Notation


- Spectroscopists sometimes use $F$ for triply degenerate; almost everyone uses $G$ and $H$ for four- and five-fold degenerate.

- $A$ and $B$ are symmetric and antisymmetric, respectively, with respect to rotation around the principal axis.

- Primes refer to behaviour with respect to reflection plane: single prime symmetric, double prime antisymmetric.

- Inversion symmetry is denoted by subscripts $g$ and $u$ (even and odd).

- Subscript numerals are counting indices.
Reduction of a Representation

- This is the application of our formula

\[ \chi(G) = \bigoplus c_\alpha \chi^\alpha(G) \]
\[ c_\alpha = g^{-1} \sum_{k \text{ classes}} N_k \chi(G_k)^* \chi^\alpha(G_k). \]

- \( E \otimes E \) in \( C_{3v} \) is (4,1,0): reduces to \( A_1 \oplus A_2 \oplus E \).
Subduction

- In the $C_s$ subgroup $\{E, \sigma^a_v\}$ of $C_{3v}$, $x$ is a basis function for $A'$ and $y$ for $A''$. Hence $E$ in $C_{3v}$ subduces to $A' \oplus A''$ in $C_s$.

- Reduction of a representation of $G$ is the analysis into a direct sum of irreps of $G$.

- Subduction of a representation of $G$ is the analysis into a direct sum of irreps of $H$, where $H \subset G$. 
Basis Functions

- Representation matrices and character tables can be used, as we have shown, to deduce basis functions for irreps.

- Actually, the way these tables are derived in the first place usually comes from looking at the transformation of various functions, which form partners, etc. Thus the tables can be derived from basis functions!

- An excellent source of basis functions is the spherical harmonics

\[
Y_{l,+m}(\theta, \phi) = N P_{l}^{m}(\cos \theta) \cos m\phi
\]

\[
Y_{l,-m}(\theta, \phi) = N P_{l}^{m}(\cos \theta) \sin m\phi,
\]

where \( P_{l}^{m}(x) \) is an associated Legendre polynomial and \( N \) is a normalization constant.
Basis Functions

- For many point groups the spherical harmonics provide basis functions for all irreps for relatively low values of $l$. For groups of very high order high $l$ values may be required.

- The pairs of functions $Y_{l,+m}$ and $Y_{l,-m}$ for given $l$ and (non-zero) $m$ form basis functions for the $m$th degenerate irrep of the linear groups. For axial groups such a pair may again provide a basis for a degenerate irrep, but sometimes the two functions will transform separately as basis functions for a nondegenerate irrep. This can easily be decided by inspection.
Separable Degeneracy

- By examining the full matrix irreps for $C_{3v}$, we might conclude that the matrix irreps for $C_3$ are

$$C_3 \text{ “Matrix Irreps”}$$

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_3$</th>
<th>$C_3^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$(E)_{11}$</td>
<td>1</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
</tr>
<tr>
<td>$(E)_{21}$</td>
<td>0</td>
<td>$\frac{\sqrt{3}}{2}$</td>
<td>$-\frac{\sqrt{3}}{2}$</td>
</tr>
<tr>
<td>$(E)_{12}$</td>
<td>0</td>
<td>$-\frac{\sqrt{3}}{2}$</td>
<td>$\frac{\sqrt{3}}{2}$</td>
</tr>
<tr>
<td>$(E)_{22}$</td>
<td>1</td>
<td>$-\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
</tr>
</tbody>
</table>
Separable Degeneracy

- However, the dimensionality of the irreps is wrong — $C_3$ is of order three. On inspection, the unitary transformation

\[
\begin{pmatrix}
2^{-1/2} & 2^{-1/2} \\
2^{-1/2}i & -2^{-1/2}i
\end{pmatrix}
\]

reduces the “E” irrep.
Separable Degeneracy

- We obtain

\[ C_3 \text{ Irreps} \]

<table>
<thead>
<tr>
<th></th>
<th>( E )</th>
<th>( C_3 )</th>
<th>( C_3^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( E1 )</td>
<td>1</td>
<td>( \omega )</td>
<td>( \omega^* )</td>
</tr>
<tr>
<td>( E2 )</td>
<td>1</td>
<td>( \omega^* )</td>
<td>( \omega )</td>
</tr>
</tbody>
</table>

where \( \omega \) and \( \omega^* \) are the so-called “complex cube roots of unity”, \( \exp(\pm 2\pi i/3) \).

- Complex irreps, complex basis functions.
Separable Degeneracy

- Energy levels belonging to these irreps are degenerate in the absence of magnetic interactions, invariant under time reversal, etc.

- Use two-dimensional real *reducible* representations and real basis functions.

- Need to remember that these two-dimensional representations are not irreducible.
Continuous Compact Groups

- The linear groups are infinite order: summation over group elements becomes \textit{integration over the group manifold}. For character projection in $C_{\infty \nu}$, for example,

\[
\mathcal{P}^\gamma f = \frac{1}{4\pi} \left\{ \int_{-\pi}^{\pi} \chi^\gamma [C(\phi)]^* C(\phi) f \, d\phi \\
+ \int_{-\pi}^{\pi} \chi^\gamma [\sigma_\nu(\alpha)]^* \sigma_\nu(\alpha) f \, d\alpha \right\}
\]

- In many cases there is no need to resort to these more elaborate tactics, as the necessary results can often be obtained by inspection.
Stabilizers of Centres

- An operator $G \in \mathcal{G}$ will generally transform centre $A$ in a molecule into its image $G(A)$. However, some operations $U$ may leave centre $A$ unchanged:

$$U(A) = A \forall U.$$ 

- Easy to show that the operations $U$ form a group $\mathcal{U}$, a subgroup of $\mathcal{G}$. A subgroup with the above property is termed the stabilizer of $A$ in $\mathcal{G}$.

- Distinct image centres can be found by enumerating left cosets $G\mathcal{U}$ and taking one operator from each distinct coset.

- The number of such cosets is $g/u$, where $u$ is the order of $\mathcal{U}$. This number is called the index of the stabilizer; it is necessarily an integer.
Example: CH₄

- Point group is $T_d$ (order 24).
- Stabilizer of the carbon is again $T_d$.
- Stabilizer of a given hydrogen is a $C_{3v}$ group (order 6), comprising the trigonal axis through the hydrogen and the three reflection planes that intersect in that axis.
- Index of the stabilizer of hydrogen is $24/6 = 4$. 

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Atomic Orbitals

- We note that virtually all atomic orbitals in use can be written as
  \[ f_A(r) = R_A(r)Y_{l m, A}(\theta, \phi), \]
  or as a linear combination of these functions, where \( R_A(r) \) is spherically symmetric about centre \( A \).

- The transformation of \( f_A(r) \) under an operator \( G \) breaks into two factors: the transformation of \( A \) under \( G \) and the transformation of \( Y_{l m, 0} \) (centred at the origin) under \( G \).

- All we need to determine the symmetry properties is then the transformation behaviour of the angular parts, since the transformation of the centre is usually trivial.
Transformation of Atomic Orbitals

- One very useful observation derives from the fact that if a centre is moved by an operation $G$, the contribution of functions on that centre to the character of $G$ in the (reducible) representation will be zero. In other words, if $G$ is not in the stabilizer of $A$, operating on functions on $A$ must produce functions on other centres, so the transformation matrix will have zero on the diagonal.
Transformation of Atomic Orbitals

Planar Symmetric BF₃ Molecule ($D_{3h}$)

- Stabilizer of B is $D_{3h}$, of F is $C_{2v}$. 
Atomic Orbitals

• An $s$ orbital on B must be totally symmetric: $a'_1$. A $p$ set must be $a''_2 \oplus e'$: the reducible representation spanned by the Cartesian axes.

• The stabilizer of $F_1$ is $C_{2v}$, so that the character of the representation spanned by an $s$ orbital on $F_1$ and its images must be zero for the operations $C_3$ and $S_3$. We have

$$
\begin{array}{ccccccc}
E & \sigma_h & 2C_3' & 2S_3' & 3C_2' & 3\sigma_v \\
3 & 3 & 0 & 0 & 1 & 1 \\
\end{array}
$$

The $a'_1$ contribution is

$$
\frac{1}{12} \left\{ 3 + 3 + 0 + 0 + 3 \times 1 + 3 \times 1 \right\} = 1,
$$

By subtracting this from the original reducible representation
we obtain

\[
\begin{array}{cccccc}
E & \sigma_h & 2C_3 & 2S_3 & 3C'_2 & 3\sigma_v \\
2 & 2 & -1 & -1 & 0 & 0
\end{array}
\]

which is \( e' \).
Atomic Orbitals

- For $p_z$ orbitals on F we have the reducible representation

\[
\begin{array}{ccccccc}
E & \sigma_h & 2C_3 & 2S_3 & 3C''_2 & 3\sigma_v \\
3 & -3 & 0 & 0 & -1 & 1 \\
\end{array}
\]

which reduces to $a''_2 \oplus e''$.

- For the $p_x$ and $p_y$ orbitals on F we have the reducible representation

\[
\begin{array}{ccccccc}
E & \sigma_h & 2C_3 & 2S_3 & 3C''_2 & 3\sigma_v \\
6 & 6 & 0 & 0 & 0 & 0 \\
\end{array}
\]

which reduces to $a'_1 \oplus a'_2 \oplus 2e'$. 
Exploiting Direct Product Groups

- There is no need to use the full group $D_{3h}$ for these manipulations. The symmetry with respect to the horizontal plane is trivial to determine: it is easier to use the group $C_{3v}$ and determine the symmetry with respect to the plane by inspection. For example, in $C_{3v}$ we obtain

$$
\begin{array}{ccc}
E & 2C_3 & 3\sigma_v \\
6 & 0 & 0 \\
\end{array}
$$

for the $p_x$ and $p_y$ orbitals on F. This reduces to $a_1 \oplus a_2 \oplus 2e$. Since all the orbitals lie in the molecular plane, the full labels must be $a'_1 \oplus a'_2 \oplus 2e'$.

- For direct product groups involving a horizontal plane or the inversion, it is generally easier to determine the symmetry with respect to these operations by inspection at the end.
Projection of Atomic Orbitals

- Projection operators

\[ \mathcal{P}^\alpha_{ii} = g^{-1} n_\alpha \sum_G D^\alpha_{ii}(G)^* G \]

and shift operators

\[ \mathcal{P}^\alpha_{ji} = g^{-1} n_\alpha \sum_G D^\alpha_{ji}(G)^* G, \]

- Obtain explicit symmetry-adapted functions from \( s \) orbitals on each \( F \) in \( BF_3 \), denoted \( s_1, s_2, \) and \( s_3 \). Use \( C_{3v} \).

\[ \mathcal{P}^{A_1} = \frac{1}{6} \left[ E + C_3 + C_3^2 + \sigma_1 + \sigma_2 + \sigma_3 \right] \]

and

\[ \mathcal{P}^{E}_{11} = \frac{2}{6} \left[ E - \frac{1}{2} C_3 - \frac{1}{2} C_3^2 + \sigma_1 - \frac{1}{2} \sigma_2 - \frac{1}{2} \sigma_3 \right]. \]
\[ P^A_{11} s_1 = \frac{1}{6} \left[ s_1 + s_2 + s_3 + s_1 + s_3 + s_2 \right] \]

\[ = \frac{1}{3} \left[ s_1 + s_2 + s_3 \right] . \]

\[ P^E_{11} s_1 = \frac{2}{6} \left[ s_1 - \frac{1}{2} s_2 - \frac{1}{2} s_3 + s_1 - \frac{1}{2} s_3 - \frac{1}{2} s_2 \right] \]

\[ = \frac{1}{3} \left[ 2s_1 - s_2 - s_3 \right] . \]
Projection of Atomic Orbitals

- We can apply a shift operator

\[
\mathcal{P}_{21}^E = \frac{2}{6} \left[ \frac{\sqrt{3}}{2} C_3 - \frac{\sqrt{3}}{2} C_3^2 - \frac{\sqrt{3}}{2} \sigma_2 + \frac{\sqrt{3}}{2} \sigma_3 \right]
\]

to the basis function of species \((e,1)\).

\[
\mathcal{P}_{21}^E \frac{1}{3} \left[ 2s_1 - s_2 - s_3 \right]
\]

\[
= \frac{\sqrt{3}}{18} \left[ 2s_2 - s_3 - s_1 - 2s_3 + s_1 + s_2 - 2s_3 + s_2 + s_1 + 2s_2 - s_1 - s_3 \right]
\]

\[
= \frac{\sqrt{3}}{3} \left[ s_2 - s_3 \right].
\]
• Operation on $s_1$ with $P^E_{22}$ or $P^E_{12}$ yields zero.
Character Projection

- We could instead apply the $e$ character projector

$$\mathcal{P}^E = n_\alpha g^{-1} \sum_{G} \chi^\alpha(G')^*G.$$ 

to $s_1$.

- We obtain

$$\mathcal{P}^E s_1 = \frac{1}{3} [2s_1 - s_2 - s_3]$$

- To find another $e$ basis function we need to project on another orbital:

$$\mathcal{P}^E s_2 = \frac{1}{3} [2s_2 - s_3 - s_1].$$

This is not even orthogonal to the result of projecting on $s_1$, much less equivalent to the partner function we found previously.
Character Projection

- We can obtain the correct partner function by orthogonalizing the second character projection result to the first. However, without reference to full matrix irreps, we still cannot identify these functions with particular symmetry species. And in general, the results of character projection, followed by orthogonalization, say, will not yield functions that can be identified with symmetry species anyway.
Character vs Full Matrix Projectors

- Character projectors are easier to use and do not require full representation matrices.

- Character projectors do not yield partner functions and usually do not give basis functions for symmetry species.

- Representation matrix information can often be obtained by “induction” from a few tables, such as those given in the Supplementary Notes.

- Application of a suitable sequence of character projectors for a chain of subgroups can give the same results.

- The most important thing is to be familiar with both approaches.