Lecture #4: Block functions, finite crystals, density of states

**General properties of Bloch waves**

Given an origin-centered reciprocal lattice:

\[ T_{nk}(\vec{R}) = \frac{M_{nk}(\vec{R})}{\sqrt{V}} e^{i \vec{K} \cdot \vec{R}} \quad \text{with} \quad M_{nk}(\vec{R} + \vec{R}') = M_{nk}(\vec{R}) \]

Expand for all \( n \) as a Fourier series:

\[ M_{nk}(\vec{R}) = \sum_{\vec{Q} \in \text{reciprocal lattice}} c_{nk}(\vec{Q}) e^{-i \vec{Q} \cdot \vec{R}} \]

Only \( \vec{Q} \in \text{Reciprocal lattice} \) give non-zero Fourier components. It's easy to prove this: Say \( \vec{Q} \) not in reciprocal lattice contributes, then \( M_{nk}(\vec{R}) \) would have a component like \( e^{i \vec{Q} \cdot \vec{R}} \) and \( M_{nk}(\vec{R} + \vec{R}') \sim e^{i \vec{Q} \cdot \vec{R}} e^{i \vec{Q} \cdot \vec{R}'} \neq M_{nk}(\vec{R}) \). \( \checkmark \) means \( \vec{Q} \) not in reciprocal lattice.

Since \( \vec{k} \) and \( \vec{R} \) lie in the first Brillouin zone, we may write

\[ \Psi_{nk}(\vec{R}) = \frac{1}{\sqrt{V}} \sum_{\vec{Q}} c_{nk}(\vec{Q}) e^{i (\vec{K} - \vec{Q}) \cdot \vec{R}} \]

\[ \Psi_{nk}(\vec{R}) = \frac{1}{\sqrt{V}} \sum_{\vec{Q}} c_{nk}(\vec{K} - \vec{Q}) e^{i (\vec{Q} - \vec{Q}) \cdot \vec{R}} \]

Which is just another way of proving Bloch's theorem.
Note: Set a reciprocal lattice vector $\mathbf{b}^* = k^*$:

$$T_{m_{n_k}}(\mathbf{b}^*) = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \mathcal{C}_{m} (\mathbf{k} + \mathbf{q}^* - \mathbf{b}^*) e^{i (\mathbf{k} + \mathbf{q}^* - \mathbf{b}^*) \cdot \mathbf{r}} = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \mathcal{C}_{m} e^{i q^* \cdot \mathbf{r}} e^{i (\mathbf{b}^* - \mathbf{q}^*) \cdot \mathbf{r}}$$

Substitute: $\mathbf{q}^* = \mathbf{q} - \mathbf{b}^*$

$$= \mathcal{T}_{m_{n_k}}^{*}(\mathbf{k})$$

Block states $\mathcal{T}_{m_{n_k}}(\mathbf{r})$ are periodic in $\mathbf{k}$, with periodicity given by each reciprocal lattice vector.

Also note:

$$\mathcal{T}_{m_{n_{k^*}}}^{*}(\mathbf{r}) = \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r} + \mathbf{k}^*) = e^{i \mathbf{k}^* \cdot \mathbf{r}} \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r}) = e^{i \mathbf{k}^* \cdot \mathbf{R}} \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r})$$

Conjugate to $\mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r}) = e^{-i \mathbf{k}^* \cdot \mathbf{R}} \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r})$

Since the momentum must be modulo $\mathbf{k}^*$ uniquely

$$\mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r}) = \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r})$$

Also:

$$\mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r}) = \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r} + \mathbf{k}^*) = (e^{i \mathbf{k}^* \cdot \mathbf{R}} \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r}))^{*} = e^{-i \mathbf{k}^* \cdot \mathbf{R}} \mathcal{T}_{m_{n_{k}}}^{*}(\mathbf{r})$$

Reduced form:

$$E_{\gamma_{n_{k}}} = \left< \mathcal{T}_{m_{n_{k}}}^{*} \mid \mathcal{T}_{m_{n_{k}}} \right> = \int d^3 \gamma \mathcal{E}_{\gamma_{n_{k}}}^{*} \gamma \mathcal{T}_{m_{n_{k}}}^{*} \gamma = \int d^3 \gamma \mathcal{E}_{\gamma_{n_{k}}}^{*} \gamma \mathcal{E}_{\gamma_{n_{k}}}$$

$$= \left< \mathcal{T}_{m_{n_{k}}} \mid \mathcal{T}_{m_{n_{k}}} \right>^{*} = E_{\gamma_{n_{k}}}$$
\[ E_{\nu K} = E_{\nu - K} \] "Kramers theorem."

This then, plus \( T_n, k + \phi = T_n, k \) implies that the "zone boundary" point \( \phi = \frac{\pi}{2} \) has special properties:

\[
\left. \frac{\partial E_{nk}}{\partial k} \right|_{\phi = \frac{\pi}{2}} = \frac{\text{f.m.}}{\text{dE}} = \frac{\left( T_{nk}, d\phi \right) \left| H_{nk} \right| T_{nk}, d\phi}{2|dE|}
\]

But:

\[
\left( T_{nk}, d\phi \right) \left| H_{nk} \right| T_{nk}, d\phi = \left( T_{nk}, \phi \right) - \left( T_{nk}, d\phi \right) \left| H_{nk} \right| T_{nk}, d\phi
\]

\[
= \left( T_{nk}, -d\phi \right) \left| H_{nk} \right| T_{nk}, -d\phi
\]

\[
= \left( T_{nk}, \phi + d\phi \right) \left| H_{nk} \right| T_{nk}, \phi + d\phi
\]

\[
\left. \frac{\partial E_{nk}}{\partial k} \right|_{\phi = \frac{\pi}{2}} = 0
\]

Similarly at \( \phi = 0 \):

\[
\left. \frac{\partial E}{\partial k} \right|_{\phi = 0} = \text{f.m.} \left( T_{nk}, d\phi \right) \left| H_{nk} \right| T_{nk}, d\phi = 0
\]

\[ \text{true for any direction, so } \frac{\partial E}{\partial k} = 0. \]

Also, \( \frac{\partial E_{nk}}{\partial k} = 0 \) at \( \phi = 0 \), then as we called critical points, we suppose that a point \( Q \) at the zone boundary and at the midpoint between two different \( \phi \)'s at critical point.

\[ \text{an arbitrary } \phi \text{ and } Q \text{ belonging line in zero!} \]

Also,

\[ \frac{\partial T_{nk}}{\partial k} = 0 \quad \text{at } \phi = 0 \quad \text{and chosen } T_{nk, \phi} \text{ real at } \phi = 0 \]

\[ \frac{\partial}{\partial k} \left( M_{nk}(k) e^{i(k-k_0)} \right) = 0 \Rightarrow \left( \frac{\partial}{\partial k} M_{nk}(k) e^{i(k-k_0)} + i(k-k_0) M_{nk}(k) e^{i(k-k_0)} \right) = 0 \Rightarrow \frac{\partial}{\partial k} M_{nk}(k) \bigg|_{k = k_0} = -i(k-k_0) M_{nk}(k)
\]

\[ M_{nk}(k) = M_{nk}(k_0) + \frac{\partial}{\partial k} M_{nk}(k_0) \cdot \bar{k} + \bar{k}(k) = M_{nk}(k_0) \left[ 1 - \bar{k} \cdot \bar{k} \right] + \bar{k}(k)
\]
Boundary conditions in a polycrystal

Real crystals have boundaries, but if we assume a perfect lattice to neglect electrons out of the crystal, a boundary condition such as \( n(\vec{a}) = 0 \) at the surface, then our assumptions leading to Bloch's theorem are now valid anymore. Namely, it is not invariant under translational of any \( \vec{R} \), and \( n_k(\vec{a} + \vec{R}) \neq n_k(\vec{R}) \).

Of course, Bloch's theorem holds approximately for the region inside a long crystal, in the sense that \( n_k \) is approximately a Bloch state over several unit cell depths inside the crystal.

A simple solution to this problem is to use periodic boundary conditions:

\[
\begin{align*}
T_{nk}(0) &= T(L), \\
\frac{e^{i2\pi n_k L}}{2\pi} &= T_{nk}(L).
\end{align*}
\]

While this is physically incorrect, it has the advantage that it satisfies exactly the assumptions behind Bloch's theorem. Consider \( \vec{R} = N_1 \vec{a}_1 + N_2 \vec{a}_2 + N_3 \vec{a}_2 \hat{a}_3 \), where \( N_k \) is the number of atoms in the direction \( \hat{a}_k \).

\[
\begin{align*}
T_{nk}(\vec{a} + \vec{R}) &= e^{i2\pi \vec{k} \cdot \vec{R}} T_{nk}(\vec{a}) = T_{nk}(\vec{R}) \\
&\Rightarrow e^{i2\pi \vec{k} \cdot \vec{R}} = 1
\end{align*}
\]

62 \( \vec{k} \cdot \vec{R} = \sum k_i N_i \hat{a}_i \), where \( N_i \) is the number of atoms in the direction \( \hat{a}_i \).

The condition satisfied is \( \vec{R} = N_1 \hat{a}_1 + N_2 \hat{a}_2 + N_3 \hat{a}_3 \hat{a}_3 \), and

\[
\vec{k} \cdot \vec{R} = (N_1 + N_2 + N_3) \hat{a}_3 \quad \text{(because } \hat{a}_i \cdot \hat{a}_j = 2\pi S_{ij} \text{)}
\]

\( \Rightarrow \vec{k} \) can only have discrete values so that a finite \( k \) of full wavelengths "fit in \( L \)."

\[ \Rightarrow \text{For } \vec{k} \in \text{1st Brillouin } \}
\]
Total of $N = N_1 N_2 N_3$ states within each band, equal to # of atoms, as expected.

In this case, we can put an integer # of half wavelengths inside $L$. At first, this means it leads to $(2N_1) (2N_2) (2N_3)$ states per band, $8 \times$ # of atom. However, in a crystal like this, all states are standing waves, so only need to count $\frac{1}{8}$ in the positive $k$ quadrant, i.e., $\frac{1}{8}$ of the $k$'s actually lead to real standing waves. ⇒ # of states per band is $N$.

Since $\vec{k} = \frac{1}{N_1} \vec{x} + \frac{1}{N_2} \vec{y} + \frac{1}{N_3} \vec{z}$, each state (each allowed vector $(v_1, v_2, v_3)$)

Consider the following lattice in $k$ space:

$$A^3 \vec{k} = A \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{1}{N_1 N_2 N_3} \frac{2 \pi}{N_1 N_2 N_3} \frac{2 \pi}{N_1 N_2 N_3} = \frac{(2\pi)^3}{V}$$

Density of states:

Because the number $N$ of atoms is so large in a crystal, we can regard $k$ as a continuous variable within the Brillouin zone. Most of the macroscopic properties are related to a narrow $E$.

$$\sum_k \rightarrow \int \frac{d^3k}{(2\pi)^3} = \int D(E) dE$$

Energy density, i.e., # of states lying between $E$ and $E+dE$.

$$D(E) = \int \frac{d^3k}{(2\pi)^3} \delta(E(E) - E) \delta(E) dE = \frac{d^3k}{(2\pi)^3}$$
But:

\[ D(\varepsilon) = \int \frac{d^3k}{(2\pi)^3} \frac{1}{|\textbf{E}|} \, d\varepsilon \]

Because \( d\varepsilon = \varepsilon \, d\varepsilon(\varepsilon) \, d\textbf{k} \).

\[ \int d^3k = \int 4\pi k^2 \, dk = \int 4\pi \frac{k^2}{(2\pi)^3} \, \frac{d\varepsilon}{d\textbf{k}} = \int \frac{V}{2\pi^2} \frac{k^3}{\hbar^3} \, d\varepsilon = \frac{mV}{2\pi^2 \hbar^3} \int \frac{2\pi^2}{\hbar^3} \, d\varepsilon \]

\[ \Rightarrow D(\varepsilon) = \frac{mV}{2\pi^2 \hbar^3} \sqrt{\frac{k^3}{\hbar^3}} \, d\varepsilon \]