

# Generation of Clebsch–Gordan coefficients for the point and double groups <sup>☆</sup>

K. Rykhlinskaya <sup>\*</sup>, S. Fritzsche

*Institut für Physik, Universität Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany*

Received 28 October 2005; received in revised form 30 November 2005; accepted 11 January 2006

Available online 24 February 2006

## Abstract

The theory of the point and double groups has been widely used in quantum physics to understand the structure and dynamical properties of molecules and solids. In order to construct wave functions for such systems, one often needs the Clebsch–Gordan coefficients for the symmetry groups. Here, we present an extension of the BETHE program to support the calculation of the Clebsch–Gordan coefficients as applied, for instance, in crystal field theory. Apart from the generation of the Clebsch–Gordan coefficients, the program also provides a simple access to the group theoretical data for all frequently applied point and double groups.

## Program summary

*Title of program:* BETHE

*Catalogue number:* ADUH\_v3\_0

*Program summary URL:* [http://cpc.cs.qub.ac.uk/summaries/ADUH\\_v3\\_0](http://cpc.cs.qub.ac.uk/summaries/ADUH_v3_0)

*Program obtainable from:* CPC Program Library, Queen's University of Belfast, N. Ireland

*Reference in CPC to previous versions:* Comput. Phys. Comm. 162 (2004) 124–142; Comput. Phys. Comm. 171 (2005) 119–132

*Catalog identifiers of previous versions:* ADUH, ADVU

*Does the new version supersede the old version?:* Yes

*Licensing provisions:* None

*Computers for which the program is designed:* All computers with a license of the computer algebra package MAPLE [Maple is a registered trademark of Waterloo Maple Inc.]

*Installations:* University of Kassel (Germany)

*Operating systems under which the program has been tested:* Linux 8.1+ and Windows 2000

*Programming language used:* MAPLE 7 and 8

*Memory required to execute with typical data:* 10–30 MB

*No. of lines in distributed program, including test data, etc.:* 11 024

*No. of bytes in distributed program, including test data, etc.:* 210 244

*Distribution format:* tar.gz

*Nature of the physical problem:* The energy levels of atoms, placed into a crystal environment, can be classified by using group theory. In order to represent, for instance, the wave functions, which are associated with these atomic levels, one often requires the Clebsch–Gordan coefficients of the underlying symmetry group of the overall system. These coefficients arise in the coupling of the electronic wave functions (subsystems) and therefore help investigate the interaction between the many-electron atom and the external field of the crystal.

*Method of solution:* In the framework of the BETHE program [K. Rykhlinskaya, S. Fritzsche, Comput. Phys Comm. 162 (2004) 124–142; K. Rykhlinskaya, S. Fritzsche, Comput. Phys Comm. (2005), in press], we previously defined data structures to deal with a large number of group parameters of the point and double groups. Among other parameters, here we also implemented the *irreducible (matrix) representations*

<sup>☆</sup> This paper and its associated computer program are available via the Computer Physics Communications homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/00104655>).

<sup>\*</sup> Corresponding author.

E-mail address: [rykhli@physik.uni-kassel.de](mailto:rykhli@physik.uni-kassel.de) (K. Rykhlinskaya).

of these groups which are utilized in the present extension of the program in order to generate the Clebsch–Gordan coefficients for the point and double groups. In practice, of course, these coefficients are obtained by means of a proper summation over the matrix elements of the irreducible representations of the group.

*Reasons for the new version:* Extension of the program.

*Summary of revision:* A number additional procedure have been created to generate the Clebsch–Gordan coefficients for the symmetry groups (Bethe\_CG\_matrix(), Bethe\_CG\_coefficient(), Bethe\_group\_direct\_product(), etc.)

*Restrictions onto the complexity of the problem:* The generation of the Clebsch–Gordan coefficients is supported for the cyclic and related groups  $C_i$ ,  $C_s$ ,  $C_n$ ,  $C_{nh}$ ,  $C_{nv}$ , the dihedral groups  $D_n$ ,  $D_{nh}$ ,  $D_{nd}$ , the improper cyclic groups  $S_{2n}$  ( $n \leq 10$ ), the cubic groups  $O$ ,  $T$ ,  $O_h$ ,  $T_h$ ,  $T_d$  as well as the icosahedral groups  $I$  and  $I_h$ . Both the point and the double groups are supported.

*Unusual features of the program:* All commands of the BETHE program are available for interactive work. Apart from the generation of the Clebsch–Gordan coefficients, the program also provides a simple access to the group theoretical data for all the groups specified above. The notation of the symmetry operations and of the irreducible representations follows the compilation by Altmann and Herzog [S. Altmann, P. Herzog, Point-Group Theory Tables, Clarendon Press, Oxford, 1994]. For a quick reference to the program, a description of all user-relevant commands is given in the (user) manual `Bethe-commands.pdf` which is distributed together with the code.

*Typical running time:* Although the program replies ‘promptly’ on most requests, the running time depends strongly on the particular task.

© 2006 Elsevier B.V. All rights reserved.

PACS: 02.20.-a; 71.70.-d

**Keywords:** Clebsch–Gordan coefficients; Coupling of subsystems; Crystal field theory; Direct product; Double group; Molecular physics; Physical chemistry; Point group

## 1. Introduction

In recent years, a large number of studies have been carried out to understand the spectra of atoms which are placed in a potential of lower than spherical symmetry [1–3]. Such a potential occurs for instance for atoms in a crystal field. In order to explore the structure of atoms, incorporated into a crystal, the experimental techniques of magnetic resonance [1] and optical absorption [3] have been applied. These techniques demonstrate the splitting of some of the degeneracies, inherent in the energy levels of the free atom. The details of this splitting depend on the symmetry of the crystal field (potential) and, therefore, can be analyzed by means of group theory. To simplify this analysis, the theory of so-called *Clebsch–Gordan* (CG) coefficients has been developed earlier, which help describe the interelectronic interaction of the atoms in the crystal field and which facilitate the construction of the wave functions of the individual levels. Apart from the crystal field theory, the CG coefficients are used also in other applications of group theory, such as the study of *vibronic effects* [4] or *magnetic circular dichroism* [5].

The CG coefficients of any (finite) group are obtained from group theory by analyzing the direct products of the irreducible representations of the group. In physics, they are best known for the  $SO_3$  rotation group, associated with the coupling of angular momenta. For the point and double groups, however, the generation of the CG coefficients often becomes rather cumbersome as it requires not only the knowledge of group theory but also the—fast and reliable—access to the parameters and representations of the group. In contrast to other group data for the point and double groups, which have been tabulated in a large number of monographs and texts [cf. Refs. [6,7]], the CG coefficients are less often available; they are given, for instance, in the compilation by Altmann and Herzog [6] but are not so simple to use because of the great number of abbreviations and conventions which had to be made in this tabulation.

An alternative *route* for generating the CG coefficients for the point and double groups is offered by computer algebra today. In order to utilize this route, we have recently developed the BETHE program [8,9], a set of MAPLE procedures which provide a simple and interactive access to the group data for the 72 most frequently applied point groups (and the associated double groups). In addition to the group data, this program also facilitates a number of standard tasks from physical chemistry, including the generation of the symmetry orbitals, normal coordinates, or the analysis of the vibrational spectra. Since the BETHE program has been found useful in various applications of group theory, here we present an extension of this code which allows the computation and the use of the CG coefficients for both the point and double groups specified above.

In the next section we briefly recall the theoretical background and the definition of the CG coefficients as well as a few of their properties. Section 3 provides a short description of the BETHE program, while a few simple examples are shown in Section 4. In Section 5, we describe the level splitting of a (two-electron) molecular ion in a tetrahedral environment including the construction of the two-particle wave functions. Finally, a short outlook onto the future development of the program is given in Section 6.

## 2. Theoretical background

The generation and use of the CG coefficients is based on group theory. However, since the theory of the *finite* groups has been discussed in a large number of texts (see, for instance, Refs. [6,7,10]), not much needs to be said here again about the definition of the *point* and *double* groups. Instead, we shall restrict ourselves to a few selected topics from the *representation theory* of groups,

just enough in order to understand the implementation and the use of the BETHE program. We shall also explain how the CG coefficients of the point or double groups can be generated by starting from the irreducible representations of the corresponding group.

### 2.1. Concept of group representations. Direct products

One of the great benefits of group theory is that it helps to classify the molecular states and properties of symmetric molecules by using the *symmetry operations* of the underlying point group. Therefore, understanding the symmetry operations of a molecule allows one to obtain the molecular geometry, i.e. the relative distances and angles of all the atoms and nuclei in the equilibrium configuration. Perhaps an even greater simplification in the description of molecules and solids can be achieved, however, by utilizing the *representations* of the group, i.e. the induced transformation (of the elements of some vector spaces  $L$ ) as obtained, for instance, in classical or quantum mechanics. Usually, a representation of a group is generated by analyzing the behavior of some vector quantity in a vector space  $L$  under the symmetry operations of the group. In quantum physics, for example, the representation theory helps classify the molecular states. Below, we shall restrict ourselves to matrix representations which are associated with an orthonormal basis  $\mathbf{e}_1, \dots, \mathbf{e}_n$  in  $L$ . For such a basis, the transformation of the vectors  $\mathbf{e}_j$  is given by

$$\mathbf{e}'_j = \hat{S}\mathbf{e}_j = \sum_{i=1}^n \mathbf{e}_i T_{ij}(\hat{S}) \quad (1)$$

for each symmetry operation  $\hat{S}$  of the group, i.e. by the set of  $n^2$  coefficients  $\{T_{ij}(\hat{S}), i, j = 1, \dots, n\}$ . Of course, such a vector space  $L$  need not refer (necessarily) to the position vectors or, more generally, vectors in  $\mathcal{R}^n$  but may denote also some function space with the (orthonormal) basis  $\{\psi_i(\mathbf{r}), i = 1, \dots, n\}$ . Similarly to Eq. (1), the transformations of these basis functions are then given by

$$\psi'_j(\mathbf{r}) = \hat{S}\psi_j(\mathbf{r}) = \sum_{i=1}^n \psi_i(\mathbf{r}) T_{ij}(\hat{S}), \quad (2)$$

where, for a given  $j$ , the expansion coefficients refer to the  $j$ th column of the matrix  $T(\hat{S})$ . Since, in general, we can choose the basis rather arbitrarily within the vector space  $L$ , the representations of a group are not defined uniquely but usually depend on the basis, i.e. the particular choice of the coordinates and further parameters. The great benefit of group theory is that, for finite groups, any representation can be decomposed into (a rather small number of) *irreducible representations* which, up to a unitary transformation, are unique and independent of the basis.

The irreducible representations of a group are of fundamental importance and useful for many practical applications. Most of the properties of these representations can be derived from the so-called *great orthogonality theorem* [7,11] which refer to the matrix elements (or characters, i.e. the traces of the corresponding matrices). One particular property of the irreducible representations concerns the ‘orthogonality relation’

$$\sum_{\hat{S}} T_{ip}^{(\alpha)}(\hat{S}) T_{jq}^{(\beta)*}(\hat{S}) = g \delta_{\alpha\beta} \delta_{ij} \delta_{pq} / n_{\alpha} \quad (3)$$

which is important for the generation of the CG coefficients. In this relation,  $T_{ip}^{(\alpha)}$  and  $T_{jq}^{(\beta)}$  are the matrix elements of the irreducible representations  $T^{(\alpha)}$  and  $T^{(\beta)}$ ;  $g$  is the order of the symmetry group  $G$  (i.e. the number of symmetry operations);  $n_{\alpha}$  is the dimension of the irreducible representation  $T^{(\alpha)}$ . The relation (3) can also be used to show that the basis functions, which belong to different irreducible representations, are orthogonal to each other.

To take advantage of the representation theory, one has to deal with the *direct product* of representations which appears frequently in quantum mechanical applications of groups. From a mathematical viewpoint, the direct product of two or more irreducible representations is equivalent to the direct products of the associated matrices and has been considered in many textbooks [7,11]. Therefore, let us remind the reader only that the direct product of a  $n \times n$  matrix  $A$  and  $m \times m$  matrix  $B$  results in the  $nm \times nm$  matrix denoted by  $A \otimes B$ . In group theory, the direct products of two irreducible representations  $T^{(\alpha)}$  and  $T^{(\beta)}$  of the symmetry group  $G$  is again a valid representation of the group, but generally reducible. Therefore, the representation  $T^{(\alpha \otimes \beta)}$  can be decomposed into its irreducible components  $T^{(\gamma)}$

$$T^{(\alpha \otimes \beta)} = \sum_{\gamma} a_{\gamma} T^{(\gamma)}, \quad (4)$$

where the coefficients  $a_{\gamma}$  are obtained from the characters of the irreducible representations  $T^{(\alpha)}$ ,  $T^{(\beta)}$  and  $T^{(\gamma)}$  involved [7,10]. The dot over the summation sign in Eq. (4) denotes that this is not the usual matrix summation but *direct sum* of matrices, which are usually not all of the same dimension. This symbol for the summation means that every matrix of the product representation

$T^{(\alpha\otimes\beta)}$  can be composed from the square matrices  $T^{(\gamma)}$ , arranged down the diagonal with zeros elsewhere. The decomposition of the direct product matrices into their block-diagonal form is achieved by means of a non-singular unitary matrix  $C^{(\alpha\beta)}$

$$(C^{(\alpha\beta)})^{-1} T^{(\alpha\otimes\beta)} C^{(\alpha\beta)} = \left\{ \begin{array}{ccc} T^{(\gamma,1)} & & \\ & \ddots & \\ & & T^{(\gamma,a_\gamma)} \\ & & & \ddots \end{array} \right\} \quad (5)$$

whose matrix elements are denoted by  $\langle \alpha i \beta k | s \gamma m \rangle$  and are known as the *Clebsch–Gordan coefficients* of the symmetry group  $G$ . In this notation  $\alpha$ ,  $\beta$  and  $\gamma$  denotes the irreducible representations  $T^{(\alpha)}$ ,  $T^{(\beta)}$  and  $T^{(\gamma)}$ , while  $i$ ,  $k$  and  $m$  denotes integer indices to enumerate the corresponding basis functions of these representations. Parameter  $s$  refers to the multiple occurrence of the irreducible representation  $\gamma$  in the direct product of  $\alpha$  and  $\beta$ .

## 2.2. Derivation and properties of the Clebsch–Gordan coefficients

As mentioned above, the CG coefficients are the elements of the unitary matrix  $C^{(\alpha\beta)}$  which enables one to transform the (matrices of the) direct product into its block-diagonal form (5). In order to derive the elements of this matrix, we can write the expansion (4) also in the form

$$T^{(\alpha\otimes\beta)} = \sum_{\gamma s} T^{(\gamma,s)}, \quad (6)$$

where  $s \in \{1..a_\gamma\}$  denotes an index that accounts for the multiplicity of the irreducible representation  $T^{(\gamma)}$ . To obtain the CG coefficients  $\langle \alpha i \beta k | s \gamma m \rangle$  explicitly, we have to insert  $T^{(\gamma)}$ , obtained from the transformation (5), into the expansion (6):

$$T^{(\alpha\otimes\beta)} = C^{(\alpha\beta)} \sum_{\gamma} a_\gamma T^{(\gamma)} (C^{(\alpha\beta)})^{-1} = C^{(\alpha\beta)} \sum_{\gamma s} T^{(\gamma,s)} (C^{(\alpha\beta)})^{-1}. \quad (7)$$

From this expression, we may find for the symmetry operation  $\hat{S}$  the matrix elements of the matrix  $T^{(\alpha\otimes\beta)}$ :

$$T_{ik,jl}^{(\alpha\otimes\beta)}(\hat{S}) = T_{ij}^{(\alpha)}(\hat{S}) T_{kl}^{(\beta)}(\hat{S}) = \sum_{\gamma smn} \langle \alpha i \beta k | s \gamma m \rangle T_{mn}^{(\gamma,s)}(\hat{S}) \langle \alpha j \beta l | s \gamma n \rangle^*. \quad (8)$$

Multiplying (8) by  $T_{m'n'}^{(\gamma')*}(\hat{S})$  and by performing the summation over all symmetry operations  $\hat{S}$  of the group  $G$ , we find

$$\sum_{\hat{S}} T_{ij}^{(\alpha)}(\hat{S}) T_{kl}^{(\beta)}(\hat{S}) T_{m'n'}^{(\gamma')*}(\hat{S}) = \sum_{\hat{S}} \sum_{\gamma smn} \langle \alpha i \beta k | s \gamma m \rangle T_{mn}^{(\gamma,s)}(\hat{S}) T_{m'n'}^{(\gamma',s)*}(\hat{S}) \langle \alpha j \beta l | s \gamma n \rangle^* \quad (9)$$

from which, taking into account the orthogonality property for the irreducible representations (3), we finally obtain

$$\sum_s \langle \alpha i \beta k | s \gamma m \rangle \langle \alpha j \beta l | s \gamma n \rangle^* = \frac{n_\gamma}{g} \sum_{\hat{S}} T_{ij}^{(\alpha)}(\hat{S}) T_{kl}^{(\beta)}(\hat{S}) T_{mn}^{(\gamma)*}(\hat{S}). \quad (10)$$

Eq. (10) can be utilized to derive all or individual CG coefficients which are associated with the three irreducible representations  $T^{(\alpha)}$ ,  $T^{(\beta)}$  and  $T^{(\gamma)}$ , respectively. This is achieved by applying the following scheme, for instance. If we consider first  $i = j$ ,  $k = l$  and  $m = n$ , at least one non-zero coefficient can be calculated up to its phase. From this coefficient, others are obtained, including the relative phase, by keeping the parameters  $i$ ,  $k$  and  $m$  fixed and varying only the indices  $j$ ,  $l$  and  $n$ . In the BETHE program, we follow the phase convention by Altmann and Herzog [6]. Using such a step-wise variation of the indices  $j$ ,  $l$ , ... it is clear, of course, that the individual CG coefficients are obtained only after the whole matrix of CG coefficients has been constructed before.

In general, the CG coefficients arise whenever a symmetry-adapted basis is needed for the (direct) product representation of two or more irreducible representations. Let us suppose that the functions  $\{\psi_i^{(\alpha)}, i = 1, \dots, n_\alpha\}$  and  $\{\psi_k^{(\beta)}, k = 1, \dots, n_\beta\}$  form orthogonal bases of the irreducible representations  $T^{(\alpha)}$  and  $T^{(\beta)}$ , respectively. Then, we may construct a set of product functions  $\{\psi_m^{(\gamma)}, m = 1, \dots, n_\gamma\}$

$$\psi_m^{(\gamma)} = \sum_{ik} \langle \alpha i \beta k | s \gamma m \rangle \psi_i^{(\alpha)} \psi_k^{(\beta)} \quad (11)$$

which transform according to the irreducible representation  $T^{(\gamma)}$ , i.e. form a basis for this representation. From the linear combination (11), a number of important properties can be seen for the CG coefficients. Since the product functions  $\psi_i^{(\alpha)} \psi_k^{(\beta)}$  form an orthogonal set (due to construction), the function  $\psi_m^{(\gamma)}$  can also be orthonormalized. Therefore, the CG coefficients obey the two

Table 1

Main commands of the BETHE program. A more detailed description of these procedures is given in the user-manual `Bethe-commands.pdf` which is distributed with the code

<code>Bethe_decompose_representation()</code>	Returns the irreducible representations which are contained in some given (reducible) representation of the group.
<code>Bethe_group()</code>	Provides the basic group data and notations.
<code>Bethe_group_direct_product()</code>	Returns the <i>direct product</i> of two or more irreducible representations.
<code>Bethe_group_irrep()</code>	Returns the matrices of the irreducible representations.
<code>Bethe_group_representation()</code>	Calculates different types of representations of a group as they occur frequently in the literature.
<code>Bethe_CG_coefficient()</code>	Generates the CG coefficient $\langle \alpha i \beta k   s \gamma m \rangle$ if all the representations and indices are given explicitly.
<code>Bethe_CG_matrix()</code>	Generates a whole array of CG coefficients $\{\langle \alpha i \beta k   s \gamma m \rangle\}$ for the three irreducible representation $\alpha$ , $\beta$ , and $\gamma$ , respectively.
<code>Bethe_CGC_are_orthogonal()</code>	Tests whether the CG coefficients satisfy the orthogonality relations (12), (13).

orthogonality relations

$$\sum_{ik} \langle \alpha i \beta k | s' \gamma' m' \rangle^* \langle \alpha i \beta k | s \gamma m \rangle = \delta_{\gamma' \gamma} \delta_{s' s} \delta_{m' m}, \quad (12)$$

$$\sum_{\gamma sm} \langle \alpha i \beta k | s \gamma m \rangle \langle \alpha i' \beta k' | s \gamma m \rangle^* = \delta_{ii'} \delta_{kk'}. \quad (13)$$

Moreover, by applying these orthogonality relations, we also obtain the transformation

$$\psi_i^{(\alpha)} \psi_k^{(\beta)} = \sum_{sm} \langle \alpha i \beta k | s \gamma m \rangle^* \psi_m^{(\gamma)}, \quad (14)$$

which is the inverse to Eq. (11) from above and refers to a ‘de-coupling’ of the subsystems in a quantum mechanical treatment.

### 3. Extension of the BETHE program

The general setup of the BETHE program need not to be explained here in much detail as it has been described in two previous papers [8,9]. Instead, we shall mainly discuss those features of the program which are required in order to make use of the code. Originally, BETHE was designed with the intention to provide a computer algebraic tool which facilitates the use of the point group symmetry (and theory) in chemistry and physics. This program is based on a set of MAPLE procedures which are available for interactive work and for constructing new commands at some higher level of the hierarchy.

In order to support the generation of CG coefficients for the point and double groups, a number of new procedures have been developed recently. The procedure `Bethe_CG_matrix()`, for instance, supports the generation of a whole matrix array of CG coefficients, while the procedure `Bethe_CG_coefficient()` just provides some individual coefficient. The procedures `Bethe_CGC_are_orthogonal()`, moreover, enables one to perform a quick test of whether the calculated CG coefficients satisfy the orthogonality properties as described above. Table 1 lists all important procedures of the BETHE program which are needed for the generation of CG coefficients. A more detailed description of these procedures is given in the file `Bethe-commands.pdf` which contains a quick reference of all user-relevant commands and which is provided together with the code.

As before, the program is distributed as a single `Bethe.tar` file of the BETHE root directory which contains the source code library, the file `.mapleinit` and a short guide for the installation. Having adapted the `.mapleinit` file in the home directory of the user (as briefly explained in a `Read.me` file of the program), the BETHE program can be invoked like any other module of MAPLE. By using the command `with(Bethe)`, the user may load all procedures and initialize the internal settings of the BETHE program:

```
> with(Bethe);

Welcome to Bethe!
```

### 4. Examples: Generation of the CG coefficients

To demonstrate the capabilities of the BETHE program, let us briefly demonstrate the computation of CG coefficients as it appears in practice. These examples describe the generation of two individual CG coefficients as well as of a whole matrix of these coefficients. In order to obtain these coefficients, of course, some group data are required and it is shown how to derive them from the program.

Let us consider the tetrahedral point group  $T_d$ . The symmetry of this group is approximately fulfilled, for instance, by the methane molecule ( $\text{CH}_4$ ), carbon tetrachloride ( $\text{CCl}_4$ ) as well as by a few others. To generate the CG coefficients for the group  $T_d$ , we first need to know the irreducible representations of the group. In the BETHE program, these irreducible representations are denoted by some string identifiers and are obtained simply by

```
> wa := Bethe_group(Td, irreps);

wa := ["A1", "A2", "E", "T1", "T2"]
```

In the output above, the first two strings "A1" and "A2" refer to one-dimensional irreducible representations, "E" to a two-dimensional one, while "T1" and "T2" are three-dimensional irreducible representations. From these irreducible representations, for example, we may consider the direct product  $A_1 \otimes E$  and ask for its irreducible components

```
> wb := Bethe_group_direct_product(Td, "A1", "E");

wb := ["E"]
```

which shows that this product is irreducible by itself as easily seen from the character of the individual representations. Since  $A_1$  is the totally symmetric representation, it does not change the character of any other representation. Therefore, to generate the CG coefficients  $\langle \alpha\beta k | sym \rangle$  of  $T_d$  only the dimension of the representations need to be taken into account in order to specify the indices  $i$ ,  $k$  and  $m$ , respectively. The dimension of an irreducible representation can be obtained by using `Bethe_group_irrep()` with the keyword *dimension*; moreover, the parameter  $s$  enumerates the multiplicity of the irreducible representation  $T^{(\gamma)}$  and refers to the integers 1, 2,  $a_\gamma$ , where  $a_\gamma$  was defined above. If the representation  $T^{(\gamma)}$  is contained more than once in the direct product  $T^{(\alpha)} \otimes T^{(\beta)}$ . With these restrictions in mind, we can calculate for instance the two CG coefficients  $\langle A_1 1 E 1 | 1 E 1 \rangle$  and  $\langle A_1 1 E 1 | 1 E 2 \rangle$  by

```
> wc_1 := Bethe_CG_coefficient(Td, "A1", 1, "E", 1, 1, "E", 1);
wc_2 := Bethe_CG_coefficient(Td, "A1", 1, "E", 1, 1, "E", 2);

wc_1 := 1

wc_2 := 0
```

and similarly for the second dimension of the representation  $E$  with  $m = 2$ , i.e. the CG coefficients  $\langle A_1 1 E 2 | 1 E 1 \rangle$  and  $\langle A_1 1 E 2 | 1 E 2 \rangle$ , respectively. Of course, the procedure would terminate with a proper ERROR message if either one of the irreducible representations or the corresponding indices is not allowed for the group given.

The choice of the irreducible representation  $A_1$  and  $E$  in the direct product above is very simple and, perhaps, no explicit computations are needed in this case. A less trivial case concerns the direct product  $E \otimes E$  which gives rise to a 4-dimensional representation and which must be reducible due to the output above. Indeed, the irreducible components of this product are given by

```
> wd := Bethe_group_direct_product(Td, "E", "E");

wd := ["A1", "A2", "E"]
```

or, symbolically,  $E \otimes E = A_1 \oplus A_2 \oplus E$ . Using the conventions from above, we can calculate the CG coefficients  $\langle E 2 E 1 | 1 A_2 1 \rangle$  and  $\langle E 2 E 1 | 1 E 1 \rangle$

```
> we_1 := Bethe_CG_coefficient(Td, "E", 2, "E", 1, 1, "A2", 1);
we_2 := Bethe_CG_coefficient(Td, "E", 2, "E", 1, 1, "E", 1);

we_1 := - 1/2
we_2 := 0
```

and could apply them in further computations.

As mentioned earlier, however, the algorithm for calculating the CG coefficients implies that one first obtains the ‘whole array’ of CG coefficients for the given combinations of irreducible representations  $\alpha$ ,  $\beta$ , and  $\gamma$  of the group before the individual coefficient can be extracted. In many applications, therefore, it seems beneficial to calculate (and obtain) all the corresponding CG coefficients together prior to other calculations. This option is supported by the command `Bethe_CG_matrix()` which returns the array of CG coefficients as associated with the product representation. For the direct product  $E \otimes E$ , for instance, we obtain

```
> wf := Bethe_CG_matrix(Td, "E", "E");
```

Table 2  
Clebsch–Gordan coefficients for the  $T_d$  group product  $E \otimes E$

$\alpha$ : $E$ $i$	$\beta$ : $E$ $k$	$\gamma$ : $m$ :	$A_1$ 1	$A_2$ 1	$E$ 1	$E$ 2
1	1		0	0	0	1
1	2		$\sqrt{2}/2$	$\sqrt{2}/2$	0	0
2	1		$\sqrt{2}/2$	$-\sqrt{2}/2$	0	0
2	2		0	0	1	0

```

wf := [
  [ 0      0      0      1]
  [
  [ 1/2    1/2
  [2      2
  [-----
  [ 2      2
  [ 1/2    1/2
  [2      2
  [----- - -----
  [ 2      2
  [
  [ 0      0      1      0]

```

an array of CG coefficients. The columns of this array can be labeled by the basis functions of the direct product in the same sequence as obtained by the procedure `Bethe_group_direct_product()`. The rows of this array refer to the basis functions of the irreducible representations, specified in the input of the procedure `Bethe_CG_matrix()`. It can be understood by means of Table 2. As seen from this table, the left column of the table shows four basis functions of the direct product  $E \otimes E$  ( $\alpha i = \{E1, E2\}$ ,  $\beta k = \{E1, E2\}$ ,  $\alpha i \beta k = \{E1E1, E1E2, E2E1, E2E2\}$ ), while the header of the table gives the bases of the irreducible representations  $\gamma m = \{A_11, A_21, E1, E2\}$ . The main body of the table then shows the CG coefficients  $\langle E1E1|E1 \rangle = 0$ ,  $\langle E1E1|E2 \rangle = 1$ ,  $\langle E1E2|A_11 \rangle = \sqrt{2}/2$ , etc. From this table, therefore, all the basis functions of the direct product  $E \otimes E$  can be obtained. For instance, the second and third columns of the body of Table 2 gives us the wave functions  $\psi_1^{A_2}$  and  $\psi_1^E$ .

$$\psi_1^{A_2} = \frac{\sqrt{2}}{2} \psi_1^E \psi_2^E - \frac{\sqrt{2}}{2} \psi_2^E \psi_1^E,$$

$$\psi_1^E = \psi_2^E \psi_2^E$$

etc. In addition, we can test the orthogonality (relations) of the CG coefficients by calling the procedure

```

> Bethe_CGC_are_orthogonal(wf);

true

```

on the output from above, i.e. on the array of CG coefficients.

Up to the present, we have restricted our examples on the (vector) point groups and, in particular, the group  $T_d$ . Instead of the vector groups, the CG coefficients are sometimes needed also for the *double* groups and the irreducible representations which are associated to these groups. A more detailed discussion of the representations of the double groups can be found in Ref. [12]. Similarly as before, we can obtain the string identifiers of the irreducible representations of the double groups by using the keyword *double*

```

> wa_dbl := Bethe_group(Td, irreps, double);

wa_dbl := ["A1", "A2", "E", "T1", "T2", "E1/2", "E5/2", "F3/2"]

```

and can use these string identifiers to calculate the CG coefficients for the direct product  $E_{1/2} \otimes E_{5/2}$  which contains the irreducible representations  $A_2$  and  $T_2$ . For the irreducible representations  $E_{1/2} \otimes E_{5/2}$ , the array of CG coefficients is given by



```
> wf_dbl := Bethe_CG_matrix(Td, "E1/2", "E5/2");
```

```

      [      1/2      1/2 ]
      [      2      2 ]
      [  0  ----  0  ---- ]
      [      2      2 ]
      [      ]
      [  1/2      1/2 ]
      [  2      2 ]
      [  ----  0  ----  0 ]
      [  2      2 ]
wf_dbl := [      ]
      [  1/2      1/2 ]
      [  2      2 ]
      [ - ----  0  ----  0 ]
      [  2      2 ]
      [      ]
      [      1/2      1/2 ]
      [      2      2 ]
      [  0  ----  0  ---- ]
      [      2      2 ]

```

Rows of the array `wf_dbl` can be marked by the basis functions of the direct product  $E_{1/2} \otimes E_{5/2}$  ( $\alpha\beta k = \{E_{1/2}1E_{5/2}1, E_{1/2}1E_{5/2}2, E_{1/2}2E_{5/2}1, E_{1/2}2E_{5/2}2\}$ ) and the columns correspond to the basis functions  $\gamma m = \{A_21, T_21, T_22, T_23\}$ . Again, the individual CG coefficient can be obtained for the double group similarly like above by using the procedure `Bethe_CG_coefficient()`.

## 5. Physical applications of the Clebsch–Gordan coefficients

In the examples above, we have shown how the CG coefficients can be generated by means of the BETHE program. However, these coefficients would probably be of little interest without their ‘physical meaning’ in the description of many-particle quantum systems and, in particular, for many-electron atoms (or ions) which are embedded in some crystal field. For such atoms, the level splitting and observed spectra can be characterized by means of the irreducible representations of the symmetry group of the crystal. Moreover, the CG coefficients of this group help to construct the wave functions of the embedded atom. In this section, therefore, we shall demonstrate how BETHE can be used to analyze the level splitting of atoms in a tetrahedral crystal environment. To facilitate the description let us briefly recall, however, how group theory occurs in the quantum mechanical treatment of atoms embedded into a crystal field.

### 5.1. Symmetry in quantum mechanics

Many important problems concerning the electronic structure of atoms, molecules and solids are described by starting from the Schrödinger equation  $\hat{H}\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r})$ . The eigenfunctions  $\psi_i(\mathbf{r})$  of the Hamiltonian  $\hat{H}$  are known as the wave functions of the quantum system considered and contain the whole quantum mechanical knowledge about the system and its behavior. If it has symmetry, however, group theory may help in the treatment by analyzing the properties of Hamiltonian and its invariance under certain group transformation. Here, the invariance of a Hamiltonian with regard to a particular symmetry group means that the states of the quantum system must “belong” to this group and that the eigenvalues  $E_i$  are associated with a certain representation of the group, while the corresponding eigenfunctions  $\psi_i(\mathbf{r})$  form a basis of this representation. Hence, the wave functions of a symmetric quantum system are the basis functions of the irreducible representations of the corresponding symmetry group.

Now, let us consider two subsystems with coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , respectively, whose wave functions transform under the group  $G$ , i.e. that the (one-particle) functions  $\psi_j^{(\alpha)}(\mathbf{r}_1)$  and  $\psi_l^{(\beta)}(\mathbf{r}_2)$  form bases for irreducible representations  $T^{(\alpha)}$  and  $T^{(\beta)}$ . Of course, the combined system with the (antisymmetrized) product functions  $\psi_j^{(\alpha)}(\mathbf{r}_1)\psi_l^{(\beta)}(\mathbf{r}_2)$  is then described by the reducible representation  $T^{(\alpha\otimes\beta)}$  and remains degenerate in this subspace (of the overall Hilbert space) if the two subsystems do not interact with one another. An interaction of the subsystems, in contrast, usually leads to a level splitting of the energies of the total system and to a ‘reduced’ degeneracy which can be obtained from Eq. (4). Since, in general, the direct product  $T^{(\alpha\otimes\beta)}$  is reducible into the irreducible components  $T^{(\gamma)}$  [cf. Section 2.1], the wave functions  $\psi_m^{(\gamma)}(\mathbf{r}_1, \mathbf{r}_2)$  of the total system (i.e. the basis functions of  $T^{(\gamma)}$ ) can be obtained as linear combinations of  $\psi_i^{(\alpha)}(\mathbf{r}_1)\psi_k^{(\beta)}(\mathbf{r}_2)$  by using the CG coefficients

$$\psi_m^{(\gamma)}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ik} \langle \alpha\beta k | \gamma m \rangle \psi_i^{(\alpha)}(\mathbf{r}_1) \psi_k^{(\beta)}(\mathbf{r}_2). \quad (15)$$



Physically, the parameters  $|\langle \alpha i \beta k | s \gamma m \rangle|^2$  gives the probability to find each of the subsystems in the one-particle states  $\psi_i^{(\alpha)}(\mathbf{r}_1)$  and  $\psi_k^{(\beta)}(\mathbf{r}_2)$ , while the total system is described by the wave function  $\psi_m^{(\gamma)}(\mathbf{r}_1, \mathbf{r}_2)$ . Therefore, the CG coefficients have to be normalized by the relation

$$\sum_{ik} |\langle \alpha i \beta k | s \gamma m \rangle|^2 = 1. \quad (16)$$

The proper normalization of the CG coefficients ensures that, if the product functions form an orthonormal set themselves, the functions  $\psi_m^{(\gamma)}(\mathbf{r}_1, \mathbf{r}_2)$  are also normalized.

### 5.2. Group-theoretical classification of levels in crystal fields

As discussed above, the level splitting of an atom embedded in a crystal field can be analyzed by means of the point group symmetry of the surrounding crystal. In fact, the atom-crystal interaction usually results into an additional level splitting of the atomic energy levels whose details can be found by using the (irreducible) representations and CG coefficients of the underlying symmetry group. Although, of course, we do not know the irreducible representations from the very beginning, we may use them to *classify* the split atomic levels in terms of the irreducible representations of the symmetry group of the crystal.

To lay down the grounds for further discussions, let us start here from the case of (effective) one-electron atom embedded in a crystal. If we omit the spin of the electron here, the (one-electron) angular states of the free atom

$$Y_{lm}(\vartheta, \varphi) = \frac{1}{2\pi} \Theta_{lm}(\vartheta) e^{im\varphi} \quad (17)$$

belong to the group  $R_3$  (the continuous group of rotations of the sphere with fixed center) and, hence, are  $(2l + 1)$  times degenerate due to the orbital angular momentum  $l$  of the electron [11]. Of course, the symmetry of the  $R_3$  rotation group is higher than the symmetry of any finite point group. The decrease in symmetry, when the atom is introduced into a crystal, then leads to the splitting of the atomic energy levels. The classification of the atomic states in the crystal field is based on the decomposition of the  $R_3$  group representation  $T$  as generated by the functions  $Y_{lm}(\vartheta, \varphi)$  into its irreducible components  $T^{(\gamma)}$  of the crystal symmetry point group. This gives rise to the decomposition

$$T = \sum_{\gamma} a_{\gamma} T^{(\gamma)}, \quad (18)$$

analogous to Eq. (4) and where  $a_{\gamma}$  denotes how often the irreducible representation  $T^{(\gamma)}$  occurs in the representation  $T$ . An explicit formula for the coefficient  $a_{\gamma}$  as well for the construction of the  $R_3$  group representation  $T$  can be found in many textbooks [7, 10, 11]. The irreducible components as obtained by the decomposition (18) serve to classify the one-electron states in the crystal field. In particular, the sum over  $\gamma$  of the integers  $a_{\gamma}$  shows the number of atomic energy levels as it will occur for the  $(2l + 1)$ -fold degenerate level of the free atom. Moreover, the degeneracy of every level is seen from the dimension of corresponding component  $T^{(\gamma)}$ .

For atoms in a crystal field, the classification of the atomic levels discussed above can be generalized to the case of many-electron atoms and ions. In this case, however, the interelectron interaction has usually to be taken into account as well. Depending on the strength of the crystal field with respect to the interelectron interaction, three cases of *weak*, *intermediate* and *strong* crystal fields are often distinguished. In the following, we will restrict our discussion to a strong crystal field. In this case, the influence of the crystal field should be considered separately for each electron *before* the interelectron interaction is taken into account as an additional perturbation. According to our discussion above, therefore, we should construct the  $R_3$  group representation for the angular part  $Y_{lm}$  of each electron independently of the occupation of the other electrons. To account for several electrons in the atom, we then take the direct product of these representations and decompose it for the symmetry group of the crystal in order to obtain information about the number and degeneracy of many-electron states in a strong crystal field. When the states of the electrons in the crystal field are classified in terms of the irreducible representations, the wave functions of these states can be constructed by use the CG coefficients (see Eq. (15)).

### 5.3. Example: Two-electron ions in a crystal environment

In order to demonstrate how the classification of the level splitting and the construction of the wave functions can be performed by the BETHE program, let us consider the  $(\text{MnO}_4)^{3-}$  molecular ion. For this ion, the optical and magnetic properties have been discussed rather often in the literature [3, 13]. Scott and coworkers [3], for instance, measured the optical absorption spectra of the  $(\text{MnO}_4)^{3-}$  molecular ion in a strong tetrahedral crystal field; their spectra show a number of bands which are clearly related to the level splitting in such a crystal environment. Different theoretical methods have been applied to obtain a theoretical interpretation of these measurements, including the molecular orbital approach by Deghoul et al. [13] based upon the density-functional theory,

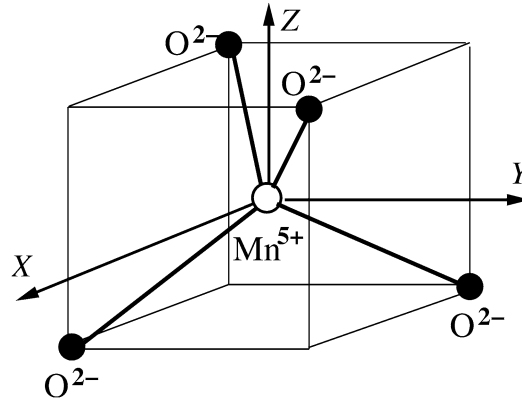


Fig. 1. Tetrahedral configuration of the molecular ion  $(\text{MnO}_4)^{3-}$ .

in order to calculate the parameters of the terms. To understand such spectra, a group theoretical classification of the terms and the construction of the wave function can be performed using the CG coefficients as defined above.

In the  $(\text{MnO}_4)^{3-}$  molecular ion, the  $3d^2$  configuration ion of  $\text{Mn}^{5+}$  is fourfold coordinated with  $\text{O}^{2-}$  ions (see Fig. 1). As seen from the figure, therefore, the  $\text{O}^{2-}$ -environment obeys a tetrahedral  $T_d$  symmetry. In accordance to the strong-field regime, the interelectronic interaction can be omitted and (the characters of) the representation, generated by the  $Y_{lm}$  part of the single electron wave function, have to be found

```
> wa := Bethe_group_representation(Td, Ylm, 2);

wa := [5, 1, 1, 1, -1, -1, -1, -1, -1, -1, -1, -1,
      -1, -1, -1, -1, -1, -1, 1, 1, 1, 1, 1, 1]
```

Here,  $T_d$  is the label of the symmetry group of the surrounding crystal,  $Y_{lm}$  a keyword which defines the kind of representation, and the third argument 2 determines the orbital quantum number  $l$  of the  $d$ -electron. The list of numbers  $wa$  stands for the characters of the representation which refer to the symmetry operations of the group  $T_d$  in the same sequence as obtained by the procedure `Bethe_group(Td, operators)`. The corresponding list of the explicitly calculated (five-dimensional) matrices of this representation could be obtained also by adding the keyword *matrix* to the list of parameters,

```
> wa_m := Bethe_group_representation(Td, Ylm, 2, matrix):
```

but are omitted here as they are not required for the further analysis. Using the (list of) characters  $wa$  from above, we find the irreducible components of this induced representation by

```
> wb := Bethe_decompose_representation(Td, wa);

wb := ["E", "T2"]
```

a result which shows immediately that the five-fold degenerate level of a single  $d$ -electron is split within a tetrahedral environment into the two-fold degenerate level  $E$  and the three-fold level  $T_2$ . In the strong field regime, these single-electron states give rise to the three two-electron configurations  $T_2T_2$ ,  $ET_2$  and  $EE$ . Let us restrict here to the latter case with the two electron belonging each to the irreducible representation  $E$ , i.e. to the product space  $E \otimes E$  for the two-electron ion. Since the wave functions of the two-electron states must transform as the irreducible components of this direct product  $E \otimes E = A_1 \oplus A_2 \oplus E$  [cf. Section 4], we see that the 4-fold degenerate level  $E \otimes E$  will be split in a strong-field tetrahedral environment into the two nondegenerate levels  $A_1$  and  $A_2$  as well as a doubly degenerate level  $E$  (of the two-electron system). In order to construct also the wave functions which correspond to these levels, the matrix  $wf$  of the CG coefficients from Section 4 can be utilized immediately. For instance, the wave functions of the levels  $A_1$  and  $A_2$  can be expressed from the product functions of two (one-electron)  $E$  states by

$$\psi_1^{A_1}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\sqrt{2}}{2} \psi_1^E(\mathbf{r}_1) \psi_2^E(\mathbf{r}_2) + \frac{\sqrt{2}}{2} \psi_2^E(\mathbf{r}_1) \psi_1^E(\mathbf{r}_2),$$

$$\psi_1^{A_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\sqrt{2}}{2} \psi_1^E(\mathbf{r}_1) \psi_2^E(\mathbf{r}_2) - \frac{\sqrt{2}}{2} \psi_2^E(\mathbf{r}_1) \psi_1^E(\mathbf{r}_2).$$

Similarly, we could construct as well the wave functions for the degenerated two-particle level  $E$ .

## 6. Summary and outlook

The BETHE program has been grown in several directions during the last few years. It presently supports the 72 most widely applied point (and corresponding double) symmetry groups and can be used to solve a number of the quantum physical problems related to the symmetry of molecules, clusters and solids. With the present extension of the program, we provide a number of procedures to calculate the CG coefficients for point and double groups. These coefficients help to analyze the splitting of the atomic energy levels in the crystal field. The interactive design of program presented may help the user in following the literature and in daily research work.

Since the BETHE program has been found useful for practical applications, it will be developed in the future. There are several extensions, which would make BETHE a much more powerful tool. In particular the problem of molecular symmetry distortion, known also as *Jahn–Teller effect*, is intended to be implemented into the BETHE package. In this problem, a theoretical analysis of the molecular adiabatic potential has to be performed by using symmetry considerations about the molecules. In addition, a more detailed treatment of the atomic energy levels into the crystal field (taking in account also the spin–orbit interaction) would be useful for studying the magnetic properties of materials. Finally, the further development of the vibrational analysis of the molecule (namely, the treatment of the nonfundamental vibrational transitions as well as of related problems, such as resonance Raman spectroscopy or the polarization of the vibrational modes and many others), which was started originally in Ref. [8], would be certainly desirable. Besides this short list of topics, there are further extensions which would make the BETHE program a more attractive tool and for which suggestions from the users are very welcome.

## Acknowledgements

One of the authors (E.R.) gratefully acknowledges financial support from Kassel University. This work has also been supported by the German Research Council under the contract FR 1251/8-1:2.

## References

- [1] H.J. Reyher, N. Hausfeld, M. Pape, J. Phys. Condens. Matter 12 (2000) 10599.
- [2] F. Fauth, E. Suard, E. Caignaert, I. Mirebeau, Phys. Rev. B 66 (2002) 184421.
- [3] M. Scott, B. Henredson, H. Gallagher, T. Han, J. Phys. Condens. Matter 9 (1997) 9893.
- [4] I. Bersuker, The Jahn–Teller Effect and Vibronic Interaction in Modern Chemistry, Plenum Press, New York, 1984.
- [5] S. Piepho, P. Schatz, Group Theory in Spectroscopy, Wiley-Interscience Publication, New York, 1983.
- [6] S. Altmann, P. Herzig, Point-Group Theory Tables, Clarendon Press, Oxford, 1994.
- [7] A. Cotton, Chemical Application of Group Theory, Wiley-Interscience Publication, New York, 1990.
- [8] K. Rykhinskaya, S. Fritzsche, Comput. Phys Comm. 162 (2004) 124–142.
- [9] K. Rykhinskaya, S. Fritzsche, Comput. Phys Comm. (2005), in press.
- [10] J.P. Elliott, P.G. Dawber, Symmetry in Physics, vols. I and II, The MacMillan Press Ltd., London, 1990.
- [11] B. Tsukerblat, Group Theory in Chemistry and Spectroscopy, Academic Press, London, 1994.
- [12] K. Balasubramanian, Relativistic Effects in Chemistry, Part A, John Wiley & Sons, New York, 1997.
- [13] F. Deghoul, H. Chermette, F. Rogemond, R. Moncorge, C. Stückl, C. Daul, Phys. Rev. B 60 (4) (1999) 2404.