2.7 Constructing Symmetry Adapted Linear Combinations

A set of equivalent functions $-f_1$, f_2 , \cdots , f_{n^-} can be used to form an n-dimensional representation. By calculating the characters for this representation and by applying the great orthogonality theorem, the representation can be expressed as a sum of irreducible representations. One might ask, "what are the n-linear combinations of f_1 , \cdots , f_n that transform like the irreducible representations?" The answer is provided by the projection operator, denoted \hat{P}^{Γ_i} .

$$\hat{P}^{\Gamma_{i}}(f_{j}) = \frac{n}{g} \sum_{R} \chi_{\hat{R}}(\Gamma_{i}) \hat{O}_{R}(f_{j})$$

Here \hat{P} is the operator that projects out of a set of equivalent functions the Γ_i irreducible representation of the point group. The n/g factor (n = dimension of the irreducible representation and g the order of the group) usually is irrelevant. The constant factor before wavefunctions is ordinarily determined by normalization conditions specific to the problem. The function f_j chosen can be any one of n belonging to the equivalent set. This operator sums over *all* the symmetry operations \hat{R} the product of the character for that operation times the transformed function $\hat{O}_R(f_j)$ by that operation. An important caveat here is that classes cannot be lumped together, as in the preceding section. For example, in the C_{3v} character table the $2\hat{C}_3$ represents the class composed of \hat{C}_3^1 and \hat{C}_3^2 operations. The three different \hat{C}_2 operations would also have to be performed separately on f_j , since they produce different results.

As a simple example, consider the O-H stretches in water (yz as molecular plane). A useful way to apply the formula is to tabulate the characters of the irreducible representations and list the effect of \hat{O}_R on one of the functions at the bottom of the table.

C_{2v}	Е	C ₂ (z)	$\sigma_v(xz)$	$\sigma_v(yz)$
A ₁	1	1	1	1
B ₁	1	-1	+1	-1
B ₂	1	-1	-1	+1
$\hat{O}_{R}(O-H_{a})$	O-H _a	O-H _b	O-H _b	O-Ha

Apply the projection operator for A_1 by multiplying the A_1 row times the \hat{O}_R row and adding them to obtain the result:

$$\overset{A}{P}^{A_{1}} (O-H_{a}) = \frac{1}{4} (O-H_{a} + O-H_{b} + O-H_{b} + O-H_{a})$$
$$= \frac{1}{2} (O-H_{a} + O-H_{b})$$

According to the earlier calculation using the orthogonality theorem it shouldn't be possible to obtain a B_1 linear combination, and indeed the projection operator yields the null result.

$${}^{A}{}^{B_{1}}(O-H_{a}) = \frac{1}{4} [(O-H_{a}) - (O-H_{b}) + (O-H_{b}) - (O-H_{a})]$$

= 0

Application of the B₂ projection operator yields:

$${}^{\wedge}_{P}{}^{B_{2}} (O-H_{a}) = \frac{1}{4} [(O-H_{a}) - (O-H_{b}) - (O-H_{b}) + (O-H_{a})]$$
$$= \frac{1}{2} [(O-H_{a}) - (O-H_{b})]$$

The above linear combinations correspond to the symmetric (A_1) and antisymmetric (B_2) stretches of water depicted in Figure 2.2. Whenever only two equivalent real functions are involved, then the correct linear combinations will always be the sum and difference functions. Symmetry labels can be assigned by inspection. The water molecule does indeed exhibit two distinct O-H IR stretches in its infra-red spectrum at 3652 and 3756 cm⁻¹.



Figure 2.2 The A 1 and B 2 stretching vibrations of water.

Whenever degenerate representations are involved, the task of constructing symmetry adapted linear combinations becomes more difficult. Consider the ammonia molecule and its N-H stretching vibrations (Figure 2.3).



Figure 2.3 The N-H stretching coordinates for ammonia

In the C_{3v} point group, the characters for the 3-dimensional representation spanned by the three N-H stretches would be (3 0 1). The $\stackrel{A}{E}$ operation takes the three equivalent bonds into themselves, a $\stackrel{A}{C}_3$ operation mixes them all (*i.e.*, none go into \pm themselves to give a nonzero diagonal element in the transformation matrix), and a $\stackrel{A}{\sigma}_v$ leaves one bond unchanged (a +1 on the diagonal) but interchanges the other two (0 on the diagonals). The (3 0 1) character representation reduces to A₁ + E. In applying the projection operator, it is convenient to construct a table that separates the classes as follows.

C _{3v}	Ê	C ₃	C ₃ ²	$\sigma_v{}^a$	$\sigma_v{}^b$	$\sigma_v{}^c$
A ₁	1	1	1	1	1	1
A ₂	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0
Ô _R (N-H _a)	(N-H _a)	(N-H _b)	(N-H _c)	(N-H _a)	(N-H _c)	(N-H _b)
Ô _R (N-H _b)	(N-H _b)	(N-H _a)	(N-H _c)	(N-H _c)	(N-H _b)	(N-H _a)

The $3\hat{\sigma}_v$ are superscripted according to whether they contain H_a, H_b, or H_c. To project out the A₁ linear combination multiply the first and fourth rows to obtain:

 $[2(N-H_a) + 2(N-H_b) + 2(N-H_c)] = 2N[(N-H_a) + (N-H_b) + (N-H_c)]$ The constant *N* is determined by the normalization condition specific to vibrational wavefunctions (discussed in Chapter 5). One linear combination of the 2-dimensional E representation can be generated by multiplying rows 3 and 4.

 $N[2(N-H_a)-(N-H_b)-(N-H_c)]$

Another independent function can be obtained by multiplying rows 3 and 5 to give

 $N[2(N-H_b) - (N-H_a) - (N-H_c)]$

Although these two functions form a basis for the E representation, they are not orthogonal. *The sum and difference of two similarly normalized functions are orthogonal*, and this fact can be used to construct an orthogonal pair of functions that transform like the E representation.

 $N[(N-H_a) + (N-H_b) - 2(N-H_c)]$

 $N[3(N-H_a) - 3(N-H)_b] = 3N[(N-H_a) - (N-H_b)]$

This particular orthogonal linear combination is not unique, since other linearly independent pairs of orthogonal combinations are possible. For example, the pair of functions shown below serve

 $N[2(N-H_a) - (N-H_b) - (N-H_c)]$ $3N[(N-H_b) - (N-H_c)]$

equally well as an E representation. The situation resembles the diverse choices possible for the x and y axes in C_{3v} . Any orthogonal pair of unit vectors perpendicular to the 3-fold axis work equally well.

2.8 Products of Irreducible Representations and Selection Rules

Most chemists are familiar with the Laporte selection rule that $g \rightarrow g$ or $u \rightarrow u$ electronic transitions in atoms, diatomic molecules, and all molecules with inversion symmetry are dipole forbidden. This arises from a consideration of the integral for the dipole moment of a transition between two electronic states ψ and ψ' . The transition intensity is proportional to the integral

 $\int \psi d\psi' d\tau$, which runs over the electronic coordinates for the molecule. Since the dipole moment $d = e \cdot \vec{r}$, then d behaves like a vector \vec{r} and can be reduced to x, y, and z parts. A rule often cited is that the symmetry of a product function is even if the number of times odd functions appear in the product is even. The symmetry of a product function is odd if the number of times odd functions appear in the product is odd. For example, Figure 2.4a displays the odd functions y = x and $y = \sin x$ along with the even function $y = \cos x$. The product of the two odd



Figure 2.4a - Plots of the odd functions y = x and y = sin(x) with the even function y = cosx for the interval $-2 \le x \le 2$.

and even functions gives an even product function shown in Figure 2.4b. With even functions, the integral from x = 0 to $x = \infty$ is the same as from x = 0 to $x = -\infty$ and will have a nonzero value over the total $\pm \infty$ range. By contrast, in Figure 2.5a the odd function y = x and



Figure 2.4b - Plot of the odd-odd-even product function from 2.4a, which yields an even function.



Figure 2.5a - Plot of the odd function y = x and even functions $y=(\sin x)^2$ and $y = \cos x$ for the interval $-2 \le x \le 2$.

the even functions $y = (sinx)^2$ and y = cos x give an odd product function shown in Figure 2.5b.



Figure 2.5b - Plot of the odd even even product function from 2.5a, which yields an odd function.

Since the curve inverts its sign about the origin, the integral from x = 0 to $x = \infty$ will have the opposite sign of that from x = 0 to $x = -\infty$. Thus, the two segments of the integral cancel and the total integral is exactly zero.

The behavior of even and odd functions can be viewed in the context of the character table for the C_i group.



The C_i group is a subgroup for any molecule that contains an inversion center. The rightmost column in the character table provides information that rotation around the x, y, or z axes (R_x , R_y , R_z) each transform like an A_g irreducible representation. The vectors x,y,z (and hence the dipole moment operator components along these axes) each transform like A_u . The symmetry representation of product functions can be computed by multiplying the corresponding 1-dimensional matrix representations (*i.e.*, the characters). *Thus the symmetry of x(sinx)(cosx) is given by the direct product of the characters* for $A_u \otimes A_g = (1 \cdot 1 \cdot 1 = 1 \text{ for E and } -1 \cdot 1 \cdot 1 = 1$

for i) = A_g . The rule that only integrals of even functions are nonzero becomes a rule that *only integrals of a function transforming like the totally symmetric representation are nonzero*. These conclusions can be generalized to all point groups.

Suppose f_1 transforms like Γ_1 and f_2 like Γ_2 . How does the product function f_1f_2 transform? *This question is answered by the direct product representation*

$$\Gamma(f_1f_2) = \Gamma(f_1) \times \Gamma(f_2)$$

The characters of $\Gamma(f_1f_2)$ are easily calculated by the formula $\chi_R^{A}(f_1f_2) = \chi_R^{A}(f_1) \chi_R^{A}(f_2)$.

C _{3 v}	E	2C ₃	$3\sigma_v$	
A1	1	1	1	z
A ₂	1	1	-1	
Е	2	-1	0	(x,y)

For example, in C_{3v} if f_1 transforms like E and f_2 like A_2 then:

$$X(f_1f_2) = 2 -1 0 = E$$

If f_1 transforms like E and f_2 like E, then:

$$X(f_1f_2) = 4 \quad 1 \quad 0 = A_1 + A_2 + E$$

Notice that the latter direct product produces a four-dimensional reducible representation. For all groups, *the integral of a function over all space is nonzero only if the function transforms like the totally symmetric representation for that group.* In the preceding example:

The second integral is nonzero by virtue of the A_1 piece in the direct product.

2.9 Use of Rotation Subgroups to Simplify Problems

The application of group theory becomes tedious in high symmetry molecules. Application of the projection operator to an octahedral complex requires the calculation of transformations for 48 symmetry operations. It is often possible to work the problem in a subgroup with fewer operations. The most useful approach, with the least chance for error, is to work in the pure rotation subgroup of a particular group. For example, if a problem is solved in O instead of O_h it cuts the work by one-half. To recover the O_h representations the functions in the lower symmetry subgroup need be combined by taking appropriate sums and differences to account for the inversion

symmetry. The reason for choosing rotation subgroups is that they determine the fundamental degeneracies possible in a problem. The other symmetry operations merely determine subscripts and superscripts. Several such correlations are given in Table II.3. The extension to other groups is straightforward. Complete correlation tables for each group to all of its subgroups may be found in the reference by Wilson, Decius, and Cross at the end of this chapter.

Consider the application of this method to determine the π -orbitals of the cyclopentadienide anion. First, note the correlation between the **D**_{5h} C₅H₅⁻ species and its pure rotation subgroup **D**₅. Since **D**_{5h} consists of E, C₅, σ_h , 5C₂, $5\sigma_v$, and S₅ symmetry elements the

O _h	0	D _{6h}	D ₆	C _{6v}	C ₆	T _d	Т
A _{1g}	A ₁	A _{1g}	A ₁	A ₁	А	A_1	А
A _{2g}	A2	A _{2g}	A ₂	A ₂	А	A_2	А
Eg	Е	B _{1g}	B ₁	B ₁	В	E	Е
T _{1g}	T_1	B _{2g}	B ₂	B ₂	В	T ₁	Т
T _{2g}	T2	E _{1g}	E_1	E_1	E_1	T_2	Т
A _{1u}	A ₁	E _{2g}	E_2	E_2	E_2		
A _{2u}	A2	A _{1u}	A ₁				
Eu	Е	A _{1u}	A ₁				
T_{1u}	T_1	A _{2u}	A2				
T_{2u}	T2	B _{1u}	B_1				
		B _{2u}	B ₂				
		B _{2u}	B ₂				
		E _{1u}	E ₁				
		E _{2u}	E ₂				

Table II 3. Correlation Between Groups and Their Pure Rotation Subgroups

removal of the σ_h , $5\sigma_v$, and S_5 elements leaves **D**₅. The table below blocks out the D₅ character table from the D_{5d} tables in boldface type. The last line in the table contains the characters

D_{5h}	E	2C5	$2C_5^2$ $5C_2$	σ	ħ	$2S_5 2S_5^3$	$5\sigma_v$		1
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°	2 cos 144°	0	2	$2\cos 72^{\circ}$	2 cos 144°	0	(x,y)
E_2	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	$2\cos 72^{\circ}$	0	$(x^2 - y^2, xy)$
A_1	1	1	1	1	-1	-1	-1	-1	
A2~	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°	-2 cos 144°	0	$(R_x, R_y) (xz, yz)$
E_2	2	2 cos 144°	$2\cos 72^{\circ}$	0	-2	-2 cos 144°	-2 cos 72°	0	
$\Gamma(\pi)$	5	0	0	-1	-5	0	0	1	

for the five equivalent p_{π} orbitals on carbon in the $C_5H_5^-$ ion, Figure 2.6, under the various operations of the point group. This reduces to $(5\ 0\ 0\ -1\ -5\ 0\ 0\ 1) = A_2^{\prime\prime} + E_1^{\prime\prime} + E_2^{\prime\prime}$ in D_{5h} .



Figure 2.6 The five equivalent π -orbitals in the cyclopentadienide ion.

The correlation table shown below can be constructed by comparing the characters in the D_5 and D_{5h} group. For example, the A₂ representation in D_5 , which has a -1 character for C₂ and +1 for E, C₅, and C₅² correlates with either the A₂' or A₂'' representations of D_{5h} . they have identical characters for the listed operations.

D _{5h}	$\rightarrow D_5$	\rightarrow C ₅
A ₁ ´	A ₁	A
A ₂ ´	A ₂	A
E ₁ ´	E ₁	E1
E ₂ ´	E ₂	E ₂
A_1	A ₁	A
A ₂ ~	A ₂	A
E ₁ ~	E ₁	E1
E ₂ ~	E ₂	E2

The D_5 group blocked out in the D_{5h} character table is identical to the section below it for the double primed representations. Thus the double primed and primed representations correlate similarly. By similar reasoning the correlation extends to the C_5 group derived in section 2.3. Therefore the π -orbitals of $C_5H_5^-$ obey the correlation.

This correlation allows us to conclude that the A representation projected out in C_5 will correspond to A_2 in the higher symmetry D_{5h} group. A correlation can also be made between E_1 and E_1 and between E_2 and E_2 . This problem can therefore be uniquely solved in C_5 . Caution is necessary when applying this method to problems where the results might be ambiguous. If the problem contained both A_1 and A_2 functions in D_{5h} , then in C_5 this corresponds to two A functions. Then linear combinations of the two A functions would have to be used to construct the desired A_1 and A_2 representations. Alternatively, the problem could be solved in D_5 , where the correlation would not be ambiguous.

For the C₅H₅⁻ ion in the lower symmetry character table C₅, the transformed orbitals π_1 - π_5 behave as follows:

C5	Е	C5	C_{5}^{2}	C ₅ ³	C5 ⁴
A	1	1	1	1	1
E_1	2	$2 \cos \frac{2\pi}{5}$	$2 \cos \frac{4\pi}{5}$	$2 \cos \frac{4\pi}{5}$	$2 \cos \frac{2\pi}{5}$
E_2	2	$2 \cos \frac{4\pi}{5}$	$2 \cos \frac{2\pi}{5}$	$2 \cos \frac{2\pi}{5}$	$2 \cos \frac{4\pi}{5}$
$\hat{\theta}_{\hat{R}}(\pi_1)$	π_1	π_2	π3	π_4	π_5
$\hat{\theta}_{\hat{R}}(\pi_2)$	π_2	π_3	π_4	π_5	π_1

From this the A representation, which correlates to A_2 in D_{5h} , is given by

$$A_2'' = N(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5)$$

Two similarly normalized E_1 functions can be projected from the last 2 rows of the preceding table.

$$\begin{split} E_1{}^a &= N[2\pi_1 + 0.618\pi_2 - 1.618\pi_3 - 1.618\pi_4 + 0.618\pi_5] \\ E_1{}^b &= N[2\pi_2 + 0.618\pi_3 - 1.618\pi_4 - 1.618\pi_5 + 0.618\pi_1] \end{split}$$

The sum and difference give an orthogonal pair of wavefunctions, which correlate to E_1 in D_{5h} .

$$E_{1} \stackrel{\sim}{\sim} \begin{cases} N[2.618\pi_{1} + 2.618\pi_{2} - \pi_{3} - 3.236\pi_{4} - \pi_{5}] \\ N[1.382\pi_{1} - 1.382\pi_{2} - 2.236\pi_{3} + 2.236\pi_{5}] \end{cases}$$

A similar procedure yields the E_2 " orbital set.

$$E_{2} \sim \begin{cases} N[0.382\pi_{1} + 0.382\pi_{2} - \pi_{3} + 1.236\pi_{4} - \pi_{5}] \\ N[3.618\pi_{1} - 3.618\pi_{2} + 2.236\pi_{3} - 2.236\pi_{5}] \end{cases}$$

The symmetries of these π wavefunctions are sketched in Figure 2.7. The orbital with no nodal plane between π orbitals, A₂^{''}, is the most stable one. The next higher energy orbitals should be



 E_1 , which have one nodal plane, and then E_2 , with two such planes. Of course, the plane of the paper is a nodal plane for all the orbitals, since they are $p\pi$ in nature.

Figure 2.7 The A $_2$ ", E $_1$ ", and E $_2$ " Symmetry Combinations of π -Orbitals in the Cyclopentadienide Anion.

2.10 Additional Readings

Atkins, P. W.; Child, M. S.; Phillips, C. S. G.; *Tables for Group Theory*: Oxford University Press; London, 1970.

Butler, P. H. *Point Group Symmetry Applications: Methods and Tables*: Plenum Press, New York, 1981.

Salthouse, J. A.; Ware, M. J. *Point Group Character Tables and Related Tables*: Cambridge Univ. Press, 1972.

Thomas, A. D.; Wood, G. V. Group Tables: Shiva Publ; Orpington, Kent, 1980.

Wilson, E. B. Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*. Dover: New York, 1980. Contains a complete set of correlation tables for the symmetry point groups.

2.11 Problems

1)

Reduce the following representations:

a) $\underline{\text{In } D_{2h}}$
$\underline{E} \underline{C_{2(z)}} \underline{C_{2(y)}} \underline{C_{2(x)}} \underline{i} \underline{\sigma(xy)} \underline{\sigma(xz)} \underline{\sigma(yz)}$
4 0 0 0 0 4 0 0
b) $\underline{\text{In } D_{3d}}$
$\underline{E} \underline{2C_3} \underline{3C_2} \underline{i} \underline{2S_6} \underline{3\sigma_d}$
3 0 -1 1 -2 1
c) In O_h
$\underline{E} \underline{8C_3} \underline{6C_2} \underline{6C_4} \underline{3C_2} \underline{i} \underline{6S_4} \underline{8S_6} \underline{3\sigma_h} \underline{6\sigma_d}$
7 1 1 -1 3 1 1 1 5 -1

2) The p_x, p_y, and p_z orbitals are so named because they behave like the functions x, y, and z in their nodal properties. To what irreducible representations do these functions belong to in the C_{2v}, D_{2d}, and D_{4h} point groups if they are located on an atom which lies at a position where all symmetry elements intersect?

3) How would d_{xy} , d_{xz} , and d_{yz} functions transform under the conditions of problem 2?

4) Show all possible subgroups of D_{6h} that also contain a C_6 axis, and construct a correlation table for these groups.

5) Construct the C_6 character table for real functions just as we did in the text for C_5 .

- 6) Use the C_6 character table derived above to calculate the symmetry adapted linear combinations of π -orbitals in benzene.
- 14) Use symmetry to deduce a qualitative MO diagram for N_2O .

Answers to Problems:

- 1) a) $a_g + b_{1g} + b_{2u} + b_{3u}$
 - b) $a_{2u} + e_g$
 - c) $a_{1g} + a_{2g} + e_g + t_{2u}$
- 2) These transform the same way as the functions x,y, and z given in the character table. When you work the problem you may obtain an answer that differs from that in the book if you do not choose the same direction as x and y as they did. In that case deduce what orientation the character table assumes for x and y. There usually isn't any ambiguity in the choice of z, because it coincides with the unique symmetry axis.
- Calculate this by taking the direct product for the two representations. For example, xz will transform like the direct product of the representation for x and z, which you deduced in problem 2.
- There a total of 18 different subgroups for D_{6h}, but only four contain a C₆ axis (note the group S₆ is also a subgroup of D_{6h}).

D _{6h}	D ₆	C _{6h}	C _{6v}	C ₆
A _{1g}	A_1	Ag	A ₁	А
A _{2g}	A ₂	Ag	A ₂	А
B _{1g}	B ₁	Bg	B ₂	В
B _{2g}	B ₂	Bg	B ₁	В
E _{1g}	E_1	E _{1g}	E_1	E_1
E _{2g}	E_2	E _{2g}	E_2	E_2
A _{1u}	A ₁	A _u	A ₂	А
A _{2u}	A ₂	A _u	A ₁	А
B _{1u}	B ₁	B _u	B ₁	В
B _{2u}	B ₂	B _u	B ₂	В
E_{1u}	E ₁	E _{1u}	E_1	E_1
E_{2u}	E_2	E_{2u}	E_2	E_2

Note the flipping of B_2 and B_1 and A_2 and A_1 in C_{6v} required by the correspondence between characters for the common symmetry elements.

C ₆	Е	C ₆	C ₃	C ₂	C_{3}^{2}	C ₆ ⁵
A	1	1	1	1	1	1
В	1	-1	1	-1	1	-1
E ₁	2	1	-1	-2	-1	1
E ₂	2	-1	-1	2	-1	-1

5) The character table is given below in its real form.

6) The Γ_{π} listed at the bottom of the C₆ character table above reduces to A + B + E₁ + E₂. If we call the pi orbitals π_1 through π_6 , then use of the projection operator gives:

$$\begin{split} \Psi(A) &= N(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5 + \pi_6) \\ \Psi(B) &= N(\pi_1 - \pi_2 + \pi_3 - \pi_4 + \pi_5 - \pi_6) \\ \Psi(E_{1a}) &= N(2\pi_1 + \pi_2 - \pi_3 - 2\pi_4 - \pi_5 + \pi_6) \\ \Psi(E_{1b}) &= N(\pi_2 + \pi_3 - \pi_5 - \pi_6) \\ \Psi(E_{2a}) &= N(2\pi_1 - \pi_2 - \pi_3 + 2\pi_4 - \pi_5 - \pi_6) \\ \Psi(E_{2b}) &= N(\pi_2 - \pi_3 + \pi_5 - \pi_6) \end{split}$$

These wavefunctions can be correlated back to the correct representation in D_{4h} symmetry by looking at their symmetry properties. For example, the A function must be A_{1g}, A_{2g}, A_{1u}, or A_{2u} in D_{6h}. It consists of the in phase combination of all 6 π orbitals and it is u with respect to inversion symmetry. From the character table, A_{1u} and A_{2u} can be distinguished by their different behavior under either C₂' operation. Since the function in question goes into -1 itself under a C₂' perpendicular to the C₆ axis, this implies that it is an A_{2u} function. Similarly $\Psi(B)$ corresponds to $\Psi(B_{2g})$ with the choice that the C₂' axis passes through opposite carbons in the ring. If we had taken C₂' to bisect a side of the hexagonal ring, then it would be B_{1g}. It is interesting that no such ambiguity exists for the A representations in this point group. For the E representations it is a bit more complex, because both orbitals must be considered together to find the characters. We note that both $\Psi(E_{1a})$ and $\Psi(E_{1b})$ are g orbitals, so the character for the identity will be +2. Thus, they correspond to $\Psi(E_{1g}^a)$ and $\Psi(E_{1g}^b)$ in D_{6h}. On the other hand, both $\Psi(E_{2a})$ and $\Psi(E_{2b})$ are u functions. They correspond to $\Psi(E_{2u}^a)$ and $\Psi(E_{2u}^b)$ in the D_{6h} point group.