

Born - von Karman boundary conditions and Fourier transforms for a Bravais lattice

We generalize the idea of periodic (or Born-von Karman boundary conditions to electron states on a Bravais lattice

B.L. vectors $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$
 n_1, n_2, n_3 integers.

For a BL of finite size we have $0 \leq n_i < N_i$
 $N = N_1 N_2 N_3$ is total number of points in the BL.

Total volume of this finite BL is

$$V = \underbrace{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}_{\text{volume of primitive cell}} N$$

We want our electron wavefunctions to be periodic on such a finite BL

$$\psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r})$$

As we saw earlier for free electrons, this imposes a constraint on the wave vectors $\vec{k}$ that can appear in the Fourier transform of $\psi(\vec{r})$.

Write $\psi(\vec{r})$ in terms of its Fourier transform

$$\psi(\vec{r}) = \sum_{\vec{k}} e^{i \vec{k} \cdot \vec{r}} c_{\vec{k}}$$

$\uparrow$ Fourier coefficients for $\psi(\vec{r})$

Then

$$\begin{aligned}\psi(\vec{r} + N_i \vec{a}_i) &= \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{r} + N_i \vec{a}_i)} c_{\vec{k}} \\ &= e^{iN_i \vec{k} \cdot \vec{a}_i} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} c_{\vec{k}} \\ &= e^{iN_i \vec{k} \cdot \vec{a}_i} \psi(\vec{r})\end{aligned}$$

$\Rightarrow$ must have $e^{iN_i \vec{k} \cdot \vec{a}_i} = 1$ for all $\vec{k}$
that appear in Fourier transform of $\psi(\vec{r})$

Write $\vec{k}$ in terms of the primitive vectors of the RL

$$\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3 \quad x_i \text{ are not in general integers}$$

$$\text{Then } e^{iN_i \vec{k} \cdot \vec{a}_i} = e^{iN_i 2\pi x_i} = 1$$

$$\Rightarrow x_i N_i = m_i \text{ integer}$$

$$x_i = \frac{m_i}{N_i}$$

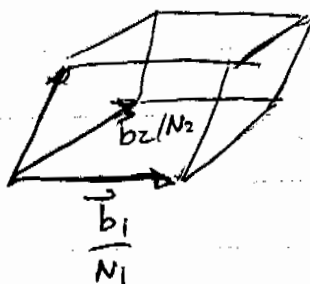
So the allowed wavevectors are

$$\boxed{\vec{k} = \frac{m_1}{N_1} \vec{b}_1 + \frac{m_2}{N_2} \vec{b}_2 + \frac{m_3}{N_3} \vec{b}_3}$$

where m_1, m_2, m_3 are integers.

This is the Born - von Karman boundary conditions

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volume per allowed wavevector in $\vec{k}$ -space is the volume of the parallelepiped formed by the vectors $\frac{\vec{b}_i}{N_i}$

$$= \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1 N_2 N_3} = \frac{(2\pi)^3}{N (\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3))}$$

$$= \frac{(2\pi)^3}{v N} = \frac{(2\pi)^3}{V} \quad \begin{matrix} V = v N \\ = \text{total volume BL} \end{matrix}$$

where $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the primitive cell of the B.L. and $\frac{(2\pi)^3}{v}$ is the volume of the primitive cell of the R.L.

Note: volume per allowed wavevector $\frac{(2\pi)^3}{v}$ is same as we had for free electrons.

Number of allowed $\vec{k}$ values in any primitive cell of the R.L. is

$$\frac{\left[\frac{(2\pi)^3}{v} \right]}{\left[\frac{(2\pi)^3}{v N} \right]} = N \quad \text{number of wvs in BL}$$

Number of allowed $\vec{k}$ values in any primitive cell of the R.L., for example the 1st BZ, is N

We now define the Fourier transform and its inverse that is consistent with the allowed wavevectors $\vec{k}$ of the Born-von Karman boundary conditions

$$\text{IF } \boxed{\psi(\vec{r}) \equiv \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} c_{\vec{k}}}$$

↑ sum over all $\vec{k}$ that obey Born-von Karman boundary conditions

then the inverse Fourier transform is

$$\boxed{c_{\vec{k}} = \frac{1}{V} \int_V d^3r e^{-i\vec{k} \cdot \vec{r}} \psi(\vec{r})}$$

Proof:

$$\frac{1}{V} \int_V d^3r e^{-i\vec{k} \cdot \vec{r}} \psi(\vec{r}) = \sum_{\vec{k}'} c_{\vec{k}'} \frac{1}{V} \int_V d^3r e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}}$$

since both $\vec{k}$ and $\vec{k}'$ satisfy Born-von Karman boundary conditions, we can write

$$\vec{k}' - \vec{k} = \frac{m_1}{N_1} \vec{b}_1 + \frac{m_2}{N_2} \vec{b}_2 + \frac{m_3}{N_3} \vec{b}_3$$

with m_1, m_2, m_3 integers.

Also we can write

$$\vec{r} = x_1 \vec{a}_1 + x_2 \vec{a}_2 + x_3 \vec{a}_3 \quad 0 \leq x_i \leq N_i$$

since $\vec{r}$ is not in general a BL vector, the x_i are any real values (not necessarily integers)

Now

$$\int_V d^3r = v \int_0^{N_1} dx_1 \int_0^{N_2} dx_2 \int_0^{N_3} dx_3 \quad \text{since } V = v N$$

$v = \text{vol primitive cell}$

and

$$(\vec{k}' - \vec{k}) \cdot \vec{r} = 2\pi \left(\frac{m_1}{N_1} x_1 + \frac{m_2}{N_2} x_2 + \frac{m_3}{N_3} x_3 \right)$$

$$\text{So } \frac{1}{V} \int d^3r e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \frac{v}{V} \prod_{i=1}^3 \left[\int_0^{N_i} dx_i e^{2\pi i \frac{m_i}{N_i} x_i} \right]$$

do for example the x_1 integral

$$\int_0^{N_1} dx_1 e^{2\pi i \frac{m_1}{N_1} x_1} = \frac{e^{2\pi i m_1} - 1}{2\pi i \frac{m_1}{N_1}}$$

$$= \begin{cases} 0 & m_1 \neq 0 \text{ since } m_1 \text{ integer} \\ N_1 & m_1 = 0 \text{ (take limit } m_1 \rightarrow 0) \end{cases}$$

So

$$\begin{aligned} \frac{1}{V} \int d^3r e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} &= \frac{v N_1 N_2 N_3}{V} \delta_{\vec{k}', \vec{k}} \\ &= \delta_{\vec{k}', \vec{k}} \end{aligned}$$

$\uparrow$ zero unless $\vec{k} = \vec{k}'$

$$\text{So } \sum_{\vec{k}'} c_{\vec{k}'} \frac{1}{V} \int d^3r e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \sum_{\vec{k}'} c_{\vec{k}'} \delta_{\vec{k}', \vec{k}} = c_{\vec{k}}$$

Bloch's Theorem

Now we prove Bloch's Theorem by substituting the Fourier transform in the Schrödinger Equ.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + U(\vec{r}) \psi = \epsilon \psi$$

where $U(\vec{r})$ is the ionic potential
and ϵ is the eigenvalue = electron energy

Substitute in the Fourier transforms

$$\psi(\vec{r}) = \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} c_{\vec{k}}$$

$$U(\vec{r}) = \sum_{\vec{k}'} e^{i\vec{k}' \cdot \vec{r}} U_{\vec{k}'}$$

to get

$$\begin{aligned} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \left[\frac{\hbar^2 k^2}{2m} c_{\vec{k}} + \sum_{\vec{k}''} \sum_{\vec{k}'} e^{i(\vec{k}'' + \vec{k}') \cdot \vec{r}} U_{\vec{k}'} c_{\vec{k}''} \right] \\ = \epsilon \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} c_{\vec{k}} \end{aligned}$$

Now ~~the~~ transform summation variable in the 2nd term to $\vec{k} = \vec{k}'' + \vec{k}'$ so $\vec{k}'' = \vec{k} - \vec{k}'$

$$\Rightarrow \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) c_{\vec{k}} + \sum_{\vec{k}'} U_{\vec{k}'} c_{\vec{k} - \vec{k}'} \right] = 0$$

$$\text{write } \epsilon_k^0 = \frac{\hbar^2 k^2}{2m}$$

$$\Rightarrow \epsilon_k^0 c_k + \sum_{k'} U_{k'} c_{k-k'} = \epsilon c_k$$

Now the ionic potential $U(\vec{r})$ is periodic on the Bravais lattice, i.e.

$$U(\vec{r} + \vec{R}) = U(\vec{r}) \text{ for all } \vec{R} \text{ in BL}$$

$\Rightarrow$ the only wave vectors $\vec{k}$ that appear in its Fourier transform are the wave vectors $\{\vec{K}\}$ of the reciprocal lattice.

$$U(\vec{r} + \vec{R}) = \sum_{\vec{k}} e^{i\vec{k} \cdot (\vec{r} + \vec{R})} U_{\vec{k}} = \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{R}} e^{i\vec{k} \cdot \vec{r}} U_{\vec{k}}$$

$$U(\vec{r}) = \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} U_{\vec{k}}$$

these can be equal only if $e^{i\vec{k} \cdot \vec{R}} = 1$ for any $\vec{R}$ in BL
 $\Rightarrow \vec{k}$ must be a $\vec{K}$ in the R.L.

So the sum on $\vec{k}'$ in above becomes a sum on $\vec{K}$

$$\Rightarrow \epsilon_k^0 c_k + \sum_{\vec{K}} U_{\vec{K}} c_{k-\vec{K}} = \epsilon c_k$$

note: $U_{\vec{K}} = \frac{1}{V} \int_V d^3r e^{-i\vec{K} \cdot \vec{r}} U(\vec{r})$
 $= \frac{1}{v} \int_C d^3r e^{-i\vec{K} \cdot \vec{r}} U(\vec{r})$

where C is any primitive cell of the B.L. This follows from fact that $U(\vec{r})$ is periodic on the B.L.

Also, we can assume $U_{K=0} = 0$ due to charge neutrality, since

$$U(\vec{r}) = \int d^3r' \frac{\rho(r')}{|\vec{r} - \vec{r}'|}$$

$\rho(\vec{r})$ is total charge density from all ions and electrons

$$U_{K=0} = \frac{1}{V} \int d^3r' \rho(r') \int d^3r \frac{1}{|\vec{r} - \vec{r}'|}$$

independent of $\vec{r}'$ if
using periodic boundary conditions
if charge neutral

$$\propto \int d^3r' \rho(\vec{r}') = 0$$

Thus we see that the periodic ionic potential $U(\vec{r})$ only couples wavevectors $\vec{k}$ to the wave vectors $\vec{k}' = \vec{k} - \vec{K}$, with $\vec{K}$ in the RL. These $\vec{k}'$ are just the wave vectors one gets from scattering of the electron off the Bragg planes.

$$\epsilon_k^0 c_k + \sum_{k'} U_{k'} c_{k-k'} = \epsilon c_k$$

apply the above to the wave-vector $\vec{k}-\vec{k}'$

$$\epsilon_{k-k}^0 c_{k-k} + \sum_{k'} U_{k'} c_{k-k-k'} = \epsilon c_{k-k}$$

or relabeling the summation vector in the 2nd term
 $\vec{k}+\vec{k}' \rightarrow \vec{k}'$

$$\epsilon_{k-k}^0 c_{k-k} + \sum_{k'} U_{k'-k} c_{k-k'} = \epsilon c_{k-k}$$

As $\vec{k}$ in the above varies through the wavevectors in the R.L. we get ~~for~~ a set of linear equations for the Fourier coefficients $\{c_{k-k}\}$, $\vec{k}$ in R.L.

Above can be viewed as a matrix eigenvalue problem for the ^{eigen}-vector $\{c_{k-k}\}$ (viewing k as the index of the vector, and ϵ as the eigenvalue).

Solution gives

$$\psi(\vec{r}) = \sum_k e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} c_{k-k} = e^{i\vec{k} \cdot \vec{r}} \sum_k e^{-i\vec{k}' \cdot \vec{r}} c_{k-k}$$

Define $u_k(\vec{r}) \equiv \sum_k e^{i\vec{k} \cdot \vec{r}} c_{k-k}$

then eigenstates have the form

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$$

where $u_k(\vec{r}+\vec{R}) = u_k(\vec{r})$ i.e. $u(\vec{r})$ is periodic on the B.L.

This is Bloch's theorem

If we label the R.L. wavevectors as $\vec{K}_i$, the Schrodinger Eqn takes the matrix form

$$\begin{pmatrix} E_k^0 & U_{K_1} & U_{K_2} & U_{K_3} & \dots \\ U_{-K_1} & E_{k-K_1}^0 & U_{K_2-K_1} & U_{K_3-K_1} & \\ U_{-K_2} & U_{K_1-K_2} & E_{k-K_2}^0 & U_{K_3-K_2} & \\ U_{-K_3} & U_{K_1-K_3} & U_{K_2-K_3} & E_{k-K_3}^0 & \\ \vdots & & & & \ddots \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-K_1} \\ c_{k-K_2} \\ c_{k-K_3} \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_k \\ c_{k-K_1} \\ c_{k-K_2} \\ c_{k-K_3} \\ \vdots \end{pmatrix}$$

Note: Since $U(\vec{r})$ is a real function,

$$U_{\vec{k}}^* = \frac{1}{V} \int_V d^3r e^{i\vec{k}\cdot\vec{r}} U(\vec{r}) = U_{-\vec{k}}$$

Hence the above matrix is Hermitian as it should be to guarantee it is diagonalizable with real eigenvalues

Also: If the ~~crystal~~ ^{crystal} has inversion symmetry, i.e. $U(\vec{r}) = U(-\vec{r})$, then $U_{\vec{k}} = \frac{1}{V} \int_V d^3r e^{-i\vec{k}\cdot\vec{r}} U(\vec{r}) = \frac{1}{V} \int_V d^3r e^{-i\vec{k}\cdot\vec{r}} U(-\vec{r})$
 $= \frac{1}{V} \int_V d^3r e^{i\vec{k}\cdot\vec{r}} U(\vec{r}) = U_{-\vec{k}} = U_{\vec{k}}^*$ is real

Note: If we let $\vec{k} \rightarrow \vec{k} + \vec{k}_0$ in the above matrix equation, the only result is a permutation of the rows and columns since the set $\{\vec{k} + \vec{k}_0\} = \{\vec{k} + \vec{k}_0 + \vec{k}\}$ since $\vec{k}_0 + \vec{k}$ is vector in the R.L. if both $\vec{k}_0$ and $\vec{k}$ are.

Hence the eigenvectors and eigenvalues are periodic functions of wavevector with periodicity given by the R.L. That is, if

$$\psi_{k,n}(\vec{r}) = \sum_{\vec{k}} e^{i(\vec{k} - \vec{k}_0) \cdot \vec{r}} c_{\vec{k} - \vec{k}_0} \quad \text{with eigenvalue } E_n(\vec{k})$$

is the n^{th} eigenvector and eigenvalue of the matrix then $\psi_{k,n}$ and

$$\begin{aligned} \psi_{\vec{k} + \vec{k}_0, n}(\vec{r}) &= \psi_{\vec{k}, n}(\vec{r}) \\ E_n(\vec{k} + \vec{k}_0) &= E_n(\vec{k}) \end{aligned} \quad \left. \begin{array}{l} \text{periodic in} \\ \vec{k} \rightarrow \vec{k} + \vec{k}_0 \\ \text{for any } \vec{k}_0 \text{ in R.L.} \end{array} \right\}$$

Therefore the unique states are specified by a wave vector $\vec{q}$ in the 1st BZ (called the "crystal momentum") and the discrete "band index" n that labels the different eigenvalues of the above matrix for a given value of $\vec{q}$.

(all other $\vec{k}$ values can always be written as $\vec{k} = \vec{q} + \vec{R}$ where $\vec{q}$ is in 1st BZ and $\vec{R}$ is in R.L.)

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 and let $V \rightarrow 0$, 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 and 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 ~~the~~ ^{a unique} R.L. vector closest to $\vec{k}$ and $\vec{q}$ 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.

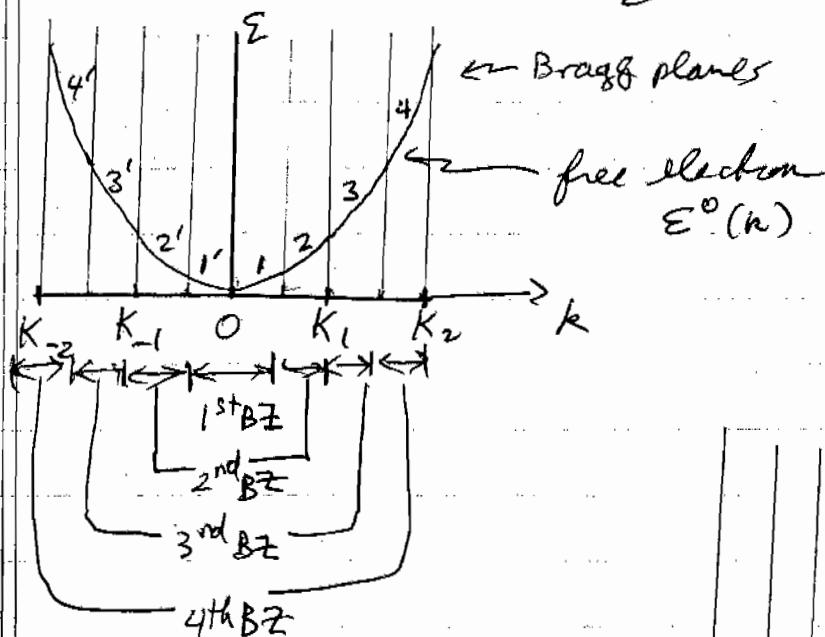
Then for any $\vec{k} = \vec{g} + \vec{K}$ in the n^{th} Brillouin Zone

write $E^0(\vec{k}) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (\vec{g} + \vec{K})^2}{2m} = E_n(\vec{g})$

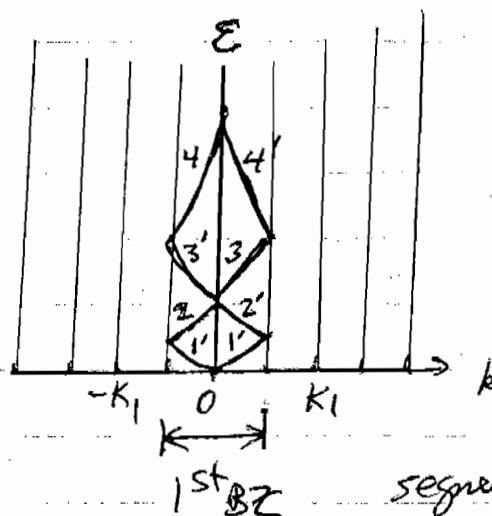
energy at crystal momentum $\vec{g}$
in band index "n"

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 $K_n = \left(\frac{2\pi}{a}\right)n$, $n=0, \pm 1, \pm 2, \dots$
Bragg planes at $k = \frac{K_n}{2} = \left(\frac{\pi}{a}\right)n$



can translate the section of curve in n^{th} BZ back into 1st BZ by subtracting appropriate K from k



representing free electron states by $\vec{g}$ in 1st BZ.

Integers label corresponding sections of the curves in the two equivalent representations

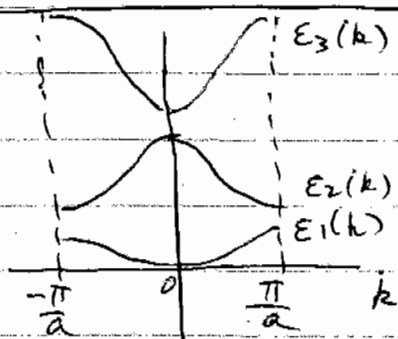
segments of curve labeled n or n' came from the n^{th} BZ of free electrons

Comments.

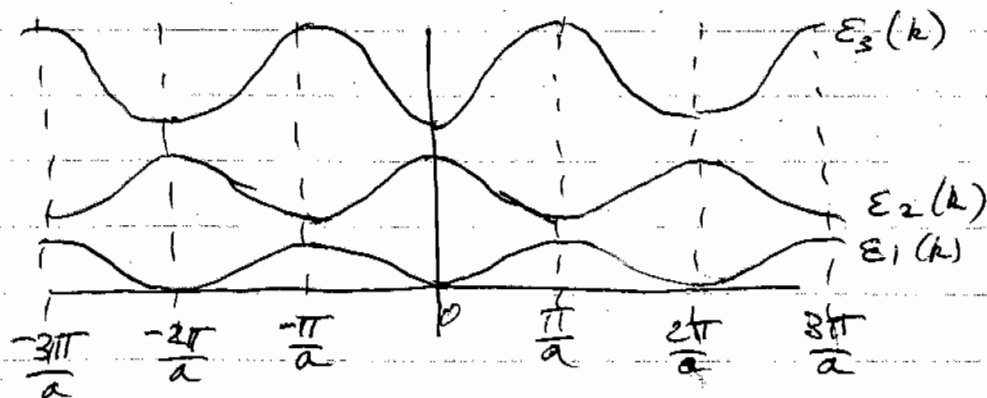
- ① Because $\vec{k}$ enters the matrix equation as a parameter via the terms $E_{\vec{k}+\vec{K}}$, we expect that the eigenvalues $E_n(\vec{k})$ are smooth continuous functions of $\vec{k}$.
- ② Because $E_n(\vec{k})$ is periodic in $\vec{k}$, $E_n(\vec{k}+\vec{K}) = E_n(\vec{k})$, we ~~expect~~ ^{must have} that $E_n(\vec{k})$ has a maximum and a minimum and varies continuously between them. This is why $E_n(\vec{k})$ is referred to as an energy band.
- ③ Since $\psi_{kn}(\vec{r}) = \sum_{\vec{K}} e^{i(\vec{k}+\vec{K}) \cdot \vec{r}} c_{\vec{k}+\vec{K}}$ 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 $\vec{K}$. 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 momentum of an electron is ~~only~~ "conserved" modulo a R.L. vector $\vec{K}$.

④ Because $\psi_{kn}(\vec{r})$ and $E_n(\vec{k})$ are periodic in $\vec{k}$ -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

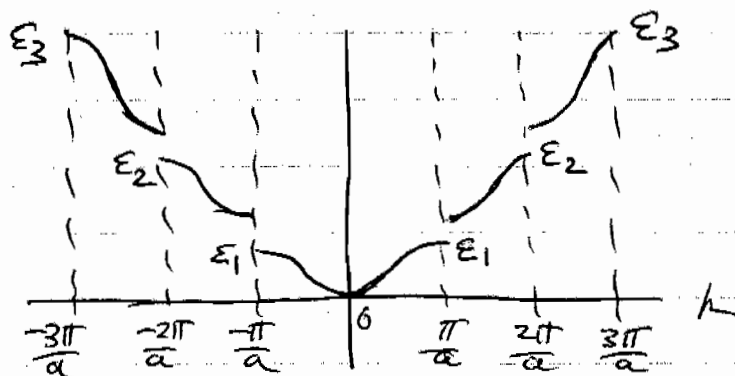
Reduced Zone scheme : restrict $\vec{k}$ to 1st BZ for all energy bands n



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



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



Note: However one represents the band structure,
 each band contains only N ^{distinct} ~~also~~ allowed
 values of $\vec{k}$ consistent with the Born-von Karman
 boundary conditions. $\Rightarrow$ each band can contain
 $2N$ electron states (2 for spin $\uparrow$ or $\downarrow$)
 $N = \#$ ^{primitive cells} ~~atoms~~ in crystal (= $\#$ ions if we have a simple
 BC and not a lattice with a basis)

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

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

$$= \frac{1}{\hbar} \vec{\nabla}_{\vec{k}} E_n(\vec{k}) \quad \leftarrow \text{looks just like group velocity, but is exact result}$$

$\uparrow$ gradient with respect to $\vec{k}$ for expectation value of $\vec{v}$ in eigenstate

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

$$\vec{V}_k = \frac{1}{\hbar} \frac{\partial \epsilon_k}{\partial \vec{k}}$$

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

$$H_{\vec{k}} u_{\vec{k}} = \epsilon_{\vec{k}} u_{\vec{k}} \quad (1)$$

where

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

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

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

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

where Ω is a primitive cell

From (2) we have $\frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} H_{\vec{k}} u_{\vec{k}} = \epsilon_{\vec{k}} \frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} u_{\vec{k}} \quad (4)$

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

$$\frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}} u_{\vec{k}}^* = \epsilon_{\vec{k}} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} u_{\vec{k}}^* \quad (5)$$

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

$$\epsilon_{\vec{k}} \frac{\partial}{\partial \vec{k}} \int_{\Omega} |u_{\vec{k}}|^2 d^3 \vec{x} = \int_{\Omega} \left[\frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} H_{\vec{k}} u_{\vec{k}} + \frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}} u_{\vec{k}}^* \right] d^3 \vec{x}$$

(6)

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

$$\begin{aligned} \int_{\Omega} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{\vec{k}} u_{\vec{k}}^* d^3\vec{x} &= \left[\int_{\Omega} u_{\vec{k}} H_{\vec{k}} \frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} d^3\vec{x} \right]^* \\ &= \int_{\Omega} u_{\vec{k}}^* H_{\vec{k}} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} d^3\vec{x} \end{aligned} \quad (7)$$

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

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

However, (1) and (3) directly imply

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

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

$$\begin{aligned} \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}} &= \int_{\Omega} u_{\vec{k}}^* \frac{\partial H_{\vec{k}}}{\partial \vec{k}} u_{\vec{k}} d^3\vec{x} \\ &= \frac{\hbar^2}{m} \int_{\Omega} u_{\vec{k}}^* \left(\frac{1}{i} \nabla + \vec{k} \right) u_{\vec{k}} d^3\vec{x} \end{aligned}$$

or

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