Lecture #3: Bravais lattices, Reciprocal lattice, x-ray scattering

Bravais lattice is a lattice that is "truly periodic" in the sense that you can't zoom out any atom, or any group of atoms.

Example: \( \ldots \ldots \ldots \ldots \) (The only possible Bravais in 1d!)

Not a Bravais!

Definition: For dimension \( d \), give a set of \( d \) primitive vectors that fill the space for a single cell \( \vec{a}_1, \vec{a}_2, \vec{a}_3, \ldots \), define a Bravais lattice as the set of points:

\[
R = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3
\]

For \( m_i = -\infty, \ldots, -2, -1, 0, 1, 2, 3, \ldots, \infty \)

Example: Simple cubic lattice (cc)

Body-centered lattice (bc)

\[
\begin{align*}
\vec{a}_1 &= a \hat{x} \\
\vec{a}_2 &= a \hat{y} \\
\vec{a}_3 &= \frac{a}{2} (\hat{x} + \hat{y} + \hat{z})
\end{align*}
\]
Face centred cubic (fcc)

\[
\begin{align*}
\hat{a}_1 &= \frac{a}{2} (\hat{x} + \hat{y}) \\
\hat{a}_2 &= \frac{a}{2} (\hat{x} + \hat{z}) \\
\hat{a}_3 &= \frac{a}{2} (\hat{y} + \hat{z})
\end{align*}
\]

Simple cubic (sc)

\[
\begin{align*}
\hat{a}_1 &= a \hat{x} \\
\hat{a}_2 &= a \left( \hat{x} + \sqrt{3} \hat{y} \right) \\
\hat{a}_3 &= c \hat{z}
\end{align*}
\]
We showed that the wavevectors \( \mathbf{k} = \pm \frac{N}{a} \mathbf{b}_{\|} \) have special properties because they are associated to electrons with wavelength \( \lambda = \frac{2a}{N} \) that are perfectly reflected when incident on the lattice. In a multidimensional system, there are many different ways to form Bragg reflectors:

Three examples of parallel planes that can form Bragg reflectors or "Bragg planes".

Note: Not all "planes" form Bragg reflectors. Example:

A 2d or 3d crystal has an infinite set of parallel planes, where distance \( \frac{N}{2a} \) from one plane to all the way to zero. But only a subset of these are Bragg planes.
For Bragg planes, the interplane vector \( \mathbf{\hat{a}} \) has to be equal to a sum of primitive vectors.
\[
\mathbf{\hat{a}}(\text{Bragg}) = N_1 \mathbf{\hat{a}}_1 + N_2 \mathbf{\hat{a}}_2 + N_3 \mathbf{\hat{a}}_3
\]
For all other planes, the interplane vector \( \mathbf{\hat{a}} \) here equals to an integer fraction of the \( \mathbf{\hat{a}}(\text{Bragg}) \).
To find the set of wavevectors \( \mathbf{\hat{q}} \) Bragg, it is useful to study the set of all plane waves \( \mathbf{\hat{q}} \) that have the periodicity of the lattice:
\[
e^{i \mathbf{\hat{q}} \cdot \mathbf{r}} = e^{i \mathbf{\hat{q}} \cdot \mathbf{R}}
\]
The family of \( \mathbf{\hat{q}} \) satisfying this for all \( \mathbf{R} \) defines the reciprocal lattice (That is, the "Fourier lattice")

Or equivalently:
\[
\mathbf{\hat{q}} \cdot \mathbf{R} = 2\pi N \quad \text{for some integer } N.
\]
Write \( \mathbf{\hat{q}} = \mathbf{\hat{q}}_1 \mathbf{\hat{b}}_1 + \mathbf{\hat{q}}_2 \mathbf{\hat{b}}_2 + \mathbf{\hat{q}}_3 \mathbf{\hat{b}}_3 \) with \( \mathbf{\hat{q}}_i \) integers, where

the \( \mathbf{\hat{b}}_i \)'s are a set of orthogonal vectors satisfying \( \mathbf{\hat{a}}_i \cdot \mathbf{\hat{b}}_i = 2\pi \delta_{ij} \):

\[
\begin{align*}
\mathbf{\hat{b}}_1 &= \frac{2\pi (\mathbf{\hat{a}}_2 \times \mathbf{\hat{a}}_3)}{\mathbf{\hat{a}}_1 \cdot (\mathbf{\hat{a}}_2 \times \mathbf{\hat{a}}_3)} \\
\mathbf{\hat{b}}_2 &= \frac{2\pi (\mathbf{\hat{a}}_3 \times \mathbf{\hat{a}}_1)}{\mathbf{\hat{a}}_2 \cdot (\mathbf{\hat{a}}_3 \times \mathbf{\hat{a}}_1)} \\
\mathbf{\hat{b}}_3 &= \frac{2\pi (\mathbf{\hat{a}}_1 \times \mathbf{\hat{a}}_2)}{\mathbf{\hat{a}}_3 \cdot (\mathbf{\hat{a}}_1 \times \mathbf{\hat{a}}_2)}
\end{align*}
\]

Hence, we can write \( \mathbf{R} = N_1 \mathbf{\hat{a}}_1 + N_2 \mathbf{\hat{a}}_2 + N_3 \mathbf{\hat{a}}_3 \):
\[
\mathbf{\hat{q}} \cdot \mathbf{R} = \left( N_1 \mathbf{\hat{q}}_1 \mathbf{\hat{b}}_1 \cdot \mathbf{\hat{a}}_1 + N_2 \mathbf{\hat{q}}_2 \mathbf{\hat{b}}_2 \cdot \mathbf{\hat{a}}_2 + N_3 \mathbf{\hat{q}}_3 \mathbf{\hat{b}}_3 \cdot \mathbf{\hat{a}}_3 \right) = 2\pi N \left( \mathbf{\hat{q}}_1 N_1 + \mathbf{\hat{q}}_2 N_2 + \mathbf{\hat{q}}_3 N_3 \right) = 2\pi \mathbf{N}
\]
The set of vectors $\mathbf{q}$ define a lattice just as the set of vectors $\mathbf{r}$ define a lattice in real space.

- Each vector $\mathbf{q}$ points perpendicular to a set of planes in the real lattice $\mathbf{R}$.
- Each $2\pi\mathbf{q}$ corresponds to an interplane distance $2\pi/a$ parallel in the real lattice $\mathbf{R}$.

1d lattice: $\mathbf{R} = m\mathbf{a} + n\mathbf{b}$

Reciprocal: $\mathbf{q} = \frac{2\pi}{a} \mathbf{a} + \frac{2\pi}{b} \mathbf{b}$

Cubic lattice:

In a 1d system, the Brillouin zone is the set of $k$'s in reciprocal space between $-\pi/a$ and $\pi/a$. In higher dimensions, the equivalent zone has boundaries at $\pm \frac{T}{2}$, where $T$ is the smallest possible Bragg plane in a given direction.

This leads to a simple rule to construct the Brillouin zone in higher dimensions:

1) Construct reciprocal lattice
2) Start from the origin, draw lines to nearest neighbors
3) Bisect these lines with planes; the cell extending from the origin all the way to these planes is the Brillouin zone.
Energy gaps open up at the boundaries of the Brillouin zone, just as in the 1D case. The zone around this way is called the Wigner-Seitz cell. The Wigner-Seitz method can be applied to find a primitive cell for any lattice. For real space lattices, it leads to a consistent (more symmetrical) cell than the parallelepiped we had before.

Wigner-Seitz cell of the triangular lattice.

X-ray scattering

The reciprocal lattice is nicely connected to X-ray scattering.

Suppose an incident wave \( \mathbf{A}_n = e^{i \mathbf{k}_n \cdot \mathbf{r}_n - wt} \) scattering off atom \( A \), generating a scattered wave \( \mathbf{A}_{\text{scat}} = e^{i \mathbf{k}_{\text{scat}} \cdot \mathbf{r}_n - wt} \).

Note, \( \mathbf{k} = \mathbf{k}_0 \) (elastic scattering) but \( \mathbf{k} \) not in the incident direction \( \mathbf{R}_0 \).

The total wave amplitude of atom \( B \) is given by (for \( \mathbf{R}_B = \mathbf{R}_0 \), \( \mathbf{R}_A = \mathbf{0} \)):

\[
A_{\text{tot}} (\mathbf{R}_B) = A_{\text{in}} (\mathbf{R}_B) + A_{\text{scat}} (\mathbf{R}_B) = e^{i \mathbf{k}_0 \cdot \mathbf{R}_B - wt} + e^{i \mathbf{k} \cdot \mathbf{R}_B - wt} = e^{i (\mathbf{k}_0 + \mathbf{k}) \cdot \mathbf{R}_B - wt} (1 + e^{i \mathbf{B} \cdot \mathbf{R}_B})
\]
where \( \mathbf{s} = (\mathbf{R} - \mathbf{R}_0) \) is the scattering vector.

The intensity at \( \mathbf{R}_0 \) is hence proportional to

\[
I \propto |A_{mm}|^2 = \left(1 + e^{i\frac{\mathbf{s} \cdot \mathbf{R}_0}{\lambda}}\right)\left(1 + e^{-i\frac{\mathbf{s} \cdot \mathbf{R}_0}{\lambda}}\right) = 2 \left[1 + c_0(\mathbf{s} \cdot \mathbf{R}_0)\right].
\]

This is the standard interference pattern of two coherent sources.

In the case of a lattice, we must sum over all scattered waves generated by each "atom \( \mathbf{R}_0 \)."

This leads to (using \( \mathbf{R}_0 \to \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \)):

\[
A_{mm} = 1 + \sum e^{i\frac{\mathbf{s} \cdot \mathbf{R}}{\lambda}} = 1 + \sum e^{i(n_1 \mathbf{s} \cdot \mathbf{a}_1 + n_2 \mathbf{s} \cdot \mathbf{a}_2 + n_3 \mathbf{s} \cdot \mathbf{a}_3)}
\]

\[\text{incident wave} \quad \uparrow \quad \text{summed over all scattered waves from all the atoms} \quad \text{from zero amplitude}\]

In this case, most of the time the phase factors will cancel out unless they are added coherently.

There is constructive interference only when the following three conditions are met simultaneously:

\[
\mathbf{s} \cdot \mathbf{a}_1 = 2\pi n_1, \quad \mathbf{s} \cdot \mathbf{a}_2 = 2\pi n_2, \quad \mathbf{s} \cdot \mathbf{a}_3 = 2\pi n_3
\]

with \( n_1, n_2, n_3 \) integers.

This is the same as saying that

\[
\mathbf{s} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3
\]

or \( \mathbf{s} \) must be a reciprocal lattice vector.
The three conditions are very stringent. For a given \( F \), \( \sigma \) only has two degrees of freedom, the azimuthal and longitudinal angle of \( \Phi \) (\( \Phi = 0 \)).

For the X-ray scattering to be met, one must use the following two methods to get a criterion of inputs:

- **Laue Method**: Broad range of input wavelengths ("white" light). Determines the orientation of the crystal but does not determine its lattice spacing.

- **Powder Diffraction**:
  - Use monochromatic light.
  - Scatters the \( \sigma \) angle, by grinding the crystal into a powder (many small micrometers).
  - Allows determination of \( a \) and crystal structure.

\[ \sum_{\text{basis}} e^{i \vec{\mathbf{g}} \cdot \vec{\mathbf{R}}_{\text{basis}}} \]

\[ S(\vec{g}) = \sum_{\text{basis}} e^{i \vec{\mathbf{g}} \cdot \vec{\mathbf{R}}_{\text{basis}}} = 1 + e^{i \vec{\mathbf{g}} \cdot \vec{\mathbf{a}}} \]

**Example:**

Let's look at the 1d lattice of space \( \sigma \) on a lattice with a basis. The Bravais has \( \sigma \) and there are two atoms in the unit, \( \vec{\mathbf{R}}_1 = \sigma \) and \( \vec{\mathbf{R}}_2 = 2 \sigma \).

For reciprocal in \( \vec{\mathbf{g}} = N \frac{2\pi}{a} \hat{\mathbf{a}} \): This has two times more atoms than the "usual" \( \hat{\mathbf{g}} = N \frac{2\pi}{a} \hat{\mathbf{a}} \).

\[ S(N \frac{2\pi}{a}) = 1 + e^{iN \frac{2\pi}{a}} = \begin{cases} 0 & \text{for } N \text{ odd} \\ 2 & \text{for } N \text{ even} \end{cases} \]

The structure factor "zeros" the addition.