

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

General properties of Bloch functions

Bloch's theorem:

$$\psi_{n\vec{k}}(\vec{r}) = \frac{u_{n\vec{k}}(\vec{r})}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \quad \text{with } u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$$

Expand the cell func as a Fourier series:

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{Q} \text{ in reciprocal lattice}} c_{n\vec{k}}(\vec{Q}) e^{-i\vec{Q}\cdot\vec{r}}$$

Only  $\vec{Q} \in$  Reciprocal Lattice gives non-zero Fourier components. It's easy to prove this: Say  $\vec{q}$  not in reciprocal lattice contributes; then  $u_{n\vec{k}}(\vec{r})$  would have a component like  $e^{i\vec{q}\cdot\vec{r}}$ , and  $u_{n\vec{k}}(\vec{r}+\vec{R}) \sim e^{i\vec{q}\cdot\vec{R}} e^{i\vec{q}\cdot\vec{r}} \neq u_{n\vec{k}}(\vec{r})$ .  
 $\neq 1$  because  $\vec{q}$  is not in reciprocal lattice.

Since  $\vec{k}$  can be chosen to lie in the 1<sup>st</sup> Brillouin zone, we may write

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{Q}} c_{n\vec{k}}(\vec{Q}) e^{i(\vec{k}-\vec{Q})\cdot\vec{r}}$$

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{Q}} c_n(\vec{k}-\vec{Q}) e^{i(\vec{k}-\vec{Q})\cdot\vec{r}}$$

which is just another way of expressing Bloch's theorem.

2)

Note: Add a reciprocal lattice vector to  $\vec{k}$ :

$$\psi_{m, \vec{k} + \vec{\phi}'}(\vec{n}) = \frac{1}{\sqrt{V}} \sum_{\vec{R}} c_m(\vec{k} + \vec{\phi}' - \vec{\phi}) e^{i(\vec{k} + \vec{\phi}' - \vec{\phi}) \cdot \vec{n}} = \frac{1}{\sqrt{V}} \sum_{\vec{R}''} c_m(\vec{k} - \vec{\phi}'') e^{i(\vec{k} - \vec{\phi}'') \cdot \vec{n}}$$

Substitute:  $\vec{\phi}'' = \vec{\phi} - \vec{\phi}'$   $\rightarrow$   $= \psi_{m, \vec{k}}(\vec{n})$

► Bloch states  $\psi_{m, \vec{k}}(\vec{n})$  are periodic in  $\vec{k}$ , with periodicity given by each reciprocal lattice vector.

Also note:

$$\hat{T}_{\vec{R}} \psi_{m, \vec{k} + \vec{\phi}}(\vec{n}) = \psi_{m, \vec{k} + \vec{\phi}}(\vec{n} + \vec{R}) = e^{i(\vec{k} + \vec{\phi}) \cdot \vec{R}} \psi_{m, \vec{k} + \vec{\phi}}(\vec{n}) = e^{i\vec{k} \cdot \vec{R}} \psi_{m, \vec{k} + \vec{\phi}}(\vec{n})$$

↓

Compare to  $\hat{T}_{\vec{R}} \psi_{m, \vec{k}}(\vec{n}) = e^{i\vec{k} \cdot \vec{R}} \psi_{m, \vec{k}}(\vec{n})$

Since the quantum numbers  $m$  and  $\vec{k}$  specify  $\psi_{m, \vec{k}}$  uniquely  $\Rightarrow \psi_{m, \vec{k}}(\vec{n}) = \psi_{m, \vec{k} + \vec{\phi}}(\vec{n})!$

Also:  $\hat{T}_{\vec{R}} \psi_{m, \vec{k}}^*(\vec{n}) = \psi_{m, \vec{k}}^*(\vec{n} + \vec{R}) = (e^{i\vec{k} \cdot \vec{R}} \psi_{m, \vec{k}}(\vec{n}))^* = e^{-i\vec{k} \cdot \vec{R}} \psi_{m, \vec{k}}^*(\vec{n})$

↑

$\psi_{m, \vec{k}}^*(\vec{n}) = \psi_{m, -\vec{k}}(\vec{n})$

This implies:

$$E_{m, -\vec{k}} = \langle \psi_{m, -\vec{k}} | \hat{H} | \psi_{m, -\vec{k}} \rangle = \int d^3n \psi_{m, -\vec{k}}^*(\vec{n}) \hat{H} \psi_{m, -\vec{k}}(\vec{n}) = \int d^3n \psi_{m, \vec{k}}(\vec{n}) \hat{H} \psi_{m, \vec{k}}^*(\vec{n})$$

$$= \langle \psi_{m, \vec{k}} | \hat{H} | \psi_{m, \vec{k}} \rangle^* = E_{m, \vec{k}}$$

↑  
Hamiltonian!

$$\Rightarrow \boxed{E_{n\vec{k}} = E_{n,-\vec{k}}} \text{ "Kramers theorem"}$$

This then, plus  $\psi_{n,\vec{k}+\vec{\phi}} = \psi_{n\vec{k}}$  implies that the "zone boundary" point  $\vec{k} = \frac{\vec{\phi}}{2}$  has special properties:

$$\frac{\partial E_{n\vec{k}}}{\partial k} \Big|_{\vec{k} = \frac{\vec{\phi}}{2}} = \lim_{d\vec{k} \rightarrow 0} \frac{\langle \psi_{n,\frac{\vec{\phi}}{2}+d\vec{k}} | H | \psi_{n,\frac{\vec{\phi}}{2}+d\vec{k}} \rangle - \langle \psi_{n,\frac{\vec{\phi}}{2}-d\vec{k}} | H | \psi_{n,\frac{\vec{\phi}}{2}-d\vec{k}} \rangle}{2|d\vec{k}|}$$

But


$$\begin{aligned} \langle \psi_{n,\frac{\vec{\phi}}{2}-d\vec{k}} | H | \psi_{n,\frac{\vec{\phi}}{2}-d\vec{k}} \rangle &= \langle \psi_{n,\frac{\vec{\phi}}{2}-d\vec{k}-\vec{\phi}} | H | \psi_{n,\frac{\vec{\phi}}{2}-d\vec{k}-\vec{\phi}} \rangle \\ &= \langle \psi_{n,-d\vec{k}-\frac{\vec{\phi}}{2}} | H | \psi_{n,-d\vec{k}-\frac{\vec{\phi}}{2}} \rangle \\ &= \langle \psi_{n,\frac{\vec{\phi}}{2}+d\vec{k}} | H | \psi_{n,\frac{\vec{\phi}}{2}+d\vec{k}} \rangle \end{aligned}$$

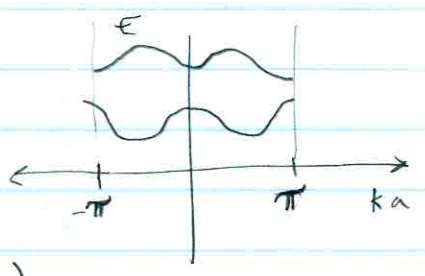
$$\Rightarrow \boxed{\frac{\partial E_{n\vec{k}}}{\partial k} \Big|_{\vec{k} = \frac{\vec{\phi}}{2}} = 0}$$

Similarly at  $\vec{k} = \vec{0}$ :

$$\frac{\partial E}{\partial k} \Big|_{\vec{k} = \vec{0}} = \lim_{d\vec{k} \rightarrow 0} \frac{\langle \psi_{n,d\vec{k}} | H | \psi_{n,d\vec{k}} \rangle - \langle \psi_{n,-d\vec{k}} | H | \psi_{n,-d\vec{k}} \rangle}{2|d\vec{k}|} = 0$$

$\Rightarrow$  true for any direction, so  $\nabla_{\vec{k}} E_{n\vec{k}} = \vec{0}$ .

Also,  $\nabla_{\vec{k}} E_{n\vec{k}} = \vec{0}$  at other  $\vec{k} \neq \vec{0}$ ; these are the so-called critical points. We suppose that a point  $\vec{k}$  at the zone bound and at the midpoint between two different  $\vec{\phi}$ 's is a critical point.   
  $\Rightarrow$  direction of  $E$  w.r.t  $\vec{k}$  along this line is zero!



Also,  $\nabla_{\vec{k}} \psi_{n\vec{k}} = \vec{0}$  at (Use  $\psi_{n\vec{k}}^* = \psi_{n,-\vec{k}}$  and choose  $\psi_{n\vec{k}}$  real at  $\vec{k} = \vec{0}$ )  
 critical point such as  $\vec{k} = \vec{0}$ .

$$\begin{aligned} \Rightarrow \nabla_{\vec{k}} (u_{n\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}) = \vec{0} &\Rightarrow (\nabla_{\vec{k}} u_{n\vec{k}}(\vec{r})) e^{i\vec{k} \cdot \vec{r}} + i \vec{k} u_{n\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} = \vec{0} \Rightarrow \nabla_{\vec{k}} u_{n\vec{k}}(\vec{r}) \Big|_{\vec{k} = \vec{0}} = -i \vec{k} u_{n\vec{k}}(\vec{r}) \\ \Rightarrow u_{n\vec{k}}(\vec{r}) = u_{n\vec{0}}(\vec{r}) + \nabla_{\vec{k}} u_{n\vec{k}} \Big|_{\vec{k} = \vec{0}} \cdot \vec{k} + O(k^2) &= u_{n\vec{0}}(\vec{r}) [1 - i \vec{k} \cdot \vec{r}] + O(k^2) \end{aligned}$$

④

Boundary conditions in a finite crystal

Real crystals have boundaries; but if we assume a potential barrier to eject electrons out of the crystal, or a boundary condition such as  $\psi(\vec{r})=0$  at the surfaces, then our assumptions leading to Bloch's theorem are not valid anymore. Namely,  $\psi$  is not invariant under translations of any  $\vec{R}$ , and  $\psi_{nk}(\vec{r}+\vec{R}) \neq e^{i\vec{k}\cdot\vec{R}}\psi_{nk}(\vec{r})$ .

Of course, Bloch's theorem holds approximately for the region inside a large crystal, in the sense that  $\psi_{nk}$  is approximately a Bloch state over several unit cells deep inside the crystal.

A simple solution to this problem is to use periodic boundary conditions: (OKS Born-von Karman bound cond.)

$$\psi_{nk}(0) = \psi_{nk}(L), \quad \frac{\partial \psi_{nk}(0)}{\partial x} = \frac{\partial \psi_{nk}(L)}{\partial x}$$

While this is unphysical, it has the advantage that it satisfies exactly the assumptions behind  $2^D$ 's

theorem. Consider  $\vec{R} = N_1\vec{a}_1 + N_2\vec{a}_2 + N_3\vec{a}_3$ , where  $N_i$  is the <sup>total</sup> # of atoms in the direction  $i$ .

$$\psi_{nk}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_{nk}(\vec{r}) = \psi_{m\vec{k}}(\vec{r})$$

$$\Rightarrow e^{i\vec{k}\cdot\vec{R}} = 1$$

$$\Leftrightarrow \vec{k}\cdot\vec{R} = \vec{k}\cdot[N_1\vec{a}_1 + N_2\vec{a}_2 + N_3\vec{a}_3] = 2\pi N$$

The condition is satisfied  $\vec{k} = \frac{\nu_1}{N_1}\vec{r}_1 + \frac{\nu_2}{N_2}\vec{r}_2 + \frac{\nu_3}{N_3}\vec{r}_3$ , and

$$\vec{k}\cdot\vec{R} = (\nu_1 + \nu_2 + \nu_3)2\pi \quad (\text{because } \vec{r}_i \cdot \vec{r}_j = 2\pi \delta_{ij})$$

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

$$\Rightarrow \text{For } \vec{k} \in 1^{\text{st}} \text{ Brillouin, } \begin{cases} \nu_1 = -\frac{N_1}{2}, -\frac{N_1}{2}+1, \dots, \frac{N_1}{2} \\ \nu_2 = -\frac{N_2}{2}, \dots, \frac{N_2}{2} \\ \nu_3 = -\frac{N_3}{2}, \dots, \frac{N_3}{2} \end{cases}$$

⇒ Total of  $N = N_1 N_2 N_3$  states inside each Band; equal to # of atoms, as expected.

We get the same result if we use "impenetrable" bound. cond.

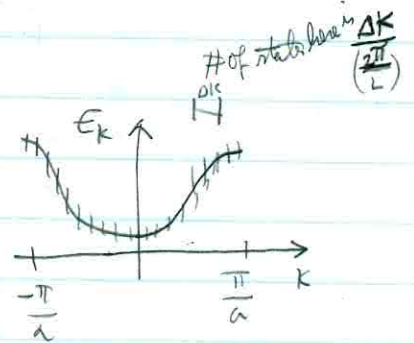
In this case, we can fit an integer # of half wavelengths inside  $L$ . At first, this seems to lead to  $(2N_1)(2N_2)(2N_3)$  states per band,  $8 \times$  # of atoms. However, in a crystal like

this all states are standing waves ⇒ only need to count  $\vec{k}$ 's in the positive  $\vec{k}$  quadrant, i.e.,  $\frac{1}{8}$  of the  $\vec{k}$ 's actually lead to new standing waves ⇒ # of states per band is  $N$ .

Since  $\vec{k} = \frac{\nu_1}{N_1} \vec{r}_1 + \frac{\nu_2}{N_2} \vec{r}_2 + \frac{\nu_3}{N_3} \vec{r}_3$ , each state (each allowed vector  $(\nu_1, \nu_2, \nu_3)$ )

occupies the following volume in  $\vec{k}$  space:

$$\Delta^3 k = \frac{\vec{r}_1}{N_1} \cdot \left( \frac{\vec{r}_2}{N_2} \times \frac{\vec{r}_3}{N_3} \right) = \frac{1}{\underbrace{N_1 N_2 N_3}_{N_{\text{atoms}}}} \frac{(2\pi)^3}{\underbrace{|\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}_{V_{\text{cell}}}} = \frac{(2\pi)^3}{V} //$$



Density of states

Because the number  $N$  of atoms is so large in a crystal, we can regard  $\vec{k}$  as a continuous variable within the Brillouin zone. Most of the macroscopic properties are related to a sum over  $\vec{k}$ ,

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

energy density of states, i.e., # of states with energy between  $E$  and  $E+dE$ .

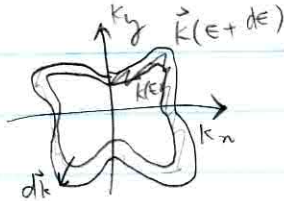
$$D(E) = \int \frac{d^3 k}{(2\pi)^3} \delta(E(\vec{k}) - E) \quad \text{because} \quad \int D(E) dE = \int \frac{d^3 k}{(2\pi)^3}$$

⑥

But:

$$D(E) = \int \frac{d\sigma_{\vec{k}}}{(2\pi)^3 V} \frac{1}{\underbrace{|\vec{v}_{\vec{k}}|}_{\sim \frac{dE}{d\vec{k}}}}$$

Because  $dE = \vec{v}_{\vec{k}}(\vec{k}) \cdot d\vec{k}$ .



Examples:

1) Free electrons in 3D

$$E = \frac{\hbar^2 k^2}{2m}$$

$$\int \frac{d^3k}{(2\pi)^3 V} = \int \frac{4\pi k^2 dk}{(2\pi)^3 V} = \int \frac{4\pi k^2}{(2\pi)^3 V} \frac{dE}{\frac{dE}{d\vec{k}}} = \int \frac{V}{2\pi^2} k^2 \frac{dE}{\frac{\hbar^2}{m} k} = \frac{mV}{2\pi^2 \hbar^2} \int \sqrt{2mE} dE$$

$$\Rightarrow D(E) = \frac{mV}{2\pi^2 \hbar^2} \sqrt{\frac{2m}{\hbar^2}} \sqrt{E} \propto \sqrt{E}$$

