An efficient code for calculation of the $6\text{C}$, $9\text{C}$, and $12\text{C}$ symbols for $C_{3v}$, $T_d$, and $O_h$ point groups

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Abstract

A new code designed to calculate the $6\text{C}$, $9\text{C}$, and $12\text{C}$ symbols for $C_{3v}$, $T_d$, and $O_h$ point groups is presented. The program is based on an algorithm that uses the symmetry property between pair and impair representations. This algorithm allows one to speed up the $C$-symbols calculation and increase the efficiency of spectroscopic programs based on the irreducible tensorial formalism.

Program summary

Program title: 6912C
Catalogue identifier: AEKZ_v1_0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AEKZ_v1_0.html
Program obtainable from: CPC Program Library, Queen’s University, Belfast, N. Ireland
No. of lines in distributed program, including test data, etc.: 1214
No. of bytes in distributed program, including test data, etc.: 22097
Distribution format: tar.gz
Programming language: C++
Computer: Any computer with C, C++ compiler
Operating system: Linux SUSE, Windows XP64
RAM: 400 Kb
Classification: 4.2, 16.2, 16.3
Nature of problem: Spectroscopy of symmetric atmospheric molecules.
Solution method: The program is based on an algorithm that uses the symmetry property between pair and impair representations.
Running time: The test program provided takes a few seconds for $C_{3v}$, a few minutes for $T_d$ and a few days for $O_h$.

1. Introduction

Spectroscopic investigations of polyatomic molecules play an important role for atmospheric applications. The most of atmospheric molecules included in spectroscopic banks [1,2] are high symmetry molecules. For example the need for reliable high-resolution methane parameters is significant for modeling of planetary atmospheres, like those of the Giant Planets. Since infrared spectroscopy is generally the best diagnostic tool to study CH4 in these environments, it appears essential to be able to model its absorption very precisely. Since years the irreducible tensor formalism [3,4] (see also references therein) has been successfully applied for calculating rovibrational spectra of high symmetry molecules [5–7]. Several programs, such as STDS [8], MIRS [9], and HTDS [10,11] based on tensor formalism [5] have been developed. These programs use the empirically adjusted effective Hamiltonian [5] and the full nuclear Hamiltonian expressed in terms of normal-mode irreducible tensor operators obtained from the ab initio PES [12,13]. The ab initio-based effective Hamiltonian [12]...
is quite similar to classical effective Hamiltonian [5] but it can be constructed up to higher orders and for high exited states. The program performance is very important because of increasing the number of Hamiltonian parameters and basis functions. The calculations involving the effective Hamiltonian for high exited states can be also very cumbersome and can require a program optimization. It was found that one of the bottlenecks is slow calculation of the 9C [5,11] (other notations: X [4], 9Γ [6]) and 12C symbols. The 12C symbols are required only for intensity calculations while 9C are used for line position calculations. In addition, the 9C symbols are used in variational programs applied for calculation of multi-dimensional irreducible matrix elements [13–15]. As a rule, the 9C symbols are calculated in terms of a sum of products of three 6C symbols [5,6], and only when one of the representations in the 9C symbol is \( A_1 (A_{1g}) \), a simplified formula can be used. This method of calculation can be very time consuming. It is often sufficient to know whether a 9C symbol is zero — in most cases, it results from the number of different representations in the 9C symbol. Taking into account the limited number of representations in point groups, the calculations of the 6C, 9C and 12C symbols are more easy than calculations of similar symbols for the angular momentum coupling coefficients \( 6f, 9f, \) and \( 12f \) [16–18]. However, the optimization of the program for calculating the 9C and 12C symbols is required for various practical applications.

2. 6C symbol calculation

The 6C symbol is defined as [4]:

\[
\begin{vmatrix}
C_1 & C_2 & C_{12} \\
 C_3 & C & C_{23}
\end{vmatrix} = \sum_{\sigma_1,\sigma_2,\sigma_3} F(C_1, C_2, C_{12}) F(C_1, C, C_{23}) F(C_3, C_2, C_{23}) F(C_3, C, C_{12}).
\]

(1)

where \( F(C_1, C_2, C_{12}) \) is 3C symbol [3,4,19]. Note that a 6C symbol is nonvanishing, only if all four factors in the right-hand part of Eq. (1) conform to the triangle rule. The symmetry properties of the 6C and 9C symbols have been considered in [3,4]. The \( T_d \) symmetry group has three even representations (\( A_1, E, \) and \( F_2 \)), and two odd representations (\( A_2 \) and \( F_1 \)). The associated representations for the Octahedral Group have been considered in Appendix B of [4]. Each irreducible representation \( g \) of the octahedral group has associated with it another irreducible representation \( C \), according to the rule \( C = A_2 \times C \). Clearly, \( A_1 = A_2, \tilde{F}_2 = F_1, \tilde{E}_2 = E_1 \). When one of the representations in the 6C symbol is \( A_1 \), it is expressed as [4]:

\[
\begin{vmatrix}
A_1 & C_2 & C_3 \\
 C_4 & C_5 & C_6
\end{vmatrix} = \delta_{C_2 C_3} \delta_{C_5 C_6} \Delta(C_4, C_5, C_1) \Delta(C_4, C_2, C_6)(-1)^{C_2 + C_4 + C_5} \frac{1}{\sqrt{|C_2||C_5|}}.
\]

(2)

For \( A_2 \), one can use the similar expression:

\[
\begin{vmatrix}
A_2 & C_2 & C_3 \\
 C_4 & C_5 & C_6
\end{vmatrix} = \delta_{C_2 \tilde{C}_3} \delta_{C_5 \tilde{C}_6} \Delta(C_4, C_5, C_2) \Delta(C_4, C_2, C_6)(-1)^{C_2 + \tilde{C}_4 + C_5 + (C_3 + C_6)}(C_2, C_4, C_5)\Delta(E, \phi, \theta) \frac{1}{\sqrt{|C_2||C_5|}}.
\]

(3)

When none of representations \( C_2, C_4, C_5 \) is \( E \), or \( C_2 = C_5, S = 1 \) in Eq. (3). In addition, \( S(C_2, C_4, C_5) = (-1)^{C_2 + \tilde{C}_3 + (C_2, C_4, C_5)\Delta(E, \phi, \theta)} \) is invariant to permutations of \( C_2 \) and \( C_5 \). Thus, for \( C_3 \), \( \tilde{C}_3 \), and \( T_d \) groups, the 6C symbols that have at least one one-dimension representation can be obtained using the simplified expressions (2), (3). Other 6C symbols can be easily calculated, because the number of nonvanishing symbols is limited. Despite that the expression (3) is quite simple, it never has been mentioned in the papers [4–6]. Eq. (3) will help us simplify the calculations of the 9C and some of 12C symbols that have one-dimensional representation.

For \( O_h \) group, an associated representation \( C \) is defined according to the rule \( C = A_1 u \times C \) so \( \tilde{C}_2 = C_{\tilde{u}} \). From the 6C symbol definition (1), we deduce:

\[
\begin{vmatrix}
C_1 & C_2 & C_3 \\
 C_4 & C_5 & C_6
\end{vmatrix} = \begin{vmatrix}
\tilde{C}_1 & \tilde{C}_2 & \tilde{C}_3 \\
\tilde{C}_4 & \tilde{C}_5 & \tilde{C}_6
\end{vmatrix}.
\]

(4)

At the same time, Eq. (3) is valid for any subgroup \( g \) of \( O \) that is isomorphic to \( T_d \) symmetry group. For \( O_h \) group, any 6C symbol can be reduced to 6C symbol containing only \( g \) representations. After this, one can use programs for calculating 6C symbols for \( T_d \) group (Eq. (3) is valid for \( T_d \)). Thus, for \( O_h \) symmetry group, any 6C symbol containing one-dimensional representations can be obtained using Eqs. (2)–(4).

3. 9C symbol calculation

The number of nonvanishing 9C symbols is considerably more than that for 6C symbols. The 9C symbol is defined as [4]:

\[
\begin{vmatrix}
C_1 & C_2 & C_{12} \\
 C_3 & C_4 & C_{34} \\
 C_{13} & C_{24} & C
\end{vmatrix} = \sum_{X} \begin{vmatrix}
C_1 & C_2 & C_{12} \\
 C_3 & C_4 & C_{34} \\
 X & C & C_{13}
\end{vmatrix} \begin{vmatrix}
C_3 & C_4 & C_{34} \\
 C_1 & C_2 & C_{12} \\
 X & C & C_{13}
\end{vmatrix} \begin{vmatrix}
C_{13} & C_{24} & C
\end{vmatrix}.
\]

(5)

If \( C_1 = A_1 (A_{1g}) \), the following expression can be used:

\[
\begin{vmatrix}
A_1 & C_2 & C_2 \\
 C_3 & C_4 & C_{34} \\
 C_{13} & C_{24} & C
\end{vmatrix} = (-1)^{C_2 + \tilde{C}_1 + C_{24} + C_{34}} \sqrt{|C_2||C_3|} \begin{vmatrix}
C_2 & C_4 & C_{24} \\
 C_3 & C_4 & C_{34}
\end{vmatrix} \delta_{C_2 C_3} \delta_{C_3 C_4}.
\]

(6)
For $T_d$ and $C_{3v}$ groups, and for any subgroup $g$ of $O_h$, the 9C symbols can be evaluated by the equation:

$$
\begin{align*}
\begin{bmatrix}
A_2 & C_2 & C_2 \\
C_3 & C_4 & C_{34} \\
C_3' & C_{34} & C
\end{bmatrix} = & (-1)^{j_2+c_1+c_2+c_{34}} \begin{bmatrix}
C_2 & C_4 & C_{34} \\
C_3 & C_3 & C_3 \\
C_3' & C_{34} & C
\end{bmatrix} \delta_{c_2'j_2} \delta_{c_3'j_3} \delta_{c_{34}'j_{34}} S(C_2,C_4,C_{34}) S(C_3,C_{34},C).
\end{align*}
$$

(Eqns. (6), (7) allow us to obtain most of the 9C symbols. For $T_d$ group, the total number of 9C symbols is $S^9 = 1953125$, but there are only 19683 symbols that contain no $A_1$ and $A_2$ representations. Below, we consider only 9C symbols that contain no one-dimensional representation and conform to the triangle rule for rows and columns. The number of such symbols (without taking into account the symbol symmetry properties) is 6033. These symbols are listed in Table C3.1 (see Appendix C in [4]). A 9C symbol containing only $F_1$ and $F_2$ either is trivial zero (when the number of $F_1$ representations is odd) or $1/24$ (for even number of $F_1$ representations). There are only 5779 9C symbols with the following number of the $E$ representations: 1, 2, 3, 5, or 9. 9C symbol containing nine $E$ representations is equal to $\frac{1}{\sqrt{2}}$. When the number of $E$ representations is 4, 6, 7, or 8, a 9C symbol is trivial zero. When the number of $E$ representations is 2 or 5, a 9C symbol is always nonvanishing. A 9C symbol containing only one $E$ representation is nonvanishing only if total parity of four $F$ representations in the same column as $E$ and in the same row as $E$, is even. A 9C symbol containing three $E$ representations can be evaluated using the following rules. When all three $E$ representations are diagonal elements of a 9C symbol, it is nonvanishing only if for every $E$ representation total parity of four $F$ representations in the same column as $E$ and in the same row as $E$, is even. Then all three $E$ representations are together in one row (column), a 9C symbol is vanishing only if the total parity of six $F$ representations is positive. Thus, to evaluate whether a 9C symbol is vanishing, it is often sufficient to check its conformance to the triangle rule and calculate the number of the $E, F_1, F_2$ representations. There are 4145 nonvanishing 9C symbols that contain only $E$ and $F$ representations. Note that there is a nonvanishing 6C symbol $\bar{E} = \frac{1}{24}$ in which representations in triangles $\Delta(E, F_1, F_2)$ and $\Delta(E, F_2, F_2)$ have different parity: $(-1)^{F_1 + F_2} \neq (-1)^{F_2 + F_2}$.

### 4. 12C symbol calculation

In this paper, we use the following definition of 12C symbols similar to that for 12j symbols of the first kind [20]:

$$
\begin{align*}
\begin{bmatrix}
a_1 & a_2 & a_3 & a_4 \\
b_1 & b_2 & b_3 & b_4 \\
c_1 & c_2 & c_3 & c_4
\end{bmatrix} = & (-1)^S \sum_X (-1)^X \begin{bmatrix}
a_1 & c_1 & X \\
c_2 & a_2 & b_1 \\
a_3 & c_3 & X \\
c_4 & a_4 & b_3 \\
c_1 & a_1 & b_4
\end{bmatrix},
\end{align*}
$$

(Eq. (8) differs from the 12C symbol definition used for calculations of line intensities in [21]. At the same time, Eq. (8) allows us to use the symmetry properties and the triangle rule for 12j symbols described by the octagonal graphical scheme [20].

$$
\begin{align*}
\begin{bmatrix}
a_1 & a_2 & a_3 & a_4 \\
b_1 & b_2 & b_3 & b_4 \\
c_1 & c_2 & c_3 & c_4
\end{bmatrix} = & \begin{bmatrix}
a_2 & a_3 & a_4 & c_1 \\
b_2 & b_3 & b_4 & b_1 \\
c_2 & c_3 & c_4 & a_1
\end{bmatrix} = \begin{bmatrix}
a_4 & a_3 & a_2 & a_1 \\
b_3 & b_2 & b_1 & b_4 \\
c_4 & c_3 & c_2 & c_1
\end{bmatrix},
\end{align*}
$$

$$
\begin{align*}
\begin{bmatrix}
a_1' & a_2 & a_3 & a_4 \\
b_1 & b_2 & b_3 & b_4 \\
c_1 & c_2 & c_3 & c_4
\end{bmatrix} = & (-1)^{S+c_1+c_2+c_3+c_4+c_4} \begin{bmatrix}
a_3 & c_3 & c_1 \\
c_3 & a_4 & b_3 \\
a_1 & a_3 & b_2
\end{bmatrix} \frac{1}{\sqrt{a_2||c_4}} \delta_{c_4,b_4} \delta_{a_2,b_1}.
\end{align*}
$$

For $T_d$, $C_{3v}$ groups, and any subgroup $g$ of $O_h$ group, we have:

$$
\begin{align*}
\begin{bmatrix}
A_2 & a_2 & a_3 & a_4 \\
b_1 & b_2 & b_3 & b_4 \\
c_1 & c_2 & c_3 & c_4
\end{bmatrix} = & (-1)^S (-1)^{\bar{c}_1} S(c_1,c_2,a_2) S(c_1,a_4,c_4) \begin{bmatrix}
A_2 & a_2 & \bar{c}_1 \\
a_3 & c_3 & c_1 \\
a_4 & a_4 & b_3
\end{bmatrix} \frac{1}{\sqrt{a_2||c_4}} \delta_{c_4,b_4} \delta_{a_2,b_1},
\end{align*}
$$

$$
\begin{align*}
\begin{bmatrix}
a_1 & a_2 & a_3 & a_4 \\
b_1 & b_2 & b_3 & b_4 \\
c_1 & c_2 & c_3 & c_4
\end{bmatrix} = & \begin{bmatrix}
A_1 & a_2 & c_4 \\
c_4 & b_3 & c_3 \\
a_1 & a_3 & b_2
\end{bmatrix} \frac{1}{\sqrt{a_1||c_1}} \delta_{c_1,b_1} \delta_{a_1,c_2},
\end{align*}
$$

$$
\begin{align*}
\begin{bmatrix}
a_1 & a_2 & a_3 & a_4 \\
b_1 & b_2 & b_3 & b_4 \\
c_1 & c_2 & c_3 & c_4
\end{bmatrix} = & (-1)^{a_1+c_1+a_3+c_3} \begin{bmatrix}
a_4 & a_4 & c_1 \\
c_4 & b_3 & c_3 \\
a_1 & a_3 & b_2
\end{bmatrix} \frac{1}{\sqrt{a_1||c_1}} \delta_{c_1,b_1} \delta_{a_1,c_2} S(b_2,c_3,c_1) S(b_2,a_3,a_1).
\end{align*}
$$

The calculations of matrix elements for the transition moment operators involve direction cosines. In the space-fixed frame, the dipole moment transforms as $A_2$ for $T_d$, $C_{3v}$ groups or $A_1u$ for $O_h$ group, so 12C symbols involved in calculations of the dipole moment matrix elements contain at least one-dimensional representation. Thus, for $T_d$ group, the 12C symbols can be calculated using simplified formulas (10).
5. Discussion and conclusion

The primary aim for this study was to develop an efficient program designed to calculate 9C and 12C symbols. It is desirable that this program could:

- Store 9C and 12C symbols in RAM by allocating a minimum amount of memory.
- Quickly fill the required data array.
- Quickly access required C symbols stored in memory or calculate them in a reasonable time.

Often, it is sufficient to evaluate whether a 9C symbol is vanishing. In this case, it is not necessary to calculate it. For example, when recoupling three big binary trees [22], it is unlikely that the final recoupling coefficient is nonvanishing. In this scenario, before performing calculations, it is recommended to ensure that none of the recoupling coefficients is zero. Otherwise, the matrix element is trivial zero. The C program designed to calculate the 6C, 9C and 12C symbols and its short description is given in electronic Supplementary materials. This program can be used for modeling highly excited vibration–rotation spectra [8,9] and variational calculations of energy levels for symmetry molecules [13–15,23]. Note that this program is much more efficient with respect to the program reported in the paper [9].

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.cpc.2011.11.012.

References