Comment - For free electrons the energy eigenstates are specified ~~for~~ by a wave vector $\vec{k}$ that can take a value anywhere in k-space. For an electron in a periodic potential, we said eigenstates should be specified by a discrete band index n and a crystal momentum $\vec{q}$ that must lie only in the 1st BZ. But if we take the problem of the periodic potential ad let $U \to 0$, we recover the free electron case. So how can these two ways of labeling eigenstates both be valid?

Answer: We can represent even free electron states using the band index n ad 1st BZ $\vec{q}$ as quantum numbers. For any $\vec{k}$, anywhere in k-space, we can always write $\vec{k} = \vec{q} + \vec{K}$ where $\vec{K}$ is a unique ~~the~~ R.L. vector closest to $\vec{k}$ ad $\vec{q}$ therefore must be in the 1st B.Z. This follows from the equivalence of all points in the R.L. (since it is a Bravais lattice) and from the definition of the 1st BZ as the set of wave-vectors ~~closest~~ closer to the origin than to any other $\vec{K}$ in the R.L.

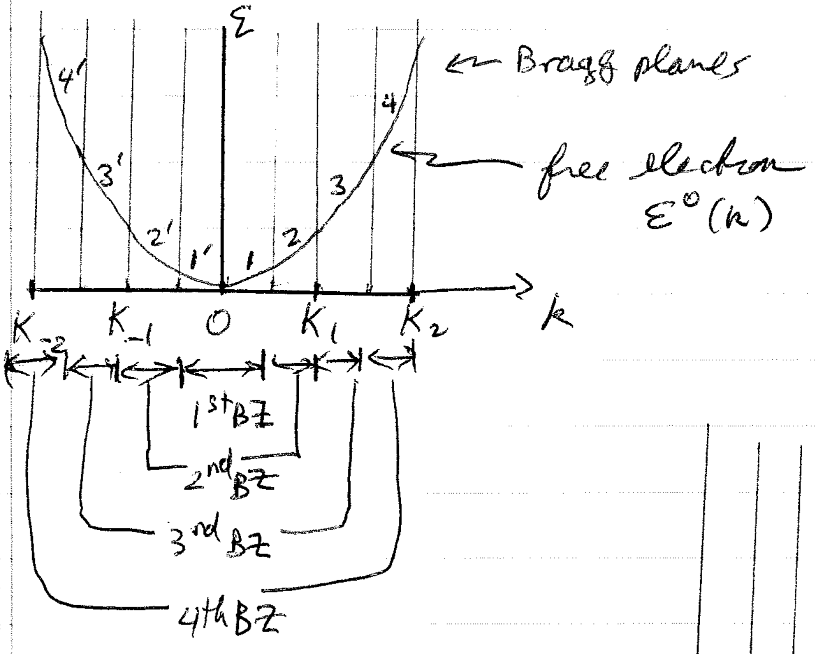
Then for any $\vec{k} = \vec{q} + \vec{K}$ in the nth Brillouin Zone

write $\mathcal{E}^0(k) = \dfrac{\hbar^2 k^2}{2m} = \dfrac{\hbar^2 (\vec{q} + \vec{K})}{2m} = \mathcal{E}_n(\vec{q})$

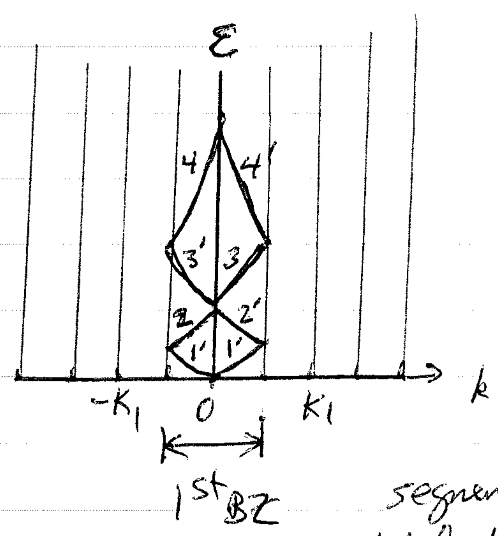
energy at crystal momentum $\vec{q}$ in band index "n"

Thus the band index gives the B.Z. in which the corresponding free electron wavevector $\vec{k}$ lies.

Ex: in a 1D B.L. of lattice constant a
R.L. vectors are $K_n = \left(\frac{2\pi}{a}\right) n$, $n = 0, \pm 1, \pm 2, \ldots$
Bragg planes at $k = \frac{K_n}{2} = \left(\frac{\pi}{a}\right) n$



can translate the section of curve in nth BZ back into 1st BZ by subtracting appropriate K from $\vec{k}$.



representing free electron states by $\vec{q}$ in 1st BZ.
Integers label corresponding sections of the curves in the two equivalent representations

segments of curve labeled n or n' came from the nth BZ of free electrons

Comments:

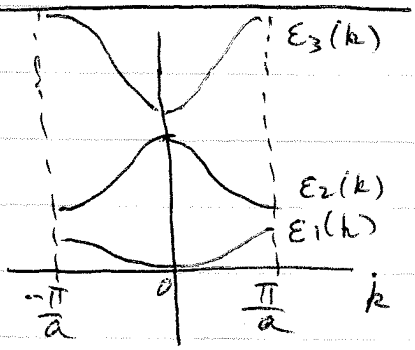
① Because $\vec k$ enters the matrix equation as a parameter via the terms ε^0_{k+K}, we expect that the eigenvalues $\varepsilon_n(\vec k)$ are smooth continuous functions of $\vec k$.

② Because $\varepsilon_n(\vec k)$ is periodic in $\vec k$, $\varepsilon_n(\vec k+\vec K) = \varepsilon_n(\vec k)$, we ~~expect~~ must have that $\varepsilon_n(\vec k)$ has a maximum and a minimum and varies continuously between them. This is why $\varepsilon_n(\vec k)$ is referred to as an energy band

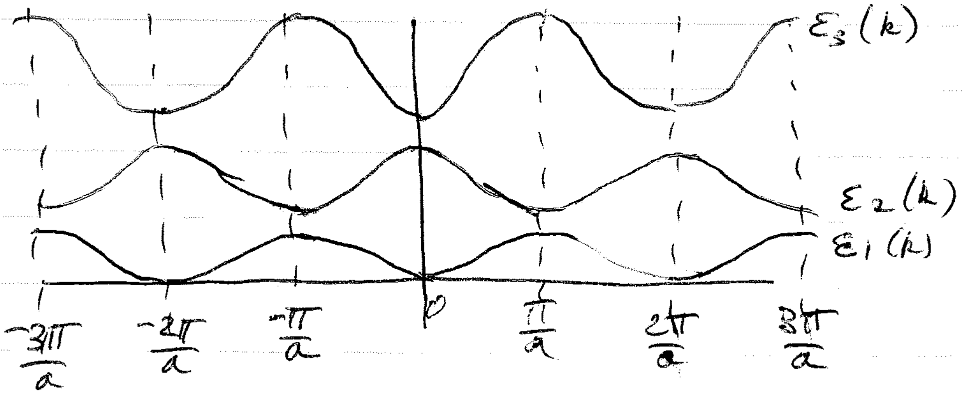
③ Since $\psi_{kn}(\vec r) = \sum_K e^{i(k-K)\cdot\vec r} c_{k-K}$ is no longer a pure plane wave, ψ_{kn} is NOT an eigenstate of momentum. This is reasonable since with the periodic potential turned on the system no longer has translational invariance. However the system does have invariance in translations by B.L. vectors $\vec R$. This is why ψ_{kn} mixes only wavevectors related to $\vec k$ by $\vec k' = \vec k - \vec K$ for $\vec K$ in R.L. Because of this difference, $\vec k$ is called the "crystal momentum" – it is not the true momentum. In collisions, the crystal ~~true~~ momentum of an electron is "conserved" modulus a R.L. vector $\vec K$.

④ Because $\psi_{kn}(\vec{r})$ and $\varepsilon_n(\vec{k})$ are periodic in k-space, the states $\vec{k}$ and $\vec{k}+\vec{K}$ are not physically different. Nevertheless it is sometimes convenient to represent states by a $\vec{k}$ that is not in the 1st BZ. This is most often done when one wants to make closer analogy to free electrons. One therefore has three commonly used schemes for representing band structure. We illustrate these in 1D

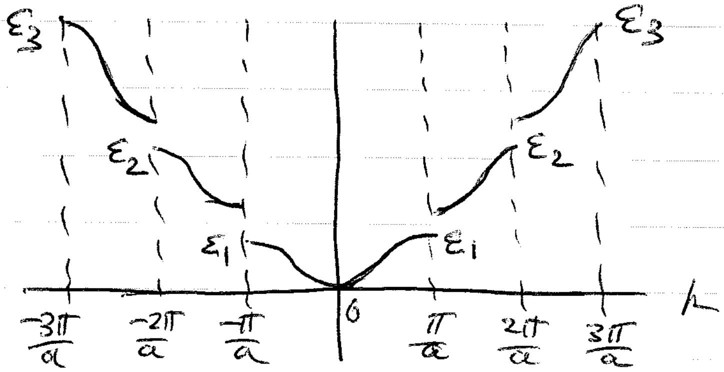
Reduced Zone scheme : restrict $\vec{k}$ to 1st BZ for all energy bands n



Repeated Zone scheme : show all values of $\vec{k}$, with $\varepsilon_n(\vec{k})$ periodic in $\vec{k}$



Extended Zone scheme : show energy bad n ~~#~~ using $\vec{k}$ vectors in n^{th} BZ.



Note: However one represents the bad structure, each band contains only N ~~all~~ distinct allowed values of $\vec{k}$ consistent with the Born-von Karman boundary conditions. ⇒ each band can contain 2N electron states (2 for spin ↑ or ↓)

N = # ~~ions~~ primitive cells in crystal (= # ions if we have a simple BL and not a lattice with a basis)

⑤ If one computes the expectation of velocity in a Bloch ~~std~~ electron state, one finds

$$\vec{v}_n(\vec{k}) = \langle \psi_{nk} | \frac{\hbar}{i} \vec{\nabla} | \psi_{nk} \rangle = \int d^3r \; \psi^*_{nk}(\vec{r}) \, \frac{\hbar}{i} \vec{\nabla} \psi_{nk}(\vec{r})$$

$$= \frac{1}{\hbar} \vec{\nabla}_k \, \varepsilon_n(\vec{k})$$

← looks just like group velocity, but is exact result for expectation value of $\vec{v}$ in eigenstate

↑ gradient with respect to $\vec{k}$

proof follows.

Main point is that the eigenstates of an electron in a periodic potential, although they are not eigenstates of momentum, nevertheless have a well defined, generally finite, value for their average velocity. Therefore, in spite of the interaction of the electron with the periodic potential, the electron in its eigenstate moves with a steady velocity even if no net force (for example from an electric field) is applied to it. This is contrast to Drude's classical picture in which collisions between the electron and the ions served to randomize any initial electron velocity on the collision time scale τ. The reason Drude's picture does not hold is because of the wave nature of the electron and its phase coherent scattering off the ions.

A nonperturbative proof for $\boxed{\vec{V}_{\vec{k}} = \frac{1}{\hbar}\frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}}}$

The Bloch function is known to be of the form [ignore band index]

$$\psi_{\vec{k}}(\vec{x}) = e^{i\vec{k}\cdot\vec{x}}\, u_{\vec{k}}(\vec{x})$$

where $u_{\vec{k}}(\vec{x})$ is periodic in the Bravais lattice and satisfies

$$H_{\vec{k}}\, u_{\vec{k}} = \mathcal{E}_{\vec{k}}\, u_{\vec{k}} \qquad (1)$$

where

$$H_{\vec{k}} = \frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + \vec{k}\right)^2 + U(\vec{x}) \qquad (2)$$

Note that $H_{\vec{k}}$ is Hermitian for any $\vec{k}$.

Suppose $u_{\vec{k}}(\vec{x})$ is normalized as

$$\int_{\Omega} |u_{\vec{k}}|^2 d^3\vec{x} = 1 \qquad (3)$$

where Ω is a primitive cell

From (2) we have

$$\frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} H_{\vec{k}}\, u_{\vec{k}} = \mathcal{E}_{\vec{k}} \frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} u_{\vec{k}} \qquad (4)$$

Taking complex conjugate of eq. (4) yields [using $H_{\vec{k}}^* = H_{-\vec{k}}$]

$$\frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}}\, u_{\vec{k}}^* = \mathcal{E}_{\vec{k}} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} u_{\vec{k}}^* \qquad (5)$$

Adding (4) and (5) and integrating over the primitive cell Ω we get

$$\mathcal{E}_{\vec{k}} \frac{\partial}{\partial \vec{k}} \int_{\Omega} |u_{\vec{k}}|^2 d^3\vec{x} = \int_{\Omega} \left[\frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} H_{\vec{k}}\, u_{\vec{k}} + \frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}}\, u_{\vec{k}}^* \right] d^3\vec{x} \qquad (6)$$

Since $H_{-\vec{k}}$ is Hermitian,

$$\int_{\Omega} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}}\, u^*_{\vec{k}}\, d^3\vec{x} = \left[\int_{\Omega} u_{\vec{k}}\, H_{-\vec{k}} \frac{\partial u^*_{\vec{k}}}{\partial \vec{k}}\, d^3\vec{x} \right]^*$$

$$= \int_{\Omega} u^*_{\vec{k}}\, H_{\vec{k}} \frac{\partial u_{\vec{k}}}{\partial \vec{k}}\, d^3\vec{x} \qquad (7)$$

Thus, (3), (6) and (7) together imply

$$\int_{\Omega} \left[\frac{\partial u^*_{\vec{k}}}{\partial \vec{k}} H_{\vec{k}}\, u_{\vec{k}} + u^*_{\vec{k}}\, H_{\vec{k}} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} \right] d^3\vec{x} = 0 \qquad (8)$$

However, (1) and (3) directly imply

$$\mathcal{E}_{\vec{k}} = \int_{\Omega} u^*_{\vec{k}}\, H_{\vec{k}}\, u_{\vec{k}}\, d^3\vec{x} \qquad (9)$$

Differentiate eq. (7) with respect to $\vec{k}$ and exploit (8) we have

$$\frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}} = \int_{\Omega} u^*_{\vec{k}} \frac{\partial H_{\vec{k}}}{\partial \vec{k}} u_{\vec{k}}\, d^3\vec{x}$$

$$= \frac{\hbar^2}{m} \int_{\Omega} u^*_{\vec{k}} \left(\frac{1}{i} \nabla + \vec{k} \right) u_{\vec{k}}\, d^3\vec{x}$$

or

$$\frac{1}{\hbar} \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}} = \frac{1}{m} \int_{\Omega} \psi^*_{\vec{k}} \left(\frac{\hbar}{i} \nabla \right) \psi_{\vec{k}}\, d^3\vec{x} = \vec{V}_{\vec{k}}$$

Density of states

$g(\varepsilon)$ = # single electron states per unit energy, per unit ~~area~~ volume, at energy ε

$g_n(\varepsilon)$ is density of states in band n

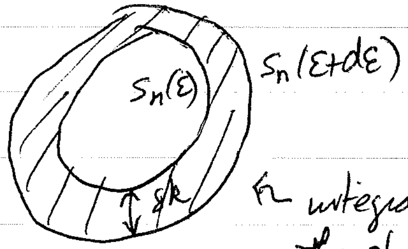
$$g(\varepsilon) = \sum_n g_n(\varepsilon)$$

$$g_n(\varepsilon) = \int_{\vec{k} \text{ in } 1^{st} BZ} \frac{d^3k}{4\pi^3}\, \delta(\varepsilon_n(\vec{k}) - \varepsilon) \quad \leftarrow \text{includes factor of 2 for spin}$$

Alternatively

$$g_n(\varepsilon)\, d\varepsilon = \int \frac{d^3k}{4\pi^3} \times \begin{cases} 1 & \text{if} \quad \varepsilon \le \varepsilon_n(\vec{k}) \le \varepsilon + d\varepsilon \\ 0 & \text{otherwise} \end{cases}$$

Let $S_n(\varepsilon)$ be the surface in $\vec{k}$-space of constant energy ε, and let $\delta k(\vec{k})$ be the perpendicular distance between $S_n(\varepsilon)$ and $S_n(\varepsilon + d\varepsilon)$



← integral computes the shaded volume

$$g_n(\varepsilon)\, d\varepsilon = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3}\, \delta k(\vec{k})$$

surface area
× width
= volume

But we have

$$\mathcal{E} + d\mathcal{E} = \mathcal{E} + |\vec{\nabla}_k \mathcal{E}_n| \, \delta k(\vec{k})$$

since $\vec{\nabla}_k \mathcal{E}_n$ is normal to surface $S_n(\mathcal{E})$

$$\Rightarrow \quad d\mathcal{E} = |\vec{\nabla}_k \mathcal{E}_n| \, \delta k(\vec{k})$$

$$\Rightarrow \quad \delta k(\vec{k}) = \frac{d\mathcal{E}}{|\vec{\nabla}_k \mathcal{E}_n|}$$

$$\boxed{g_n(\mathcal{E}) = \int_{S_n(\mathcal{E})} \frac{dS}{4\pi^3} \frac{1}{|\vec{\nabla}_k \mathcal{E}_n(\vec{k})|}}$$

Since the band energies $\mathcal{E}_n(\vec{k})$ are periodic in $\vec{k}$ on the RL they are bounded above and below. Hence there are $\vec{k}_0$ where $\mathcal{E}_n(\vec{k}_0)$ is a local max or min. At such values $\vec{\nabla}_k \mathcal{E}_n(\vec{k})$ vanishes and the integrand in g_n diverges. One can show that these divergences are integrable in 3D, hence $g_n(\mathcal{E})$ stays finite, but $\frac{dg_n}{d\mathcal{E}}$ will have a divergence. Such singularities are called van Hove singularities

If there is a van Hove singularity on the Fermi surface (ie at a $\vec{k}_0$ such that $\mathcal{E}_n(\vec{k}_0) = \mathcal{E}_F$) this can cause some anomalous looking behavior in quantities that depend on $\frac{dg}{d\mathcal{E}}$.

Energy gaps in the Weak Potential Approximation

Assume U is a weak perturbation

Consider the effect of the periodic potential U on the free electron state with wavevector $\vec{k}$ and energy ε_k^0. The potential will mix in plane waves with wavevectors $\vec{k}-\vec{K}$, for $\vec{K}$ in the R.L., and it will shift the energy eigenvalue from ε_k^0 to a new ε. For weak $U(\vec{r})$, ε is close to ε_k^0.

Schrodingers equation for the Fourier coefficients c_k of the electron eigenstate is

$$(*) \qquad (\varepsilon - \varepsilon^0_{k-K})\, c_{k-K} = \sum_{K' \neq K} U_{K'-K}\, c_{k-K'}$$

The right hand side can be no bigger than $O(U)$ (since by normalization we will assume all $|c_{k-K}| \leq 1$).

$\Rightarrow$ The left hand side can be no bigger than $O(U)$

① Suppose $\vec{k}$ is not near any Bragg plane on an energy scale of $O(U)$, i.e. $|\varepsilon_k^0 - \varepsilon_{k-K}^0| \gg U$ for all $\vec{K}$ in the R.L.
Then it is only $(\varepsilon - \varepsilon_k^0)$ that can be small; $(\varepsilon - \varepsilon^0_{k-K})$ must be bigger than $O(U)$ for all $\vec{K} \neq 0$.

$\Rightarrow$ we must have $c_{k-K} \sim O(U)$ for all $\vec{K} \neq 0$

Since we start with the free electron state at $\vec{k}$, then $c_k \sim O(1)$.

From (*) setting $\vec{K}=0$ we have

$$(\mathcal{E}-\mathcal{E}^0_k)\, c_k = \sum_{K' \neq 0} U_{K'}\, c_{k-K'}$$

but since $U_{K'} \sim O(U)$, and $c_{k-K'} \sim O(U)$,
~~and $c_k \sim O(1)$ the left hand~~
the right hand side is $O(U^2)$.
Since $c_k \sim O(1)$ we must then have

$$(\mathcal{E}-\mathcal{E}^0_k) \sim O(U^2)$$

So when $\vec{k}$ is <u>not</u> near any Bragg plane, the scattered waves mix in an amount $c_{k-K} \sim O(U)$ and the energy shifts $(\mathcal{E}-\mathcal{E}^0_k) \sim O(U^2)$

The periodic potential has relatively little effect on the free electron state if U small.