- 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

$$h\phi_{o_i}(\underline{r}) = \epsilon_{o_i}\phi_{o_i}(\underline{r})$$

$$h = -\frac{\nabla^2}{2} + V^{eff}(\underline{r})$$

What can we use this for?

(i) as it stands: directly for systems $\geq$ 1 electrons in otherwise empty space

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

Chapter 4: Lattice periodicity

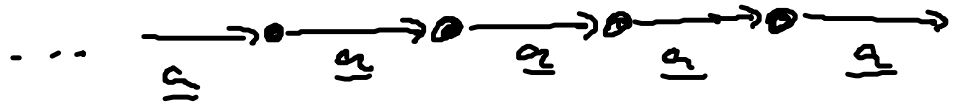
4.1 Symmetry

(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



translational symmetry

Most periodic structures also have some kind of further symmetry (rotation, reflection, inversion, ...)

In better order

Single-particle eqs.: Nuclear positions → $n(\underline{r})$ → $V^{eff}(\underline{r})$ (symmetry) → (same symmetry)

$\underline{\nabla}^2$: invariant under translation, rotations, ...

$\Leftrightarrow$ nuclear system determines symmetry

Periodic crystal: Translational symmetry.

$$\underline{R}_n = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3 \qquad n_i \text{ integers}$$

"primitive vectors" (lattice vectors)

Translation operator

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

Apply to Hamiltonian:

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

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

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

$$T_{\underline{R}_n} h \varphi_{o_i}(\underline{r}) = h T_{\underline{R}_n} \varphi_{o_i}(\underline{r}) = \epsilon_o \varphi_{o_i}(\underline{r}+\underline{R}_n)$$

$$= \epsilon_o T_{\underline{R}_n} \varphi(\underline{r})$$

if $\varphi_{o_i}(\underline{r})$ is eigenfunction with ϵ_o

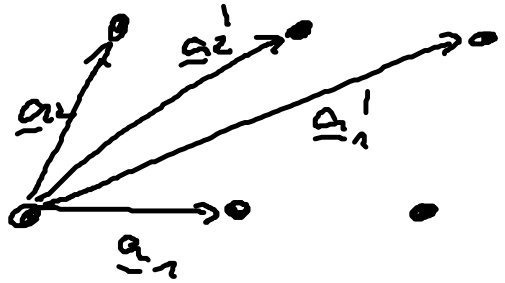
$\rightarrow$ $T_{\underline{R}_n} \varphi_{o_i}(\underline{r})$ is also eigenfunction

This does not mean $\varphi_{o_i}(\underline{r}) \overset{?}{=} \varphi_{o_i}(\underline{r}+\underline{R}_n)$

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

define "Bravais lattice"

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

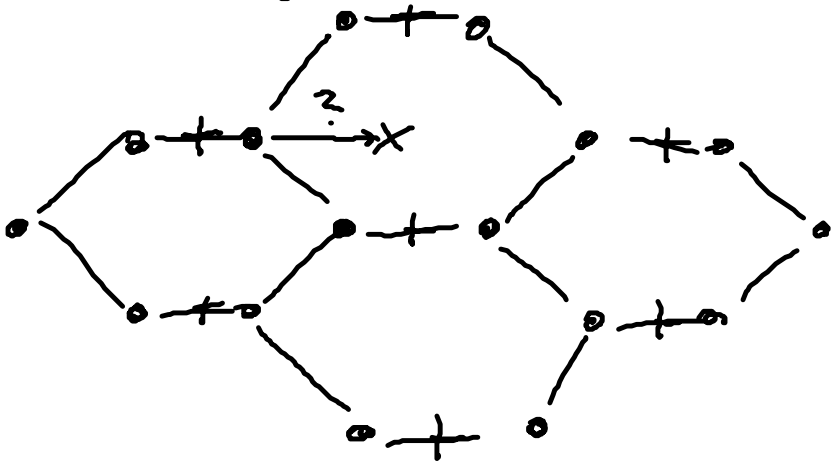


$\underline{a}_1, \underline{a}_2$ are not unique.

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

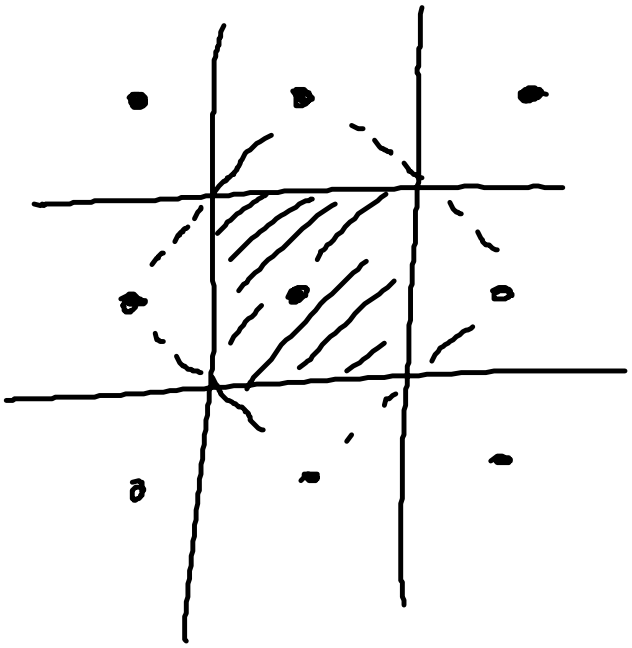
●—● "basis"

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

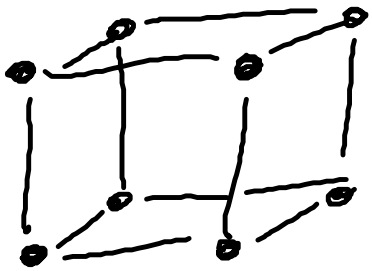
- contains exactly one point of the lattice
- can be used to "tile" (ie. fill) entire space by periodic repetition

- Special primitive cell: Wigner – Seitz cell
  = region closer to a given lattice point than to any other $\underline{R}_n$.

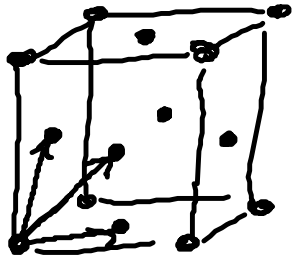
example:



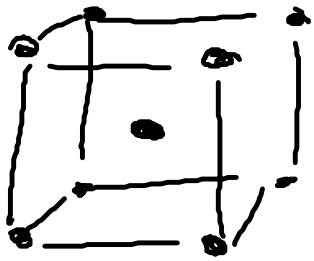
Note: Sometimes non-primitive cells are more illustrative than primitive ones (conventional cells)



simple cubic



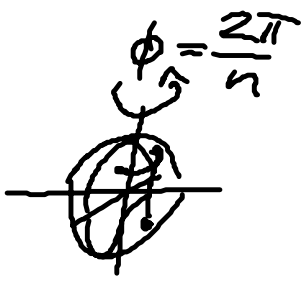
face-centered cubic (fcc



body-centered cubic (bcc)

Crystal symmetries

[• Translation]

- Rotation
  - a) C_n "normal rotation" → 
  - b) S_n improper rotation = normal rotation followed by reflection

- σ Reflection (by a plane)
- i inversion ($\underline{r} \to -\underline{r}$)
- $\widehat{T R_\phi}$ screw rotation
  - T: translation
  - R_ϕ: general rotation by ϕ
- $\widehat{T \sigma}$ glide symmetry

point symmetries ≡ operations that leave (at least) one point of the lattice fixed

→ $C, S, \sigma, i, [E]$

$[E]$: unit element

Combining operations:

$$c = a \otimes b$$

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

The set of symmetry op's 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 $\{T_{\underline{R}_n}\}$ on the lattice (subgroup)

$$T_{\underline{R}_n} \otimes T_{\underline{R}_m} = T_{\underline{R}_n} \otimes T_{\underline{R}_n} = T_{\underline{R}_m + \underline{R}_n}$$

commute → Abelian

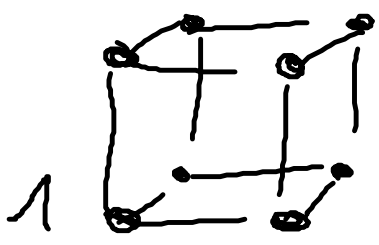
Subgroup → Subset U of G that is in itself closed with respect to $\otimes$

"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 (real 1600 733)
- $\otimes i$ — 24

48 op.

note: reflections not listed explitly:

$$\sigma_v = i \otimes C_2$$

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

"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 → 10 classes
- O (O_h <u>without</u> i) → 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 $(n > 6)$

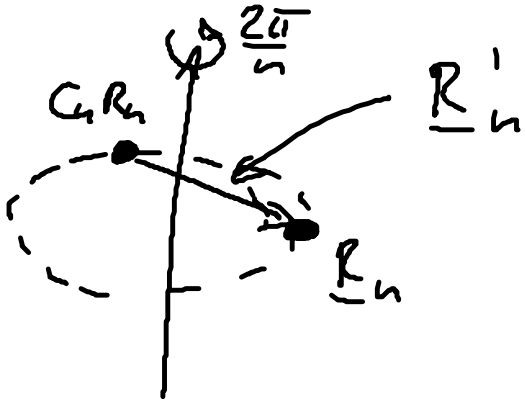
Proof: $\underline{R}_n = n_1 \underline{a} + n_2 \underline{a}_2 + n_3 \underline{a}_3$

Let $\underline{a}_1$ be the shortest possible $\underline{R}_n$

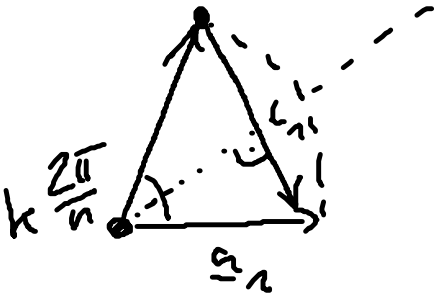
If $\{\underline{R}_n\}$ has C_n (n integer)

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

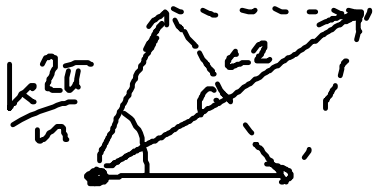
Consider: $\underline{R}'_n = \underline{R}_n - C_n \underline{R}_n$



$\underline{a}_1$: shortest in $\{\underline{R}_n\}$ $\quad (k C_n)\underline{a}_1 \in \{\underline{R}_n\}$



$$\left|\underline{a}_1 - \underbrace{(k C_n)\underline{a}_1}_{\underline{V}}\right| = L_1$$



$$\left|\underline{a}_1 + (k C_n)\underline{a}_1\right| = L_2$$

$L_1 \geq |\underline{a}_1|$ by def. unless $L_1 = 0$

$$\left|\sin\left(\frac{k\pi}{n}\right)\right| = \frac{L_1}{2|\underline{a}_1|} \geq \frac{1}{2} = \sin\frac{\pi}{6}$$

$\Rightarrow n \leq 6$

$$\left|\cos\frac{k\pi}{n}\right| = \frac{L_2}{2|\underline{a}_1|} \geq \frac{1}{2} \quad \text{⊥}$$

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

G	A_1	A_2	...
A_1	$A_1 \otimes A_1$	$A_1 \otimes A_2$	...
A_2	$A_2 \otimes A_1$	$A_2 \otimes A_2$	...
⋮	⋮	⋮	

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

Crystals with a basis:

lowers symmetry comp to underlying Bravais lattice

for O_h:

O → no inversion

T_d → point group of tetrahedron

T → same but no reflection symmetry

T_h → $T \otimes i$

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

→ exercises.

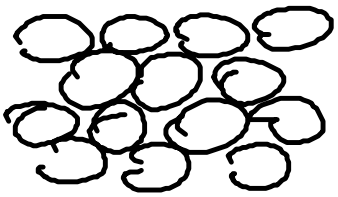
Finally: What types of structures are there?
(Bravais lattice + basis)

32 cryst. point groups

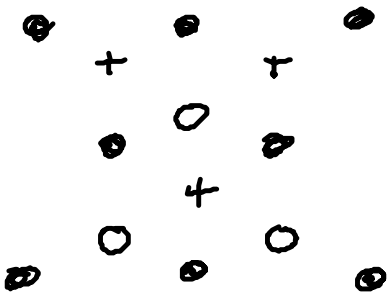
230 space groups

Close-packed structures

hard spheres filling as much volume as possible?

 → hex. plane

3D: stack hex. planes



A-B stacking
"hex close packed"
hcp

A-B-C stacking
fcc structure