Cyclic Groups

Consider \( C_N \), the cyclic group consisting of the operations \( C_N, C_N^2, C_N^3, ..., C_N^{N-1}, C_N^N = E \). Because all the operations are in the different classes, there are \( N \) irreducible representations and they are all one dimensional. This means that the characters are the same as the matrices - just numbers.

Character Tables for Cyclic Groups

\[
\begin{array}{c|ccccccc}
\Gamma & C_N & C_N^2 & C_N^3 & \cdots & C_N^{N-1} & C_N^N = E \\
\hline
\Gamma_1 & \xi & \xi^2 & \xi^3 & \cdots & \xi^{N-1} & \xi^N \\
\Gamma_2 & \xi^2 & \xi^4 & \xi^6 & \cdots & \xi^{2N-2} & \xi^{2N} \\
\Gamma_3 & \xi^3 & \xi^6 & \xi^9 & \cdots & \xi^{3N-3} & \xi^{3N} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\Gamma_{N-1} & \xi^{N-1} & \xi^{2N-2} & \xi^{3N-3} & \cdots & \xi^{-2} & \xi^{N(N-1)} \\
\Gamma_N & \xi^N & \xi^{2N} & \xi^{3N} & \cdots & \xi^{-1} & \xi^{N^2} \\
\end{array}
\]

\( \xi = \exp(2\pi i / N) \)
**Example**

★ Use the $C_6$ group to find the characters of the reducible representation obtained using the 6 carbon $p\pi$ orbitals of benzene as a basis — then find the irreducible reps. spanned by this rep.

★ Draw the complex coefficients of the orbitals for each irreducible representation.

★ Draw real counterparts of these orbitals.

<table>
<thead>
<tr>
<th>$C_6$</th>
<th>$E$</th>
<th>$C_6$</th>
<th>$C_6^2$</th>
<th>$C_6^3$</th>
<th>$C_6^4$</th>
<th>$C_6^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^0 = \Gamma^6$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^1$</td>
<td>$\epsilon$</td>
<td>$\epsilon^2$</td>
<td>$\epsilon^3$</td>
<td>$\epsilon^4$</td>
<td>$\epsilon^5$</td>
<td>$\epsilon^6$</td>
</tr>
<tr>
<td>$\Gamma^2$</td>
<td>$\epsilon^3$</td>
<td>$\epsilon^4$</td>
<td>$\epsilon^6$</td>
<td>$\epsilon^8$</td>
<td>$\epsilon^{10}$</td>
<td>$\epsilon^{12}$</td>
</tr>
<tr>
<td>$\Gamma^3$</td>
<td>$\epsilon^4$</td>
<td>$\epsilon^8$</td>
<td>$\epsilon^{12}$</td>
<td>$\epsilon^{16}$</td>
<td>$\epsilon^{20}$</td>
<td>$\epsilon^{24}$</td>
</tr>
<tr>
<td>$\Gamma^4$</td>
<td>$\epsilon^5$</td>
<td>$\epsilon^{10}$</td>
<td>$\epsilon^{15}$</td>
<td>$\epsilon^{20}$</td>
<td>$\epsilon^{25}$</td>
<td>$\epsilon^{30}$</td>
</tr>
<tr>
<td>$\Gamma^5$</td>
<td>$\epsilon^6$</td>
<td>$\epsilon^{12}$</td>
<td>$\epsilon^{18}$</td>
<td>$\epsilon^{24}$</td>
<td>$\epsilon^{30}$</td>
<td>$\epsilon^{36}$</td>
</tr>
</tbody>
</table>

**$C_6$ Group**

$\epsilon = \exp(2\pi i / 6)$

<table>
<thead>
<tr>
<th>$C_6$</th>
<th>$E$</th>
<th>$C_6$</th>
<th>$C_6^2$</th>
<th>$C_6^3$</th>
<th>$C_6^4$</th>
<th>$C_6^5$</th>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^1$</td>
<td>$\epsilon$</td>
<td>$\epsilon^2$</td>
<td>$\epsilon^3$</td>
<td>$\epsilon^4$</td>
<td>$\epsilon^5$</td>
<td>$\epsilon^6$</td>
</tr>
<tr>
<td>$\Gamma^2$</td>
<td>$\epsilon^2$</td>
<td>$\epsilon^4$</td>
<td>$\epsilon^6$</td>
<td>$\epsilon^8$</td>
<td>$\epsilon^{10}$</td>
<td>$\epsilon^{12}$</td>
</tr>
<tr>
<td>$\Gamma^3$</td>
<td>$\epsilon^3$</td>
<td>$\epsilon^6$</td>
<td>$\epsilon^9$</td>
<td>$\epsilon^{12}$</td>
<td>$\epsilon^{15}$</td>
<td>$\epsilon^{18}$</td>
</tr>
<tr>
<td>$\Gamma^4$</td>
<td>$\epsilon^4$</td>
<td>$\epsilon^8$</td>
<td>$\epsilon^{12}$</td>
<td>$\epsilon^{16}$</td>
<td>$\epsilon^{20}$</td>
<td>$\epsilon^{24}$</td>
</tr>
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</tr>
</tbody>
</table>

Let $\psi_1$ be a basis function that belongs to $\Gamma^1$, then

$C_6\psi_1 = \epsilon \psi_1, \ C_6^2\psi_1 = \epsilon^2 \psi_1, \ldots, \ C_6^5\psi_1 = \epsilon^5 \psi_1$

Write $\psi_1$ as a combination of $p\pi$ basis functions,

$\psi_1 = \phi_1 + c_1 \phi_2 + c_2 \phi_3 + c_3 \phi_4 + c_4 \phi_5 + c_5 \phi_6$

$C_6\psi_1 = C_6\left(\phi_1 + c_1 \phi_2 + c_2 \phi_3 + c_3 \phi_4 + c_4 \phi_5 + c_5 \phi_6\right) = \epsilon \psi_1$

$\phi_1 + c_2 \phi_2 + c_3 \phi_3 + c_4 \phi_4 + c_5 \phi_5 + c_6 \phi_6 = \epsilon \psi_1$

$c_1 = 1 \Rightarrow c_2 = \epsilon^* = \epsilon^{-1}$

$c_2 = \epsilon^{-1} = c_1 \epsilon \Rightarrow c_3 = \epsilon^2$
Translation Group (1-dimension)

The one-dimensional translation group is just a particular cyclic group of order $N$. The trans-polyacetylene below is an example of a system with translational symmetry.

1-D Translation Group Char. Table

This has the same appearance as the $C_N$ group’s character table:

$$
\begin{array}{cccccccc}
\Gamma^1 & t^1 & t^2 & t^3 & \ldots & t^{N-1} & t^N = E \\
\Gamma^2 & \varepsilon & \varepsilon^2 & \varepsilon^3 & \ldots & \varepsilon^{N-1} & \varepsilon^N \\
\Gamma^3 & \varepsilon^2 & \varepsilon^4 & \varepsilon^6 & \ldots & \varepsilon^{2N-2} & \varepsilon^{2N} \\
\Gamma^4 & \varepsilon^3 & \varepsilon^6 & \varepsilon^9 & \ldots & \varepsilon^{3N-3} & \varepsilon^{3N} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\Gamma^{N-1} & \varepsilon^{N-1} & \varepsilon^{2N-2} & \varepsilon^{3N-3} & \ldots & \varepsilon^{(N-1)^2} & \varepsilon^{N(N-1)} \\
\Gamma^N & \varepsilon^N & \varepsilon^{2N} & \varepsilon^{3N} & \ldots & \varepsilon^{N(N-1)} & \varepsilon^{2N} \\
\end{array}
$$

Character Table for $T_N$, rewritten

All the IRs of $T_N$ have the form:

$$
\varepsilon = e^{2\pi i / N}
$$

$$
\begin{array}{cccccccc}
\Gamma^j & t^j & t^{2j} & t^{3j} & \ldots & t^{(N-1)j} & t^N = E \\
\Gamma^j & \varepsilon^j & \varepsilon^{2j} & \varepsilon^{3j} & \ldots & \varepsilon^{(N-1)j} & \varepsilon^N \\
\end{array}
$$

We make the substitution $k = \left( \frac{1}{a} \right) \times \left( \frac{j}{N} \right)$, where $-\frac{1}{2a} < k \leq \frac{1}{2a}$

Making the substitution, $\varepsilon^j = (e^{2\pi i / N})^j = e^{2\pi ik}$. This is rewritten to yield

$$
\begin{array}{ccccc}
\Gamma(k) & E & t & t^2 & t^3 & \ldots & t^{N-1} \\
\Gamma(k) & e^{2\pi i (k+u)} & e^{2\pi i (k+2u)} & e^{2\pi i (k+3u)} & \ldots & e^{2\pi i (k+Nu)} \\
\end{array}
$$
Examples

* Find the characters of the reducible representation obtained using the N hydrogen 1s orbitals of a hypothetical H-atom chain (with N atoms) as a basis — then find the irreducible reps. spanned by this rep.

* Follow the same procedure (i) using the longitudinal stretching vectors as a basis, (ii) using the transverse stretching vectors as a basis, (iii) using $p_\alpha$ orbitals as a basis.

$[\text{Pt(CN)}_4]^{-2+\chi}$

Chains in $\text{K}_2[\text{Pt(CN)}_4]$ and $\text{K}_2[\text{Pt(CN)}_4]\text{Br}_{3-5}3\text{H}_2\text{O}$

$[\text{Pt(CN)}_4]^2$: $d(\text{Pt-Pt}) = a = 3.48$ Å

$[\text{Pt(CN)}_4]^1.7$: $d(\text{Pt-Pt}) = a = 2.88$ Å

$\alpha_p - \alpha_d = 8|\beta| \quad \beta = -1$

$\beta_{pd} = \beta \quad \beta_{pp} = 2\beta \quad \beta_{dp} = 1.5\beta$

The tetracyanoplatinates crystallize such that square planar Pt(CN)$_4^{2-}$ species stack upon each other as indicated in the illustration below. (Steric factors cause the square planar ions to stack in a staggered fashion, but we’ll proceed as if the stacking is eclipsed, i.e., as if there is just one Pt(CN)$_4^{2-}$ ion per unit cell.) Pt-Pt distances are markedly shortened (from 3.48 Å to 2.88 Å) when the platinum is oxidized by reaction with Br$_2$ — that results in the intercalation of some additional bromide ions (Br$^-$) into voids between the chains in the solid state structure.
Consider only the largest Pt-Pt $\sigma$ overlaps involving the $5d_z^2$ orbital (occupied for this $d^8$ complex) and the $6p_z$ orbital (a high-lying unoccupied orbital that is stabilized to some extent by overlap with the CN $\pi^*$ orbitals).

Set up the $2 \times 2$ $k$-dependent Hückel-like secular equation and solve it to obtain analytical $k$-dependent expressions for each of the two band curves. Draw a one-dimensional band dispersion diagram that includes bands that derive from the $5d_z^2$ and the $6p_z$ orbitals. Use these parameters:

$$\alpha_p - \alpha_d = 8|\beta| \quad \beta = -1$$

$$\beta_{dd} = \beta \quad \beta_{pp} = 2\beta \quad \beta_{dp} = 1.5\beta$$

Mark the Fermi levels for both systems. Explain why the Pt-Pt distances shrink upon oxidation. Show the lowest energy allowed optical transitions for both systems.

$$\alpha_p - \alpha_d = 8|\beta| \quad \beta = -1$$

2-dimensional Layers

**Bloch’s Theorem in 2– or 3–D**

$$\varphi_k(r + R) = e^{2\pi i k \cdot R} \varphi_k(r) \quad R = ua + vb + wc \quad k = k_x a^* + k_y b^* + k_z c^*$$

- Orbitals and bands for a square net of Hydrogen atoms
- Orbitals and bands for graphite
Selection Rules for Crystals: Vertical Transitions

Intensity, \( I \propto \left| \int \psi_i^* \mathcal{H}'(t) \psi_f \, d\tau \right|^2 \)

where \( \mathcal{H}'(t) \) is the perturbation of the molecule (solid) caused by the electric field of the radiation, and the electromagnetic wave propagating in the \( z \)-direction

\[
\mathcal{H}'(t) = \frac{E_0}{2} \sum_s q_s X_s \left[ e^{2\pi i (s-k_x + i\lambda_{\text{photon}}) x} + e^{-2\pi i (s-k_x + i\lambda_{\text{photon}}) x} \right]
\]

(See Eqs. 16 & 17 in Handout on "Transitions Between Stationary States")

\[
\psi_i \propto \psi_{\text{free}}(r) e^{2\pi i (s-k_x) x} \quad \text{Important terms to consider} \sim \int e^{i\omega \tau} e^{2\pi i (k_x-k_y) y} \, d\tau
\]

\[
\psi_f \propto \psi_{\text{free}}(r) e^{2\pi i (s-k_y) y} \quad I = 0 \quad \text{unless} \quad k_y = k_x, + k_{\text{photon}} = 0
\]

but \( |k_{\text{photon}}| \ll |k_x|, |k_y| \) (\( \lambda_{\text{photon}} \gg \lambda_t, \lambda_e \)), \( \therefore \) transition forbidden unless \( k_y = k_x = 0 \)

Allowed transitions are vertical, \( k_f = k_i \)

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2-D Square H array - Band

2-D Graphite (Graphene) \( \pi \) Bands
PES Measurements of Graphite

Densities of States for 1D, 2-D, 3-D