Computation of Symmetry Orbitals for Point Groups

Hirohide NAKAMATSU*, Hirohiko ADACHI** and Takeshi MUKOYAMA***

A program is presented for the construction of symmetry-adaped basis functions for molecular orbitals, employing the projection operator technique. It is written in a language of Mathemeatica and the way of using the program is described. A line of input data produces the symmetry orbitals for the point group of molecule and an input file for a program named "SCAT" which puts the discrete-variational $X\alpha$ molecular orbital method into practice.

I. INTRODUCTION

One of time-consuming parts in the molecular orbital calculations is to obtain matrix elements. The matrix can be reduced in a way based on symmetrical properties of the molecule. The group theory is applied to handle the properties. The basis functions for the irreducible matrix are called symmetry orbitals. They are useful not only to reduce the number of integrations for the matrix, but also to characterize the spatial distribution of electrons and the interactions between the molecular orbitals.

There are two categories of algorithms to construct the symmetry orbitals for the point group. Tools of the group theory such as a projection operator are used directly to get the relevant quantities of symmetry orbitals.[1,2] In the other technique, the symmetry orbitals are derived with the orthogonal transformation matrices for atomic orbitals (AO's) which are found on the process of reducing the matrices of overlap between the AO's.[3] The latter technique is suitable for numerical calculation in FORTRAN. The former technique can specify the common symbols of representations for the symmetry orbitals and produces a simpler form of symmetry orbitals, because the axes are prescribed in space. Therefore, the symmetry orbitals generated by the former technique are convenient for analyzing spatial features of the molecular orbitals (MO's). However, the implementation of the technique requires programming for mathematical symbolic operations.

In the present paper, a procedure for constructing the symmetry orbitals by the projection operator is described, followed by explanation how to use the program employing the operator. A line of input data gives the symmetry orbitals and an input

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* 中松 博英: Laboratory of Nuclear Radiation, Institute for Chemical Reserch, Kyoto University, Uji, Kyoto 611.

** 足立 裕彦: Hyogo University of Teacher Education, Shimokume, Yashiro-cho, Kato-gun, Hyogo 673-14

*** 向山 毅: Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

file for a program "SCAT"[4] based on the descrete-variational $X\alpha$ (DV-$X\alpha$) molecular orbital method. As the projection operator technique needs the symbolic operations and a check on the results needs numerical calculations, the present program has been written in a language Mathematica (Wolfram Research, Inc.)[5] which runs on a lot of computers from personal computers to workstations and mainframes. Test runs of the program were done on Macintosh IIcx and Sun 4/1.

II. COMPUTATIONAL METHOD

2.1 Generation of Symmetry Orbitals

The projection operator for the μth irreducible representation of a point group is defined as follows:

$$\hat{P}_{\mu;st} = \frac{n_\mu}{h} \sum_i^h \Gamma_\mu^*(R_i)_{st} \, \hat{R}_i, \tag{1}$$

where n_μ is the dimension of μth representation, h is the order of group and $\Gamma_\mu^*(R_i)_{st}$ is the complex conjugate of matrix element ofr the sth row and tth column of representation for the oprator $\hat{R}_i$. An arbitrary function $\phi(r)$ operated by the $\hat{P}$ gives a symmetry orbital f :

$$f_{\mu;st} = \hat{P}_{\mu;st} \, \phi(r). \tag{2}$$

If the function $\phi(r)$ has no components of the symmetry orbitals belonging to the representation $\Gamma_{\mu;st}$, the operation results in zero. Reference 2 provides a proof that the $f_{\mu,st}$ is one of the functions of irreducible basis.
The transformation of function by a spatial operator is perfomed in the following equation:

$$\hat{R}\phi(r) = \phi(\hat{R}^{-1}r). \tag{3}$$

A general form of expression is used in the case where the function $\phi(r;S_i)$ has the origin of coodinate system S_i differing from the origin of symmetry operation:

$$\hat{R}\phi(r; S_i) = \phi(\hat{R}^{-1}r; \hat{R}S_i). \tag{4}$$

This relation is illustrated with the aid of Fig. 1. A site S_1 is transferred to S_2 by the operator $\hat{R}$ and the axis X_1 for the site S_1 is transformed to X'_2. The axis X'_2 should be transformed to X_2 which is in the same direction as the original axis is. This transformation is done at the local origin S_2 by the inverse operator $\hat{R}^{-1}$.
The following atomic orbitals φ_{nlm} are often adopted in the linear combination of AO (LCAO) approximation:

$$\varphi_{nlm}(r; \nu) = u_{nl}(r; \nu) \, Y_{lm}(\theta, \phi; \nu), \tag{5}$$
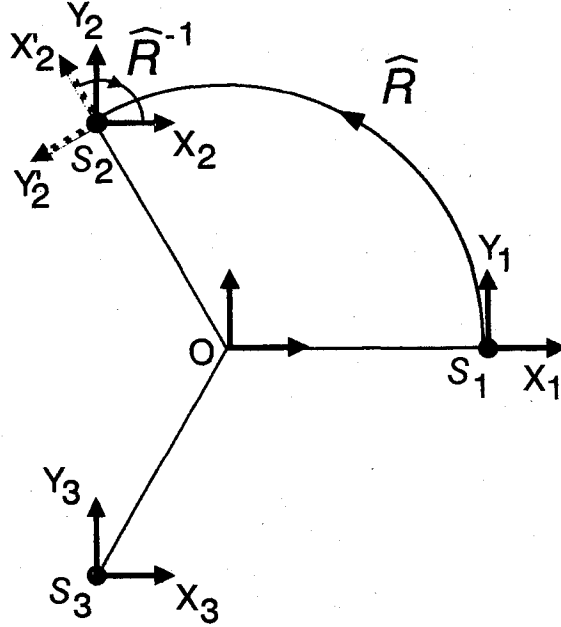
Fig. 1. Symmetry operation for a function located at the origin different from that for the symmetry.

where u_{nl} is a radial function, functions Y_{lm} are the spherical harmonics and ν is used instead of S_i for simplicity of typography. The radial function is a numerical solution of atomic calculation in the DV-Xα method and a power of r multiplied by an exponential function for the Slater-type orbitals (STO's). It has a spherical symmetry and can be omitted on handling the symmetrical properties. The symmetry orbitals $f_{i;l}$ without the radial parts are given by:

$$f_{i;l} = \hat{P}_{\mu;st} \, Y_{lm}(\theta, \phi; \nu), \tag{6}$$

$$= \sum_{\nu, m} w_{\nu m;i} \, Y_{lm}(\theta, \phi; \nu), \tag{7}$$

The summation is carried out over ν and m except for l because the spatially transformed Y_{lm} is expressed in terms of the Y_{lm} with the same l value:

$$\hat{R} Y_{lm}(\theta, \phi; \nu) = \sum_{m'} c_{m';lm} \, Y_{lm'}(\theta, \phi; \nu). \tag{8}$$

The symmetry-adapted basis functions $\chi_{i;nl}$ for the LCAO are finally expressed with the $w_{\nu m;i}$ derived in Eq.(7):

$$\chi_{i;nl} = \sum_{\nu, m} w_{\nu m;i} \, u_{nl}(r; \nu) Y_{lm}(\theta, \phi; \nu). \tag{9}$$

Using a close relation between Y_{lm} and Y_{l-m}, real forms of spherical harmonics y_{lm} are derived by:

$$y_{lm} = \frac{1}{\sqrt{2}} (Y_{lm} + (-1)^m Y_{l-m}) \quad ; m > 0, \tag{10}$$

$$= \frac{i}{\sqrt{2}} (Y_{lm} - (-1)^m Y_{l-m}) \quad ; m < 0, \tag{11}$$

$$= Y_{lm} \qquad\qquad ; m = 0. \tag{12}$$

In the present program, the y_{lm} with the equal l are multiplied by a constant for simplicity of symbolic operation without affecting the results and defined in an initialization routine of the program. The $f_{i;l}$ with the y_{lm} is produced in the present program and the $\chi_{i;nl}$ is constructed in the DV-Xα program SCAT according to the $f_{i;l}$.

2.2 Classification of Symmetry Orbitals

The symmetry orbitals are derived from the y_{lm} located at one of the equivalent atomic sites by the projection operator. During the process, duplication of the symmetry orbitals takes place. After eliminating the duplicates, it is confirmed that the number of symmetry orbitals is equal to the number of original y_{lm}'s for all the atoms.

The derived orbitals in a degenerate representation are classified in order to be orthogonal to the orbitals in the other blocks. Overlap integrals $<g_j \mid \chi_i>$ are evaluated to judge the orthogonality. Test functions g_j are defined in the program and when the overlap integral is not zero, the function f_i belongs to the same block as the test function. It is requested only that the symmetrical properties are reflected in the integral values. The integrals are replaced by the following summation:

$$<g_j \mid \chi_i> \rightarrow \sum_k g_j(r_k) \chi'_i(r_k), \tag{13}$$

$$\chi'_i(r) = \sum_{v,m} w_{vm;i}(r - r_v) y_{lm}(r - r_v), \tag{14}$$

where a simple radial function $(r - r_v)$ located at the atom site v is introduced into the χ'_i which is used instead of χ_i. The points r_k arise from transformation of a point at a general position by all the operations in the point group. This classification technique with overlap integrals is useful for checking the results in a way independent of the group theory tools, though the projection operator can be utilized for the classification and checking.

III. DESCRIPTION OF INPUT DATA

The program is called symOrb, which is read into Mathematica with a command "<<symOrb". When a command "?symOrb" is inputted, a help message is returned which contains a format of input data, explanation of the parameters and examples. The program is in a form of function: symOrb ["group name", sites, {linit, lfin}, "file name", start number]. The input parameter of group name means the name of point group and is specified by the Shönflies symbols such as C3, C3v, Oh, etc. The parameter of sites needs the coordinates of representative points which are defined later. The
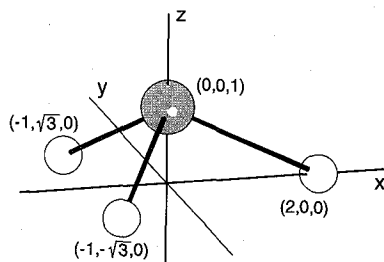
Fig. 2. Example of atomic positions.

format is {x, y, z,} and for two or more representative points, the sets of coordinates are listed in a pair of braces, e.g., {{x_1, y_1, z_1}, {x_2, y_2, z_2},...}. (Default={0, 0, 0}) The parameter {lint, lfin} indicates the range of angular momentum quantum number l. A value {0, 1}, for example, results in the symmetry orbitals with the s and p orbitals. A value {0, 3} denotes the quantum numbers for s, p, d and f states. (Default={0, 1}) The input of file name causes the output of results to the file. When the name is not specified, nothing is written in any file. The numbering of sites begins at the parameter of start number. This is used to get additional symmetry orbitals for the existing symmetry orbital file. (Default=1)

The representative points are explained for a tetratomic molecule with C_{3v} symmetry as shown in Fig. 2. Four atomic sites in the molecule are classified into two: {0, 0, 1} and the other. The latter three sites are equivalent, which means that permutations occur among them when the group operations are carried out. One of the equivalent sites is called a representative point in the present program. A list {{0, 0, 1}, {2, 0, 0}} is specified as the input of representative points for the function "symOrb". It is sufficient that the set of atom sites has the same symmetrical properties as the molecule has. The present example of representative points is applicable to various NH_3-shaped molecules such as NF_3, PCl_3. When the actual coordinates of molecules are used in place of the {{0, 0, 1}, {2, 0, 0}}, the same results will be obtained in a longer calculation time.

The principal axis of symmetry operations is taken as the z axis, which agrees with the common usage. The way of taking the x and y directions follows the custom usage according to a character table in Ref. 6. Some different definitions of the x and y directions are encountered in the papers. For example, the coordinate system for the H_2S molecule adopted in the present program is different from the usage in Ref. 7. The reverse definition of B_1 and B_2 representations appears.

Examples of input data are shown below.

symOrb["C3v", {1, 0, 0}, {0, 1}]
    (* These three input lines result in the same symmetry orbitals *)
symOrb["C3v", {−1, Sqrt[3], 0}, {0, 1}]   (* Sqrt[3] means $\sqrt{3}$ *)
symOrb["C3v", {1.23, 0, 1.5}, {0, 1}]
symOrb["C3v", {{1, 0, 0}, {0, 0, 0}}, {{0, 1}}, "symC3v"]   (* NH_3 *)
    (* This input makes the results written in a file "symC3v" *)

symOrb["C2v", {{1, 0, 0}, {0, 0, 0}}, {{0, 1}}];   (* H$_2$O *)

symOrb["C3v", {{0, 0, 0}, {1, 0, 0}, {1, 0, 0}, {2, 1, 0}}, {0, 3}, "symC3v"];
    (* P(CF$_3$)$_3$ *)

symOrb["C3", {{1, 0, 0}, {1, 1, 0}, {0, 0, 0}, {0, 0, 0}}]
    (* C$_2$H$_6$; HCCH twisted angle$\neq$nπ/6 *)

IV. TEST RUN

Figure 3 shows a test run to construct the symmetry orbitals for a NH$_3$-shaped molecule with the s and p orbitals. The first line(a) is necessary at the beginning of using the program "symOrb". The next line(b) is the input data. The messages(c) appear during the calculation and include the correspondence between the atom sites and the coordinates. The lines in the example mean that the site a01 is located at (1, 0, 0), the site a02 ($-1/2$, $\sqrt{3}/2$, 0) and so on. The first three sites a01, a02, a03 are equivalent and make up one group. The site a04 alone forms the other group. The lines(d) show the symmetry orbitals without the radial functions and have a structure

```
                       (* Ammonia-type    20sec. SUN 4/1 *)
<<symOrb                                              ⌐ (A)
                                                      ⌐
symOrb["C3v", {{1,0,0},{0,0,0}},{0,1}, "file-NH3" ]   ⌐ (B)

  End of rSA
  End of setProj
Atomic positions: {{a01, a02, a03}, {a04}}  ->
                 1    Sqrt[3]          1   -Sqrt[3]            (C)
{{{1, 0, 0}, {-(-), -------, 0}, {-(-), --------, 0}}, {{0, 0, 0}}}
                 2      2              2      2

  End of sym
  End of remoDup
Generated SO's: 16, Expected SO's: 16
Normal End.

{{{a1 /z  C3v}, {a2}, {e/x, e/y}},

  {{6 a04 y00, 2 a01 y00 + 2 a02 y00 + 2 a03 y00,             (D)

   6 a04 y10, 2 a01 y10 + 2 a02 y10 + 2 a03 y10,

   Sqrt[3] a02 y1-1 - Sqrt[3] a03 y1-1 + 2 a01 y11 - a02 y11 - a03 y11},

   {2 a01 y1-1 - a02 y1-1 - a03 y1-1 - Sqrt[3] a02 y11 + Sqrt[3] a03 y11},

   {4 a01 y00 - 2 a02 y00 - 2 a03 y00, 4 a01 y10 - 2 a02 y10 - 2 a03 y10,

   6 a04 y11,

   -(Sqrt[3] a02 y1-1) + Sqrt[3] a03 y1-1 + 4 a01 y11 + a02 y11 + a03 y11,

   Sqrt[3] a02 y1-1 - Sqrt[3] a03 y1-1 + 3 a02 y11 + 3 a03 y11},

   {2 Sqrt[3] a02 y00 - 2 Sqrt[3] a03 y00, 6 a04 y1-1,

   2 Sqrt[3] a02 y10 - 2 Sqrt[3] a03 y10,

   4 a01 y1-1 + a02 y1-1 + a03 y1-1 + Sqrt[3] a02 y11 - Sqrt[3] a03 y11,

   3 a02 y1-1 + 3 a03 y1-1 - Sqrt[3] a02 y11 + Sqrt[3] a03 y11}}}
```

Fig. 3.   Test run output on display.

```
5 al /z  C3v
0    1    1
0    4  6.000000
0    3    1
0    3  2.000000      0   2  2.000000      0   1  2.000000   (A)
```

Omitted for space

```
**  Nsym, Isyml, Jsyml  **
  4
  1    1    1    1          (B)
  1    1    1    0
```

```
C3v  Positions of atoms
4
1.    0.    0.    1
-0.5   0.866025   0.   2    (C)
-0.5  -0.866025   0.   3
0.    0.    0.    4
```

Fig. 4.   Contents of test run output file after the formatting.

{{names}, {symmetry orbitals}}. Symmetry orbitals belonging to a representation A_1 constitute the wavefunctions in a_1 one-electron states. The results for the a_1 orbitals mean as follows:

$6y_{00}(a_4),$

$2y_{00}(a_1)+2y_{00}(a_2)+2y_{00}(a_3),$

$6y_{10}(a_4),$

$2y_{10}(a_1)+2y_{10}(a_2)+2y_{10}(a_3),$

$\sqrt{3}y_{1-1}(a_2)-\sqrt{3}y_{1-1}(a_3)+2y_{11}(a_1)-y_{11}(a_2)-y_{11}(a_3).$

Figure 4 shows the contents of output file "file-NH3" which has been processed by a formatting FORTRAN program named "FORMSYM". The formatted file will be directly obtained with the next version of symOrb coded in the second version of Mathemetica. The lines(A) are the symmetry orbital data for the DV-Xα program "SCAT". The lines(B) are parameters concerned with the reading of symmetry orbital data. They are required in the main input file F05 for the program "SCAT". The lines(C) show the coordinates of atomic sites.

Note added in proof: The classification procedure explained in the section 2.2 has been replaced with that according to a relationship in the group theory. The method is described by Meyer [§ 3 in *Int. J. Quant. Chem.*, **33**, 445 (1988)]. The numerical integration in the text is still used to check the obtained symmetry orbitals.

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