

• Recap:

- have explored modern approaches to e-e interaction via mean-field Ansatz
 - Hartree / Hartree-Fock
 - Density functional theory → Ongoing active research area!

Effective single-particle equations

$$\hbar \nabla^2 \phi_i(\mathbf{r}) = \epsilon_{0,i} \phi_i(\mathbf{r})$$

$$\hbar = -\frac{\nabla^2}{2} + V^{\text{eff}}(\mathbf{r})$$

What can we use this for?

(i) as it stand: directly for systems $\geq 10^2$ atoms in otherwise empty space

(ii) extended condensed matter: $\sim 10^{23}$ atoms?

Chapter 4: Lattice periodicity

4.1 Symmetry

(translational symmetry,
point symmetries, "other symmetries",
"group theory")

Many solids: "crystals"

"A crystal is a solid having ^{an} essentially discrete diffraction pattern"

Subset of all crystals: periodic solids

Apply to Hamiltonian:

$$T_{\underline{R}_n} \psi(\underline{r}) = \psi^{\text{eff}}(\underline{r} + \underline{R}_n) = \psi^{\text{eff}}(\underline{r})$$

$$T_{\underline{R}_n} \nabla^2 f(\underline{r}) = \nabla^2 f(\underline{r} + \underline{R}_n) = \nabla^2 T_{\underline{R}_n} f(\underline{r})$$

$\rightarrow T_{\underline{R}_n}, h$ commute.

$$\begin{aligned} T_{\underline{R}_n} h \psi_0(\underline{r}) &= h T_{\underline{R}_n} \psi_0(\underline{r}) = \epsilon_0 \psi_0(\underline{r} + \underline{R}_n) \\ &= \epsilon_0 T_{\underline{R}_n} \psi_0(\underline{r}) \end{aligned}$$

if $\psi_0(\underline{r})$ is eigenfunction with ϵ_0

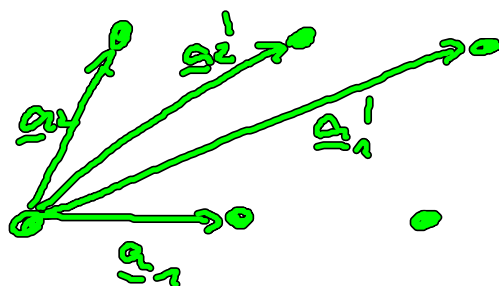
$\rightarrow T_{\underline{R}_n} \psi_0(\underline{r})$ is also eigenfunction

This does not mean $\psi_0(\underline{r}) \neq \psi_0(\underline{r} + \underline{R}_n)$

Vectors \underline{a}_i : "primitive vectors"

define "Bravais lattice"

Set of points $\{\underline{R}_n\}$

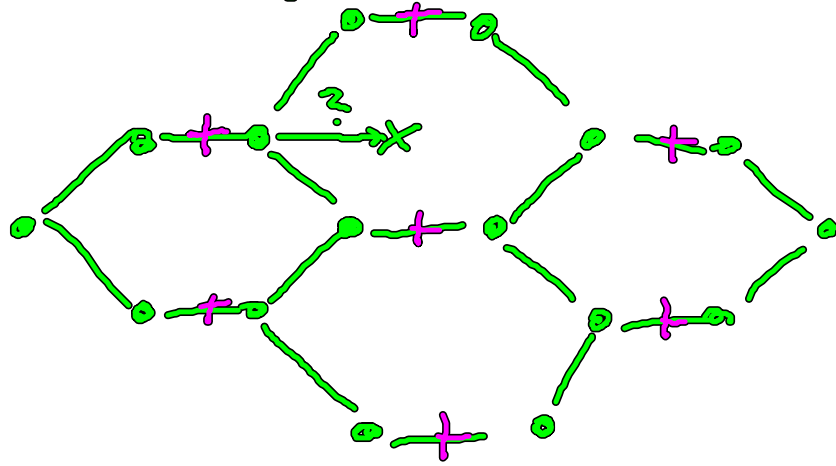


$\underline{a}_1, \underline{a}_2$
are not unique.

if a Bravais lattice has a given symmetry,

an arbitrary unit cell defined by $\underline{a}_1, \underline{a}_2$
does not necessarily have that symmetry by itself.

Not every apparently symmetric set of points
is a Bravais lattice



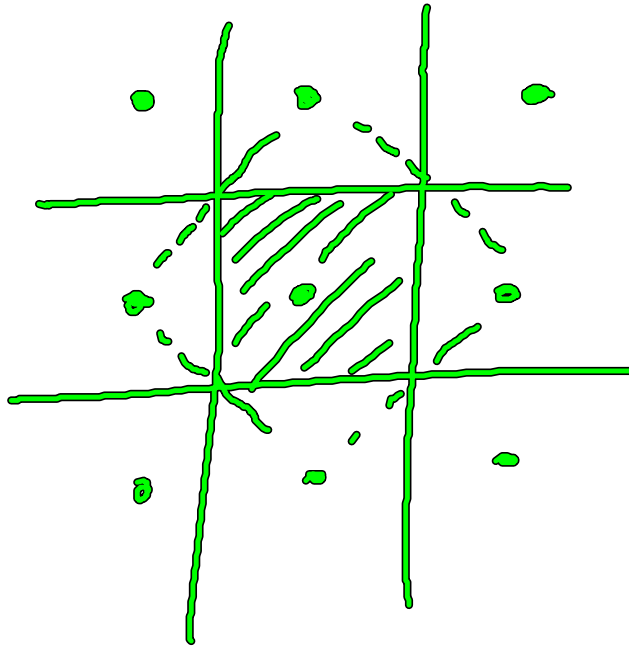
+ Bravais lattice
● → "basis"

"primitive unit cell" defined by $\underline{a}_1, \underline{a}_2$:

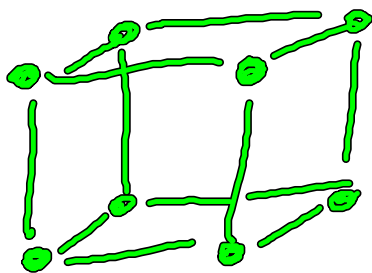
- contains exactly one point of the lattice
- can be used to "tile" (i.e. fill) entire space by periodic repetition

• Special primitive cell: Wigner-Seitz cell
= region closer to a given lattice point than to any other \mathbb{R}^n .

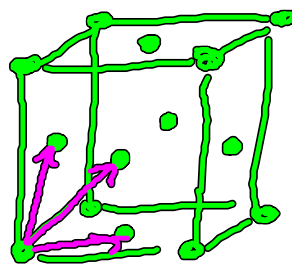
example:



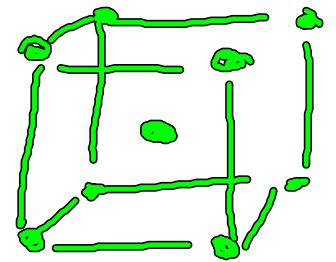
Note : Sometimes non-primitive cells are more illustrative than primitive ones (conventional cells)



simple cubic



face-centered cubic (fcc)



body-centered cubic (bcc)

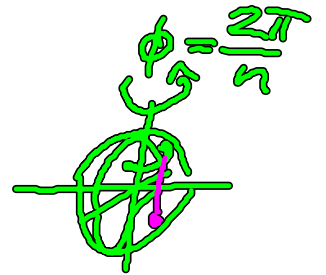
Crystal symmetries

[• Translation]

• Rotation

a) C_n

"normal rotation" \rightarrow



b) S_n

improper rotation
= normal rotation followed
by reflection

• σ

Reflection (by a plane)

• i

inversion ($r \rightarrow -r$)

• $\hat{T} R_\phi$
 \nearrow translation
 \uparrow general rotation
 by ϕ

SCREW rotation

• $\hat{T} \sigma$

glide symmetry

point symmetries \equiv operators that leave (at least)
one point of the lattice fixed

$\rightarrow C, S, \sigma, i, [E]$
 \uparrow
 unit element

Combining operators:

$C = a \otimes b$

e.g. $\sigma = C_n^{-1} \otimes S_n$

The set of symmetry ops for a given object (e.g. lattice) form a group G .

- $a, b \in G \Rightarrow a \otimes b \in G$

- associative law

$$a \otimes (b \otimes c) = (a \otimes b) \otimes c$$

- neutral element: $a \otimes E = E \otimes a = a$

- inverse element: $a \otimes a^{-1} = E = a^{-1} \otimes a$

E.g. all translations $\{T_{R_n}\}$ on the lattice

(subgroup)

$$T_{R_n} \otimes T_{R_m} = T_{R_n} \otimes T_{R_m} = T_{R_n + R_m}$$

commute \rightarrow Abelian

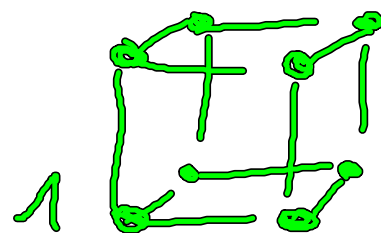
Subgroup \rightarrow Subset U of G that

is in itself closed with respect to \otimes

'Coset' of Subgroup: $a \otimes U \neq U \otimes a$
left coset right coset

The point group of a cube " O_h "

- E



- C_4 rotate about $x, y, z, -x, -y, -z$ by $\frac{2\pi}{4}$ 6
 - C_2 rotate x, y, z by $\frac{2\pi}{2}$ 3
 - C_2' rotate $\frac{2\pi}{2}$ about diagonals of cube sides 6
 - C_3 rotation about space diagonals by $\frac{2\pi}{3}$ 8
 - i
- Wed 1600
733
-
- 24
48 op.

note: reflections not listed explicitly:

$$\sigma_v = i \otimes C_2$$

$$\sigma_d = i \otimes C_2'$$

"Class" (Class of conjugate elements)

a and b are part of a class

if $a = c^{-1} b c$ with c from the group

For example, E is its own class.

- $O_h \rightarrow 10$ classes
- O (O_h without i) $\rightarrow 5$ classes above

The set of symmetries for a
Bravais lattice + basis

=: "Space Group" (point symmetries, translations,
combinations)

Bravais lattices:

The total number of possible symmetry
operations is finite

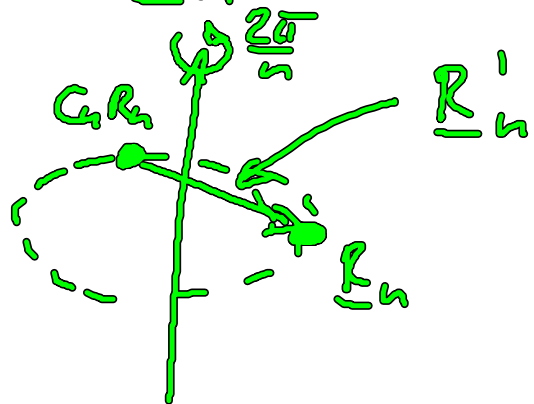
E.g. C_2 , C_3 , C_4 , C_6
but not C_5
 C_n ($n > 6$)

Proof: $\underline{R}_n = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3$
Let \underline{a}_1 be the shortest possible \underline{R}_n

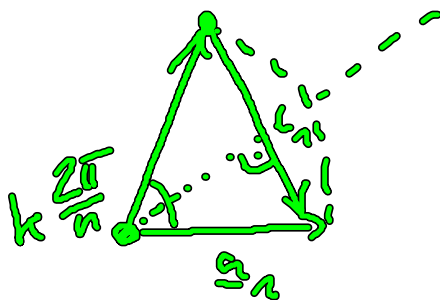
If $\{\underline{R}_n\}$ has C_n (n integer)

then $C_n \underline{R}_n \in \{\underline{R}_n\}$

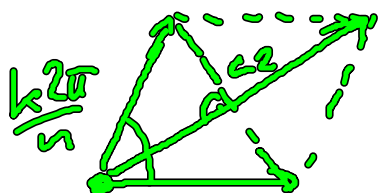
Consider: $R'_n = R_n - C_n R_n$



\underline{a}_n : shortest $i \in \{R_n\}$ $(k C_n) \underline{a}_n \in \{R_n\}$



$$|\underline{a}_n - (k C_n) \underline{a}_n| = L_1$$



$$|\underline{a}_n + (k C_n) \underline{a}_n| = L_2$$

$L_1 \geq |\underline{a}_n|$ by def. unless $L_1 = 0$

$$\left| \sin\left(\frac{k\pi}{n}\right) \right| = \frac{L_1}{2|\underline{a}_n|} \geq \frac{1}{2} = \sin\frac{\pi}{6}$$

$$\Rightarrow n \leq 6$$

$$\left| \cos\frac{k\pi}{n} \right| = \frac{L_2}{2|\underline{a}_n|} \geq \frac{1}{2} \quad \text{for } k=1$$

but this is not true

e.g. for $n=5$
if $k=2$

C_5 cannot appear in periodic crystals
but "quasicrystals"

C_5 possible

C_{12} also possible

- need at least two tiles
- no periodicity although highly ordered.

The number of different lattices (loosely)

- Two groups are equivalent if
 - same number of elements
 - multiplication tables are identical

Γ	A_1	A_2	\dots
A_1	$A_1 \otimes A_1$	$A_1 \otimes A_2$	\dots
A_2	$A_2 \otimes A_1$	$A_2 \otimes A_2$	\dots
\vdots	\vdots	\vdots	

- There are 7 different point groups for Bravais lattices.
- There are 14 different space groups \equiv Bravais lattices

Crystals with a basis:

lowers symmetry comp to underlying Bravais lattice

for O_h :	O	\rightarrow	no inversion
	T_d	\rightarrow	point group of tetrahedron
	T	\rightarrow	same but no reflection symms
	T_h	\rightarrow	$T \otimes i$

note point groups can be written as matrices (3x3)

\rightarrow exercise.

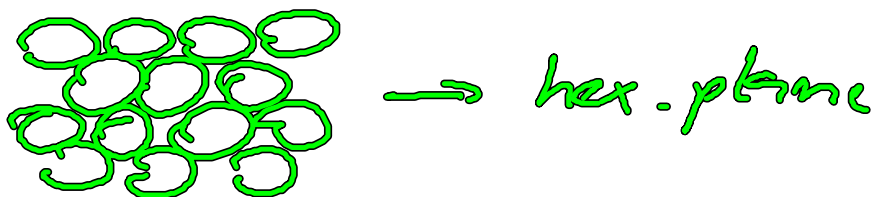
Finally: What types of structures are there?
(Bravais lattice + basis)

32 cryst. point groups

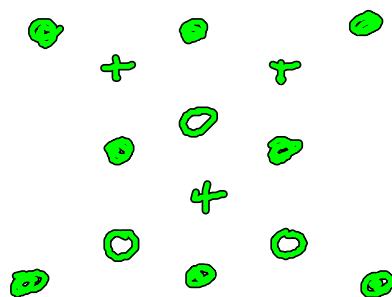
230 space groups

Close-packed structures

hard spheres filling as much volume as possible?



3D: stack hex. planes



A-B stacking
"hex close packed"
hcp

A-B-C stacking
fcc structure