Lecture 9: Applications of Group Theory, Part I

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Tensors and Molecular Properties: Scalars

Molecule with point group symmetry $\mathcal{G} = \{a, b, \ldots\}$
Tensor rank 0: Scalars, inner products, distances

- "Overlap" between two eigenstates $(\psi_1|\psi_2)$
- (Scalar) operator matrix elements $(\psi_1|\mathbf{O}\psi_2)$
- Hamiltonian, other scalar operators and their traces
- Energies (electronic, vibrational, etc.), charge, isotropic couplings, polarizabilities etc.
- s functions in $\mathbf{O}$
- Invariant under all symmetry operations, hence totally symmetric or zero

Tensors and Molecular Properties: Vectors

Tensor rank 1: Vectors

- Molecular orbitals (describing eigenstates)
- Molecular vibrations (describing eigenmodes)
- Polar vectors: Dipole moment, electric field, translation
- Axial (pseudo) vectors: Angular momenta (orbital+spin), magnetic field, rotations
- Vector operators
- p functions in $\mathbf{O}$
- Underlying vector space may be decomposed into IRREP spaces
- May transform according to any IRREP; however, polar vectors are odd (ungerade) and axial vectors are even (gerade)

Tensors and Molecular Properties: Tensors

Rank 2 tensors:

- (Traceless) quadrupole moment, polarizability, magnetizability, NMR shielding, vector couplings (e.g. 2 angular momenta)
- Two-electron wavefunctions
- spherical d functions in $\mathbf{0}$
- Transform as tensor product of vector REPS
- Second-rank tensors are even (gerade)

Higher rank tensors: Nonlinear response properties, couplings of three and more vectors, etc.

Constructing Tensor Representations

- The tensor product of two REPS Γ_1 and Γ_2 with REP spaces S_1 and S_2 is the REP $\Gamma_1 \otimes \Gamma_2$ on $S_1 \otimes S_2$ with REP matrices

$$\mathbf{P}_{\Gamma_1 \otimes \Gamma_2}(a) = \mathbf{P}_{\Gamma_1}(a) \otimes \mathbf{P}_{\Gamma_2}(a)$$

  $\forall a \in \mathcal{G}$.
- The tensor product of two $n \times n$ and $m \times m$ matrices $\mathbf{A}, \mathbf{B}$ is called Kronecker product and is a $nm \times nm$ matrix

$$\mathbf{A} \otimes \mathbf{B} = \begin{pmatrix} A_{11}\mathbf{B} & A_{12}\mathbf{B} & \cdots \\ A_{21}\mathbf{B} & A_{22}\mathbf{B} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

- The character of a tensor product is the simple product of the characters of the factors:

$$\chi_{\Gamma_1 \otimes \Gamma_2}(a) = \chi_{\Gamma_1}(a)\chi_{\Gamma_2}(a)$$

- The tensor product of two IRREPs is generally not reducible
- Subduction of a tensor product of two IRREPs into a direct sum of IRREPs: Clebsch-Gordan reduction

Example: Nuclear Displacements of Water

- Γ_C: Representation of C_{2v} spanned by all Cartesian displacements of all atoms. Dimension: $3N = 9$
- Rather than constructing all 9×9 REP matrices by hand, we note that

$$S_C = S_{\mathbf{r}} \otimes S_p,$$

where S_p is an N-dimensional vector space of ordered N-tuples of atoms. For example,

$$\mathbf{e}_O = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{e}_{H_1} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \mathbf{e}_{H_2} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

denotes the O and the two H atoms.

Example: Nuclear Displacements of Water

- REP matrices ("nuclear exchange tables"):

$$\Gamma_p = \left\{ \mathbf{P}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \mathbf{P}(C_2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \right.$$
$$\left. \mathbf{P}(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \mathbf{P}(\sigma_v') = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \right\}$$

- Easily compute characters without setting up REP matrices

$$\chi_C(a) = \chi_{\mathbf{r}}(a)\chi_p(a),$$

because $\Gamma_C = \Gamma_{\mathbf{r}} \otimes \Gamma_p$:

	E	C_2	σ_v	$\sigma_{v'}$
Γ_C	9	-1	3	1