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GENERATION OF SYMMETRY-ADAPTED FUNCTIONS FOR MOLECULAR CALCULATIONS

Lubomír SKÁLA
Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 12116 Prague 2, Czechoslovakia

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PROGRAM SUMMARY

Title of program: SYMMET

Catalogue number: AAPD

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Computer: ICL 4-72; *Installation*: University Regional Computing Centre, Prague

Computer on which it is operable: IBM 360/370 (FORTRAN H compiler)

Operating system: MULTIJOB

Programming language used: FORTRAN (IBM version)

High speed storage required: 2208 words

No. of bits in a word: 32

Overlay structure: none

No. of magnetic tapes required: none

Other peripherals used: line printer

No. of cards in combined program and test deck: 1254

Card punching code: EBCDIC

Keywords: electronic structure, molecule, symmetry-adapted function, point group, irreducible representation

Nature of physical problem
The group theory is used for the classification of energy states of molecules and the transformation of the eigenvalue problem to a quasidiagonal form.

Method of solution
Symmetry-adapted linear combinations of the basis functions and other information are obtained by means of the symmetrizing operator.

Restrictions on the complexity of the problem
All the most important point groups are included. There is no restriction on the number of the basis functions.

Typical running time
The running time is usually negligible in comparison with other steps of the electronic structure calculation. The test run took 30 s on an ICL 4-72.

LONG WRITE-UP

1. Some relevant group theoretical results

The generalized matrix eigenvalue problem

$$Hc = ESc, \tag{1}$$

where

$$H_{\mu\nu} = \int \phi_\mu^* \hat{H} \phi_\nu \, d\tau , \tag{2}$$

$$S_{\mu\nu} = \int \phi_\mu^* \phi_\nu \, d\tau \tag{3}$$

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and $\{\phi_\mu\}$ are the LCAO basis functions is one of the most frequently solved problems in quantum chemistry.

It is known [1] that for a molecule which has a point symmetry it is possible to introduce a new symmetry-adapted basis in which the Hamiltonian H and also the overlap matrix S have a quasidiagonal form. Symmetry-adapted linear combinations of the basis functions can be found by applying the symmetrizing operator to the basis functions ϕ_μ, $\mu = 1, ..., N$

$$\phi_t^{(i)} = \frac{d_i}{|G|} \sum_{R \in G} D^i(R)^*_{ts} R\phi_\mu \,. \tag{4}$$

Here, G is a point group with elements $R, S, ...$, $D^i(R)$ is the matrix representative of R and is of dimension d_i, $|G|$ is the order of group G and $\phi_t^{(i)}$ is a symmetry-adapted function belonging to row t of the irreducible representation Γ_i. The subscript s is fixed during the calculation.

We re-write formula (4) in a more convenient form

$$\phi_\mu^s = \sum_\nu Q_{\nu\mu}\phi_\nu \tag{5}$$

which states that the symmetry adapted functions ϕ_μ^s are linear combinations of the original functions ϕ_ν. The coefficients of the linear combination are arranged in the matrix Q column by column.

The Hamiltonian and overlap matrix have in this basis a quasidiagonal form

$$\{Q^T H Q\}_{\text{quasi}} = \begin{bmatrix} \square & & 0 \\ & \square & \\ 0 & & \ddots \end{bmatrix}, \tag{6}$$

$$\{Q^T S Q\}_{\text{quasi}} = \begin{bmatrix} \square & & 0 \\ & \square & \\ 0 & & \ddots \end{bmatrix} \tag{7}$$

and the original eigenvalue problem becomes

$$\{Q^T H Q\}_{\text{quasi}} c_{\text{quasi}} = E\{Q^T S Q\}_{\text{quasi}} c_{\text{quasi}} \,. \tag{8}$$

Two functions $\phi_t^{(i)}$ belong to different blocks if they correspond to different irreducible representations i or to different rows t of the same representation. For an irreducible representation of order n, the blocks corresponding to $t = 1, ..., n$ are the same assuming the same order of functions ϕ_μ to which the symmetrizing operator is successively applied. Therefore, in this case it is sufficient to calculate and diagonalize only one from these blocks. Having the eigenvalues and eigenvectors of the quasidiagonal eigenvalue problem (8) the original eigenvectors can be obtained by the back transformation

$$c = Qc_{\text{quasi}} \,. \tag{9}$$

During this transformation, the originally identical eigenvectors corresponding to $t = 1, ..., n$ become linearly independent so that all necessary eigenvectors are correctly obtained. Assuming the eigenvectors c_{quasi} to be normalized, the eigenvectors c are also normalized.

2. Description of the program

The code consists of two subroutines SYMMET and ASSGRP and four BLOCK DATA.

The subroutine SYMMET is called by the main program written by the user. It calls the subroutine ASSGRP. The subroutine SYMMET verifies first whether the molecule has the symmetry specified by the user. After that the matrix Q and other necessary information is calculated.

The following types of real basis functions can be used: s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$. The form of the radial part of these functions can be arbitrary. Transformation properties of these 9 functions for alltogether 72 different symmetry operations are stored in BLOCK DATA. These 72 symmetry operations enable to work with the following point groups: C_i, C_2, C_{1h}, C_{2v}, D_2, C_{2h}, C_4, S_4, C_3, D_3, C_{3v}, C_6, C_{3h}, D_4, C_{4v}, D_{2d}, D_6, C_{6v}, D_{3h}, T, O and T_d. In cases when the molecule has symmetry C_i, it is possible to perform the direct product of an arbitrary from the above mentioned groups with the group C_i. It enables one to take into account further groups including O_h. All information about the groups, i.e. names of the groups and their irreducible representations, the list of their operations and the elements of the matrix representatives are stored in BLOCK DATA. If the user does not give any from the above mentioned groups explicitly, the program uses all these groups (multiplied by C_i if the molecule has this symmetry) and selects from them the group giving the lowest order of the blocks of the quasidiagonal Hamiltonian matrix. If there is more than one such group, it takes that one leading to the greatest number of

blocks. If there is yet more than one such group the last of them is taken.

3. COMMON variables

The common blocks contain the following information:

COMMON SYM1

1) Characters or elements of the matrices $D^i(R)_{ts}$ for $s = 1$ (arrays PCI, ..., PO). For isomorphic groups, they are given for one group only.

2) The list of group operations (arrays OCI, ..., OTD).

3) Names of irreducible representations (arrays RCI, ..., RTD).

To avoid complex arithmetic, complex conjugated one-dimensional irreducible representations are taken as one two-dimensional reducible representation (groups C_4, S_4, C_3, C_6, C_{3h} and T).

If a symmetry operation is applied to a given basis function ϕ_μ, a linear combination of the basis functions is obtained. In order to describe it completely, one must give:

1) The number of functions in the linear combination (COMMON SYM2, arrays NE, ..., NSGV3).

2) The type of the functions in the linear combination (COMMON SYM3, arrays IE, ..., ISGV3).

3) The coefficients of the linear combination (COMMON SYM4, arrays CE, ..., CSGV3).

Four BLOCK DATA are used to store this information in the common blocks.

The last common block SYM5 consists of working arrays. For a given group, the information stored in SYM1, ..., SYM4 is transferred to SYM5 by means of the subroutine ASSGRP.

4. Description of formal parameters

All input data are transferred to the subroutine SYMMET by means of its formal parameters. They have the following meaning.

LOGICAL*1 SEARCH – If SEARCH = T and GROUP = 0, the symmetry giving the greatest reduction of the order of the eigenvalue problem will be found by SYMMET. If GROUP ≠ 0, the value of SEARCH has no meaning.

INTEGER*4 GROUP – If GROUP = 0, no symmetry is given by the user. If SEARCH = F, return to the calling program. Other values have the following meaning: 1 = C_i, 2 = C_2, 3 = C_{1h}, 4 = C_{2v}, 5 = D_2, 6 = C_{2h}, 7 = C_4, 8 = S_4, 9 = C_3, 10 = D_3, 11 = C_{3v}, 12 = C_6, 13 = C_{3h}, 14 = D_4, 15 = C_{4v}, 16 = D_{2d}, 17 = D_6, 18 = C_{6v}, 19 = D_{3h}, 20 = T, 21 = O, 22 = T_d. All group operations are considered with respect to the origin of the coordinate systems. The coordinate system for D_{6h} and its subgroups C_3, D_3, C_{3v}, C_6, C_{3h}, D_6, C_{6v} and D_{3h} (or for their direct product with C_i) must be oriented in such a way that one corner of the hexagon (triangle) is directed in the direction of y-axis. In the opposite case, the subroutine SYMMET does not find the symmetry; in case of SEARCH = T and GROUP = 0 a subgroup instead of the correct group will be probably found.

LOGICAL*1 MULTCI – If MULTCI = T, the subroutine SYMMET verifies first whether the molecule has the symmetry C_i. If this is the case, the direct product of the given group with C_i is considered. If SEARCH = T and GROUP = 0, its value has no meaning as the program tests whether the molecule has the symmetry C_i in any case.

INTEGER*4 NSET – The total number of basis sets. The basis set must consist of s or p_x, p_y, p_z or d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, $d_{3z^2-r^2}$ functions, respectively.

INTEGER*4 SET(NSET) – The values of SET(I) can be arbitrary except that they must be different for different basis sets. The same basis sets are those which have the same angular (s, p or d) and radial part. They can be located on different atoms. For example, for the basis sets 1s(H_1), 1s(H_2), 1s(O), 2s(O), 2p(O) of the H_2O molecule, one can put 1s(H_1) = 1s(H_2) = 1, 1s(O) = 2, 2s(O) = 3, 2p(O) = 4.

REAL*8 XSET(NSET), YSET(NSET), ZSET(NSET) – XSET(I), YSET(I) and ZSET(I) are the Cartesian coordinates of the Ith basis set. Arbitrary units can be used, however, the basis sets must be in symmetric positions with an accuracy better than 0.0001 units. The square of this value is given in the DATA statement in the subroutine SYMMET (variable ZERO2) and can be changed.

INTEGER*4 NAO – The total number of atomic orbitals. The atomic orbitals are numbered from 1 to NAO.

INTEGER*4 AOL(NSET), AOU(NSET) – The atomic orbitals of the Ith basis set have the numbers AOL(I), ..., AOU(I).

INTEGER*4 TYPAO(NAO) – TYPAO(I) is the type of the Ith atomic orbital. The type is coded in the following way: 1 = s, 2 = p_x, 3 = p_y, 4 = p_z, 5 = d_{xy}, 6 = d_{xz}, 7 = d_{yz}, 8 = $d_{x^2-y^2}$, 9 = $d_{3z^2-r^2}$. p- or d-functions in a given set must be arranged in the order 2, 3, 4 or 5, 6, 7, 8, 9, respectively.

LOGICAL*1 PRINT – If PRINT = F, no information is printed during the calculation.

INTEGER*4 NDIM – The dimension used in the declaration of the matrix Q in the calling program. It can be different from NAO.

The results are in the following formal parameters:

LOGICAL*1 SYM – If SYM = F, the molecule has not the given symmetry (for 1 ⩽ GROUP ⩽ 22) or no symmetry was found (for SEARCH = T and GROUP = 0) or symmetry adapted functions were not successfully generated or no reduction of the order of the eigenvalue problem was obtained.

REAL*4 NAME – The name of the symmetry (FORMAT(A4)).

INTEGER*4 NBLOCK – The number of blocks of the quasidiagonal eigenvalue problem.

INTEGER*4 LOW(20), UPP(20) – LOW(I) and UPP(I) give the position of the Ith block.

REAL*4 REPR(2,20) – The Ith block corresponds to the irreducible representation (REPR(J, I), J = 1,2) (FORMAT(2A4)).

LOGICAL*1 COPY(20) – If COPY(I) = T, the Ith block corresponds to the second or third row of a two- or three-dimensional representation so that this block need not be diagonalized.

REAL*8 Q(NDIM, NDIM) – The coefficients of the symmetry-adapted linear combinations of the basis functions stored column by column.

GROUP – If input GROUP = 0 and output SYM = T the input GROUP is replaced by GROUP found by the program. In other cases, it remains unchanged.

There is one machine-dependent constant in the program. The constant MACHEP should be the smallest positive real number for which 1 + MACHEP > 1 on the computer (DATA statement in the subroutine SYMMET). It is used in the test of a linear dependence of symmetry-adapted linear combinations. Its value is not critical.

5. Output and error diagnostic

If PRINT = T, the following output is printed:

1) The information whether the given symmetry (and C_i if MULTCI = T) was found or not.

2) The list of the blocks with their orders and the names of the corresponding irreducible representations.

3) In the case when SEARCH = T and GROUP = 0 the information ad 1) and 2) for all groups starting from GROUP = 1 to GROUP = 22. The group giving the greatest reduction of the order of the eigenvalue problem is then taken.

If PRINT = T, the error diagnostic is printed in the following cases:

1) The molecule has not a given symmetry.

2) MULTCI = T and the symmetry C_i was not found (warning).

3) The number of symmetry-adapted functions is different from NAO.

4) No reduction of the order of the eigenvalue problem was obtained.

6. Test run

The test run corresponds to two identical atoms with s, p, d-basis. The coordinates of the atoms are (0, 0, −1) and (0, 0, 1). All necessary data are given in the DATA statement in the main program.

Acknowledgements

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Reference

[1] C.J. Bradley and A.D. Cracknell, The mathematical theory of symmetry in solids (Clarendon Press, Oxford, 1972).

TEST RUN OUTPUT

```
SYMMETRY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       AG            9
  2       AU            9

SYMMETRY C2

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A     G       5
  2       B     G       4
  3       A     U       5
  4       B     U       4

SYMMETRY C1H

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A'    G       5
  2       A''   G       4
  3       A'    U       4
  4       A''   U       5

SYMMETRY C2V

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       4
  2       B2    G       2
  3       A2    G       1
  4       B1    G       2
  5       A1    U       4
  6       B2    U       2
  7       A2    U       1
  8       B1    U       2

SYMMETRY D2

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A     G       4
  2       B3    G       2
  3       B1    G       1
  4       B2    G       2
  5       A     U       1
  6       B3    U       2
  7       B1    U       4
  8       B2    U       2

SYMMETRY C2H

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       AG    G       5
  2       BG    G       4
  3       AU    U       5
  4       BU    U       4

SYMMETRY C4

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A     G       3
  2       B     G       2
  3       E     G       4
  4       A     U       3
  5       B     U       2
  6       E     U       4

SYMMETRY S4

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A     G       3
  2       B     G       2
  3       E     G       4
  4       A     U       2
  5       B     U       3
  6       E     U       4

SYMMETRY C3

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A     G       3
  2       E     G       6
  3       A     U       3
  4       E     U       6

SYMMETRY D3

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       3
  2       E     G       3
  3       E     G       3
  4       A2    U       3
  5       E     U       3
  6       E     U       3

SYMMETRY C3V

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       3
  2       E     G       3
  3       E     G       3
  4       A1    U       3
  5       E     U       3
  6       E     U       3

SYMMETRY C6

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A     G       3
  2       E1    G       2
  3       E2    G       4
  4       A     U       3
  5       E1    U       2
  6       E2    U       4

SYMMETRY C3H

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A'    G       3
  2       E'    G       2
  3       E''   G       4
  4       A''   U       3
  5       E'    U       4
  6       E''   U       2

SYMMETRY D4

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       3
  2       B1    G       1
  3       B2    G       1
  4       E     G       2
  5       E     G       2
  6       A2    U       3
  7       B1    U       1
  8       B2    U       1
  9       E     U       2
 10       E     U       2

SYMMETRY C4V

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       3
  2       B1    G       1
  3       B2    G       1
  4       E     G       2
  5       E     G       2
  6       A1    U       3
  7       B1    U       1
  8       B2    U       1
  9       E     U       2
 10       E     U       2

SYMMETRY D2D

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       3
  2       B1    G       1
  3       B2    G       1
  4       E     G       2
  5       E     G       2
  6       A1    U       1
  7       A2    U       1
  8       B2    U       3
  9       E     U       2
 10       E     U       2

SYMMETRY D6

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       3
  2       E2    G       1
  3       E2    G       1
  4       E1    G       2
  5       E1    G       2
  6       A2    U       3
  7       E2    U       1
  8       E2    U       1
  9       E1    U       2
 10       E1    U       2

SYMMETRY C6V

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1    G       3
  2       E2    G       1
  3       E2    G       1
  4       E1    G       2
  5       E1    G       2
  6       A1    U       3
  7       E2    U       1
  8       E2    U       1
  9       E1    U       2
 10       E1    U       2

SYMMETRY D3H

MULTIPLIED BY C1

WAS FOUND

BLOCK REPRESENTATION ORDER

  1       A1'   G       3
  2       E'    G       1
  3       E'    G       1
  4       E''   G       2
  5       E''   G       2
  6       A2''  U       3
  7       E'    U       2
  8       E'    U       2
  9       E''   U       1
 10       E''   U       1

SYMMETRY T

WAS NOT FOUND

SYMMETRY O

WAS NOT FOUND

SYMMETRY TD

WAS NOT FOUND
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SYMMETRY D3H
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MULTIPLIED BY C1

WAS FOUND

AS A RESULT OF SEARCHING FOR THE GROUP

GIVING THE GREATEST REDUCTION OF THE ORDER OF THE EIGENVALUE PROBLEM

BLOCK REPRESENTATION ORDER

  1       A1'  G       3
  2       E'   G       1
  3       E'   G       1
  4       E''  G       2
  5       E''  G       2
  6       A2'' U       3
  7       E'   U       2
  8       E'   U       2
  9       E''  U       1
 10       E''  U       1


SYM T

NAME D3H

GROUP 19

NBLOCK 10

REPR       LOW UPP COPY

A1'  G      1   3    F
E'   G      4   4    F
E'   G      5   5    T
E''  G      6   7    F
E''  G      8   9    T
A2'' U     10  12    F
E'   U     13  14    F
E'   U     15  16    T
E''  U     17  17    F
E''  U     18  18    T

Q

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