Molcas point group handling.

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Abstract: *Symmetry helps in QC computations. Also it facilitates input and output, by providing a classification of states and orbitals. It is also necessary in order to understand and compare to experimental results.*

In MOLCAS (as for most program packages) orbitals and states are symmetry adapted to the point groups D_2h and its subgroups.

In the following slides, we will learn how to use symmetry in inputs and how to understand the symmetry information in the results.

Molcas point group handling.

Symmetry groups: Default is C_1(no symmetry). Input for D_{2h} or its subgroups (D_{2h}, C_{2v}, C_{2h}, D_2, C_2, C_s, C_i) is specified in GATEWAY (or SEWARD) as one, two, or three symmetry generators.

Example: The reflection operator with Schönflies symbol σ_{xy} will change sign of the z coordinate but leaves the x and y unchanged. The rotation operator with Schönflies symbol $C_2(z)$ will change the sign of the x and y coordinates, but not of z. These two symmetry operators generate the point group C_{2h}.

Example: The same group can also be generated e.g. by the two generators σ_{xy} and i,where i is the inversion operator which changes the sign of all three coordinates, i.e. $\mathbf{r} \to -\mathbf{r}$

The operators and point groups that Molcas can handle are precisely those that change the sign of one or more components of the nuclear coordinates.

The possible symmetry generators.

The possible symmetry operators are written using letters X,Y,Z in Molcas:

Molcas	Schönflies	Image of $\mathbf{r} = (x, y, z)$ is:
X	σ_{yz}	$(-x, y, z)$
Y	σ_{xz}	$(x, -y, z)$
Z	σ_{xy}	$(x, y, -z)$
XY	C_z	$(-x, -y, z)$
XZ	C_y	$(-x, y, -z)$
YZ	C_x	$(x, -y, -z)$
XYZ	i	$-\mathbf{r} = (-x, -y, -z)$

The point group can be specified by the input keyword Symmetry in GATEWAY, followed by one to three symmetry operators, which generate the group, e.g.

```
    Symmetry
     Y X                        or        Symmetry = X Y
```

Symmetry input in GATEWAY: H_2O.

```
&GATEWAY &END
Title
 H2O geom optim, using the ANO-S basis set.
Symmetry
  Y  X
Basis set
O.ANO-S...3s2p1d.
O  0.0000   0.0000 0.0000    Angstrom
End of basis
Basis set
H.ANO-S...2s1p.
H  0.7586   0.0000  0.5043   Angstrom
End of basis
End of input
```

Other symmetry inputs in GATEWAY: H_2O.

Please note that there are several different ways that input can be given to GATEWAY:

```
&GATEWAY &END          &GATEWAY &END          &GATEWAY &END
Title                  Title                  Title
 H2O, 6-31G* basis  Any title line            This is the first
COORD                  COORD                   and this the second
 H2O.xyz               H2O.xyz                 of three title lines
GROUP                  GROUP                  COORD= H2O.xyz
 Y  X                  FULL                   GROUP=NOSYM
BASIS=6-31G*           BASIS=6-31G*           BASIS
End of input           End of input           6-31G*
                                              End of input
```

Here are three examples, using the keyword COORD to specify the name of an 'XYZ file'.
Keywords GROUP and BASIS, if used, should be after COORD. Note, in the third example, the
use of NOSYM inhibits symmetry. GROUP=FULL is the default. It also may move the
molecules. This can be inhibited by NOMOVE.

The symmetry input, summary:

- The symmetry point group is specified in GATEWAY by keyword GROUP.

- You can specify a precise set of generators by using the symbols "x", "y", ..., "xyz".

- The order, and possibly the name used, of the irreps will depend on the order and type of the generators (Ex: 'X Y',' Y X', or 'XY X' could all be used for the same group).

- You can let GATEWAY decide which group to use by using GROUP=FULL. The set of generators chosen may be different, and/or in different order, than you would have chosen.

- You can use no symmetry at all: GROUP=NOSYM.

- The 'old' input can also be used, keyword SYMMETRY. This can also be placed in SEWARD instead of GATEWAY. But then the coordinates must be given in the input, together with basis set information, **and symmetry unique coordinates only**, i.e. old style input. This may be convenient, and it is necessarily the only type of input if you use inline basis sets.

Symmetry output: H_2O.

From GATEWAY:

```
--- Group Generators ---
Reflection in the xz-plane
Reflection in the yz-plane



Character Table for C2v


              E    s(xz) s(yz) C2(z)
      a1      1      1     1      1   z
      b1      1     -1     1     -1   y, yz, Rx
      b2      1      1    -1     -1   x, xz, Ry
      a2      1     -1    -1      1   xy, Rz, I
```

From SEWARD:

```
Basis set specifications :
Symmetry species            a1  b1  b2  a2
Basis functions             11   4   7   2
```

Order and labelling of irreps.

The QC programs all print out the table of atomic coordinates. All orbital lists give standard symmetry labels of the irreps, but their order depend on your symmetry specifications. This may e.g. interchange b_1, b_2 and b_3 labels, compared to IUPAC standards.

For the same reason, it is quite common to see conflicting irrep labels in the literature.

Symmetry output from SCF: H2O.

```
Cartesian coordinates:
-------------------------------------------------
No.  Label      X          Y          Z

-------------------------------------------------

 1    O         0.00000    0.00000    0.00000
 2    H         1.43354    0.00000    0.95295
 3    H        -1.43354    0.00000    0.95295

-------------------------------------------------

Nuclear repulsion energy =    9.643629


Orbital specifications :
Symmetry species               1    2    3    4
                              a1   b1   b2   a2
Frozen orbitals                0    0    0    0
Occupied orbitals              3    1    1    0
Deleted orbitals               0    0    0    0
Total number of orbitals      11    4    7    2
Number of basis functions     11    4    7    2
```

The SCF orbitals are symmetry orbitals.

```
Molecular orbitals for symmetry species 1: a1


        Orbital          1          2          3          4          5
        Energy     -20.5486    -1.3768    -0.5845     0.1122     0.4937
        Occ. No.     2.0000     2.0000     2.0000     0.0000     0.0000


   1 O    1s        -1.0004    -0.0415     0.0338    -0.1171    -0.1231
   2 O    2s        -0.0029     0.7002     0.4567    -0.9257    -0.7620
   3 O    3s        -0.0004    -0.0659     0.0754    -0.3193    -0.3408
   4 O    2pz       -0.0014     0.0724    -0.8213    -0.2858    -0.2152
   5 O    3pz        0.0005    -0.0434     0.0101    -0.1425    -1.1063
   6 O    3d0        0.0000     0.0017    -0.0222    -0.0031    -0.0025
   7 O    3d2+      -0.0002     0.0084    -0.0064    -0.0105    -0.0499
   8 H    1s         0.0013     0.2950    -0.2983     0.9874     0.6368
   9 H    2s         0.0001    -0.0598     0.0549     0.6612     0.1489
  10 H    2px       -0.0010    -0.0616     0.0484    -0.0306    -0.3183
  11 H    2pz       -0.0007    -0.0356    -0.0198    -0.0206    -0.0811
```

Molecular orbitals for symmetry species 2: b1

Orbital	1	2
Energy	-0.5177	0.5499
Occ. No.	2.0000	0.0000

			1	2
1	O	2py	0.9558	0.0243
2	O	3py	0.0313	1.0590
3	O	3d1-	0.0215	0.0039
4	H	2py	0.0638	-0.1300

Molecular orbitals for symmetry species 3: b2

Orbital	1	2	3
Energy	-0.7698	0.2540	0.5552
Occ. No.	2.0000	0.0000	0.0000

			1	2	3
1	O	2px	0.6299	1.2134	-1.5852
2	O	3px	-0.1044	0.7924	-2.0016
3	O	3d1+	0.0344	0.0446	-0.0362
4	H	1s	0.5377	-3.1469	3.3586
5	H	2s	-0.0932	-2.0792	1.3211
6	H	2px	-0.0469	0.0979	-0.2668
7	H	2pz	-0.0513	0.0666	-0.1448

SLAPAF, MCLR, McKinley:

In input to SLAPAF, it may be necessary to use a symmetry operator, to distinguish symmetry-equivalent atoms:

```
R1 = BOND O H
A1 = ANGLE H O H(X)
```

All the vibrational frequencies are computed by MCLR/McKinley, also for vibrations that break the symmetry (Output has been edited) :

```
Symmetry a1          0.00           1748.78           4135.24
Intensity:      0.387E-11      0.976E+02         0.426E+02


Symmetry b1          i21.17            0.00
Intensity:      0.284E+03      0.237E-05

Symmetry b2          i22.59            0.00           4247.54
Intensity:      0.943E+02      0.811E-07         0.152E+03
```

Higher symmetry groups:

Higher symmetry groups can contain threefold axes, improper rotations, fivefold axes, etc. They have irreducible representations with dimension two or more, and orbitals or wave functions can be symmetry degenerate. Such groups are not supported by Molcas, even if some subgroups can be used. This has two consequences:

(1) The calculations can break symmetry, i.e. the computed electronic wave function has lower symmetry than that implied by the nuclear coordinates. This may lead to hysteresis phenomena and similar problems.

(2) Symmetry-equivalent components of degenerate orbitals may belong to different irreps of the subgroup and complicate the specification of states and interpretation of results.

GSSORB usually gives accurately symmetry-adapted orbitals also for higher symmetry.

RASSCF can be forced to respect linear symmetries (C , Cv, Dh) by keyword LINEAR, and atoms (O(3)) by keyword ATOM.