Lecture 8: Symmetry Adapted Bases

Filipp Furche

Chem 150/250 Fall 2023

10/13/2023

UCIrvine

http://ffgroup.chem.uci.edu

Bases of IRREP Spaces

- Decomposition of REP space S_Γ into IRREP spaces:

$$S_\Gamma = S_\alpha \oplus S_\beta \oplus \cdots$$

- A set of vectors $\{\mathbf{v}_{\alpha i} | i = 1, \ldots, d_\alpha n_\alpha\}$ forming a basis of S_α is called symmetry adapted. For unitary REPs, bases can be chosen orthonormal, i.e., $(\mathbf{v}_{\alpha i}|\mathbf{v}_{\alpha j}) = \delta_{ij}$.
- The symmetry adapted basis vectors belonging to *different* IRREPs, and thus

$$(\mathbf{v}_{\alpha i}|\mathbf{v}_{\beta j}) = \delta_{\alpha\beta}\delta_{ij}$$

- The $\{\mathbf{v}_{\alpha i}\}$ form a symmetry-adapted basis of S_Γ.

Determining Symmetry Adapted Bases

- IRREP projection operator $\mathbf{\Pi}_{\alpha\,k}$: Projects $\mathbf{x} \in S_\Gamma$ onto IRREP space S_α, k-th "column",

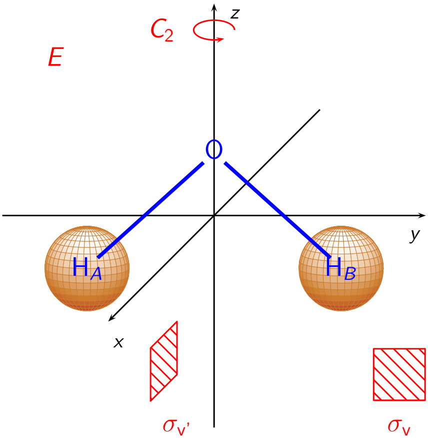
$$\mathbf{\Pi}_{\alpha\,k} = \frac{d_\alpha}{g} \sum_{a \in \mathcal{G}} \mathbf{P}^*_{\alpha\,kk}(a)\mathbf{P}(a). \tag{1}$$

- Requires knowledge of IRREP matrices $\mathbf{P}_{\alpha\,kk}(a)$
- Orthogonalization not necessary if IRREP multiplicity is 1.
- Character projection operator: Projects onto any column of IRREP space S_α,

$$\mathbf{\Pi}_\alpha = \sum_{k=1}^{d_\alpha} \mathbf{\Pi}_{\alpha\,k} = \frac{d_\alpha}{g} \sum_{a \in \mathcal{G}} \chi^*_\alpha(a)\mathbf{P}(a). \tag{2}$$

- Always requires column orthogonalization for more than 1D IRREPs.

Example: Hydrogen 1s SALCs in Water



Example: Hydrogen 1s SALCs in Water

- The two 1s atomic orbitals $\{\psi_A, \psi_B\}$ form basis of a two-dimensional REP space $S_{\Gamma_{2s}}$
- For qualitative purposes, use complete neglect of differential overlap (CNDO) to construct ON basis of Γ_{2s}:

$$(\psi_A|\psi_A) = (\psi_B|\psi_B) = 1, \quad (\psi_A|\psi_B) = 0$$

  [$(\cdot|\cdot)$ is Hilbert space inner product]
- The resulting Γ_{2s} representation of C_{2v} is reducible with REP matrices

	E	C_2	σ_v	$\sigma_{v'}$
P	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

Example: Hydrogen 1s SALCs in Water

- IRREP decomposition: $\Gamma_{2s} = A_1 \oplus B_1$
- Projection operators:

$$\mathbf{\Pi}_{A_1} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad \mathbf{\Pi}_{B_1} = \frac{1}{2}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

- Projection of either unit vector and normalization yields

$$\psi_{A_1} = \frac{1}{\sqrt{2}}(\psi_A + \psi_B), \quad \psi_{B_1} = \frac{1}{\sqrt{2}}(\psi_A - \psi_B)$$