Lecture 9

Announcements: HW2 is now posted

Due 10/10 (11:59 pm central)

Recap: Space groups $G \trianglerighteq T$ ← Bravais lattice translations

230 Space groups:

73 Symmorphic $G = T \rtimes \bar{G}$

- $\bar{G} < G$ $g \in G \Rightarrow g = \{E|\vec{t}\}\{R|\vec{0}\}$ for $\vec{t} \in T$, $R \in \bar{G}$

- Hermann Maugin symbol [letter][pt group symbol]

157 nonsymmorphic $\bar{G} \not< G$

- $G = \bigcup_{i=0}^{n-1} T\{R_i | \vec{d}_i\}$ $R_i \in \bar{G}$ at least one $\vec{d}_i$ **Must** be a fraction of a Bravais lattice translation
- Typically contain screw rotations and/or glide reflections
- Hermann-Mauguin symbols use subscripts for screws & letters for glides

for any space group $R \in \bar{G}$, $\vec{t} \in T$ $\quad R\vec{t} \in T$

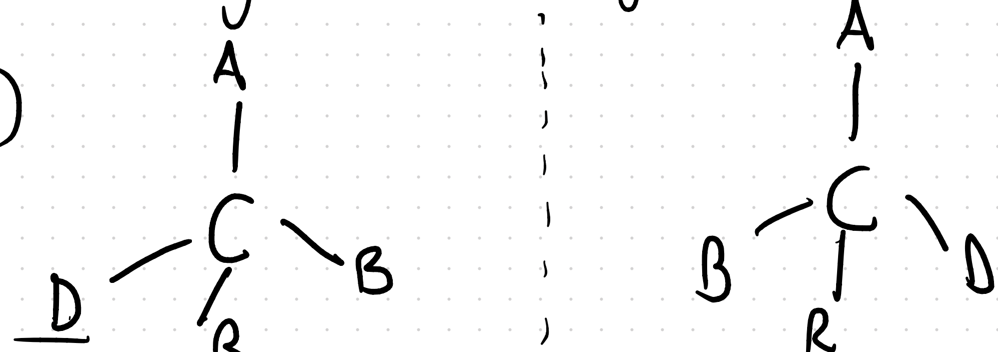
Screw rotation: $\left(\{C_{n\hat{z}} \mid \alpha\hat{z}\}\right)^n = \{E \mid n\alpha\hat{z}\} \in T$

$$\Rightarrow \alpha\hat{z} = \frac{p}{n}\vec{e} \qquad p < n$$

Chiral Crystals: crystal structure has a handedness

given a chiral crystal if we reverse the orientation of coordinates we get a different crystal

Ex: (molecule)



Right handed Left handed

Chiral materials cannot have any orientation-reversing symmetries

Definition of orientation: $\vec{e}_1, \vec{e}_2, \vec{e}_3$ fixed primitive lattice vectors

$$\mathcal{O} = \text{sign}\left[\vec{e}_1 \cdot (\vec{e}_2 \times \vec{e}_3)\right] \begin{cases} +1 & \text{RH coordinate system} \\ -1 & \text{LH coordinate system} \end{cases}$$

I. All rotations preserve orientation

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

$\det R = +1$

$$R\vec{e}_1 \cdot (Re_2 \times Re_3) = \varepsilon^{ijk} (R_{in} e_1^n)(R_{jm} e_2^m)(R_{kl} e_3^l)$$

$$= \left[\varepsilon^{ijk} R_{in} R_{jm} R_{kl}\right] e_1^n e_2^m e_3^l$$

$$= \det R \, \varepsilon_{nml} \, e_1^n e_2^m e_3^l$$

$$= e_1 \cdot (e_2 \times e_3)$$

$\rightarrow$ rotations leave $\circlearrowleft$ unchanged

2. Spatial inversion I reverses orientation

$$I\vec{e}_i = -\vec{e}_i$$

$$Ie_1 \cdot (Ie_2 \times Ie_3) = -e_1 \cdot (e_2 \times e_3)$$

$$O \to -O$$

$\Rightarrow$ $I \times$ any rotation also flips orientation

- mirror
- glide
- rotoinversion IC_4 or IC_6

65 space groups w/ no orientation reversing symmetries

- translations
- rotations
- screw rotations

$\boxed{\text{Söhnke}}$ space groups

any chiral crystal has one of these 65 as its space group

$$P4 = \{T, C_{4\hat{z}}\}$$

$$I\, P4\, I^{-1} = P4$$

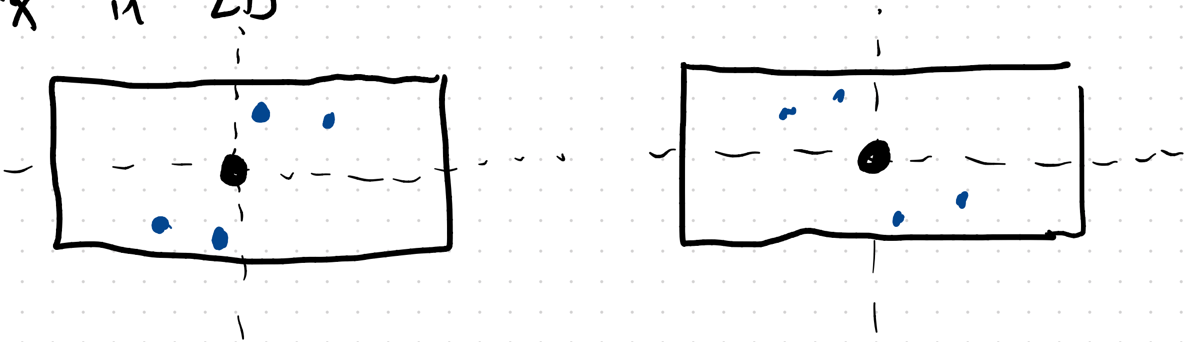
$$P4_1 = \langle \{T, \{C_{4z} | \tfrac{1}{4}\hat{z}\}\} \rangle$$

$$I\, P4_1\, I^{-1} = \langle \{T, \{C_{4z} | -\tfrac{1}{4}\hat{z}\}\} \rangle$$

$= \langle T, \{C_{4z} | \frac{3}{4}\hat{z}\} \rangle$

$= P4_3$

Ex in 2D

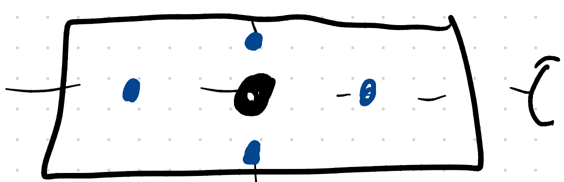


enantiomers

$\mathrm{sign}(\varepsilon_{ij} e_1^i e_2^j)$

P2 - this is a Söhnke space groups

this is a chiral structure



$\leftarrow$ not chiral

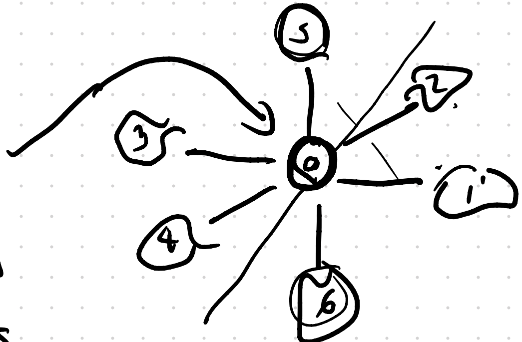
$Pmm2$ – has orientation reversing symmetries

How space group symmetries constrain the spectrum of H

Warmup: 0D crystal (no Bravais lattice translations, only pt group symmetries) – molecules

Octahedral symmetry:

Valence electrons in d orbitals ($l=2$)



Pt group 432 (O)

$$\langle C_{4z}, C_{3,111} \rangle = G$$

$\hat{x}+\hat{y}+\hat{z}$

The electrons feel a potential

$$U(\vec{x}) = U_0(\vec{x}) + \sum_{i=1}^{6} U_i(\vec{x})$$

$$g \in G \quad U(g^{-1}x) = U(\vec{x})$$

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

$$H_{mm'} = \langle l=2\, m | H | l=2, m' \rangle$$

Schur's lemma: if we find a basis for our Hilbert space $\mathcal{H} = \{|l=2, m_z\rangle\}$ in terms of irreps of $\bar{G}$

$$= \bigoplus_i V_i \qquad \rho_i : \bar{G} \to U(V_i)$$

then in this basis

$$H = \begin{array}{c|c} & \begin{array}{ccc} V_1 & V_2 & \cdots \end{array} \\ \hline \begin{array}{c} V_1 \\ V_2 \\ \vdots \end{array} & \left(\begin{array}{c|c|c} H_{11} & H_{12} & \cdots \\ \hline H_{21} & H_{22} & \\ \hline \vdots & \vdots & \ddots \end{array}\right) \end{array}$$

each H_{ij} will be constrained by Schur's lemma

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

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

$\rightarrow$ Eigenstates of H can be labelled by irreps of $\bar{G}$

$|G| = 24$

	1	4	2_{100}	3	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

1: $\{E\}$

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

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

3: $\{C_{3,111} +$

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

d-orbitals transform in $\ell=2$ irrep of $SO(3)$

$$\rho_{\ell=2} : (\hat{n}, \theta) \to e^{-i\hat{n}\cdot\vec{J}\theta} \qquad \vec{J} \text{ - spin-2 matrices}$$

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

$$\bar{G} < \underline{SO(3)}$$

$$\eta : 432 \to U(\mathcal{H})$$

$$\eta(g) = \rho_{\ell=2}(g) \text{ for } g \in 432 \qquad \eta = \rho_{\ell=2} \downarrow \bar{G}$$

restrictions

we want to know how to write η as a sum of irreps of G

to find this, we can use characters

$$\boxed{\chi_\eta}$$

irreps

$$\eta \cong \bigoplus_i n_i \sigma_i$$

$$n_i = \langle \chi_{\sigma_i}, \chi_\eta \rangle$$

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

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

$$\eta(C_{2z}) = e^{-i\pi J_z} = \begin{pmatrix} 1 & & & & \\ & -1 & & & \\ & & 1 & & \\ & & & -1 & \\ & & & & 1 \end{pmatrix} \to \chi_\eta(2_{100}) = +1$$

Trick for remaing two:

$$\chi_\eta(g) = \operatorname{tr} \rho_{\ell=2}(g) = \operatorname{tr} \rho_{\ell=2}(R)\,\rho_{\ell=2}(g)\,\rho_{\ell=2}(R^{-1})$$

for any R in $SO(3)$

$$\operatorname{tr} \eta(C_{3,111}) = \operatorname{tr} \rho_{\ell=2}(C_{3z}) = \operatorname{tr} e^{-i\frac{2\pi}{3}J_z}$$

$$= \operatorname{tr} \begin{pmatrix} e^{-4\pi i/3} & & & & \\ & e^{-2\pi i/3} & & & \\ & & 1 & & \\ & & & e^{2\pi i/3} & \\ & & & & e^{4\pi i/3} \end{pmatrix}$$

$$= -1$$

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

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

	1	4	2_{100}	3	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

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

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

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

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