state in

One can obtain the relevant expression of transformation matrix elements for the case $N_1 = 2$, $N_2 = 1$ from (16) transposing $j_1 \leftrightarrow j_2$ and $J_2 \rightarrow J_1$. The simplified expression (16) was used to check numerically the general formulae (8) for all cases of $l^3, l=1,2$ and 3.

b) $N_1 = 3, N_2 = 0$ or $N_1 = 0, N_2 = 3$

Let us now consider the case when all three electrons are in one $jj$ subshell, namely $j^3$. Inserting the expressions of the transformation matrices for a shell of two equivalent electrons into (8) we obtain:

\[
(l^3 \alpha LS|\nu_{l}^{j} J) = \frac{1}{4} \sqrt{[L, S][j]} \sum_{\alpha' L' S'} (l^3 \alpha LS||l^2(\alpha' L'S')l) \sqrt{[L', S'](1 + (-1)^{L'+S'}) \times \sum_{J'} (j^2(J'), j||j^3\nu J)}.
\]

For $(j^2(J'), j||j^3\nu J)$ we use analytical expression

\[
(j^2(J'), j||j^3\nu J) = \frac{\delta(j', J_0)\delta(jjJ_0)(1 + (-1)^{J_0})}{\sqrt{1 + 2 [J_0]}} \frac{(1 + (-1)^{j-J})}{2\sqrt{3}} \sqrt{[J_0, J'] \{ j, j, J' \}}.
\]

where parameter $J_0$ should be chosen to satisfy two conditions: triangular condition $\delta(jjJ_0)$ should be satisfied and $J_0$ should be even. The expression (18) is valid when the quantum number $J$ is sufficient to classify the state in $jj$ coupling.

Inserting (18) into (17) we arrive at the expressions similar to (14). Then analogically to (15) we found the property

\[
\sum_{\alpha' L' S'} (l^3 \alpha LS||l^2(\alpha' L'S')l) \sqrt{[L', S'](1 + (-1)^{L'+S'}) \times \sum_{J'} (j^2(J'), j||j^3\nu J)}.
\]
\[= \sum_{\alpha' L' S'} (l^3 \alpha LS||l^2 (\alpha' L'S')l) \sqrt{|L, S'|} (1 + (-1)^{L'+S'}) \]
\[\times \sum_{J'} [J'] \left\{ \begin{array}{ccc} j & j & J' \\ J & j & J_0 \end{array} \right\} \left\{ \begin{array}{ccc} l & l & L' \\ s & s & S' \end{array} \right\} \left\{ \begin{array}{ccc} l & L & L' \\ s & S & S' \end{array} \right\} \left\{ \begin{array}{ccc} j & j & J' \\ j & J & J_0 \end{array} \right\}. \] (19)

Using (19) we find the following simplified expressions for the case of \( N_i = 3 \):

\[ (l^3 \alpha LSJ|j^3_{\nu J}) = \frac{\sqrt{3}}{2} \sqrt{|L, S, J_0|} [j]^j \left( \frac{(-1)^{j-J}}{1 + 2 [J_0]} \right) \]
\[\times \sum_{\alpha' L' S'} (l^3 \alpha LS||l^2 (\alpha' L'S')l) \sqrt{|L', S'|} (1 + (-1)^{L'+S'}) \left\{ \begin{array}{ccc} l & l & L' \\ s & s & S' \end{array} \right\} \left\{ \begin{array}{ccc} l & L & L' \\ s & S & S' \end{array} \right\} \left\{ \begin{array}{ccc} j & j & J_0 \\ j & J & J_0 \end{array} \right\}. \] (20)

Formulas like Eq. (16) and (20) are simpler for calculations compared to general recurrent relation (8). We can even more simplify such formulas with the use of known algebraic expressions for CFP’s in \( LS \) and \( jj \) couplings. Such expressions and the relevant computer code may be useful as an independent check of more general programs for \( LS-jj \) matrix elements calculation. Similar expressions may be found for a number of other special cases of electronic configurations, but they are rather complicated and, therefore, of a little use.

4 Conclusion

Numerical values of the transformation matrices from \( jj \) to \( LS \) coupling scheme in general may be found making use of the recurrent formulae of the kind (8). The relevant calculation procedure is very time consuming, therefore the alternative ways, even if they are suitable only for some particular cases, are of interest.

The use of analytical expressions for the coefficients of fractional parentage, both in \( LS \) and \( jj \) couplings, allowed us to obtain the comparatively simple algebraic formulas for the abovementioned transformation matrices in the case of particular electronic configurations.

References

[1] A. A. Nikitin and Z. B. Rudzikas, Foundations of the Theory of the Spectra of Atoms and Ions (Nauka, Moscow, 1983, in Russian).

[2] Z. B. Rudzikas, Theoretical Atomic Spectroscopy (Cambridge University Press, Cambridge, 1997).
[3] Z. B. Rudzikas and J. V. Čiplys, Physica Scripta, V. 16, p. 217 (1969).

[4] G. Gaigalas, Z. Rudzikas and C. Froese Fischer, ”Reduced coefficients (subcoefficients) of fractional parentage for p-, d- and f-shells,“, At. Data Nucl. Data Tables, V. 70, p. 1-39 (1998).

[5] G. Gaigalas, S. Fritzsche and Z. Rudzikas, ”Reduced coefficients of fractional parentage and matrix elements of the tensor $W_{k_i k_j}$ in jj coupling” At. Data Nucl. Data Tables, V. 76, p. 235-269 (2000).

[6] K. G. Dyall and I. P. Grant, ”Phase conventions, quasi-spin and the jj–LS transformation coefficients” J. Phys. B., V. 15, p. L371-L373 (1982).

[7] J. S. Kičkin, A. A. Slepcov, V. J. Sivcev and Z. B. Rudzikas, ”Correlation between wave functions of many-electron atoms in various coupling schemes” Lithuanian J. Phys., V. 16, p. 217-229 (1976) [in Russian].