

APPENDIX 8 USE OF CHARACTER TABLES

Ref. CO1; EWK,172; AT1,121; TI; LE2,420

Many excellent discussions of the applications of group theory to problems in molecular quantum mechanics are available in the literature. Here we only define the notation and list a few equations which are useful for the application of character tables to problems in this book. Our purpose is to provide material for review and easy reference.

The point groups of interest consist of symmetry operations which exist because of molecular symmetry elements. The operations are:

<u>Symbol</u>	<u>Effect</u>
E	identity operation
σ	reflection through a plane
i	inversion through the center of symmetry
C_n	rotation by $2\pi/n$
S_n	rotation by $2\pi/n$ followed by reflection in the plane \perp to the rotation axis

The operation R can be represented by the matrix $\{\Gamma(R)_{nm}\}$ which produces the desired transformation of a set of basis vectors u_n . Thus

$$Ru_m = \sum_n \Gamma(R)_{nm} u_n$$

The matrix elements provide sufficient representations of the operators because they have the same multiplication table as the operators. Accordingly, $R_1R_2 = R_3$ corresponds to the matrix product

$$\sum_j \Gamma(R_1)_{ij} \Gamma(R_2)_{jk} = \Gamma(R_3)_{ik}$$

The trace of such a matrix is called the character of the representation. For example, if R is represented by $\Gamma(R)$, the character is

$$\chi(R) = \sum_n \Gamma(R)_{nn}$$

We are concerned with two applications of group theory; namely (a) the simplification of the solution of the Schrödinger equation for molecules having symmetry and (b) the

determination of selection rules for transitions that are induced by radiation. The former is possible because the eigenfunctions of the Hamiltonian which have the same eigenvalue are bases for the irreducible representations of the symmetry group to which the molecule belongs. In general, eigenfunctions which transform according to different irreducible representations of the molecular symmetry group will have different eigenvalues, except in cases of accidental degeneracy which are not related to symmetry. The eigenvalue problem can thus be simplified and sometimes solved completely by choosing basis functions at the outset which transform according to the irreducible representations of the symmetry group. The construction of such functions is simplified by making use of the unnormalized projection operator,

$$P_j = \sum_R \chi_j^*(R)R$$

which operates on an arbitrary function ϕ to generate a linear combination of functions transforming according to the j th irreducible representation. Thus

$$u_j = P_j \phi = \sum_R \chi_j^*(R)R\phi \quad (1)$$

The complete basis is obtained by operating on ℓ distinct functions where ℓ is the dimension of the j th irreducible representation. The resulting functions may not be orthogonal. In some problems there are n -functions ϕ which are related by symmetry. When Eq. (1) is applied to such a set with $n > \ell$, the resulting n linear combinations are not necessarily linearly independent and the solutions may not be unique. It is always possible, however, to construct a set of ℓ linearly independent functions from such a set.

Simplifications occur in the eigenvalue problem because matrix elements of the type

$$\int u_i^* \hat{H} u_j d\tau$$

vanish when u_i and u_j transform according to different irreducible representations of the symmetry group. Such integrals can be non-zero only when the representation of the integrand is totally symmetric or contains the totally symmetric representation. Since \hat{H} transforms according to the totally symmetric representation of the molecular symmetry group, the integral will vanish unless the direct product of the representations of u_i and u_j contains the totally symmetric representation. It can be shown that this only occurs when the representations of u_i and u_j are identical, i.e. $\Gamma_i = \Gamma_j$.

In order to determine selection rules in molecular spectroscopy we need to consider integrals of the type

$$\int u_i^* \hat{H}' u_f d\tau$$



where \hat{H}' is a perturbation and u_i and u_f are eigenfunctions of the unperturbed Hamiltonian. The integral will vanish unless the direct product of the representations of u_i and u_j is equal to or contains the representation of \hat{H}' . In specific problems the symmetry of \hat{H}' is known and the transformation properties of u_i and u_f must be determined. Often we are concerned only with the number of allowed transitions, e.g. in infrared and Raman spectroscopy. In such cases the apparatus of group theory can be used to obtain directly the number of eigenfunctions n_i which transform according to the i th irreducible representation of the symmetry group. The procedure is to select a set of basis functions (vectors) which are sufficient for the description of the symmetry behavior of the eigenfunctions. The resulting representation (set of matrices) $\Gamma(R)$ is usually reducible, but it contains the irreducible representations associated with each of the eigenfunctions; i.e.

$$\Gamma(R) = \sum_i n_i \Gamma_i(R) \tag{2}$$

The number of times the i th irreducible representation is contained in the reducible representation $\Gamma(R)$ is given by

$$n_i = \frac{1}{h} \sum_R \chi(R) \chi_i^*(R) \tag{3}$$

where h is the order of the group (no. of symmetry elements) and $\chi(R)$ is the character of R in the reducible representation.

If the representations of both u_i and u_f are known for the integral above, then the representation based on their direct product is required. In practice only the characters of this representation are needed. Consider the general case where the sets $\{u\}$ and $\{v\}$ are bases for the representations Γ_i and Γ_f , respectively. The direct product of the two sets, i.e. the set of products $u_i v_f$, is the basis for the direct product representation

$\Gamma_{if} = \Gamma_i \times \Gamma_f$. It can be shown that the character for the operation R in the direct product representation is given by

$$\chi_{if}(R) = \chi_i(R) \chi_f(R) \tag{4}$$

where $\chi_i(R)$ and $\chi_f(R)$ are the characters of R in the representations Γ_i and Γ_f , respectively.

It is possible that $\{u\}$ and $\{v\}$ are bases for the same irreducible representation Γ_i . Then Eq. (4) gives $\chi_{ii}(R) = \chi_i^2(R)$. This relation is sufficient for the one-dimensional representations; however, when Γ_i is degenerate new complications arise. We consider two cases of special interest in spectroscopy.

(1) Excited vibrational states: A vibrational frequency ν having d -fold degeneracy is associated with a set of d normal modes. These modes (normal coordinates) form the basis for the d -dimensional representation Γ of the molecular point group. If the i th mode of

this set has the vibrational quantum n_i , then the total excitation of these modes can be indicated by the constant

$$n = \sum_{i=1}^d n_i$$

It can be shown that the total vibrational wave function for the degenerate set transforms as $[\Gamma^n]^+$ which is the symmetric direct product of Γ with itself n times (LE2,422). This situation differs from the one considered above because there is only one set of basis functions. Consider for example the case where $n = 2$. If two different d -fold degenerate sets, x_i ($i = 1, \dots, d$) and y_i ($i = 1, \dots, d$), were involved then the direct product would contain d^2 elements $x_i y_i$. When $\{x\} \equiv \{y\}$, only $d(d+1)/2$ products can be formed. All of the basis functions in the direct product set are symmetric functions of the types x_i^2 or $x_i y_j + x_j y_i = x_i x_j + x_j x_i$. The $d(d-1)/2$ antisymmetric combinations $x_i y_j - x_j y_i$ clearly vanish in this case. It can be shown that the character for R in the symmetric direct product representation for a doubly excited state ($n = 2$) is given by

$$\chi_{\Gamma\Gamma}(R)^+ = \frac{1}{2} [\chi_{\Gamma}(R)^2 + \chi_{\Gamma}(R^2)] \quad (5)$$

This equation holds for symmetric direct products $(\Gamma \times \Gamma)^+$ for representations Γ of any dimension. The generalizations of Eq. (5) to triply excited ($n = 3$) and higher states do, however, depend on the degeneracies involved (HE2,258; WDC,152).

(2) Excited electronic states: As discussed in Chapter 9 the many-electron wave functions for molecules must obey the Pauli exclusion principle. Consider for example the ground state of the benzene molecule. According to Problem 9.16 the configuration for the π -electrons can be written as $(a_{2u})^2(e_{1g})^4$. The repeated application of Eq. (4) neglecting spin restrictions gives the following resolution of this configuration into states:

$$3A_{1g} + 3A_{2g} + 5E_{2g}$$

However, the exclusion principle severely limits the number of possibilities and, in fact, permits only the A_{1g} state with $S = 0$ for this or any other closed shell system (see Problem 11.17).

For a degenerate state (transforming like Γ) containing two electrons, symmetric and antisymmetric spin functions corresponding to $S = 1$ and $S = 0$, respectively, are found. The allowed states, i.e. those combinations of spatial and spin functions which satisfy the exclusion principle, are obtained by associating the singlet ($S = 0$) spin function with spatial functions which transform like representations resulting from the symmetric direct product of Γ with itself; and the triplet ($S = 1$) spin functions with the spatial functions which transform like representations resulting from the antisymmetric direct product $(\Gamma \times \Gamma)^-$

of Γ with itself. The characters for $(\Gamma \times \Gamma)^+$ are obtained with Eq. (5) while the characters for $(\Gamma \times \Gamma)^-$ are obtained from the equation:

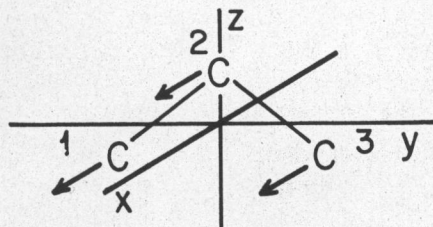
$$\chi_{\Gamma\Gamma}(\mathbf{R})^- = \frac{1}{2} [\chi_{\Gamma}(\mathbf{R})^2 - \chi_{\Gamma}(\mathbf{R}^2)] \quad (6)$$

When more than two equivalent electrons are present, the calculation becomes much more involved. The reader should consult the article by Ford (listed below) and the references contained therein for discussions of the general case. The symmetric group algebra which is required for the construction of properly antisymmetrized many-electron wave functions is explained in MA,158.

Ref: D. I. Ford, J. Chem. Ed. 49, 336 (1972).

Example 1: Construction of symmetry orbitals for the π -electrons in the allyl radical using $2p_x$ basis functions.

The allyl radical which is treated in Problems 9.12 and 9.13 has C_{2v} symmetry, i.e. it has the following symmetry elements: E, C_2 , $\sigma_v(xz)$ and $\sigma'_v(yz)$.



We denote the $2p_x$ orbitals by ϕ_1, ϕ_2 , and ϕ_3 . Then R operating on ϕ_1 gives:

$$E\phi_1 = \phi_1; \quad C_2\phi_1 = -\phi_3; \quad \sigma_v(xz)\phi_1 = \phi_3; \quad \sigma'_v(yz)\phi_1 = -\phi_1$$

and using Eq. (1):

$$\begin{aligned} P(A_1)\phi_1 &= \phi_1 - \phi_3 + \phi_3 - \phi_1 = 0 \\ P(A_2)\phi_1 &= \phi_1 - \phi_3 - \phi_3 + \phi_1 = 2(\phi_1 - \phi_3) \\ P(B_1)\phi_1 &= \phi_1 + \phi_3 + \phi_3 + \phi_1 = 2(\phi_1 + \phi_3) \\ P(B_2)\phi_1 &= \phi_1 + \phi_3 - \phi_3 - \phi_1 = 0 \end{aligned}$$

The function ϕ_3 gives nothing new, but for ϕ_2 we find:

$$E\phi_2 = \phi_2; \quad C_2\phi_2 = -\phi_2; \quad \sigma_v(xz)\phi_2 = \phi_2; \quad \sigma'_v(yz)\phi_2 = -\phi_2$$

and

$$P(A_1)\phi_2 = \phi_2 - \phi_2 + \phi_2 - \phi_2 = 0; \quad P(A_2)\phi_2 = 0; \quad P(B_1)\phi_2 = 4\phi_2; \quad P(B_2)\phi_2 = 0$$

Thus, there are two combinations which transform according to B_1 and one which transforms according to A_2 . When normalized these become

$$B_1: \frac{1}{\sqrt{2}} (\phi_1 + \phi_3), \phi_2; \quad A_2: \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)$$

These are, of course, the same functions which were derived intuitively in Problem 9.13.

Example 2: A representation for C_{2v} based on the $2p_x$ orbitals of the allyl radical.

The MO's for the π -electrons are linear combinations of the $2p_x$ orbitals which (1) diagonalize the Hamiltonian and (2) transform according to the irreducible representations of the molecular symmetry group. Suppose that we choose the functions ϕ_1 , ϕ_2 , and ϕ_3 as bases for a three-dimensional representation of C_{2v} . The matrices for this reducible representation can be written out quite easily:

$$E \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix}$$

$$C_2 \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} -\phi_3 \\ -\phi_2 \\ -\phi_1 \end{pmatrix}$$

$$\sigma_V(xz) \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} \phi_3 \\ \phi_2 \\ \phi_1 \end{pmatrix}$$

$$\sigma'_V(yz) \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \end{pmatrix} = \begin{pmatrix} -\phi_1 \\ -\phi_2 \\ -\phi_3 \end{pmatrix}$$

The characters for this representation are thus

	E	C_2	$\sigma_V(xz)$	$\sigma'_V(yz)$
$\Gamma(2p_x)$	3	-1	1	-3

The application of Eq. (3) then immediately gives the number of times each of the irreducible representations are contained in $\Gamma(2p_x)$ and thus the number of eigenfunctions which transform according to each of the irreducible representations. The results are (using the character table for C_{2v}):

$$n(A_1) = (1/4)(3 - 1 + 1 - 3) = 0$$

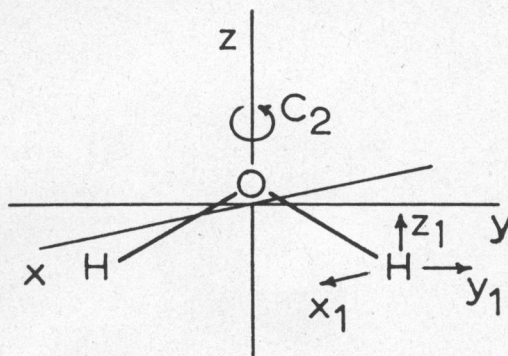
$$n(A_2) = (1/4)(3 - 1 - 1 + 3) = 1$$

$$n(B_1) = (1/4)(3 + 1 + 1 + 3) = 2$$

$$n(B_2) = (1/4)(3 + 1 - 1 - 3) = 0$$

Example 3: Determination of the symmetries of the normal modes of vibration for H_2O and

the identification of infrared and Raman active modes. The structure of the H₂O molecule is shown below:



In order to represent the motion of the atoms in a molecule we use a set of $3N$ cartesian vectors, three of which are shown above. These vectors provide a basis for a 9 dimensional representation of C_{2v} . Consider for example the operation C_2 :

$$\begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & +1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & +1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & +1 \end{pmatrix} \begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_{H2} \\ y_{H2} \\ z_{H2} \\ x_0 \\ y_0 \\ z_0 \end{pmatrix} = \begin{pmatrix} -x_{H2} \\ -y_{H2} \\ z_{H2} \\ -x_{H1} \\ -y_{H1} \\ z_{H1} \\ -x_0 \\ -y_0 \\ z_0 \end{pmatrix}$$

The column vector after rotation was constructed by inspection and the matrix was then set up to give the desired effect. As explained previously we only need the character (trace) of this matrix which is -1 . It should be clear that only atoms which are "unmoved" by the symmetry operation can contribute to the character, i.e. only atoms which lie on the corresponding symmetry element can contribute. For the operation $\sigma_v(xz)$ only the oxygen atom is unmoved and for it $x_0, y_0, z_0 \rightarrow x_0, -y_0, z_0$. Therefore $\chi(\sigma_{xz}) = +1$. Similarly, O, H1, and H2 all lie on σ_{yz} and each contributes $+1$ to give $\chi(\sigma_{yz}) = +3$. The

characters for Γ_g are shown below:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ_g	9	-1	+1	+3

This representation can be reduced using Eq. (3).

$$n(A_1) = \frac{1}{4} (9 - 1 + 1 + 3) = 3$$

$$n(A_2) = \frac{1}{4} (9 - 1 - 1 - 3) = 1$$

$$n(B_1) = \frac{1}{4} (9 + 1 + 1 - 3) = 2$$

$$n(B_2) = \frac{1}{4} (9 + 1 - 1 + 3) = 3$$

Thus $\Gamma_g = 3A_1 + A_2 + 2B_1 + 3B_2$. The character table for C_{2v} in Appendix 8 indicates that the three translations x, y, z and the three rotations R_x, R_y, R_z provide a basis for the representation

$$\Gamma(\text{trans, rot}) = A_1 + A_2 + 2B_1 + 2B_2$$

This leaves for the genuine vibrations:

$$\Gamma(\text{vib}) = 2A_1 + B_2$$

The normal coordinates for atomic motion are three in number with two transforming like A_1 and one like B_2 .

The transition moment for a harmonic oscillator was considered in Problem 10.12. For the fundamental transition ($v'' = 0 \rightarrow v' = 1$) the x -component of the transition moment is proportional to

$$\int \psi^{v'=1} x \psi^{v''=0} d\tau \quad (1)$$

But since $\psi^{v''=0}$ is totally symmetric and $\psi^{v'=1}$ transforms like the normal coordinate Q , this integral will vanish unless x transforms according to the same irreducible representation as Q , i.e. for the integrand to be totally symmetric the product xQ must be totally symmetric. The general rule is:

I. The fundamental vibration for a given normal coordinate will be active in the infrared spectrum only if the normal coordinate transforms according to the same irreducible representation of the molecular symmetry group as one or more of the Cartesian coordinates.

Raman scattering results from an induced electric dipole moment. In place of the Cartesian coordinate in (1) a component of the polarizability tensor must be substituted. e.g.

$$\int \psi^{v'=1} \alpha_{xy} \psi^{v''=0} d\tau$$

The component α_{xy} transforms as xy , α_{xz} as xz , and so on. The general rule is:

II. The fundamental vibration for a given normal coordinate will be active in the Raman spectrum only if the normal coordinate transforms according to the same irreducible representation of the molecular symmetry group as one or more of the components of the polarizability tensor.

Applying rules I and II to the H_2O molecule we find that there are two A_1 modes, both of which are infrared and Raman active. There is one B_2 mode which is also infrared and Raman active. Therefore, three frequencies will be found in the infrared spectrum and the same three frequencies will be found in the Raman spectrum. Information is also available about the polarization of the scattered light (Raman lines). It turns out that only those fundamentals associated with totally symmetric modes will be polarized. In the case of H_2O the B_2 mode will give rise to a depolarized Raman line.

Example 4: Determination of the symmetries and multiplicities of the excited states arising from the configuration $(a_1)^1(e)^2$ of the cyclopropenyl radical.

This C_{3v} system is discussed in Problem 9.15. The $(a_1)^1$ electron causes no problems. The representation is A and the spin is $1/2$, i.e. the symbol is 2A_1 . For the pair $(e)^2$, however, we must be careful with the exclusion principle. For $S = 0$ and $S = 1$ we require symmetric and antisymmetric spatial functions, respectively. The necessary characters are given in the table below for the E representation of C_{3v} :

R	E	C_3	σ_v
R^2	E	C_3^2	E
$\chi(R)$	2	-1	0
$\chi(R)^2$	4	1	0
$\chi(R^2)$	2	-1	2
$\chi(R)^+$	3	0	2
$\chi(R)^-$	1	1	-1

The characters $\chi(R)^+$ and $\chi(R)^-$ have been obtained using Eqs. (5) and (6), respectively.

Equation (3) then permits the following reductions

$$S = 0: (ExE)^+ = A_1 + E, \quad S = 1: (ExE)^- = A_2$$

Combining these with the appropriate multiplicities then gives

$$(e)^2 \rightarrow {}^1A_1 + {}^1E + {}^3A_2$$

The complete set of states is obtained from the product

$${}^2A_1 \times ({}^1A_1 + {}^1E + {}^3A_2) = {}^2A_1 + ({}^2A_1 \times {}^1E) + ({}^2A_1 \times {}^3A_2) = {}^2A_1 + {}^2E + {}^4A_2 + {}^2A_2$$

This last resolution has been carried out with Eqs. (3) and (4) and the C_{3v} character table. The multiplicities are obtained from simple vector addition, i.e. $S_1 + S_2 \rightarrow S_1 + S_2$, $S_1 + S_2 - 1, \dots, |S_1 - S_2|$.

In this appendix some of the most widely used character tables are reproduced. The irreducible representations Γ_i are listed at the left of each table in the conventional notation: A, B (one-dimensional representations), E (two-dimensional representation), T (three-dimensional representations). Across the top, the classes of symmetry operations are given. In applying Eq. (3) the coefficients of these classes must be taken into account.

Character Tables

1. The C_n Groups ($n = 2, 3, 4, 5, 6$)

C_2	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	-1	x, y, R_x, R_y	yz, xz

C_3	E	C_3	C_3^2		$\epsilon = \exp(2\pi i/3)$
A	1	1	1	z, R_z	$x^2 + y^2, z^2$
E	$\begin{Bmatrix} 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon \end{Bmatrix}$			$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (yz, xz)$

C_4	E	C_4	C_2	C_4^3		
A	1	1	1	1	z, R_z	$x^2 + y^2, z^2$
B	1	-1	1	-1		$x^2 - y^2, xy$
E	$\begin{Bmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{Bmatrix}$				$(x, y) (R_x, R_y)$	(yz, xz)

C_5	E	C_5	C_5^2	C_5^3	C_5^4		$\epsilon = \exp(2\pi i/5)$
A	1	1	1	1	1	z, R_z	$x^2 + y^2, z^2$
E_1	$\begin{Bmatrix} 1 & \epsilon & \epsilon^2 & \epsilon^{2*} & \epsilon^* \\ 1 & \epsilon^* & \epsilon^{2*} & \epsilon^2 & \epsilon \end{Bmatrix}$					$(x, y) (R_x, R_y)$	(yz, xz)
E_2	$\begin{Bmatrix} 1 & \epsilon^2 & \epsilon^* & \epsilon & \epsilon^{2*} \\ 1 & \epsilon^{2*} & \epsilon & \epsilon^* & \epsilon^2 \end{Bmatrix}$						$(x^2 - y^2, xy)$

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5		$\epsilon = \exp(2\pi i/6)$
A	1	1	1	1	1	1	z, R_z	$x^2 + y^2, z^2$
B	1	-1	1	-1	1	-1		
E_1	$\begin{Bmatrix} 1 & \epsilon & -\epsilon^* & -1 & -\epsilon & \epsilon^* \\ 1 & \epsilon^* & -\epsilon & -1 & -\epsilon^* & \epsilon \end{Bmatrix}$						(x, y) (R_x, R_y)	(xz, yz)
E_2	$\begin{Bmatrix} 1 & -\epsilon^* & -\epsilon & 1 & -\epsilon^* & -\epsilon \\ 1 & -\epsilon & -\epsilon^* & 1 & -\epsilon & -\epsilon^* \end{Bmatrix}$							$(x^2 - y^2, xy)$

2. The C_{nv} Groups ($n = 2, 3, 4, 5, 6$)

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A ₁	1	1	1	1	z	x^2, y^2, z^2
A ₂	1	1	-1	-1	R_z	xy
B ₁	1	-1	1	-1	x, R_y	xz
B ₂	1	-1	-1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A ₁	1	1	1	z	$x^2 + y^2, z^2$
A ₂	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	$(x^2 - y^2, xy)$ (xz, yz)

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A ₁	1	1	1	1	1	z	$x^2 + y^2, z^2$
A ₂	1	1	1	-1	-1	R_z	
B ₁	1	-1	1	1	-1		$x^2 - y^2$
B ₂	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A ₁	1	1	1	1	z	$x^2 + y^2, z^2$
A ₂	1	1	1	-1	R_z	
E ₁	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	(x, y) (R_x, R_y)	(xz, yz)
E ₂	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0		$(x^2 - y^2, xy)$

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A ₁	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A ₂	1	1	1	1	-1	-1	R_z	
B ₁	1	-1	1	-1	1	-1		
B ₂	1	-1	1	-1	-1	1		
E ₁	2	1	-1	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)
E ₂	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$

3. The C_{nh} Groups (n = 2,3,4,5,6)

C _{2h}	E	C ₂	i	σ _h		
A _g	1	1	1	1	R _z	x ² , y ² , z ² , xy
B _g	1	-1	1	-1	R _x , R _y	xz, yz
A _u	1	1	-1	-1	z	
B _u	1	-1	-1	1	x, y	

C _{3h}	E	C ₃	C ₃ ²	σ _h	S ₃	S ₃ ⁵		ε = exp(2πi/3)
A'	1	1	1	1	1	1	R _z	x ² + y ² , z ²
E'	$\left\{ \begin{array}{ccc} 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon \end{array} \right.$						(x, y)	(x ² - y ² , xy)
A''	1	1	1	-1	-1	-1	z	
E''	$\left\{ \begin{array}{ccc} 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon \end{array} \right.$						(R _x , R _y)	(xz, yz)

C _{4h}	E	C ₄	C ₂	C ₄ ³	i	S ₄ ³	σ _h	S ₄		
A _g	1	1	1	1	1	1	1	1	R _z	x ² + y ² , z ²
B _g	1	-1	1	-1	1	-1	1	-1		x ² - y ² , xy
E _g	$\left\{ \begin{array}{cccc} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{array} \right.$								(R _x , R _y)	(xz, yz)
A _u	1	1	1	1	-1	-1	-1	-1	z	
B _u	1	-1	1	-1	-1	1	-1	1		
E _u	$\left\{ \begin{array}{cccc} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{array} \right.$								(x, y)	

C _{5h}	E	C ₅	C ₅ ²	C ₅ ³	C ₅ ⁴	σ _h	S ₅	S ₅ ⁷	S ₅ ³	S ₅ ⁹		ε = exp(2πi/5)
A'	1	1	1	1	1	1	1	1	1	1	R _z	x ² + y ² , z ²
E ₁ '	$\left\{ \begin{array}{cccccc} 1 & \epsilon & \epsilon^2 & \epsilon^{2*} & \epsilon^* & 1 \\ 1 & \epsilon^* & \epsilon^{2*} & \epsilon^2 & \epsilon & 1 \end{array} \right.$										(x, y)	
E ₂ '	$\left\{ \begin{array}{cccccc} 1 & \epsilon^2 & \epsilon^* & \epsilon & \epsilon^{2*} & 1 \\ 1 & \epsilon^{2*} & \epsilon & \epsilon^* & \epsilon^2 & 1 \end{array} \right.$											(x ² - y ² , xy)
A''	1	1	1	1	1	-1	-1	-1	-1	-1	z	
E ₁ ''	$\left\{ \begin{array}{cccccc} 1 & \epsilon & \epsilon^2 & \epsilon^{2*} & \epsilon^* & -1 \\ 1 & \epsilon^* & \epsilon^{2*} & \epsilon^2 & \epsilon & -1 \end{array} \right.$										(R _x , R _y)	(xz, yz)
E ₂ ''	$\left\{ \begin{array}{cccccc} 1 & \epsilon^2 & \epsilon^* & \epsilon & \epsilon^{2*} & -1 \\ 1 & \epsilon^{2*} & \epsilon & \epsilon^* & \epsilon^2 & -1 \end{array} \right.$											

C_{6h}	E	C_6	C_3	C_2	C_3^2	C_6^5	i	S_3^5	S_6^5	σ_h	S_6	S_3		$\epsilon = \exp(2\pi i/6)$
A_g	1	1	1	1	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
B_g	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
E_{1g}	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$	ϵ	$-\epsilon^*$	-1	$-\epsilon$	ϵ^*	1	ϵ	$-\epsilon^*$	-1	$-\epsilon$	ϵ^*	(R_x, R_y)	(xz, yz)
		ϵ^*	$-\epsilon$	-1	$-\epsilon^*$	ϵ	1	ϵ^*	$-\epsilon$	-1	$-\epsilon^*$	ϵ		
E_{2g}	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$	$-\epsilon^*$	$-\epsilon$	1	$-\epsilon^*$	$-\epsilon$	1	$-\epsilon^*$	$-\epsilon$	1	$-\epsilon^*$	$-\epsilon$		$(x^2 - y^2, xy)$
		$-\epsilon$	$-\epsilon^*$	1	$-\epsilon$	$-\epsilon^*$	1	$-\epsilon$	$-\epsilon^*$	1	$-\epsilon$	$-\epsilon^*$		
A_u	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	z	
B_u	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
E_{1u}	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$	ϵ	$-\epsilon^*$	-1	$-\epsilon$	ϵ^*	-1	$-\epsilon$	ϵ^*	1	ϵ	$-\epsilon^*$	(x, y)	
		ϵ^*	$-\epsilon$	-1	$-\epsilon^*$	ϵ	-1	$-\epsilon^*$	ϵ	1	ϵ^*	$-\epsilon$		
E_{2u}	$\left\{ \begin{array}{l} 1 \\ 1 \end{array} \right.$	$-\epsilon^*$	$-\epsilon$	1	$-\epsilon^*$	$-\epsilon$	-1	ϵ^*	ϵ	-1	ϵ^*	ϵ		
		$-\epsilon$	$-\epsilon^*$	1	$-\epsilon$	$-\epsilon^*$	-1	ϵ	ϵ^*	-1	ϵ	ϵ^*		

4. The D_{nh} Groups ($n = 2, 3, 4, 5, 6$)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	1	-1	1	1	1	-1	R_z	
E_1'	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	(x, y)	
E_2'	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0		$(x^2 - y^2, xy)$
A_1''	1	1	1	1	-1	-1	-1	-1		
A_2''	1	1	1	-1	-1	-1	-1	1	z	
E_1''	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	-2	$-2\cos 72^\circ$	$-2\cos 144^\circ$	0	(R_x, R_y)	(xz, yz)
E_2''	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	-2	$-2\cos 144^\circ$	$-2\cos 72^\circ$	0		

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

5. The S_4 Group

S_4	E	S_4	C_2	S_4^3			
A	1	1	1	1	R_z	$x^2 + y^2, z^2$	
B	1	-1	1	-1	z	$x^2 - y^2, xy$	
E	$\begin{pmatrix} 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}$				(x, y)	(R_x, R_y)	(xz, yz)

6. The Cubic Groups

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

7. The $C_{\infty v}$ and $D_{\infty h}$ Groups

$C_{\infty v}$	E	$2C_{\infty}^{\phi}$...	$\infty\sigma_v$			
$A_1 \equiv \Sigma^+$	1	1	...	1	z	$x^2 + y^2, z^2$	
$A_2 \equiv \Sigma^-$	1	1	...	-1	R_z		
$E_1 \equiv \Pi$	2	$2\cos\phi$...	0	(x, y)	(R_x, R_y)	(xz, yz)
$E_2 \equiv \Delta$	2	$2\cos 2\phi$...	0			$(x^2 - y^2, xy)$
$E_3 \equiv \Phi$	2	$2\cos 3\phi$...	0			
...			

