Lecture 10: Applications of Group Theory, Part II

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Chem 150/250 Fall 2023

10/20/2022

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Conservation Laws

A system "has a symmetry" associated with $\mathcal{G}$ iff the Hamiltonian is totally symmetric under all symmetry operations, i.e.,

$$\hat{P}(a)\hat{H}\hat{P}^{-1}(a) = \hat{H} \quad \forall a \in \mathcal{G}$$

or equivalently $[\hat{H}, \hat{P}(a)] = 0$.

As a consequence, the eigenstates of $\hat{H}$ transform according to IRREPs of $\mathcal{G}$. This is closely related to Noether's theorem, "symmetries induce conservation laws".

Symmetries and Conservation Laws

Examples:

- Rotational (SO(3)) symmetry: Angular momentum conservation. IRREPs are $2l+1$-dimensional, spanned by integer spherical harmonics
- Spin rotation (SU(2)) symmetry: Total spin conservation. IRREPs are $2l+1$-dimensional, spanned by integer or half integer spherical harmonics
- Translation symmetry: Momentum conservation. IRREPs are spanned by reciprocal lattice vectors
- Parity: Inversion symmetry. IRREPs are even (g) and odd (u)
- Point group symmetry: All molecular eigenstates (orbitals, vibrations, etc.) transform according to an IRREP of $\mathcal{G}$

Matrix Elements

Necessary condition for a matrix element

$$M(\alpha, \beta, \gamma) = (\psi_\alpha | \hat{O}_\beta \phi_\gamma)$$

to be non-zero:

$$\alpha \otimes \beta \otimes \gamma \text{contains the totally symmetric IRREP}$$

Generalization: Wigner-Eckart Theorem

Examples

- Dipole moment:

$$\boldsymbol{\mu} = q(\psi_\alpha | \hat{\mathbf{r}} \psi_\alpha)$$

  Nonzero if $\alpha \otimes \Gamma_{\mathbf{r}} \otimes \alpha$ or $\Gamma_{\mathbf{r}} \otimes \alpha \otimes \alpha$ contains totally symmetric IRREP. Since $\alpha \otimes \alpha$ always contains the totally symmetric IRREP, the dipole moment is non-zero if $\Gamma_{\mathbf{r}}$ contains the totally symmetric IRREP. Applies to each component of $\boldsymbol{\mu}$.
- It follows that molecules with inversion symmetry do not have a permanent dipole moment.
- Transition dipole moment:

$$\boldsymbol{\mu}_{\alpha\beta} = q(\psi_\alpha | \hat{\mathbf{r}} \chi_\beta)$$

  Nonzero if $\alpha \otimes \Gamma_{\mathbf{r}} \otimes \beta$ contains the totally symmetric IRREP. Special case: Transitions from closed-shell ground states. α is totally symmetric IRREP, so the condition simplifies to $\Gamma_{\mathbf{r}} \otimes \beta$ containing the totally symmetric IRREP. Hence β must be one of the IRREPs contained in $\Gamma_{\mathbf{r}}$ ("electronically (dipole) allowed transitions")

Examples

- Optical activity / circular dichroism: The circular dichroism intensity is proportional to

$$\boldsymbol{\mu}_{\alpha\beta} \cdot \boldsymbol{m}_{\beta\alpha},$$

where

$$\boldsymbol{\mu}_{\alpha\beta} = \frac{q}{2mc}(\psi_\alpha|\hat{\mathbf{l}}\chi_\beta)$$

is the magnetic transition dipole moment. Necessary condition for scalar product of a polar and axial vector to be non-zero:

$$\Gamma_{\mathbf{r}} \otimes \Gamma_{\mathbf{l}}$$

must contain totally symmetric IRREP

- Stronger condition: Improper rotations (no S_n axes with $n > 0$) must be absent, since the scalar product $\boldsymbol{\mu}_{\alpha\beta} \cdot \boldsymbol{m}_{\beta\alpha}$ is a pseudoscalar (odd parity under improper rotation).

Examples

- IR selection rule: Electronic dipole moment derivative wrt normal mode X_α,
$$\frac{\partial \boldsymbol{\mu}}{\partial X_\alpha}$$
is nonzero if $\Gamma_{\mathbf{r}} \otimes \alpha$ is totally symmetric, i.e., X_α changes the (permanent) dipole moment.
- Raman selection rule: Electronic polarizability derivative wrt normal mode X_α,
$$\frac{\partial \mathbf{P}}{\partial X_\alpha}$$
is nonzero if $\Gamma_{\mathbf{P}} \otimes \alpha$ is totally symmetric. $\mathbf{P}$ is second-rank symmetric tensor, so $\Gamma_{\mathbf{P}}$ contains the totally symmetric IRREP (isotropic part) plus 5 elements transforming as 5 spherical d functions. Hence totally symmetric modes are Raman active.
- Inversion symmetric molecules: X_α is either IR or Raman active, because IR activity implies odd symmetry whereas Raman activity implies even symmetry.