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ORIGINAL PAPER

Asymptotic behavior of Clebsch–Gordan coefficients

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Abstract
In this study, the Clebsch–Gordan coefficients are expressed using the generalized hypergeometric functions of unit argument and binomial coefficients, and their behavior as a function of quantum numbers is examined. The Clebsch–Gordan coefficients are also numerically computed for integer and non-integer quantum numbers. Subsequently, the convergence between the Clebsch–Gordan and asymptotic Clebsch–Gordan coefficients is investigated based on the orbital angular momentum quantum numbers.

Keywords Clebsch–Gordan coefficients · Vector addition coefficients · Wigner coefficients · Classical limits of the Clebsch–Gordan coefficients · Generalized hypergeometric functions

1 Introduction

The Clebsch–Gordan (CG) coefficients, also referred to as vector addition coefficients, and the Wigner coefficients describe how individual angular momentum states may be coupled to yield the total angular momentum of atomic systems [1–4]. CG coefficients play a crucial role in applications for quantum physics and chemistry to study the physical and chemical properties of atoms, molecules, solids, and other fields of physics.

Approximate methods are used to understand multi-electron atoms or molecules' physical and chemical properties. Using an approximate method, basis sets such as Slater-type, Gaussian, and Bessel-type orbitals are selected. The common feature of these basis sets is that their angular parts consist of spherical harmonics. A large number of molecular integrals must be calculated to find the physical property of an atom or molecule numerically. The angle-dependent part of molecular integrals involves the product of two or more spherical harmonics. Such integrals are called

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angular momentum coupling coefficients. It is well known that all angular momentum coupling coefficients can be evaluated as the sums of products of CG coefficients. Accordingly, it is important to calculate CG coefficients accurately in a very short CPU time.

CG coefficients are expressed as factorial functions [5–10] and binomial coefficients [11–14] as finite sums. The fact that the sums remain finite depends on the condition that the factorial functions in the denominator are negative integers. As long as this condition is satisfied, these formulae are suitable for numerically calculating CG coefficients. By employing the sum expressions that involve gamma functions provided by Tarter in Ref. [15], CG coefficients, written in terms of factorial parts, can be further represented using the generalized hypergeometric functions of unit argument [16]. The usual expressions of CG coefficients, as presented in Refs. [5–10], are given in terms of the generalized hypergeometric functions of unit argument by Eqs. (21) to (26) on pp. 240 and 241 of Ref. [17].

Several authors calculate CG coefficients using recursion formulae to avoid the risk of numerical instabilities. The recursion relationship is guaranteed stable for arbitrarily large sets of quantum numbers. Ritchie presented simple two-term and three-term recursion relationships for rapidly and accurately calculating CG coefficients [18, 19]. Ritchie proposed expressing CG coefficients as a sum of three binomial products, called an unnormalized CG coefficient, with the remaining gamma function product term treated as a normalization term. This factorization of CG coefficients allows the unnormalized CG coefficients to be calculated precisely in integer arithmetic [20, 21]. Recently, Xu introduced an improved recursive computation method for CG coefficients based on separating the recurrence process into sign recursion and exponent recursion [22].

The behavior of CG coefficients for the highest values of the orbital angular momenta, called "classical limits", is of interest in connection with specific applications and from the mathematical point of view. The expressions for the asymptotic CG (ACG) coefficients were obtained in Refs. [23–27] when the quantum numbers satisfy the condition $L, l_1 \gg l_2$. Kintish et al. have given how the asymptotic behaviors of selected *3j* and *9j* symbol coefficients and their unitary counterparts are obtained [28]. Dowker was related to the permutation symmetry of *3j* symbols, yielding an extension of the classical limit established by Edmonds [29].

CG coefficients given by Racah [6] or Fock [7], Wigner [8], and Shimpuku [11] are defined as functions of the factorial functions. CG coefficients contain finite sums in all these expressions where the quantum numbers are integers. The lower and upper limits of the summation index are determined according to the negative values of the factorial terms in the denominator. Since the factorials of negative integers approach infinity, these expressions give very accurate results when quantum numbers are integers. However, when the quantum numbers are not integers, the expressions in the denominator will not be infinite. In this case, it is necessary to determine where to cut the expressions in the summation index for the sums to give a numerical value. These formulae for CG coefficients in Refs. [5–10] are given by Eqs. (21–26) in terms of the generalized hypergeometric functions of unit argument in Ref. [17]. Equations other than Eqs. (25, 26) in Ref. [17] do not give correct results except for some quantum states. The problem with these formulae arises from the fact that in some allowed quantum states, factorials of negative integers appear in the coefficients, or the generalized hypergeometric functions of the unit argument do not converge.

This study uses symmetry relations of the generalized hypergeometric functions of unit argument and Weierstrass infinite-product definition for negative factorials to overcome these problems [30]. All equations from (21) to (26) in Ref. [17] have been rewritten in terms of binomial coefficients using the newly obtained relations. Despite their different mathematical structures, all these equations yield the same numerical results for very high quantum numbers (on the order of millions). The fact that the relations we rewrote for CG coefficients have simple mathematical structures enables these formulas to be programmed easily. The most important advantage of these equations we have written is that the CPU time is very short, which is essential in calculating molecular integrals. The behavior of CG coefficients depending on the selected quantum sets was examined, and two- and three-dimensional graphs were plotted. Special values of CG coefficients were determined using the equations provided by the generalized hypergeometric functions of unit argument for the special values of the angular momentum quantum numbers l_1, l_2, L and the momentum projections (m_1, m_2, M). The values of the orbital angular momentum quantum numbers, which make CG coefficients zero when triangular conditions and selection rules are not satisfied, were obtained by analyzing the drawn graphs. Numerical results for both integer and non-integer quantum numbers were obtained using the formulae rewritten for CG coefficients in Sect. 2, and these values were compared with existing literature. The study also investigated whether CG coefficients from the proposed relations satisfy orthogonality and symmetry relations. In Sect. 3, new mathematical expressions, orthogonality relation, and special values were derived for ACG coefficients. The compatibility between ACG and CG coefficients was examined by altering the quantum sets.

All computer programs are written in Mathematica programming language. Programs run using Intel(R) Core (TM) i7-6500U CPU @ 2.50 GHz computer.

2 Clebsch–Gordan coefficients

The expressions of CG coefficients on pp. 240 and 241 in Ref. [17] may be represented as the following form

$$C^{LM}_{l_1m_1,l_2m_2} = N^{LM}_{l_1m_1,l_2m_2}\,{}_3F_2\left[\begin{array}{c} a,b,c \\ d,e \end{array}\middle|1\right] \tag{1}$$

where $N^{LM}_{l_1m_1,l_2m_2}$ is normalization coefficient and ${}_3F_2\left[\begin{array}{c} a,b,c \\ d,e \end{array}\middle|1\right]$ is the generalized hypergeometric function of unit argument. According to the Eqs. (21–26) in Ref. [17], the arguments of the normalization coefficients and the generalized hypergeometric functions of the unit argument in this definition change.

The phase of CG coefficients may be chosen in different ways. The phase convention proposed in Ref. [4] is universally accepted. Under such a phase definition, CG coefficients satisfy the relations as follows [17]

$$\begin{array}{ll} C^{l_1+l_2 m_1+m_2}_{l_1 m_1, l_2 m_2} > 0 & C^{LM}_{l_1 m_1, l_2 -l_2} > 0 \\ (-1)^{l_1+l_2-L} C^{LM}_{l_1 m_1, l_2 l_2} > 0 & (-1)^{l_1-m_1} C^{LL}_{l_1 m_1, l_2 m_2} > 0 \\ (-1)^{l_2+m_2} C^{l_1-l_2 M}_{l_1 m_1, l_2 m_2} > 0 & \end{array} \tag{2}$$

These conditions and special values of CG coefficients provide the convenience of checking the accuracy of the programs written in the shortest time and efficiently.

The equations except for Eqs. (25, 26) in Ref. [17] are unsuitable for some values that quantum numbers can take in numerical calculations. During calculating the normalization coefficients or the generalized hypergeometric functions of unit argument in these equations, uncertain numerical values with defined limits arise in some allowed values of the quantum numbers. To get rid of these ambiguities, Eqs. (11, 12) in Ref. [31], symmetry relations of the generalized hypergeometric functions of unit argument [32, 33] should be used. After these operations are performed, if the factorial parts are written in binomial coefficients, CG coefficients are given by Eqs. (21–26) in Ref. [17] are rewritten as follows:

Van der Waerden [5], Racah [6]

$$\begin{aligned} C^{LM}_{l_1 m_1, l_2 m_2} = \delta_{M, m_1+m_2} \sqrt{\frac{2L+1}{l_1+l_2+L+1}} F\left(l_1+l_2-m_1-m_2, l_1+l_2-L\right) \\ \left\{ \frac{F\left(2l_1, l_1+m_1\right) F\left(2l_2, l_2+m_2\right) F\left(2l_1+2L, l_1+l_2+L\right)}{F\left(2l_2, l_1+l_2-L\right) F(2L, L+M) F\left(2l_1+2L, 2l_1\right)} \right\}^{\frac{1}{2}} \\ {}_3F_2\left[\begin{matrix} -l_1-l_2+L, -l_1+m_1, -l_1-l_2-L-1 \\ m_1+m_2-l_1-l_2, -2l_1 \end{matrix} \middle| 1 \right] \end{aligned} \tag{3}$$

Racah [6], Fock [7]

$$\begin{aligned} C^{LM}_{l_1 m_1, l_2 m_2} = \delta_{M, m_1+m_2} \sqrt{\frac{2L+1}{l_1+l_2+L+1}} F\left(l_1+L+m_2, l_2+m_2\right) F\left(l_2+L-m_1, l_1-m_1\right) \\ \left\{ \frac{F(2L, L+M) F\left(2l_1+2l_2, l_1+l_2+L\right)}{F\left(2l_1, l_1+m_1\right) F\left(2l_2, l_2+m_2\right) F\left(2L, l_1-l_2+L\right) F\left(2l_1+2l_2, 2l_1\right)} \right\}^{\frac{1}{2}} \\ {}_3F_2\left[\begin{matrix} -l_1+m_1, -l_2+m_1-M, -l_1-l_2-L-1 \\ -l_2-L+m_1, -L-M-l_1+m_1 \end{matrix} \middle| 1 \right] \end{aligned} \tag{4}$$

Wigner [8]

$$C^{LM}_{l_1m_1,l_2m_2} = \delta_{M,m_1+m_2}(-1)^{l_2-L-m_1}\sqrt{\frac{2L+1}{l_1+l_2+L+1}}\frac{1}{F(l_1+l_2+L,l_2+m_1-M)}$$
$$\left\{\frac{F(2l_2,l_2+m_2)F(2l_1,l_1+m_1)F(2L,L+M)F(2L,l_1-l_2+L)F(2l_1+2l_2,2l_1)}{F(2l_1+2l_2,l_1+l_2+L)}\right\}^{\frac{1}{2}}$$
$$ {}_3F_2\left[\begin{matrix}-L-M,-l_1-l_2-L-1,-l_1+l_2-L\\ -l_1+m_1-L-M,-2L\end{matrix}\middle|1\right] \tag{5}$$

Majumdar [9]

$$C^{LM}_{l_1m_1,l_2m_2} = \delta_{M,m_1+m_2}(-1)^{l_2+m_2}\sqrt{\frac{2L+1}{l_1+l_2+L+1}}F(l_2+L-m_1,l_1-m_1)$$
$$\left\{\frac{F(2L,L+M)F(2l_2,l_2+m_2)F(2l_1+2l_2,l_1+l_2+L)}{F(2l_1,l_1+m_1)F(2L,l_1-l_2+L)F(2l_1+2l_2,2l_1)}\right\}^{\frac{1}{2}} \tag{6}$$
$$ {}_3F_2\left[\begin{matrix}l_1-l_2-L,-l_1-l_2-L-1,-l_2-m_2\\ -2l_2,-l_2-L-m_2+M\end{matrix}\middle|1\right]$$

Bandzaitis and Yutsis [10]

$$C^{LM}_{l_1m_1,l_2m_2} = \delta_{M,m_1+m_2}(-1)^{l_2+m_2}\sqrt{\frac{2L+1}{l_1+l_2+L+1}}F(l_2+L+m_1,l_1+m_1)$$
$$\left\{\frac{F(2L,L+M)F(2l_2,l_2+m_2)F(2l_1+2L,l_1+l_2+L)}{F(2l_1,l_1+m_1)F(2l_2,l_1+l_2-L)F(2l_1+2L,2l_1)}\right\}^{\frac{1}{2}} \tag{7}$$
$$ {}_3F_2\left[\begin{matrix}l_1-l_2-L,-l_1-l_2-L-1,-L-M\\ -2L,-l_2-L-m_1\end{matrix}\middle|1\right]$$

Bandzaitis and Yutsis [10]

$$C^{LM}_{l_1m_1,l_2m_2} = \delta_{M,m_1+m_2}(-1)^{l_1-m_1}\sqrt{\frac{2L+1}{l_1+l_2+L+1}}F(l_2+L-m_1,l_1-m_1)F(l_1+l_2-M,L-M)$$
$$\left\{\frac{F(2l_2,l_2+m_2)F(2l_1+2L,l_1+l_2+L)}{F(2L,L+M)F(2l_1,l_1+m_1)F(2l_2,l_1+l_2-L)F(2l_1+2L,2l_1)}\right\}^{\frac{1}{2}}$$
$$ {}_3F_2\left[\begin{matrix}-l_1-l_2-L-1,-l_1+m_1,-L+M\\ -l_1-l_2+M,-l_2-L+m_1\end{matrix}\middle|1\right] \tag{8}$$

where $F(a,b)$ represents the binomial coefficients.

CG coefficients given by Eqs. (3–8) are mathematically equivalent and easily computed numerically. The calculated CG coefficients for some selected integer and non-integer quantum numbers are shown in Table 1. The numbers in parentheses in the 7th column of Table 1 indicate the relevant reference numbers. As seen in Table 1, Eqs. (3–8) provided in this study satisfy all symmetry relationships for CG coefficients relations given in Refs. [1–3].

Table 1 CG coefficients are tabulated for integer and non-integer quantum numbers

l_1	m_1	l_2	m_2	L	$C^{LM}_{l_1m_1,l_2m_2}$	Literature
2	2	2	− 2	0	0.447213595499957939281834733746255	[17]
5/2	3/2	5/2	− 1/2	1	− 0.478091443733757455987526871877250	[17]
3	0	2	1	1	− 0.292770021884559953806315390872030	[17]
3	1	3	− 1	0	0.377964473009227227214516536234180	[17]
3	2	5/2	− 3/2	3/2	− 0.218217890235992381266097485415619	[17]
11/2	− 5/2	9/2	9/2	5	− 0.518874521662770825598088677365213	[11]
5	2	1	1	6	0.738548945875996396405443960751458	[11]
6	4	5	− 4	8	0.371510262122030924038281785659454	[11]
11/2	− 3/2	9/2	− 7/2	10	0.437679640253302234775351466909291	[11]
6	6	7/2	5/2	19/2	0.606976978666883994176535959937783	[11]
11/2	11/2	5	3	21/2	0.462910049886275730783283388292000	[11]
15	2	20	− 3	9	− 0.207128377200859542074494317223818	[13]
25	12	35	− 17	40	− 0.102439678889182401706342466360153	[13]
40	− 2	37	1	49	− 0.125134852685479680179749481300492	[13]
60	18	52	− 15	80	0.132731595612954623084204774338178	–
60	− 18	52	15	80	0.132731595612954623084204774338178	–
52	− 15	60	18	80	0.132731595612954623084204774338178	–
60	18	80	− 3	52	0.107190433363976649435883787202672	–
80	− 3	52	− 15	60	− 0.115067866913218666640495307964221	–
80	3	60	− 18	52	0.107190433363976649435883787202672	–
52	15	80	3	60	− 0.115067866913218666640495307964221	–

The comparison of numerical results obtained in the last column with the literature and the numerical results obtained by using symmetry relations in the last 7 rows are given

Figure 1a–c show graph of CG coefficients versus l_1, l_2, and L orbital angular momentum numbers, respectively. As can be seen from Fig. 1, CG coefficients oscillate approximately periodically. In Fig. 1a–c, the amplitudes of CG coefficients are not constant. In the graphs (a) and (b) drawn for the constant L value, the amplitudes of CG coefficients decrease against increasing l_1 and l_2 values. In diagram (c), illustrated by changing the L value, the amplitude decreases and continues increasing. Figure 1d shows the three-dimensional behavior of CG coefficients versus l_1 and l_2.

The behavior of CG coefficients as functions of magnetic quantum numbers is illustrated in Fig. 2a–c for constant orbital angular momentum quantum numbers.

It is well known that CG coefficients will be zero unless triangular conditions are satisfied simultaneously. However, some CG coefficients can be "accidentally" zero even if the conditions are fulfilled. In Fig. 1, the points where CG coefficients are zero correspond to the locations where the triangular conditions are satisfied. Still, the generalized hypergeometric functions of the unit argument evaluate to zero. For $15 \leq l_1 \leq 60$, $l_2 = 45$, and $L = 60$, the approximate values of the first 15 nodes, read from the drawn graph using Mathematica's "Get Coordinates" command, are given in Table 2.

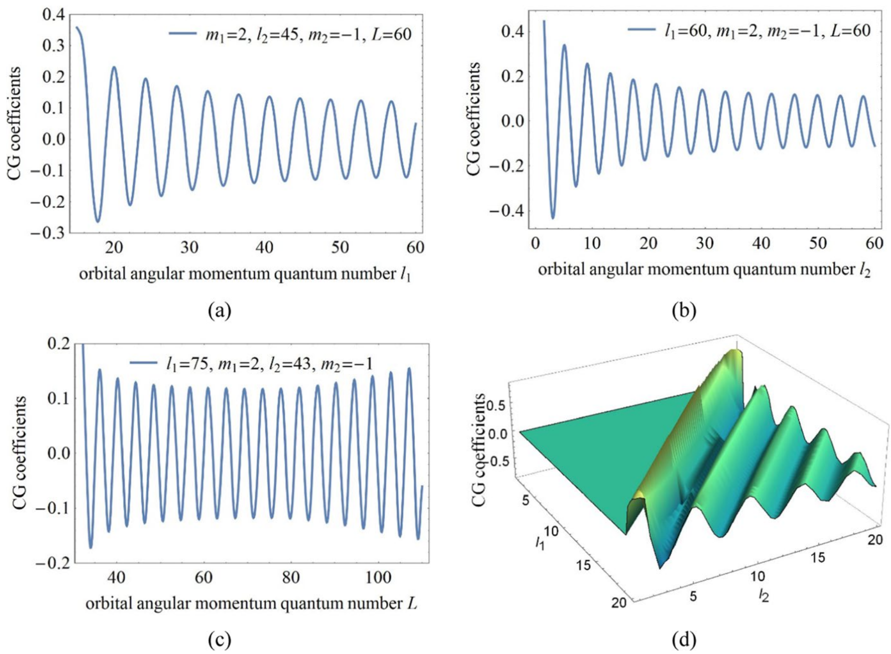

Fig. 1 CG coefficients are shown as a function of orbital angular momentum quantum numbers for a range of magnetic quantum numbers ($m_1 = 2, m_2 = -1$). **a** $15 \le l_1 \le 60$. **b** $1 \le l_2 \le 60$. **c** $32 \le L \le 108$. **d** 3D graph of CG coefficients versus l_1 and l_2 orbital angular momentum quantum numbers ($L = 20$)

In this study, the special values provided by the generalized hypergeometric functions of the unit argument are used to rewrite the special values of CG coefficients given extensively listed in Ref [17].

The generalized hypergeometric functions	Special values of CG coefficient
${}_3F_2\left[\begin{matrix}-2L-1,-L+M,\ -L+M\\ -L+M,\ -L+M\end{matrix}\middle\vert 1\right]$ $= (-1)^{L-M}F(2L,L-M)$	$C^{LM}_{LM,00} = 1$
${}_3F_2\left[\begin{matrix}-2l_1-2l_2-1,0,\ 0\\ 0,\ -2l_2\end{matrix}\middle\vert 1\right] = 1$	$C^{l_1+l_2 l_1+l_2}_{l_1 l_1,l_2 l_2} = 1$
${}_3F_2\left[\begin{matrix}-2l_1-2l_2-1,0,-2l_2\\ -2l_2,-2l_2\end{matrix}\middle\vert 1\right] = 1$	$C^{l_1+l_2 l_1-l_2}_{l_1 l_1,l_2 -l_2} = \sqrt{\frac{1}{F(2l_1+2l_2,2l_1)}}$
${}_3F_2\left[\begin{matrix}-2l_1-1,-l_1+m_1,m_1+m_2\\ -2l_1+m_1+m_2,-l_1+m_1\end{matrix}\middle\vert 1\right] = \sqrt{\frac{F(2l_1,l_1+m_1)}{F(2l_1,l_1+m_2)}}$	$C^{00}_{l_1 m_1,l_2 m_2} = (-1)^{l_1-m_1}\frac{\delta_{m_1,-m_2}}{\sqrt{2l_1+1}}$
${}_3F_2\left[\begin{matrix}-2l_1-2l_2,-1,0\\ -1,-2l_2\end{matrix}\middle\vert 1\right] = 1$	$C^{l_1+l_2-1 l_1+l_2-1}_{l_1 l_1-1,l_2 l_2} = -\sqrt{\frac{l_2}{l_1+l_2}}$
${}_3F_2\left[\begin{matrix}-2l_1-2l_2,0,0\\ -1,-2l_2+1\end{matrix}\middle\vert 1\right] = 1$	$C^{l_1+l_2-1 l_1+l_2-1}_{l_1 l_1,l_2 l_2-1} = \sqrt{\frac{l_1}{l_1+l_2}}$

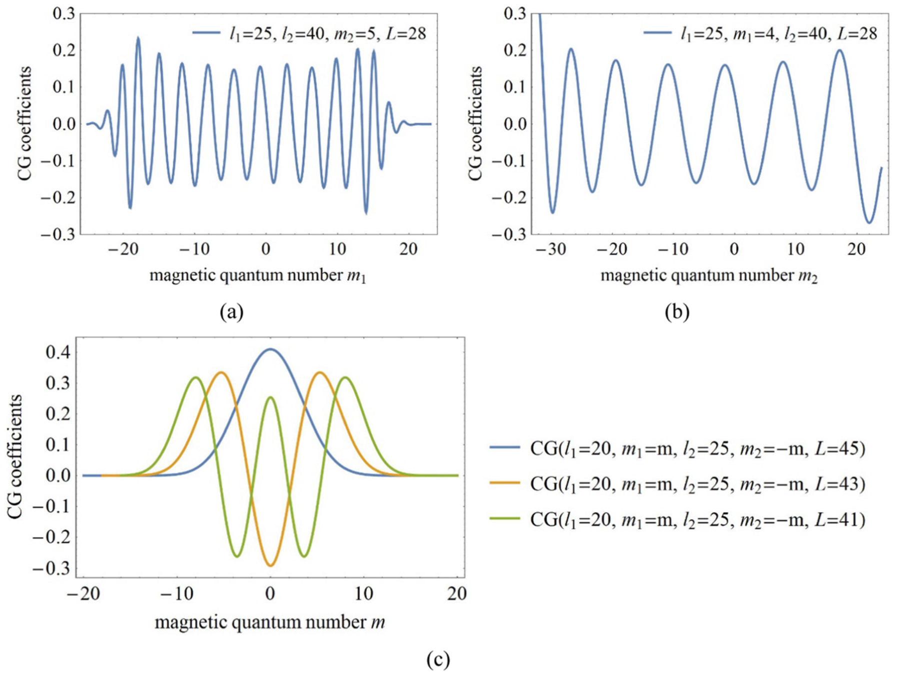

Fig. 2 Oscillatory behavior of CG coefficients in the intervals **a** $-25 \le m_1 \le 25$. **b** $-35 \le m_2 \le 25$. **c** $-20 \le m \le 20$

3 Asymptotic behavior of the Clebsch–Gordan coefficients

The analytical expressions for ACG coefficients given by Refs. [23, 24] are rewritten in terms of binomial coefficients with some modifications as follows

$$
\begin{aligned}
c^{LM}_{l_1m_1,l_2m_2} \approx & \sqrt{F\left(l_2+m_2, l_2-\beta\right)F\left(l_2+\beta, l_2-m_2\right)} \\
& \left(\frac{L-M+1/2}{2L+1}\right)^{l_2} \sum_{s=a}^{b} (-1)^{l_2-\beta-s} \frac{F\left(l_2-m_2, s\right)F\left(l_2-\beta, s\right)}{F\left(m_2+\beta+s, s\right)\left(tan\frac{\theta}{2}\right)^{l_2+m_2+2s}}
\end{aligned} \tag{9}
$$

where $\beta = L - l_1$. The intervals of the summation index have been determined by following conditions.

$$
\begin{aligned}
b &= Min\left\{l_2 - m_2, l_1 + l_2 - L\right\} \\
a &= \begin{cases} 0, & l_1 < m_2 + L \\ l_1 - m_2 - L, & l_1 > m_2 + L \end{cases}
\end{aligned} \tag{10}
$$

In Eq. (9), θ is the angle between the momentum L and the z-axis can be expressed as follows.

Table 2 For the arbitrarily chosen fixed values of l_2 and L, points where CG coefficients are zero

$l_1 = (15, 60) l_2 = 45 L = 60$																	
m_1	m_2	M	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
2	−1	1	16.7	18.9	21.1	23.2	25.2	27.3	29.4	31.4	33.5	35.4	37.5	39.6	41.5	43.6	45.6
1	−1	0	16.4	18.5	20.6	22.6	24.7	26.9	28.8	30.9	32.9	34.9	36.9	38.9	41.0	43.1	45.1
0	−1	−1	16.1	18.2	20.2	22.3	24.3	26.3	28.4	30.3	32.4	34.4	36.4	38.5	40.5	42.5	44.5
−1	−1	−2	15.8	17.8	19.8	21.8	23.8	25.8	27.8	29.8	31.8	33.8	35.9	37.9	40.0	42.0	44.0
−2	−1	−3	15.6	17.5	19.4	21.4	23.3	25.3	27.3	29.4	31.3	33.3	35.4	37.4	39.4	41.4	43.5
2	0	2	16.5	18.7	20.8	22.9	25.0	27.0	29.0	31.1	33.1	35.1	37.1	39.1	41.1	43.1	45.1
2	1	3	16.5	18.6	20.6	22.7	24.7	26.7	28.7	30.7	32.7	34.7	36.7	38.6	40.6	42.6	44.6

All triangular conditions and selection rules are satisfied at these points

$$tan\frac{\theta}{2} = \sqrt{\frac{L-M+1/2}{L+M+1/2}} = \frac{c^{L+\frac{1}{2}M-\frac{1}{2}}_{LM,\frac{1}{2}-\frac{1}{2}}}{c^{L+\frac{1}{2}M+\frac{1}{2}}_{LM,\frac{1}{2}\frac{1}{2}}} \tag{11}$$

The following formula relates the behavior of ACG coefficients with representations of finite rotation functions [24]

$$c^{LM}_{l_1m_1,l_2m_2} \approx (-1)^{l_2}\delta_{M-m_1,m_2} d^{l_2}_{m_2,L-l_1}(\theta) \tag{12}$$

This formula was mentioned by Edmonds [1]. We derive a formula for ACG from the definition of recursion relations for finite rotation functions and Eq. (9) in terms of trigonometric functions and ACG coefficients.

$$\begin{aligned} c^{LM}_{l_1m_1,l_2m_2} =& c^{L0}_{l_10,l_20} c^{l_1+m_20}_{l_10,l_20} K_{m_2\beta}(0) \\ &+ 2\sum_{s=1}^{l_2} c^{l_1+m_20}_{l_1-s,l_2s} c^{L0}_{l_1-s,l_2s} K_{m_2\beta}(s\theta) \end{aligned} \tag{13}$$

where we denote

$$K_{m_1m_2}(\theta) = sin\left(\theta - \frac{Mod\left(m_1-m_2,4\right)-1}{2}\pi\right) \tag{14}$$

and

$$\theta = Arccos\left(\frac{M}{L+1/2}\right) \tag{15}$$

Both Eqs. (9) and [(12) or (13)] are used to calculate ACG coefficients numerically; the results are completely in agreement with each other. ACG coefficients are satisfied following orthogonality relation.

$$\sum_{s=-l_2}^{l_2} c^{LM}_{l_1m_1,l_2s} c^{L'M}_{l_1'm_1,l_2s} = \delta_{LL'}\delta_{l_1l_1'} \tag{16}$$

4 Results and discussions

In this study, CG coefficients were calculated using Eqs. (3–8), and the accuracy of our results was checked using orthogonality and symmetry relationships. The numerical results obtained from these equations, presented in Table 1, were compared with those in the literature [11, 13, 17] and with results generated using the command in Mathematica programming language. Our numerical values are

Table 3 CPU times for the CG coefficients

l_1	m_1	l_2	m_2	L	CPU times (second)						
					Equation (3)	Equation (4)	Equation (5)	Equation (6)	Equation (7)	Equation (8)	Mathematica Eq. (17)
2	1	2	1	4	0	0	0	0	0	0	0
20	10	20	10	40	0	0	0	0	0	0	0
200	10	200	10	400	0	0	0	0	0	0	0.015625
2000	10	2000	10	4000	0.015625	0.015625	0.031250	0.031250	0.015625	0.015625	0.125000
20,000	100	20,000	100	40,000	0.281250	0.734375	1.000000	0.531250	0.625000	0.625000	4.796875
200,000	100	200,000	100	400,000	2.828125	9.781250	15.187500	4.125000	6.640625	5.093750	156.64025

in complete agreement with both the literature and the results of the Mathematica CG command given by Eq. (17). To calculate the numerical results of the CG coefficients using the command line provided by Eq. (17) and Eqs. (3–8), the required CPU times in seconds are given in Table 3. As seen from Table 3, among all equations, Eq. (3) has the shortest running time in all selected quantum states. At high values of quantum numbers, a considerable difference was observed between the running times of the Mathematica command line given in Eqs. (3–8) and (17). In quantum mechanical systems, hundreds of thousands of CG coefficients must be calculated to calculate a physical quantity. This shows the importance of calculating CG coefficients in a short time. The running time of Eqs. (3–8) has not been compared with the values in the literature because computers with different features are used.

$$\mathrm{ClebschGordan}[\{\mathrm{l1}, \mathrm{m1}\}, \{\mathrm{l2}, \mathrm{m2}\}, \{\mathrm{L}, \mathrm{M}\}] \tag{17}$$

ACG coefficients were numerically calculated in the range of $100 \le l_1 \le 2,000,050$ using Eq. (9), and the results are presented in Table 4. The accuracy of the results was verified through the orthogonality relation provided by Eq. (16). To facilitate a comparison between CG and ACG coefficients, CG coefficients were calculated utilizing these quantum sets and are detailed in Table 4. Table 4 shows that CG and ACG coefficients exhibit a very gradual convergence. Figure 3 illustrates the overlap between CG and ACG coefficients in response to the orbital angular momentum quantum numbers in the range $52 \le l_1 \le 75$, with $l_2 = 23$, $m_2 = -2$, $L = 75$, and $M = -2$. While these coefficients yield significantly different numerical results for small values of the l_1 quantum numbers, it has been observed that they converge slowly as the quantum numbers increase. Even at very high quantum numbers, this approximation remains within single

Table 4 Numerical values of CG and ACG coefficients for very high quantum numbers

l_1	m_1	l_2	m_2	L	M	$C^{LM}_{l_1 m_1, l_2 m_2}$	$c^{LM}_{l_1 m_1, l_2 m_2}$
100	5	50	−3	150	2	0.25548852192936475045	0.24687294038836336605
500	5	50	−3	550	2	0.25869051355731599254	0.25516984718244435831
1000	5	50	−3	1050	2	0.25846575745897489230	0.25655842390320664255
10,000	5	50	−3	10,050	2	0.25810191171984115663	0.25789708927763605043
50,000	5	50	−3	50,050	2	0.25806163139315841425	0.25802040809747868049
100,000	5	50	−3	100,050	2	0.25805650195393040116	0.25803587408143466317
150,000	5	50	−3	150,050	2	0.25805478746344074460	0.25804103194134032442
250,000	5	50	−3	250,050	2	0.25805341418620378665	0.25804515914118298640
300,000	5	50	−3	300,050	2	0.25805307063283173052	0.25804619106782365208
400,000	5	50	−3	400,050	2	0.25805264105943644521	0.25804748104739066992
500,000	5	50	−3	500,050	2	0.25805238324516473558	0.25804825507314173664
750,000	5	50	−3	750,050	2	0.25805203941085622191	0.25804928715182508525
1,000,050	5	50	−3	1,000,050	2	0.25805186745858024120	0.25804980321017413331
2,000,050	5	50	−3	2,000,050	2	0.25805160948626172857	0.25805057732145796498

Numerical values of ACG coefficients that are compatible with CG coefficients are underlined

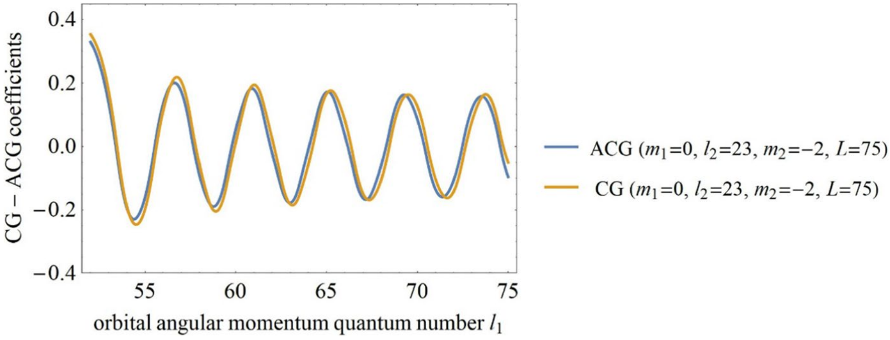

Fig. 3 Graph of CG and ACG coefficients change as a function of quantum number l_1 in interval $52 \le l_1 \le 75$

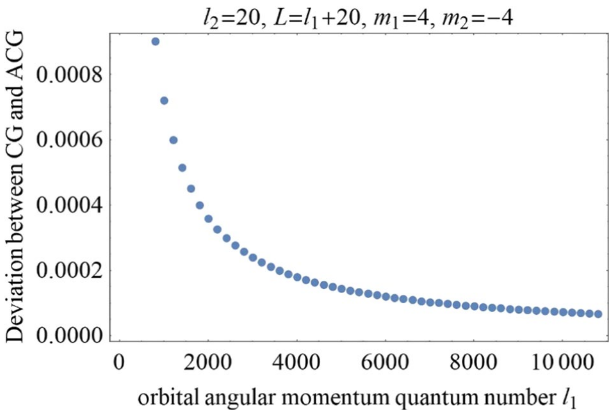

Fig. 4 The plot of $\Delta^{LM}_{l_1m_1,l_2m_2}$ versus l_1 angular momentum quantum numbers

digits. Table 4 shows that the orbital quantum number needs to be in the order of 100,000 for the next digit to be compatible.

The amount of deviation between CG and ACG coefficients, $\Delta^{LM}_{l_1m_1,l_2m_2}$, for the given quantum sets, is calculated with the formula given below, and the results are illustrated in Fig. 4 as a function of the l_1 quantum numbers. According to Fig. 4, the difference between CG and ACG is maximum at small values inversely proportional to the angular momentum quantum number and slowly approaches each other as l_1 increases.

$$\Delta^{LM}_{l_1m_1,l_2m_2} = \left| C^{LM}_{l_1m_1,l_2m_2} - c^{LM}_{l_1m_1,l_2m_2} \right| \tag{18}$$

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Declarations

Competing interests The authors have no competing interests.

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References

1. A.R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1960)
2. M.E. Rose, *Elementary Theory of Angular Momentum* (Dover Publications, INC., New York, 1957)
3. R.N. Zare, *Angular Momentum, Understanding Spatial Aspects in Chemistry and Physics* (Wiley, New York, 1988)
4. E.U. Condon, G.H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935)
5. B.L. Van der Waerden, *Die Gruppentheoretische Methode in der Quantenmechanik* (Springer, Berlin, 1932)
6. G. Racah, Phys. Rev. **62**, 438–462 (1942)
7. V.A. Fock, JETP **10**, 383–393 (1940)
8. E.P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press, New York, 1959)
9. S.D. Majumdar, Prog. Theor. Phys. **20**, 798–803 (1958)
10. A. Bandzaitis, A. Yutsis, Litov. Fiz. Sb. **4**, 45–49 (1964)
11. T. Shimpuku, Prog. Theor. Phys. Suppl. **13**, 1–135 (1960)
12. S.T. Lai, Y.N. Chiu, Comput. Phys. Commun. **61**, 350–360 (1990)
13. I.I. Guseinov, A. Özmen, Ü. Atav, H. Yüksel, J. Comput. Phys. **122**, 343–347 (1995)
14. L. Wei, Comput. Phys. Commun. **120**, 222–230 (1999)
15. C.B. Tarter, J. Math. Phys. **11**, 3192–3195 (1970)
16. J.-C. Pain, Eur. Phys. J. A **56**(296), 1–13 (2020)
17. D.A. Varshalovich, A.N. Moskalev, V.K. Khersonskii, *Quantum Theory of Angular Momentum, Irreducible Tensors, Spherical Harmonics, Vector Coupling Coefficients, 3 nj Symbols* (World Scientific, Singapore, Hong Kong, 1988)
18. D. Ritchie, High performance algorithms for molecular shape recognition (2011), https://tel.archives-ouvertes.fr/tel-00587962
19. D. Ritchie, Whole number recursion formulae for high order Clebsch–Gordan coupling coefficients, hal-01851097 (2018)
20. R. Suresh, R.K. Srinivasa, Appl. Math. Inf. Sci. **5**, 44–52 (2011)
21. R.E. Tuzun, P. Burkhardt, D. Secrest, Comput. Phys. Commun. **112**, 112–148 (1998)
22. G. Xu, J. Quant. Spectrosc. Radiat. Transf. **254**, 107210 (2020)
23. A.R. Edmonds, Angular Momenta in Quantum Mechanics, CERN 55-26, Geneva (1955)
24. P.J. Brussaard, H.A. Tolhoek, Physica **23**, 955–971 (1957)
25 Ya.A. Smorodinskiy, L.A. Shelepin, Usp. Fiz. Nauk. (Sov.) **106**, 3–45 (1972)
26 M.E. Rose, *Multipole Fields* (Wiley, New York, 1955)
27. E.L. Akim, A.A. Levin, Dokl. Acad. Nauk USSR **138**, 503–505 (1961)
28. D.H. Kintish, L. Zamick, B. Kleszyk, Phys. Rev. C **90**, 027302 (2014)
29. J.S. Dowker, Note on an improved classical limits of Clebsch–Gordan coefficients (2023). https://arxiv.org/abs/2302.07737

30. G.B. Arfken, H.J. Weber, *Mathematical Methods for Physicists* (Academic Press, London, 1995)
31. N. Yükçü, E. Öztekin, Comput. Math. Math. Phys. **53**, 1–7 (2013)
32 A.P. Prudnikov, Y.A. Brychkov, O.I. Marichev, *Integrals and Series, Vol. 3, More Special Functions* (Gordon and Breach, New York, 1990)
33. https://functions.wolfram.com/HypergeometricFunctions/Hypergeometric3F2/17/02/06/