Lecture 6: Representations

Filipp Furche

Chem 150/250 Fall 2023

10/13/2023

UCIrvine

http://ffgroup.chem.uci.edu

Definition

- A representation is a map $\Gamma : \mathcal{G} \to a$ from a group $\mathcal{G}$ onto an operator algebra A s. t.

  $$\mathbf{P}(a) \cdot \mathbf{P}(b) = \mathbf{P}(a \cdot b)$$

  $\forall a, b \in \mathcal{G}, \forall \mathbf{P}(a), \mathbf{P}(b) \in A$.
- The domain of A is called "representation space" S, i.e., $A = S \otimes S$. If it has finite dimension n, each operator corresponds to an $n \times n$ matrix.
- Symmetry operations are represented by orthogonal/unitary operators with determinant $+1$ (C_n, E) or -1 (S_n, σ).

Determining Representation Matrices

1. Choose a convenient orthonormal basis $\{\mathbf{e}_i\}$ of S.
2. For each element $a \in \mathcal{G}$, construct the representation matrix element
$$P_{ij}(a) = (\mathbf{e}_i|\mathbf{P}(a)\mathbf{e}_j)$$
by considering the action of $\mathbf{P}(a)$ on each basis vector $\mathbf{e}_j$.
3. You may check your result by verifying that each representation matrix is unitary and has determinant ± 1.

Example: C_{2v}, $\Gamma_{\mathbf{r}}$

The representation $\Gamma_{\mathbf{r}}$ ("polar vector representation") of C_{2v} is spanned by the unit vectors $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$. Determine the representation matrices.

- $\mathrm{C}_{2v} = \{E, C_2, \sigma_v, \sigma_v'\}$
- Representation matrices:

$$\Gamma_{\mathbf{r}} = \left\{ \mathbf{P}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \mathbf{P}(C_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \right.$$

$$\left. \mathbf{P}(\sigma_v) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \mathbf{P}(\sigma_v') = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\}$$

Characters

- The character of a group element a in a representation Γ is

$$\chi_\Gamma(a) = \mathrm{tr}\left\{\mathbf{P}(a)\right\} = \langle \mathbf{P}(a) \rangle = \sum_{i=1}^{n} P_{ii}(a).$$

- Example: C_{2v}, $\Gamma_\mathbf{r}$

	E	C_2	σ_v	$\sigma_{\mathrm{v}'}$
$\Gamma_\mathbf{r}$	3	-1	1	1

- Characters are convenient, but often not sufficient (e.g. for non-Abelian symmetry)