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A Treatment of Symmetry in MO Calculations

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A method of using molecular symmetry in MO calculations is described. The method consists of determining the point group of the molecule, and establishing equivalence tables for atoms equivalent under various applicable symmetry operations. Ways of setting up symmetry orbitals are outlined. The determination of the symmetry species of molecular orbitals, of configurations and states of molecules are described.

Over the past several years we have developed a general, automatic treatment of molecular symmetry for MO calculations. Although developed within a single system, as subroutines of a single computer program (CNDO/S) [1], we feel these methods are sufficiently general to be adaptable to any program, and to be useful in many other contexts. Consequently, we offer herewith a description of this system.

The only input required to the program, and particular to the symmetry handling routines are the coordinates and the atomic numbers of the atoms [1]. At the time that the coordinate cards are read, each atom is assigned an order number (i.e., the atoms are numbered in the order of the appearance of the coordinate cards). To provide a record, the coordinates, with atomic and order numbers, are printed out. In addition, a "diagram" of the molecule is "drawn" by the high speed printer by projecting the molecule on the coordinate plane in which its dimensions are maximal.

The first step is a translation of the origin to the center of mass of the system. Next, a coordinate transformation to the principal axis system is performed.[1] For this purpose, the moment of inertia matrix (MIM) is calculated and diagonalized.[2]

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[1] Only if the molecule under consideration is an *ion* (i.e., carries a net charge), is this step modified; in this case the origin transformation is made to the centroid of positive charge. This is done so that a calculation of the dipole moment as $\Sigma_i \langle er_i \rangle$, which is origin independent for neutral systems, retains its meaning for charged ones.

[2] Since this is a 3×3 matrix, it may, of course, be solved in any other convenient way. The presence of diagonalization routines in most MO programs makes diagonalization convenient.

At this point, three cases which require distinct handling become distinguishable: the asymmetric, the symmetric, and the spherical top, characterized by no degeneracies in the eigenvalues of the MIM, one degenerate pair and one distinct value, and three degenerate values, respectively. The treatments of these cases will be discussed further in the next section. The eigenvectors of the MIM can now serve directly as a transformation matrix, rotating the coordinates into the principal axis system. This is always done for asymmetric top molecules. However, for symmetric and spherical tops, where two or all three eigenvectors are arbitrary, nothing is gained; on the contrary, matters are often obscured if this rotation is carried out. For the symmetric top, a rotation of the distinct axis into the z-axis is performed; no other rotations are performed, on the assumption that the orientation of the molecule chosen by the investigator is likely to be more useful than the arbitrary orientation achieved by the program.

DETERMINATION OF POINT GROUP AND EQUIVALENCE TABLES

After the molecule is properly oriented, we proceed to the determination of the point group, and at the same time accumulate information subsequently needed about the equivalence of atoms. This information is collected in two tables for each symmetry element, the ON table and the BY table, which are discussed in more detail in a later section.

Asymmetric Tops

Only eight point groups need to be considered for asymmetric tops: C_1, C_2, C_s, C_i, C_{2v}, C_{2h}, D_2, and D_{2h}. All symmetry operations are binary, i.e., relate at most two atoms. Since we have converted our coordinate system to a principal axis system, all symmetry axes coincide with the coordinate axes, all planes of symmetry coincide with the planes defined by two coordinate axes, and the center of symmetry (if one exists) lies at the origin.[3] At most, three symmetry elements are needed to define the point group. The ones we have chosen are indicated in Table I.

We begin by examining the xy-plane. We scan all atoms, and place into an ON table the order number of any atoms lying in this plane (i.e., for which $z = 0 \pm .01$ A). For any atom which does *not* lie on the plane, we scan all other atoms to find one for which $x_i = x_j$, $y_i = y_j$ and $z_i = -z_j$, all within .01 A. For safety, one may further verify that the atomic numbers of the equivalently located atoms are equal, although we have chosen to omit this test since it seems highly improbable to find unlike atoms, in pairs, at appropriate coordinates. Once one corresponding atom has been found, the scan is terminated since it would require

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[3] This holds even for charged molecules since the centroid of positive charge must coincide with the center of gravity if a center of symmetry exists.

TABLE I

The Symmetry Elements Chosen to Define the Various Point Groups of Asymmetric Top Molecules[a]

	C_1	C_2	C_s	C_i	C_{2v}	C_{2h}	D_2	D_{2h}
σ_{xy}	√	√	(A)	√	√	A	√	A
σ_{xz}	√	√	(A)	√	A	√	√	A
σ_{yz}	√	√	(A)	√	A	√	√	A
$C_2{}^2$	√	A		√			A	
$C_2{}^x$							A	
i	√		√ (*if* σ_{xy})	B		B		

[a] Means element checked, letters A through C refer to the format of the equivalence tables and indicate symmetry elements used to classify the molecule. A letter in parentheses indicates that one, but only one, of the elements is present.

coincident atoms to find a second match; as a check of coordinates this seems expensive and unreliable, hence it is not done. When a match has been found, the pair of atoms is inscribed into the BY table.

If we encounter an atom which lies neither on the plane, nor has a matching partner, the element (in this case the xy-plane) is rejected as a symmetry element, and we proceed to the next plane. In this manner all three planes, xy, xz and yz are checked. If all three are planes of symmetry, the molecule belongs to D_{2h} ; if two (xz and yz) are, it belongs to C_{2v}, and the determination is complete. If only one plane was a symmetry plane, and this was not xy, the molecule transforms as C_s ; if the plane was xy, we next check for a center.

All atoms i are checked for the presence of a partner j at $x_j = -x_i$, $y_j = -y_i$ and $z_j = -z_i$; if one is found, the order numbers of atoms i and j are entered into a BY table. If no partner is found, we check whether the atom lies at the origin; if so, its order number is stored in an ON table. The first atom we encounter which does not have an equivalent partner, nor lies at the origin, indicates that the molecule has no center of symmetry. If a center of symmetry is found in this manner (after σ_{xy} had been established), the molecule belongs to point group C_{2h}, if no center is found, the assignment is C_s.

If no plane of symmetry was found, we test the z-axis to determine if it is a 2-fold axis ($x_i = y_i = 0 \pm .01$ A for atoms on the axis, $x_i = -x_j$, $y_i = -y_j$, $z_i = z_j$ within .01 A for related pairs). If the z-axis *is* a symmetry axis, we check the y-axis (or x-axis) to distinguish C_2 and D_2 ; if the z-axis is *not* an axis we test for a center of symmetry to distinguish C_1 and C_i. This procedure uniquely determines the point group of any asymmetric top molecule.

Symmetric tops are slightly more difficult, since we have to determine the order of the unique axis, which has been made to coincide with the z-axis by the principal axis transformation. We deal here with several groups of point groups; C_p, C_{ph}, C_{pv}, D_p, D_{ph}, D_{pd} and S_{2p}, with all values of $p > 2$.

To proceed to the determination of p, we scan all atoms, collecting into an ON table the order numbers of all atoms lying on the z-axis (i.e., $x_i = y_i = 0 \pm .01$ A). For all atoms i not lying on the axis, we calculate the distance $\rho_i = (x_i^2 + y_i^2)^{1/2}$ from the z-axis. For each such atom i we now find all other atoms, j, k,..., which have the same values of z and ρ:

$$z_i = z_j = z_k = \ldots, \text{ Within .01 A,}$$
$$\rho_i = \rho_j = \rho_k = \ldots, \text{ Within .01 A.}$$

Unlike in the case of the asymmetric top, here we verify that the atomic numbers match. Atoms found in this way to be related by the z-axis are entered into a BY table. Since we know that the z-axis is a p-fold symmetry axis, at the end of this procedure all atoms must have been entered in the ON table, or be a member of a group in the BY table. Next we must ascertain that atoms in each group are truly equivalent under C_p. To do so let us define the angle α_{ij} which the radius vectors ρ_i and ρ_j from the z-axis to atoms i and j subtend at the z-axis. A necessary condition[4] for equivalence is that the angle α_{ij} between all nearest neighbors be the same. Calculation of the distance r_{ij} (or its square) between the pair of atoms i and j is equivalent to determination of the angle (and easier). Thus, we calculate r_{ij}^2 from each atom i to each atom j in the group, search for the smallest value, and test if, for each atom i, there are two (and just two) r_{ij}^2 which have this minimum value. If this condition is fulfilled, the group may be accepted as a group of equivalent atoms; if the condition is not fulfilled, we check equally with the second smallest distance (and in case of failure, successively larger distances). If the second smallest distance appears twice for each atom, we have two equivalent sets at the same value of z.

We thus have assigned all atoms which do not lie on the axis to groups. Each group should number p, or a small integral multiple of p atoms. We shall now assume that the number of atoms in the group with the lowest number is just p and thus that the z-axis is a p-fold axis.[5] We verify that the number in the other groups

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[4] Although this condition is not mathematically sufficient, it seems extremely improbable that we shall ever treat a molecule in which this insufficiency matters. See also footnote 5 below.

[5] We can conceive of hypothetical molecules in which we encounter only groups with various multiples of p but not with p itself; e.g. a sandwich compound of benzene, a central atom, and a planar cyclononatetraenyl radical would have a 3-fold axis, and equivalent groups of 6C's, 6H's, 9C's and 9H's. It seems, however, extremely improbable that such a molecule will ever be treated, and in the programs we have made no provision for this eventuality.

are either p, or a small multiple of (2 or 3 times) p. Since we have previously determined that the molecule is a symmetric top, we expect this procedure to be successful in determining the value of p, with a value of $p > 2$. Should the value of p obtained in this way be two, we still have the possibility of point groups D_{2d} or S_4. To check for this possibility we test for a S_4 axis.

In order to test for the presence of an S_4 axis, we rotate the molecule around the z-axis until one of the atoms, i, in the twofold equivalent groups lies in the xz-plane (if it does not already lie there). We then check for the presence of two other atoms, j and k, with $z_j = z_k = -z_i$, $x_j = x_k = y_i = 0$, $y_j = -y_k = x_i$, all within 0.01 A. We continue this process for at least one atom in each group. If all these tests are successful, a S_4 axis is established, and the molecule belongs to either D_{2d} or S_4. The two cases are readily distinguished by rotating the molecule again about the z-axis, this time by 45°, and testing whether the x-axis is now a 2-fold axis (D_{2d}) or not (S_4), in exactly the manner used for the asymmetric tops.

In case we have not found a p-fold axis with $p > 2$, nor an S_4 axis, we must conclude that the degeneracy in the MIM was accidental, and treat the molecule as an asymmetric top. Here, the lack of a unique determination of the principal axes may cause difficulties, but a rotation of some (or a maximum number) of atoms into the xz-plane may help. If the number of atoms in the various groups established in the determination of p does not behave in the expected way, we print an error message, and abandon the problem, at least until the reason for the lack of expected behavior is established.

Following determination of p in C_p, we test for σ_h and σ_v planes; the tests are quite analogous to those described for asymmetric top. A σ_h-plane must be the xy-plane, which is first tested. A σ_v plane is a plane which includes the z-axis and one member of a group of p atoms. If none of these originally lay in the xz-plane, we have found it convenient to further rotate the molecule around the z-axis to place an atom into this plane. A test for a single σ_v plane, and later for a single σ_d plane and $C_2(d)$ axis suffices, since the C_p axis generates the remainder of these elements from the first one. At this point D_{ph} is uniquely identified by the presence of all three symmetry elements, (C_p, σ_h and σ_v), C_{pv} by C_p and σ_v; C_{ph} by C_p and σ_h.

If neither σ_h nor σ_v was present, we proceed to test for a diagonal axis ($C_2(d)$), which is an axis normal to the z-axis and bisecting the angle between a pair of adjacent atoms of a p-fold group. This test is again most conveniently made by rotating the molecule around the z-axis until the desired axis coincides with the x-axis. If a $C_2(d)$ axis is found, the molecule belongs to point group D_p or D_{pd}, which are distinguished by testing for a σ_d plane. This would be the xz-plane in the orientation of the molecule used to test for the $C_2(d)$ axis. If σ_d is present, we have D_{pd}, if absent, D_p.

If no elements of symmetry beyond C_p have been found the molecule transforms as C_p or S_{2p}. The decision is readily made by testing for an S_{2p} axis by comparing each group of p atoms at a position $z_i \neq 0$ with a corresponding group at $-z_i$, and verifying that the groups are rotated relative to one another around the z-axis by an angle of $2\pi/2p$.

As for the asymmetric top, ON and BY tables are created for each symmetry element present. The maximum number of required symmetry elements is still three, of which one is the p-fold axis. The sequence of operations required in the case of each of the point groups of symmetric tops is indicated in Table II.

TABLE II

The Symmetry Elements Chosen to Define the Point Group of Symmetric Top Molecules[a]

	C_p	C_{pv}	C_{ph}	D_p	D_{pd}	D_{ph}	S_{2p}
C_p	C	C	C	C	C	C	C
σ_h	√	√	A	√	√	A	√
σ_v[b]	√	*A*	√	√	√	*A*	√
$C_2(d)$[c]	√			A	A		√
σ_v[c]				√	*A*		
S_{2p}	√						*C*

[a] Cf. Footnote to Table I.
[b] Through an atom.
[c] Halfway between atoms.

Spherical tops are even more complicated, since now we must find 3, 4 or 5 fold axes without the benefit of a principal axis transformation. First, a special equivalence table is readily constructed by calculating the distance of all atoms from the center of gravity, and assuming equivalent all those having the same distance and atomic number. Again, for most commonly treated molecules, we may assume that all such atoms are equivalent, although hypothetical molecules are readily generated for which this is not the case.

Next, the orders of the various axes must be determined. We have so far been unable to find a truly general recipe for this process. Probably sufficient for most cases is to test axes passing through any of a group of equivalent atoms and the center, and axes bisecting the angle between the radius vectors to pairs of nearest neighbor equivalent atoms. Once one such an axis is found, it is not difficult to generate the other appropriate axes (three mutually perpendicular C_4's in the O groups, four tetrahedrally oriented C_3's in the O and T groups, and the C_5's of the I groups), or to find the planes which will distinguish between T, T_d and T_h, between O and O_h, and between I and I_h. Since we have not programmed this problem we shall not discuss it further.

USE OF THE EQUIVALENCE TABLES

Having now determined the point group of the molecule and constructed equivalence tables for the atoms, we are in a position to apply this information in a number of different ways. It should be noted that, depending on the point group, a number of different equivalence tables are extant, and different formats may have to be used. As indicated, for each symmetry element found, we have two tables, ON and BY. The ON table gives the atoms that lie *on* the element, the BY tables the atoms that are related *by* the element. For twofold axes and planes, format A is used; it gives the number of atoms and the order numbers of each in the ON table, and the number of pairs of atoms, and, in successive words the order numbers of the members of the pair in the BY table. For the center, in a special format B, the ON table consists only of two words, a 1 or 0 depending on whether or not an atom lies on the center, and in a second word the order number of the atom on the center. The BY table has the A format. For axes of higher order the ON table has the A format, but the BY table, format C, contains the number of groups, the number in each group, and the order numbers of each group. Each pair (format A) or group (format C) is given only once, with order numbers in ascending order.

Construction of Symmetry Orbitals and Transformation of Integral Tables

The equivalence tables have all the information required to construct symmetry orbitals and the transformation matrices to transform integrals from an atomic orbital basis to a symmetry orbital basis. Although we have not chosen to make this transformation in our programs it is evident that the process is straightforward. The only additional information required is the behavior and relation of atomic orbitals under the symmetry transformations, information which we shall see below is readily obtained and already incorporated in later sections of our programs.

Assignment of Symmetry Species to Molecular Orbitals.

The equivalence tables, coupled with the atomic orbital symmetry information, can readily be used to determine the irreducible representation in which any given molecular orbital (based on an a.o. basis) transforms. If the transformation discussed in the preceding paragraph is made, this assignment is, of course, no longer required, since the basis members being combined in a MO all belong to the same irreducible representation. To classify a given MO, in a special subroutine, the equivalence tables are examined separately for each symmetry element concerned. First, the ON table is examined. The MO coefficients of each basis member of each atom in the ON table are tested. The first coefficient which is nonzero[6] determines the behavior, i.e., symmetric or antisymmetric, of the orbital under the element in

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[6] That is, greater than an arbitrarily chosen threshhold value.

question, depending on the behavior of the a.o. the coefficient represents. Thus, in the case of a C_{2v} molecule, if the first nonzero coefficient encountered on the xz-plane belongs to a p_y orbital, the MO is antisymmetric relative to that plane (i.e., transforms as either a_2 or b_1). If, instead of the p_y coefficient, the coefficient of the s or any other p orbital was nonzero, the MO would be symmetric with respect to the xz-plane.

Next, all subsequent entries of the ON table are similarly tested. However, since the symmetry of the MO has now been established, the result of the test is merely compared with the previous result. If a conflict arises, a special routine is invoked which is discussed below.

After the ON table has been examined in this fashion, the BY table is similarly checked. If the coefficient of a given orbital of the first of a pair of atoms is nonzero, its value is compared with the value of the corresponding coefficient of the second atom. If the two are equal[7] or equal and opposite in sign,[7] tests will be made whether the symmetry behavior agrees with that previously established. If none was previously established, the first set of coefficients encountered is used to establish the behavior, and all subsequent ones are checked. As an example, take again the coefficients of the p_y orbitals of a pair of atoms related by the xz-plane in a C_{2v} molecule. If the coefficients are equal,[7] the behavior is antisymmetric, if their sum is zero,[7] the MO is symmetric.

If the coefficient corresponding to the first of the pair of atoms is zero,[6] but the second nonzero,[6] the same tests are made. If either coefficient is nonzero,[6] and neither the sum nor the difference is nonzero,[7] or if the result of the determination is at variance with a previously determined behavior, the same corrective action routine mentioned above is called, cf. below.

When dealing with point groups in which more than one symmetry element is necessary (cf. Tables I and II), the process is repeated separately for each element, and the information is then combined into an irreducible representation. The process is repeated for each molecular orbital.

In case the symmetry checking leads to a conflict, the first assumption is that we are dealing with a group of accidentally or essentially degenerate orbitals. We then call a subroutine which determines whether the orbital under examination is degenerate[8] with the one above or the one below in energy. If this is not the case, an error message is printed, and the calculation continues as if the molecule transforms as C_1, or, at the programmer's option, may be abandoned at this point.

If we have encountered degenerate orbitals, the subsequent treatment differs depending on the point group of the molecule. If the point group has no degenerate representations, the degeneracy must be accidental; consequently a linear com-

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[7] Again, if the absolute value of the difference, or of the sum, is less than an arbitrary value.

[8] That is, whether the absolute value of the difference of the orbital energies is less than an arbitrary predetermined value.

bination of the degenerate orbitals can be formed to make the coefficients of the orbital conform to the expected symmetry. Once this is done, the symmetry checking of the degenerate orbitals is started all over.

However, if we are dealing with truly degenerate orbitals, transforming in the degenerate representations, we have found two alternative procedures. The first consists in treating the molecule as if it transformed as the highest nondegenerate subgroup of its true point-group. In that case, the above procedure is applicable: degenerate orbitals are resolved by linear combinations into pairs of orbitals transforming as the distinct representations of the nondegenerate subgroups. This procedure has been found generally applicable, giving adequate results for closed shell systems; only the orbital labeling is now appropriate to the subgroup rather than the true point group. A reversal of the procedures used for reducing symmetry, as, say, in the method of descending symmetries [2], can readily be applied to obtain the appropriate species symbols for the degenerate species. However, when we are dealing with partially occupied degenerate sets of orbitals, this procedure is inadequate.

An alternative procedure is to deal with groups of degenerate orbitals jointly. This is achieved by forming the sum of squares of the pairs of orbitals, i.e., in the LCAO formalism and subject to the ZDO approximation (as used in CNDO), by summing the squares of the coefficients of corresponding AO's in the set of degenerate orbitals. This sum of squares always transforms as the totally symmetric representation. Groups of orbitals are assigned to e (or t) representations by the fact of degeneracy, coupled with the failure of the symmetry checks on the individual orbitals.

The further distinction between various e (or t) species can frequently be made by use of binary symmetry elements for which the behavior of all components of a degenerate set (and hence any linear combination thereof) is the same. Thus g and u species can always be distinguished by examining the behavior of the individual orbitals with respect to i, primed and doubly primed species (e.g. e' and e'') by their behavior with respect to σ_h. Other such classifications depend on the individual point groups; thus e_1 and e_2 in C_{6v} or D_6 are distinguishable by the antisymmetric or symmetric behavior, respectively, under $C_6{}^3$, and e_{1g}, e_{1u}, e_{2g}, e_{2u} of D_{6h} by combinations of any two of $C_6{}^3$, σ_h and i. However, this resolution is not always straightforward, and may have to be programmed separately for many of the less common point groups. For the C_5 groups, e.g., there is no simple test available to distinguish between e_1 and e_2 species.

It is questionable, however, whether the second procedure outlined here has much merit over the use of the highest subgroup. For closed shells the results are the same by both, although the labeling is improved by the second procedure. For open shells, on the other hand, unless a multideterminant function is introduced, the SCF scheme breaks up the degeneracy, and nothing is gained.

In the manner outlined in this section we are able to classify all molecular orbitals, virtual as well as occupied ones, according to the irreducible representation of the appropriate point group.

The Direct Product and Selection Rules

Since we are principally interested in electronic spectra, we must next form the direct product representation of pairs of orbitals to obtain the irreducible representation of a configuration. This is readily achieved by use of a direct product table. A single table serves for all nondegenerate point groups, cf. Table III. Similar tables can be created for the degenerate representations, including the reduction of reducible representations arising in the products of degenerate representations.

The selection rules, which avoid the necessity to make the calculation of oscillator strength in the case of forbidden transitions, are contained similarly in small tables, which, for each representation in each point group, give a yes–no type information.

TABLE III

Direct Product Table of Nondegenerate Point Groups[a]

	I							
J	1	2	3	4	5	6	7	8
1	1	2	3	4	5	6	7	8
2	2	1	4	3	6	5	8	7
3	3	4	1	2	7	8	5	6
4	4	3	2	1	8	7	6	5
5	5	6	7	8	1	2	3	4
6	6	5	8	7	2	1	4	3
7	7	8	5	6	3	4	1	2
8	8	7	6	5	4	3	2	1

	C_1	C_2	C_s	C_i	C_{2h}	C_{2v}	D_2	D_{2h}
1	A	A	A'	G	A_g	A_1	A	A_{1g}
2		B	A''	U	A_u	A_2	B_1	A_{1u}
3					B_g	B_1	B_2	B_{1g}
4					B_u	B_2	B_3	B_{1u}
5								B_{2g}
6								B_{2u}
7								B_{3g}
8								B_{3u}

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[a] Where I and J stand for the irreducible representations of each point group, according to the following table.

Configuration Interaction

With the irreducible representation of each configuration directly available, it is now easy to make tremendous savings in the calculation of configuration interaction. Since only configurations transforming in the same irreducible representation interact, a simple test allows to eliminate much of the calculation (even 50% in the case of only two representations). As the calculation of the CI matrix is often the "rate-determining" step in such a calculation, the savings are tremendous. In addition, if desired, the CI matrix may be blocked, and diagonalized in symmetry blocks. This procedure seems, however, worthwhile only in case of really large matrices, since the overhead of handling the separate matrices and recombining them at the end cuts deeply into the savings achieved. We use this technique only when we wish to diagonalize CI matrices the size of which exceeds the readily available storage in the computer. In this case we create blocked matrices, one row at a time, and dump these on disk (auxiliary storage). We then retrieve them, one matrix at a time, and rewrite the eigenvector matrices on disk, holding the eigenvalues in separate vectors in core. This greatly simplifies the sorting by energy and remerging after all matrices are diagonalized.

The symmetry of the states resulting from a CI calculation are also readily determined, even when the CI matrix is diagonalized as a whole. Since only configurations of the same species combine, it suffices to ascertain the species of the leading term of any CI expansion, or even of any term having a significant coefficient. Since the species of the individual configurations is available, this is of course readily accomplished.

Higher Excited States

With the irreducible representation of each M.O. available, it has become readily possible to define, in symmetry terms, the nature of excited configurations. This has led to an open shell program capable of calculating excited states of molecules by invoking the *Aufbau* principle, not for all orbitals at once, but for each irreducible representation separately [3]. The input to such a program involves a table of the number of doubly occupied and singly occupied orbitals in each representation, and at each iteration the orbital occupation is determined according to this table. This procedure is essential since, as iterations are carried out, one frequently encounters crossing of orbitals of different symmetry; consequently, in the absence of this type of symmetry constraint, frequently convergence is not obtained.

APPENDIX

In this appendix are presented the input data required and the equivalence tables generated in a very simple application of the symmetry handling routines described in this paper. Formaldehyde ($H_2C{=}O$) is chosen as the example.

TABLE A1

Data Used

Generated	Input			
Order number	Coordinates x	y	z	Atomic number
1	0	0	1.21	8
2	0	0	0	6
3	.944	0	−.545	1
4	−.944	0	−.545	1

TABLE A2

Equivalence Tables Generated

		No. of atoms	Order no			
σ_{xz}	ON Table	4	1	2	3	4
σ_{yz}	ON Table	2	1	2	–	–
		No. of pairs	Order no			
σ_{xz}	BY Table	0	–	–	–	–
σ_{yz}	BY Table	1	3	4	–	–

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