Group theory and QM

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Chemical applications of group theory F. Albert Cotton Chapter 5
Outline

• Wavefunctions are bases for irreducible representations
• The direct product
• Identifying nonzero matrix elements
Wavefunction as a basis for irreps.

Nondegenerate case:

\[ \mathcal{H} \Psi = E \Psi \]
\[ R \mathcal{H} = \mathcal{H} R \]
\[ \mathcal{H} R \Psi_i = E_i R \Psi_i \]
\[ R \Psi_i = \pm 1 \Psi_i \]

Degenerate case:

\[ \mathcal{H} \sum_j a_{ij} \Psi_j = \mathcal{H} a_{i1} \Psi_{i1} + \mathcal{H} a_{i2} \Psi_{i2} + \cdots + \mathcal{H} a_{ik} \Psi_{ik} \]
\[ = E_i a_{i1} \Psi_{i1} + E_i a_{i2} \Psi_{i2} + \cdots + E_i a_{ik} \Psi_{ik} \]
\[ = E_i \sum_j a_{ij} \Psi_{ij} \]

\[ \int \sum_j a_{ij} \Psi_j^* a_{ij} \Psi_j \, d\tau = \sum_j a_{ij}^2 = 1 \]

These are already irreducible representations.
Wavefunction as a basis for irreps.

$E_i$ is $k$-fold degenerate:

$$\mathcal{H} R \Psi_{il} = E_i R \Psi_{il}$$

$$R \Psi_{il} = \sum_{j=1}^{k} r_{jl} \Psi_{ij}$$

$$S \Psi_{ij} = \sum_{m=1}^{k} s_{mj} \Psi_{im}$$

$$T \Psi_{il} = \sum_{m=1}^{k} t_{ml} \Psi_{im}$$
Example

$p_x, p_y$ orbitals of nitrogen atom in ammonia:

\[ p_x = \Psi, \sin \theta \cos \phi \]
\[ p_y = \Psi, \sin \theta \sin \phi \]

E:

\[ E p_x = E(\sin \theta_1 \cos \phi_1) = \sin \theta_2 \cos \phi_2 = \sin \theta_1 \cos \phi_1 = p_x \]
\[ E p_y = E(\sin \theta_1 \sin \phi_1) = \sin \theta_2 \sin \phi_2 = \sin \theta_1 \sin \phi_1 = p_y \]

C₃:

\[ C_3 p_x = C_3(\sin \theta_1 \cos \phi_1) = \sin \theta_2 \cos \phi_2 \]
\[ = (\sin \theta_1)(-\frac{1}{2})(\cos \phi_1 + \sqrt{3} \sin \phi_1) \]
\[ = -\frac{1}{2} \sin \theta_1 \cos \phi_1 - (\sqrt{3}/2) \sin \theta_1 \sin \phi_1 \]
\[ = -\frac{1}{2} p_x - (\sqrt{3}/2)p_y \]

\[ C_3 p_y = C_3(\sin \theta_1 \sin \phi_1) = \sin \theta_2 \sin \phi_2 \]
\[ = (\sin \theta_1)(-\frac{1}{2})(\sin \phi_1 - \sqrt{3} \cos \phi_1) \]
\[ = (\sqrt{3}/2) \sin \theta_1 \cos \phi_1 - \frac{1}{2} \sin \theta_1 \sin \phi_1 \]
\[ = (\sqrt{3}/2)p_x - \frac{1}{2}p_y \]

\[ \sigma_v: \]

\[ \sigma_v p_x = \sigma_v(\sin \theta_1 \cos \phi_1) = \sin \theta_2 \cos \phi_2 = \sin \theta_1 \cos \phi_1 = p_x \]
\[ \sigma_v p_y = \sigma_v(\sin \theta_1 \sin \phi_1) = \sin \theta_2 \sin \phi_2 = -\sin \theta_1 \sin \phi_1 = -p_y \]
Example

\[ p_x = \Psi_x \sin \theta \cos \phi \]
\[ p_y = \Psi_x \sin \theta \sin \phi \]

\[
\begin{bmatrix}
1 & 0 & \frac{1}{2} \\
0 & 1 & -\frac{\sqrt{3}}{2} \\
\frac{1}{2} & -\frac{\sqrt{3}}{2} & 1
\end{bmatrix}
\begin{bmatrix}
p_x \\
p_y
\end{bmatrix}
= E
\begin{bmatrix}
p_x \\
p_y
\end{bmatrix}
\]
\[ \chi(E) = 2 \]

\[
\begin{bmatrix}
-\frac{1}{2} & \frac{\sqrt{3}}{2} \\
\frac{\sqrt{3}}{2} & -\frac{1}{2}
\end{bmatrix}
\begin{bmatrix}
p_x \\
p_y
\end{bmatrix}
= C_3
\begin{bmatrix}
p_x \\
p_y
\end{bmatrix}
\]
\[ \chi(C_3) = -1 \]

\[
\begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}
\begin{bmatrix}
p_x \\
p_y
\end{bmatrix}
= \sigma_v
\begin{bmatrix}
p_x \\
p_y
\end{bmatrix}
\]
\[ \chi(\sigma_v) = 0 \]
The direct product (external)

R is a symmetry operation, $X_m$ and $Y_m$ are two set of functions which are bases for the representation of the group

$$RX_i = \sum_{j=1}^{m} x_{ji} X_j$$
$$RY_k = \sum_{l=1}^{n} y_{lk} Y_l$$

It is also true that

$$RX_iY_k = \sum_{j=1}^{m} \sum_{l=1}^{n} x_{ji} y_{lk} X_j Y_l = \sum_{j} \sum_{l} z_{jl,ik} X_j Y_l$$

Then $z_{jl,ik}$ is element $(mn)\times(mn)$ matrix

**The characters of the representation of a direct product are equal to the products of the characters of the representations based on the individual sets of functions.**

**PROOF:** This theorem is easily proved as follows:

$$\chi_\pi(R) = \sum_{jl} z_{jl,il} = \sum_{j=1}^{m} \sum_{l=1}^{n} x_{ji} y_{lk} = \chi_\pi(R)\chi_\nu(R)$$

<table>
<thead>
<tr>
<th>Cₜ</th>
<th>E</th>
<th>C₂</th>
<th>2C₄</th>
<th>2σₓ</th>
<th>2σₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>


$A_1A_2 = A_2$
$E^2 = (A_1 + A_2 + B_1 + B_2$
$B_1E = E$
$A_1EB_2 = E$
The direct product

\[ \int_{-\infty}^{\infty} y \, dx \begin{cases} 0 & \text{if } y \text{ is odd} \\ \text{Not zero} & \text{if } y \text{ is even} \end{cases} \]

Only if one of the irreducible representations occurring in the sum is the totally symmetric one will the integral have a value other than zero.

\[ a_i = \frac{1}{\hbar} \sum_R \chi(R)\chi_i(R) \]

\[ a_i = \frac{1}{\hbar} \sum_R \chi_{AB}(R)\chi_i(R) \]

\[ a_1 = \frac{1}{\hbar} \sum_R \chi_{AB}(R) \]

\[ \chi_{AB}(R) = \chi_A(R)\chi_B(R) \]

\[ a_1 = \frac{1}{\hbar} \sum_R \chi_A(R)\chi_B(R) \]

The representation of a direct product, \( \Gamma_{AB} \), will contain the totally symmetric representation only if the irreducible \( \Gamma_A \) = the irreducible \( \Gamma_B \).

\[ a_1 = \delta_{AB} \quad \text{Q.E.D.} \]
Example group $D_4$

### Character table for point group $D_4$

<table>
<thead>
<tr>
<th></th>
<th>$D_4$</th>
<th>$E$</th>
<th>$2C_4(z)$</th>
<th>$C_2(z)$</th>
<th>$2C_2'$</th>
<th>$2C_2''$</th>
<th>linear functions, rotations</th>
<th>quadratic functions</th>
<th>cubic functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>-</td>
<td>$x^2+y^2, z^2$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$A_2$</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-</td>
<td>$z, R_z$</td>
<td>-</td>
<td>$z^3, z(x^2+y^2)$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>-</td>
<td>$x^2, y^2$</td>
<td>$xyz$</td>
<td>$xyz$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>-</td>
<td>$xy$</td>
<td>$z(x^2-y^2)$</td>
<td>$z(x^2-y^2)$</td>
</tr>
<tr>
<td>$E$</td>
<td>+2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$(x, y)$ ($R_x, R_y$)</td>
<td>$(xz, yz)$</td>
<td>$(xz^2, yz^2)$</td>
</tr>
</tbody>
</table>

\[
E \quad 2C_4 \quad C_2 \quad 2C'_2 \quad 2C''_2
\]

\[
\begin{array}{cccc}
4 & 0 & 4 & 0 \\
4 & 0 & 0 & 0
\end{array}
\]

\[
a_{A_1} = \frac{1}{2} [4 + 0 + 4 + 0 + 0] = 1
\]

\[
\frac{\int \psi_i H \psi_j \, d\tau}{\int \psi_i \psi_j \, d\tau} = E
\]

\[
\int f_A f_B f_C \, d\tau
\]

An energy integral $\int \psi_i H \psi_j \, d\tau$ may be nonzero only if $\psi_i$ and $\psi_j$ belong to the same irreducible representation of the molecular point group.
Spectral transition probabilities

\[ h\nu = E_i - E_j \]
\[ I \propto \int \psi_i \mu \psi_j \, d\tau \]

For electric dipole operator:

\[ \mu = \sum_i e_i x_i + \sum_i e_i y_i + \sum_i e_i z_i \]
\[ I_x \propto \int \psi_i x \psi_j \, d\tau \]
\[ I_y \propto \int \psi_i y \psi_j \, d\tau \]
\[ I_z \propto \int \psi_i z \psi_j \, d\tau \]

An electric dipole transition will be allowed with \( x, y, \) or \( z \) polarization if the direct product of the representations of the two states concerned is or contains the irreducible representation to which \( x, y, \) or \( z, \) respectively, belongs.

\[ B_{1g} x A_{2u} x B_{2u} = 1, 1, 1, 1, 1, 1, 1, 1, 1, 1 = A_{1g} \]
Summary

• Eigenfunctions of a system are bases for irreps.
• Direct product of irreducible representations.
• Identifying nonzero matrix elements.