Lecture 8

① If G is a space group then $T \triangleleft G$

the point group $\bar{G} = G/T$

② if $R \in \bar{G}$, then R is either

- a rotation by $0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}, \pi$
- spatial inversion I : $(x, y, z) \to (-x, -y, -z)$
- the composition of $I \times$ an allowed rotation

32 point groups in 3D

Note: not every Bravais lattice $T = \langle \vec{e}_1, \vec{e}_2, \vec{e}_3 \rangle$

the group generated by $\vec{e}_1, \vec{e}_2, \vec{e}_3$

is compatible w/ every point group

14 classes of Bravais lattice

To form a space group, we want to combine a Bravais lattice T, a compatible pt group $\overline{G}$

$G = T \rtimes \overline{G}$, 73 symmorphic space groups

$= \{ \{E|\vec{t}\}\{R|0\} \}$

$\rightarrow$ $\bar{G} \subset G$ for symmorphic space groups

Notation: [Letter][Hermann-Mauguin for pt group]

tells us
Bravais lattice

tells us point group

Ex: space group $\underbrace{P}_{\text{primitive orthorhombic}}\underbrace{mm2}_{\text{point group } mm2}$ $= \langle C_{2z}, M_x, M_y \rangle$

$\vec{e}_1 = (a,0,0)$ a, b, c are distinct

$\vec{e}_2 = (0,b,0)$ lengths

$\vec{e}_3 = (0,0,c)$

Full list of lattice types, letters, and primitive lattice vectors: Table 3.1 in Bradley and Cracknell

But: 157 space groups are not semidirect products

Non-symmorphic space groups

$$G = T \cup T\{\bar{g}_1 | \vec{d}_1\} \cup T\{\bar{g}_2 | \vec{d}_2\} \cup \ldots \cup T\{\bar{g}_{n-1} | \vec{d}_{n-1}\}$$

if G is nonsymmorphic, at least one of these $\vec{d}_i$ has to be a fraction of a Bravais lattice translation

Screw rotation or a glide reflection

$\{C_{n\hat{p}} \mid \vec{d}\}$ $\vec{d}$ has a component along the axis of rotation

denoted n_l ← fractional translation - if we take the screw to the nth power, we get a translation by l primitive lattice vectors

order of rotation

2_1 $\left(\left\{C_{2z} \middle| \frac{c\hat{z}}{2}\right\}\right)^2 = \{E \mid c\hat{z}\}$ - a single lattice translation

$3_1 = \left\{C_{3z} \middle| \frac{c\hat{z}}{3}\right\}$ $(3_1)^3 = \{E \mid c\hat{z}\}$

$3_2 = \{C_{3z} | \frac{2c}{3}\hat{z}\}$ $\quad (3_2)^3 = \{E | 2c\hat{z}\}$

$4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5$

Glide reflection (glide mirror) - mirror reflection w/ a translation not orthogonal to the invariant plane

Ex: $\{M_z | \frac{a}{2}\hat{x}\} = g$ $\quad g: (x, y, z) \to (x + \frac{a}{2}, y, -z)$

$g^2 = \{E / a\hat{x}\}$

Herman Maugin symbol

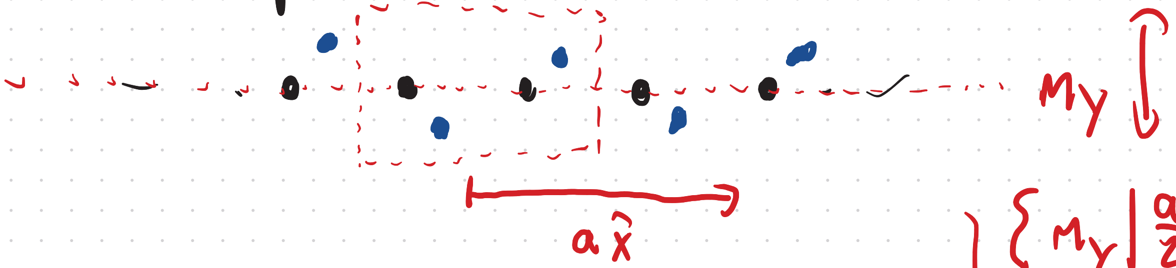
m - mirror (not glide)

a, b, c - glide w/ translation along cartesian direction n – glide along a face diagonal

d – glide along a body diagonal

e – multiple glides w/ same mirror plane

Ex: quasi-1d system



$$\boxed{\{M_y \,|\, \tfrac{a}{2}\hat{x}\}}$$

Glides and screws fix no points in space

Screw $\{C_{n\hat{n}} \,|\, \vec{d}\}$

Glide $\{M_{\hat{n}} \mid \vec{d}\}$

$157 + 73 = 230$ total 3D space groups

Ex: $P2_13$

Primitive cubic lattice

$\vec{e}_1 = (a, 0, 0)$

$\vec{e}_2 = (0, a, 0)$

$\vec{e}_3 = (0, 0, a)$

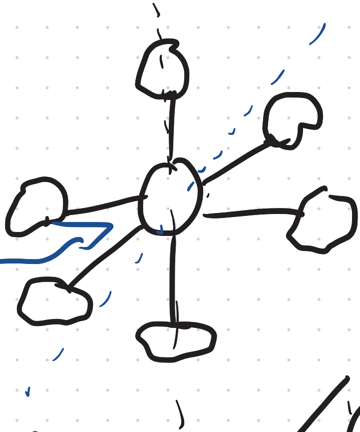
↳ point group has HM symbol 23 - cubic point group

twofold rotation is a screw

How do space group symmetries constrain the spectrum of the Hamiltonian

Warmup: 0D crystal (no Bravais lattice translations)

Molecule



Has valence electrons in d orbitals ($\ell=2$)

Octahedral symmetry

O (432)

Schönflies

H-M. notation

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

Hamiltonian invariant under 432

→ eigenstates of H can be labelled by irreps of 432
(Schur's lemma)

→ 5 d orbitals to start - we can decompose these into irreps of 432

	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 $\{C_{4x}, C_{4y}, C_{4z}, C_{4x}^{-1}, C_{4y}^{-1}, C_{4z}^{-1}\}$

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

3: $\{C_{3,111}, C_{3,11-1}, C_{3,1,-1,1}, C_{3,-1,1,1}$ + inverse$\}$

2_{110}: $\{C_{2,110}, C_{2,101}, C_{2,011}, C_{2,1,-1,0},$

$C_2\ 10{-}1,\ C_2, 01\bar{1}\}$

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

$$\eta(\theta, \hat{n}) = e^{-i\hat{n}\cdot\vec{J}\theta}$$

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

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

spin-2 matrices

η restricted to elements in 432 gives us a representation

$$\eta(E) = \begin{pmatrix} 1 & & & & \\ & 1 & & & \\ & & 1 & & \\ & & & 1 & \\ & & & & 1 \end{pmatrix} \qquad \chi_\eta(E) = 5$$

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

$$\eta(C_{2z}) = e^{-iJ_z\left(\frac{2\pi}{2}\right)} = \begin{pmatrix} 1 & & & & \\ & -1 & & & \\ & & 1 & & \\ & & & -1 & \\ & & & & 1 \end{pmatrix} \qquad \chi_\eta(C_{2z}) = +1$$

To evaluate $\chi_\eta(C_{3,111})$ and $\chi_\eta(C_{2,110})$

we can use a shortcut

$\mathfrak{g}$ η is actually a representation of $SO(3)$

$$C_{3,111} = R_{\theta\hat{y}} C_{3z} R_{\theta\hat{y}}^{-1}$$

$$\eta(C_{3,111}) = \eta(R_{\theta\hat{y}})\eta(C_{3z})\eta(R_{\theta\hat{y}}^{-1})$$

$$\chi_\eta(C_{3,111}) = \operatorname{tr} e^{-i\frac{2\pi}{3}J_z} = -1$$

$$C_{2,110} = R_{\theta 1\text{-}10} C_{2z} R_{\theta 1\text{-}10}$$

$$\chi_\eta(C_{2,110}) = \chi_\eta(C_{2z}) = +1$$

	E	4	2_{100}	3	2_{110}
$\chi_\eta =$	5	-1	1	-1	1

inner product of characters

$$\langle \chi_\rho, \chi_\eta \rangle = \frac{1}{24}\Big(\chi_\rho(E)\chi_\eta(E) + 6\chi_\rho^*(C_{4z})\chi_\eta(C_{4z}) + 3\chi_\rho^*(C_{2z})\chi_\eta(C_{2z}) + 8\chi_\rho^*(C_{3111})\chi_\eta(C_{3111}) + 6\chi_\rho^*(C_{2,110})\chi_\eta(C_{2,110})\Big)$$

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

	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

$$\langle \chi_E, \chi_\eta \rangle = 1$$

$$\langle \chi_{T_2}, \chi_\eta \rangle = 1$$

$$\eta = E \oplus T_2$$

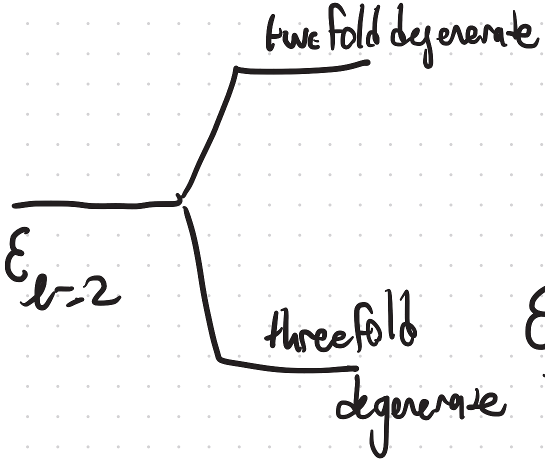
$$H_{molecule} = H_{isolated\ atom} + V$$

$H_{isolated\ atom}$: SO(3)

V: 432 symmetry

$$\langle 2m | H_{isolated\ atom} | 2m' \rangle = \varepsilon_{l=2}\,\delta_{mm'}$$

"crystal field effect"



$\varepsilon_{l=2} + \varepsilon_E$ ← two states transform in the E irrep of 432

$\varepsilon_{l=2} + \underline{\varepsilon_{T_2}}$ ← three states transform in the T_2 irrep of 432

states in E

States in T_2

Schur's lemma:

$$
\eta(g) = \left(\begin{array}{c|c} \rho_E(g) & 0 \\ \hline 0 & \rho_{T_2}(g) \end{array}\right)
\qquad
H = \begin{array}{cc} \overbrace{\qquad\qquad}^{H_{EE}} & \overbrace{\qquad\qquad\qquad}^{H_{TE}} \\ \left(\begin{array}{cc|ccc} \varepsilon_{l=2}+\varepsilon_E & & & & \\ & \varepsilon_{l=2}+\varepsilon_E & & 0 & \\ \hline & & \varepsilon_{l=2}+\varepsilon_{T_2} & & \\ & 0 & & \varepsilon_{l=2}+\varepsilon_{T_2} & \\ & & & & \varepsilon_{l=2}+\varepsilon_{T_2} \end{array}\right) \\ H_{ET} & H_{TT} \end{array}
$$

$$
[H_{EE}, \rho_E(g)] = [H_{TT}, \rho_{T_2}(g)] = 0
$$

$$
H_{TE}\,\rho_{T_2}(g) = \rho_E(g)\,H_{TE} \longrightarrow H_{TE} = 0
$$

$$
H_{ET}\,\rho_E(g) = \rho_{T_2}(g)\,H_{ET} \longrightarrow H_{ET} = 0
$$

Next time - Beyond 0D

ϕ_1: $\{C_{4z} \,|\, \frac{1}{4}\hat{z}\}$

ϕ_3: $\{C_{4z} \,|\, -\frac{1}{4}\hat{z}\}$