A Computer-Algebraic Approach to the Study of the Symmetry Properties of Molecules and Clusters

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Zusammenfassende deutsche Darstellung der in englischer Sprache abgefassten Doktorarbeit:

Eine Computer-algebraische Methode zur Untersuchung der Symmetrie-Eigenschaften von Molekülen und Clustern

Ziel dieser Dissertation war, mit Hilfe computer-algebraischer Methoden ein Werkzeug zur Untersuchung der Symmetrieeigenschaften von Molekülen und Clustern zu entwickeln. Das MAPLE Paket BETHE gestattet es, gruppentheoretische Daten zu extrahieren und zu manipulieren und damit Symmetrieanwendungen zu vereinfachen (Kap. 2). Zunächst werden die Vorteile von BETHE beim Erzeugen der gruppentheoretischen Daten gezeigt. In der aktuellen Version können die Symmetriedaten für 72 häufig benutzte Punktgruppen sowie der zugehörigen Doppelgruppen erzeugt werden. Der Schwerpunkt dieser Arbeit liegt im Bereich der Anwendungen dieses Programmpakets in der Physik der Moleküle und Cluster (Kap. 3). Neben der Untersuchung der optischen Eigenschaften von Molekülen in Abhängigkeit von der jeweiligen Symmetriegruppe wird auch gezeigt, wie BETHE zum Verständnis der Feldaufspaltung in Kristallen beitragen kann und wie die zugehörigen Wellenfunktionen berechnet werden können. Einige der heutigen Fähigkeiten von BETHE werden an Hand mehrerer ausgearbeiteten Beispielen gezeigt. Obwohl wir nicht auf alle Details ausführlich eingehen können zeigen diese Beispiele doch die umfassenden Möglichkeiten computer-algebraischer Techniken bei der Untersuchung symmetrieabhängiger Eigenschaften von Molekülen und Clustern.

In dieser Dissertation wurde besonderer Wert auf die Vielseitigkeit des BETHE Pakets gelegt, damit neue Anwendungen problemlos implementiert werden können (Kap. 4). Diese Erweiterungen sind sinnvoll, da die schwierigsten Teile dieser künftigen Anwendungen bereits im BETHE Paket enthalten sind. So werden zum Beispiel die Vibrationskoordinaten (Normalkoordinaten) als Funktion der kartesischen Einheitsvektoren, die für die Wilsonsche Methode benötigt werden, oder auch die Clebsch-Gordan Koeffizienten, die für das Jahn-Teller-Problem benötigt werden, bereits in der vorliegenden Programmversion erzeugt. Für das Jahn-Teller-Problem scheint der Gebrauch des CA Werkzeugs sogar unvermeidlich zu sein, weil dieses Problem einen analytischen Zugang zum adiabatischen Potential erfordert und deshalb durch einen numerischen Algorithmus nicht behandelt werden kann.

Die Fähigkeiten des BETHE Pakets werden durch die oben erwähnten Anwendungen noch nicht ausgeschöpft. Es gibt verschiedene Richtungen, in die das BETHE Programm in der Zukunft weiterentwickelt werden kann. Beispiele hierfür sind (i) die Untersuchung magnetischer Eigenschaften von Festkörpern und von (ii) optischen Übergängen. Die Implementierung dieser Erweiterungen wird das BETHE Programm zu einem noch flexibleren und mächtigeren Werkzeug machen.

Contents

Chapter 1

Introduction

Since the middle of the last century the numerical computational techniques have been widely applied in all branches of modern physics and chemistry. Even in the theoretical physics, where the analytical approach was dominated for a very long time, the numerical computations have become an accepted instrument. During the last decades, however, the use of computers in science makes turn from purely numerical to the *symbolic* or *computer-algebraic* (CA) computations. The CA solutions, or combinations of the new symbolic techniques with the previously developed numerical algorithms, are very promising. Therefore, they seem to be increased in the nearest future. The reason for such an increase is the number of advantages of the computer algebra in the theoretical research. These advantages are

- the reach mathematical basis, built into the CA systems, i. e. knowledge of all the mathematical rules, which are necessary to treat the mathematical expressions;
- fast and reliable symbolic manipulation;
- interactive style of work, i. e. the possibility to work "step-by-step" and, therefore, to examine the computation process on different stages;

These (as well as many other) advantages have led CA to find its way to many different areas of physics and chemistry, including the quantum chemistry, biophysics and many others. One of the areas, in which the use of CA is highly desirable, is the treatment of many-particle systems, such as molecules and clusters. The high complexity of these systems restricts the use of numerical computations and requires some additional simplifications, which are easier to realize within the CA approach.

Since most of the molecules and clusters possess a symmetry, the powerful simplification can be followed from the symmetry consideration. Moreover, sometimes symmetry appears even irreplaceable in order to recognize the properties and behavior of molecules and clusters. The basic mathematical tool for dealing with symmetry is the *group theory*. During the last fifty years this theory has found its way into almost all branches of modern physics and chemistry [1, 2] and has helped achieve simplifications of great power. In practice, however, the application of the molecular symmetries in physics and chemistry may become rather cumbersome. Although, nominally, the basic relations of group theory are widely known, there are several shortcomings

which make the access to the group data inefficient and difficult to use. Apart from an often very compressed compilation of the group data in some tables or appendixes of textbooks, only parts of these data are usually displayed explicitly and without providing the user with the additional algorithms and abbreviations. Even in Ref. [3], which is found as the most complete tabulation of the group-theoretical data, some parameters are not easy to extract. Moreover, the number of different notations, used in the literature for the group-theoretical parameters, also may to make difficult the access to the group data. These reasons make the practical use of the group theory very difficult.

An alternative and very promising route for dealing with the symmetry and the group theory is offered by computer-algebraic systems today. Several powerful CA systems, such as MATHEMATICA or MAPLE, are available and can be utilized to develop new algorithms and tools for applying group–theoretical methods in physics and chemistry. A number of CA packages, which support the definition and manipulation of the group-theoretical parameters, has been created. For instance, GAP [4], SYMMGRP.MAX [5] and many others. However, most of these packages are developed to provide the mathematical basis of the symmetry and are not appropriate to be used in the practical research.

Nevertheless, there is a big number of physical and chemical tasks, in which the CA approach can be very helpful. For instance,

- search for symmetries and appropriate molecular coordinates;
- derivation of the normal coordinates and modes of molecules and clusters;
- derivation of selection rules and spectral activities for the vibrational transitions of the molecule;
- level spitting of atoms in external crystal fields;
- studying of the magnetic properties of material;
- analysis of vibronic interaction and the Jahn-Teller effect;
- construction of molecular symmetry orbitals for quantum computations;
- use of Racah's algebra;

and many others. The features of the CA approach to some of these tasks are briefly analyzed in Ref. [6]. In order to develop the use of computer algebra for dealing with the symmetry application, we developed the program BETHE, which is described in this thesis work. This program has been created within the framework of MAPLE. It provides the group-theoretical data for most frequently applied point and double groups as well as the manipulation of these data (see Chapter 2). Using the group-theoretical data, the program also supports several applications of the symmetry. In this thesis work only three applications are considered: (i) the generation of the molecular geometry and symmetries (Section 3.1); (ii) the vibrational analysis of the molecule (Section 3.2), which includes the generation of the spectroscopy selection rules for the nonfundamental vibrational transitions; and (iii) the analysis of the atomic behavior and

splitting of atomic terms due to the external crystal field (Section 3.3). The last task includes a big number of particular cases (one- and many-electron atom, weak and strong crystal field, spin-orbit interaction and others).

The important feature of the BETHE program is its flexible structure, which allows to adapt it for a wide range of applications. Therefore, some ideas for the possible future applications are collected in Chapter 4. For instance, the program realization of the Wilson's method is suggested in Section 4.1. This method continues the vibrational analysis of the molecule. It helps to define the relationship between the vibrational frequencies and molecular force constants. Apart from the Wilson's method, there is a well known phenomenon from molecular physics, known as the *Jahn–Teller effect*. This effect consists in the spontaneous distortion of a molecule due to its vibrational motion and depends on the interaction between the electrons and the nuclei. The theory of this effect is based, again, upon a group–theoretical analysis of the adiabatic potential of the (polyatomic) molecule when the electronic states become nearly degenerated. The question about the *geometrical stability* of the molecule is then related to the search of the minimum of the potential surface and can be answered by means of the BETHE package. The theoretical background of the Jahn-Teller effect and suggestions for its program realization are described in detail in Section 4.2. The summary of results and short outlook can be found in Chapter 5, while the Appendix contains the description of all procedures, implemented into the BETHE. Finally, the three papers on the development of the BETHE package, which have been published (or accepted for publication) during the last years, are included at the end of this thesis work.

Chapter 2

BETHE - A computer-algebraic tool for dealing with symmetry

The BETHE program has been developed to provide a simple and reliable access to the point group data as required by many applications. Following a brief overview about the program, we shall explain below how these data can be manipulated in order to solve some particular tasks. Owing to the interactive design of BETHE, we expect this program of quite common interest, both in teaching the basic elements of the group theory as well as for advanced research studies. Therefore, in this chapter we explain how to use this program in order to extract and manipulate the group data. Dealing with the BETHE is illustrated by a big number of examples.

2.1 Symmetry and the group theory

The group theory is probably one of the most powerful mathematical tools which is used in quantum mechanics and spectroscopy. Being applied to some quantum-mechanical systems, this theory allows to simplify the treatment of these systems. Since the group theory has been worked out a long time ago, here we shall not to go into the mathematical details, but assume the reader to be familiar with basic concepts of the group theory. From the large number of available texts on this theory, we refer the reader to the classical books of Wigner [1], Heine [2], or Elliot and Dawber [7] and many others. Therefore, in this section we give only a brief outlook of the group theory in order to recall the terminology and notation of the following applications.

The symmetry of a physical object is known to be determined by the set of transformations that brings the object to a geometrical configuration, indistinguishable from the original. Such transformations are called typically *symmetry operations*. In some more details, five kinds of symmetry operations are usually distinguished, including (i) the identity operation $\hat{E}$ (which leaves the object as it is), (ii) an $n-$fold rotation $\hat{C}_n$ about some axis, or (iii) the inversion $\hat{i}$ of all coordinates at the origin. Moreover, there are (iv) reflection $\hat{\sigma}$ at some mirror plane, or — in a combined form — (v) n-fold rotations about some axis, followed by a reflection through a plane which is perpendicular to this axis ($\hat{S}_n$). The symmetry operations are associated with three different types of *symmetry elements*, such as a line, plane, or some particular point, with

respect to which one or several symmetry operations can be carried out. The set of symmetry operations, inherent in some physical object, constitute a symmetry group and are known to form (finite) subgroup of the continuous group O_3 of rotations in three-dimensional space [7, 8]. Since the molecule or cluster must not be shifted in the space by carrying out these operators, at least one point has to be fixed in space. Therefore, the groups of operators, described above, are called *point* groups. These groups are of major interest in chemical sciences. The most complete tabulation of the group data has been compiled by Altmann and Herzig [3] and has been utilized as one of the main references in the design of the BETHE program.

While the point groups just allow the geometrical transformation of some object, it is possible to add the concept of electron spin to these groups. These extended groups are usually called *double* groups [8, 9]. They basically arise from the observation that the spin function for a particle with spin s=1/2 is invariant only under the rotation of 4π (around any axis in the space). This means, however, that the rotation $\hat{E}$ by 2π does not give rise to the identity, but only $\hat{E}^2 = \tilde{E}$. Referring to the spin space of the particle, of course, the (new) element $\tilde{E}$ commutes with all rotations $\hat{R}_a$. Hence, for given a group G of such rotations, the corresponding double group $\tilde{G}$ is generated by appending the new elements $\tilde{E}\,\hat{R}_a = \tilde{R}_a,\ a = 1, ..., g$ to the group. As a consequence, the number of symmetry operations is doubled when compared to the number of the corresponding point group, i.e. without spin. Obviously, if a group contains the rotation $\hat{C}_n$ as one of the symmetry operators, then $\hat{C}_n^n = \tilde{E}$ and $\hat{C}_n^{2n} = \hat{E}$ in the case of the double groups. Since the double group is obtained simply by "doubling" the number of symmetry operations (due to the non-identical rotation about 2π), all operator strings appear basically twice for the double group, with one of them having a leading capital letter "R". In the BETHE program we always support both, the point groups and the corresponding double groups. The double groups are important in various chemical applications including, for example, the theory of transition metal ions and in relativistic quantum chemistry. For instance, the generation of molecular symmetry orbitals, supported by the BETHE package [10], makes extensive use the double group parameters.

2.2 Program organization

The BETHE program, created within the framework of MAPLE, has been designed as an interactive tool to facilitate the use of the symmetry group theory in physics and chemistry. The main emphasize was placed on providing a user-friendly tool, which requires neither a detailed knowledges about the theoretical background, nor the abbreviations and notations, used in the literature.

In the present version of the program, BETHE provides the group data for all finite groups of common interest, including the cyclic and their 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, I_h. The table of classification of these groups in terms of the *group families* is presented in Ref. [11]. For each of the groups, mentioned above, we provide the definition of the symmetry operators, the multiplication law, character tables, the matrices of the irreducible representations as well as the numbers of other

Table 2.1: Main commands of the BETHE program.

Bethe_decompose_representation()	Determines the irreducible components of given reducible group representation.
Bethe_group()	Provides the basic point group data and notations.
Bethe_group_chain()	Displays the chain structure of the point group.
Bethe_group_character()	Returns the character of a given irreducible representation and symmetry operation.
Bethe_group_class()	Returns all symmetry operations of the same class.
Bethe_group_direct_product()	Returns the *direct product* of two irreducible representations.
Bethe_group_Euler()	Returns the three Euler angles (α, β, γ) for a given symmetry operation.
Bethe_group_irrep()	Returns the matrix representation of a given irreducible representation and symmetry operation.
Bethe_group_multiplication()	Returns the *product* operation of two symmetry operations.
Bethe_group_parameter()	Specifies the symmetry operations in different parameterizations.
Bethe_group_representation()	Evaluates a few particular group representations as displayed in Table 3.
Bethe_group_subduction()	Returns the irreducible components, which appear in the decomposition of the group Glabel to the lower-symmetry group.
Bethe_group_subduction_O3()	Returns the irreducible components, which appear in the decomposition of the O_3 group representation to the lower-symmetry group.
Bethe_group_symmetry()	Determines the symmetry of a given set of points.
Bethe_group_tabulation()	Prints the group theoretical data in a table format.

parameters. As said before, all these data are supported for both, the point and double groups.

The BETHE program has been organized in a hierarchical order. It includes more than hundred procedures which can be invoked either interactively or simply as a language elements in order to build up commands at some higher level of the hierarchy. In practice, however, only less than 20 procedures need to be known by the user. These procedures are briefly explained in Table 2.1 to provide the reader with the first impression about the BETHE program. In order to distinguish these commands from MAPLE's internal functions, they all start with the prefix `Bethe_`. More detailed information about the arguments and the output of these procedures can be obtained from the Appendix. Therefore, we do not explain most of the procedures in details. Let us only make mention of the command `Bethe_group()`. This command is one of the most important procedures of the BETHE toolbox. It provides all the basic information about a particular group, such as the number and names of the symmetry operations, the number of classes, irreducible representations and many others. The group label (Glabel) is used in this procedure (as well as in many other procedures) as a first argument in order to specify the symmetry group. A list of all presently supported group labels is returned by calling

Table 2.2: Optional arguments of the command `Bethe_group(Glabel,...)`.

Keyword(s)	Output of the procedure
crystallographic	Boolean value *true* for the crystallographic groups or *false*.
crystal_system	Name of the crystallographic system.
cubic	Boolean value *true* for the cubic groups or *false*.
cyclic	Boolean value *true* for the cyclic groups or *false*.
dihedral	Boolean value *true* for the dihedral groups or *false*.
examples	Prints a few examples.
group_table	Prints a summary about all the presently supported point groups.
icosahedral	Boolean value *true* for the icosahedral groups or *false*.
implemented	Boolean value *true* for the implemented group or *false*.
irreps	List of irreducible representation identifiers.
irreps, double	List of irreducible representations identifiers in the double group.
No_Altmann	Number of the tabulation by Altmann & Herzig [3].
No_class	Number of classes.
No_class, double	Number of classes in the double group.
No_irregular	Number of irregular classes.
No_irreps	Number of irreducible representations.
No_irreps, double	Number of irreducible representations in the double group.
No_operators	Number of symmetry operations
No_operators, double	Number of symmetry operations in the double group.
No_regular	Number of regular classes.
operator_details	Prints a description of all symmetry operations.
operators	List of symmetry operation identifiers.
operators, double	List of symmetry operation identifiers in the double group.
proper	Boolean value *true* for proper groups or *false* (improper groups).
spinor_irreps	List of spinor irreducible representation identifiers.
subgroups	List of subgroup labels.
symmetry_elements	Prints a description of all symmetry elements.

the procedure `Bethe_group()` without arguments. A second argument of the `Bethe_group()` command is the keyword, which allows to specify the type of extracted group-theoretical data. All presently supported keywords are displayed in the Table 2.2 in alphabetic order. Of course, the output depends on the given parameters and can be either a number, boolean value, a string, or simply a NULL expression if the procedure just prints some information. Finally, third argument - keyword *double* - may be used to obtain the corresponding double group theoretical data, if appropriate.

Consider, for example, the symmetry group D_{3h} which is obtained from dihedral group D_3 by adding three vertical mirror planes and one horizontal plane. The symmetry of this group is fulfilled approximately by the *eclipsed ethane* molecule C_2H_6 (see Fig. 2.1). The symmetry elements and operations of this group are shown below, as returned by the program.

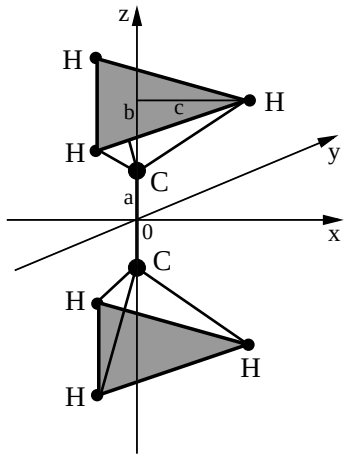

Figure 2.1: Geometry of the eclipsed ethane molecule C_2H_6.

- Symmetry operations of the D_{3h} group:

```
> Bethe_group(D3h, operators);

     ["E", "C3+", "C3-", "C21‘", "C22‘", "C23‘", "S3-", "S3+",
          "sigma_h", "sigma_v1", "sigma_v2", "sigma_v3"]

> Bethe_group(D3h, operators, double);

      ["E", "C3+", "C3-", "C21‘", "C22‘", "C23‘", "S3-", "S3+",
           "sigma_h", "sigma_v1", "sigma_v2", "sigma_v3",
     "RE", "RC3+", "RC3-", "RC21‘", "RC22‘", "RC23‘", "RS3-", "RS3+",
          "Rsigma_h", "Rsigma_v1", "Rsigma_v2", "Rsigma_v3"]
```

- Definition of the symmetry operations.

```
> Bethe_group(D3h, operator_details);

   Description of symmetry operations for the point group  D3h:
   ------------------------------------------------------------
   E         Identity operation
   C3+       Clockwise rotation about the z(principal)-axis by 2*Pi/3
   C3-       Anticlockwise rotation about the z(principal)-axis by 2*Pi/3
   sigma_h   Reflection through the horizontal (x-y) plane
   sigma_v1  Reflection through the (sigma_v1)-plane given by the z-axis
             and the azimuth angle phi = 0
   .
   .
```

- Explanation of the symmetry elements.

```
> Bethe_group(D3h, symmetry_elements);

     Symmetry elements of the point group  D3h:
     ------------------------------------------
      C_3       3-fold principal axis along the z-axis
      S_3       3-fold improper axis along the z-axis
      sigma_h   Horizontal (x-y) reflection plane
      sigma_v1  Vertical reflection plane
                including the z-axis and with azimuth angle phi = 0
      .
      .
```

During the last years, the BETHE program has been published in the Computer Physics Communications library in several steps [10]-[12]. The full package is distributed by a tar file of the BETHE root directory (`Bethe.tar`), which contains the source code library, file `.mapleinit`, guide for installation as well as the documentation for the program. The BETHE program can be invoked like any other module of MAPLE. Then, by using the command `with(Bethe)` user may load all procedures and initialize the internal settings of the BETHE package:

```
> with(Bethe);

                        Welcome to Bethe
                   version from 02 January 2006


              Bethe_save_framework = nonrelativistic

[AO, Abasis, Bethe_CGC_are_orthogonal, ...
```

2.3 Interactive work with the group data

As shown in the previous section, the BETHE package helps to extract the group theoretical data for particular group. However, the computer-algebraic approach, which realized within the BETHE package, allows not only extraction, but also interactive use of these data. In this section we demonstrate, how the symmetry operations of the group D_{3h}, obtained by the command `Bethe_group()`, can be used to obtain the advanced group-theoretical information. As seen from the output of the previous section, all symmetry operations are handled by means of appropriate string identifiers. For each of these strings, we can determine the parameterization of this symmetry operation in terms of Euler angles α, β, γ

```
> Bethe_group_Euler(D3h, "C3+"), Bethe_group_Euler(D3h, "sigma_v1");
```

```
        2 Pi
[0, 0, ----], [0, Pi, 0].
        3
```

Apart from this (most widely applied) type of parameterization, one can determine other types of parameterization. For instance, in terms of the angle φ and pole $\mathbf{n}$ of rotation

```
> Bethe_group_parameter(D3h, "C3+"), Bethe_group_parameter(D3h, "sigma_v1");
```

```
                    2 Pi
                  [----, [0, 0, 1]], [Pi, [0, 1, 0]].
                     3
```

or in terms of the so-called *quaternion parameters*

```
> Bethe_group_parameter(D3h, "C3+",quaternion), Bethe_group_parameter(D3h,
"sigma_v1", quaternion);
```

```
                     [       1/2]
                     [      3   ]
               [1/2, [0, 0, ----]], [0, [0, 1, 0]]
                     [       2  ]
```

Moreover, one of the important group properties, that the product of any two operators must also be a member of the group, can be easily confirmed in the program

```
> Bethe_group_multiplication(D3h, "C3+", "sigma_v1"),
Bethe_group_multiplication(D3h, "RC3+", "Rsigma_v1");
```

```
                  "sigma_v3", "Rsigma_v3".
```

The whole "multiplication table" is then simply obtained by cycling through all pairs of symmetry operators.

2.4 Group representations

2.4.1 Irreducible representations

The symmetry operations of the group would be of minor interest, if they would not give rise to the so-called *induced transformations* in some given vector space L. The relations between the symmetry operations and their induced transformations lead to the great simplifications in describing the molecular systems. Typically, such induced transformations can be expressed by the matrices and are called the *representations* T of the group (by assigning one matrix to each of the symmetry operators $\hat{R}_a$). The representation matrices fulfill the same 'multiplication rule' like the symmetry operations: $T(\hat{R}_a)\,T(\hat{R}_b) = T(\hat{R}_a\hat{R}_b)$ and $T(\hat{E}) = 1$. The vector space L, in which these representations are found, is then called the *representation space* of T and

its dimension is the dimension of this representation [7]. In physics, we may usually restrict ourselves to matrix representations as obtained by choosing an orthonormal basis $\mathbf{e}_1$, ..., $\mathbf{e}_n$ in L: $T_{ji}(\hat{R}_a) = \langle \mathbf{e}_j | T(\hat{R}_a) | \mathbf{e}_i \rangle$. More generally, the space L may be considered not only as a vector space, but also as function space with the orthonormal basis $\varphi_1, ..., \varphi_n$. The set of functions φ_i, $i = 1, ..n$ is called *basis functions* of the irreducible representation T. Since, in general, we can choose the basis rather arbitrarily, the representations of a group are not unique but depend of course on the choice of the coordinates and further parameters.

One of the great benefits of group theory arises from the fact that, for finite groups, any representation can be decomposed into — a rather small number of — *irreducible representations*, which are unique and independent of the basis up to some unitary transformation. In this decomposition, of course, the sum of the dimensions of the involved irreducible components must be equal to the dimension of the considered vector space L. In the BETHE program the so-called *Mullican* notation is used to identify the irreducible representations. For the D_{3h} point group, for instance, the string identifiers of irreducible representations are

```
> Bethe_group(D3h, irreps);

    ["A1‘", "A2‘", "E‘", "A1‘‘", "A2‘‘", "E‘‘"]
```

In this notation the one–dimensional representations are labeled by A or B in dependence of whether the character of the rotation about the principal axis is $+1$ or -1, respectively. In addition, the two–, three– and four–dimensional representations are labeled by E, T, and F. The five– and six–dimensional representations, appearing in some high-order groups, are denoted by H and I, respectively. Integer subscript is used to indicate the symmetry with respect to the binary axes, perpendicular to the main rotational axis, while primes and double primes denote the symmetry with respect to the horizontal reflection plane. First irreducible representation in the list, returned by the procedure `Bethe_group(Glabel, irreps)`, is always *totally symmetric*, that is it has the characters $\chi = +1$ for all of the symmetry operations of the underlying group. In addition to the point group (vector) representations, the list of the double group irreducible representations includes also so-called *spinor* representations, marked by the half-integer subscript.

```
> Bethe_group(D3h, irreps, double);

    ["A1‘", "A2‘", "E‘", "A1‘‘", "A2‘‘", "E‘‘", "E1/2", "E3/2", "E5/2"]
```

The number of the spinor representations not exceed the number of the vector representations. For each of these representations, the BETHE program provides either the explicit matrix or simply the character, that means the trace of corresponding matrix. The characters are sufficient for most practical applications. For instance, for the (two-dimensional) irreducible representation $E‘$ of the group D_{3h} the character and explicit matrix can be obtained as

```
> Bethe_group_character(D3h, "E‘","C3+"), Bethe_group_irrep(D3h, "E‘","C3+");
```

```
                [                1/2                        ]
                [- 1/2 - 1/2 I 3                0           ]
           -1,  [                                           ]
                [                                      1/2  ]
                [        0              - 1/2 + 1/2 I 3     ]
```

or, for the spinor representation $E_{1/2}$

```
> Bethe_group_character(D3h,"E1/2","C3+"),Bethe_group_irrep(D3h,"E1/2","C3+");
```

```
                [              1/2                      ]
                [1/2 - 1/2 I 3                0         ]
            1,  [                                       ]
                [                                  1/2  ]
                [       0              1/2 + 1/2 I 3     ]
```

Moreover, the list of characters (matrices) for all operators as defined above can be obtained

```
> Bethe_group_character(D3h, "E‘"), Bethe_group_irrep(D3h, "E‘"):
```

```
                    [2, -1, -1, 0, 0, 0, -1, -1, 2, 0, 0, 0]
```

where the full printout of matrices is omitted here by using a double point at the end of the line. The characters of a group representation are often denoted by χ and can be used, for instance, to determine the number of (inequivalent) irreducible representations, which are 'involved' in some reducible representation (see below). From these few examples it becomes clear how the corresponding data for other representations and symmetry operations can be extracted from the BETHE program.

2.4.2 Reducible representations and their reduction

Equally to the irreducible representations of the symmetry group, so-called *reducible* representations are of the great importance in various applications. For instance, in the vibrational spectroscopy the representation, generated by a set of $3N$ Cartesian basis vectors (for N-atomic molecule) is useful [13]. Another applications require to construct the reducible representation generated not by the vectors, but by the mathematical functions [14]. A number of reducible representations can be generated within the BETHE package by calling the procedure `Bethe_group_representation(Glabel, ...)`. The second argument of this procedure is the keyword, which specifies the type of required representation. In Table 2.3 we display the presently supported keywords of this procedure.
Let us demonstrate, how to obtain the representation, generated by the set of spherical harmonics Y_{lm} of rank 1. To achieve this, the keyword `Ylm` has to be used. Moreover, the third argument $l = 1$ specifies the parameter l of the function Y_{lm}. This reducible representation can be obtained either in terms of characters for every symmetry operation of the group D_{3h}

Table 2.3: Optional arguments of the procedure `Bethe_group_representation(Glabel, ...)`.

Keyword	Output of the procedure
polar_vector	Representation, generated by the polar vector $\mathbf{r}$=(x, y, z).
axial_vector	Representation, generated by the axial vector $\mathbf{R}$=(R_x, R_y, R_z).
Ylm	Representation, generated by the spherical harmonics of rank l, i.e. of $Y_{lm}(\theta, \varphi)$, $m = l, l-1, ..., -l$.
jm	Representation, generated by the spinor function $\|jm\rangle$ of half-integer rank j, i.e. of $\|jm\rangle$, $m = j, j-1, ..., -j$.
cartesian_tensor	Representation, generated by the cartesian tensor functions of given *rank*.
Euler	Euler representation of the group
regular	Regular representation of the group
total	Total matrix representation of the group for a given set of atomic displacements
vibrational	Representation of the vibrational motion for a given set of atomic displacements

```
> wa := Bethe_group_representation(D3h, Ylm, 1);

                wa := [3, 0, 0, -1, -1, -1, -2, -2, 1, 1, 1, 1]
```

or in terms of explicit matrices

```
> wa_mat := Bethe_group_representation(D3h, Ylm, 1, matrix);

                          [                 1/2                             ]
           [1    0    0]  [- 1/2 + 1/2 I 3       0            0           ]
           [             ]  [                                               ]
wa_mat := [[0    1    0], [        0             1            0           ], ...
           [             ]  [                                               ]
           [0    0    1]  [                                        1/2]     
                          [        0             0    - 1/2 - 1/2 I 3   ]
```

As seen from result, the obtained representation is three-dimensional. Generally, the dimension of reducible representations is not restricted. Some representations, especially those, which are used in the vibrational spectroscopy, are of the very large dimension. To simplify the dealing with such (highly-dimensional) representations, we can transform each matrix of the reducible representation into a number of irreducible representation matrices. This can be achieved by applying the so-called *reduction formula* [7, 8]

$$T \;=\; \dot{\sum_{\gamma}} m_\gamma \, T^{(\gamma)} \tag{2.1}$$

$$m_\gamma \;=\; \frac{1}{h} \sum_{R} \chi_{\hat{R}} \, \chi^{(\gamma)}_{\hat{R}}, \tag{2.2}$$

where T is the reducible representation and $T^{(\gamma)}$ are irreducible representations of the group, while the number m_γ indicates how many times every irreducible representation $T^{(\gamma)}$ is found in the reducible representation T. Moreover, h denotes the order of the group, $\hat{R}$ - the symmetry operation of the group, χ - the character of the reducible representation T and $\chi^{(\gamma)}_{\hat{R}}$ - the character of the irreducible representations $T^{(\gamma)}$. The dot over the summation sign in the Eq. (2.1) denotes that this is not the usual matrix summation but the *direct sum* of matrices [15]. This symbol for the summation means that by use of some transformation, the reducible representation matrix T can be presented as a set of irreducible representation matrices $T^{(\gamma)}$, arranged down the diagonal (see Ref. [12] for details). The BETHE program provides the reduction of the reducible representation to the irreducible component, based on the reduction formulas (2.1) and (2.2)

```
> Bethe_decompose_representation(D3h, wa);

          ["E‘", "A2‘‘"]
```

As seen from result, the three-dimensional reducible representation `wa` consists on the irreducible components E‘ and A_2“.

2.4.3 Direct product of the representation and its decomposition

In some applications of symmetry the so-called *direct product* of irreducible representations is important. The direct product of irreducible representations is equivalent to the direct product of corresponding matrices. Although the matrix direct product is widely known [16, 17], we will briefly remind, 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 $A \otimes B$. The character of direct product matrix $A \otimes B$ is given by the product of the characters of matrices A and B. In the group theory the direct product $T^{(\alpha)} \otimes T^{(\beta)}$ 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, it can be decomposed to the irreducible components $T^{(\gamma)}$ according to the expressions (2.1) and (2.2) where $T = T^{(\alpha)} \otimes T^{(\beta)}$ and the coefficients m_γ are obtained from the characters of the irreducible representations $T^{(\alpha)}$, $T^{(\beta)}$ and $T^{(\gamma)}$ involved. Decomposition of the irreducible representation direct product can be achieved in the BETHE package. For instance, for the group D_{3h} the program can return characters of the direct product of E‘ with A‘$_1$ or with itself

```
> Bethe_group_direct_product(D3h, "E‘", "A1‘", characters);
Bethe_group_direct_product(D3h, "E‘", "E‘", characters);

                  [2, -1, -1, 0, 0, 0, -1, -1, 2, 0, 0, 0]
                  [4,  1,  1, 0, 0, 0,  1,  1, 4, 0, 0, 0]
```

Apart from the characters, the explicit matrices of the direct product representations can be returned by use of keyword *matrix*. Moreover, then program can automatically produce the decomposition of the direct product

```
> Bethe_group_direct_product(D3h, "E‘", "A1‘"),
Bethe_group_direct_product(D3h, "E‘", "E‘");
```

```
["E‘"], ["A1‘", "A2‘", "E‘"]
```

As seen from result, the two-dimensional direct product $E‘ \otimes A1‘$ is irreducible (since the totally symmetric irreducible representation $A‘_1$ does not change any other representation), while the four-dimensional direct product $E‘ \otimes E‘$ is decomposed to the three irreducible components $A‘_1$, $A‘_2$ and $E‘$.

The direct product of the irreducible representation with itself $T^{(\alpha)} \otimes T^{(\alpha)}$ can be divided on the so-called *symmetrized* and *antisymmetrized* parts. These parts are denoted by $\left[T^{(\alpha)} \otimes T^{(\alpha)}\right]$ and $\{T^{(\alpha)} \otimes T^{(\alpha)}\}$ respectively; of course, $\left[T^{(\alpha)} \otimes T^{(\alpha)}\right] + \{T^{(\alpha)} \otimes T^{(\alpha)}\} = T^{(\alpha)} \otimes T^{(\alpha)}$. The meaning of the symmetrized and antisymmetrized parts of the direct product refers to the basis functions of the direct product representation, as described in Ref. [8, 18]. Therefore, we do not give the detailed explanation of it. Note only, that the basis functions of the symmetrized part keep the form under the interchange of the parent irreducible representations basis functions, while the basis functions of the antisymmetric part reverse the sign. The symmetrized and antisymmetrized parts of the direct product can be obtained by the BETHE program using the corresponding keywords

```
> Bethe_group_direct_product(D3h, "E‘", "E‘", symmetrized);
Bethe_group_direct_product(D3h, "E‘", "E‘", antisymmetrized);

                    ["A1‘", "E‘"], ["A2‘"]
```

The totally symmetric irreducible representation of the group is always included into the symmetrized part.

In this Chapter the capability of the BETHE package to extract and manipulate the group theoretical data is demonstrated. In the next Chapter we will show, how these data can be used in different applications in physics and chemistry.

Chapter 3

Application of BETHE on physics of molecules and clusters

As said before, the theory of symmetry plays a very important role in modern physics and chemistry. The symmetry consideration helps to solve a number of research problems. In this chapter we demonstrate how the computer-algebraic approach can simplify the dealing with particular symmetry applications. These applications include the derivation of molecular symmetry, the interaction of molecules with the radiation field as well as behavior of atomic energy levels in the external crystal field. The examples from the BETHE, presented in this chapter, give the impression of what this program is able to do.

3.1 Molecular geometry and symmetries

A simple, but very frequently occurring task in physical chemistry refers to the specification of the molecular symmetry and geometry [19, 21]. If the symmetry of a molecule or cluster is known, for instance, we might raise the question about the atomic coordinates. Certainly, it can be achieved if the coordinates are given for just one or few atoms from each set of equivalent atoms under the symmetry operations of the group. Vice versa, we may wish to determine the (highest) symmetry of a molecule if the atomic coordinates are given.

To demonstrate how to simplify this task by use the BETHE package, let us consider again the eclipsed ethane molecule (C_2H_6), mentioned in the previous chapter. This molecule is known to obey a D_{3h} symmetry with the two carbon atoms on the central axis, "sandwiched" between two identical parallel H_3 rings, as displayed in Fig. 2.1. Therefore, there are two sets of equivalent atoms: two carbon atoms and six atoms of hydrogen. To define the symmetry of every atom, we can choose one carbon atom at the position $(0, 0, a)$ along the z-axis, while one of the hydrogen atoms - at the position $(b, 0, c)$ (see Fig. 2.1). Using the BETHE program, we obtain

```
> w_carbon := Bethe_generate_sites(D3h, [0,0,a]); w_hydrogen :=
Bethe_generate_sites(D3h, [b,0,c]);

                        w_carbon := [[0, 0, a], [0, 0, -a]]
```

```
                                        1/2                 1/2
                                   b 3                 b 3
w_hydrogen := [[b, 0, c], [- b/2, - ------, c], [- b/2, ------, c], [b, 0, -c],
                                     2                   2

                      1/2                 1/2
                 b 3                 b 3
    [- b/2, - ------, -c], [- b/2, ------, -c]]
                   2                   2
```

Sometimes it is useful to determine the symmetry of a molecule, if the coordinates of all the equivalent atoms are given explicitly. For example, we may ask, whether the (two sets of the) carbon and hydrogen atoms altogether obey a C_{3h} symmetry

```
> Bethe_group_symmetry(C3h, w_carbon, w_hydrogen);

                        true
```

or even a D_{3d} symmetry

```
> Bethe_group_symmetry(D3d, w_carbon, w_hydrogen);

                        false.
```

These two answers are, of course, not very surprising because C_{3h} group is known to be a subgroup of D_{3h}, while the D_{3d} group is not. Moreover, for a given set of coordinates (of equivalent atoms), we can determine automatically the group with highest symmetry

```
> Bethe_group_symmetry(highest, w_carbon, w_hydrogen);

                        D3h
```

which confirms our assumption above about the symmetry of eclipsed ethane.

Of course, the examples, presented above, are trivial. However, they show how one can easily generate the atomic coordinates and symmetries and utilize them in other applications, for instance for determining the normal coordinates of a molecule as we consider in the [11].

3.2 Molecular vibrations and vibrational spectroscopy

Of course, in most cases the generation of the molecular geometry and symmetry is not self-sufficient, but only intermediate problem of some more important applications. One of such applications is the molecular vibrations and vibrational spectroscopy. Vibrational spectroscopy is known as the experimental tool in order to resolve the structure and bonds of molecules, or to understand their adsorption at surfaces [22, 24]. Two experimental methods of vibrational

spectroscopy are widely used today: infrared and Raman spectroscopy which are based on quite different physical principles. While, for instance, infrared spectroscopy concerns the absorption of (infrared) light by a molecule, owing to its vibrational frequencies, Raman spectroscopy refers to the scattering of light. The infrared spectroscopy can therefore be taken as a direct measurement of the vibrational frequencies whereas, in Raman spectroscopy, they just occur as the differences in the frequencies of the incident and the Raman–scattered light, respectively. For the interpretation of the vibrational spectra and derivation of the geometrical structure of underlying molecule and clusters, so-called *selection rules* are widely used. These rules are rather different for infrared and Raman excitations of the molecule. Whereas in infrared spectroscopy the occurrence of a vibrational transition requires a change in the electric dipole moment of the molecule, Raman lines go along with a change in the polarizability during the vibration. Therefore, the selection rules for infrared and Raman transitions are widely used to interprete the vibrational spectra and to derive the geometrical structure of the underlying molecules and clusters.

For the treatment of the observed infrared and Raman spectra the theory of the point group is used to extract most relevant information about the molecules. In particular, the point group theory can define the spectral activity of polyatomic molecules or, by other words, to answer the question, which vibrational transition is allowed in the infrared and Raman spectra [18, 25, 27]. Therefore, in this section we demonstrate how to apply the BETHE package for the analysis of the vibrational spectra. We start from the analysis of vibrational transitions and their classification. Since the group-theoretical approach to the vibrational analysis was described in Ref. [11] we will recall it very briefly just in order to demonstrate how computer algebra may simplify the vibrational analysis, even if the complex molecule is involved in the experiment.

3.2.1 Classification of vibrational transitions

According to the Born-Oppenheimer approximation, we can consider the molecular vibrations independently of the states and motion of electrons. The vibrational motion of the N-atomic molecule, in which its interatomic distances and internal angles change periodically without producing any rotation or translation of the molecule as a whole, can be simply classified in terms of $3N-6$ *normal modes*. Most easily this is seen by means of the total vibrational wave function

$$\Psi(n_1, n_2, ..., n_{3N-6}) = \prod_{n_k} \psi_{n_k}(Q_k) \tag{3.1}$$

which can be presented as the product of the oscillator functions $\psi_{n_k}(Q_k)$, associated with the normal coordinates Q_k, $k = 1, 2, ..., 3N-6$ [11]. For a wide range of temperatures and pressures the molecule is found predominantly in the vibrational ground state, where all $n_k = 0$. Several types of transitions from the ground state to the excited vibrational states can be distinguished in the molecule:

- *Fundamental transitions:* These transitions connect the ground level and the first excited level with just a single quantum incorporated in one of the normal modes. For instance,

$n_j = 1$ while $n_k = 0$ for $k \neq j$. The fundamental transitions are typically more intense that any other kind of transition by at least one order of magnitude; their typical frequencies are in the infrared region of about $\sim$ 100-5000cm^{-1}.

- *Overtones:* These transitions occur when a mode is excited *beyond* the first excited level with a single quantum. It means, that $n_j > 1$, $n_k = 0$ for $k \neq j$. Since the transition to the first excited level is fundamental, transitions from the ground level to the m-th excited level is called $(m-1)$-*th overtone*.

- *Combination bands:* These transitions are observed if more than one vibration is excited. By other words, a molecule has acquired two or more vibrational quanta, distributed among two or more modes $(n_i \geq 1, n_j \geq 1, ..., k \neq i, j, ...)$

- *Hot bands* are observed when an already excited vibration is further excited. The intensity of the hot band is usually very weak. However, since the population of the initial state increase with increasing the temperature, the intensity of the hot band will increase with temperature. Hence the name "hot band" [18].

- Occasionally so-called *difference bands* can be detected. These bands occur when the molecule, which is already in a vibrationally excited state, gains another vibrational quantum, while losing the one it possessed originally. Such bands are rare, since few molecules exist initially in excited states except at high temperatures [14].

Before to analyze the vibrational transitions, the vibrational motion of the molecule should be classified. This classification can be performed by the group theoretical considerations. Having generated the reducible vibrational representation $T^{(vib)}$ of a molecule as described in the [13], the normal vibrations can be obtained from the decomposition of this representation into its irreducible components according to the expressions (2.1) and (2.2)

$$T^{(vib)} = \sum_{\alpha} m_\alpha T^{(\alpha)} \tag{3.2}$$

From this decomposition one can define the symmetry type $T^{(\alpha)}$ of every normal mode and a number m_α of modes with a particular symmetry $T^{(\alpha)}$. Moreover, the degree of degeneracy for every frequency refers to the dimension of corresponding irreducible representation $T^{(\alpha)}$. The number of vibrational modes of the molecule is given by the total number of irreducible representations, appearing in the Eq. (3.2).

3.2.2 Selection rules for the infrared and Raman spectroscopy

The group-theoretical basis for determination the spectral activities of the vibrational modes is described in [13, 14, 18]. The computer algebraic approach to the vibrational problem is explained in Ref. [11]. Moreover, in the section 4.2 of this paper a number of examples how to determine the spectral activity of fundamental transitions is presented. In this section we will

deal only with the overtones and combination bands – most frequently occurred nonfundamental transitions. For these transitions we will apply the selection rules, which tell us whether the particular vibrational mode is active in one or the other or both types of the spectra.

The spectral activity of the molecules can be defined by analyzing the irreducible components which are associated with the upper and lower states of some given transition. However, in case of the nonfundamental transitions, care has to be taken about the degeneracy of the normal modes involved and the number of photons. Consider, for instance, overtone. In case of the nondegenerate vibrations, the spectral activity of overtone can be defined similarly as of the fundamentals. The only distinction occurs, if the number of photons n_j is *even*. In this case the final state (overtone) function is always totally symmetric. To illustrate this, we use, to be successive, the example of M_3 molecule with three identical atoms at the corners of an equilateral triangle (for instance, the carbon atoms in cyclopropane). The classification of the vibrational modes and selection rules for fundamental vibrational transitions of this molecule were performed in Ref. [11]. For the first overtone (transition from the ground to the second excited state) of this molecule in the A_1' vibrational mode we have

```
> Bethe_spectral_activity(D3h, "A1'", infrared, 2);

                    false

> Bethe_spectral_activity(D3h, "A1'", Raman, 2);

                     true
```

where the number of photons is provided by the fourth argument. As seen from the output, the first overtone of the A_1' mode is forbidden in the infrared spectrum but allowed in the Raman spectrum.

In order to determine the possible symmetries of the excited states for degenerate modes a number of general formulas have been derived in the literature [18]. For the doubly-degenerate vibrational mode, for example, the characters $\chi_\nu(\hat{R})$ of the vibrational representation of every symmetry operation $\hat{R}$ have to be calculated for the ν-th level using the recursion formula

$$\chi_\nu(\hat{R}) = 1/2 \left[\chi(\hat{R})\chi_{\nu-1}(\hat{R}) + \chi(\hat{R}^\nu) \right], \tag{3.3}$$

where $\chi(\hat{R}^\nu)$ is the character for the operation $\hat{R}$, carried out ν times. Being decomposed to the irreducible components by the usual technique (see Eq.(2.1)and (2.2)), this representation gives a number of irreducible components. These components define the symmetry of corresponding level of doubly degenerate vibration. Then the spectral activity of the degenerate mode can be determined. This quite tedious process is realized within the BETHE package. For instance, for the doubly-degenerate E' vibration of M_3 molecule we have

```
> Bethe_spectral_activity(D3h, "E'", infrared, 2);

                     true

> Bethe_spectral_activity(D3h, "E'", Raman, 2);
```

```
                    true
```

The first overtone of the E' vibration is allowed in both spectra. Spectral activity of the triply-degenerate vibrations, where the recursion formula for characters has a form Ref. [18]

$$\chi_\nu(\hat{R}) = \frac{1}{3}\left[2\chi(\hat{R})\chi_{\nu-1}(\hat{R}) + \frac{1}{2}\left\{\chi(\hat{R}^2) - \chi^2(\hat{R})\right\}\chi_{\nu-2}(\hat{R}) + \chi(\hat{R}^\nu)\right], \tag{3.4}$$

can be also defined in the BETHE package.

Combination bands are not much more complicated. As said before, the combination transition process includes several vibrations. In this case the symmetry of excited state can be obtained from the *direct product* of the symmetries of particular modes. If some of the included modes are degenerate, one has to use the expression (3.3) or (3.4) to evaluate corresponding symmetry. The transition moment integral, calculated with the corresponding symmetry of final state gives the desired answer about the allowance of the combination transition. Consider the example of combination, where the transition in the mode A_1' to the second excited state occur together with the transition of E' mode to the first excited state. Using the BETHE package we obtain

```
> Bethe_spectral_activity(D3h, ["A1', "E'"], infrared, [2,1]);

                    true

> Bethe_spectral_activity(D3h, ["A1', "E'"], Raman, [2,1]);

                    true
```

This result shows, that the combination $\{A_1' : 0 \to 2; E' : 0 \to 1\}$ will be allowed in both spectra. It does not mean, that this combination will be strong in both spectra. It only means, that it may have some nonzero value.

Thus, we have shown, how overtones and combination bands can be treated by the BETHE package. Although these transitions are generally much less intense then the fundamental transitions, they may in some cases be more pronounced than a weak fundamentals. Of course, the presence of such intense nonfundamental transitions in the infrared and Raman spectra can introduce complications in the vibrational analysis. Occasionally, however, they can be useful, since totally inactive fundamentals may be active as overtones or combination bands in the infrared or Raman spectra, and this can give approximate frequencies for such vibrations [28, 29]. Therefore, the analysis of the nonfundamental activity, supported by the BETHE package is very important.

3.3 Crystal field splitting

Apart from the vibrational spectroscopy, the symmetry properties of a system are reflected also by the splitting of the ground-state levels of ions, placed into an (external) crystal field. The behavior of the energy levels in the crystal field helps to recognize the structure of atoms and ions and to understand the nature of the bonding in transition metal complexes [30, 31, 32]. In

this section we explain, how BETHE package helps to analyze such systems. Since the discussion of the energy levels in the crystal field reveals the relationship between the wavefunctions, the energy levels of the quantum system and the irreducible representations of its symmetry group, the use of the symmetry theory in the quantum mechanic will be briefly recalled. Some details about group-theoretical treatment of the crystal filed splitting reader can find also in Ref. [12].

3.3.1 Use of symmetry in the quantum mechanics. Wigner theorem.

The basis functions of the irreducible representations, mentioned in the Section 2.4.1, would be of minor interest, if they did not have the physical meaning. In quantum physics these functions can be interpreted as a wave functions of the molecular systems and help to classify these systems in accordance to their symmetry. Actually, the behavior of the stationary quantum system is determined by the wave function ψ, which is solution of the Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n, \tag{3.5}$$

where $\hat{H}$ is the Hamiltonian of the system, E_n is the energy of n-th level (i. e. its eigenvalue) and ψ_n s the corresponding eigenfunction. Let us assume the fixed positions in the space for every nuclei in the molecule. Then the Hamiltonian contains the kinetic energy operators of all valence electrons, the Coulomb energy of their repulsion as well as the potential energy of electron-nuclei interaction. Obviously, the point group symmetry operations $\hat{R}$ change neither the electron kinetic energy nor the interaction between electrons. Moreover, even the potential energy of the electron-nuclear interaction is not changed under the symmetry operations (because all nuclei are going into the undistinguished positions). Therefore, the Hamiltonian is *invariant* under the point group transformations. Mathematically, this statement can be expressed as $T(\hat{R})\ \hat{H}\ T^{-1}(\hat{R}) = \hat{H}$ for all operations $\hat{R}$ of the symmetry group G. The invariance of the Hamiltonian under a particular group of transformations means that the quantum system "belongs to" this symmetry group. In this case each of the eigenvalues E of the Hamiltonian is associated with a certain representation of the group G, while the corresponding eigenfunctions $\psi_i(\mathbf{r})$ $(i = 1, .., s)$ form a basis of this representation. Moreover, the degeneracy of the energy level E is equal to the dimension s of this representation. Thus, each energy level of the system is related to a certain irreducible representation of the symmetry group. Corresponding wavefunctions form the basis of these irreducible representations. Every of these functions belongs to some component of an irreducible representation (or to row of corresponding matrix) of the symmetry group. This statement is called the *Wigner theorem*. This theorem allows to classify the quantum states of the symmetry system according to the irreducible representations of its symmetry group.

3.3.2 One-electron states in a crystal field

In order to explain the qualitative behavior of an atomic levels in a crystal field, we start from the atom, having the single electron in the valence shell of the transition metal. It is known, that the states of this atom belong to the continuous group O_3 Ref. [7, 8] and can be described by the spherical functions $Y_{lm}(\vartheta, \varphi)$. These functions are known to be degenerate in

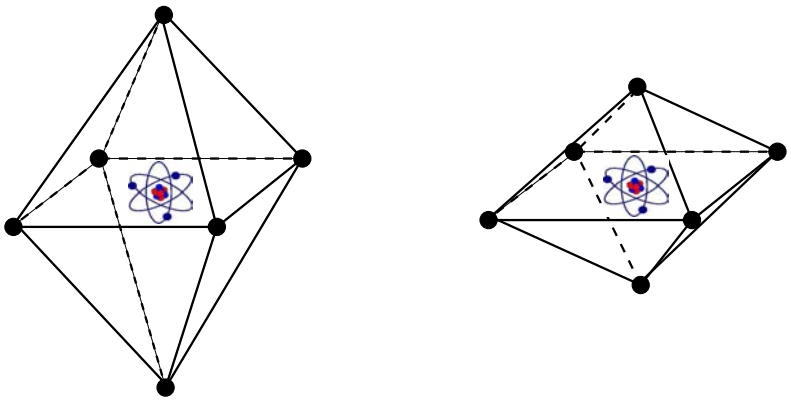

Figure 3.1: Atom in the crystal environment of an a) octahedral configuration O_h; b) tetrahedral configuration D_{4h}.

$m = -l, -l+1, ..., l$ for the free atom and can be presented as

$$Y_{lm}(\vartheta, \varphi) = \frac{1}{2\pi}\Theta_{lm}(\vartheta)e^{im\varphi}, \tag{3.6}$$

(leaving out the radial and the spin part of the wave function for the present). The symmetry of O_3 group is higher then the symmetry of any finite point group. If atom is placed into the crystal environment, its symmetry is decreased. Lowering the symmetry results in the splitting of energy levels. Therefore, the classification of the atomic states in the crystal field is based on the decomposition of the O_3 group representation to the irreducible components of the crystal symmetry point group, as described in section 3.4.2. In order to make this decomposition, the representations of the crystal symmetry point group in the basis of the spherical functions $Y_{lm}(\vartheta, \varphi)$ have to be found. As shown in Ref. [8, 13] the matrix representation, generated by such a function for any rotation by the angle α has a form

$$T^{(l)}(\hat{R}_\alpha) = \begin{vmatrix} e^{il\alpha} & 0 & \dots & 0 & 0 \\ 0 & e^{i(l-1)\alpha} & 0 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & e^{-i(l-1)\alpha} & 0 \\ 0 & 0 & \dots & 0 & e^{-il\alpha} \end{vmatrix} \tag{3.7}$$

In the BETHE program we can evaluate this representation for the atom in the crystal environment. Consider, for instance, the atom, placed into the octahedral environment. It means, that this atom is sixfold coordinated with crystal atoms, as shown on Fig. 3.1 a). Clusters of such type are mentioned very often in the literature. For instance, the manganese oxide cluster MnO_6, which is important for the phenomenon of *colossal magnetoresistance* [33]; another example - chromium bromide $CrBr_6$, magnetic properties of which are discussed in Ref. [34]. The behavior of the atomic energy levels of the central atom in the field of crystal atoms can help to clarify the magnetic structure of these clusters.

Let us start from the assumption, that the atom, placed into octahedral environment, has one d-electron in the valence shell. Although the full symmetry of the octahedron is O_h, we can

gain all required information about the d-orbital by using only the pure rotational subgroup O, because O_h may be obtained from O by adding the inversion operator. However, d-orbitals are even to the inversion, so that it is only the pure rotational operators of O will bring us new information. Thus for the point group O we obtain the representation, generated by Y_{lm} functions for d-electron

```
> Bethe_group_representation(O, 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]
```

where the `Ylm` is the keyword and the third argument $l = 2$ refers to a single d-electron, Here we have restricted ourselves to the characters of the representation. The full matrix representation would be obtained from the same command by adding the keyword *matrix* as a fourth argument.

The representation, generated by $Y_{lm}(\vartheta, \varphi)$ functions is (generally) reducible in the crystal point group. Therefore the irreducible components of this representation can be obtained according to the Eq. (2.1) and (2.2). These components serve to classify the one-electron states in crystal field. In particular, the sum over γ of the integers m_γ 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 $T^{(\gamma)}$. Decomposition of the representation, generated by $Y_{lm}(\vartheta, \varphi)$ functions, to the irreducible components is provided by the program

```
> Bethe_decompose_representation(O, wa);

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

i.e. the five-fold degenerate level of the d electron is split by the octahedral environment into two levels, the doublet E and the triplet T_2. This is seen from the Fig. 3.2 a) and b). This diagram (as well as other splitting diagrams of this section) is purely qualitative and does not demonstrate the relative energies of the levels. For other symmetries of the external crystal field, of course, the representation $T^{(l)}$ in Eq. (3.6) might be irreducible, leaving the ionic level degenerated as before.

As the result of some additional interactions and perturbations, the shape of the external crystal can be distorted. In this case, owing to the reduction of the symmetry of the system, a further level splitting is expected. If, for example, the octahedral symmetry of the crystal field from above is reduced to a D_{4h} symmetry (as shown on Fig. 3.1 b), the further level splitting of the E and T_2 levels can be obtained by carrying out a subduction of the group

```
> Bethe_group_subduction(O, "E", D4); Bethe_group_subduction(O, "T2", D4);

        ["A1", "B1"]
        ["B2", "E"]
```

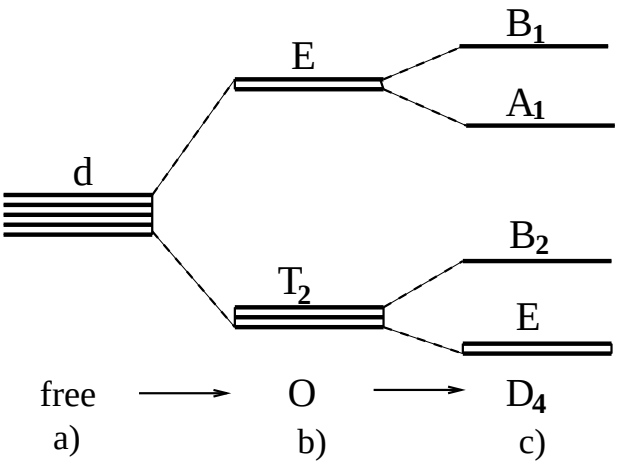

Figure 3.2: d-level splitting in the crystal field: a) d-level of free atom; b) splitting in the octahedral environment; c) splitting in the tetragonal environment.

and which shows that each of these levels is split now into a pair of (sub-) levels with only one (E) still being degenerate (see Fig. 3.2 c)). Here the group label D_{4h} is changed to D_4 by the same reason as for O_h symmetry.

3.3.3 Many-electron states in a crystal fields

The method of the classification of one-electron states in crystal field, explained before, can be quite easily generalized also to the case of the many-electron atom or ion, taking Pauili's principle into account. Owing to the coupling scheme and the inter-electron interaction, however, two cases need to be distinguished: the case, when the crystal field is *weak* in comparison with the electron-electron interaction within the valence shell and the case of the *strong* field, where the crystal field is stronger, then the electron-electron interaction. Consider first the case of the weak crystal field. If we neglect the spins of electrons, the splitting of a given (LS-) term with total angular momentum L is the same as for a single l-shell electron. It arises from the fact, that the $\Phi(\phi)$ factor of the wave function for L term is $e^{iM\phi}$ in exact analogy to the factor $e^{im\phi}$ in the wave function of single electron. For instance, for atoms or ions with an outer d^2 configuration, we have the five LS terms ^3F, ^1D, ^3P, ^1G and ^1S Ref. [13]. To get the splitting of these terms we have to (i) generate the representation of Y_{LM} functions for every term and (ii) decompose these representation to the irreducible components (like in previous section). The irreducible components, obtained in this decomposition, classify the splitting of many-electron terms. Within the BETHE program, these two steps can be done automatically by the procedure `Bethe_group_subduction_O3()`, which generate the irreducible components of the spherical harmonic Y_{LM} representation with given L. For instance, for the terms, mentioned above, we have

```
> we_S:=Bethe_group_subduction_O3(O, 0); we_P:=Bethe_group_subduction_O3(O, 1);
we_D:=Bethe_group_subduction_O3(O, 2); we_F:=Bethe_group_subduction_O3(O, 3);
we_G:=Bethe_group_subduction_O3(O, 4);
```

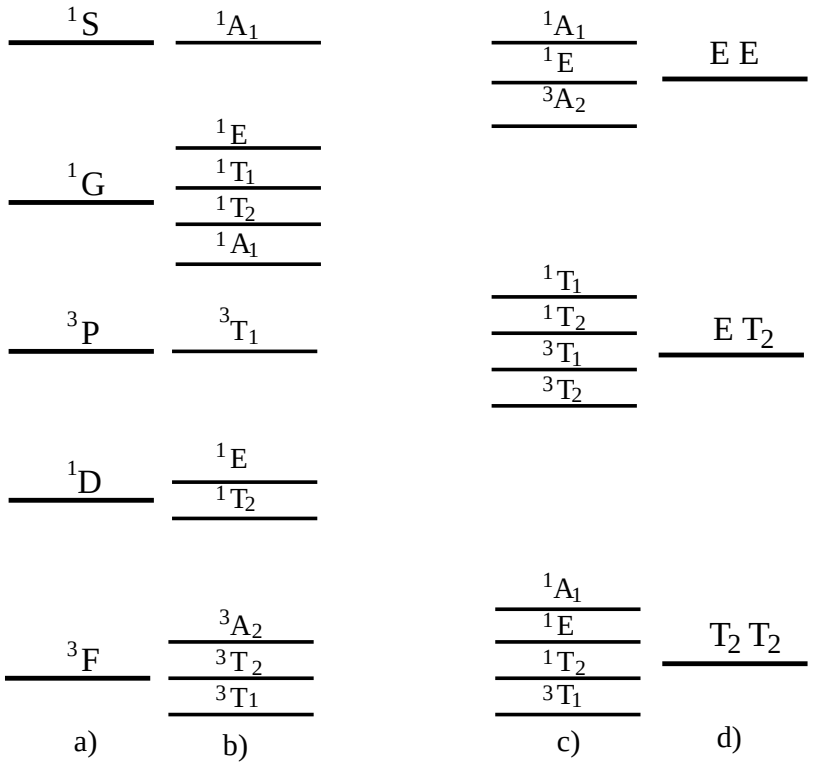

Figure 3.3: Energy levels of d^2-ion in an octahedral crystal field: (a)free atomic states; (b) a weak crystal field; (c) a strong crystal field and weak interelectronic repulsion; (d) infinitely strong crystal field (degeneracy of the energy levels is not shown).

```
we_S := ["A1"]
we_P := ["T1"]
we_D := ["E", "T2"]
we_F := ["A2", "T1", "T2"]
we_G := ["A1", "E", "T1", "T2"]
```

This result is demonstrated on Fig. 3.3 a) and b). Note, that the spin multiplicity of the split terms will be the same like for the original LS terms, because the crystal field does not interact directly with the spin of electrons.

The classification of the atomic states in the crystal filed, given before, is followed from the approach, where the crystal field is considered as a perturbation influencing the electronic states of a free atom or ion. Such approach can be used only if the crystal field is weak in comparison with the interelectron interaction. A rather different level splitting is found if the crystal field becomes comparable or even stronger than the interaction among the electrons in the valence shell. In this case the action of the crystal field on each electron should be considered first and then the interelectron interaction is taken into account as a perturbation. According to this scheme, in the first stage of classification, we omit the interelectron interaction. The representations (3.6), generated by one-electron wave functions have to be found for every electron separately, and then decomposed to the irreducible components. Consider again an atom with

d^2 configuration, placed in the strong octahedral field. Using the results from above for the splitting of a single d-electron (see section 4.3.2), we have the one two-dimensional component E and one three-dimensional component T_2. In the strong crystal field the electrons begin to couple in certain way, giving rise to a set of states of the entire configuration. For example, for two d-electrons in the presence of the strong field we have three possible configurations EE, ET_2 and T_2T_2. To define the symmetry properties of the corresponding states, we have to take the direct product of the representations of the single electrons. Decomposition of this direct product classifies the term splitting in the presence of the strong crystal field. For instance, for the configuration T_2T_2 we obtain

```
> wd := Bethe_group_direct_product(O, "T2", "T2");

          wd := ["A1", "E", "T1", "T2"].
```

This result shows that the degenerate level T_2T_2 is split in the crystal environment into four sublevels with symmetries A_1, E, T_1 and T_2 (see Fig. 3.3 c)-d)). Behavior of the levels in the configurations EE and ET_2 can be obtained by the same procedure. As seen from the Fig. 3.3, there exist a one-to-one correspondence between the states of the atom in the weak and in the strong crystal field.

Similarly like above for the one-electron terms, the BETHE program help to define the splitting of the many electron levels in the low-symmetry crystal filed, i.e. when the symmetry of the surrounding crystal is distorted.

3.3.4 Spin-orbit interaction in a crystal field

In the previous sections we have shown how to determine the splitting of the states, characterized by integer values of the angular momentum quantum number l or L. There are, however, many cases of interest in which the concept of electron spin is important and we may want to determine the splitting of a state, characterized by its total angular momentum J. This will be the thing of importance in the number of phenomena, such as Zeeman effect and many others [35, 36]. Since the concept of electron spin is included, the theory of the point groups can not be applied to analyze such splitting. Therefore, one needs to use the *double* symmetry groups.

Consider the spin-orbit splitting in the case of one d-electron in an O cubic field. Like before, we should consider separately the cases of the strong and weak (in comparison with the spin-orbit interaction) crystal fields. If the cubic field is stronger than the spin-orbit interaction, we should neglect the spin-orbit interaction at the first stage and define how the degenerate state of free d-electron is split in the crystal field

```
> Bethe_group_subduction_O3(O, 2);

          ["E", "T2"]
```

We obtain two levels, related to the irreducible representations T_2 and E. With allowance of spin the orbital multiplet $^2T_2$ will be not three-, but six-fold degenerate. To obtain the splitting of this level resulting from the spin-orbit interaction, we need to take the direct product of the irreducible representation T_2 and the irreducible representation $E_{1/2}$ of the double group O

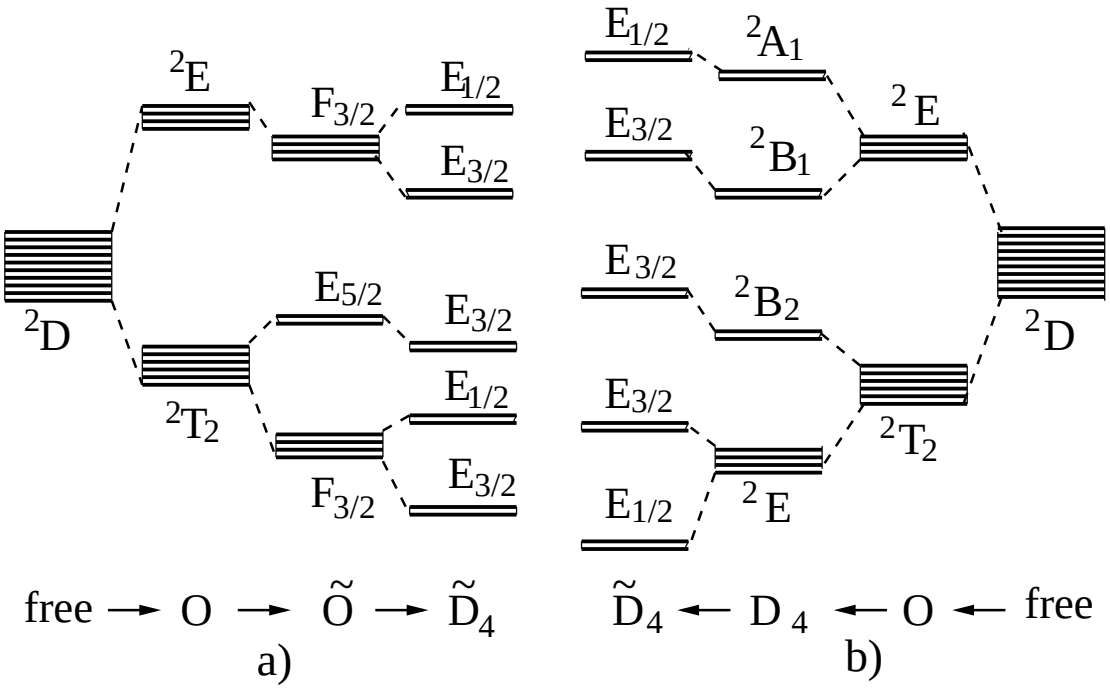

Figure 3.4: D-level splitting in the octahedral and tetrahedral fields (a) according to the scheme $free \longrightarrow O \longrightarrow \tilde{O} \longrightarrow \tilde{D}_4$; (b) according to the scheme $free \longrightarrow O \longrightarrow D_4 \longrightarrow \tilde{D}_4$.

```
> Bethe_group_direct_product(O, "T2", "E1/2");

          ["E5/2", "F3/2"]
```

According to the Wigner theorem, each irreducible representation is related to a certain energy level. It means that the spin-orbit interaction splits the $^2T_2$ term into a doublet $E_{5/2}$ and quadruplet $F_{3/2}$, called fine-structure levels (see Fig. 3.4 a)). Appearance of the double valued irreducible representations for one-electron atom is reasonable: the fine structure levels in a crystal field are enumerated either by single-valued irreducible representations (for even number of electrons) or by double-valued irreducible representations (for odd number of electrons). Similarly we can consider the term ^2E, for which we obtain

```
> Bethe_group_direct_product(O, "E", "E1/2");

          ["F3/2"]
```

The existence of one irreducible representation indicates that in the cubic field term ^2E is not split by the spin-orbit interaction.

Imagine now that the octahedral complex O is tetragonally distorted to the D_4 symmetry. If the tetragonal field is weaker than the spin-orbit interaction, we need to make the subduction of the O group irreducible representations, obtained above, to the group D_4. We obtain

```
> Bethe_group_subduction(O, "E5/2", D4);
Bethe_group_subduction(O, "F3/2", D4);
```

```
[["E3/2"]], [["E1/2", "E3/2"]]
```

Corresponding splitting is shown on Fig. 3.4(a). The scheme, realized before is $free \longrightarrow O \longrightarrow \tilde{O} \longrightarrow \tilde{D}_4$

Consider the case, where tetrahedral field is strong in comparison with the spin-orbit interaction. In this case it seems to be reasonable to take into account the crystal field, not focusing the attention on the spin-orbit interaction as the first consideration. In other words it is convenient to proceed from the tetragonal components of $^2T_2$ and ^2E following the reduction from O to D_4.

```
> Bethe_group_subduction(O, "T2", D4); Bethe_group_subduction(O, "E", D4);
```

```
[["B2", "E"]], [["A1", "B1"]]
```

and then include the spin-orbit interaction by the direct product with the double-valued irreducible representation (scheme $free \longrightarrow O \longrightarrow D_4 \longrightarrow \tilde{D}_4$)

```
> Bethe_group_direct_product(D4, "B2", "E1/2");
Bethe_group_direct_product(D4, "E", "E1/2");
Bethe_group_direct_product(D4, "A1", "E1/2");
Bethe_group_direct_product(D4, "B1", "E1/2");
```

```
["E3/2"], ["E1/2", "E3/2"], ["E1/2"], ["E3/2"]
```

This result, of course, coincide (qualitatively) with the result already obtaining. The transition from a weak to a strong spin-orbit interaction is expressed by the Fig. 3.4 b).

Of course, we can suppose already at the beginning, that in the system with one d-electron the spin-orbit interaction is stronger, then the crystal octahedral field, or realize the scheme $free \longrightarrow \tilde{O}$. According to this scheme, we should start from the total angular momentum J of the system. For the atom with one d-electron (angular momentum of the system $l = 2$ and spin $s = 1/2$) we have to find possible total angular momenta $J = 3/2, 5/2$ and make a subduction of corresponding representation to the irreducible components of the octahedral group

```
> Bethe_group_subduction_O3(O, 3/2); Bethe_group_subduction_O3(O, 5/2);
```

```
["F3/2"], ["E5/2", "F3/2"]
```

This subduction demonstrate qualitatively the same splitting like in the scheme $free \longrightarrow O \longrightarrow \tilde{O}$.

Up to now only the spin-orbit splitting of one-electron term was described. Let us consider briefly the spin-orbit splitting of many-electron terms. The states of many-electron atoms are numbered by two parameters: S (total spin of the system) and T (irreducible representation of the electron term). To classify the fine-structure levels of ST term, one has to carry out a number of manipulations. First of all the irreducible components of the representation T_s, generated by the spin function have to be found. Then we form the direct product $T \otimes T_s$.

The irreducible components of this direct product gives the desired answer about the splitting of many-electron term.

Consider the ${}^4T_2$ term of the d^3 ion in the octahedral field. We have S =3/2, $T = T_2$. By using the BETHE program we can find the irreducible components of the representation, generated by the spin

```
> Bethe_group_subduction_O3(O, 3/2);

          ["F3/2"]
```

Then we take the direct product $F_{3/2} \otimes T_2$

```
> Bethe_group_direct_product(O, "F3/2", "T2");

          ["E1/2", "E5/2", "F3/2", "F3/2"]
```

The result shows, that the level ${}^4T_2$ will be split in the octahedral field to the two doubly degenerate levels $E_{1/2}$ and $E_{5/2}$ and two four-fold degenerate levels $F_{3/2}$.

3.3.5 Wave functions of split levels.

In the previous sections we described how the MAPLE package BETHE can be used in order to classify the splitting of atomic energy levels in the crystal field. The emphasize was placed to demonstrate the flexibility of the BETHE package, where user can suppose different relations between the interactions in the crystal and classify the corresponding splitting. Apart from the classification, the BETHE package can be used in order to generate the wave functions of the split levels. These functions are constructed from the basis functions of the irreducible representations by means of the Clebsch-Gordan decomposition. The concept of the irreducible representation basis functions and the Clebsch-Gordan coefficients for the symmetry group are described in details in Ref. [12]. Moreover, several examples, concerning the generation of the wave function for the split levels without taking in account the spin-orbit interaction are presented in this reference. Therefore, we will focus only on the wave functions of the fine-structure levels (when the spin-orbit interaction is taken into account).

Knowing the irreducible representations $T^{(\gamma)}$, describing the fine structure levels, the corresponding wavefunctions $\psi_m^{(\gamma)}$ ($m = 1..dim\{T^{(\gamma)}\}$) can be constructed by means of the Clebsch-Gordan decomposition

$$\psi_m^{(\gamma)} = \sum_{ik} \langle \alpha i \beta k | s \gamma m \rangle \, \psi_i^{(\alpha)} \, \psi_k^{(\beta)} \tag{3.8}$$

where α labels the irreducible representations $T^{(\alpha)}$ of the electron term and β labels the irreducible representations $T^{(\beta)}$ of the spin function. The integer indices i and k enumerate the corresponding basis functions of these representations and s is the index to account the multiplicity of the irreducible representation $T^{(\gamma)}$; $\langle \alpha i \beta k | s \gamma m \rangle$ are the Clebsch-Gordan coefficients, which can be generated by the BETHE package. Consider the example of one d-electron in the octahedral filed in the state ${}^2T_2$ taking into account the spin-orbit interaction. The

classification of states for this example was produced in section 4.3.4. Corresponding splitting is demonstrated on Fig. 3.4 a). Since we have one d-electron, the spin part of this electron refers to the double-valued irreducible representation $E_{1/2}$. In the case under consideration th expression (3.8) has the form

$$\psi_m^{(\gamma)} = \sum_{ik} \langle T_2\, i\, E_{1/2}\, k | s\, \gamma\, m \rangle\, \psi_i^{(T_2)}\, \psi_k^{(E_{1/2})} \tag{3.9}$$

where $\gamma = \{E_{5/2}, F_{3/2}\}$, i, k and m denote integer indices to enumerate the basis functions of corresponding irreducible representations. To construct these wave functions we have to use the Clebsch-Gordan coefficients for the direct product $T_2 \otimes E_{1/2}$. Although the BETHE group can generate every coefficient separately by the procedure `Bethe_CG_coefficient()`, it seems beneficial to calculate the whole matrix of the Clebsch-Gordan coefficients

```
> CG_mat := Bethe_CG_matrix(0, "T2", "E1/2");
```

```
        [           1/2                       1/2                       1/2         ]
        [           3                         3                         3           ]
        [   0     - ----         0          - ----          0         - ---- - 1/2 I ]
        [           3                         3                         6           ]
        [                                                                           ]
        [   1/2                 1/2                       1/2                       ]
        [  3                   3                         3                          ]
        [  ----     0           ----          0           ---- + 1/2 I        0       ]
        [   3                   3                         6                         ]
        [                                                                           ]
        [    1/2            1/2                           1/2                       ]
        [   3              3                             3                          ]
        [ - ----    0      ---- - 1/2 I        0       - ---- + 1/2 I        0       ]
        [    3              6                             6                         ]
CG_mat = [                                                                          ]
        [           1/2                     1/2                         1/2         ]
        [          3                       3                           3            ]
        [   0      ----         0        - ---- + 1/2 I       0         ---- - 1/2 I  ]
        [           3                       6                           6           ]
        [                                                                           ]
        [           1/2                     1/2                             1/2     ]
        [          3                       3                               3        ]
        [   0      ----         0        - ---- - 1/2 I       0           - ----     ]
        [           3                       6                               3       ]
        [                                                                           ]
        [   1/2              1/2                              1/2                   ]
        [  ----     0      - ---- - 1/2 I       0           - ----          0       ]
        [   3                6                                3                     ]
```

This array can be understood by means of Table 3.1 The left column of this table shows six basis function of the direct product $T_2 \otimes E_{1/2}$ ($\alpha, i = \{T_2, 1;\ T_2, 2;\ T_2 3;\}$, $\beta, k = \{E_{1/2}, 1;\ E_{1/2}, 2;\}$, $\alpha, i, \beta, k = \{T_2, 1, E_{1/2}, 1;\ T_2, 1, E_{1/2}, 2;\ T_2, 2, E_{1/2}, 1;\ ...\}$), while the header of this table gives the bases of the irreducible representations $\gamma m = \{E_{5/2}1,\ E_{5/2}2,\ F_{3/2}1,\ ...\}$. The main body of the table shows corresponding Clebsch-Gordan coefficients. From these coefficients the wave

Table 3.1: Clebsch-Gordan coefficients for the O group product $T_2 \otimes E_{1/2}$.

$\alpha:$ T_2 i	$\beta:$ $E_{1/2}$ k	$\gamma:$ $m:$	$E_{5/2}$ 1	$E_{5/2}$ 2	$F_{3/2}$ 1	$F_{3/2}$ 2	$F_{3/2}$ 3	$F_{3/2}$ 4
1	1		0	$-\frac{\sqrt{3}}{3}$	0	$-\frac{\sqrt{3}}{3}$	0	$-\frac{\sqrt{3}}{6}-\frac{I}{2}$
1	2		$\frac{\sqrt{3}}{3}$	0	$\frac{\sqrt{3}}{3}$	0	$\frac{\sqrt{3}}{6}+\frac{I}{2}$	0
2	1		$-\frac{\sqrt{3}}{3}$	0	$\frac{\sqrt{3}}{6}-\frac{I}{2}$	0	$-\frac{\sqrt{3}}{6}+\frac{I}{2}$	0
2	2		0	$\frac{\sqrt{3}}{3}$	0	$-\frac{\sqrt{3}}{6}+\frac{I}{2}$	0	$\frac{\sqrt{3}}{6}-\frac{I}{2}$
3	1		0	$\frac{\sqrt{3}}{3}$	0	$-\frac{\sqrt{3}}{6}-\frac{I}{2}$	0	$-\frac{\sqrt{3}}{3}$
3	2		$\frac{\sqrt{3}}{3}$	0	$-\frac{\sqrt{3}}{6}-\frac{I}{2}$	0	$-\frac{\sqrt{3}}{3}$	0

functions of the split levels can be constructed. For instance, from first and fourth columns we have

$$\Psi_1^{E_{5/2}} = \frac{\sqrt{3}}{3}\Psi_1^{T_2}\Psi_2^{E_{1/2}} - \frac{\sqrt{3}}{3}\Psi_2^{T_2}\Psi_1^{E_{1/2}} + \frac{\sqrt{3}}{3}\Psi_3^{T_2}\Psi_2^{E_{1/2}}, \tag{3.10}$$

$$\Psi_2^{F_{3/2}} = -\frac{\sqrt{3}}{3}\Psi_1^{T_2}\Psi_1^{E_{1/2}} + (-\frac{\sqrt{3}}{6}+\frac{I}{2})\Psi_2^{T_2}\Psi_2^{E_{1/2}} + (-\frac{\sqrt{3}}{6}-\frac{I}{2})\Psi_3^{T_2}\Psi_1^{E_{1/2}}, \tag{3.11}$$

Using same procedure we can construct the wave functions of the split levels for any type of splitting, described in this section. Thus we have shown, that the BETHE package can be very useful in analyzing of the term splitting in the crystal field and construction of corresponding wave functions.

Chapter 4

Possible future applications

From the examples, presented in the previous Chapter, the present capabilities of the BETHE program can be seen for determining the crystal field splitting or the generation of the molecular spectroscopic activities. However, there are several other applications, which would make BETHE a much more powerful tool. In this section we would like to describe several *future applications*, which could be easily developed on the basis BETHE package.

4.1 Frequencies of the molecular vibrations: Wilson‘s method

Although the group theory is quite powerful tool for the analysis of the vibrational spectra, it suggests only *qualitative* way for analyzing the problems of molecular vibrations. Indeed, the group theoretical approach provides the methods how to determine the number and the symmetry type of molecular normal modes, the vibrational coordinates of the molecule as well as the molecular spectral activity (see Sections 3.2 and [11]). Nevertheless, the group theory can not tell us anything about the expected frequency of a particular vibration. However, there is also a *quantitative* way to solve the vibrational problem which makes use of symmetry considerations. This way help to recognize how the frequencies of the vibrations, which can be obtained from the experiment, are related to the masses of the atoms, the bond angles and bond lengths and most particularly to the *force constants* of the individual bonds and interbond angles [37]. To describe the relationship between he vibrational frequencies and force constants, the so-called *Wilson's method of F and G matrices* is used [13, 38, 39]. In this section we briefly describe this method. To illustrate the realization of Wilson's method, we present the example how to generate the relationship between the frequencies and force constants for particular molecule. In the end of current section the approximate design of *Maple* procedures, which are necessary in order to realize the Wilson's method within the BETHE package, is presented. Note, that the realization of the Wilson's method requires the generation of the vibrational normal coordinates Q_i in terms of the internal displacement vectors of the molecule. Generation of these coordinates is supported by the BETHE package and was described in detail in Ref. [11]. Therefore, we suppose reader to be familiar with the principles of these coordinates generation.

4.1.1 Vibrational secular equation

Let us analyze the molecular vibrational process by setting up the expressions for the kinetic and potential energies of the molecule. We will employ the classical mechanics because it yields a solution of the vibrational problem, which is easier to visualize than the quantum-mechanical solution. Using a system of coordinates moving with the N-atomic molecule, we can present the kinetic energy of this molecule as

$$2T = \sum_{\alpha=1}^{N} m_\alpha \left[\left(\frac{d\triangle x_\alpha}{dt} \right)^2 + \left(\frac{d\triangle y_\alpha}{dt} \right)^2 + \left(\frac{d\triangle z_\alpha}{dt} \right)^2 + \right]. \tag{4.1}$$

The coordinates $\triangle x_1, ..., \triangle z_N$ can be replaced by a new set of coordinates $q_1, ..., q_{3N}$, defined as follows

$$q_1 = \sqrt{m_1}\triangle x_1,\ q_2 = \sqrt{m_1}\triangle y_1,\ q_3 = \sqrt{m_1}\triangle z_1,\ q_4 = \sqrt{m_2}\triangle x_2,\ etc. \tag{4.2}$$

In fact they are the mass-weighted cartesian displacement coordinates. In terms of the time derivatives of these coordinates, the kinetic energy is

$$2T = \sum_{i=1}^{3N} \dot{q}_i^2. \tag{4.3}$$

The potential energy will be some function of coordinates q's. Suppose, that in the equilibrium position the potential energy must to have a minimum and, therefore, the first derivatives $\frac{\partial V}{\partial q_i} = 0$. Then, for sufficiently small amplitudes of vibration (when higher terms are neglected) the potential energy can be expressed as

$$2V = \sum_{i,j=1}^{3N} f_{ij} q_i q_j, \tag{4.4}$$

in which the f_{ij}'s are constants, given by

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 \tag{4.5}$$

with $f_{ij} = f_{ji}$.

Since kinetic energy T is a function of velocities only and potential energy V is a function of the coordinates only, the Newton's equation of motion can be written in the form

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_j} + \frac{\partial V}{\partial q_j} = 0, j = 1, 2, ..., 3N. \tag{4.6}$$

Substitution of the expressions for T and V given above then yields the equations

$$\ddot{q}_j + \sum_{i=1}^{3N} f_{ij} q_i = 0, j = 1, 2, ..., 3N \tag{4.7}$$

This is a set of $3N$ simultaneous second-order linear differential equations. Possible solutions of these equations are

$$q_i = A_i \cos\sqrt{\lambda}t + \epsilon, \tag{4.8}$$

where A_i, λ and ϵ are properly chosen constants. If this expression is substituted in the differential equations (4.7), a set of algebraic equations results:

$$\sum_{i=1}^{3N}(f_{ij}-\delta_{ij}\lambda)A_i = 0, j = 1, 2, ..., 3N, \tag{4.9}$$

in which δ_{ij} is the Kronecker delta symbol. The (4.9) is the set of the linear algebraic equations in the $3N$ unknown amplitudes A_i. The nonvanishing solution of the system (4.9) exists only for very special values of λ, which satisfy the so-called *secular equation*

$$\begin{vmatrix} f_{11}-\lambda & f_{12} & f_{13} & ... & f_{1,3N} \\ f_{21} & f_{22}-\lambda & f_{23} & ... & f_{2,3N} \\ ... & ... & ... & ... & ... \\ f_{3N,1} & f_{3N,2} & f_{3N,3} & ... & f_{3N,3N}-\lambda \end{vmatrix} = 0 \tag{4.10}$$

The elements of this determinant are the coefficients of the unknown amplitudes A_i in the set of equations (4.9). Generally it consist of $3N$ rows and columns (since there are $3N$ unknowns A_i). Each root λ_k corresponds to a set of amplitudes A_{ik} and consequently to one of the solutions (4.8) of the original equations of motion.

For the construction of the secular equation it is not necessary to use the cartesian coordinates q_i. One can use another coordinates, in terms of which the kinetic and potential energies are, respectively, quadratic forms in the velocities and coordinates respectively. For instance, we can use the internal coordinates of the molecule s_i, given by changes of the interatomic distances and interbond angles. These coordinates describe only the internal vibrational motion, without taking into account the rotational and translational motion of a hole molecule in the space. In terms of the $(3N-6)$ internal coordinates the kinetic energy of vibration can be written in the form

$$2T = \sum_{ij}(g^{-1})_{ij}\dot{s}_i\dot{s}_j \tag{4.11}$$

where the coefficients $(g^{-1})_{ij}$ are the elements of inverted matrix g (see below), which involves the masses and certain spatial relationship of the atoms. The potential energy, expressed in the same internal coordinates can be presented as

$$2V = \sum_{ij} f_{ij}s_i s_j \tag{4.12}$$

where f_{ij} are corresponding force constants. A term such as $f_{ii}s_i^2$ represents the potential energy of stretching a given bond or bending a given angle, while the cross terms represent the energies of interaction between such motions. Therefore, the vibrational problem leads to a secular equation

$$\begin{vmatrix} f_{11}-(g^{-1})_{11}\lambda & f_{12}-(g^{-1})_{12} & ... & f_{1n}-(g^{-1})_{1n} \\ f_{21}-(g^{-1})_{21} & f_{22}-(g^{-1})_{22}\lambda & ... & f_{2n}-(g^{-1})_{2n} \\ ... & ... & ... & ... \\ f_{n1}-(g^{-1})_{n1} & f_{n2}-(g^{-1})_{n2} & ... & f_{nn}-(g^{-1})_{nn}\lambda \end{vmatrix} = 0 \tag{4.13}$$

where $n = 3N - 6$.

The secular equation (4.13) is of the fundamental importance in the study of vibration. However, in most cases this equation is of a high degree. Therefore, the method how to simplify this equation is needed. This methods is provided by the symmetry consideration and is called *symmetry factorization* of the secular equation. To perform this factorization, we need to use the so-called *symmetry coordinates* or vibrational normal coordinates Q_i, expressed in terms of the internal coordinates of the molecule [11]. The kinetic energy T of the molecule can be expressed in terms of the vibrational coordinates Q_i as

$$2T = \sum_{jl} (G^{-1})_{jl} \dot{Q}_j \dot{Q}_l, \tag{4.14}$$

while the potential energy as

$$2V = \sum_{jl} F_{jl} Q_j Q_l \tag{4.15}$$

Here the F_{jl} are again force constants, but pertain to vibrations described by the symmetry coordinates $Q_j Q_l$ and matrix G represents the kinetic energy of a molecule in terms of the normal coordinates Q_i. In these coordinates the secular equation (4.13) will have a form

$$|F - G^{-1}\lambda| = 0 \tag{4.16}$$

or

$$|FG - E\lambda| = 0 \tag{4.17}$$

in which F, G and E are matrices and the entire left-hand side of the equation is a determinant. F is a matrix of force constants, which brings the potential energies of the vibrations into the equation, G is a matrix that brings the kinetic energies into the equation and E is a unit matrix. Every parameters λ depend on the particular vibrational frequencies ν and are defined by $\lambda = 4\pi^2 c^2 \nu^2$.

4.1.2 Generation of the secular equation

The relationship between the frequencies of particular vibrations and the force constants can be obtained from the master equation (4.17), introduced in the previous section. To generate this secular equation for a particular molecule, we should start from the matrices f and g. Then, by use the symmetry consideration, we obtain the matrices F and G in the symmetry factorized form. Finally, the secular equation in form (4.17) can be obtained. Solution of this equation gives us the relationship between the force constants f_{ik} and the frequencies of particular vibrations.

The F matrix

Consider again an example of M_3 molecule (symmetry group D_{3h}). The vibrational analysis of this molecule is produced in Section 3.2 and Ref. [11]. The $3N - 6 = 3$ internal displacements

s_i of this molecule are presented by three interatomic distances r_1 and r_2 and r_3 as shown on Fig. 4.1. The set of force constants for the M_3 molecule can be expressed as a square array, where the rows and columns are labeled by the internal displacements. Thus we have the f matrix, or matrix of the f_{ik}

	r_1	r_2	r_3
r_1	f_{11}	f_{12}	f_{13}
r_2	f_{12}	f_{22}	f_{23}
r_3	f_{13}	f_{23}	f_{33}

In this matrix the element f_{21} is replaced by f_{12}, f_{31} by f_{13} and f_{32} by f_{23} because of the general requirement that the matrix be symmetrical about its diagonal. Moreover, since all three internal displacements are *equivalent* (that is, they can be transformed to each other by the symmetry operations of the D_{3h} group), we can also make the substitution $f_{11} = f_{22} = f_{33}$ and $f_{12} = f_{13} = f_{23}$. Finally, we have only two force constants f_{11} and f_{12}. This result is not unexpected: although the M_3 molecule has three vibrational modes, two of them belong to one doubly degenerate irreducible representation E' (see Ref. [11]). Therefore, these modes have the same frequency. It means that only two frequencies are inherent in this molecule and therefore, as a minimum two force constants should be found. Generally, the number of force constants for polyatomic molecule can be determined from the vibrational reducible representation of the molecule $T^{(vib)}$ (see Ref. [11]). If m_γ specifies how many times every irreducible representation $T^{(\gamma)}$ appears in the $T^{(vib)}$, then the number of the force constants n_f is defined as

$$n_f = \sum_\gamma m_\gamma (m_\gamma + 1)/2 \tag{4.18}$$

As determined in the [11], the vibrational representation for the M_3 molecule is $T^{(vib)} = A_1' + E'$. Therefore, $m_{A_1'} = 1$, $m_{E'} = 1$ and $n_f = 1 \times \frac{2}{2} + 1 \times \frac{2}{2} = 2$, as obtained before.

Thus, we have obtained the f matrix in the form

$$f = \begin{vmatrix} f_{11} & f_{12} & f_{12} \\ f_{12} & f_{11} & f_{12} \\ f_{12} & f_{12} & f_{11} \end{vmatrix} \tag{4.19}$$

This is the force constants matrix for the M_3 molecule. To provide the easiest route for dealing with this matrix, we can make the *symmetry factorization* of this matrix. As said before, this factorization can be achieved by use the vibrational normal coordinates Q_i. These coordinates, associated with three vibrational modes of M_3 molecule, have been generated in Ref. [11] in terms of the internal displacements as

$$\begin{aligned} Q_1(A_1') &= \tfrac{1}{\sqrt{3}} r_1 + \tfrac{1}{\sqrt{3}} r_2 + \tfrac{1}{\sqrt{3}} r_3 \\ Q_2(E') &= \tfrac{1}{\sqrt{2}} r_1 - \tfrac{1}{\sqrt{2}} r_3 \\ Q_3(E') &= -\tfrac{1}{\sqrt{6}} r_1 + \tfrac{2}{\sqrt{6}} r_2 - \tfrac{1}{\sqrt{6}} r_3 \end{aligned} \tag{4.20}$$

and are shown graphically on Fig. 4.1. In order to simplify the matrix f, we need to express

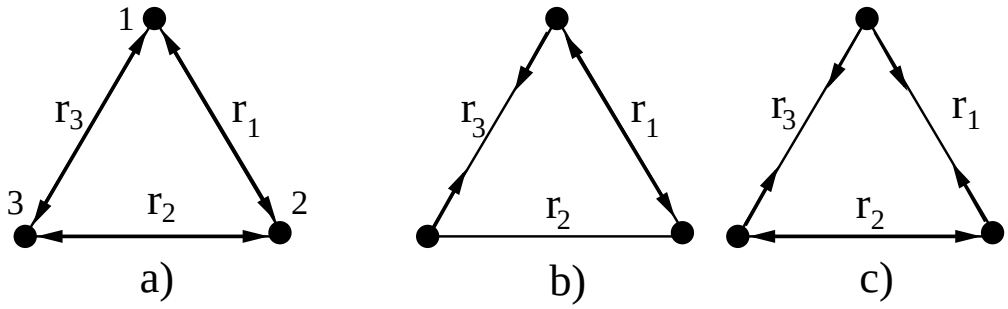

Figure 4.1: Vibrational modes of M_3 complex in terms of the internal displacement vectors: a)$Q_1(A_1')$, b)$Q_2(E')$, c)$Q_3(E')$.

each of the two equations of the potential energy (4.12) and (4.15) in matrix notation:

$$2V = \mathbf{s'fs} \tag{4.21}$$

$$2V = \mathbf{Q'FQ} \tag{4.22}$$

by writing the s_i as a column matrix $\mathbf{s}$ and the Q_j as a column matrix $\mathbf{Q}$, and taking $\mathbf{s'}$ and $\mathbf{Q'}$ as the corresponding row matrices. Moreover, the relationship between the internal coordinates and the symmetry coordinates can be written in matrix form:

$$\mathbf{Q} = \mathbf{Us} \tag{4.23}$$

where (for the M_3 molecule) matrix $\mathbf{U}$ is

	r_1	r_2	r_3
Q_1	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$
Q_2	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$
Q_3	$-\frac{1}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$

Since matrix $\mathbf{U}$ describes a linear orthogonal transformation between the coordinates Q_i and r_i, the inverse of the matrix $\mathbf{U}$ its simply its transpose $\mathbf{U'}$. Thus, (4.23) may be rewritten as

$$\mathbf{s} = \mathbf{U^{-1}Q'Q} \tag{4.24}$$

and we have

$$\mathbf{s'} = (\mathbf{U'Q})' = \mathbf{Q'U}. \tag{4.25}$$

We can now equate the right-hand sides of two equations(4.21), and employ relations (4.23) and (4.25). Finally, we obtain

$$\mathbf{UfU'} = \mathbf{F} \tag{4.26}$$

We thus obtain a simple matrix equation for transforming the f matrix into the F matrix. For the M_3 molecule this can be presented as

$$\mathbf{F = Uf'U} = \begin{vmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{6}} & \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \end{vmatrix} \begin{vmatrix} f_{11} & f_{12} & f_{12} \\ f_{12} & f_{11} & f_{12} \\ f_{12} & f_{12} & f_{11} \end{vmatrix} \begin{vmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & 0 & \frac{2}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} \end{vmatrix} \tag{4.27}$$

Thus, we obtain the F matrix in the symmetry factorized form.

$$\mathbf{F} = \begin{vmatrix} f_{11}+2f_{12} & 0 & 0 \\ 0 & f_{11}-f_{12} & 0 \\ 0 & 0 & f_{11}-f_{12} \end{vmatrix} \tag{4.28}$$

The G matrix

The generation of G matrix can be produced similarly as for the F matrix. As before, we start from the constructing of g matrix, which was introduced in Eq. (4.11)). For the M_3 molecule this matrix generally has a form

$$g = \begin{vmatrix} g_{11} & g_{12} & g_{13} \\ g_{12} & g_{22} & g_{23} \\ g_{13} & g_{23} & g_{33} \end{vmatrix} \tag{4.29}$$

where the requirement that the matrix should be symmetrical about its diagonal is taking into account. Elements of g matrix can be expressed in terms of the atomic masses and the dimensions of the molecule. Commonly used matrix elements g_{ij} are tabulated in the form of general expressions for different types of internal coordinates s_i and s_j involved. The specific parameters of any molecule should be inserted into these expressions. Such a tabulation and direction for its use is given, for instance, in Ref. [13, 38]. For the M_3 molecule it is found that $g_{11} = \mu_1 + \mu_2$, $g_{12} = \mu_2 \cos(\theta_{12})$, $g_{13} = \mu_1 \cos(\theta_{13})$, $g_{22} = \mu_2 + \mu_3$, $g_{23} = \mu_3 \cos(\theta_{23})$ and $g_{33} = \mu_1 + \mu_3$, where μ_i is the reciprocal mass of i atom and θ_{ij} is the angle between i-th and j-th bonds. Since the three atoms of M_3 molecule are identical and placed in the corners of equilateral triangle, we have $\mu_1 = \mu_2 = \mu_3 = \mu$, $\theta_{12} = \theta_{12} = \theta_{23} = 2\pi/3$. Therefore, for the M_3 molecule g matrix has the form

$$g = \begin{vmatrix} 2\mu & -\mu/2 & -\mu/2 \\ -\mu/2 & 2\mu & -\mu/2 \\ -\mu/2 & -\mu/2 & 2\mu \end{vmatrix} \tag{4.30}$$

The (symmetry factorized) G matrix may be constructed by the procedure analogous to that used for the F matrix (see Eq. (4.27))

$$\mathbf{G} = \mathbf{U}g\mathbf{U}' = \begin{vmatrix} \mu & 0 & 0 \\ 0 & 5/2\mu & 0 \\ 0 & 0 & 5/2\mu \end{vmatrix} \tag{4.31}$$

Now the relationship between the frequencies of the fundamental modes and a set of force constants can be recognized from the explicit form of the secular equation (4.17).

$$\begin{vmatrix} f_{11}+2f_{12} & 0 & 0 \\ 0 & f_{11}-f_{12} & 0 \\ 0 & 0 & f_{11}-f_{12} \end{vmatrix} \begin{vmatrix} \mu & 0 & 0 \\ 0 & 5/2\mu & 0 \\ 0 & 0 & 5/2\mu \end{vmatrix} - \begin{vmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_2 \end{vmatrix} = 0 \tag{4.32}$$

The root λ_2 of the secular equation occurs twice, because one of the normal modes is doubly degenerate and there are two independent normal modes of vibration with the same frequency.

This is the end of the symmetry analysis. From here the problem of generation the relationship between the vibrational frequencies and force constants is a purely computational one.

Note, that after the symmetry factorization, the secular equation not always takes on such a simple diagonal form like Eq. (4.32). For instance, the three-dimensional secular equation for the molecule of water, constructed in Ref. [13], is symmetry factorized into one 2×2 block and a one 1×1 block. Moreover, for most molecules – in contrast to the M_3 molecule – the number of the force constants exceeds the number of molecular vibrational modes. The most generally applicable procedure for dealing with this problem is to measure the frequencies of *isotopically substituted* molecules (for instance, involving the deuterium). Such molecules provide new sets of equations involving different frequencies , but give rise to the same force constants.

4.1.3 Realization of the Wilson's method within the Bethe framework.

The Wilson's method, described above, makes extensive use of the symmetry. Therefore, it can be easily realized by means of the BETHE program. Having specified the atomic coordinates of particular molecule as the input of the problem, the user can obtain from the BETHE the expressions for the force constants in terms of the vibrational frequencies (or vice versa) (see Eq. 4.32) for this molecule. The most difficult problem, which arises at the program realization of Wilson's method, is the generation of the g matrix. As said before, the elements of this matrix are tabulated in form of the general expressions for different types of molecular bonds. Therefore, the storage procedure for keeping the g_{ij} elements need to be created. Remaining parameters, such as internal coordinates and the vibrational normal coordinates, which are necessary for the Wilson's method, are already available by the BETHE package.

If the number and the symmetry types of the vibrational modes and the symmetry coordinates for these modes are supposed to be known, the following steps should be done to generate the relationship between the frequencies and force constants:

- Generation of the U-matrix (4.23), which express the transformation between the internal displacement vectors and the vibrational normal coordinates;
- Generation of the f-matrix (4.19), taking into account the symmetry of this matrix about the diagonal and equivalency of some internal displacements;
- Generation of the F-matrix in the symmetry-factored form (4.28);
- Tabulation of the elements of g-matrix for different types of internal coordinates s_i and s_j;
- Generation of the g-matrix in the general form (4.29) and in the explicit form (4.30);
- Generation of the G-matrix in the symmetry-factored form (4.31);
- Construction of the secular equations $FG - E\lambda = 0$ (4.32);
- Generation of the relationships $F_{ij}(\lambda_k)$;

Table 4.1: Commands of the BETHE program, to realize the Wilson-method

Bethe_generate_U_matrix()	Generates the transformation matrix between the internal s and symmetry S vibrational coordinates.
Bethe_generate_f_matrix()	Generates the force constants matrix f.
Bethe_generate_F_matrix()	Generates the (symmetry factored) force constants matrix F.
Bethe_generate_g_matrix()	Generates the matrix g.
Bethe_g_matrix_elements()	Returns the elements of the matrix g.
Bethe_generate_G_matrix()	Generates the (symmetry factored) matrix G.
Bethe_generate_secular_equation()	Generates the secular equation $FG - E\lambda = 0$.

All of these steps can be realized on the basis of the package BETHE. In Table 4.1 the approximate list of procedures (without specification of the input-output parameters) is shown. Apart from these "working" procedures, the "testing" procedures for confirmation of some results can be provided. For instance, the number of independent force constants in the f matrix can be compared with the number n_f of the force constants, calculated from the vibrational reducible representation of the molecule (see Eq. (4.18)). Therefore, the procedure `Bethe_test_force_constants_number()`, returning the boolean variables *true* or *false*, is recommended to create.

4.2 Vibrational-electronic coupling and the Jahn-Teller effect

In the previous section the Wilson's method for determining the relationship between the vibrational frequencies and force constants has been suggested to realize within the BETHE package. Another application of symmetry, which could be implemented into the BETHE, is the problem of spontaneous distortion of the molecular symmetry, known as the *Jahn-Teller distortion* or *Jahn-Teller effect*. This effect consists in the instability and spontaneous distortion of the nuclei configuration of a molecule in degenerate electronic state. The presence of the Jahn-Teller (JT) effect was supposed by Landau in the year 1934. Later it was verified by Jahn and Teller and shown [40] to be true for all nonlinear molecular systems.

The theoretical treatment of the JT effect makes use of the symmetry and of the group theory. This theory helps not only to predict the distortions of the molecular symmetry, but also to find the final - stable - configuration of the molecule. Use of the CA approach to analyze the JT distortion seems to be very effective. Therefore, we suggest to implement the also the JT effect into the BETHE package. This section provides a brief explanation of the (quite complicated) theoretical background of this effect. The details about the JT effect can be found in Refs. [41, 45]. We start from the short outlook of the adiabatic approximation. Then the JT effect is introduced as the deviation from this approximation. In the next sections the JT theorem is provided, which allows to deduce a number of qualitative results without performing specific calculations. Moreover, the methods how to construct and analyze the adiabatic potential of the molecule are also presented. Finally, in section 5.2.5 we make the suggestions for the

extension of the BETHE package.

4.2.1 Adiabatic approximation and vibronic interaction

It is known, that the structure and properties of a molecular system are determined by the motion of its electrons and by their interaction. The motion and interaction of electrons are governed by the quantum mechanical laws. However, because of the mathematical difficulties, the quantum mechanical treatment of the molecular structure in most cases can be carried out only if some simplifying approximations are introduced. Let us start from the adiabatic or Born-Oppenheimer approximation, which is one of the most important simplifications in quantum mechanics. This approximation is based on the fundamental inequality of the masses and velocities of electrons and nuclei. Since the nuclei mass is about 2000 times that of the electron, the velocity of the latter is much greater than that of the former. Therefore, it can be assumed that every fixed position of the nuclei corresponds to a stationary electronic state and that the motions of the nuclei are governed by the average field of the electrons. This assumption enables us to ignore at the beginning the nuclei motions when solving the electronic part of the problem, and then to use the mean electronic energy as the potential for the nuclear motion.

To illustrate these stages, let us divide the total Hamiltonian of the Schrödinger equation into three components:

$$H = H_r + H_Q + V(r, Q) \tag{4.33}$$

where H_r is the electronic component, including the kinetic energy of the electrons and the interelectronic electrostatic interaction, H_Q is the kinetic energy of the nuclei and $V(r, Q)$ is the energy due to interaction of the electrons with the nuclei and internuclear repulsion (r and Q denote the whole set of coordinates of the electrons r_i, $i = 1, 2, ..., n$ and nuclei Q_α, $\alpha = 1, 2, ..., N$, respectively). The operator $V(r, Q)$ can be expanded as a series of small displacements of the nuclei about the point $Q_\alpha = Q_{\alpha 0} = 0$ (chosen as origin):

$$V(r, Q) = V(r, 0) + \sum_\alpha \left(\frac{\partial V}{\partial Q}\right)_0 Q_\alpha + \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right)_0 Q_\alpha Q_\beta + ... \tag{4.34}$$

If the first term of this expansion is regarded as the potential energy of the electrons in the fixed nuclei, one can solve the electronic part of the Schrödinger equation

$$\left[H_r + V(r, 0) - \varepsilon'_k\right] \varphi_k(r) = 0 \tag{4.35}$$

and obtain a set of energies ε'_k and wave functions $\varphi_k(r)$ for the given nuclear configuration corresponding to the point $Q_{\alpha 0}$. In order to see how these solutions vary under nuclear displacements, the full Schrödinger equation

$$(H - E)\Psi(r, Q) = 0 \tag{4.36}$$

must be solved. According to the adiabatic approximation, the solution $\Psi(r, Q)$ of the Eq. (4.36) can be expanded in terms of electronic functions $\varphi_k(r)$,

$$\Psi(r, Q) = \sum_k \chi_k(Q)\varphi_k(r) \tag{4.37}$$

where the expansion coefficients $\chi_k(Q)$ are functions of the nuclear coordinates. Substituting equation (4.37) into equation (4.36), after some transformations one obtains the following system of coupled equations for the functions $\chi_k(Q)$:

$$[H_Q + \varepsilon_k(Q) - E]\,\chi_k(Q) + \sum_{m \neq k} W_{km}(Q)\chi_m(Q) = 0 \tag{4.38}$$

In this system $W_{km}(Q)$ denotes the electronic matrix element of the so-called *vibronic interaction*. This VIBRONIC interaction arises when the VIBRations of the nuclei generate the mixing of the electrONIC states and can be expressed as that part of the electron-nuclear interaction $V(r,Q)$, which depends on Q,

$$W(r,Q) = V(r,Q) - V(r,0) = \sum_{\alpha} \left(\frac{\partial V}{\partial Q}\right)_0 Q_\alpha + \frac{1}{2}\sum_{\alpha,\beta} \left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right)_0 Q_\alpha Q_\beta + ... \tag{4.39}$$

The vibronic interaction is especially strong in the case of the electronic degeneracy. The member

$$\varepsilon_k(Q) = \varepsilon'_k + W_{kk}(Q) \tag{4.40}$$

of the system (4.38) is the potential energy of the nuclei in the mean field of the electrons in state $\varphi_k(r)$. It is seen from the coupled system of equations (4.38) that if vibronic mixing of different electronic states can be ignored ($W_{km}(Q) = 0$ for $k \neq m$), the coupling between these states vanishes and the system (4.38) decomposes into a set of simple equations:

$$[H_Q + \varepsilon_k(Q) - E]\,\chi_k(Q) = 0 \tag{4.41}$$

each of which, for given k, represents the Schrödinger equation for the nuclei moving in the mean field of the electrons in state $\varphi_k(r)$.

In other words, if the motions of the nuclei and electrons are separated, the problem as a whole can be solved in two stages. In the first stage, the electronic states $\varphi_k(r)$ are determined as solutions of equation (4.35) and used to calculate the potential energy of the nuclei $\varepsilon_k(Q)$ by equation (4.41). In the second stage the wave functions $\chi_k(Q)$ and energies E of the nuclei are determined by the equation (4.41), the total wave function being $\Psi(r,Q) = \varphi_k(r)\chi_k(Q)$. This is the simple adiabatic approximation. Criterion for this approximation is that terms of the vibronic mixing $W_{km}(Q)$ of different electronic states in equation (4.38) can be ignored, or

$$\hbar\omega \ll |\varepsilon'_m - \varepsilon'_k| \tag{4.42}$$

where $\hbar\omega$ is the energy quantum of vibrations in the electronic state k or m and ε'_m and ε'_k are electronic states. By other words, the adiabatic approximation can be used, only if the electronic states of the system are not degenerate.

4.2.2 Deviation from the adiabatic approximation. Vibronic constants.

The adiabatic approximation, described above, is very important for number of applications. However, in some systems the electrons do not follow the motion of nuclei, while the nuclear

states are determined not only by the average field of the electrons. The resulting coupling between the electronic and nuclear motions is the essential deviation from the adiabatic approximation.

Consider a molecular system in which the electronic states are degenerate or there are near-lying electronic states. For these electronic states criterion (4.42) is not satisfied and vibronic interaction plays a significant role in determining the molecular properties. This interaction $W_{km}(Q)$ is given by the equation (4.39) and contains linear, quadratic, cubic, etc., terms. In most cases it is enough to take into account the linear and quadratic terms. To simplify the further analysis of the vibronic interaction, we will use the symmetry approach. Within this approach, the nuclei coordinates Q_α can be specified as the *normal vibrational coordinates* in terms of the Cartesian displacement vectors (see Ref. [11]). In order to determine these coordinates, first of all the initial configuration of the molecule should be defined. Of course, in a number of cases this configuration can be taken from the experiment. However, it is not always possible to determine the initial configuration exactly. Therefore, the initial nuclear configuration must be chosen at the point, where the electronic states are degenerate. Since the electronic degeneracy is related to the symmetry of molecular system, the initial configuration is one of highest symmetry. As described in Ref. [11], the normal coordinates Q_α can be classified in terms of the irreducible representations T of the molecular symmetry group and their components γ. Therefore, in the normal coordinates $Q_{T\gamma}$ the operator of vibronic interaction (4.39) may be written in the form

$$W(r,Q) = \sum_{T\gamma} \left(\frac{\partial V}{\partial Q_{T\gamma}}\right)_0 Q_{T\gamma} + \frac{1}{2} \sum_{T^{(1)}\gamma_1} \sum_{T^{(2)}\gamma_2} \left(\frac{\partial^2 V}{\partial Q_{T^{(1)}\gamma_1} \partial Q_{T^{(2)}\gamma_2}}\right)_0 Q_{T^{(1)}\gamma_1} Q_{T^{(2)}\gamma_2} \quad (4.43)$$

Coefficients of this expansion are the derivatives of the electron-nuclear interaction. The matrix elements of these coefficients are the constants of vibronic coupling or *vibronic constants*. These constants are of fundamental importance in the analysis of vibronic interaction effect. They characterize the measure of coupling between the electronic structure and nuclear displacements, i.e. the measure of influence of the nuclear displacements on the electron distribution. If we denote the electronic states by appropriate irreducible representations $T, T', ...$ of the molecular symmetry group and suppose, that the states T and T' are not degenerate, then the matrix element

$$F_{\bar{T}}^{TT'} = \left\langle T \left| \left(\frac{\partial V}{\partial Q_{\bar{T}}}\right) \right| T' \right\rangle \quad (4.44)$$

is called the *linear vibronic constant*. Following the rules of group theory, $F_{\bar{T}}^{TT'}$ is nonzero if and only if the direct product $T \otimes T'$ contains the irreducible representation $\bar{T}$. If T or T' or both are degenerate, a set of linear vibronic constants $F_{\bar{T}\bar{\gamma}}^{T\gamma T'\gamma'}$ must be introduced instead $F_{\bar{T}}^{TT'}$. However, according to the Wigner-Eckart theorem [8, 46], we can obtain following relation between different components of the linear vibronic constants:

$$F_{\bar{T}\bar{\gamma}}^{T\gamma T'\gamma'} = F_{\bar{T}}^{TT'} \left\langle \bar{T}\bar{\gamma} T'\gamma' | T\gamma \right\rangle, \quad (4.45)$$

where $\left\langle \bar{T}\bar{\gamma} T'\gamma' | T\gamma \right\rangle$ are the Clebsch-Gordan coefficients for the symmetry group (see Ref. [3]). Therefore, if one knows at least one vibronic constant of certain symmetry, all the others can be

easily calculated by (4.45) using the Clebsch-Gordan coefficients. Some of the linear vibronic constants have a clear physical meaning. For instance, the diagonal vibronic constant $F_{\bar{T}}^{TT}$ has the sense of the force, with which the electrons in state T affect the nuclei in the direction of the normal coordinate $Q_{\bar{T}}$. According to the group theoretical condition, the constant $F_{\bar{T}}^{TT}$ is nonzero if the symmetrized(!) part $[T \otimes T]$ of the direct product $T \otimes T$ contains $\bar{T}$ (see Section 2.4.3). For nondegenerate T the direct product $[T \otimes T]$ always results in the totally symmetric irreducible representation. Therefore, the nuclei configuration can be distorted only in the direction of totally symmetric displacement, which does not change the symmetry of the system. If the electronic state T is degenerate, the symmetrized part of the direct product $[T \otimes T]$ contains nontotally symmetric representations. Therefore, the molecular symmetry can be distorted *nonsymmetrically*. These nonsymmetrical distortions are essential in the JT effect.

Similarly to the linear vibronic constants, the quadratic (or second-order) vibronic constants can be introduced as

$$K_{\bar{T}\bar{\gamma}}^{(TT')} = \frac{1}{2}\left\langle T\left[\left(\frac{\partial^2 V}{\partial Q_{T^{(1)}\gamma_1}\partial Q_{T^{(2)}\gamma_2}}\right)_0\right]T'\right\rangle \tag{4.46}$$

The totally symmetric part of the diagonal matrix element (4.46) forms the curvature of the adiabatic potential and appears as its essential component $\frac{1}{2}\sum_{T\gamma} K_{\bar{T}}^{T} Q_{\bar{T}\bar{\gamma}}^2$. Corresponding constant $K_{\bar{T}}^{T}$ is called *force constant*. The remaining terms and the nondiagonal matrix elements contain the quadratic vibronic constant $G_{\bar{T}}^{TT'}$, which must be distinguished from the force constant (see Refs. [41, 43] for details).

4.2.3 Jahn-Teller theorem

The vibronic constants, introduced in the previous section, allow to formulate the so-called *Jahn-Teller theorem*, which predicts the nonsymmetrical molecular distortions. This theorem is based on the group-theoretical analysis of the behavior of the adiabatic potential of a molecule near the point of electronic degeneracy. Suppose, that by solving the electronic Schrödinger equation (4.35) for the nuclei fixed at the point $Q_{\bar{T}\bar{\gamma}} = 0$ we obtain an f-fold degenerate electronic term, i. e. f states $\varphi_k(r), k = 1, 2, ..., f$ with identical energies $\varepsilon'_k = \varepsilon_0$. To answer the question how these energy levels vary under nuclear displacements $Q_{\bar{T}\bar{\gamma}} \neq 0$, the adiabatic potential near the point of degeneracy must be determined. It can be done by estimating the effect of the vibronic interaction terms $W(r, Q)$ on the energy level ε'_k. For sufficiently small nuclear displacement $Q_{\bar{T}\bar{\gamma}}$ the AP $\varepsilon_k(Q)$ can be obtained as a solution of the secular equation

$$|W_{ij} - \varepsilon| = 0 \tag{4.47}$$

where W_{ij} are the matrix elements of the vibronic interaction operator (4.39) calculated with the wave functions of the degenerate term. The presence of this term is assumed because of the high symmetry of the system. Note, that since the totally symmetric displacements do not change the symmetry of the system, we will omit these displacements. Moreover, the second order terms of vibronic interaction operator may also be omitted due to the assumed small

values of $Q_{\bar{T}\bar{\gamma}}$. Therefore, matrix elements of the vibronic interaction operator are

$$W_{T\gamma T\gamma'} = \sum_{\bar{T}\bar{\gamma}} F^{T\gamma T\gamma'}_{\bar{T}\bar{\gamma}} Q_{\bar{T}\bar{\gamma}} = \sum_{\bar{T}\bar{\gamma}} F^{T}_{\bar{T}} Q_{\bar{T}\bar{\gamma}} \left\langle \bar{T}\bar{\gamma} T\gamma' | T\gamma \right\rangle \tag{4.48}$$

where $F^T_{\bar{T}}$ are the linear vibronic constants (4.44). If at least one of these constants s nonzero, then at least one of the roots ε of the equation (4.47) contains not only quadratic, but also linear terms in appropriate displacement $Q_{\bar{T}\bar{\gamma}}$ and, therefore, the adiabatic potential $\varepsilon_k(Q)$ has no minimum at the point $Q_{\bar{T}\bar{\gamma}} = 0$ with respect to this displacement. The question whether the vibronic constant $F^T_{\bar{T}}$ is zero or not may be answered by means group-theoretical rule, mentioned in previous section. Examining all types of the degenerate terms of all symmetry point groups, Jahn and Teller showed, that *for any orbital degenerate term T of any molecular system there are nontotally symmetric displacements $\bar{T}$ with respect to which at least one of the vibronic constants is nonzero, $F^T_{\bar{T}} \neq 0$. Therefore, the adiabatic potential of this term has no minimum in the point $Q_{\bar{T}\bar{\gamma}} = 0$.* This statement is just the JT theorem. The proof of this theorem by means of an examination of all types of degenerate terms in all symmetry point groups allows to reveal the JT active modes. These modes are the nuclei displacements $Q_{\bar{T}\bar{\gamma}}$ for which the vibronic constant $F^T_{\bar{T}}$ is nonzero and which remove the electron degeneracy of the electronic term T.

4.2.4 Adiabatic potential and stability of the molecular configuration

As follows from the the JT theorem, at the point of the nuclei configuration, where the electronic state is degenerate, the surface of the potential energy of the nuclei in the mean field of electrons has no minimum. The question arises whether this surface possesses any minimum and where this minimum is situated. Or, more generally, what is the stable configuration of the nuclei in the presence of the JT effect. To answer this question the shape of the adiabatic potential $\varepsilon(Q_{\bar{T}\bar{\gamma}})$ in the space of all nuclear displacements $Q_{\bar{T}\bar{\gamma}}$ must be determined. For the f-fold degenerate electronic state T the adiabatic potential has f sheets $\varepsilon_k(Q)$ $k = 1, 2, ..., f$, which intersect at the point of degeneracy. To determine $\varepsilon_k(Q_{\bar{T}\bar{\gamma}})$ we should first separate the totally symmetric part of the diagonal matrix elements of the vibronic interactions, which give rise to the constant $K^T_{\bar{T}}$ (see Eq. (4.46)). Then the f sheets of the adiabatic potential of an f-fold degenerate electronic term are given by the following expressions

$$\varepsilon_k(Q_{\bar{T}\bar{\gamma}}) = \frac{1}{2} \sum_{\bar{T}\bar{\gamma}} K^T_{\bar{T}} Q^2_{\bar{T}\bar{\gamma}} + \varepsilon^\nu_k(Q_{\bar{T}\bar{\gamma}}),\ k = 1, 2, ..., f \tag{4.49}$$

where $\varepsilon^\nu_k(Q_{\bar{T}\bar{\gamma}})$ are the roots of the secular equation

$$|W^\nu_{\gamma\gamma'}(Q_{\bar{T}\bar{\gamma}}) - \varepsilon^\nu| = 0;\ \gamma, \gamma' \in T\ (\gamma, \gamma' = 1, 2, ..., f) \tag{4.50}$$

in which the diagonal matrix elements $W^\nu_{\gamma\gamma'}(Q_{\bar{T}\bar{\gamma}})$ do not contain the totally symmetric part of the quadratic terms used in the force constant formation.

Here we illustrate, how to construct and analyze the adiabatic potential for a particular molecule. Then we consider the octahedral molecule of type ML_6 (symmetry group O_h). The JT distortion of such molecule is discussed very often in the literature [47, 48]. The shape

of this molecule is shown on Fig. 4.2 a). By calling the irreducible representation of the group O_h

```
> Bethe_group(Oh, irreps);

        ["A1g", "A2g", "Eg", "T1g", "T2g", "A1u", "A2u", "Eu", "T1u", "T2u"]
```

we define, which electronic states are presented in the ML_6 molecule. Consider the doubly degenerate electronic state E_g (so-called E_g-term). The systems with E_g- or E_u-term are very widely spread, but in the same time quite simple to illustrate the JT effect. First of all we need to define the JT active vibrational (or normal) modes of this molecule. To achieve this, we need to specify the molecule ML_6 as a collection of individual atoms, situated as shown on the Fig. 4.2 a).

```
> ML6 := molecule(atom( M, [ 0, 0, 0]),
                  atom(L1, [ 0, 0, a]),
                  atom(L2, [ 0, 0, -a]),
                  atom(L3, [ 0, a, 0]),
                  atom(L4, [ 0, -a, 0]),
                  atom(L5, [ a, 0, 0]),
                  atom(L6, [ -a, 0, 0]));

         ML6 := molecule(atom( M, [0, 0, 0]), atom(L1, [0, 0, a]),
                         atom(L2, [0, 0, -a]), atom(L3, [0, a, 0]),
                         atom(L4, [0, -a, 0]), atom(L5, [a, 0, 0]),
                         atom(L6, [-a, 0, 0]))
```

The vibrational modes of this molecule can be found as described in Ref. [11]:

```
> VR := Bethe_group_representation(Oh, vibrational, ML6);
Bethe_decompose_representation(Oh, VR);

      VR := [15, -1, -1, -1,  0,  0,  0,  0,  0,  0,  0,  0, 1, 1, 1, 1,
              1,  1,  1,  1,  1,  1,  1,  1, -3,  5,  5,  5, 0, 0, 0, 0,
              0,  0,  0,  0, -1, -1, -1, -1, -1, -1,  3,  3, 3, 3, 3, 3]

               ["A1g", "Eg", "T2g", "T1u", "T1u", "T2u"]
```

Then we need to define, which of these vibrational modes will be JT active in the E_g state (i.e. will destroy the octahedral symmetry in this state). According to the JT theorem we should find the symmetrized part of the direct product $E_g \otimes E_g$

```
> Bethe_group_direct_product(Oh, "Eg", "Eg", symmetrized);

               ["A1g", "Eg"]
```

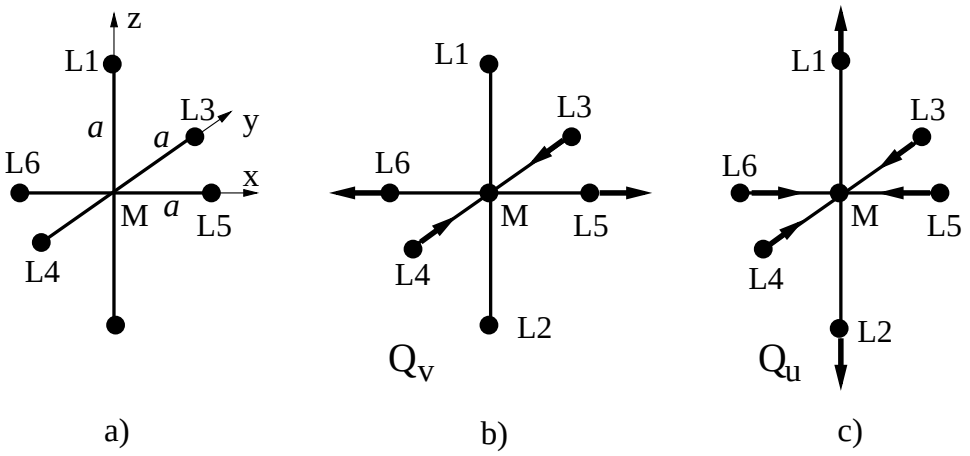

Figure 4.2: Shape of octahedral ML_6 molecule (a) and its normal displacements Q_v (b) and Q_u (c).

The result shows, that nonzero parts of the vibronic interaction operator $W^{\nu}_{\gamma\gamma'}(Q_{\bar{\Gamma}\bar{\gamma}})$ for E_g term contain only type E_g nontotally symmetric displacements $Q_{\bar{\Gamma}\bar{\gamma}}$ (the totally symmetric displacement is not taken into account). Let us take the symbol e_g for this representation, in order to distinguish it from the state of the molecule. Therefore, we specify corresponding JT problem as the $E_g - e_g$ problem. It means, that the octahedral molecule in degenerate state E_g will be distorted in the direction of two normal coordinates $Q_{e_g u}$ and $Q_{e_g v}$ of the irreducible representation e_g. Since both included irreducible representations have the subscript g, we can omit this subscript. Then the corresponding JT problem will be considered as $E - e$ problem. The two components Q_{eu} and Q_{ev} of the normal displacements e (later we denote them Q_u and Q_v) can be defined in the BETHE package as two sublists of the list `Q`

```
> Q := Bethe_normal_coordinates(Oh, ML6, "Eg", Cartesian);
```

```
                                      1/2       1/2    1/2         1/2
                                     3         3      3           3
Q:=[[0, 0, 0, 0, 0, 0, 0, 0, 0, 0,- ---, 0, 0,---, 0,---, 0, 0,- ---, 0, 0],
                                     12        12     12          12

                    1         1      -1        1      -1        1
   [0, 0, 0, 0, 0, --, 0, 0, ---, 0, --, 0, 0, --, 0, --, 0, 0, --, 0, 0]]
                    6         6      12        12     12        12
```

These sublists define the displacements of cartesian coordinates (x, y, z) of every atom, in the same sequence as specified in the variable `ML6`. These coordinates are shown graphically on Fig. 4.2 b)-c). Taking into account the Eq. (4.45), and retaining only the linear order vibronic interaction terms, we can write the explicit form of the secular equation (4.50) for the $E - e$

problem as (see [43])

$$\begin{bmatrix} F_e^E Q_u - \varepsilon^\nu & -F_e^E Q_v \\ -F_e^E Q_v & -F_e^E Q_u - \varepsilon^\nu \end{bmatrix} = 0 \tag{4.51}$$

where

$$F_e^E = \left\langle U \left| \left(\frac{\partial V}{\partial Q_u} \right)_0 \right| U \right\rangle . \tag{4.52}$$

This equation can be solved directly for ε^ν.

$$\begin{array}{c} \varepsilon_\pm^\nu(Q_u, Q_v) = \pm F_e^E \sqrt{Q_u^2 + Q_v^2} \\ \varepsilon_k(Q_u, Q_v) = \frac{1}{2} K_e^E (Q_u^2 + Q_v^2) \pm F_e^E \sqrt{Q_u^2 + Q_v^2} \end{array} \tag{4.53}$$

or, if to use the polar coordinates $Q_u = \rho\cos(\phi)$, $Q_v = \rho\sin(\phi)$,

$$\begin{array}{c} \varepsilon_\pm^\nu(\rho, \phi) = \pm F_e^E \rho \\ \varepsilon_k(\rho, \phi) = \frac{1}{2} K_e^E \rho^2 \pm F_e^E \rho \end{array} \tag{4.54}$$

The surface of this adiabatic potential has the form of the rotation surface, called the "Mexican hut" and shown on the Fig. 4.3. As seen from this figure, the octahedral system ML_6 will be distorted along the bottom of the surface to the tetrahedral symmetries and various continuously from one configuration to another (points a, b, c, d, e).

If in the equation (4.50) the second order terms are taken into account, the adiabatic potential is defined in polar coordinates as

$$\varepsilon_k(\rho, \phi) = \frac{1}{2} K_e^E \rho^2 \pm \rho \sqrt{F_e^2 + G_e^2 \rho^2 + 2 F_e G_e \rho \cos(3\phi)} \tag{4.55}$$

where G_e is the quadratic vibronic constant. The surface of this adiabatic potential is more complicated and shown on Fig. 4.4. Three minima (points 1, 3 and 5) of the AP correspond to the three distortions of the ML_6 molecule, as shown on the Fig. 4.5. .

4.2.5 Determining of the stable molecular configuration.

In the previous section we demonstrate, how to construct the adiabatic potential for the ML_6 molecule. The points (or curves) of minimum of this potential correspond to the stable configuration of the molecule. The question arises, how to find these configurations, knowing the values of the Q_v and Q_u at the minima points. Consider, for instance, the extremal point 3 in Fig. 4.4. This point is defined by to the polar angle $\varphi = 2\pi/3$. Therefore, in this point

$$Q_u = -\frac{\rho}{2}, Q_v = \frac{\sqrt{3}\rho}{2} \tag{4.56}$$

where the constant ρ can be expressed by means the constants F_e^E, G_e^E and K_e^E. To find a new atomic coordinates of the ML_6 we need to know the amplitudes of the Q_u and Q_v vibrations. However, the label of the symmetry group of the distorted molecule can be found qualitatively. To achieve this, we need to add every cartesian coordinate of ML_6 by the small increment according to the normal coordinates in point 3. It can be illustrated by the Table 4.2. The first

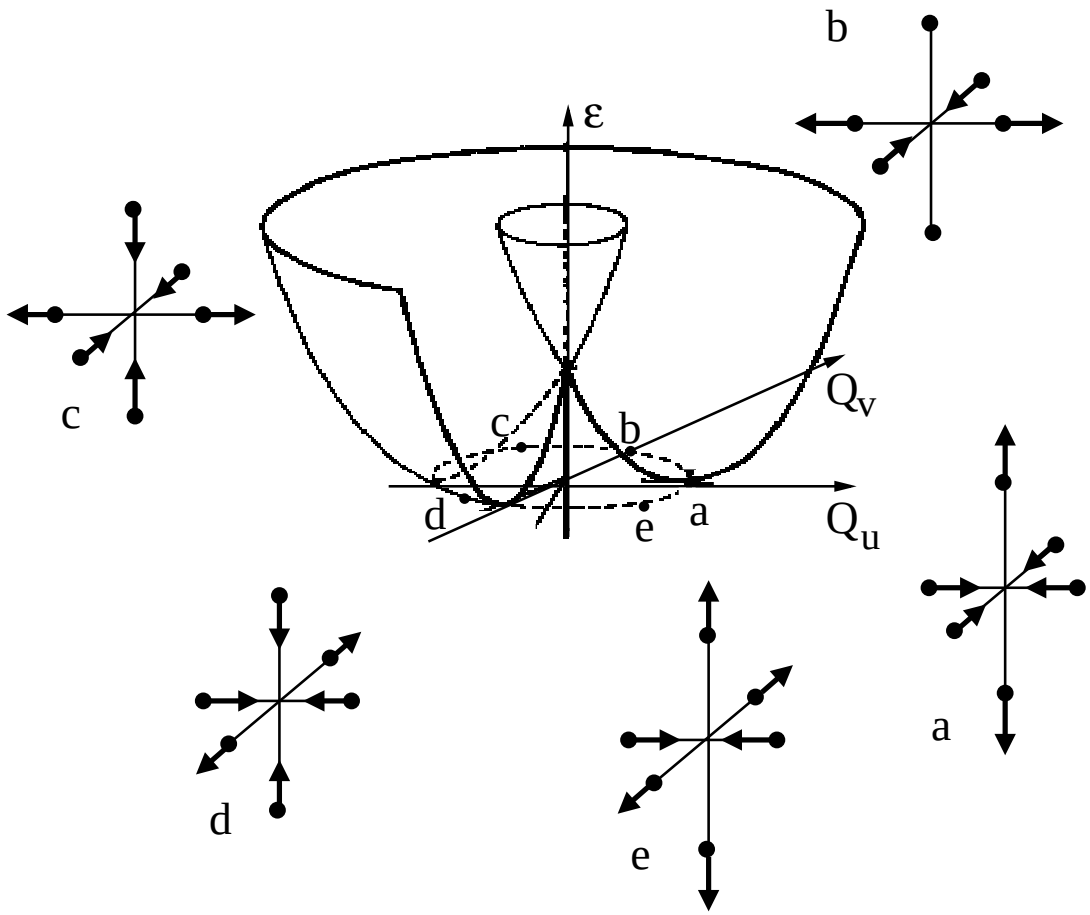

Figure 4.3: Adiabatic potential of the octahedral molecule neglecting quadratic terms of vibronic interaction (from www.mi.infm.it).

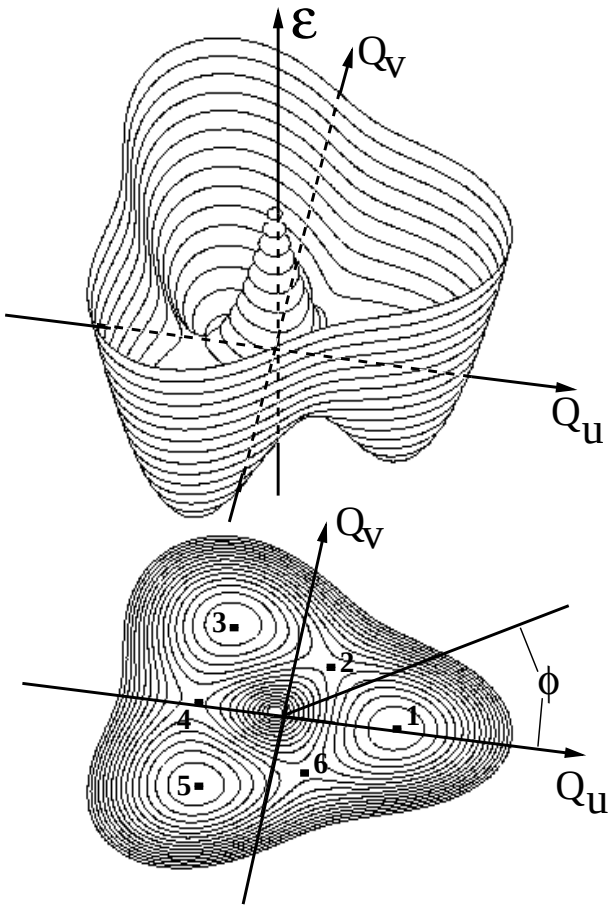

Figure 4.4: Adiabatic potential of the octahedral molecule taking into account quadratic terms of vibronic interaction (from www.mi.infm.it).

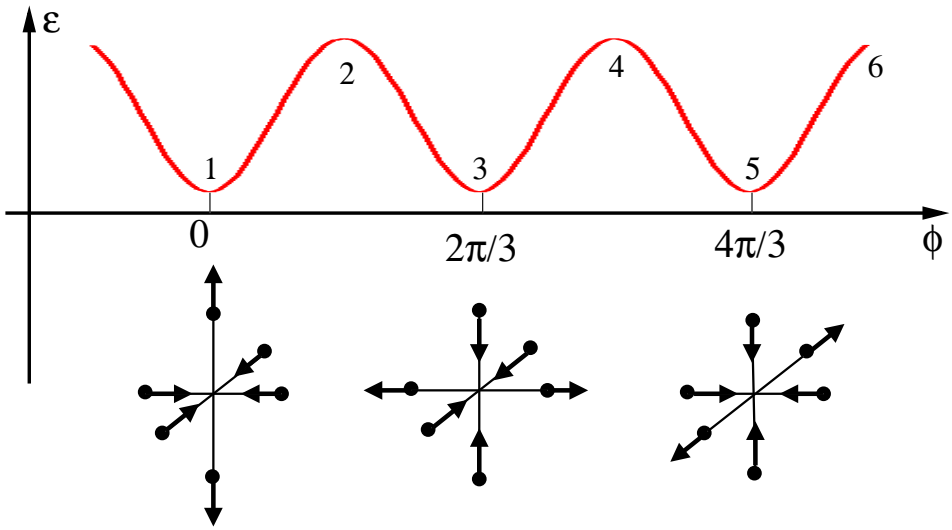

Figure 4.5: Section of the lowest sheet of the adiabatic potential of the octahedral molecule taking into account quadratic terms of vibronic interaction.

Table 4.2: Determining of the atomic coordinates in the distorted ML_6 molecule.

Atom		Initial coordinate	Displacement Q_u	Displacement Q_v	Displacement $-Q_u/2+\sqrt{3}Q_v/2$	Distorted configuration
M	x:	0	0	0	0	0
	y:	0	0	0	0	0
	z:	0	0	0	0	0
L1	x:	0	0	0	0	0
	y:	0	0	0	0	0
	z:	a	$\frac{1}{6}$	0	$-\frac{1}{12}$	$a-\frac{1}{12}$
L2	x:	0	0	0	0	0
	y:	0	0	0	0	0
	z:	$-a$	$-\frac{1}{6}$	0	$\frac{1}{12}$	$-a+\frac{1}{12}$
L3	x:	0	0	0	0	0
	y:	a	$-\frac{1}{12}$	$-\frac{\sqrt{3}}{12}$	$-\frac{1}{12}$	$a-\frac{1}{12}$
	z:	0	0	0	0	0
L4	x:	0	0	0	0	0
	y:	$-a$	$\frac{1}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{1}{12}$	$-a+\frac{1}{12}$
	z:	0	0	0	0	0
L5	x:	a	$-\frac{1}{12}$	$\frac{\sqrt{3}}{12}$	$\frac{1}{6}$	$a+\frac{1}{6}$
	y:	0	0	0	0	0
	z:	0	0	0	0	0
L6	x:	$-a$	$\frac{1}{12}$	$-\frac{\sqrt{3}}{12}$	$-\frac{1}{6}$	$-a-\frac{1}{6}$
	y:	0	0	0	0	0
	z:	0	0	0	0	0

column of this table contents the names of the ML_6 atoms. The second column gives the initial atomic coordinates of ML_6 as defined in the variable `ML6`. The third and fourth columns show the displacements of these coordinates Q_u and Q_v. The fifth column defines the displacement of every coordinate in the point 3 of Fig. 4.5 according to the (4.56). Finally, sixth column is obtained by the summation of the initial coordinates (second column) and displacement in point 3 (fifth column). By other words, this column contains the qualitatively coordinates of every atom in the distorted configuration of ML_6 molecule. Taking these coordinates from the last column, we can define the (highest) symmetry of the molecule in the point 3

```
> ML6new := [[0,0,0],[0,0,a-1/12],[0,0,-a+1/12], [0,a-1/12,0],[0,-a+1/12,0],
[a-1/6,0,0],[-a-1/6,0,0]]:
Bethe_group_symmetry(highest, ML6new);

            D2h
```

where the printout of variable `ML6new` is omitted due to the double point at the end. As expected, the symmetry of the distorted molecule is D_{2h}. The same technique can be used to

define the symmetry of the molecule in any other minimal point of the adiabatic potential.

4.2.6 Realization of the Jahn-Teller problem within the Bethe framework.

The determination of the JT active displacements, the adiabatic potential and the stable configuration of the symmetry molecules can be performed by the BETHE package. To achieve this, following steps should be done:

- Determination of the degenerate states of the molecule;
- Generation of the vibrational modes and the normal coordinates of the molecule in terms of the Cartesian displacements;
- Determination of the Jahn-Teller active vibrational modes;
- Construction of the secular equation (4.51) taking into account the Clebsch-Gordan coefficients. The vibronic constants are presented in this equation as the parameters;
- Generation of the adiabatic potential (4.54) or (4.55) in terms of the normal coordinates Q_i where the force constants are presented as the parameters;
- Determination the minimum point of the adiabatic potential;
- Determination of the molecular configuration in the points of minimum;

The first and second steps are already supported by the BETHE package and have been presented in the previous sections. The third step - determination of the Jahn-Teller active displacements - also can be done by using the procedure `Bethe_group_direct_product()`. However, it looks reasonable to organize the special procedure `Bethe_JT_activity()`, which will define the JT active modes automatically (similar to the procedure `Bethe_spectral_activity()` of the vibrational analysis). Then the procedures for the remaining steps, in which the adiabatic potential of the molecule should be constructed and analyzed, should be created. Note, that the Clebsch-Gordan coefficients, which are necessary for the adiabatic potential, are generated by the procedure `Bethe_CG_coefficient()`. It should be emphasized, that the vibronic constants are not defined directly. They are used as the parameters and the points of minimum of the adiabatic potential will be defined in terms of these constants. In the last step the stable configuration of the molecule should be defined, as described above. The approximate list of procedures, which need to be created in order to realize the JT problem within the BETHE package is presented in Table 4.3.

Table 4.3: Commands of the BETHE program, to realize the Jahn-Teller problem

Bethe_JT_activity()	Defines, whether the given vibrational mode is JT active.
Bethe_secular_equation()	Returns a secular equation in terms of the normal coordinates Q_i and vibronic constants $K_{\bar{T}}^T$, $G_{\bar{T}}^T$, $F_{\bar{T}}^T$ and adiabatic potential ε.
Bethe_secular_equation(..., solution)	Returns a solution of secular equation in terms of the normal coordinates Q_i and vibronic constants $K_{\bar{T}}^T$, $G_{\bar{T}}^T$, $F_{\bar{T}}^T$ and adiabatic potential ε.
Bethe_adiabatic_potential()	Returns the adiabatic potential ε as a function of the normal coordinates Q_i and vibronic constants $K_{\bar{T}}^T$, $G_{\bar{T}}^T$, $F_{\bar{T}}^T$
Bethe_adiabatic_potential(..., min)	Returns the minima points of adiabatic potential in terms the vibronic constants $K_{\bar{T}}^T$, $G_{\bar{T}}^T$, $F_{\bar{T}}^T$
Bethe_JT_distortion()	Returns the stable configuration of molecule either in terms of the atomic coordinates or as a name of corresponding symmetry group

Chapter 5

Summary and Outlook

This thesis work was dedicated to use the CA approach for dealing with the group symmetries and studying the symmetry properties of molecules and clusters. The MAPLE package BETHE, created to extract and manipulate the group-theoretical data and to simplify some of the symmetry applications, was introduced in Chapter 2. First of all the advantages of using BETHE to generate the group theoretical data was demonstrated. In the current version, the data of 72 frequently applied point groups can be used, together with the data for all of the corresponding double groups. The emphasize of this work was placed to the applications of this package in physics of molecules and clusters (Chapter 3). Apart from the analysis of the spectral activity of molecules with point-group symmetry, it was demonstrated how BETHE can be used to understand the field splitting in crystals or to construct the corresponding wave functions. Several examples are worked out in Chapter 3 to display (some of) the present features of the BETHE program. While we cannot show all the details explicitly, these examples certainly demonstrate the great potential in applying computer algebraic techniques to study the symmetry properties of molecules and clusters.

A special attention was placed in this thesis work on the flexibility of the BETHE package, which makes it possible to implement another applications, as described in Chapter 4. This implementation is very reasonable, because some of the most complicated steps of the possible future applications are already realized within the BETHE. For instance, the vibrational coordinates in terms of the internal displacement vectors for the Wilson's method (Section 4.1) and the same coordinates in terms of cartesian displacement vectors as well as the Clebsch-Gordan coefficients for the Jahn-Teller problem (Section 4.2) are generated in the present version of the program. For the Jahn-Teller problem, moreover, use of the CA tool seems to be even inevitable, because this problem demands an analytical access to the adiabatic potential and, therefore, can not be realized by the numerical algorithm.

However, the ability of the BETHE package is not exhausted by applications, mentioned in this thesis work. There are various directions in which the BETHE program could be developed in the future. Apart from (i) studying of the magnetic properties of materials [49, 51] and (ii) optical transitions [8], interest can be pointed out for (iii) the vibronic spectroscopy [41, 42], and many others. Implementation of these applications into the package can make BETHE a much more powerful tool.

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Appendix: Description of procedures and global variables of the BETHE package.

Global variables of the BETHE program

The following global variable is initialized by (first) invoking the BETHE program and can be re–defined by means of the procedure Bethe_set().

- Bethe_save_framework = *nonrelativistic*

Procedures for the BETHE program

Auxiliary procedures

- **Abasis(string$_{\rm atom}$, [a$_1$,a$_2$,a$_3$],[n$_1$,l$_1$],[n$_2$,l$_2$],...)** *bethe_a*

  Auxiliary procedure to represent an atomic basis set $\{\langle \mathbf{r} \mid \mathbf{a}\ n_1 l_1 m\rangle\,,\ \langle \mathbf{r} \mid \mathbf{a}\ n_2 l_2 m\rangle\,,\ \ldots\}$ which is centered at the position $\mathbf{a} = (a_1, a_2, a_3)$ and which is characterized by means of string$_{\rm atom}$.

  Output: An unevaluated call to Abasis() is returned.

  Argument options: (string$_{\rm atom}$,[a$_1$,a$_2$,a$_3$],[n$_1$,kappa$_1$],[n$_2$,kappa$_2$],...) to represent a relativistic orbital basis $\{\langle \mathbf{r} \mid \mathbf{a}\ n_1\kappa_1 m\rangle\,,\ \langle \mathbf{r} \mid \mathbf{a}\ n_2\kappa_2 m\rangle\,,\ \ldots\}$ if a *relativistic* framework is used.

  Additional information: A few minor tests are made on the parameters list with regard to the number and type of the arguments. ♣ If the quantum numbers n_i and l_i are given numerically, they must be integers and must fulfill the relation $n_i \geq l_i + 1$. ♣ The last parameter string$_{\rm atom}$ can be used to characterize either the sort of the atom or the one–particle basis to which the orbital belongs.

  See also: AO(), SO(), Bethe_set().

- **AO([a$_1$,a$_2$,a$_3$],n,l,m,string$_{\rm atom}$)** *bethe_a*

Auxiliary procedure to represent a (nonrelativistic) atomic orbital $\langle \mathbf{r} \,|\, \mathbf{a}\, nlm \rangle$ which is centered at the position $\mathbf{a} = (a_1, a_2, a_3)$ and which is characterized by means of $\text{string}_{\text{atom}}$.

Output: An unevaluated call to AO([a_1,a_2,a_3],n,l,m,$\text{string}_{\text{atom}}$) is returned.

Argument options: ([a_1,a_2,a_3],n,kappa,m,$\text{string}_{\text{atom}}$) to represent a relativistic atomic Dirac orbital $\langle \mathbf{r} \,|\, \mathbf{a}\, n\kappa m \rangle$ if a *relativistic* framework is used.

Additional information: A few minor tests are made on the input parameters with regard to the number and type of the arguments. ♣ If the quantum numbers n, l and/or m are given numerically, they must be integers and must fulfill the relations $n \geq l + 1$ and $|m| \leq l$. ♣ The last parameter $\text{string}_{\text{atom}}$ can be used to characterize either the sort of the atom or the one–particle basis to which the orbital belongs.

See also: SO(), Bethe_set().

- **atom(string$_{\text{Sy}}$)** *bethe_a*

Auxiliary procedure to represent an atom with symbol Sy in the Periodic Table of Elements.

Output: An unevaluated call to atom($\text{string}_{\text{Sy}}$) is returned.

Argument options: ($\text{string}_{\text{Sy}}$,[$a_1$,$a_2$,$a_3$]) to represent an atom with symbol Sy at the atomic site $\mathbf{a} = (a_1, a_2, a_3)$. An unevaluated call to atom($\text{string}_{\text{Sy}}$,[$a_1$,$a_2$,$a_3$]) is returned. ♣ ($\text{string}_{\text{Sy}}$,*mass* = m) to represent an atom with symbol Sy and atomic weight m.

Additional information: A few minor checks are made on the parameter list which concern (i) the proper type of arguments. ♣ Usually, $\text{string}_{\text{Sy}}$ represents an atom in terms of it symbol in the Periodic Table of Elements; a few examples are "H", "He", or "Li". The use of such predefined symbols is however not necessary. ♣ Atomic coordinates are usually treated in Å units; 1 Å = 10^{-10} m. ♣ Further properties of the atom can be *added* to the parameter list if they are given in terms of equations, i.e. in the form *keyword* = value.

See also: Bethe_set(), SO().

- **molecule(atom$_1$, atom$_2$, ...)** *bethe_a*

Auxiliary procedure to represent an molecule in terms of its individual atoms.

Output: An unevaluated call to molecule(atom_1,atom_2,...) is returned.

Argument options: (atom_1,atom_2,*distance* = d) to represent a diatomic molecule at the equilibrium distance d.

Additional information: A few minor checks are made on the parameter list that all arguments represent either (i) atoms or (ii) describe further properties in terms of equations. ♣ Further properties of the atom can be *added* to the parameter list if they are given in terms of equations *keyword* = value.

See also: Bethe_molecule().

- **SO(Glabel,[a_1,a_2,a_3],n,l,m,string$_{\rm IR}$,mu,nu,string$_{\rm atom}$)** *bethe_a*

  Auxiliary procedure to represent a symmetry orbital $\langle \mathbf{r} \,|\, (G\mathbf{a})\ nlm;\ T^{(\alpha)}\mu\nu \rangle$ of the irreducible representation $T^{(\alpha)}$ of the group $\mathcal{G}$ (with label Glabel) which is characterized by means of string$_{\rm atom}$.

  Output: An unevaluated call to SO(Glabel,[a_1,a_2,a_3],n,l,m,string$_{\rm IR}$,mu,nu,string$_{\rm atom}$) is returned.

  Argument options: (Glabel,[a_1,a_2,a_3],n,kappa,m,string$_{\rm IR}$,mu,nu,string$_{\rm atom}$) to represent a relativistic symmetry orbital $\langle \mathbf{r} \,|\, (G\mathbf{a})\ n\kappa m;\ T^{(\alpha)}\mu\nu \rangle$ if a *relativistic* framework is used.

  Additional information: A few minor tests are made on the parameters list with regard to the number and type of the arguments. ♣ If the quantum numbers n, l and/or m are given numerically, they must be integers and must fulfill the relations $n \geq l+1$ and $|m| \leq l$. ♣ The last parameter string$_{\rm atom}$ can be used to characterize either the sort of the atom or the one–particle basis to which the orbital belongs.

  See also: AO(), Bethe_set().

Main procedures

- **Bethe_angular_j(kappa)** *bethe_b*

  Return the total angular momentum j for a given relativistic angular momentum quantum number κ.

  Output: A half–integer is returned.

  See also: AO(), SO().

- **Bethe_angular_l(kappa)** *bethe_b*

  Return the (orbital) angular momentum quantum number $l = abs(\kappa) - 1$ for $\kappa < 0$ or $l = \kappa$ for $\kappa > 0$ for a given κ.

  Output: An integer is returned.

  See also: AO(), SO().

- **Bethe_CG_coefficient(Glabel, string$_{\rm IR_\alpha}$, i, string$_{\rm IR_\beta}$, s, k, string$_{\rm IR_\gamma}$,m)** *bethe_b*

  Calculates the Clebsch–Gordan (or Wigner) coefficient $\langle \alpha i,\, \beta k \,|\, s\gamma m \rangle$ for the three irreducible representations α, β, and γ of the group with label Glabel with the string identifiers string$_{\rm IR_\alpha}$, string$_{\rm IR_\beta}$ and string$_{\rm IR_\gamma}$.

  Output: A number is returned.

Additional information: The irreducible representation γ with the string identifier $\text{string}_{\text{IR}_\gamma}$ has to be 'part of' the direct product $T^{(\alpha\otimes\beta)}$, i.e. $T^{(\alpha\otimes\beta)} = \ldots \oplus T^{(\gamma)} \oplus \ldots$. The procedure terminates with a proper ERROR message if this is not fulfilled. To determine the irreducible representations, which are contained in the direct product above, the procedure Bethe_group_direct_product() can be invoked. ♣ The indices i, k, and l enumerate the basis functions of corresponding irreducible representations and, therefore, have to be less or equal the irreducible representation dimensions. To determine the dimension of an irreducible representation of a given group, the procedure Bethe_group_irrep(..., dimension) can be utilized.The parameter s enumerates the multiplicity of the irreducible representation γ and differs from 1 only if the representation γ is contained in the direct product $\alpha \times \beta$ more then 1 time. The procedure terminates with an ERROR message if the parameters i, k, l and s are typed wrong.

See also: Bethe_group_direct_product(), Bethe_CG_matrix().

- **Bethe_CG_matrix(Glabel, string$_{\text{IR}_\alpha}$, string$_{\text{IR}_\beta}$)** $^{bethe\_b}$

  Generates the matrix of the (non–vanishing) Clebsch–Gordan (or Wigner) coefficient for the two irreducible representations α, β with the string identifiers $\text{string}_{\text{IR}_\alpha}$ and $\text{string}_{\text{IR}_\beta}$.

  Output: A unitary matrix is returned.

  Additional information: Elements of this matrix $\langle \alpha i, \beta k \mid s\gamma m \rangle$ appears in the intersection of the αi, βk rows with the $s\gamma m$ columns. ♣ The irreducible representation γ are the irreducible components of the direct product $\alpha \times \beta$. These components are calculated automatically. ♣ The dimension of the returned matrix is the $mn \times mn$, where m and n are the dimensions of the irreducible representations stringIR_1 and stringIR_2

  See also: Bethe_group_direct_product(), Bethe_CGC_are_orthogonal().

- **Bethe_CGC_are_orthogonal(mat)** $^{bethe\_b}$

  Tests whether the CG coefficients, which form the matrix *mat*, are orthogonal each other.

  Output: A boolean variable TRUE or FALSE is returned.

  Additional information: The CG coefficients are orthogonal each other if the conditions

$$\sum_{ik} \langle \alpha i \beta k \mid s'\gamma' l' \rangle^* \langle \alpha i \beta k \mid s\gamma l \rangle = \delta_{\gamma\gamma'}\delta_{ss'}\delta_{ll'} \tag{5.1}$$

$$\sum_{\gamma sl} \langle \alpha i \beta k \mid s\gamma l \rangle \langle \alpha i' \beta k' \mid s\gamma l \rangle^* = \delta_{ii'}\delta_{kk'} \tag{5.2}$$

  are fulfilled.

  See also: Bethe_CG_coefficient().

- Bethe_chains_relations(*invariant*) $^{bethe-pg-data}$

  Return a list of subchains from which all the *invariant* group chains can derived.

Output: A list is returned.

Argument options: (*subduction*) to return a list of subchains from which all the *subductions* can derived.

Additional information: The list of subchains are generated from the graphs 1–12 as displayed by Altmann & Herzig (1994, paragraph 9). ♣ All subchains are listed in alphabetical order and in the form [Glabel_up, Glabel_low] where the orders of the corresponding group labels fulfill the relation h_up $\geq$ h_low.

See also: Bethe_group_chain().

- Bethe_cos(m, n) $^{bethe-pg-data}$

  Calculates the value of cos(m/n)*Pi.

  Output: A number is returned.

- **Bethe_decompose_representation(Glabel, [chi$_1$, chi$_2$, ..., chi$_k$], [string$_{\mathrm{SO_1}}$, string$_{\mathrm{SO_2}}$, ..., string$_{\mathrm{SO_k}}$])** $^{bethe\_b}$

  Determines how many times each irreducible representation of the group $\mathcal{G}$ with label Glabel is contained in a reducible representation with characters [chi$_1$,chi$_2$,...chi$_k$] where k is the number of the symmetry operations [string$_{\mathrm{SO_1}}$,string$_{\mathrm{SO_2}}$, ...,string$_{\mathrm{SO_k}}$] of the group Glabel.

  Output: A list of irreducible representation identifiers [string$_{\mathrm{IR_1}}$,string$_{\mathrm{IR_2}}$,...] of the given group is returned.

  Argument options: (Glabel,[chi$_1$,chi$_2$,...,chi$_k$]) to return the same result if the characters are given in the *internal* standard order, i.e. as obtained by a call to the procedure Bethe_group(Glabel,*symmetry_operations*).
  ♣ (Glabel,[chi$_1$,chi$_2$,...,chi$_k$], *spin_reps*) to return the same result for the list of the spinor representations of the group Glabel.
  ♣ (Glabel,[matrix$_1$,matrix$_2$,...,matrix$_k$],[string$_{\mathrm{SO_1}}$,string$_{\mathrm{SO_2}}$,...,string$_{\mathrm{SO_k}}$]) to return the same result if the reducible matrix representation is given explicitly.
  ♣ (Glabel,[matrix$_1$,matrix$_2$,...,matrix$_k$]) to return the same result if the reducible matrix representation is given explicitly and if they are given in the *internal* standard order.
  ♣ (Glabel, string$_{\mathrm{IR_a}}$, string$_{\mathrm{IR_b}}$,...) to return the same decomposition for the product representation associated to string$_{\mathrm{IR_a}}$ $\times$ string$_{\mathrm{IR_b}}$ $\times$ ...
  ♣ (Glabel, *polar_vector*) to return a list of irreducible representation names [string$_{\mathrm{IR_a}}$, string$_{\mathrm{IR_b}}$, ...] of group Glabel, which describe the transformation of the polar vector $\mathbf{r}$ = (x, y, z);
  ♣ (Glabel, *axial_vector*) to return the list of irreducible representation names which describe the transformation of the axial vector $\mathbf{R} = (R_x, R_y, R_z)$;
  ♣ (Glabel, *cartesian_tensor*, rank) to return the same for the representation of a cartesian tensor function of rank *rank*.

Additional information: At the output, an irreducible string identifier $\text{string}_{\text{IR}}$ appears as many times as it arises in the given reducible representation. The order of the irreducible string identifiers is undetermined. ♣ The *internal* standard order of the symmetry operations is those as obtained by a call to Bethe_group(Glabel, operators). ♣ Decomposition of the double group representations is also supported by the program. In this case k is considered as a number of the symmetry operations of corresponding double group.

See also: Bethe_group_representation().

- Bethe_Djmm(j, m, mp, alpha, beta, gamma) *bethe_b*

  Returns a Wigner D-function if j,m,mp are given numerically. Formula 4.3(1) from Varshalovich et al. (1988) is used.

  Output: A number or an unevaluated function call is returned.

- Bethe_djmm(j, m, mp, beta) *bethe_b*

  Returns a Wigner d-function if j,m,mp are given numerically. Formula 4.3(2) from Varshalovich et al. (1988) is used.

  Output: A number or an unevaluated function call is returned.

- Bethe_direct_product(M1, M2) *bethe_b*

  Calculates the direct (Kronecker) product of matrix M1 and matrix M2.

  Output: A $n_1 n_2 \times n_1 n_2$ matrix is returned where n_1, n_2 are dimensions of the matrices M1 and M2 respectively.

  Additional information: The matrices M1 and M2 have to be square.

- Bethe_function_return(m, listmol, listvib) *bethe_b*

  Return a list of numbers for drawing the atoms molecule with coordinates *listmol* in the different positions of vibration like defined by the list *listvib* for m oscillations.

  Output: A list is returned.

  Additional information: A normal coordinate in terms of the cartesian displacement vectors should be used.

  See also: molecule(), Bethe_function_display().

- **Bethe_generate_AO($\text{string}_{\text{atom}}$, [$a_1$,$a_2$,$a_3$,[$n_1$,$l_1$],[$n_2$,$l_2$],...)** *bethe_b*

  Generates a list of atomic orbitals (including all possible m's) at the position $\mathbf{a} = (a_1, a_2, a_3)$ and for an atom with the identifier $\text{string}_{\text{atom}}$.

  Output: A list of (unevaluated) calls to AO() with proper quantum numbers is returned.

  Argument options: ($\text{string}_{\text{atom}}$,[$a_1$,$a_2$,$a_3$],[$n_1$,kappa$_1$], [$n_2$,kappa$_2$],...) to generate a list of relativistic orbitals (including all possible m's) if a *relativistic* framework is used.

Additional information: All atomic orbitals are located at the same site $\mathbf{a} = (a_1, a_2, a_3)$. ♣ All principal quantum numbers n_i and (orbital) angular momentum numbers l_i or κ_i must be of type integer.

See also: AO().

- **Bethe_generate_AO_basis(Glabel,$\mathbf{AO}_1$,$\mathbf{AO}_2$,...)** *bethe_b*

Generates an atomic basis by applying all symmetry operations of the point group $\mathcal{G}$ with label Glabel to the atomic orbitals AO_1, AO_2, ...

Output: A list of (unevaluated) calls to AO() with proper quantum numbers and with positions of all *equivalent* atomic sites **a** is returned.

Additional information: To generate an atomic basis, it is typically enough to provide the corresponding orbitals at one of the *equivalent* sites, i.e. atomic sites which are equivalent under the symmetry operations of the group $\mathcal{G}$. ♣ Although returned in a list structure, it is ensured that each atomic orbital only occurs once in the list.

See also: Bethe_generate_AO().

- **Bethe_generate_sites(Glabel,[$\mathbf{a}_x$,$\mathbf{a}_y$,$\mathbf{a}_z$])** *bethe_b*

Generates all *equivalent* sites of the point $\mathbf{a} = (a_x, a_y, a_z)$ under the symmetry operations of the point group $\mathcal{G}$ with label Glabel.

Output: A list of sites [$[\mathrm{a}_x^{(1)},\mathrm{a}_y^{(1)},\mathrm{a}_z^{(1)}]$, $[\mathrm{a}_x^{(2)},\mathrm{a}_y^{(2)},\mathrm{a}_z^{(2)}]$, $[\mathrm{a}_x^{(3)},\mathrm{a}_y^{(3)},\mathrm{a}_z^{(3)}]$, ...] is returned.

Argument options: (Glabel,$[\mathrm{a}_x,\mathrm{a}_y,\mathrm{a}_z]$, $[\mathrm{b}_x,\mathrm{b}_y,\mathrm{b}_z]$, ...) to generate the same but for different sites $\mathbf{a} = (a_x, a_y, a_z)$, $\mathbf{b} = (b_x, b_y, b_z)$, ...; a list of lists is returned. ♣ The input $\mathbf{a} = (a_1, a_2, a_3)$ is always returned as first operand $[[\mathrm{a}_1^{(1)},\mathrm{a}_2^{(1)},\mathrm{a}_3^{(1)}]$, ...] of the output. ♣ The present version only supports *cartesian* coordinates.

See also: Bethe_group().

- **Bethe_generate_SO(SO(Glabel, $[\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3]$, n, l, m, $\mathbf{string}_{\mathrm{IR}}$, mu, nu, $\mathbf{string}_{\mathrm{atom}}$))** *bethe_b*

Expands a given symmetry orbital $\langle \mathbf{r} \,|\, (G\mathbf{a})\ nlm;\ T^{(\alpha)}\mu\nu \rangle$ of the group $\mathcal{G}$ and with one of the atoms centered at position $\mathbf{a} = (a_1, a_2, a_3)$ in terms of the atomic orbitals with quantum numbers n and l, centered at all *equivalent* sites.

Output: A list $[[\mathrm{c}_1, \mathrm{AO}_1],[\mathrm{c}_2, \mathrm{AO}_2]$, ...] is returned where c_i are the mixing coefficients and where AO_i describes an atomic orbital at one of the equivalent sites of the molecule.

Argument options: (SO,*print*) to print the expansion in terms of atomic orbitals in a line mode which is much simpler to read. A NULL expression is returned in this case.

Additional information: If the keyword *print* is used, one line $\mathrm{c}_i \times \mathrm{AO}_i()$ is printed for each atomic orbital involved in the expansion. ♣ The expansion coefficients are normalized due to $\sum_i c_i^2 = 1$

See also: Bethe_generate_AO().

- **Bethe_generate_SO_basis(Glabel,Abasis$_1$, Abasis$_2$,...)** *bethe_b*

  Generates a *complete* but linear independent set of symmetry orbitals for the point group $\mathcal{G}$ with label Glabel from the set of atomic orbitals as given by the basis sets Abasis$_1$, Abasis$_2$, ...

  Output: A list of unevaluated calls to SO() is returned.

  Argument options: (Glabel,Abasis$_1$,Abasis$_2$,...,*explicit*) to generate an explicit representation of the (set of) symmetry orbitals in terms of the corresponding atomic orbitals, [[[c$_1$, AO$_1$],[c$_2$, AO$_2$], ...], ...].
  ♣ (Glabel,Abasis$_1$,Abasis$_2$,...,*print*) to print the complete but linear independent basis of symmetry orbitals in line mode. A NULL expression is returned in this case.
  ♣ (Glabel,Abasis$_1$,Abasis$_2$,...,*explicit,print*) to generate and print an explicit representation of all symmetry orbitals in terms of atomic orbitals. A NULL expression is returned in this case.

  Additional information: To generate a symmetry orbital basis, it is typically enough to provide the corresponding orbitals in the atomic basis set *Abasis* for just one of the *equivalent* sites, i.e. for one of the atomic sites which are equivalent under the symmetry operations of the group $\mathcal{G}$.

  See also: Bethe_generate_AO_basis().

- **Bethe_group()** *bethe_b*

  Returns a list of all point groups (labels) which are presently supported by the BETHE package.

  Output: A list of Glabel's is returned.

  Argument options: (Glabel,*implemented*) to return *true* if the point groups $\mathcal{G}$ with label Glabel is supported by the BETHE program and *false* otherwise. ♣ (Glabel,*No_class*) or (Glabel,*No_class,double*) to return the number of classes in the group or the or the corresponding double group. ♣ (Glabel,*No_regular*) to return the number of regular classes in the group. ♣ (Glabel,*No_irregular*) to return the number of irregular classes in the group. ♣ (Glabel,*No_irreps*) or (Glabel,*No_irreps,double*)to return the number of irreducible representations of the group or the corresponding double group. ♣ (Glabel,*No_operators*) or (Glabel,*No_operators*, *double*)to return the number of symmetry operations of the group or the corresponding double group. ♣ (Glabel,*No_Altmann*) to return the number of the table in the main reference book by Altmann & Herzig (1994). ♣ (Glabel,*crystallographic*) to return *true* if the group label indicates a crystallographic point group and *false* otherwise. ♣ (Glabel,*crystal_system*) to return, if Glabel denotes a crystallographic group, the name of of the crystallographic system (such as triclinic, rhombic, ...) and FAIL otherwise. ♣ (Glabel,*cubic*) to return *true* if the Glabel indicates a cubic point group and *false* otherwise. ♣ (Glabel,*cyclic*) to return *true* if the Glabel indicates a cyclic point group and *false* otherwise. ♣ (Glabel,*dihedral*) to return *true* if the Glabel indicates a dihedral point group and *false* otherwise. ♣ (Glabel,*icosahedral*) to return *true* if the Glabel indicates

a icosahedral point group and *false* otherwise. ♣ (Glabel,*proper*) to return *true* if the Glabel indicates a proper point group and *false* otherwise. ♣ (Glabel,*subgroup*) to return a list of the subgroups for the group Glabel. ♣ (Glabel,*irreps*) or (Glabel,*irreps*,*double*) to return a detailed list of all irreducible representations of the group or the corresponding double group. ♣ (Glabel,*operators*) or (Glabel,*operators*, *double*) to return a detailed list of all symmetry operations of the group or the corresponding double group. ♣ (*group_table*) to print a detailed tabulation about all presently supported point groups including the international (short and long) notation of the group as well as the notation due to Schönfliess. ♣ (Glabel,*operator_details*) to print a detailed list about all symmetry operations of the group or the corresponding double group. ♣ (Glabel,*spinor_irreps*) to return a list of the spinor (double valued) irreducible representations of the group Glabel. ♣ (Glabel,*symmetry_elements*) to print a detailed list about all symmetry elements (with respect to space fixed coordinates) of the group, i,.e. the choice of principal axis, the center of symmetry, the reflection planes, etc. ♣ (Glabel,*examples*) to print a table with a number of molecules which obey this group.

Short description of all keywords	
crystallographic	Boolean value *true* or *false*
crystall_system	Prints a name of the crystal system
cubic	Boolean value *true* or *false*
cyclic	Boolean value *true* or *false*
dihedral	Boolean value *true* or *false*
examples	Prints a few examples
group_table	Prints a summary about all presently supported point groups
icosahedral	Boolean value *true* or *false*
implemented	Boolean value *true* or *false*
irreps	List of irreducible representation identifiers
irreps, double	List of irreducible representations identifiers in the double group
No_Altmann	Number of the tabulation by Altmann & Herzig (1994)
No_class	Number of classes
No_class, double	Number of classes in the double group
No_irregular	Number of irregular classes
No_irreps	Number of irreducible representations
No_irreps, double	Number of irreducible representations in the double group
No_operators	Number of symmetry operations
No_operators, double	Number of symmetry operations in the double group
No_regular	Number of regular classes
operator_details	Prints a description of all symmetry operations
operators	List of symmetry operation identifiers
operators, double	List of symmetry operation identifiers in the double group
proper	Boolean value *true* or *false*
spinor_irreps	List of spinor irreducible representation identifiers
subgroup	List of the subgroups
symmetry_elements	Prints a description of all symmetry elements

Additional information: Each irreducible representation of the group is described by an individual string identifier which is used in the input and output of many commands. ♣ The irreducible representations of the standard and the double groups have different

string identifiers. ♣ For the optional argument (Glabel,*operator_details*), the procedure prints a short description of all the symmetry operations of the point group $\mathcal{G}$:

```
Description of symmetry operations for the point group  C2v:
------------------------------------------------------------
  E         Identity operation
  C2        Clockwise rotation about the z(principal)-axis by Pi
  sigma_x   Reflection through the (y-z) plane
  sigma_y   Reflection through the (x-z) plane
```

♣ For the optional argument (*group_table*), the procedure prints a list of all presently supported groups in the form:

```
                        Notation
Glabel Schoenfliess  Full    Short   Group description
-------------------------------------------------------------------
 Cs        C_s         m       m     Group of horizontal reflection
 CI        C_i        ^1      ^1     Imroper cyclic group
 C2        C_2         2       2     Proper cyclic group
 C3        C_3         3       3     Proper cyclic group
 ...
```

♣ For the optional argument (Glabel,*symmetry_elements*), the procedure prints a short description of all the symmetry elements of the point group $\mathcal{G}$:

```
Symmetry elements of the point group  C2v:
------------------------------------------
C_2       2-fold principal axis along the z-axis
sigma_y   Vertical (x-z) reflection plane
sigma_x   Vertical (y-z) reflection plane
```

- **Bethe_group_chain(Glabel)** *bethe_b*

Returns a list of *invariant* group chains which contain the group with label Glabel.

Output: A list of lists is returned.

Argument options: (Glabel_1,Glabel_2,...) to return a list of *invariant* group chains which contain all the given group labels. ♣ (Glabel_1,...,*down*) to return the *invariant* group chains which start with Glabel_1. ♣ (Glabel_1,...,*up*) to return the *invariant* group chains which terminate with Glabel_1. ♣ (Glabel_1,...,*subduction*) to return the *subduction* group chains which include the given Glabels.

Additional information: The group chains are given as a list of group labels in descending order of the group order, i.e. by starting with the group of highest symmetry. ♣ The *subduction* group chains are defined independently from the invariant group chains.

See also: Bethe_group().

- **Bethe_group_character(Glabel, string$_{\mathrm{IR}}$,string$_{\mathrm{SO}}$)** $^{bethe\_b}$

  Returns the character χ for the irreducible representation string$_{\mathrm{IR}}$ and the symmetry operation string$_{\mathrm{SO}}$ for the point group $\mathcal{G}$ with label Glabel.

  Output: A number is returned.

  Argument options: (Glabel, string$_{\mathrm{IR}}$) to return the characters for all the symmetry operations χ_1, χ_2, ... of the point group. A list of numbers is returned which refer to the symmetry operations of the group in the same sequence as obtained by Bethe_group(Glabel, operators). ♣ (Glabel, string$_{\mathrm{IR}}$,*double*) to return the same for the corresponding double group.

  See also: Bethe_group().

- **Bethe_group_class(Glabel, string$_{\mathrm{SO}}$)** $^{bethe\_b}$

  Returns a list of all symmetry operation identifiers, i.e. [string$_{SO_1}$, string$_{SO_2}$, ...] which belong to the same class as string$_{SO}$ for the point group with label Glabel. String$_{SO}$ is also included in this list so that the list contains at least one element.

  Output: A list is returned.

  Argument options: (Glabel, string$_{\mathrm{SO}}$,*order*) to return the order of this class. A number is returned in this case. ♣ (Glabel, string$_{\mathrm{SO}}$,*double*) to return the list of all symmetry operation identifiers, i.e. which belong to the same class as string$_{\mathrm{SO}}$ for the double group with label Glabel. ♣ (Glabel, string$_{\mathrm{SO}}$, *double,order*) to return the order of double group class.

  See also: Bethe_group().

- **Bethe_group_direct_product(Glabel, string$_{\mathrm{IR_a}}$,string$_{\mathrm{IR_b}}$,...)** $^{bethe\_b}$

  Returns the *direct product* of the irreducible representations string$_{\mathrm{IR_a}}$ $\otimes$ string$_{\mathrm{IR_b}}$ $\otimes$ ... in terms of such irreducible representation identifiers

  Output: A list of irreducible representation identifiers [string$_{\mathrm{IR_1}}$, string$_{\mathrm{IR_2}}$, ...] is returned.

  Argument options: (Glabel, string$_{\mathrm{IR_a}}$, string$_{\mathrm{IR_a}}$,..., *symmetrized*) to return the *symmetrized* part of the direct product of the irreducible representation string$_{\mathrm{IR_a}}$ with itself. ♣ (Glabel, string$_{\mathrm{IR_a}}$, string$_{\mathrm{IR_a}}$,..., *antisymmetrized*) to return the *antisymmetrized* part of the direct product of the irreducible representation string$_{\mathrm{IR_a}}$ with itself. ♣ (Glabel, rep_list$_a$, rep_list$_b$, ...) to calculate the direct product of the two or more (reducible or

irreducible) representations, rep_list$_{\mathrm{IR_a}}$ $\otimes$ rep_list$_{\mathrm{IR_b}}$ $\otimes$ ..., if these representations are given explicitly. ♣ (Glabel, rep_list$_a$, rep_list$_a$, ..., *symmetrized*) to calculate the *symmetrized* part of the direct product of the representation rep_list$_a$ with itself. ♣ (Glabel, rep_list$_a$, rep_list$_a$, ..., *antisymmetrized*) to calculate the *antisymmetrized* part of the direct product of the representation rep_list$_a$ with itself. ♣ (Glabel, string$_{\mathrm{IR_a}}$, rep_list$_b$) to calculate the direct product of the irreducible representation string$_{\mathrm{IR_a}}$ and the explicitly given representation rep_list$_b$. ♣ (Glabel, ..., *matrices*) to return the matrix representation of the direct product explicitly within a list structure; a list of matrices is returned. ♣ (Glabel, ..., *characters*) to return the characters of the direct product representation; a list of numbers is returned.

Additional information: The result of this procedures is similar as obtained by Altmann & Herzig (1994), tables Tn.8. ♣ Since the irreducible components in the direct product are the same for the point and double groups (as far as the irreducible representations are the same), no distinction need to be made for these two groups with the same label Glabel. ♣ A representation can be given explicitly within a list of matrices structure, where every matrix is assigned to each symmetry operator of the group Glabel. Of course, all these matrices must have the same dimension and their sequence must agree with the sequence of symmetrized operators as obtained from Bethe_group(Glabel, *operators*) or Bethe_group(Glabel, *operators*, *double*), respectively. ♣ If a group representation is given explicitly, the number of list elements must agree with the number of symmetry operators in either the vector or the double group with label Glabel, from which the kind of the group is derived (if necessary).

See also: Bethe_group(), Bethe_group_irrep_manifold().

- **Bethe_group_Euler(Glabel, string$_{\mathrm{SO}}$)** $^{bethe\_b}$

Returns the three Euler angles α, β, γ for the symmetry operation string$_{\mathrm{SO}}$ of the point group $\mathcal{G}$ with label Glabel.

Output: A list of three angles [alpha, beta, gamma] is returned.

Argument options: (Glabel, string$_{\mathrm{SO}}$, *matrix*) to return the rotation matrix due to the symmetry operator string$_{\mathrm{SO}}$.

Additional information: The values of the Euler angles are taken from Altmann & Herzig (1994), table Tn.1. ♣ The Euler angles only specify 'pure' rotations; additional informations about the reflection planes, the center of inversion, or whether the symmetry operation belongs to the point or double group may be required in order to characterize the symmetry operations in general. ♣ The Euler angles of the *point group* operation are returned even if the symmetry operation belongs to the corresponding *double group*. ♣ If a third argument *matrix* is given, the 3×3 rotation matrix is returned including a proper inversion at the origin of the coordinates, if necessary for this operation; note, however, that a 3×3 rotation matrix is not sufficient to specify the symmetry operations of the double group uniquely.

See also: Bethe_group(), Bethe_group_character().

- Bethe_group_inverse(Glabel, string$_{\rm SO}$) $^{bethe\_b}$

  Returns the inverse symmetry operation to the operation string$_{\rm SO}$ for the point group with label Glabel.

  Output: A string is returned.

  Argument options: (Glabel, string$_{\rm SO_1}$,string$_{\rm SO_2}$,...) to return the inverse symmetry operation to the product operation string$_{\rm SO_1}$ $\otimes$ string$_{\rm SO_2}$ $\otimes$ ...

  Additional information: In the present version, the inverse is found for symmetry operations from the point and double group.

  See also: Bethe_group().

- **Bethe_group_irrep(Glabel, string$_{\rm IR}$,string$_{\rm SO}$)** $^{bethe\_b}$

  Returns the matrix of the irreducible representation string$_{\rm IR}$ for the symmetry operation string$_{\rm SO}$ of the point group with label Glabel.

  Output: A matrix is returned.

  Argument options: (Glabel, string$_{\rm IR}$, string$_{\rm SO}$,mu,nu) to return the matrix element [mu, nu]. A number is returned in this case. ♣ (Glabel, string$_{\rm IR}$, *dimension*) to return the dimension of the irreducible representation with string identifier string$_{\rm IR}$. ♣ (Glabel, string$_{\rm IR}$) to return the matrix representation for all the symmetry operations of the point group. A list of matrices is returned which refer to the symmetry operations of the group in the same sequence as obtained by Bethe_group(Glabel,operators). ♣ (Glabel, string$_{IR}$, string$_{SO}$,mu, nu, *real*) to calculate a real matrix element for the multidimensional irreducible representations. A real number is returned in this case.

  Additional information: To get a real matrix element for the multidimensional irreducible representations, the pair of imaginary elements need to be transformed into pair of real elements. It can be done by adding and subtracting the two matrix elements for each representation and dividing the resulting characters by the greatest common denominator.

  See also: Bethe_group().

- **Bethe_group_irrep_manifold(Glabel, string$_{\rm IR_\alpha}$, string$_{\rm IR_\beta}$, string$_{\rm IR_\gamma}$)** $^{bethe\_b}$

  Returns the coefficient m_γ in the expansion of the direct product

  $$T^{(\alpha)} \times T^{(\beta)} = \dot{\sum_{\gamma}} m_\gamma T^{(\gamma)}$$

  where $T^{(\alpha)}$, $T^{(\beta)}$, and $T^{(\gamma)}$ refer to three irreducible representations of the point group Glabel, denoted as string$_{\rm IR_\alpha}$, string$_{\rm IR_\beta}$, string$_{\rm IR_\gamma}$.

Output: A number is returned.

Additional information: Even if $T^{(\alpha)}$ and $T^{(\beta)}$ are irreducible, the representation $T^{(\alpha)} \times T^{(\beta)}$ is generally not irreducible but can be decomposed due to the relation above where the weights are given by

$$m_\gamma \;=\; \frac{1}{h} \sum_\gamma c_p \, \chi_p^{(\gamma)} \, \chi_p^{(\alpha)} \, \chi_p^{(\beta)} \, .$$

Here, h denotes the order of the group, c_p the order of the class, and χ is the character of the corresponding irreducible representation (Elliot & Dawber 1979). ♣ The irreducible representations of corresponding *double groups* are also supported by the program.

See also: Bethe_group(), Bethe_symmetry_operations().

- **Bethe_group_multiplication(Glabel, string$_{\rm SO_a}$,string$_{\rm SO_b}$)** *bethe_b*

Returns the *product operation* of the two symmetry operations string$_{\rm SO_a}$ and string$_{\rm SO_b}$ of the point group $\mathcal{G}$ with label Glabel as defined by Altmann & Herzig (1994) Tn.2-3.

Output: A string$_{\rm SO}$ is returned.

Argument options: (Glabel, string$_{\rm SO_a}$,string$_{\rm SO_b}$,*double*) to returns the *product operation* of the two symmetry operation string$_{\rm SO_a}$ and string$_{\rm SO_b}$ for the corresponding double group of $\mathcal{G}$.

Additional information: If A, B are the symmetry operations associated to the symmetry operation strings string$_{\rm SO_a}$ and string$_{\rm SO_b}$, the results is the string$_{\rm SO}$ identifier which belong to the product operation AB.

See also: Bethe_group().

- **Bethe_group_parameter(Glabel, string$_{\rm SO}$)** *bethe_b*

Returns the rotation angle and the unit vector which define the symmetry operation string$_{\rm SO}$ of the point group $\mathcal{G}$ with label Glabel as defined by Altmann & Herzig (1994) Tn.1.

Output: A list $[\phi, [n_1, n_2, n_3]]$ is returned.

Argument options: (Glabel, string$_{\rm SO}$,*U_rotation*) to return the set of angles (ϕ, Θ, Φ) of the symmetry operation string$_{\rm SO}$. ♣ (Glabel, string$_{\rm SO}$,quaternion) to return the quaternion parameters λ and $\mathbf{\Lambda}$ of the same symmetry operation as defined by Altmann & Herzig (1994).

Additional information: A parameterization of the symmetry operations in terms of ϕ and the unit vector (n_1, n_2, n_3) is equivalent to the (more common) Euler angles.

See also: Bethe_group_Euler().

- **Bethe_group_representation(Glabel, *polar_vector*)** *bethe_b*

  Calculates the characters for the representation which describes the transformation of a polar vector $\mathbf{r} = (x, y, z)$ as induced by the group (elements) with label Glabel.

  Output: A list of numbers is returned which describe the characters of the symmetry operations in the same sequence as obtained from Bethe_group(Glabel,operators).

  Argument options: (Glabel, *polar_vector,double*) to calculate the same list of operators but for the double group. ♣ (Glabel, *polar_vector*, *matrix*) or (Glabel, *polar_vector*, *matrix*, *double*) to calculate an explicit matrix representation; a list of matrices is returned. ♣ (Glabel, *axial_vector*) to calculate the characters for the representation which describes the transformation of a axial vector $\mathbf{R} = (R_x, R_y, R_z)$ as induced by the group. ♣ (Glabel, *axial_vector,double*) to calculate the same list of operators but for the double group. ♣ (Glabel, *axial_vector*, *matrix*) or (Glabel, *axial_vector*, *matrix*, *double*) to calculate an explicit matrix representation; a list of matrices is returned. ♣ (Glabel, *Ylm*,l) to calculate the characters for the transformation of the spherical harmonics of (spherical tensor) rank l, i.e. of $Y_{lm}(\theta, \phi)$, $m = l, l-1, ..., -l$ as induced by the point group. ♣ (Glabel, *Ylm*,l,*matrix*) to calculate the explicit matrix representation; a list of $(2l+1) \times (2l+1)$ matrices is returned. ♣ (Glabel, *jm*,j) to calculate the characters for the transformation of the spinor functions $|jm\rangle$ of half–integer (spherical tensor) rank j, i.e. of $|jm\rangle$ $m = j, j-1, ..., -j$ as induced by the point group. ♣ (Glabel, *total*,[[a_{1x},a_{1y},a_{1z}],[a_{2x},a_{2y},a_{2z}],...]) to calculate the characters for a set of 'atomic displacements', centered at $\mathbf{a}_1 = (a_{1x}, a_{1y}, a_{1z})$, $\mathbf{a}_2 = ...$ ♣ (Glabel, *total*,[[a_{1x},a_{1y},a_{1z}],[a_{2x},a_{2y},a_{2z}],...], *matrix*) to return the total matrix representation for the same set of atomic displacements explicitly. ♣ (Glabel, *total*, molecule) to calculate the characters for the atoms of molecule, defined by the procedure molecule(). ♣ (Glabel, *total*, molecule, *matrix*) to return the total explicit matrix representation for the atoms of molecule, defined by the procedure molecule(). ♣ (Glabel, *regular*) to calculate the characters of the *regular representation* of the group.
  ♣ (Glabel, *regular*, *matrix*) to calculate the explicit matrix representation of the regular representation. ♣ (Glabel, *regular*, *double*) to calculate the characters of the *regular representation* of the double group. ♣ (Glabel, *vibrational*,[[a_{1x},a_{1y},a_{1z}],[a_{2x},a_{2y},a_{2z}],...]) to calculate the characters of the *vibrational representation* for the set of atoms centered at $\mathbf{a}_1 = (a_{1x}, a_{1y}, a_{1z})$, $\mathbf{a}_2 = ...$ ♣ (Glabel, *vibrational*, molecule) to calculate the characters of the *vibrational representation* for the atoms of molecule, defined by the procedure molecule(). ♣ (Glabel, *Euler*) to return the Euler representation. A list of matrices is returned. ♣ (Glabel, *vibrational*, [[a_{1x}, a_{1y}, a_{1z}], [a_{2x}, a_{2y}, a_{2z}],..]) to calculate the characters of representation which describe the transformation of the vibrational vectors. A list of characters is returned. ♣ (Glabel, *cartesian_tensor*, rank, *matrix*) to return an explicit matrix representation of the group as generated by a set of cartesian tensor functions of the given *rank*. A list of matrices is returned. ♣ (Glabel, *cartesian_tensor*, rank) to return the characters of the representation as generated by a set of cartesian tensor functions of the given *rank*.

Additional information: In the output, the sequence of characters and matrices always refer to the *standard sequence* of the symmetry operations as obtained by a call to Bethe_group(Glabel, operators).

See also: Bethe_group(), molecule().

- **Bethe_group_subduction(Glabel, string$_{\rm IR}$, Glabel$_{\rm sub}$)** $^{bethe\_b}$

Returns the irreducible components, which appear in the decomposition of the Glabel group representation string$_{\rm IR}$ to the group Glabel$_{\rm sub}$ as defined by Altmann & Herzig (1994) Tn.9.

Output: A list of strings is returned.

Additional information: The representation string$_{\rm IR}$ should be irreducible in the group Glabel. Since the group Glabel$_{\rm sub}$ is the subgroup of group Glabel, this representation is (generally!) reducible in the group Glabel$_{\rm sub}$. ♣ The procedure terminates with proper ERROR message, if the string$_{\rm IR}$ is not irreducible representation of the group Glabel. ♣ If group Glabel$_{\rm sub}$ is not a subgroup of the group Glabel, the FAIL is returned.

See also: Bethe_decompose_representation().

- **Bethe_group_subduction_O3(Glabel, l)** $^{bethe\_b}$

Returns the irreducible components, which appear in the decomposition of the 0_3 group representation, generated by the spherical functions $Y_{lm}(\vartheta, \varphi)$ for given l, to the group Glabel as defined by Altmann & Herzig (1994) Tn.10.

Output: A list of strings is returned.

Additional information: The parameter l has to be either integer or half-integer. If this condition is not fulfilled, the procedure terminates with proper ERROR message. ♣ 0_3 group representation is constructed as a set of ($2l$ + 1-dimensional) matrices, which are necessary in order to generate the group symmetry transformations of the spherical functions $Y_{lm}(\vartheta, \varphi)$.

See also: Bethe_decompose_representation(), Bethe_group_representation().

- **Bethe_group_symmetry(Glabel, [[$\mathbf{a}_1$,$\mathbf{a}_2$,$\mathbf{a}_3$], [$\mathbf{b}_1$,$\mathbf{b}_2$,$\mathbf{b}_3$],...])** $^{bethe\_b}$

Defines, whether the (atomic) sites $\mathbf{a}, \mathbf{b}, ...$ are equivalent under the point group Glabel transformations.

Output: A boolean variable *true* or *false* is returned.

Argument options: (*which*, [[a_1,a_2,a_3], [b_1,b_2,b_3],...]) to return a list of group labels, under which the atomic sites $\mathbf{a}, \mathbf{b}, ...$ are equivalent. A list is returned. ♣ (*highest*, [[a_1,a_2,a_3], [b_1,b_2,b_3],...]) to return a group label of highest order group, under which the atomic sites $\mathbf{a}, \mathbf{b}, ...$ are equivalent.

Additional information: To determine the point symmetry, it is enough to determine all the equivalent sites of the atom at site **a** under the symmetry operations of every point group and to compare these sites with the given list of atomic sites $\mathbf{a}, \mathbf{b}, ...$

See also: Bethe_generate_sites().

- **Bethe_group_tabulation(Glabel)** *bethe_b*

  Prints the group theoretical data in a neat format as appropriate, for instance, for a quick comparison with the tables of Altmann & Herzig(1994).

  Output: A NULL expression is returned.

  Argument options: (Glabel, *Cartesian_tensor*) to print, in addition, the cartesian tensor table for given group (Tn.5), ♣ (Glabel, *characters*) to print, in addition, the character table for given group (Tn.4), ♣ (Glabel, *direct_product*) to print, in addition, the direct product table for given group (Tn.8), ♣ (Glabel, *multiplication*) to print, in addition, the multiplication table for given group (Tn.2), ♣ (Glabel, *parameters*) to print, in addition, the parameters table for given group, i. e. the Euler angles (α, β, γ), the angle and axis of the rotation (ϕ, $\mathbf{n}$), and the quaternion parameters (λ, Λ) (Tn.1), ♣ (Glabel, *subduction*) to print, in addition, the subduction table for given group (Tn.9), ♣ (Glabel, *subduction_O3*) to print, in addition, the subduction from O_3 table for given group (Tn.10).

  Additional information: The standard printout of this procedure includes (i) the different notations and short description of the given group, (ii) the order of the group, (iii) the numbers of point and double point group classes, (iv) the number of the corresponding tabulation of the given group by Altmann & Herzig(1994), (v) an indicator of crystallographic point group, (vi) the lists of the point and double point group operators enclosing in brackets all operators of the same class, (vii) the numbers of regular and irregular classes, (viii) the number of irreducible representation for point and double point groups, (ix) a number of examples molecules for this symmetry, (x) a list of invariant group chains, and (xi) a list of subduction group chains.

  See also: Bethe_group().

- Bethe_group_tabulation_cartesian_tensor(Glabel) *bethe_b*

  Prints a cartesian tensor table of the given group in a neat format as appropriate, for instance, for a quick comparison with the tables Tn.5 of Altmann & Herzig(1994).

  Output: A NULL expression is returned.

  See also: Bethe_group_tabulation(), Bethe_group_tensor().

- Bethe_group_tabulation_characters(Glabel) *bethe_b*

  Prints a character table of the given group in a neat format as appropriate, for instance, for a quick comparison with the tables Tn.4 of Altmann & Herzig(1994).

  Output: A NULL expression is returned.

  See also: Bethe_group_tabulation(), Bethe_group_characters().

- Bethe_group_tabulation_direct_product(Glabel) $^{bethe\_b}$

  Prints a direct product table of the given group in a neat format as appropriate, for instance, for a quick comparison with the tables Tn.8 of Altmann & Herzig(1994).

  Output: A NULL expression is returned.

  See also: Bethe_group_tabulation(), Bethe_group_direct_product().

- Bethe_group_tabulation_multiplication(Glabel) $^{bethe\_b}$

  Prints a multiplication table of the given group in a neat format as appropriate, for instance, for a quick comparison with the tables Tn.2 of Altmann & Herzig(1994).

  Output: A NULL expression is returned.

  See also: Bethe_group_tabulation(), Bethe_group_multiplication().

- Bethe_group_tabulation_parameters(Glabel) $^{bethe\_b}$

  Prints a table of parameters (Euler angles (α, β, γ), angle and pole of rotation $(\phi, \mathbf{n})$ and the quaternion parameters (λ, Λ) of the given group in a neat format as appropriate, for instance, for a quick comparison with the tables Tn.1 of Altmann & Herzig(1994).

  Output: A NULL expression is returned.

  See also: Bethe_group_tabulation(), Bethe_group_parameters().

- Bethe_group_tabulation_subduction(Glabel) $^{bethe\_b}$

  Prints a subduction table of the given group in a neat format as appropriate, for instance, for a quick comparison with the tables Tn.9 of Altmann & Herzig(1994).

  Output: A NULL expression is returned.

  See also: Bethe_group_tabulation(), Bethe_group_subduction().

- Bethe_group_tabulation_subduction_O3(Glabel) $^{bethe\_b}$

  Prints a subduction from O_3 table of the given group in a neat format as appropriate, for instance, for a quick comparison with the tables Tn.10 of Altmann & Herzig.

  Output: A NULL expression is returned.

  See also: Bethe_group_tabulation(), Bethe_group_subduction_O3().

- **Bethe_group_tensor(Glabel, string$_{\mathrm{fun}}$)** $^{bethe\_b}$

  Returns the list [rank, string$_{\mathrm{IR}}$]. which shows a rank of the symmetry function, decoded by string$_{\mathrm{fun}}$ and corresponding irreducible representation string$_{\mathrm{IR}}$ (or list of representations) as defined by Altmann & Herzig (Tn.5).

  Output: A list is returned.

  Argument options: (Glabel, string$_{\mathrm{IR}}$, rank) to return a list of the basis functions of the irreducible representation string$_{\mathrm{IR}}$ with corresponding rank.

Additional information: Only rank 1, 2 or 3 is available.

See also: Bethe_symmetry_tensors().

- **Bethe_group_test(Glabel)** $^{bethe\_b}$

  Carries out and reports about a number of tests on the group Glabel.

  Output: A NULL expression is returned.

  Argument options: (Glabel, *characters*) to test only the orthogonality relation for irreducible representation characters as provided by the procedure Bethe_group_test_characters() ♣ (Glabel, *direct_product*) to test only the property, that the direct product of two representations is the sun of the symmetrized direct product and antisymmetrized direct product, as provided by the procedure Bethe_group_test_direct_product() ♣ (Glabel, *irreps*) to test only orthogonality relations for the irreducible representations of the group Glabel as provided by the procedure Bethe_group_test_irreps() ♣ (Glabel, *multiplication*) to test only the multiplication rules for the symmetry operations of the group Glabel as provided by the procedure Bethe_group_test_multiplication() ♣ (Glabel, *simple*) to make a number of simple tests of the group Glabel as provided by the procedure Bethe_group_test_simple()

- Bethe_group_test_characters(Glabel) $^{bethe\_b}$

  Test the implementation of the character table for given point group due to the required orthogonality

$$\sum_a \chi^{(\alpha)}(G_a)\chi^{(\beta)*}(G_a) \;=\; g\,\delta_{\alpha\beta}\,.$$

  Output: A NULL expression is returned.

  Additional information: The procedure prints the proper message if the condition of characters orthogonality is not fulfilled.

  See also: Bethe_group_test(), Bethe_group_characters().

- Bethe_group_test_direct_product(Glabel) $^{bethe\_b}$

  Carries out and reports about whether the squared direct product of every irreducible representation of group Glabel is equal to the sum of the symmetrized and antisymmetrized parts of direct product.

  Output: A NULL expression is returned.

  Additional information: The procedure prints the proper message if the condition of direct products equality is not fulfilled. ♣ Test is carried for both of point and double point group representations.

  See also: Bethe_group_test(), Bethe_group_direct_product().

- Bethe_group_test_irreps(Glabel) $^{bethe\_b}$

Carries out and reports about the test of orthogonality of the irreducible representations of the point and the double group

$$\sum_a T_{ip}^{(\alpha)}(G_a) T_{jq}^{(\beta)*}(G_a) \;=\; \frac{g}{s_\alpha}\,\delta_{\alpha\beta}\,\delta_{ij}\,\delta_{pq}\,.$$

Output: A NULL expression is returned.

Additional information: The procedure prints the proper message if the condition of irreps orthogonality is not fulfilled.

See also: Bethe_group_test(), Bethe_group_irreps().

- Bethe_group_test_multiplication(Glabel) $^{bethe\_b}$

  Carries out and reports about the test the 'multiplication table' of the group. For each element G_a, test that $G_a\,G_b$, $b = 1, ..., g$ generates again all symmetry operations.

  Output: A NULL expression is returned.

  Additional information: The procedure prints the proper message if the condition of symmetry operation multiplication is not fulfilled.

  See also: Bethe_group_test(), Bethe_group_multiplication().

- Bethe_group_test_simple(Glabel) $^{bethe\_b}$

  Carries out and reports about a number of simple tests: (i) number of classes = number of irreps for both point and double cases; (ii) order of group divided by the order to subgroups must be an integer; (iii) number of symmetry operators = group order for both point and double cases; (iv) class order must be integral divisor of a group order; (v) class criterium $G_a = G_n G_b G_n^{-1}$ of all symmetry operators of the same class;

  Output: A NULL expression is returned.

  Additional information: The procedure prints the proper message if the conditions of (i) - (v) are not fulfilled.

  See also: Bethe_group_test(), Bethe_group().

- **Bethe_group_time_reversal(Glabel, string$_{\rm IR}$)** $^{bethe\_b}$

  Returns the symmetry behavior of the irreducible representation string$_{\rm IR}$ under time reversal.

  Output: A string with the time reversal classification is returned.

  Additional information: Addition of time-reversal operator (which is symmetry operator for the Hamiltonian of many physical systems) to an existing symmetry group can lead to increased degeneracy of wave functions of system. Irreducible representations of group with time reversal can be classified by (i) equivalent to a real representations, (ii) not equivalent to their complex conjugate representations, (iii) equivalent to their complex conjugate representations, but not to a real representations.

  Notation for time reversal classification (I is the representation string$_{\rm IR}$, I^* - its complex conjugate):

	I, I^*	Vector representation	Spinor representation
a	Real and equal	No extra degeneracy	Doubled degeneracy
b	Complex and inequivalent	Doubled degeneracy	Doubled degeneracy
c	Complex and equivalent	Doubled degeneracy	No extra degeneracy

See also: Bethe_symmetry_characters().

- **Bethe_implemented()** $^{bethe-pg-data}$

  Returns a list of a currently implemented point groups.

  Output: A list is returned.

  Additional information: Point group identifiers are returned in terms of their group labels [Glabel$_1$, Glabel$_2$, ...]. ♣ Corresponding double groups are also supported by the program.

  See also: Bethe_group().

- **Bethe_internal_coordinates(Glabel, mol)** $^{bethe\_b}$

  To specify the internal coordinates of the molecule *mol*.

  Output: A list of lists $[[[a_{ix}, a_{iy}, a_{iz}], [a_{jx}, a_{jy}, a_{jz}]], [[a_{lx}, a_{ly}, a_{lz}], [a_{mx}, a_{my}, a_{mz}], [a_{nx}, a_{ny}, a_{nz}]], [[\,], [\,]], ...]$ is returned.

  Argument options: (Glabel, mol, *stretching*) to return the stretching vibrational vectors. A list of lists $[[[a_{ix}, a_{iy}, a_{iz}], [a_{jx}, a_{jy}, a_{jz}]], [[\,], [\,]], ...]$ is returned in this case. ♣ (Glabel, mol, *bending*) to return the same for the bending vibrational vectors. A list of lists $[[[a_{ix}, a_{iy}, a_{iz}], [a_{jx}, a_{jy}, a_{jz}], [a_{kx}, a_{ky}, a_{kz}]], [[\,], [\,], [\,]], ...]$ is returned in this case.

  Additional information: The molecule is defined by the procedure molecule(). ♣ The stretching internal coordinate can be specified as a vector between two different atoms i and j, having the coordinates $[a_{ix}, a_{iy}, a_{iz}], [a_{jx}, a_{jy}, a_{jz}]$, while bending internal coordinates can be specified as an angle between three atoms i, j and k, having the coordinates $[a_{ix}, a_{iy}, a_{iz}], [a_{jx}, a_{jy}, a_{jz}], [a_{kx}, a_{ky}, a_{kz}]$. ♣ The number of output list member depends of the molecule. ♣ If the number of internal coordinates exceeds the number of normal vibrations, the list of the internal coordinates contains so-called *redundant coordinates*, which are not independent of other internal coordinates.

- Bethe_Kronecker(a, b) $^{bethe\_b}$

  Returns 1, if a = b and 0 otherwise.

  Output: A number is returned.

- **Bethe_linearly_independent([[a$_1$, a$_2$, a$_3$,...], [b$_1$, b$_2$, b$_3$,...], ...])** $^{bethe\_b}$

  Extracts the linearly independent sublists from the list [[a$_1$, a$_2$, a$_3$,...], [b$_1$, b$_2$, b$_3$,...], ...].

  Output: A list of lists is returned.

Additional information: In the output the members of sublists are linearly independent to each other.

See also: .

- Bethe_matrices_are_equal(M1, M2, dim) $^{bethe\_b}$

  Returns *true* if the matrices M1 and M2, which must have both the dimension *dim* are equal to each other and *false* otherwise.

  Output: A boolean value of *true* or *false* is returned.

  Additional information: Matrices are considered to be equal if they have the same dimension *dim* and module of the difference between each pair of corresponding matrix elements ≤ 0.001.

- Bethe_nonequivalent_angles(Glabel, mol) $^{bethe\_b}$

  Generates the list of NONEQUIVALENT interbond angles of the molecule *mol* in terms of the atomic coordinates.

  Output: A list of lists [[$a_x^{(1)}$,$a_y^{(1)}$,$a_z^{(1)}$], [$a_x^{(2)}$,$a_y^{(2)}$,$a_z^{(2)}$], [$a_x^{(3)}$,$a_y^{(3)}$,$a_z^{(3)}$]], [[], [], []], ...] is returned.

  Argument options:

  Additional information: To define a molecule, the procedure molecule() can be used. ♣ Angles, which are nonequivalent, can not be transformed into each other by the symmetry operations of the group Glabel.

  See also: Bethe_nonequivalent_atoms(), Bethe_nonequivalent_distances().

- Bethe_nonequivalent_atoms(Glabel, mol) $^{bethe\_b}$

  Generates the list of NONEQUIVALENT atoms of the molecule *mol* in terms of the atomic coordinates.

  Output: A list of lists [[$a_x^{(1)}$,$a_y^{(1)}$,$a_z^{(1)}$], [],...] is returned.

  Argument options:

  Additional information: To define a molecule, the procedure molecule() can be used. ♣ Atoms, which are nonequivalent, can not be transformed into each other by the symmetry operations of the group Glabel.

  See also: Bethe_nonequivalent_angles(), Bethe_nonequivalent_distances().

- Bethe_nonequivalent_distances(Glabel, mol) $^{bethe\_b}$

  Generates the list of NONEQUIVALENT interatomic distances of the molecule *mol* in terms of the atomic coordinates.

  Output: A list of lists [[$a_x^{(1)}$,$a_y^{(1)}$,$a_z^{(1)}$], [$a_x^{(2)}$,$a_y^{(2)}$,$a_z^{(2)}$]], [[], []], ...] is returned.

  Argument options:

Additional information: To define a molecule, the procedure molecule() can be used. ♣ Interatomic, which are nonequivalent, can not be transformed into each other by the symmetry operations of the group Glabel.

See also: Bethe_nonequivalent_atoms(), Bethe_nonequivalent_angles().

- **Bethe_normal_coordinates(Glabel, mol, string$_{\rm IR}$, *Cartesian*)** $^{bethe\_b}$

Calculates the vibrational coordinates of a molecule *mol* according with the irreducible representation string$_{\rm IR}$ in terms of its $3N$ Cartesian atomic coordinates.

Output: A list of lists $[[c_{1x}^{(1)}, c_{1y}^{(1)}, ..., c_{Nz}^{(1)}], [c_{1x}^{(2)}, c_{1y}^{(2)}, ..., c_{Nz}^{(2)}], ...]$ is returned.

Argument options: (Glabel, mol, string$_{\rm IR}$, *stretching*) to calculate the stretching normal coordinates of a molecule according with the irreducible representation string$_{\rm IR}$ in terms of stretching internal coordinates of a molecule, defined in the procedure Bethe_internal_coordinates(..., stretching). A list of lists $[[c_1^{(1)}, c_2^{(1)}, c_3^{(1)}, ...], [c_1^{(2)}, c_2^{(2)}, c_3^{(2)},$ $...], ...]$ is returned in this case. ♣ (Glabel, mol, string$_{\rm IR}$, *stretching*, listint$_{\rm str}$) to calculate the stretching normal coordinates of a molecule *mol* according with the irreducible representation string$_{\rm IR}$ in terms of stretching internal coordinates of a molecule, defined by the user as a listint$_{\rm str}$ $= [[[a_{ix}, a_{iy}, a_{iz}], [a_{jx}, a_{jy}, a_{jz}]], [[\,], [\,]], ...]$. A list of lists $[[c_1^{(1)}, c_2^{(1)}, c_3^{(1)}, ...], [c_1^{(2)}, c_2^{(2)}, c_3^{(2)}, ...], ...]$ is returned in this case. ♣ (Glabel, molecule, string$_{\rm IR}$, *bending*) to calculate the bending normal coordinates of a molecule according with the irreducible representation string$_{\rm IR}$ in terms of bending internal coordinates of a molecule, defined in the procedure Bethe_internal_coordinates(..., bending). A list $[[c_1^{(1)}, c_2^{(1)}, c_3^{(1)}, ...], [c_1^{(2)}, c_2^{(2)}, c_3^{(2)}, ...], ...]$ is returned in this case. ♣ (Glabel, molecule, string$_{\rm IR}$, *bending*, listint$_{\rm bnd}$) to calculate the bending normal coordinates of a molecule according with the irreducible representation string$_{\rm IR}$ in terms of bending internal coordinates of a molecule, defined by the user as a listint$_{bnd} = [[[a_{ix}, a_{iy}, a_{iz}], [a_{jx}, a_{jy}, a_{jz}],$ $[a_{kx}, a_{ky}, a_{kz}]], [[\,], [\,], [\,]], ...]$. A list $[[c_1^{(1)}, c_2^{(1)}, c_3^{(1)}, ...], [c_1^{(2)}, c_2^{(2)}, c_3^{(2)}, ...], ...]$ is returned in this case.

Additional information: To define a molecule, the procedure molecule() can be used. ♣ For a given molecule, all the atomic coordinates must be specified explicitly, and these coordinates must obey the symmetry of the point group Glabel. The procedure terminates with a proper ERROR message if these conditions are not fulfilled. ♣ The set of internal coordinates, specified by the user should be complete, that is all of the internal coordinates have to go each other under the symmetry operations of a group. The procedure terminates with a proper ERROR message if these conditions are not fulfilled. ♣ The normal coordinates Q_i, calculated in terms of the Cartesian coordinates, are defined as a coordinate transformation in the form

$$Q_i = Q_i(x_1, y_1, z_1, x_2, y_2, z_2, ..., x_{3N}, y_{3N}, z_{3N}) =$$

$$c_{1x}^{(i)} x_1 + c_{1y}^{(i)} y_1 + c_{1z}^{(i)} z_1 + c_{2x}^{(i)} x_2 + c_{2y}^{(i)} y_2 + c_{2z}^{(i)} z_2 + ...$$

This list can contain also the coordinates of the translational and rotational motion, if corresponding modes are inherent in given irreducible representation string$_{\rm IR}$. ♣ The

internal coordinates Q_i are defined as a coordinate transformation

$$Q_i = Q_i(r_1, r_2, r_3, ...) = c_1^{(i)} r_1 + c_2^{(i)} r_2 + c_3^{(i)} r_3 + ...$$

where every member $c_j^{(i)}$ defines the increment of a proper internal coordinate as obtained from the procedure Bethe_internal_coordinates(). ♣ Sequence of atomic Cartesian coordinates $x_1, y_1, z_1, x_2, y_2, z_2, ..., x_{3N}, y_{3N}, z_{3N}$ is defined by a molecule, while sequence of internal (stretching or bending) coordinates $r_1, r_2, r_3, ...$ is defined by a procedure Bethe_internal_coordinates(). ♣ List of the normal coordinates can contain the *equivalent normal coordinates*, obtained from the equivalent internal (or cartesian) coordinates.

See also: Bethe_internal_coordinates().

- Bethe_normal_coordinates_bending(Glabel, mol, listint$_{\rm bnd}$, string$_{\rm IR}$, ldim) $^{bethe\_b}$

  Calculates the normal coordinates of a molecule *mol* in terms of its internal (bending) displacements vectors, defined by the variable listint$_{\rm bnd}$ according to the *ldim* component of the irreducible representation $string_{\rm IR}$.

  Output: A list of lists $[[c_{1x}^{(1)}, c_{1y}^{(1)}, ..., c_{Nz}^{(1)}], [c_{1x}^{(2)}, c_{1y}^{(2)}, ..., c_{Nz}^{(2)}], ...]$ is returned.

  Argument options:

  Additional information: To define a molecule, the procedure molecule() can be used. ♣ For a given molecule, all the atomic coordinates must be specified explicitly, and these coordinates must obey the symmetry of the point group Glabel. The procedure terminates with a proper ERROR message if these conditions are not fulfilled. ♣ The set of internal coordinates, defined by the variable listint$_{bnd}$ should be complete, that is all of the internal coordinates have to go each other under the symmetry operations of a group. The procedure terminates with a proper ERROR message if these conditions are not fulfilled. ♣ The internal bending coordinates Q_i are defined as a coordinate transformation

  $$Q_i = Q_i(\alpha_1, \alpha_2, \alpha_3, ...) = c_1^{(i)} \alpha_1 + c_2^{(i)} \alpha_2 + c_3^{(i)} \alpha_3 + ...$$

  where every member $c_j^{(i)}$ defines the increment of a proper internal coordinate as obtained from the procedure Bethe_internal_coordinates(). ♣ List of the normal coordinates can contain the *equivalent normal coordinates*, obtained from the equivalent internal coordinates.

  See also: Bethe_internal_coordinates(), Bethe_normal_coordinates().

- Bethe_normal_coordinates_cartesian(Glabel, molecule, string$_{\rm IR}$, ldim) $^{bethe\_b}$

  Calculates the normal coordinates of a molecule *mol* in terms of its cartesian displacements vectors, defined automatically by the procedure, according to the *ldim* component of the irreducible representation $string_{\rm IR}$.

  Output: A list of lists $[[c_{1x}^{(1)}, c_{1y}^{(1)}, ..., c_{Nz}^{(1)}], [c_{1x}^{(2)}, c_{1y}^{(2)}, ..., c_{Nz}^{(2)}], ...]$ is returned.

Argument options:

Additional information: To define a molecule, the procedure molecule() can be used. ♣ For a given molecule, all the atomic coordinates must be specified explicitly, and these coordinates must obey the symmetry of the point group Glabel. The procedure terminates with a proper ERROR message if these conditions are not fulfilled. ♣ The normal coordinates Q_i, calculated in terms of the Cartesian coordinates, are defined as a coordinate transformation in the form

$$Q_i = Q_i(x_1, y_1, z_1, x_2, y_2, z_2, ..., x_{3N}, y_{3N}, z_{3N})$$
$$= c_{1x}^{(i)} x_1 + c_{1y}^{(i)} y_1 + c_{1z}^{(i)} z_1 + c_{2x}^{(i)} x_2 + c_{2y}^{(i)} y_2 + c_{2z}^{(i)} z_2 + ...$$

This list can contain also the coordinates of the translational and rotational motion, if corresponding modes are inherent in given irreducible representation $\text{string}_{\text{IR}}$.

♣ Sequence of atomic Cartesian coordinates $x_1, y_1, z_1, x_2, y_2, z_2, ..., x_{3N}, y_{3N}, z_{3N}$ is defined by the molecule. ♣ List of the normal coordinates can contain the *equivalent normal coordinates*, obtained from the equivalent cartesian coordinates.

See also: Bethe_normal_coordinates().

- Bethe_normal_coordinates_stretching(Glabel, mol, $\text{listint}_{\text{str}}$, $\text{string}_{\text{IR}}$, ldim) $^{bethe\_b}$

Calculates the normal coordinates of a molecule *mol* in terms of its internal (stretching) displacements vectors, defined by the variable $\text{listint}_{\text{str}}$ according to the *ldim* component of the irreducible representation $string_{\text{IR}}$.

Output: A list of lists $[[c_{1x}^{(1)}, c_{1y}^{(1)}, ..., c_{Nz}^{(1)}], [c_{1x}^{(2)}, c_{1y}^{(2)}, ..., c_{Nz}^{(2)}], ...]$ is returned.

Argument options:

Additional information: To define a molecule, the procedure molecule() can be used. ♣ For a given molecule, all the atomic coordinates must be specified explicitly, and these coordinates must obey the symmetry of the point group Glabel. The procedure terminates with a proper ERROR message if these conditions are not fulfilled. ♣ The set of internal coordinates, defined by the variable $\text{listint}_{\text{str}}$ should be complete, that is all of the internal coordinates have to go each other under the symmetry operations of a group. The procedure terminates with a proper ERROR message if these conditions are not fulfilled. ♣ The internal stretching coordinates Q_i are defined as a coordinate transformation

$$Q_i = Q_i(r_1, r_2, r_3, ...) = c_1^{(i)} r_1 + c_2^{(i)} r_2 + c_3^{(i)} r_3 + ...$$

where every member $c_j^{(i)}$ defines the increment of a proper internal coordinate as obtained from the procedure Bethe_internal_coordinates(). ♣ List of the normal coordinates can contain the *equivalent normal coordinates*, obtained from the equivalent internal coordinates.

See also: Bethe_internal_coordinates(), Bethe_normal_coordinates().

- **Bethe_normal_display(mol, norm_coord)** *bethe_b*

  Displays the vibrational motion, defined by the normal coordinate *norm_coord* of a molecule *mol* graphically.

  Output: A NULL is returned.

  Additional information: A normal coordinate in terms of the cartesian displacement vectors should be used. ♣ To define a molecule, the procedure molecule() can be used. ♣ Up to now only a two-dimensional animation is available.

  See also: molecule(), Bethe_normal_coordinates().

- Bethe_normalize_SO(SO) *bethe_b*

  Makes the coefficients of AOs normalized to unity.

  Output: A symmetry orbital in terms of atomic orbitals with normalized coefficients is returned.

  Additional information:

  See also: .

- Bethe_number_SO(Glabel, $\text{string}_{\text{IR}}$, $\text{string}_{\text{atom}}$, [$a_1$,$a_2$,$a_3$],[n,l] *bethe_b*

  Generates a number of symmetry orbitals, which have to be selected to obtain a *linearly independent* set of orbitals.

  Output: A number is returned.

  Additional information: If the number of equivalent atoms is equal to the order of the group, then the symmetry orbitals are linearly independent automatically and selection is not necessary.

  See also: .

- **Bethe_print_orbital(AO)** *bethe_b*

  Returns the string "| $\text{string}_{\text{atom}}$: ($a_1$,$a_2$,$a_3$) n=$n_o$, l=$l_o$, m=$m_o$ >" within the nonrelativistic framework in order to facilitate the printout of atomic orbitals in the line mode.

  Output: A string is returned.

  Argument options: (SO) to return the string "| $\text{string}_{\text{atom}}$: Glabel, ($a_1$,$a_2$,$a_3$) n=$n_o$, l=$l_o$, m=$m_o$; $\text{string}_{\text{IR}}(\text{mu}, \text{nu})$ >" within the nonrelativistic framework in order to facilitate the printout of symmetry orbitals in the line mode.

  Additional information: If a relativistic framework is set, either the string
  "| $\text{string}_{\text{atom}}$: ($a_1$,$a_2$,$a_3$) n=$n_o$, kappa=$\text{kappa}_o$, m=$m_o$ >" or
  "| $\text{string}_{\text{atom}}$: Glabel, ($a_1$,$a_2$,$a_3$) n=$n_o$, kappa=$\text{kappa}_o$, m=$m_o$; $\text{string}_{\text{IR}}(\text{mu}, \text{nu})$ >" is returned in this case.

  See also: AO(), SO().

- Bethe_product_contains_totally_symmetric(Glabel, string$_{\mathrm{IR}}$, listdipmom) $^{bethe\_b}$

  Defines whether the direct product of the irreducible representation string$_{IR}$ and one of the irreducible representations from the list "listdipmom" contains the totally symmetric irreducible representation of the group Glabel.

  Output: A boolean variable *true* or *false* is returned.

  Argument options:

  Additional information: The list "listdipmom" has to contain the irreducible representations of the permanent dipole moment (for the infrared absorption) or the induced dipole moment (for the Raman scattering).

  See also: Bethe_spectral_activity(), Bethe_group_representation().

- **Bethe_set(*framework = nonrelativistic*)** $^{bethe\_b}$

  Defines a nonrelativistic framework and notation for the use of the atomic orbitals, i.e. $\langle \mathbf{r} \,|\, \mathbf{a}\ nlm \rangle$.

  Output: A NULL expression is returned.

  Argument options: (*framework = relativistic*) to *define* a relativistic framework and notation for the atomic orbitals, i.e. $\langle \mathbf{r} \,|\, \mathbf{a}\ n\kappa m \rangle$ where κ is the relativistic angular momentum quantum number.

  Additional information: The information about the framework of the atomic orbitals is kept in the global variable Bethe_save_framework; its default is Bethe_save_framework = nonrelativistic. ♣ While, in the nonrelativistic framework, the group labels refer to the point groups, they refer (automatically) to the double groups of the corresponding symmetry in the relativistic case.

- Bethe_SO_are_linearly_independent(list1, list2) $^{bethe\_b}$

  Defines, whether two symmetry orbitals list1 and list2 are linearly independent each other.

  Output: A boolean variable `true` or `false` is returned.

  See also: Bethe_generate_SO_basis().

- **Bethe_SO_are_orthogonal(list$_{\mathrm{LCAO}}$)** $^{bethe\_b}$

  Defines, whether the symmetry orbitals from the list$_{\mathrm{LCAO}}$ are mutually orthogonal. An explicit representation of the symmetry orbitals in terms of the atomic orbital has to be given.

  Output: A boolean variable `true` or `false` is returned.

  Additional information: A proper message is printed if two of the symmetry orbitals from the list are not orthogonal to each other.

  See also: Bethe_generate_SO_basis().

- **Bethe_spectral_activity(Glabel, string$_{\mathrm{IR}}$, *infrared*)** $^{bethe\_b}$

  Defines, whether the normal vibration having the symmetry type string$_{\mathrm{IR}}$ is infrared active.

  Output: A boolean values true or false is returned.

  Argument options: (Glabel, string$_{\mathrm{IR}}$, *Raman*) to return the boolean value true if the normal vibration having the symmetry type string$_{\mathrm{IR}}$ is Raman active and false otherwise. ♣ (Glabel, [string$_{\mathrm{IR1}}$, string$_{\mathrm{IR2}}$, ...], infrared) to extract a list of the infrared active modes. A list of strings is returned. ♣ (Glabel, [string$_{\mathrm{IR1}}$, string$_{\mathrm{IR2}}$, ...], Raman) to extract a list of the Raman active modes. A list of strings is returned. ♣ (Glabel, string$_{\mathrm{IR}}$, *Raman*, n) to return the boolean value true if (n-1)-th overtone in the normal vibration having the symmetry type string$_{\mathrm{IR}}$ is Raman active and false otherwise. ♣ (Glabel, string$_{\mathrm{IR}}$, *infrared*, n) to return the boolean value true if (n-1)-th overtone in the normal vibration having the symmetry type string$_{\mathrm{IR}}$ is infrared active and false otherwise. ♣ (Glabel, [string$_{\mathrm{IR1}}$, string$_{\mathrm{IR2}}$, ...], infrared, [n_1, n_2, ...]) to return the boolean value true if combination of the transitions in the normal vibration having the symmetry type string$_{\mathrm{IRi}}$ from the fundamental to the n_i excited level is infrared active and false otherwise ♣ (Glabel, [string$_{\mathrm{IR1}}$, string$_{\mathrm{IR2}}$, ...], Raman, [n_1, n_2, ...]) to return the boolean value true if combination of the transitions in the normal vibration having the symmetry type string$_{\mathrm{IRi}}$ from the fundamental to the n_i excited level is Raman active and false otherwise

  See also: Bethe_normal_coordinates().

- Bethe_symmetry_characters(Glabel) $^{bethe-pg-data}$

  Return the character table of the point group with label Glabel in an internal list format.

  Output: A list is returned.

  Additional information: The character tables are provided explicitly for each point group in a list with the format: [m, n, matrix(m,n), raw_labels, traw_labels, column_labels, double_column_labels] where m,n denotes the dimension of the matrix, raw_labels is a list of irreducible representations [string$_{IR_1}$, ..., string$_{IR_m}$], traw_labels is a list of time-reversal classifications of irreducible representations, column_labels is a list of classes with list of symmetry operations [[string$_{SO_{11}}$, ..., string$_{SO_{1n}}$], [string$_{SO_{21}}$, ..., string$_{SO_{2n}}$],...] inside of each class of the corresponding point group and column_labels is a list of classes with list of symmetry operations [[string$_{SO_{11}}$, ..., string$_{SO_{1n}}$], [string$_{SO_{21}}$, ..., string$_{SO_{2n}}$],...] inside of each class of the corresponding double group. From this information, the characters can be derived for all combinations (string$_{IR}$, string$_{SO}$). Procedure is organized as a list of references to a set of subprocedures, appropriate of the families of groups (see table).

Bethe_symmetry_characters_Cis()	Cis: (Ci, Cs)
Bethe_symmetry_characters_Cn()	Cn: (C2, ..., C10)
Bethe_symmetry_characters_Cnv()	Cnv: (C2v, ..., C10v)
Bethe_symmetry_characters_Cnh()	Cnh: (C2h, ..., C10h)
Bethe_symmetry_characters_Dn()	Dn: (D2, ..., D10)
Bethe_symmetry_characters_Dnd()	Dnd: (D2d, ..., D10d)
Bethe_symmetry_characters_Dnh()	Dnh: (D2h, ..., D10h)
Bethe_symmetry_characters_Sn()	Sn: (S4, ..., S20)
Bethe_symmetry_characters_O()	O: (O, Oh, T, Th, Td)
Bethe_symmetry_characters_I()	I: (Ic, Ich)

See also: Bethe_group_character(), Bethe_group_class().

- Bethe_symmetry_description(Glabel, $\text{string}_{\text{SO}}$) $^{bethe-pg-data}$

  Returns a text string which describes the symmetry operation $\text{string}_{\text{SO}}$ for a point group with label Glabel.

  Output: A text string is returned.

  Additional information: The identifier $\text{string}_{\text{SO}}$ is usually enough to characterize the symmetry operation; the group label Glabel is used only if the string identifier itself is not unique. ♣ The procedure stores the description of all known symmetry operations in a list [[$\text{string}_{\text{SO}_1}$, Glabel/"all", "description text"], [$\text{string}_{\text{SO}_2}$, Glabel/"all", "description text"],...] where the second entry "all" is used if the corresponding string identifier represents the same symmetry operations for all groups (which contain this operation string).

  See also: Bethe_group(), , Bethe_symmetry_elements(), Bethe_symmetry_operations().

- Bethe_symmetry_elements(Glabel) $^{bethe-pg-data}$

  Return a list of strings which describes all symmetry elements of of the point group with label Glabel.

  Output: A list of strings is returned.

  Additional information: Position of the vertical reflection planes is described by angle "phi", which is azimuth angle of anticlockwise rotation of this plane around Z-axis respecting the ZX-plane. Procedure is organized as a list of references to a set of subprocedures, appropriate of the families of groups (see table).

Bethe_symmetry_elements_Cis()	Cis: (Ci, Cs)
Bethe_symmetry_elements_Cn()	Cn: (C2, ..., C10)
Bethe_symmetry_elements_Cnv()	Cnv: (C2v, ..., C10v)
Bethe_symmetry_elements_Cnh()	Cnh: (C2h, ..., C10h)
Bethe_symmetry_elements_Dn()	Dn: (D2, ..., D10)
Bethe_symmetry_elements_Dnd()	Dnd: (D2d, ..., D10d)
Bethe_symmetry_elements_Dnh()	Dnh: (D2h, ..., D10h)
Bethe_symmetry_elements_Sn()	Sn: (S4, ..., S20)
Bethe_symmetry_elements_O()	O: (O, Oh, T, Th, Td)
Bethe_symmetry_elements_I()	I: (Ic, Ich)

See also: Bethe_symmetry_operations().

- Bethe_symmetry_is_fulfilled(Glabel, mol) $^{bethe\_b}$

  Defines, whether the molecule *mol* fulfills the symmetry of the group Glabel.

  Output: A boolean variable *true* or *false* is returned.

  Argument options:

  Additional information: The molecule is defined by the procedure molecule()

  See also: .

- Bethe_symmetry_matrices(Glabel) $^{bethe-pg-data}$

  Return the table of irreducible matrix representations for the point group with label Glabel in an internal list format.

  Output: A list is returned.

  Additional information: The tables of irreducible matrix representations are provided explicitly for point groups, which have the irreducible representation with dimension ≥ 2, in a list with the format: [m, n, matrix(m,n), raw_labels, column_labels] where m,n denotes the dimension of the matrix, raw_labels is a list of matrix representations dimension ≥ 2 [$\text{string}_{\text{IR}_1}$, ..., $\text{string}_{\text{IR}_\text{m}}$], and column_labels is a list of symmetry operations [$\text{string}_{\text{SO}_1}$, ..., $\text{string}_{\text{SO}_\text{n}}$] of the corresponding point group. From this information, the matrices can be derived for all combinations ($\text{string}_{\text{IR}}$, $\text{string}_{\text{SO}}$). Procedure is organized as a list of references to a set of subprocedures, appropriate of the families of groups (see table).

Bethe_symmetry_matrices_Cis()	Cis: (Ci, Cs)
Bethe_symmetry_matrices_Cn()	Cn: (C2, ..., C10)
Bethe_symmetry_matrices_Cnv()	Cnv: (C2v, ..., C10v)
Bethe_symmetry_matrices_Cnh()	Cnh: (C2h, ..., C10h)
Bethe_symmetry_matrices_Dn()	Dn: (D2, ..., D10)
Bethe_symmetry_matrices_Dnd()	Dnd: (D2d, ..., D10d)
Bethe_symmetry_matrices_Dnh()	Dnh: (D2h, ..., D10h)
Bethe_symmetry_matrices_Sn()	Sn: (S4, ..., S20)
Bethe_symmetry_matrices_O()	O: (O, Oh, T, Th, Td)
Bethe_symmetry_matrices_I()	I: (Ic, Ich)

See also: Bethe_group_irrep().

- Bethe_symmetry_operations(Glabel) $^{bethe-pg-data}$

  Return a list of all symmetry operations of the point group with label Glabel: [[string_{SO_1}, [Euler alpha, beta, gamma], inversion], [string_{SO_2}, [Euler alpha, beta, gamma], inversion], [string_{SO_3}, [Euler alpha, beta, gamma], inversion],...].

  Output: A list of lists is returned.

  Argument options: (Glabel,*double_group*) to return the symmetry operation for the corresponding double group.

  Additional information: string_{SO} is a name of the symmetry operation oh the point group with label Glabel, [Euler alpha, beta, gamma] - list of three Euler angles for operation string_{SO} and inversion is '*true*', if the symmetry operation string_{SO} is a combination of rotation and spatial inversion and '*false*', if strong_{SO} is a pure rotation.

  Procedure is organized as a list of references to a set of subprocedures, appropriate of the families of groups (see table).

Bethe_symmetry_operations_Cis()	Cis: (Ci, Cs)
Bethe_symmetry_operations_Cn()	Cn: (C2, ..., C10)
Bethe_symmetry_operations_Cnv()	Cnv: (C2v, ..., C10v)
Bethe_symmetry_operations_Cnh()	Cnh: (C2h, ..., C10h)
Bethe_symmetry_operations_Dn()	Dn: (D2, ..., D10)
Bethe_symmetry_operations_Dnd()	Dnd: (D2d, ..., D10d)
Bethe_symmetry_operations_Dnh()	Dnh: (D2h, ..., D10h)
Bethe_symmetry_operations_Sn()	Sn: (S4, ..., S20)
Bethe_symmetry_operations_O()	O: (O, Oh, T, Th, Td)
Bethe_symmetry_operations_I()	I: (Ic, Ich)

See also: Bethe_symmetry_elements().

- Bethe_symmetry_properties(Glabel) $^{bethe-pg-data}$

Returns the list of properties of the point group with label Glabel: ["Description of the group", [group order, No. of reg. classes, No. of irreg. classes, Table-No by Altmann, crystallographic, crystall system, proper], [list of subgroups], [list of suboperators], [list of string$_{IR}$ (standard)], [list of spinor string$_{IR}$], [list of examples]]

Output: A list is returned.

Additional information:

Short description of all properties

group order	Number of the symmetry operations of the point group
No. of reg. classes	Number of regular classes
No. of irreg. classes	Number of irregular classes
Table-No by Altmann	Number of the tabulation by Altmann and Herzig (1994).
crystallographic	'*true*' or '*false*' in dependence whether Glabel is a crystallographic group or not
crystall system	Name of the crystal system (rhombic, triclinic,...) for the crystallographic groups
proper	'*true*' or '*false*' in dependence whether Glabel is a proper symmetry group or not
list of string$_{\mathrm{IR}}$	List of all irreducible representations string identifiers for the point group
list of spinor string$_{\mathrm{IR}}$	List of spinor irreducible representations string identifiers for corresponding double group
list of examples	Examples of molecules of given point group

Procedure is organized as a list of references to a set of subprocedures, appropriate of the families of groups (see table).

Bethe_symmetry_properties_Cis()	Cis: (Ci, Cs)
Bethe_symmetry_properties_Cn()	Cn: (C2, ..., C10)
Bethe_symmetry_properties_Cnv()	Cnv: (C2v, ..., C10v)
Bethe_symmetry_properties_Cnh()	Cnh: (C2h, ..., C10h)
Bethe_symmetry_properties_Dn()	Dn: (D2, ..., D10)
Bethe_symmetry_properties_Dnd()	Dnd: (D2d, ..., D10d)
Bethe_symmetry_properties_Dnh()	Dnh: (D2h, ..., D10h)
Bethe_symmetry_properties_Sn()	Sn: (S4, ..., S20)
Bethe_symmetry_properties_O()	O: (O, Oh, T, Th, Td)
Bethe_symmetry_properties_I()	I: (Ic, Ich)

See also: Bethe_group().

- Bethe_symmetry_tensors(Glabel) $^{bethe-pg-data}$

Output: A list of lists is returned.

Additional information: Returns the list of lists: [[list of irreps or products of irreps], [list of rank-1 functions], [list of rank-2 functions], [list of rank-3 functions]], which is information about the transformation behavior of the p, d, and f functions as well as the standard rotations.All symmetry functions are decoded by strings; the following strings are allowed ("no" ... no function) rank-1: "x", "y", "z", "Rx", "Ry", "Rz". rank-2: "xx", "xy", "xz", "yy", "yz", "zz", "xx-yy", "xx+yy". rank-3: "xxx", "xxy", "xxz", "xyy", "xyz", "xzz", "yyy", "yyz", "yzz", "zzz", "xxx+xyy", "xxy+yyy", "xxz+yyz", "xxx-xyy", "xxy-yyy", "xxz-yyz". Procedure is organized as a list of references to a set of subprocedures, appropriate of the families of groups (see table).

Bethe_symmetry_tensors_Cis()	Cis: (Ci, Cs)
Bethe_symmetry_tensors_Cn()	Cn: (C2, ..., C10)
Bethe_symmetry_tensors_Cnv()	Cnv: (C2v, ..., C10v)
Bethe_symmetry_tensors_Cnh()	Cnh: (C2h, ..., C10h)
Bethe_symmetry_tensors_Dn()	Dn: (D2, ..., D10)
Bethe_symmetry_tensors_Dnd()	Dnd: (D2d, ..., D10d)
Bethe_symmetry_tensors_Dnh()	Dnh: (D2h, ..., D10h)
Bethe_symmetry_tensors_Sn()	Sn: (S4, ..., S20)
Bethe_symmetry_tensors_O()	O: (O, Oh, T, Th, Td)
Bethe_symmetry_tensors_I()	I: (Ic, Ich)

See also: Bethe_group_tensors().

- **Bethe_tabulate(AO)** *bethe_b*

  Returns a table of all the quantum numbers and string identifiers of the atomic orbital AO.

  Output: A table `T` is returned.

  Argument options: (SO) to return a table of all the quantum numbers and string identifiers of the symmetry orbital SO.

  Additional information: For an atomic orbital AO, `T` has the entries `T[a], T[n], T[l], T[m], T[symbol]` in the nonrelativistic case and `T[a], T[n], T[kappa], T[m], T[symbol]` in the relativistic case. ♣ For a symmetry orbital SO, `T` has the entries `T[label], T[a], T[n], T[l], T[m], T[IR], T[mu], T[nu], T[symbol]` in the nonrelativistic case and `T[label], T[a], T[n], T[kappa], T[m], T[IR], T[mu], T[nu], T[symbol]` in the relativistic case. ♣ The entry `T[a]` returns a list of the three coordinates [a_1,a_2,a_3] which have to be interpreted in line with the predefined coordinates, see Bethe_set().

  See also: AO(), SO().

- Bethe_transform_vector(Glabel, $\text{string}_{\text{SO}}$, [$a_1$,$a_2$,$a_3$]) *bethe_b*

  Transforms the components (a_1,a_2,a_3) of a given position vector **a** under the symmetry operation $\text{string}_{\text{SO}}$ of the point group $\mathcal{G}$ with label Glabel.

Output: The three new components of the vector [$a_1 new$,$a_2 new$,$a_3 new$] are returned in a list.

Additional information: To transform the components of vector, it is enough to multiply its components with the rotation matrix of the corresponding symmetry operation $\text{string}_{\text{SO}}$, obtained by the procedure Bethe_group_Euler(..., matrix).

See also: Bethe_group_Euler().

List of Publications

During the period of this thesis work, I finished three papers which have been published or accepted for publication. A list of these publications is shown below. The detailed text of each paper is appendedto the thesis.

1. K. Rykhlinskaya, S. Fritzsche, *Use of group theory for the analysis of vibrational spectra*. Comp. Phys. Comm., 162 (2004) 124-142.

2. K. Rykhlinskaya, S. Fritzsche, *Generation of molecular symmetry orbitals for the point and double groups*. Comp. Phys. Comm., 171 (2005) 119-132.

3. K. Rykhlinskaya, S. Fritzsche, *Generation of the Clebsch-Gordan coefficients for the point and double groups*. Comp. Phys. Comm., accepted (2005).

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Erklärung

Hiermit versichere ich, daß ich die vorliegende Dissertation selbständig und ohne unerlaubte Hilfe angefertigt und andere als die in der Dissertation angegebenen Hilfsmittel benutzt habe. Alle Stellen, die wörtlich oder sinngemäß aus veröffentlichten oder unveröffentlichten Schriften entnommen sind, habe ich als solche kenntlich gemacht. Kein Teil dieser Arbeit ist in einem anderen Promotions- oder Habilitationsverfahren verwendet worden.

January 2006, Kassel

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PAPER 1

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Use of group theory for the analysis of vibrational spectra ☆

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Abstract

To facilitate the use of group theory in the analysis of vibrational spectra, a set of Maple procedures is provided generating the normal coordinates and determining the spectral activities of polyatomic molecules. Our program, called BETHE, is based on the frequently applied point groups and provides an interactive access to the group data as needed in physical chemistry and elsewhere. Owing to the demand of the users the normal coordinates of the molecules are provided either in terms of Cartesian or internal coordinates.

Program summary

Title of program: BETHE
Catalogue number: ADUH
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/ADUH
Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland
Licensing provisions: None
Computers for which the program is designed: All computers with a license of the computer algebra package MAPLE[1]
Installations: University of Kassel (Germany)
Operating systems under which the program has been tested: Linux 8.1+ and Windows 2000
Program 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.: 11 859
No. of bytes in distributed program including test data, etc.: 312 229
Distribution format: tar.gz
Nature of the physical problem: Interaction of the infrared light with the molecule can lead to the excitation of the molecular vibrations [1]. Analysis of such vibrations is performed by the point group theory and helps to interpret the molecular spectra.

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

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[1] Maple is a registered trademark of Waterloo Maple Inc.

0010-4655/$ – see front matter
doi:10.1016/j.cpc.2004.06.088

Method of solution: Point group theory is applied to determine the normal coordinates of symmetric molecules and to carry out a spectroscopic analysis of their vibrational modes. The direct product of the irreducible representations is utilized to obtain the selection rules for infrared and Raman spectroscopy.
Restrictions onto the complexity of the problem: The computation of the normal coordinates is supported for rather a large number of symmetries; in the present version the group data are provided 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} ($n \leqslant 10$), the cubic groups O, T, O_h, T_h, T_d and the icosahedral groups I, I_h.
Unusual features of the program: All commands of the BETHE program are available for interactive work. Apart from the analysis of the vibrational motion of molecules, we also provide the group theoretical data of all the presently implemented point and double groups. The notation of the symmetry operations and the irreducible representations follows the compilation by Altmann and Herzig [2]. For reference to the program, a brief description of all the available commands is given in the user manual `Bethe-commands.ps` and 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.
References:

[1] E.B. Wilson, J.C. Decius, P.C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.
[2] S. Altmann, P. Herzig, Point-Group Theory Tables, Clarendon Press, Oxford, 1994.

PACS: 02.20.-a; 33.20.Tp; 33.20.Ea; 33.20.Fb

Keywords: Fundamental transition; Infrared absorption; Irreducible representation; Normal coordinates; Point group; Raman scattering; Vibrational modes; Vibrational spectroscopy

1. Introduction

During the last decade, a large number of experiments have been carried out for studying the properties of molecules and clusters [1–3]. In order to first resolve the structure and the bonds of the molecules, the techniques of vibrational spectroscopy have often been applied. In these techniques the incident radiation is used to excite the vibrations of molecules, that is to promote a molecule to a state of higher energy, in which its vibrational amplitude is increased. Treatment of the obtained spectra can give us the information about the structure of (polyatomic) molecules.

To investigate the observed (vibrational) spectra, two experimental methods are widely used today: infrared and Raman spectroscopy [4] which are based on quite different physical principles. While, for instance, infrared spectroscopy concerns the absorption of (infrared) light by a molecule, owing to its vibrational frequencies, Raman spectroscopy refers to the scattering of light. The infrared spectroscopy can therefore be taken as a direct measurement of the vibrational frequencies whereas, in Raman spectroscopy, they just occur as the differences in the frequencies of the incident and the Raman-scattered light, respectively. However, not only the mechanisms are rather different for infrared and Raman excitations of the molecule but also the selection rules for such vibrational transitions. While, in infrared spectroscopy, the occurrence of a vibrational transition requires a change in the electric dipole moment of the molecule, Raman lines go along with a change in the polarizability during the vibration. Therefore, the selection rules for infrared and Raman transitions are widely used to interpret the vibrational spectra and to derive the geometrical structure of the underlying molecules and clusters.

The studying of vibrational spectroscopy and, in particular, evaluation of the selection rules, makes extensive use of the molecular symmetry. The symmetry considerations are known to be an inevitable tool for studying the behavior of physical systems in many branches of modern physics. In molecular physics, for instance, the point-group theory (and symmetries) provides the mathematical basis for interpretation of the spectra of molecules and crystals. In practice, however, the application of the molecular symmetries to spectroscopy problems may

become rather cumbersome. Although, nominally, the basic relations of group theory are known, there are several shortcomings which make the access to the group data inefficient and difficult to use. Apart from an often very compressed compilation of the group data in some tables or appendices of textbooks, only parts of these data are usually displayed explicitly and without providing the user with the exact definition of the symmetry operations, the matrices of the irreducible representations and further data.

Today, an alternative and promising route for dealing with group theory is offered by computer algebra. To make use of this line and in order to support the application of the point groups in molecular spectroscopy, here we present the BETHE program which helps determine the normal coordinates of symmetric molecules as well as their (spectroscopic) activities in infrared and Raman spectroscopy. Developed within the framework of MAPLE, the BETHE program provides, in addition, also the most basic group data for a number of *point-group families* including the cyclic and their related groups C_i, C_s, C_n, C_{nv} and C_{nh}, the dihedral groups D_n, D_{nd} and D_{nh}, the improper cyclic groups S_{2n} $(n = 2, \ldots, 10)$, the cubic groups O, T, O_h, T_h, T_d as well as the icosahedral groups I, I_h.

In the next section, we start with recalling some of the basic elements from the theory of the point groups as well as from the normal coordinates analysis and vibrational spectroscopy. However, no attempt will be made to explain neither the vibrational phenomena nor the experiments in detail for which we must refer to the literature. Section 3, later, provides a short description of the BETHE program and how it is implemented within the MAPLE environment. The main emphasis is of course placed on a few examples in Section 4 which illustrates the use of the program and how BETHE can be used in daily research work. Finally, a short outlook onto future extensions and applications of this package is given in Section 5.

2. Theoretical background

Let us start with some of the basic principles which are necessary to understand the BETHE program. Of course, not much need to be said here about the theory of the point groups since this theory has been presented in a large number of monographs and texts [5,6]. In this paper, moreover, we assume that the reader is familiar with the basic concepts of the (point) group theory and the analysis of vibrational spectra.

2.1. Molecular and point group symmetries

The symmetries of molecules and clusters may help simplify many of the problems which are concerned with their structure. To make the idea of molecular symmetries quantitative, of course, we must first classify these symmetry properties. As known for a long time, such a classification is achieved in terms of *symmetry operations*, which can be found for a given symmetry and which transform the molecule into an *equivalent configuration*, i.e., into one which is geometrically indistinguishable from the original configuration. For a molecule with a finite number of atoms, these symmetry operations describe rotations about a certain axis and angle, reflections through a mirror plane, inversion through a point (usually taken as the origin of the coordinates) as well as the identity operations which leaves the molecule unchanged. The combination of a rotation *and* (a successive) reflection is called an improper rotation and may also form a symmetry operation of the molecule. In the literature, different notations are found to express the symmetry operations of the point groups; in the BETHE program, we use a notation of the symmetry operations (and irreducible representations, see below) which is similar to the notation of Altmann and Herzig [6].

Mathematically speaking, the set of symmetry operations of a molecule or cluster forms a *group* and, hence, can be treated by means of group theory. Because the molecule must not be shifted in space by carrying out these operations, at least one point has to be fixed in space (and gave originally rise to the notion of the *point groups*).

Owing to the set of symmetry operations, the point groups can be arranged in terms of *group families* as shown in Table 1. Such families are formed, for instance, by the cyclic groups C_n and the symmetry groups S_n, where all

Table 1
Classification of the point groups in terms of *group families*. All these group have been implemented already into the BETHE program

C_i	C_s							
C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}	C_{9v}	C_{10v}
C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	C_{7h}	C_{8h}	C_{9h}	C_{10h}
D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}	D_{9d}	D_{10d}
D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	D_{9h}	D_{10h}
S_4	S_6	S_8	S_{10}	S_{12}	S_{14}	S_{16}	S_{18}	S_{20}
		O	T	O_h	T_h	T_d	I	I_h

symmetry operations denote proper (or improper) rotations around one or another (symmetry) axis of the molecule. Further groups with a cyclic rotation axis are the families of the C_{nh} and C_{nv} groups which, in addition, possess either a *horizontal* or *vertical* plane of reflection respectively. Further families—often with a rapidly increasing number of symmetry operations—are the dihedral groups D_n, D_{nh} and D_{nd}, the cubic groups O, T, O_h, T_d and T_h as well as the icosahedral groups I and I_h. In the BETHE program, we utilize this concept of group families for the implementation of the group data; all groups, which are printed in Table 1, are already supported by the program. In general, the symmetry of a molecule can be classified uniquely by using a systematic procedure to test the molecule for special classes of symmetry operations [5].

To take advantage of group theory, one has to deal with *representations* of the group, i.e., with (various sets of) transformations as induced by the symmetry operations in some given vector space L. In physics, we may usually restrict ourselves to matrix representations which refer to some orthonormal basis, taken in L. Obviously, however, these representations of a group are not *unique* but may depend on the basis, i.e., the choice of the coordinates as well as on further parameters. The great benefit of group theory is that any representation can be decomposed into—a rather small number of—*irreducible representations* whose characters are unique and independent of the basis. In this decomposition, the sum of the dimensions of the involved irreducible components is equal to the dimension of the reducible representation and, thus, equal to the dimension of the considered vector space L. For an irreducible representation, in contrast, no further decomposition of the vector space into invariant subspaces can be obtained. Again, several notations can be found for the irreducible representations of the point groups, known also as Mulliken symbols, in dependence on the dimension and the 'physical origin' of some given representation. As mentioned before, we follow the notation from Ref. [6] in the BETHE program.

For a given reducible representation, the irreducible components of this representation can be obtained by standard techniques [5]. For most practical applications it is not necessary to know the explicit matrices of (ir-)reducible representations, but only the *characters*, that means the traces of the corresponding matrices. The characters of a representation are often denoted by χ and can be used, for instance, to determine the number of (inequivalent) irreducible representations, which are 'involved' in some reducible representation by using the great orthogonality theorem [7], they are the characters of the irreducible representations are already known for the group under consideration.

2.2. Molecular vibrations

2.2.1. Normal modes of vibrations

Many problems of physics and chemistry require the theoretical analysis of the vibrational spectra of the molecule to determine, for instance, its spectral activity in the interaction with the radiation field or the distortion of molecular configuration under an external field. Group-theoretical arguments can be used to provide this analysis without that quantum chemical computations.

Our attention will be placed on the vibrational motion of molecules, in which its interatomic distances and internal angles change periodically without producing any translation or rotation of the molecule as a whole.

The overall vibrations of a molecule, of course, result from the superposition of a number of relatively simple vibrational motions which are known as the *normal vibrations* or *normal modes of vibration* of a molecule. The number of these modes is defined by the number of the atoms in the molecule and assumes a value of $3N - 6$ for the case of nonlinear molecules. Each of these vibrations has its characteristic frequency but—if many of them are superposed—the periods of the vibrations are difficult to discern and so it may look rather aperiodical.

To determine the normal modes of a molecule, a so-called *harmonic approximation* need to be considered for its vibrational motion [9]. Within this approximation, we start by assuming an equilibrium position for the atoms in a molecule around which they vibrate with a small amplitude. Of course, any displacements of a particular atom from this equilibrium position can be described in terms of three components along the x-, y-, and z-axes. For a whole molecule with N atoms, therefore, $3N$ components $(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$ to specify the total displacement. Below, we denote these components by $q_1, q_2, \ldots, q_{3N}$, where q_1, q_2 and q_3 refers to the x_1, y_1 and z_1 components of atom 1, q_4, q_5 and q_6 to those of atom 2, and so on. At equilibrium this position is associated with the minimum of the potential energy. Expanding this potential in a Taylor series in the coordinates q_i and by ignoring terms of order higher than the quadratic terms, we can write the Hamiltonian for the molecule in the harmonic approximation

$$H = \frac{1}{2}\sum_{i=1}^{3N} m_i \dot{q}_i^2 + \frac{1}{2}\sum_{ij} k_{ij} q_i q_j \tag{1}$$

where m_i the masses and k_{ij} the force constants.

For the sake of simplicity, instead of the treatment of the vibrational problem in the representation of the $3N$ coordinates $q_1, q_2, \ldots, q_{3N}$, it is more convenient to operate directly with the vibrational coordinates $Q_1, Q_2, \ldots, Q_{3N-6}$ which correspond to the $3N - 6$ vibrational degrees of freedom of the molecule. These normal coordinates can be defined by a linear transformation of the coordinates q_i:

$$q_i = \sum_k a_{ik} Q_k \tag{2}$$

which allows one to write the Hamiltonian (1) in the form:

$$H = \frac{1}{2}\sum_k \dot{Q}_k^2 + \frac{1}{2}\sum_k \omega_k^2 Q_k^2. \tag{3}$$

The Q_k are called the *normal coordinates* of the system along which the normal vibrations proceed and ω_k are the corresponding frequencies. In terms of the normal coordinates, therefore, the total Hamiltonian H of the molecule scan be presented just as a sum of simple harmonic oscillators with the Hamiltonian H_k, while the total wave function Ψ of the (vibrational) motion may be expressed as a product of the well-known (harmonic oscillator) wave functions $\psi_{n_k}(Q_k)$, one for each normal coordinate. The total vibrational energy is the sum of the energies of $3N - 6$ harmonic oscillators.

The great advantage of the normal coordinates is that they have to possess a certain symmetry. In other words, the normal coordinates which are related to the vibrational modes with the same frequency, form a basis of (or, as it is sometimes briefly said, 'belong to') an irreducible representation $T^{(\alpha)}$ of the molecular symmetry group. This property allow us to apply the point group theory for the classification of the normal modes according to irreducible representations of the symmetry group. A proof of this theorem about the normal modes is described in detail in many textbooks [10,11].

2.2.2. Classification of the normal vibrations

The knowledge of the symmetry type of the normal coordinates of a molecule allow us to simplify the vibrational analysis and derive its spectral properties. At the beginning of our analysis, however, we neither know the names of the irreducible representations, which correspond to the normal coordinates of the considered molecule, nor

how often these representations occur in the decomposition. Nevertheless, the symmetry properties of the normal modes as described above makes it possible to obtain the set of irreducible representations without that the normal coordinates being known explicitly.

To obtain this set or, in other words, to classify the normal vibrations, several steps have to be carried out. First of all we need to construct a $(3N-6)$-dimensional reducible representation of the symmetry group of the molecule, related to its vibrational motion. To achieve this, we have to return to the set of $3N$ atomic coordinates (or displacements) of the N atoms of the molecule. If all atoms are found in an equilibrium configuration, the set of the $3N$ displacements forms a basis of a $3N$-dimensional (reducible) representation of the group which is also as the *total* representation $T^{(\mathrm{tot})}$. In order to find this representation, we may attach local Cartesian coordinates to each of the atom and may choose that all the x axes are in parallel, and similar also for the y and z axes. Moreover, the orientation of the x_j, y_j and z_j axes must agree for all atomic coordinates with the orientation of the molecular coordinates in which the symmetry operations are expressed. For the molecule of water such an arrangement of the coordinates are shown on Fig. 1a). Then, the total representation $T^{(\mathrm{tot})}$ is just given by a matrix which represent a transformation of the $3N$-dimensional displacement vector $(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$, as induced by the group; see Ref. [5] for further details on the constructing of the total representation. Since the total representation refers to all $3N$ coordinates of the molecule, it still contains—apart from the vibrational motion of the molecule—also its translational and rotational motion. Therefore, to get the (vibrational) representation $T^{(\mathrm{vib})}$ which is related only to the vibrational modes of molecule, the translational and rotational representations need to be 'separated' from the total representation $T^{(\mathrm{tot})}$. For most cases, however, we need not to know the $3N$-dimensional matrices of the irreducible representation but may restrict ourselves just to the characters of this matrix representation. Then, the characters of vibrational representation $\chi^{(\mathrm{vib})}$ are simply obtained by subtracting the characters for an overall translation or rotation of the molecule from the characters $\chi^{(\mathrm{tot})}$ of the total representation, separately for each of the symmetry operations of the group.

Having ones obtained the vibrational representation $T^{(\mathrm{vib})}$ of a molecule, its reducible in most cases and, hence, has to be reduced into which is irreducible components $T^{(\alpha)}$ before the number of equivalent representations can be determined. For the reduction

$$T^{(\mathrm{vib})} = \sum_{\alpha} m_\alpha T^{(\alpha)} \tag{4}$$

we follow standard techniques and obtain the weights m_α in the decomposition simply from the characters (i.e., without knowing the matrices explicitly) due to

$$m_\alpha = \frac{1}{g} \sum_{p} C_p \chi_p^{(\mathrm{vib})} \chi_p^{(\alpha)*}, \tag{5}$$

where g is the order of the point group and C_p the number of group elements in the class to which also the symmetry operation p belongs. Of course, the set of irreducible representations $T^{(\alpha)}$ together with their weights m_α provides us with all the information about the number of vibrational modes of the molecule, the degeneracy of

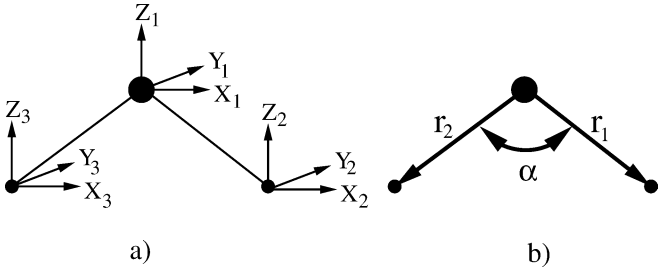

Fig. 1. Set of the basis vectors for H_2O molecule: a) Cartesian displacement vectors; b) internal displacement vectors.

the frequencies as well as the symmetry type of all the vibrational modes. While the number of vibrational modes is equal to the number of irreducible representations in the set, the dimension of the irreducible representation will refer to the degeneracy of the corresponding frequencies.

Although the Cartesian displacements are known as a popular basis for determining the symmetries of the vibrational modes and for classifying the vibrational motion of a molecule, they are not always that easy to apply in practice. In many applications in physical chemistry use is instead made of (so-called) *internal coordinates* which refer either to the interatomic distances or the bond angles at the equilibrium positions of the atoms. If a displacement of the atoms occurs, these internal coordinates are then associated with the so-called *stretching vectors* and the *bond-angle deformation vectors*. However, there is no common agreement about how the internal coordinates have to be chosen. As a rule, however, one often starts with a number of stretching vectors between some bonded atoms and then adds as many bond-angle deformation vectors as needed in order to obtain a total set of $3N - 6$ internal displacements (displacement vectors). In the H_2O molecule, for example, we need three internal displacement vectors in order to represent the three normal modes; here, a convenient way is to use the two stretching vectors r_1 and r_2, and the bond–angle deformation vector α as shown in Fig. 1b). The use of these internal coordinates then enables us to classify the stretching and bending modes separately, i.e., we obtain the two different reducible representations $T^{(\mathrm{str})}$ and $T^{(\mathrm{bend})}$, for which the stretching vectors or, respectively, the bond angles form a basis. Having these representations, they can be decomposed in a similar manner as shown in Eq. (5). Sometimes, the irreducible components of the bending and stretching modes do not agree with the irreducible components of the complete vibrational representation. In this case there is so called *redundant coordinate*. Such a coordinate can be ignored, since it does not correspond to a physically possible vibrations [9].

2.2.3. Construction of normal coordinates

As discussed above, the classification of the normal vibrations provides us with very useful information about the molecular vibrations. Beside of this classification, however, we usually need to construct the normal coordinates also explicitly, where we can start from either the Cartesian displacements or the internal displacements of the molecule. In practice, the normal coordinates, taken as a basis functions of the irreducible representations of the group, are most easily obtained by means of the *projection operator method*. In this method the property of this operator to generate the functions of the desired symmetry are utilized. In general, any projector of a irreducible representation leaves all those functions unaffected, which belong to the basis of that representation, while the function (components) of other representations are projected out. The (generalized) point group projection operator has a form

$$\widehat{P}_i^{(\alpha)} = \frac{s_\alpha}{g} \sum_a T_{ii}^{(\alpha)*}(G_a) T(G_a), \tag{6}$$

where g is the order of the group, s_α is the dimension of the irreducible representation $T^{(\alpha)}$ and where G_a refers to the set of symmetry operations of the group. Moreover, $T(G_a)$ denotes the induced matrix operation which may act in space of displacements, while $T_{ii}^{(\alpha)}(G_a)$ is one of the diagonal element of the irreducible representation matrix. If applied to the set of atomic (Cartesian) displacement vectors x_j, y_j, and z_j, the projection operator (6) gives rise to the normal displacement $Q_{\alpha i}$ of the molecule

$$\widehat{P}_i^{\alpha} x_j = Q_{\alpha i} = c_{x_1} x_1 + c_{y_1} y_1 + \cdots + c_{z_N} z_N. \tag{7}$$

The application of $\widehat{P}_i^{\alpha}$ on x_j may give zero, of course, which means that this particular displacement is not contained in the normal coordinate $Q_{\alpha i}$; to obtain this coordinate, one has to cycle through all the displacements [7]. If, instead of the Cartesian coordinates, use is made of the internal coordinates we may follow a similar procedure by applying the projection operators (6) to the sets of the stretching vectors $r_1, r_2, \ldots$ and bending angles $\alpha_1, \alpha_2, \ldots$. As a result we will have so called *symmetry-adapted linear combination* (SALC) of the basis vectors [5]. Projection operator, taken in the form (6) allows to construct the SALC for multi degenerate irreducible

representations [8]. Of course, the SALC must be normalized, which means that the sum of squares of the coefficients in the SALC must be equal one. Vibrational coordinates, constructed using this method are called usually *symmetry coordinates*. These coordinates generally are representations of the normal modes of vibration. Eventually, the symmetry coordinates can be defined separately for both, the stretching as well as the bending modes of the vibrations.

2.3. Molecular spectroscopy

2.3.1. Vibrational transitions

In the last subsections, we saw how to classify the vibrational motion of a molecule to obtain its normal (vibrational) coordinates. In the following, we shall therefore show how the information about the structure of the polyatomic molecules can be obtained from the vibrational spectrum.

As said before, we are mainly concerned with two kinds of vibrational spectroscopy, namely infrared and Raman spectroscopy. In contrast to other branches of modern spectroscopy such as (photo-)electron spectroscopy, the infrared and Raman spectra refer both to transitions between the vibrational states of the molecule, in the electronic ground or some particular excited state of the molecule. For a given electronic configuration, of course, each of the vibrational states can be characterized in terms of a (vibrational) wave function Ψ and can be labeled by some set of quantum numbers n_k which just denote the absorbed quanta in the various normal modes. For further discussion, it appears useful to distinguish now between several vibrational states of a molecule. The vibrational *ground* state refers to no quanta of excitations, i.e., $n_k = 0$ for all k, and hence to the wave function $\Psi(0, 0, \ldots, 0)$ must be invariant under all the symmetry operations of the group. For this reason, the vibrational ground state must always be transform according to the *totally symmetric* irreducible representation which has the characters $\chi = +1$ for all of the symmetry operations of the underlying point group. Above this ground state, there are several low-excited states with just a single quantum incorporated in one of the normal modes, for instance, $n_k = 1$ while all other quantum number $n_m = 0$ for $m \neq k$. This set of low-excited levels are usually called the *fundamental* (vibrational) levels of the molecule. Apart from the fundamental levels, there are further so-called *combination levels* in which two or several normal modes are excited but with just a single quantum each. Finally, all the excited states with more than one quantum absorbed in a particular normal mode are known as the *overtone* levels or briefly overtones. Those of the vibrational transitions, which connect the ground and fundamental levels are usually called *fundamental* transitions. Such a transitions generally give rise to infrared bands and Raman lines which are more intense by at least an order of magnitude than any other kinds of transitions. Therefore, we will deal only with the fundamentals here. For these transitions, typical frequencies of the absorbed light are in the infrared region of about ~ 100–$5000\ \mathrm{cm}^{-1}$. Such infrared radiation, or course, generally excites not only molecular vibrations but also rotations of the molecule as a whole. The rotational structure of the bands can be observed, in particular, in the spectra of a gaseous molecules [4]. However, in most cases the separation of vibrational energy levels is greater and the transitions occur at higher frequencies than do the rotational transitions. Therefore, here the rotational structure of the vibrational bands will be neglected.

2.3.2. Infrared and Raman spectra

At this stage of our discussion, it might be necessary to give a brief account on the methods which are available in order to observe ‘vibrational spectra’ and to obtain the sort of information that one usually wishes to extract from their analysis. Further details on this subject can be found of course in most textbooks on molecular spectroscopy, Refs. [4,12]. As mentioned before, vibrational spectra are obtained by two rather different techniques. In infrared spectroscopy, light with a broad frequency distribution is passed through some sample and the intensity of the transmitted light is observed as function of the frequency. The vibrational transitions are then obtained as minima in the absorption spectra. In Raman spectroscopy, in contrast, its not the transmitted but the scattered light which is of interest and which can be observed in (almost) any direction with respect to the incident radiation. In order to

extract the information about the scattering by the molecules, obviously, a monochromatic light source should be used.

Let us now try to understand the phenomena of vibrational transitions from a microscopic viewpoint. Both, an infrared and a Raman transitions may occur only if a change is caused in the *dipole moment* of the molecule. In particular, an infrared transition take place if a permanent dipole moment of molecule vibrates at a certain eigen frequency around some equilibrium value. Hence, an excitation of the molecule can only occur if the frequency of the incident radiation is approximately equal to the frequency of the internal moment or, respectively, the eigen frequency of the corresponding vibrational mode. In Raman spectroscopy, in contrast, we have to consider a dipole moment which is *induced* by the external light field. If, for example, we assume the molecule to be placed in some electric field $\boldsymbol{\varepsilon}$, this induced dipole moment is given by

$$\boldsymbol{\mu}_{\text{ind}} = \boldsymbol{\varepsilon}\alpha, \tag{8}$$

where α denotes the *polarizability* of the molecule, the measure for how easily the electronic configuration can be distorted by the field. Polarizability is a molecular property whose magnitude varies with the frequency ν_0 as a molecule oscillates. If a molecule is irradiated by monochromatic light of frequency ν, then light of frequency ν as well as $\nu \pm \nu_0$ is emitted by a molecule. Thus the vibrational frequencies are observed as *Raman shifts* from the incident frequency ν in the visible region. Detailed explanation of this process can be found in Ref. [13]. In general, of course, the polarizability is a 3×3 Cartesian symmetry tensor with the nine components $\alpha_{jk} = \alpha_{kj}$, $j, k = \{x, y, z\}$, which refer to the various directions in space.

2.3.3. Symmetry selection rules for infrared and Raman spectra

With this microscopic view in mind for a vibrational excitation of a molecule, we may now return to the so-called *symmetry selection rules* which apply in infrared and Raman spectroscopy. In fact, these rules determine which of the transitions, as possible due to the Ritz' combination principle, will be actually observed in the spectrum. Or, in a more spectroscopic terminology, they should tell us which of the vibrational modes are active in one or the other or both types of the spectra. As discussed before, a wave function ψ_{n_k} is assigned to each of these modes. If, in the following, we denote the total wave functions for the initial and final (vibrational) states by Ψ_i and Ψ_f, respectively, a transition from the ground to any of the fundamental levels with, say, an excitation of the jth normal mode can be written as

$$\Psi_i = \prod_k \psi_{n_k} \to \psi_{n_j} \prod_{k \neq j} \psi_{n_k} = \Psi_f. \tag{9}$$

In infrared spectroscopy, of course, this change of the wave functions must arise from the interaction of a change in the dipole moment $\boldsymbol{\mu}$ with the incident radiation. Since, for such a transition, the probability is directly proportional to the (square of the) *transition moment*

$$M_{if} = \int \mathrm{d}\tau\, \Psi_f^* \boldsymbol{\mu} \Psi_i, \tag{10}$$

an excitation of the mode j is *forbidden* in the infrared spectrum if this integral vanishes. Therefore, in order to analyze the infrared activity of a given (fundamental) transition, we have to consider the three components of the dipole moment vector μ_x, μ_y, μ_z and of the transition integral (10), respectively. In practice, however, we need not deal with the wave functions in (10) explicitly, since we know from group theory that all these integrals become zero unless the direct product of the irreducible representations, associated with the integral functions $\Gamma(\Psi_i)$, $\Gamma(\mu_{x,y,z})$, $\Gamma(\Psi_f)$, contains also the *totally symmetric* irreducible representation [13]. This follows from the fact that if the this direct product does not contain the totally symmetric irreducible representation, all components of the integrand are nonsymmetric with respect to one or more symmetry and the integral over all space vanishes. To construct this direct product, we have to define the symmetries of the three components of the integral (10). Of course, the ground-state wave function Ψ_i always forms a basis for the totally symmetric representation of the

group, while the wave functions of final states Ψ_f are the same as those of the vector that describes the vibrational modes. Finally, the symmetry properties of the dipole moment components μ_x, μ_y and μ_z are the same as those of a translational vector (x, y, z) along the same axis. Therefore, in order to decide whether the transition moment (10) vanishes, we need to form the (three) direct products

$$\Gamma(\Psi_i) \times \left\{ \begin{matrix} \Gamma(x) \\ \Gamma(y) \\ \Gamma(z) \end{matrix} \right\} \times \Gamma(\Psi_f) \tag{11}$$

which arises from the totally symmetric representation of the vibrational ground state, the irreducible representations of any of the translational vector components x, y, or z, and the irreducible representation of the vibrational mode j. If any of these products will by itself contain the totally symmetric irreducible representation of the molecular point group, the corresponding fundamental transition is said to be infrared active.

The selection rules for Raman spectroscopy can be derived along similar lines. Since a vibrational transition will occur only if the polarizability α changes in course of the vibration, a Raman transition requires a nonvanishing transition moment of the type

$$M_{if} = \int \mathrm{d}\tau\, \Psi_f^* \alpha \Psi_i . \tag{12}$$

Its again possible to analyze this expression by group-theoretical arguments and by making use of the fact that the components α_{jk} of the polarizability tensor obeys the same symmetries like the product of the corresponding coordinates. To find the selection rules for a Raman activity of some transitions, therefore, we just need to analyze the direct products of three irreducible representations with the second one being replaced by those of x^2, y^2, z^2, xy, yz, or zx, respectively.

3. Outline to the BETHE program

The BETHE program has been designed as an interactive tool in order to facilitate the application of point-group techniques in physics and chemistry. In the present version, we support the group data for a number of *point-group families*, including the cyclic and their related groups C_n, C_{nv} and C_{nh}, the symmetry groups S_{2n}, the dihedral groups D_n, D_{nd} and D_{nh} $(n = 2, \ldots, 10)$, the cubic groups O, T, O_h, T_h, T_d as well as the icosahedral groups I, I_h (see Table 1). For these groups, the BETHE program provides the definition of the symmetry operators (within various types of parameterization), the character tables, the notation and matrices of the irreducible representations as well as the decomposition of different types of direct products into their irreducible components. Both, the *point* and the *double* groups are equally well supported by the program. Owing to the simple and interactive but still quite general access to the group data, this program might be helpful not only for occasional use but also for more advanced research work. In this first version of BETHE, emphasis is placed on the determination of the normal coordinates of the vibrating molecules and clusters with internal symmetry and to their spectroscopic activity. The graphical presentation of the molecule and animation of the molecular vibration process is also available in the BETHE program.

Following MAPLE's philosophy, the BETHE program has been organized in a hierarchical order. It presently includes about 70 procedures which can be either invoked interactively or simply *used* as a language element in order to built up commands at some higher level of the hierarchy. In practice, however, only about 10 (main) procedures need to be known by the user; they are listed and briefly explained in Table 2 for a first impression about the BETHE program. More detailed information about their arguments and the output of these commands can be obtained from a user manual which is distributed with the code. In addition, a few examples are displayed below to illustrate some of the basic features of the program.

Table 2
Main commands of the BETHE program

molecule( )	Represent a molecule in terms of its individual atoms.
Bethe_decompose_representation( )	Returns the irreducible representations, which are contained in the in the (reducible) representation.
Bethe_group( )	Provides the basic point group data and notations.
Bethe_group_character( )	Provides the character of a given irreducible representation and symmetry operation.
Bethe_group_direct_product( )	Returns the *direct product* of the irreducible representations.
Bethe_group_irrep( )	Provides the matrix representation of a given irreducible representation and symmetry operation.
Bethe_group_representation( )	Calculates the representation which describes the transformation of a vibrational vector as induced by the symmetry group.
Bethe_group_projector( )	Evaluates the generalized projection operator which projects vector from the space L into the subspace L_α of the irreducible representation $T^{(\alpha)}$.
Bethe_normal_coordinates( )	Calculates the *normal coordinates* of a molecule in terms of its Cartesian displacement vectors or internal displacement vectors.
Bethe_normal_display( )	Displays the vibrational motion of a molecule graphically.
Bethe_spectral_activity( )	Determines, whether the vibrational mode of molecule is infrared or Raman active.

As known from MAPLE's recent upgrades, most of its internal commands make use of rather short names and often of some abbreviations to a given mathematical context. Although this convention might be favorable for a frequent application of the commands, it has the disadvantage that these names are usually not that easy to remember. In the BETHE program, therefore, we follow a slightly different concept by introducing names from which the purpose of the procedure can be derived (or, at least, be kept in mind). This concept sometimes results in rather long names but may simplify the application and design (or readability) of new code which still need to be implemented. Moreover, all the commands of the BETHE program begin with the additional prefix `Bethe_` to distinguish them from MAPLE's internal functionality.

In the future, we intent to develop BETHE along several lines. For several applications additional group data such as the Clebsch–Gordon coefficients or symmetrized basis functions are needed and could be derived from the data which are available. The access to such data however will require the implementation of additional (or new) algorithms and, possibly, new data structures. Last but not least we intend, of course, to provide further applications in physics and chemistry, i.e., further tasks which could be solved interactively by means of the BETHE program and in a similar manner as shown for the normal coordinates below.

4. Examples

In order to demonstrate the capabilities of the BETHE program, we shall collect and display here several examples. They describe the specification of a molecules in the BETHE program as well as the derivation of its normal coordinates and its spectral activity. These examples may give the reader also a first glimpse on the interactive use of the program.

4.1. Determination of the normal coordinates of a molecule

The normal coordinates of a molecule are known to provide a basis in terms of which the vibrations of the molecule can be classified. To demonstrate the basic steps in the derivation of the normal coordinates of a molecule, let us consider the (very simple) example of a M_3 complex, i.e., of a plain tri-atomic molecule with equal distances. Obviously, such a molecule has a $3 \times 3 - 6 = 3$ normal coordinates. The symmetry of this molecule is given by D_{3h} and, if we assume that one of the equivalent atoms has the coordinates $(0, 1, 0)$, we can immediately generate the full set of atomic coordinates by typing

```
> set_M3 := Bethe_generate_sites(D3h,[1, 0, 0]);
```

```
set_M3 := [[   1,          0, 0],
                          1/2
           [-1/2, - 1/2 3   , 0],
                          1/2
           [-1/2,   1/2 3   , 0]]
```

Alternatively, we may also consider the M_3 molecule just as a collection of (individual) atoms and may treat it by the variable

```
> M3 := molecule(atom(A1,[   1,          0, 0]),
                 atom(A2,[-1/2, -sqrt(3)/2, 0]),
                 atom(A3,[-1/2,  sqrt(3)/2, 0]) );

          M3 := molecule(atom(A1, [   1,          0, 0]),
                                              1/2
                         atom(A2, [-1/2, - 1/2 3   , 0]),
                                              1/2
                         atom(A3, [-1/2,   1/2 3   , 0]))
```

below, where the two (auxiliary) procedures `atom( )` and `molecule( )` have been introduced in order to keep the relevant information about either a single atom or molecule closely together. To derive the normal coordinates, of course, we need first to determine the $3N \times 3N$ total representation of the group. As described above, this representation is associated with the Cartesian displacements of all the atoms and accounts for the translational, rotational, and vibrational motion of the molecule. In fact, however, we need not to generate this representation here explicitly but may restrict ourselves to the characters of that part of the total representation which refers to the vibrations of the molecule. By means of the BETHE program, these characters are simply obtained by

```
> VR := Bethe_group_representation(D3h, vibrational, M3);

                VR := [3, 0, 0, 1, 1, 1, 3, 0, 0, 1, 1, 1]
```

By use the keyword '*vibrational*' the translational and rotational components of the representation are taken away. In this example the symmetry elements are not arranged to a classes in order to simplify the summation over the symmetry operations. From the list of characters VR we can derive the irreducible representations by carrying out the decomposition of VR into its irreducible components

```
> Bethe_decompose_representation(D3h, VR);

                ["A1'", "E'"]
```

with which the normal modes are associated. The dimensions of these (irreducible) representations give us for each component directly the number of—energetically degenerate—vibrational modes. Having once these representations, moreover, we can also obtain the normal coordinates in terms of the Cartesian displacements $[[c_{1x}^{(1)}, c_{1y}^{(1)}, \ldots, c_{Nz}^{(1)}], [c_{1x}^{(2)}, c_{1y}^{(2)}, \ldots, c_{Nz}^{(2)}], \ldots, [c_{1x}^{(3N-6)}, c_{1y}^{(3N-6)}, \ldots, c_{Nz}^{(3N-6)}]]$. In the BETHE program, this is achieved by

```
> Q_"A1'" := Bethe_normal_coordinates(D3h, M3, "A1'", Cartesian);
```

```
Q_"A1'" := [[   1,          0, 0,
                          1/2
              -1/2, - 1/2 3   , 0,
                          1/2
              -1/2,   1/2 3   , 0]
```

where the second and third parameter, `M3` and `"A1'"`, here describe the molecule and respectively the particular irreducible component as found in the decomposition of total vibrational representation. In addition, the last parameter 'Cartesian' is used as a *keyword* in order to specify that the normal coordinates are to be returned in terms of the Cartesian displacements.

Similarly, we may obtain also the other two normal coordinates which are associated with the irreducible representation `"E'"`

```
> Q_"E'" := Bethe_normal_coordinates(D3h, M3, "E'", Cartesian);
```

```
Q_"E'" := [[        0,     -1, 0,
                  1/2                    1/2
          [ 1/2 3   ,   1/2 , 0, -1/2 3   ,       1/2, 0],
          [   1,          0, 0,
                         1/2                      1/2
           -1/2,    1/2 3   , 0,   -1/2,    -1/2 3   , 0]]
```

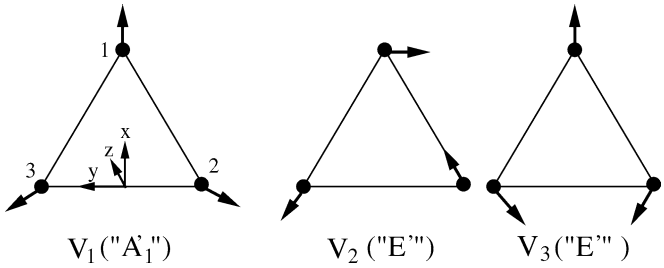

Fig. 2. Vibrational modes of the M_3 complex.

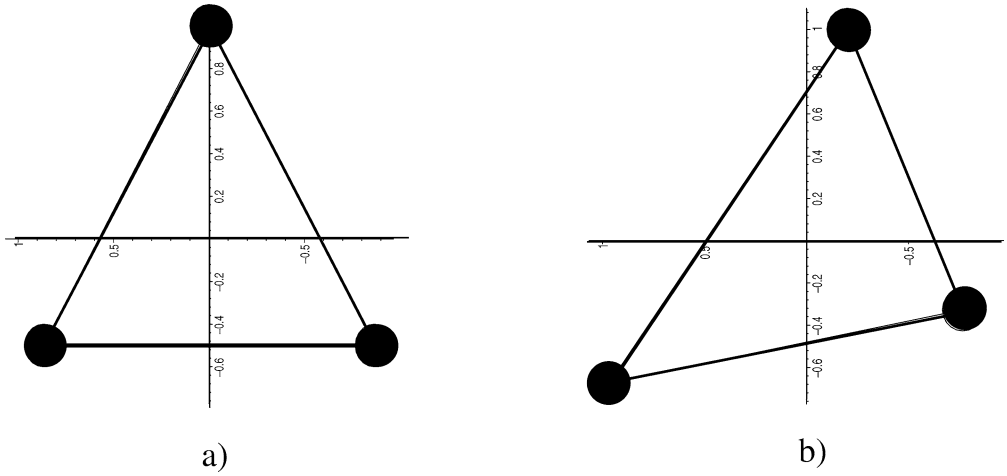

Fig. 3. Graphical presentation of the V_2"E'" vibrational mode of the M_3 complex (two frames).

where each sublists of the list `Q_"E'"` defines one of the allowed normal coordinates of irreducible representation `"E'"`. As expected, these three coordinates are of course the same as shown in Fig. 2, up to an (unimportant) unitary transformation of V_2(`"E'"`) and V_3(`"E'"`), respectively. In order to get a quick impression about the molecular vibrations of the considered structure, the normal coordinates of the molecule can be displayed also graphically.

```
> Bethe_normal_display(M3, Q_"E'"[1]);
```

Two frames from the animated picture of the V_2(`"E'"`) mode are shown in Fig. 3. Fig. 3a) shows the initial configuration of the molecule, while in Fig. 3b) the vibrationally distorted molecule is depicted.

4.2. Infrared and Raman activity of vibrational modes

The classification of the normal vibrations has provided us with the information about the number of normal modes and their symmetry type. We may utilize this information in order to derive the spectroscopic infrared and Raman activities of the molecular vibrations (and could do it even if we would not know the normal coordinates of these vibrations explicity). From Section 2, we know that the molecule M_3 has one vibration which is associated with the irreducible representation `"A1'"` and a (two-dimensional) vibration associated with the representation `"E'"`. We can ask about the infrared activity of these vibrations by typing

```
> IR_active_"A1'" := Bethe_spectral_activity(D3h, M3, "A1'", infrared);

                IR_active_"A1'" := false
```

and

```
> IR_active_"E'" := Bethe_spectral_activity(D3h, M3, "E'", infrared);

                IR_active_"E'" := true
```

Here, again, the second and third arguments describe the molecule and the symmetry of vibrational mode, respectively, while the fourth argument `infrared` serves as a keyword in order to specify the kind of the spectroscopic activity.

Of course, the activity of a vibrational modes in Raman spectroscopy can be obtained along the same lines if the keyword *Raman* is used

```
> Raman_active_"A1'" := Bethe_spectral_activity(D3h, M3, "A1'", Raman);

                Raman_active_"A1'" := true

> Raman_active_"E'" := Bethe_spectral_activity(D3h, M3, "E'", Raman);

                Raman_active_"E'" := true
```

To conclude this section, the example of the M_3 molecule shows us that only the `"A1'"` mode is active in the infrared spectrum but that the two `"E'"` modes can be found in both, the infrared and Raman spectra.

4.3. Normal coordinates in terms of internal displacement vectors

As it was mentioned already, for some physical and chemical applications the treatment of the vibrations within the framework of the Cartesian displacement vectors is not very convenient. In these cases one has to use the inter-

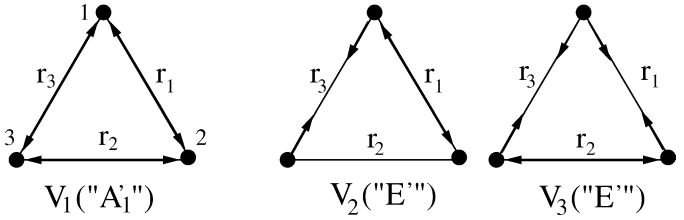

Fig. 4. Vibrational modes of M_3 complex in terms of the internal displacement vectors.

nal displacements vectors of the molecule (stretching vectors and bond angle deformation vectors). This example illustrates how to obtain the normal coordinates of the M_3 molecule in terms of the internal displacement vectors. In order to achieve this, first of all we need to specify the internal displacement vectors in terms of the names of individual atoms:

```
> M3_stretching := Bethe_internal(D3h, M3, stretching);

        M3_stretching := [[ A1, A2], [ A2, A3], [ A3, A1]]
```

Since the M_3 complex must have $3 \cdot 3 - 6 = 3$ internal coordinates, then set of three stretching vectors is enough to describe the vibrational process (in general case we could specify also the bond angle deformation vectors). The irreducible representations names, which refer to the vibrational modes of the M_3 molecule, was found in Section 4.1. Therefore, we can immediately obtain the list of the vibrational coordinates in terms of the internal displacements $[[c_1^{(1)}, c_1^{(1)}, \ldots, c_n^{(1)}], [c_1^{(2)}, c_1^{(2)}, \ldots, c_n^{(2)}], \ldots$: Now we can find the stretching vibrational coordinates of M_3 molecule:

```
> Q_str := Bethe_normal_coordinates(D3h, M3, stretching);

                    -1/2   -1/2   -1/2
Q_str := [[  3     , 3     , 3     ],
                    -1/2           -1/2
          [  2     ,       0, -2     ],
                    -1/2    -1/2   -1/2
          [ -6     , 2 6   , -6     ]]
```

Every sublist of `Q_str` defines the displacement of three vectors `M3_stretching`. The vibrations of the M_3 molecule, defined by `Q_str` are shown in Fig. 4.

4.4. Geometrical structure and the spectral properties of the H_2B–O–BH_2 molecule

The molecule M_3, whose vibrational and spectral properties was discussed in the previous subsections, is the trivial sample of the polyatomic molecule. Of course, the BETHE package may be applied for studies on more complicated molecules. In this subsection, for example, we will consider the *diboroxane* molecule H_2B–O–BH_2, which have been discussed frequently in the literature [14–16]. This molecule can obey different symmetries in dependence on the chemical environment and the process of its formation. Ab initio calculations of the geometrical structure of the diboroxane molecule, using the potential energy surface, have been performed by using the GAUSSIAN program [14]. Several experiments, based on the X-ray diffraction method as well as on the spectroscopic data was carried out to clarify this structure, however, results of these experiments was not consistent each other, Refs. [16,17]. Therefore, the further analysis of this molecule still highly desired.

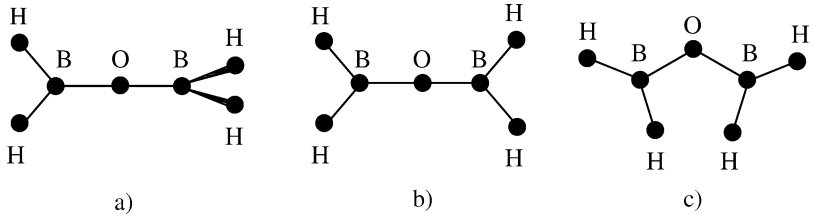

Fig. 5. Possible symmetries of the diboroxane molecule: a) D_{2d} symmetry, b) D_{2h} symmetry, c) C_{2v} symmetry.

In this contribution, we will apply the BETHE package to interpretation of the vibrational spectra of the diboroxane molecule. Of course, the types of the vibrational modes and the spectral activities of these modes will change in dependence on the two geometrical characteristics:

(i) the B–O–B linkage is linear or bend,
(ii) the BH_2 groups are coplanar or perpendicular to each other.

Therefore, we will analyze the spectral activities of the vibrational modes for three different geometries of the diboroxane molecule D_{2d}, D_{2h} and C_{2v}, which are shown in Fig. 5. First, the D_{2d} configuration will be considered. In order to specify this molecule, we need to know coordinates of at least one atom from each set of equivalent atoms, that is O, B and H atoms. Once we make the qualitative analysis, we can specify the coordinates of atoms rather arbitrarily, keeping, the molecular symmetry. Further we will specify the hole molecule in terms of individual atoms.

Apparently, the diboroxane molecule from Fig. 5a) fulfills the D_{2d} symmetry only if the O atom is at the origin of the coordinates and if the B–O–B bond is along z-axis. Let us start with specification of the atomic coordinates

```
> coord_O := [0, 0, 0]; coord_B := [0, 0, 1]; coord_H := [0.5, 0.5, 1.5];

                coord_O := [   0,   0,   0]
                coord_B := [   0,   0,   1]
                coord_H := [ 0.5, 0.5, 1.5]
```

and use this input to generate the coordinates of the other atoms from the three sets of equivalent atoms

```
> set_O := Bethe_generate_sites(D2d, coord_O);
> set_B := Bethe_generate_sites(D2d, coord_B);
> set_H := Bethe_generate_sites(D2d, coord_H);

                set_O := [[   0,    0,    0]]
                set_B := [[   0,    0,    1], [    0,    0,   -1]]
                set_H := [[ 0.5,  0.5,  1.5], [ -0.5, -0.5,  1.5],
                          [ 0.5, -0.5, -1.5], [ -0.5,  0.5, -1.5]]
```

To obtain the complete set of atomic coordinates we may simply type

```
> set_all_D2d := [op(set_O), op(set_B), op(set_H)];

            set_all_D2d := [[   0,    0,    0], [   0,    0,    1],
                            [   0,    0,   -1], [ 0.5,  0.5,  1.5],
```

```
                              [-0.5, -0.5,  1.5], [ 0.5, -0.5, -1.5],
                              [-0.5,  0.5, -1.5]]
```

This set may be utilized now in order to find the number and the symmetry types of the vibrational modes.

```
> VR_D2d := Bethe_group_representation(D2d, vibrational, set_all_D2d);
> VI_D2d := Bethe_decompose_representation(D2d, VR_D2d);

                VR_D2d := [15, -1, 1, 1, -1, -1, 5, 5]

                VI_D2d := ["A1", "A1", "A1", "B1", "B2", "B2", "B2",
                           "E",  "E",  "E",  "E"]
```

As seen from the output of the program, the D_{2d} configuration of the diboroxane molecule has 11 vibrational modes, four of which `"E"` are doubly degenerate (number of vibrational degrees of freedom for this molecule is $3 \times 7 - 6 = 15$).

Let us define now those of vibrational modes, which are infrared and Raman active

```
> IR_active := Bethe_spectral_activity(D2d, VI_D2d, infrared);
> Raman_active := Bethe_spectral_activity(D2d, VI_D2d,    Raman);

                IR_active    := [ "B2", "B2", "B2",  "E",  "E",  "E",  "E"]

                Raman_active := [ "A1", "A1", "A1", "B1", "B2", "B2", "B2",
                                  "E",  "E",  "E", "E"].
```

Thus, seven bands are common for both spectra and the Raman spectrum has four bands not found in the infrared.

Similarly to the D_{2d} configuration case we may proceed the vibrational analysis of the D_{2h} configuration (see Fig. 5b)). The complete set of coordinates `set_all_D2h` can be found by the same way. To define the symmetry of the vibrational modes, we need to specify the characters as well as the irreducible components of the D_{2h} group vibrational representation:

```
> VR_D2h := Bethe_group_representation(D2h, vibrational, set_all_D2h);
> VI_D2h := Bethe_decompose_representation(D2h, VR_D2h);

               VR_D2h := [15, -1, -1, -1, -3, 1, 9, 5]

               VI_D2h := [ "Ag",  "Ag",  "Ag", "B2g", "B3g",
                           "B3g", "B1u", "B1u", "B1u", "B1u",
                           "B2u", "B2u", "B2u", "B3u", "B3u"]
```

Therefore D_{2h} configuration of the diboroxane molecule has 15 nondegenerate normal modes of vibrations. The lists of the infrared and Raman active vibrational modes may be found then by typing

```
> IR_active := Bethe_spectral_activity(D2h, VI_D2h, infrared);
> Raman_active := Bethe_spectral_activity(D2h, VI_D2h, Raman);

                  IR_active := ["B1u", "B1u", "B1u", "B1u", "B2u", "B2u",
                                "B2u", "B3u", "B3u"]
```

```
Raman_active := [ "Ag",  "Ag",  "Ag", "B2g", "B3g", "B3g"].
```

This result illustrates the so called *mutual exclusion rule*. According to this rule, in a molecule with the center of symmetry only u (*ungerade*) modes can be infrared active and only g (*gerade*) modes can be Raman active (no mode can be both infrared and Raman active).

Spectral activity of the C_{2v} configuration of the diboroxane molecule (see Fig. 5c)) is obtained by the similar way:

```
> VR_C2v       := Bethe_group_representation(C2v, vibrational, set_all_C2v);
> VI_C2v       := Bethe_decompose_representation(C2v, VR_C2v);
> IR_active    := Bethe_spectral_activity(C2v, VI_C2v,infrared);
> Raman_active := Bethe_spectral_activity(C2v, VI_C2v,   Raman);

          VR_C2v := [15, 1, 1, 7]

          VI_C2v := ["A1", "A1", "A1", "A1", "A1", "A1", "A2", "A2",
                     "B1", "B1", "B1", "B1", "B1", "B2", "B2"]

       IR_active := ["A1", "A1", "A1", "A1", "A1", "A1", "B1", "B1",
                     "B1", "B1", "B1", "B2", "B2"]

    Raman_active := ["A1", "A1", "A1", "A1", "A1", "A1", "A2", "A2",
                     "B1", "B1", "B1", "B1", "B1", "B2", "B2"]
```

This result tells us that in the C_{2v} configuration all 15 vibrational modes are active in the Raman spectrum and only 13 modes are infrared active.

We found, that the symmetry types of the vibrational modes as well as their spectral activity are different depending on the mutual orientation of the BH_2 groups. Therefore, the use of the presented package helps define the spectral active modes of vibration and can be used for their interpretation of the spectra and the study of the geometrical structure of the diboroxane molecule and others.

5. Outlook

From our examples in Section 4, the present capabilities of the BETHE program can be seen for generating the normal coordinates and the spectroscopic activities of molecules. In the future, we will enlarge the number of applications of the program by following various lines. For more complete analysis of the vibrational spectra it would be highly desirable if the problem of molecular vibrations could be solved also quantitatively by just typing a few lines interactively. This means, that we need to address the frequencies of the particular vibrations. These frequencies are determined by the potential energy of the system and are related to the masses of the atoms, the bond angles and bond lengths. The potential energy arises from the interaction between the individual atoms and can be described in terms of the force constants. Therefore, the relationship between the frequencies of the vibrations and force constants need to be expressed. For this purpose, the use of the internal coordinates as a basis for the normal coordinates is more suitable, since the force constants, expressed in terms of the internal coordinates, have a clearer physical meaning then those, expressed in terms of Cartesian coordinates. The method of F and G matrices, developed in Ref. [9] can be used. In addition, the selection rules for the other types of the vibrational transitions, such as overtones and the combination bands, will be included into the BETHE package.

Apart from the analysis of the vibrational spectra, there are several other extensions which would make BETHE a much more powerful tool. A well known phenomenon from molecular interactions with light is the spontaneous distortion of a molecule due to its vibrational motion. This phenomenon is known as the *Jahn–Teller effect* and depends on the interaction between the electrons and the nuclei. The theory of this effect is based, again, upon a group–theoretical analysis of the adiabatic potential of the (polyatomic) molecule when the electronic states become nearly degenerated. The question about the *geometrical stability* of the molecule is then related to searching for minimum of the potential surface. The program realization of the group theory applications, mentioned above, will certainly make BETHE attractive to a wider class of users.

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PAPER 2

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Generation of molecular symmetry orbitals for the point and double groups ☆

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Abstract

Symmetry-adapted molecular basis functions are widely applied for the electronic structure computations of molecules and clusters. These functions are obtained by exploiting the symmetry of the system and often help to simplify the computations considerably. In order to facilitate their use in algebraic and numerical computations, here we provide a set of MAPLE procedures which generates these functions by means of projection operators, both within the nonrelativistic and relativistic theory. All commonly applied point and double groups are supported by the program including, in addition, the access to their group-theoretical data such as the symmetry operators, characters, or irreducible representations.

Program summary

Title of program: BETHE
Catalogue identifier: ADVU
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/ADVU
Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland
Licensing provisions: none
Computer 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 or monitors under which the program has been tested: Linux 8.1+ and Windows2000
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.: 14 190
No. of bytes in distributed program, including test data, etc.: 370 795

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

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doi:10.1016/j.cpc.2005.03.112

Distribution format: tar.gz
Nature of the physical problem: Molecular and solid-state quantum computations can be simplified considerably if the symmetry of the systems with respect to the rotation and inversion of the coordinates is taken into account. To exploit such symmetries, however, symmetry-adapted basis functions need to be constructed instead of using—as usual—the atomic orbitals as the (one-particle) basis. These so-called *symmetry orbitals* are invariant with respect to the symmetry operations of the group and are different for the point and double groups, i.e. for nonrelativistic and relativistic computations.
Method of solution: Projection operator techniques are applied to generate the symmetry-adapted orbital functions as a linear combinations of atomic orbitals.
Restrictions onto the complexity of the problem: The generation of the symmetry orbitals 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} ($n \leqslant 10$), the cubic groups O, T, O_h, T_h, T_d as well as the icosahedral groups I and I_h. In all these cases, the symmetry orbitals can be obtained for either the point or double groups by using a *nonrelativistic* or, respectively, *relativistic* framework for the computations.
Unusual features of the program: All commands of the BETHE program are available for interactive work. Apart from the symmetry orbitals generation, the program also provides a simple access to the group theoretical data for the presently implemented groups from above. The notation of the symmetry operations and the irreducible representations follows the compilation by Altmann and Herzig [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.ps` and 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.

PACS: 02.20.-a; 31.15.Hz

Keywords: Atomic and molecular orbital; Double group; Point group; Projection operator; Symmetry orbital

1. Introduction

Symmetry considerations are known to play a crucial role in (almost) all branches of modern physics, including elementary particle physics in quite a similar manner as the physics of atoms and molecules, or of the solid state. Utilizing the symmetry of a system often help simplify its theoretical description and to obtain insight into its behavior. Apart from the group-theoretical analysis of the system, however, computational tools are also required to make fully use of the symmetries. Therefore, in order to facilitate, for instance, the vibrational analysis of polyatomic molecules, we recently developed the BETHE program [1] which help determine their normal coordinates and spectral activities. In this program, the group data were implemented (or derived) for all the frequently applied point groups including 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} ($n \leqslant 10$), the cubic groups O, T, O_h, T_h, T_d as well as the icosahedral groups I and I_h.

Apart from the vibrational analysis of molecules, the generation of their *symmetry-adapted basis functions* or, briefly, *symmetry orbitals* is also of quite general interest. In particular, in a recent years a large number of investigations was carried out to study the electronic structure of molecules [2–4]. In order to resolve this structure, the (experimental) techniques of the X-ray diffraction and absorption, photoelectron spectroscopy and others have been applied. The theoretical interpretation of such experimental data requires the generation of the molecular wave functions. The symmetry orbitals can be used in order to reduce the size of the (position) space in which the molecular wave functions need to be treated explicitly. Therefore, with this paper we present the extension of the BETHE package, which provides the construction of symmetry-adapted basis functions for polyatomic molecules.

The BETHE package generates the symmetry orbitals from the set of atomic orbitals according to the LCAO method [5] by means of the group theory techniques. This method, based on the molecular symmetry properties, is

very well known in quantum chemistry. Several computer programs have been developed nowadays to construct the symmetry orbitals for selected applications (for instance, [6,7]). However, being implemented within the traditional computer languages (such as Fortran), these programs are not flexible enough to work with the algebraic properties of groups. Moreover, most of such programs support a very restricted set of either a point [6] or double [7] groups. The BETHE package is applicable for most common groups mentioned above (single and double).

In the next section, therefore, let us start with recalling some of the basic concepts in using symmetry orbitals for molecular computations. Apart from the classification of the finite groups and a brief note on the differences between the point and corresponding double groups, this includes the explicit construction of the symmetry orbitals by means of projection operators. Some general properties of the symmetry orbitals are also summarized in this section. This is followed in Section 3 by a short description of the BETHE program and how it can be used within a MAPLE environment. The examples in Section 4 later display the capabilities of the program with emphasis on the generation of the symmetry orbitals within both, a nonrelativistic and relativistic framework. A brief outlook on possible extensions of the BETHE program is finally given in Section 5.

2. Theoretical background

Since the theoretical background of the *finite groups* has been worked out long time ago, here we assume the reader to be familiar with its basic features as well as with the concept of using symmetry orbitals in molecular computations. Today, there are many texts available on this topic including, for example, the books by Elliott and Dawber [8] and Balasubramanian [9]. In the following, therefore, we restrict ourselves to rather a short account of the theory and with emphasis on the *double* groups, just enough in order to understand the implementation and the use of the program below.

2.1. Point and double group symmetries

In group theory, the symmetry of a physical object is determined by the set of transformations which leads to a geometrically indistinguishable configuration of the object. For a finite (non-spherical) system such as a molecule, these transformations are known to be the proper and improper rotations, i.e. pure rotations around some axis or rotations with an additional inversion at the origin, and are called the symmetry operations of the group. They form the (finite) subgroups of the group O_3 of orthogonal transformations in 3-dimensional space. In practice, five types of symmetry operations are usually distinguished, including (i) the identity operation $\hat{E}$ (which leaves the object as it is), (ii) an n-fold rotation $\hat{C}_n$ about some axis, and (iii) the inversion $\hat{i}$ of all coordinates at the origin. Moreover, there are (iv) reflections $\hat{\sigma}$ at some mirror plane, or—in a combined form—(v) rotations by $360°/n$ about some axis followed by a reflection through a plane which is perpendicular to it ($\hat{S}_n$; rotoreflection). The complete set of the h symmetry operations is said to form a *symmetry group* $\mathcal{G}$ and is treated by means of *group theory*. Of course, the occurrence of the various types of symmetry operations can be used also to distinguish between different *group families* as recently discussed in Ref. [1].

All the types (i)–(v) of symmetry operation, as mentioned above, refer to a *geometrical* transformation of the object. To 'add' the concept of the electron spin to the point groups, one has first to recognize that the wave function of a particle with spin $s = 1/2$ changes its sign under the rotation of 2π and is invariant only under a rotation $\hat{E}$ by 4π (around any axis in space). A rotation $\hat{E}'$ by 2π, in contrast, does not give rise to the identity ($\hat{E}'^2 = \hat{E}$). Since the element $\hat{E}'$ commutes however with all the operations $\hat{S}$ of the point group, it can be used to generate the h additional symmetry elements of the double group $\hat{\mathcal{G}}'$ by taking $\hat{E}'\hat{S} = \hat{S}'$, with the consequence that the number of symmetry operations of the group is simply *doubled* when compared to the number of the corresponding point group, i.e. without the spin. If a group contains the rotation $\hat{C}_n$ as one of the symmetry operators, moreover, we have $\hat{C}_n^n = \hat{E}'$ for the point group and $\hat{C}_n^{2n} = \hat{E}$ for the corresponding double group. Using the similar rule as for the point groups [5,8], the double group operators can be collected into the *group classes*.

The symmetry operations of an object (or its symmetry group) would be of minor interest perhaps, if they would not give rise to *induced transformations* and to a great simplification in describing the system by using group theory. In fact, the relation between the symmetry operations and their induced transformations is the topic of the *representation theory* of the groups and one of the main reasons for studying symmetries in Nature (maybe apart from their beauty). Often, such induced transformation can be expressed by matrices and are called the *representations* of the group (assigning one matrix to each of the symmetry operators). Since, in general, we may choose the basis for a representation (in some given vector space L) rather freely, the matrix representations of a group are not unique and will usually depend on the choice of the coordinates as well as on some further parameters. The great advantage in using group theory is, however, that any (reducible) representation $D(\hat{S})$ can be decomposed into—a rather small number of—*irreducible representations* $D^{(i)}(\hat{S})$, which are unique and independent of the basis up to a unitary transformation. Irreducible representations of the point groups are called usually *single-valued* or *vector* representations. In the BETHE program, the chemical (Mulliken) notation is used to denote and identify the irreducible representations, analogy to Ref. [10].

Several standard techniques exist today for determining the irreducible components of a given reducible representation [5]. Instead of an explicit matrix representation, hereby it is often sufficient to know the *characters* of the irreducible representations, i.e. the traces of the corresponding matrices. Moreover, as the number of the symmetry operations is (two times) larger for the double than for the corresponding point group, the number of the irreducible representation also increases in the case of the double groups although typically not by a factor of 2. That is, apart from the (single-valued) representations of the corresponding point group, the double group has a number of the so-called *double-valued* or *spinor* representations. In the literature these (additional) representations are marked by some half-integer superscript j, showing its dimension to be $2j + 1$. The irreducible representations for the point and double groups are shown explicitly in Ref. [10], using the well-known symmetry $D^{(i)}(\hat{S}') = \pm D^{(i)}(\hat{S})$ with the sign in dependence of the class to which the symmetry operation $\hat{S}'$ belongs.

The double groups are important for a number of applications in chemistry including, for example, the theory of the transition metal ions and relativistic molecular structure calculations based on Dirac's Hamiltonian. In the BETHE program, therefore, special attention has been paid to support the point and double groups equally well.

2.2. Construction of symmetry orbitals

For symmetric molecules, the computational costs in the electronic structure calculations can be reduced significantly if a *symmetrized* one-particle basis or, briefly, the concept of 'symmetry orbitals' is applied. In practice, this concept allows to reduce the (size of the) position space in which the molecular orbital functions need to be treated explicitly. Moreover, since the construction of the symmetry orbitals is a purely *geometrical* task (independent of the details of the electronic structure), it can be carried out algebraically for any given symmetry group and actually before the quantum-chemical computations start.

To construct the molecular orbital functions, let us begin with the atomic orbitals

$$|anlm\rangle = \frac{P_{nl}(r_a)}{r_a} Y_{lm}(\theta_a, \phi_a) \tag{1}$$

which are given in spherical coordinates (r_a, θ_a, ϕ_a) and which are centered at the position a of the atoms. Using the LCAO method (i.e. the linear combination of atomic orbitals), the molecular orbitals can be constructed from the orbital functions (1) either immediately

$$\psi_\eta = \sum_{anlm} C_{\eta,anlm} |anlm\rangle \tag{2}$$

or by first making use of an expansion in terms of symmetry orbitals

$$\psi_\eta = \sum_{\tau i \mu} B_{\eta,\tau i \mu} |\tau i \mu\rangle \tag{3}$$

which are sought to be invariant under the (symmetry) operations of the group and are characterized by the group indices i, τ, and μ, referring to one of the irreducible representations of the group. Of course, the symmetry orbitals are found again as linear combinations of atomic orbitals

$$|\tau i\mu\rangle = \sum_{am} A_{\tau i\mu,am}|anlm\rangle \tag{4}$$

with coefficients $A_{\tau i\mu,am}$ determined by the symmetry and the number of the (equivalent) atoms. In molecular computations, the coefficients $C_{\eta,anlm}$ and $B_{\eta,\tau i\mu}$ are often obtained variationally and, hence, are utilized to describe the detailed bond of the molecule apart from its symmetry.

The symmetry orbital $|\tau i\mu\rangle$ with index $\tau = (\tilde{a}nl\tilde{m}\nu)$ can be generated using group theory. In the BETHE program, the construction of this function is based on the *group projection operator* technique. To this end, the projection operator

$$\hat{P}^{(i)}_{\mu\nu} = \frac{n_i}{h}\sum_{\hat{S}} D^{(i)*}_{\mu\nu}(\hat{S})\hat{S} \tag{5}$$

is used in order to compute a bases for all the (involved) irreducible representations of the group, where h denotes the order of the group and $\hat{S}$ the symmetry operations. In this expression, moreover, the matrices $D^{(i)}(\hat{S})$ refer to the ith irreducible representation of the group with dimension n_i and with matrix elements $D^{(i)}_{\mu\nu}(\hat{S})$.

The projection operators (5) have to be applied to an (atomic) basis which includes the orbital functions of all the atoms involved in the molecule. To generate this basis, therefore, we first need to apply the symmetry operations of the group to the atomic orbitals $|anlm\rangle$ from at least one of the *equivalent* atoms in the molecule. Since, however, any spatial symmetry operation $\hat{S}$ can be presented either as a pure rotation $\hat{S} = \hat{R}$, given by the Euler angles α, β and γ, or improper rotation $\hat{S} = \hat{I}\hat{R}$, we may write

$$\hat{S}|anlm\rangle = (-1)^{l\tau_s}\sum_{m'=-l}^{l} R^{l}_{m'm}(\alpha,\beta,\gamma)\big|(\hat{S}a)nlm'\big\rangle, \tag{6}$$

where $(\hat{S}a)$ now refers to an equivalent site of the atom which was at the position a originally. The factor $(-1)^{l\tau_s}$, moreover, accounts for the parity of the atomic orbitals in case of an inversion, namely

$$\tau_s = \begin{cases} 1 & \text{if } \hat{S} \text{ contains an inversion,} \\ 0 & \text{otherwise.} \end{cases}$$

As usual, the rotation matrix $\hat{R}(\alpha,\beta,\gamma)$ is parameterized in terms of the Euler angles α,β, and γ and can be calculated, for instance, by using Wigner's formula [11]. For a given symmetry, therefore, all the *equivalent* sites of an atom are visited if the summation in Eq. (5) includes all the symmetry operators of the group. Combining Eqs. (5) and (6), the symmetry orbitals can be expressed explicitly in terms of the atomic basis by

$$|\tilde{a}nl\tilde{m}\nu i\mu\rangle = \sum_{am} C^{nl\nu i\mu}_{\tilde{a}\tilde{m},am}|anlm\rangle \tag{7}$$

with the symmetry coefficients

$$C^{nl\nu i\mu}_{\tilde{a}\tilde{m},am} = \sum_{\hat{S}} \delta_{a,\hat{S}\tilde{a}} D^{(i)*}_{\mu\nu}(\hat{S})(-1)^{l\tau_s} R^{l}_{m\tilde{m}}(\alpha,\beta,\gamma) \tag{8}$$

and where a refers to one of the equivalent atoms for the atom at position $\tilde{a}$. Moreover, since the generation of the nonrelativistic symmetry orbitals is associated to the point group symmetry, the projection operator (5) has to run through all the symmetry operators of the group.

Instead of the—nonrelativistic—atomic orbitals (1), we may start equivalently from a relativistic description of the atoms, based on Dirac's Hamiltonian [12]. In this case, the atomic orbitals (for an electron with spin $s = 1/2$) are given by the Dirac spinors

$$|an\kappa m\rangle = \begin{pmatrix} \frac{P_{n\kappa}(r_a)}{r_a}\Omega_{\kappa m}(\theta_a,\phi_a) \\ i\frac{Q_{n\kappa}(r_a)}{r_a}\Omega_{-\kappa m}(\theta_a,\phi_a) \end{pmatrix}, \tag{9}$$

where κ is the relativistic angular momentum quantum number and where, again, spherical coordinates are used and centered at the position a of the atom. The Dirac spinors consists out of the two (upper and lower) Pauli spinors with the $(s = 1/2)$ spinor spherical harmonics

$$\Omega_{\kappa m}(\theta_a,\phi_a) = \sum_{m_s}\langle lm - m_s s m_s | jm\rangle Y_{l,m-m_s}(\theta_a,\phi_a)\chi_{sm_s} \tag{10}$$

for the spin-angular part of the atomic orbitals, sometimes known also as the spherical (or Dirac) spin-orbitals. When compared with Eq. (1), the relativistic quantum number

$$\kappa = \begin{cases} -(j+1/2) = -(l+1) & \text{for } j = l+1/2, \\ j+1/2 = l & \text{for } j = l-1/2 \end{cases} \tag{11}$$

replaces the orbital angular momentum quantum number l, but now contains information about the total angular momentum j and again the parity (l) of the atomic orbital.

Since the relativistic orbitals $|an\kappa m\rangle$ in Eq. (9) always refer to a half-integer total angular momentum j, the *double-valued* irreducible representations (with the corresponding superscript j) need to be taken into account in this case in the definition of the projection operators (5). However, the summation over the symmetry operators can still be restricted to those of the corresponding point group because the contributions from the two (double group) operations $\hat{S}$ and $\hat{S}'$ are equal. If this observation is used, the order h in Eq. (5) must refer also to the order of the point group and not to the order of the double group as it appears in the formal definition.

2.3. Linear independence of the symmetry orbitals

As seen from Eq. (3), the symmetry orbitals from the last subsection are used as a basis for the molecular computations. These functions should be therefore linear independent and complete (with respect to the atomic one-particle symmetry) in order to avoid technical difficulties. In general, however, the straightforward application of the projection operators (5) leads to a number of symmetry orbitals which is larger than the number of the (underlying) atomic orbitals and, hence, to linearly-dependent orbitals. For instance, if there are A equivalent atoms $(a = 1,\ldots,A)$ in the molecule and if we consider the atomic orbitals $|anlm\rangle$ with fixed quantum numbers n and l, there are $A(2l+1)$ atomic orbitals in total but $N = Ah(2l+1)$ symmetry orbitals where h is the order of the point group. As shown in Ref. [13], it is sufficient to apply the projection operators only to one from the A equivalent atoms, reducing the number to $N = h(2l+1)$ symmetry orbitals. A linear-independent set of symmetry orbitals is therefore obtained automatically if the number of (equivalent) atoms and the order of the group are equal, $A = h$, while it is linear-dependent for $A < h$.

To derive a linear-independent set of symmetry orbitals, we shall first determine their number N_i for each irreducible representation $D^{(i)}(\hat{S})$ of the group which is given by Ref. [14]

$$N_i = \frac{1}{h}\sum_{\hat{S}}\chi^{(i)*}(\hat{S})\chi(\hat{S}), \tag{12}$$

where $\chi^{(i)}(\hat{S})$ denotes the character of the representation, corresponding to the transformation of the atomic orbitals $|anlm\rangle$. Since the matrix elements of the latter representation are

$$D_{\tilde{a}\tilde{m},am}(\hat{S}) = (-1)^{l\tau_s} R^l_{m\tilde{m}}(\hat{S})\delta_{a,\hat{S}\tilde{a}}, \tag{13}$$

the number N_i can be written

$$N_i = \frac{n_i}{h}\sum_{\hat{S}}(-1)^{l\tau_s}\chi^{(i)*}(\hat{S})\sum_{am} R^l_{mm}(\hat{S})\delta_{a,\hat{S}a} \tag{14}$$

if Eq. (6) is taken into account. Further, N_i linearly independent basis functions $|anlmvi\mu\rangle$ have to be found. The symmetry-adapted basis functions, constructed by this way are linearly independent.

3. Outline to the BETHE program

The BETHE program has been designed as an interactive tool for applications in chemistry and physics which are based on the point and double group symmetries. Hereby, the main emphasis is placed on providing a user-friendly tool which requires neither much knowledge about the group theoretical background nor about the—very large number of—names and abbreviations as used in the literature. Owing to its special design, we therefore expect the BETHE program of interest in both the teaching of the basic elements of group theory by means of the finite groups as well as in more advanced research studies. In the present version of BETHE, we support all finite groups of common interest including the cyclic and their related groups C_n, C_{nv} and C_{nh}, the symmetry groups S_{2n}, the dihedral groups D_n, D_{nd} and D_{nh} $(n = 2, \ldots, 10)$, the cubic groups O, T, O_h, T_h, T_d as well as the icosahedral groups I and I_h, respectively. While the attention in the present development of the BETHE program was mainly focused on the generation and the use of the symmetry orbitals for molecular computations, the simple access to a great deal of group-theoretical data for the point and double groups is certainly also worthwhile to mention. In the generation and expansion of the symmetry orbitals (in terms of the atomic orbitals of equivalent atoms) both, nonrelativistic and relativistic computations are equally supported. The procedures, which are necessary to generate the symmetry orbitals are listed briefly in Table 1.

The full package is distributed by a tar file of the BETHE root directory (`Bethe.tar`), which contains the source code library, file `.mapleinit`, guide for installation as well as the documentation for the program. Having adapted the `.mapleinit` file in the home directory of the user (as briefly explained in a `Read.me` file of the

Table 1
Main commands of the BETHE program. A more detailed description of these procedures is given in the user-manual `Bethe-commands.ps` which is distributed with the code

AO()	Auxiliary procedure to represent an atomic orbital $\langle \mathbf{r} \mid \mathbf{a}nlm\rangle$ which is centered at the position $\mathbf{a} = (a_1, a_2, a_3)$.
SO()	Auxiliary procedure to represent a symmetry orbital $\langle \mathbf{r} \mid (G\mathbf{a})\, nlm;\ T^{(\alpha)}\mu\nu\rangle$.
Abasis()	Auxiliary procedure to represent an atomic basis set $\{\langle \mathbf{r} \mid \mathbf{a}nlm\rangle\}$ which is centered at the position $\mathbf{a} = (a_1, a_2, a_3)$.
Bethe_generate_AO()	Generates a list of atomic orbitals (including all m's) at the site $\mathbf{a} = (a_1, a_2, a_3)$ and for an atom with the identifier $\text{string}_{\text{atom}}$.
Bethe_generate_AO_basis()	Generates an atomic basis by applying all symmetry operations of the point group $\mathcal{G}$ with label `Glabel` to the atomic orbitals AO_1, AO_2, ... of a given orbital basis.
Bethe_generate_SO()	Expands a symmetry orbital $\langle \mathbf{r} \mid (G\mathbf{a})nlm;\ T^{(\alpha)}\mu\nu\rangle$ in terms of the atomic orbitals of a set of equivalent atoms.
Bethe_generate_SO_basis()	Generates a complete, but linear independent basis of symmetry orbitals for the point group $\mathcal{G}$ with label `Glabel` from the set of atomic orbitals as described by the atomic basis sets Abasis_1, Abasis_2, ...
Bethe_group()	Provides the basic group data and notations.
Bethe_set()	Defines either a relativistic or nonrelativistic framework for the generation of the atomic orbitals and the internal interpretation of the quantum numbers.

program), the BETHE program can be invoked like any other module of MAPLE. Then, by using the command `with(Bethe)` user may load all procedures and initialize the internal settings of the BETHE package:

```
> with(Bethe);

            Welcome to Bethe!

  Bethe_save_framework := nonrelativistic
```

At any (re-) start of the program, the internal framework, as defined by the global variable `Bethe_save_framework`, is set to `nonrelativistic` as the default of the program. This initial setting of the framework which influences the internal interpretation of the quantum numbers (see below), however, can be 'overwritten' easily by means of the command `Bethe_set()`. Details about the use this global definition will become obvious in our examples in Section 4.2.

Apart from the generation of the symmetry orbitals, the BETHE program also facilitates the access to basic data of the point and double groups, following in its notation mainly the *Point-Group Theory Tables* by Altmann and Herzig [10]. It provides, for instance, the number and a detailed definition of the symmetry operations, the characters, irreducible representations, and further information by using the command `Bethe_group()` with a proper set of keywords; cf. the manual in `Bethe-commands.pdf`. In order to keep the notations as similar as they appear in the literature, we often use string identifiers for the communication with and within the program, i.e. in the input and output of many procedures and for the internal identification of the symmetry operations and irreducible representation of a particular group. A notation like $\text{string}_{\text{SO}}$ or $\text{string}_{\text{IR}}$, for instance, refers to the name of one of the symmetry operations or irreducible representations of the group, respectively. The list of all possible string identifiers for a given group (with label `Glabel`) is obtained by typing in the commands `Bethe_group(Glabel,operators)` and `Bethe_group(Glabel,irreps)`, and with an additional keyword *double* if the symmetry operations and representations of the corresponding double group are requested. Since the double group is obtained simply by 'doubling' the number of symmetry operations due to the (non-identical) rotation about 2π, all operator strings appear basically twice for the double group, with one of them having a leading capital letter "R".

4. Examples

To illustrate the use of the BETHE program, below we display and explain a few examples. They show the simple (and fast) access to the symmetry operations, irreducible representations, and to other group-theoretical data as well as the generation of symmetry orbitals for a molecule, if its symmetry and the coordinates of (at least) one atom for each sort of *equivalent* atoms are known. In all examples below we used accuracy $Digits = 6$ in order to make the output of the program more compact.

4.1. Access and use double-group data

For the sake of simplicity, let us start with the point group C_{3v} which is obtained from the cyclic group C_3 by adding three vertical mirror planes. The symmetry of this group is fulfilled approximately, for instance, by the chlorometane molecule CH_3Cl. With the BETHE program, we may first ask for the number and type of the symmetry operators which, of course, are different for the point group C_{3v} and the corresponding double group and assign them to some working variables

```
> wn  := Bethe_group(C3v, No_operators);
  wa  := Bethe_group(C3v, operators);
```

```
  wn_dbl := Bethe_group(C3v, No_operators, double);
  wa_dbl := Bethe_group(C3v, operators, double);

                                wn := 6

      wa := ["E", "C3+", "C3-", "sigma_v1", "sigma_v2", "sigma_v3"]

                                wn_dbl := 12

  wa_dbl := [ "E",  "C3+",  "C3-",  "sigma_v1",  "sigma_v2",  "sigma_v3",
              "RE", "RC3+", "RC3-", "Rsigma_v1", "Rsigma_v2", "Rsigma_v3"]
```

As mentioned before, the group data for the double groups are usually obtained by adding the keyword *double* to the list of parameters. To derive, in addition, the characters and the matrices of the irreducible representations for the C_{3v} symmetry, we first determine again the corresponding (string) identifiers which are used internally to distinguish between the different irreducible representations of the group

```
> wb := Bethe_group(C3v, irreps);
  wb_dbl := Bethe_group(C3v, irreps, double);

                  wb := ["A1", "A2", "E"]

  wb_dbl := ["A1", "A2", "E", "E1/2", "E3/2^1", "E3/2^2"]
```

For both cases, the point and the double group, we can also determine the characters and the explicit matrix representation for either a single symmetry operation

```
> wc := Bethe_group_character(C3v, "E1/2", "RC3+");
  wd := Bethe_group_irrep(C3v, "E1/2", "RC3+");

                           wc := 1

           [                1/2                        ]
           [  1/2 - 1/2 I 3                0           ]
     wd := [                                           ]
           [                                      1/2]
           [        0                1/2 + 1/2 I 3     ]
```

or for all the symmetry operators as define in the lists `wa` and `wa_dbl` above

```
> we := Bethe_group_character(C3v,"E1/2");
  we_dbl := Bethe_group_character(C3v,"E1/2", double);

                we := [2,  1,  1, 0, 0, 0]

     we_dbl := [2, 1, 1, 0, 0, 0, -2, -1, -1, 0, 0, 0]
```

In a similar way, we may determine the explicit (irreducible) matrix representations

```
> wg := Bethe_group_irrep(C3v, "E1/2");
  wh := Bethe\_group\_irrep(C3v, "E1/2", double):
```

```
                    [              1/2                      ]
          [1    0]  [1/2 - 1/2 I 3              0          ]
wg := [[          ], [                                     ],...]
          [0    1]  [                                1/2]
                    [       0            1/2 + 1/2 I 3     ]
```

where, for the sake of brevity, we only show the first two matrices and also suppress the printout for the double group by using a colon at the end of the line.

The symmetry group C_{3v} is quite simple and, perhaps, no computational tools are required to derive the characters and irreducible matrix representations for this group. In practice, however, much more complicated groups are often needed in molecular computations, for which these data are difficult or at least tedious to collect. In the following, for instance, we look at the less trivial case of a molecule with *dihedral* symmetry and demonstrate how its symmetry adapted basis functions can be derived.

4.2. Generation of the symmetry orbitals

Let us consider the *ferrocene* molecule $Fe(C_5H_5)_2$ for which the electronic and magnetic properties have been discussed recently in the literature [15,16]. It has been found of interest, in particular, for studying the transition metal complexes and the nanostructured materials. This molecule consists of an iron atom "sandwiched" between two identical parallel C_5H_5 rings. Although ferrocene is known to exist also in D_{5d} symmetry (staggered ferrocene), here we consider the symmetry D_{5h} (eclipsed ferrocene) as displayed in Fig. 1. As seen from the figure, there are three sorts of atoms which transform equivalently under the action of the symmetry operations of the group. They are formed by (i) the central iron atom, (ii) the ten carbon atoms and (iii) the ten hydrogen atoms. Below, we generate the symmetry orbitals for the carbon atoms within both, the nonrelativistic and relativistic framework, while the symmetry orbitals for the central Fe atom and hydrogen atoms follow from using very similar lines.

We start with a `nonrelativistic` framework for the atomic and symmetry orbitals as this is the *default* of the BETHE program. As usual, there is associated an atomic basis with each set of equivalent atoms which need to be sufficient for the description of the molecule. However, in order to keep the output of the following (interactive) commands at a feasible size, let us just consider the $2p$ orbitals ($n = 2$, $l = 1$) as a part of the basis for the carbon

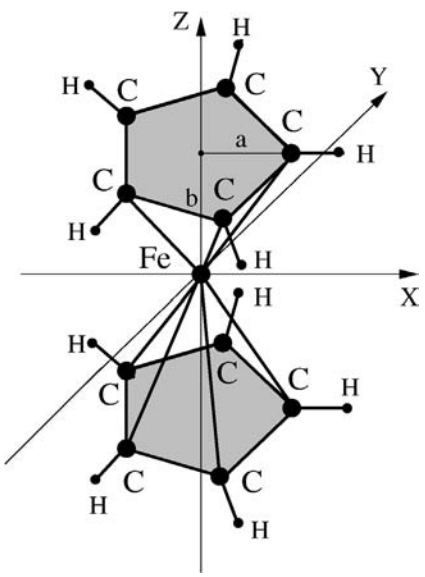

Fig. 1. Geometry of the ferrocene molecule $Fe(C_5H_5)_2$.

atoms. By adopting the distance between the z-axis and (any of) carbon atom as `a` and the distance from the iron atom to the plane of C_5H_5 as `b` (cf. Fig. 1), this basis is defined in BETHE simply by typing

```
>  basis_C := Abasis(atom_C, [a,0,b], [2,1]);

      basis_C := Abasis(atom_C,[a,0,b],[2,1])
```

where the first list, `[a,0,b]`, from the parameters above refers to the position of one of the (equivalent) carbon atoms and the second list, `[2,1]`, to the principal and orbital angular momentum quantum numbers of the $2p$ orbital. The command `Abasis()` is an auxiliary procedure which returns its input *unevaluated* and which simply serves for keeping the relevant information together. Instead of a *single* orbital list `([2,1])` any number of such lists for specifying the orbitals could be followed as additional parameters in order to enlarge the atomic basis for this sort of atoms. By giving the principal and orbital angular quantum momentum numbers, however, all the magnetic substates $|nlm\rangle$ are then taken into account automatically.

To specify the orbital basis for one of the equivalent sites is sufficient to generate a list of symmetry orbitals associated with this sort of atoms and the given symmetry

```
> Bethe_generate_SO_basis(D5h, basis_C, print);

     1) D5h | atom_C [a, 0, b], n=2, l=1, m= 1;  A1‘(1, 1) >
     2) D5h | atom_C [a, 0, b], n=2, l=1, m= 0;  A1‘(1, 1) >
     3) D5h | atom_C [a, 0, b], n=2, l=1, m= 1;  A2‘(1, 1) >
     4) D5h | atom_C [a, 0, b], n=2, l=1, m= 1;  E1‘(1, 1) >
     5) D5h | atom_C [a, 0, b], n=2, l=1, m= 0;  E1‘(1, 1) >
     6) D5h | atom_C [a, 0, b], n=2, l=1, m=-1;  E1‘(1, 1) >
     7) D5h | atom_C [a, 0, b], n=2, l=1, m= 1;  E1‘(2, 1) >
     8) D5h | atom_C [a, 0, b], n=2, l=1, m= 0;  E1‘(2, 1) >
      .
      .
    29) D5h | atom_C [a, 0, b], n=2, l=1, m= 0; E2‘‘(2, 1) >
    30) D5h | atom_C [a, 0, b], n=2, l=1, m=-1; E2‘‘(2, 1) >
```

where the third argument, `print`, has been used to force the program to print the symmetry orbitals in a line mode; a NULL expression is returned in this case. As seen from the output, each line represents one of the symmetry orbitals in a notation similar to Eq. (7). The last column in this output clearly indicates the irreducible representation of the group D_{5h}, including the indices of the matrix elements in the matrix representation. Of course, this is still a rather formal classification of the symmetry orbitals without knowing their expansion in terms of the atomic orbitals at the different (but equivalent) sites of the molecule. The same command can be invoked in order to obtain such an explicit expansion by adding the keyword *explicit* as one of the last arguments:

```
> Bethe_generate_SO_basis(D5h, basis_C, explicit, print);

         1. SO: D5h | atom_C [a, 0, b], n=2, l=1, m= 1;  A1‘(1, 1) >
       -------------------------------------------------------

    1)      -.223606+0.*I, |[             a,              0,  b], n=2, l=1, m=-1>
    2)-.0690983+.212662*I, |[ a*cos(2/5*Pi), -a*sin(2/5*Pi),  b], n=2, l=1, m=-1>
    3)-.0690983-.212662*I, |[ a*cos(2/5*Pi),  a*sin(2/5*Pi),  b], n=2, l=1, m=-1>
    4)  .180901+.131432*I, |[-a*cos(1/5*Pi), -a*sin(1/5*Pi),  b], n=2, l=1, m=-1>
    5)  .180901-.131432*I, |[-a*cos(1/5*Pi),  a*sin(1/5*Pi),  b], n=2, l=1, m=-1>
```

```
     .
     .
   28) .0690983+.212662*I, |[ a*cos(2/5*Pi), -a*sin(2/5*Pi), -b], n=2, l=1, m= 1>
   29) .0690983-.212662*I, |[ a*cos(2/5*Pi),  a*sin(2/5*Pi), -b], n=2, l=1, m= 1>
   30) -.180901+.131432*I, |[-a*cos(1/5*Pi), -a*sin(1/5*Pi), -b], n=2, l=1, m= 1>

        2. SO:  D5h | atom_C [a, 0, b], n=2, l=1, m= 0;  A1'(1, 1) >
      ------------------------------------------------------
    1)           0., |[             a,              0, b], n=2, l=1, m=-1>
    2)           0., |[ a*cos(2/5*Pi), -a*sin(2/5*Pi), b], n=2, l=1, m=-1>
    3)           0., |[ a*cos(2/5*Pi),  a*sin(2/5*Pi), b], n=2, l=1, m=-1>
    4)           0., |[-a*cos(1/5*Pi), -a*sin(1/5*Pi), b], n=2, l=1, m=-1>
     .
     .
```

Again, the line mode (keyword `print`) is used to list the contributions from the atomic orbitals at different sites and with different m-quantum numbers. For each symmetry orbital, the expansion coefficients are normalized to $\sum_i c_i^2 = 1$. Without the optional argument `print`, the expansion of the symmetry orbitals are returned in a list structure [SO_1, SO_2, ...] which can be processed further, cf. the manual file `Bethe-commands.pdf`. A similar but slightly more sophisticated list structure is also returned for an `explicit` expansion of the symmetry orbitals, allowing to make use of the output for other computations.

The last paragraphs clearly showed how easily we may generate the symmetry-adapted basis if a nonrelativistic notation (framework) is assumed for the atomic orbitals. In fact, the program supports the generation of these symmetry orbitals for the 72 most common finite point groups. In relativistic computations, the relativistic angular momentum quantum number κ 'replaces' the orbital momentum l and provides the information about the parity and total angular momentum of the orbitals. To generate the symmetry orbitals within a *relativistic* framework, we may follow very similar lines as before by first 're-defining' the framework to *relativistic*

```
> Bethe_set(framework = relativistic);

     Framework is changed to relativistic
```

To keep the output of the BETHE commands feasible for displaying it within this work, again, let us restrict ourselves to the $2p_{1/2}$ relativistic orbital ($n = 2$, $\kappa = 1$) as the atomic basis for the carbon atoms

```
> basis_C := Abasis(atom_C, [a,0,b], [2,1]);

     basis_C := Abasis(atom_C, [a,0,b], [2,1])
```

where the second list in the input, $[\kappa, m] = [2, 1]$, now automatically refers to the relativistic quantum numbers. Again, either a *formal* list of all symmetry orbitals

```
> Bethe_generate_SO_basis(D5h, basis_C, print);

     1) D5h | atom_C [a, 0, b], n=2, kappa=1, m=-1/2; E1/2(1, 1) >
     2) D5h | atom_C [a, 0, b], n=2, kappa=1, m= 1/2; E1/2(1, 1) >
     3) D5h | atom_C [a, 0, b], n=2, kappa=1, m=-1/2; E1/2(2, 2) >
     4) D5h | atom_C [a, 0, b], n=2, kappa=1, m= 1/2; E1/2(2, 2) >
     5) D5h | atom_C [a, 0, b], n=2, kappa=1, m=-1/2; E3/2(1, 1) >
```

```
      .
      .
    19) D5h | atom_C [a, 0, b], n=2, kappa=1, m=-1/2; E9/2(2, 2) >
    20) D5h | atom_C [a, 0, b], n=2, kappa=1, m= 1/2; E9/2(2, 2) >
```

or their explicit expansion in terms of the (relativistic) atomic orbitals are obtained by typing the same command as before at MAPLE's prompt

```
> Bethe_generate_SO_basis(D5h, basis_C, explicit, print);

  1. SO: D5h | atom_C [a, 0, b], n=2, kappa=1, m=-1/2; E1/2(1, 1) >
  ------------------------------------------------------------

  1)       .316227+0.*I, |[             a,              0, b], n=2, kappa=1, m=-1/2>
  2) .0977197-.300750*I, |[ a*cos(2/5*Pi), -a*sin(2/5*Pi), b], n=2, kappa=1, m=-1/2>
  3) .0977197+.300750*I, |[ a*cos(2/5*Pi),  a*sin(2/5*Pi), b], n=2, kappa=1, m=-1/2>
  4) -.255833-.185874*I, |[-a*cos(1/5*Pi), -a*sin(1/5*Pi), b], n=2, kappa=1, m=-1/2>
    .
    .
 19)            0.+0.*I, |[ a*cos(2/5*Pi),  a*sin(2/5*Pi),-b], n=2, kappa=1, m= 1/2>
 20)            0.+0.*I, |[-a*cos(1/5*Pi), -a*sin(1/5*Pi),-b], n=2, kappa=1, m= 1/2>

  2. SO: D5h | atom_C [a, 0, b], n=2, kappa=1, m= 1/2; E1/2(1, 1) >
  ------------------------------------------------------------
  .
  .
```

In comparison to the nonrelativistic case from above, the last column now displays the *spinor representation* of the symmetry orbitals by using the group-theoretical data for the corresponding double group. Of course, this is in close relation and agreement with the half-integer total angular momenta of the relativistic orbitals, $s_{1/2}, p_{1/2}, p_{3/2}, d_{3/2}, \ldots$.

For practical computations, obviously the symmetry orbitals should be orthogonal and complete (for the given one-particle symmetry), by removing all the linear-dependent symmetry orbitals. In the BETHE program, this orthogonalization is carried out internally during the execution of the program and can be tested simply, if one starts from the explicit expansion of these symmetry orbitals in terms of the atomic orbitals as explained above. To test for this orthogonality, the procedure `Bethe_SO_are_orthogonal()` is provided

```
> list_SO := Bethe_generate_SO_basis(D5h, basis_C, explicit):
  Bethe_SO_are_orthogonal(list_SO);

     true
```

and confirms the expected result. In the first line, now the list structure returned for the expansion coefficients and atomic orbitals is utilized to perform this test in detail.

5. Outlook

The examples in Section 4 display (some of) the present features of the BETHE program and clearly demonstrate how computer-algebra can be used today for applying group theory in chemistry and physics. In the present version of the BETHE program, the data of the 72 most frequently applied point groups can be utilized, not counting the

corresponding double groups. Of course, there are a number of different directions, in which the BETHE program could be developed in the future, including (a) the vibrational analysis of molecules as an extension of Ref. [1]; (b) tools for investigating the level splitting of atoms in external crystal fields (ligand field theory); (c) the study of magnetic properties of materials if the point and double groups are combined with the time reversion (operation) in order to generate the magnetic point or the color groups, respectively. For the analysis of molecular spectra, moreover, (d) the spontaneous distortion of the symmetry of molecules due to the electronic-vibrational coupling in the molecular motion, which is known as the *Jahn–Teller effect* from the literature, might be also interesting. Related or additional suggestions from the site of the users are therefore very welcome. Other group-theoretical data such as various commonly applied regular and irregular representations of the finite groups, their Clebsch–Gordan coefficients, and others are perhaps of more mathematical interest but could be derived, if a few additional algorithms are designed and implemented.

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Generation of Clebsch–Gordan coefficients for the point and double groups ☆

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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
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*

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

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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} ($n \leqslant 10$), 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 Herzig [S. Altmann, P. Herzig, 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.

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 Herzig [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 $\mathbf{e}_1, \ldots, \mathbf{e}_n$ in L. For such a basis, the transformation of the vectors $\mathbf{e}_j$ is given by

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

for each symmetry operation $\hat{S}$ of the group, i.e. by the set of n^2 coefficients $\{T_{ij}(\hat{S}),\ i, j = 1, \ldots, n\}$. 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 $\{\psi_i(\mathbf{r}),\ i = 1, \ldots, n\}$. Similarly to Eq. (1), the transformations of these basis functions are then given by

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

where, for a given j, the expansion coefficients refer to the jth 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'

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

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_α 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 $T^{(\gamma)}$

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

where the coefficients a_γ 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 $C^{(\alpha\beta)}$

$$(C^{(\alpha\beta)})^{-1}T^{(\alpha\otimes\beta)}C^{(\alpha\beta)} = \begin{Bmatrix} T^{(\gamma,1)} & & & \\ & \ddots & & \\ & & T^{(\gamma,a_\gamma)} & \\ & & & \ddots \end{Bmatrix} \tag{5}$$

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 α, β and γ 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 γ in the direct product of α and β.

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

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

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):

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

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

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

Multiplying (8) by $T^{(\gamma')*}_{m'n'}(\hat{S})$ and by performing the summation over all symmetry operations $\hat{S}$ of the group G, we find

$$\sum_{\hat{S}} T^{(\alpha)}_{ij}(\hat{S}) T^{(\beta)}_{kl}(\hat{S}) T^{(\gamma')*}_{m'n'}(\hat{S}) = \sum_{\hat{S}} \sum_{\gamma s m n} \langle \alpha i \beta k | s \gamma m \rangle T^{(\gamma,s)}_{mn}(\hat{S}) T^{(\gamma',s)*}_{m'n'}(\hat{S}) \langle \alpha j \beta l | s \gamma n \rangle^* \tag{9}$$

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

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

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 Herzig [6]. Using such a step-wise variation of the indices $j, l, \ldots$ 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 $\{\psi^{(\alpha)}_i,\ i = 1, \ldots, n_\alpha\}$ and $\{\psi^{(\beta)}_k,\ k = 1, \ldots, n_\beta\}$ form orthogonal bases of the irreducible representations $T^{(\alpha)}$ and $T^{(\beta)}$, respectively. Then, we may construct a set of product functions $\{\psi^{(\gamma)}_m,\ m = 1, \ldots, n_\gamma\}$

$$\psi^{(\gamma)}_m = \sum_{ik} \langle \alpha i \beta k | s \gamma m \rangle \psi^{(\alpha)}_i \psi^{(\beta)}_k \tag{11}$$

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 $\psi^{(\alpha)}_i \psi^{(\beta)}_k$ form an orthogonal set (due to construction), the function $\psi^{(\gamma)}_m$ 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

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

orthogonality relations

$$\sum_{ik} \langle \alpha i \beta k \vert s' \gamma' m' \rangle^* \langle \alpha i \beta k \vert s \gamma m \rangle = \delta_{\gamma\gamma'} \delta_{ss'} \delta_{mm'}, \tag{12}$$

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

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

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

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 (CH_4), carbon tetrachloride (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 $\langle \alpha i \beta k | s \gamma m \rangle$ 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_γ, where a_γ 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 $\langle A_1 1E1 | 1E1 \rangle$ and $\langle A_1 1E1 | 1E2 \rangle$ 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 $\langle A_1 1E2 | 1E1 \rangle$ and $\langle A_1 1E2 | 1E2 \rangle$, 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 $\langle E2E1 | 1A_2 1 \rangle$ and $\langle E2E1 | 1E1 \rangle$

```
> 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);

                1/2
               2
     we_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 α, β, and γ 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 $E \otimes E$

α:	β:					
E	E	γ:	A_1	A_2	E	
i	k	m:	1	1	1	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

```
        [ 0        0       0    1]
        [                        ]
        [ 1/2       1/2          ]
        [2          2            ]
        [----      ----    0    0]
        [ 2         2            ]
wf  :=  [                        ]
        [ 1/2       1/2          ]
        [2          2            ]
        [----    - ----    0    0]
        [ 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 $\gamma m = \{A_1 1, A_2 1, E1, E2\}$. The main body of the table then shows the CG coefficients $\langle E1E1|E1\rangle = 0$, $\langle E1E1|E2\rangle = 1$, $\langle E1E2|A_1 1\rangle = \sqrt{2}/2$, 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 ψ_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 $E_{1/2} \otimes E_{5/2}$ ($\alpha i \beta k = \{E_{1/2}1E_{5/2}1, E_{1/2}1E_{5/2}2, E_{1/2}2E_{5/2}1, E_{1/2}2E_{5/2}2\}$) and the columns correspond to the basis functions $\gamma m = \{A_2 1, T_2 1, T_2 2, T_2 3\}$. 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

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

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

$$\sum_{ik} \left| \langle \alpha i \beta k | s \gamma m \rangle \right|^2 = 1. \tag{16}$$

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

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

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 then 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

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

analogous to Eq. (4) and where a_γ denotes how often the irreducible representation $T^{(\gamma)}$ occurs in the representation T. An explicit formula for the coefficient a_γ 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 γ of the integers a_γ 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 $(MnO_4)^{3-}$ 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 $(MnO_4)^{3-}$ 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,

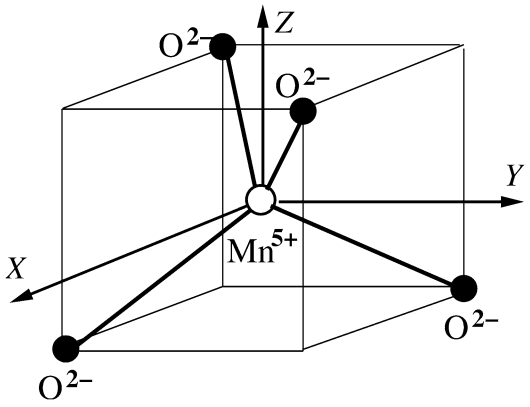

Fig. 1. Tetrahedral configuration of the molecular ion $(MnO_4)^{3-}$.

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 $(MnO_4)^{3-}$ molecular ion, the $3d^2$ configuration ion of Mn^{5+} is fourfold coordinated with O^{2-} ions (see Fig. 1). As seen from the figure, therefore, the 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, `Td` is the label of the symmetry group of the surrounding crystal, `Ylm` 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.

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