Lecture 9

Announcement: HW2 is posted
due 3/6

Recap: Space groups $G \triangleright T \leftarrow$ Bravais lattice

230 space groups in 3D

73: $G = T \rtimes \bar{G}$ symmorphic

$\bar{G}$ = point group

$\bar{G} < G = \bigcup_{i=0}^{n-1} T\{R_i|\vec{0}\}$ $R_i \in \bar{G}$

$g \in G \Rightarrow g = \{\vec{R}|\vec{t}\}$ $R \in \bar{G}$, $\vec{t} \in T$

- Hermann Mauguin notation: [letter][pt grp symbol]

157 · nonsymmorphic $\bar{G} \not\subset G$

$$G = \bigcup_{i=0}^{n-1} T\{R_i | \vec{d}_i\}$$

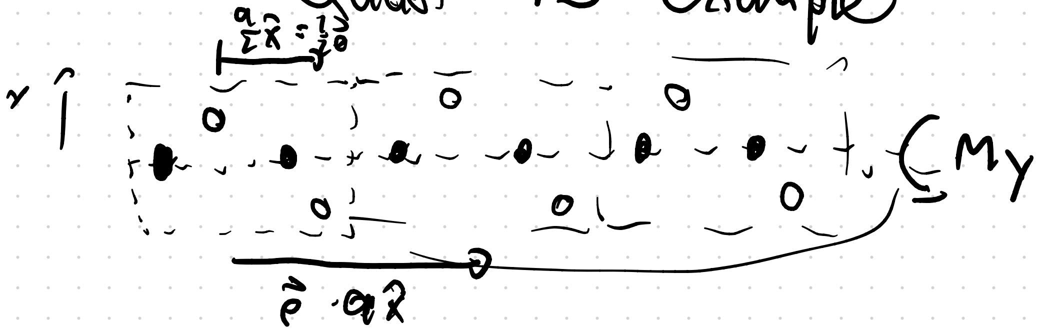
$R_i \in \bar{G}$

$\vec{d}_i$ - at least one must be a fraction of a Bravais lattice translation

- Typically contain screw rotations or glide reflections

- Hermann-Mauguin symbol: subscripts for screw rotations &
letters for glide reflections

Quasi-1D example



$$G = \left\{ \{E \mid n a\hat{x},\ n \in \mathbb{Z}\},\ \{M_y \mid \tfrac{a}{2}\hat{x} + n a\hat{x},\ n \in \mathbb{Z}\} \right\}$$

$$\bar{G} \cong G/T = \{E, M_y\}$$

but $M_y \notin G$

only $\{M_y \mid \frac{a}{2}\hat{x}\} \in G$

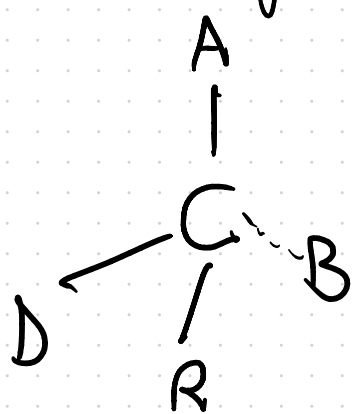
$$G = T \cup T\{M_y \mid \tfrac{a}{2}\hat{x}\}$$

Symmetries of Chiral crystals:

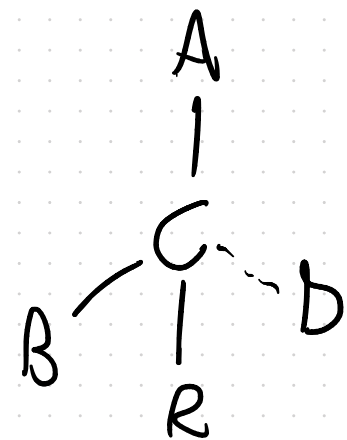
Crystal structure that has a handedness:

if we reverse orientation, we get a different crystal

Ex (molecule)



Right handed



Left handed

Crystals w/ a handedness cannot have orientation-reversing symmetries

Orientation for a crystal: $\vec{e}_1, \vec{e}_2, \vec{e}_3$ be fixed primitive lattice vectors

$$\Theta = \text{sign}\left[\vec{e}_1 \cdot (\vec{e}_2 \times \vec{e}_3)\right] = \begin{cases} +1 & \text{right-handed} \\ -1 & \text{left handed} \end{cases}$$

1. All rotations preserve orientation

$(\hat{n}, \theta) \longrightarrow R_{ij}$ 3x3 rotation matrix $R^T = R^{-1}$

$\det R = 1$

$$R\vec{e}_1 \cdot (R\vec{e}_2 \times R\vec{e}_3) = \det R \left[\vec{e}_1 \cdot (e_2 \times e_3)\right]$$

$$\text{sign}\left[R\vec{e}_1 \cdot (Re_2 \times Re_3)\right] = \underbrace{\text{sign}\det R}_{1}\ \text{sign}\left[\vec{e}_1 \cdot (e_2 \times e_3)\right]$$

(2) translations also preserve orientation

(3) spatial inversion reverses orientation

$$I : \vec{e}_i \to -\vec{e}_i$$

$$I\vec{e}_1 \cdot (Ie_2 \times Ie_3) = -\vec{e}_1 \cdot (-e_2 \times -\vec{e}_3) = -\vec{e}_1 \cdot (e_2 \times e_3)$$

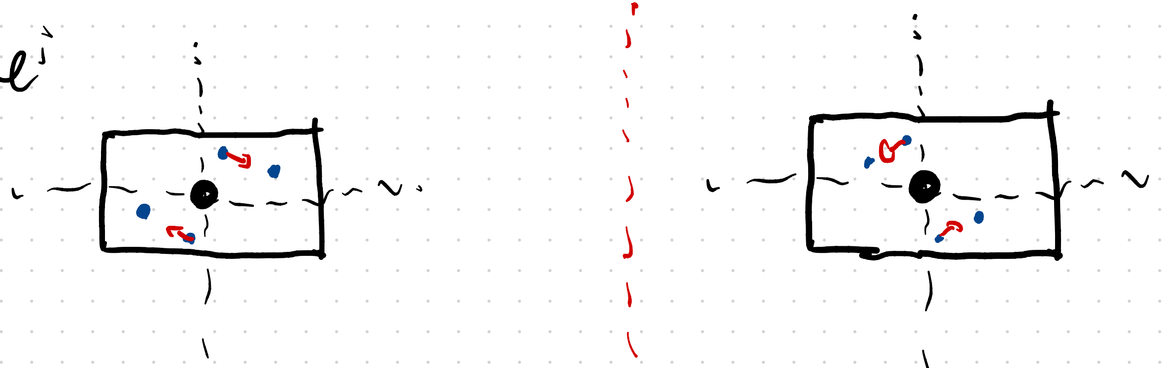
→ $I \times$ any rotation also flips orientation

Mirror symmetries
glide reflections
"rotoinversion" symmetries IC_4, IC_6, IC_3

65 space groups w/ no orientation-reversing symmetries
- translations
- rotations
- screw rotations

Söhnke space groups ← any crystal w/ chirality/handedness has one of these as its symmetry group

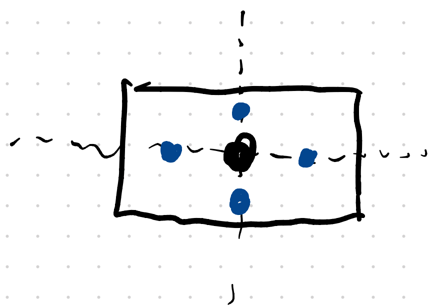
Example:



P2 P2

enantiomers

This is a chiral structure

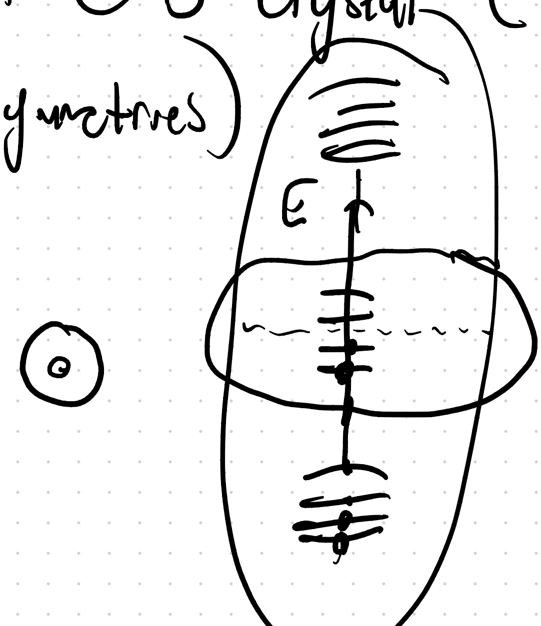


not chiral
M_x, M_y symmetries

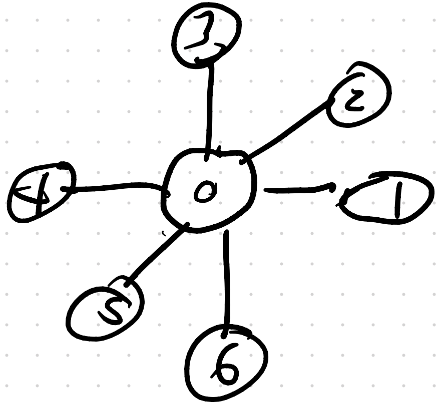
Pmm2

How do space groups constrain the spectrum of H

Warmup example: 0D crystal (no Bravais lattice, only point group symmetries)



$V = \{|\text{valence states}\rangle\}$



valence electrons @ atom 0 now feel an external potential

$$U(\vec{x}) = \sum_{i=0}^{6} V_i(\vec{x})$$

look for the symmetries that leave $U(\vec{x})$ invariant

$$\bar{G} = \{ g \in O(3) \mid U(g^{-1}\vec{x}) = U(\vec{x}) \}$$

Schur's lemma: valence states $V = \bigoplus_i V_i$

where $\rho_i : \bar{G} \to U(V_i)$ are irreps of $\bar{G}$

$$H = \frac{p^2}{2m} + U(\vec{x})$$

matrix elements of H in this basis

$$[H] = \begin{array}{c|cccc} & V_1 & V_2 & V_3 & \cdots \\ \hline V_1 & H_{11} & H_{12} & H_{13} & \\ V_2 & H_{21} & H_{22} & H_{23} & \\ V_3 & & \ddots & & \\ \vdots & & & & \end{array}$$

$$H_{ij} : V_j \to V_i$$

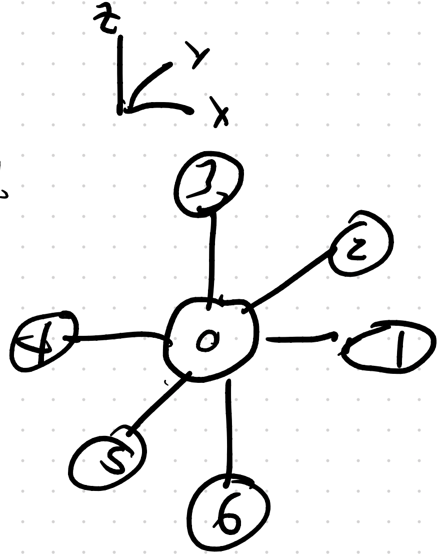
$$H_{ij}\, \rho_j(g) = \rho_i(g)\, H_{ij}$$

Schur's lemma:

if $\rho_i \not\cong \rho_j$ then $H_{ij} = 0$

if $\rho_i = \rho_j$ then $H_{ij} = \lambda \, Id$

Example:



Molecule w/ octahedral symmetry

Valence States $V = \{$d-orbital states$\}$

$V = \{ |\ell = 2, m\rangle \mid m = -2, -1, 0, 1, 2 \}$

$\bar{G} = \langle C_{4z}, C_{3,111} \rangle$ point group 432 (O)

1 $\quad 1: \{E\}$

3 $\quad 2_{100}: \{C_{2,x}, C_{2,y}, C_{2,z}\}$

8 $\quad 3: \{C_{3,111}, C_{3,11\bar{1}}, C_{3,1\bar{1}1}, C_{3,\bar{1}11}$ + inverses$\}$

6 $\quad 2_{110}: \{2_{110}, 2_{1\bar{1}0}, 2_{011}, 2_{01\bar{1}}, 2_{101}, 2_{10\bar{1}}\}$

6 $\quad 4: \{C_{4,x}, C_{4,y}, C_{4,z}$ + inverses

$1 \mid 4 \quad 2_{100} \quad 3 \quad 2_{110}$

A_1	1	1	1	1	1
A_2	1	-1	1	1	-1
E	2	0	2	-1	0
T_2	3	-1	-1	0	1
T_1	3	1	-1	0	-1

d-orbitals transform in the $l=2$ irrep of SO(3))

$$\rho_{l=2}(\hat{n},\theta) \to e^{-i\hat{n}\cdot\vec{J}\theta}$$

$$J_x = \frac{1}{2}\begin{pmatrix} 0 & 2 & & & 0 \\ 2 & 0 & \sqrt{6} & & \\ & \sqrt{6} & 0 & \sqrt{6} & \\ & & \sqrt{6} & 0 & 2 \\ 0 & & & 2 & 0 \end{pmatrix} \qquad J_y = \frac{1}{2i}\begin{pmatrix} 0 & 2 & & & \\ -2 & 0 & \sqrt{6} & & \\ & -\sqrt{6} & 0 & \sqrt{6} & \\ & & -\sqrt{6} & 0 & 2 \\ & & & -2 & 0 \end{pmatrix}$$

$$J_z = \begin{pmatrix} 2 & & & & \\ & +1 & & 0 & \\ & & 0 & & \\ & 0 & & -1 & \\ & & & & -2 \end{pmatrix}$$

$$432 = \overline{G} < SO(3)$$

$$\eta : \overline{G} \to U(V)$$

$$\eta(g) = \rho_{\ell=2}(g) \text{ for } g \in \overline{G}$$

$$\eta = \rho_{\ell=2} \downarrow \bar{G}$$ restricted representation

reducible rep of $\bar{G}$

irreducible representation of $SO(3)$

We can use characters : χ_η

$$\chi_\eta(g) = \mathrm{tr}[\eta(g)] = \mathrm{tr}[\rho_{\ell=2}(g)]$$

$$\eta(E) = e^{-i0} = \begin{pmatrix} 1 & & & & \\ & 1 & & & \\ & & 1 & & \\ & & & 1 & \\ & & & & 1 \end{pmatrix} \rightarrow \chi_\eta(E) = 5$$

$$\eta(C_{4z}) = e^{-i\frac{\pi}{2}J_z} = \begin{pmatrix} -1 & & & \\ & -i & & \\ & & 1 & \\ & & & i \\ & & & & -1 \end{pmatrix} \rightarrow \chi_\eta(C_{4z}) = -1$$

$$\eta(C_{2z}) = e^{-i\pi J_z} = \begin{pmatrix} 1 & & & & \\ & -1 & & & \\ & & 1 & & \\ & & & -1 & \\ & & & & 1 \end{pmatrix} \rightarrow \chi_\eta(C_{2z}) = +1$$

Trick for the remaining two:

$$\chi_\eta(g) = \mathrm{tr}\left[\rho_{\ell=2}(g)\right] \quad g \in \bar{G}$$

$$= \mathrm{tr}\left[\rho_{\ell=2}(g')\rho_{\ell=2}(g)\rho_{\ell=2}(g')^{-1}\right] \quad \begin{array}{l} g\in\bar{G} \\ g'\in SO(3) \end{array}$$

$$\chi_\eta(C_{3,111}) = \mathrm{tr}\left[\rho_{\ell=2}(C_{3z})\right]$$

$$= \mathrm{tr}\left[e^{-i2\pi/3\, J_z}\right] = \mathrm{tr}\begin{pmatrix} e^{4\pi i/3} & & & & \\ & e^{-2\pi i/3} & & & \\ & & 1 & & \\ & & & e^{2\pi i/3} & \\ & & & & e^{4\pi i/3} \end{pmatrix}$$

$$= -1$$

$$\chi_\eta(C_{2,110}) = \mathrm{tr}\left[\rho_{\ell=2}(C_{2z})\right] = +1$$

$$\chi_\eta = \begin{array}{ccccc} 1 & 4 & 2_{100} & 3 & 2_{110} \\ \end{array}$$
$$\chi_\eta = (5, -1, 1, -1, 1)$$

$$\langle \chi_e, \chi_\eta \rangle = \frac{1}{24}\Big(\chi_\rho^*(E)\chi_\eta(E) + 6\chi_\rho^*(4)\chi_\eta(4) + 3\chi_\rho^*(2_{100})\chi_\eta(2_{100}) + 8\chi_\rho^*(3)\chi_\eta(3) + 6\chi_\rho^*(2_{110})\chi_\eta(2_{110}) \Big)$$

A_1	1	1	1	1	1
A_2	1	-1	1	1	-1
E	2	0	2	-1	0
T_2	3	-1	-1	0	1
T_1	3	1	-1	0	-1

$$\langle \chi_E, \chi_\eta \rangle = \frac{1}{24}(10 + 0 + 6 + 8 + 0) = \underline{1}$$

$$\langle \chi_{T_2}, \chi_\eta \rangle = \frac{1}{24}(15 + 6 - 3 + 0 + 6) = \underline{1}$$

$$\chi_\eta = \chi_E + \chi_{T_2}$$

$$\eta \cong E \oplus T_2$$