

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

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 2<sup>nd</sup> 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~~ get a set of linear equations for the Fourier coefficients  $\{c_{k-k}\}$ ,  $\vec{k}$  in RL.

Above can be viewed as a matrix eigenvalue problem for the <sup>eigen-</sup>vector  $\{c_{k-k}\}$  (viewing  $\vec{k}$  as the index of the vector, and  $\epsilon$  as the eigenvalue).

Solution gives

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

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

Then eigenstates have the form

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

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

This is Bloch's theorem

If we label the R.L. wavevectors as  $\vec{K}_2$ , the Schrödinger Eqn takes the matrix form

$$\begin{pmatrix} \epsilon_{\vec{k}}^0 & U_{\vec{k}_1} & U_{\vec{k}_2} & U_{\vec{k}_3} & \dots \\ U_{-\vec{k}_1} & \epsilon_{\vec{k}-\vec{k}_1}^0 & U_{\vec{k}_2-\vec{k}_1} & U_{\vec{k}_3-\vec{k}_1} & \\ U_{-\vec{k}_2} & U_{\vec{k}_1-\vec{k}_2} & \epsilon_{\vec{k}-\vec{k}_2}^0 & U_{\vec{k}_3-\vec{k}_2} & \\ U_{-\vec{k}_3} & U_{\vec{k}_1-\vec{k}_3} & U_{\vec{k}_2-\vec{k}_3} & \epsilon_{\vec{k}-\vec{k}_3}^0 & \\ \vdots & & & & \ddots \end{pmatrix} \begin{pmatrix} c_{\vec{k}} \\ c_{\vec{k}-\vec{k}_1} \\ c_{\vec{k}-\vec{k}_2} \\ c_{\vec{k}-\vec{k}_3} \\ \vdots \end{pmatrix} = \epsilon \begin{pmatrix} c_{\vec{k}} \\ c_{\vec{k}-\vec{k}_1} \\ c_{\vec{k}-\vec{k}_2} \\ c_{\vec{k}-\vec{k}_3} \\ \vdots \end{pmatrix}$$

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~~ <sup>crystal</sup> has inversion symmetry, i.e.  $U(\vec{r}) = U(-\vec{r})$ , then

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

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

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

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

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

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

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

$$\propto \int d^3r' g(\vec{r}') = 0 \quad \text{if charge neutral}$$

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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.

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 eigen vectors and eigen values are periodic functions of wave vector 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  $n^{\text{th}}$  eigen vector and eigen value of the matrix then  $\psi_{k,n}$  and

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

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

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

Comment - For free electrons the energy eigenstates are specified ~~by~~ 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~~ <sup>a unique</sup> 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~~ <sup>closer</sup> 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

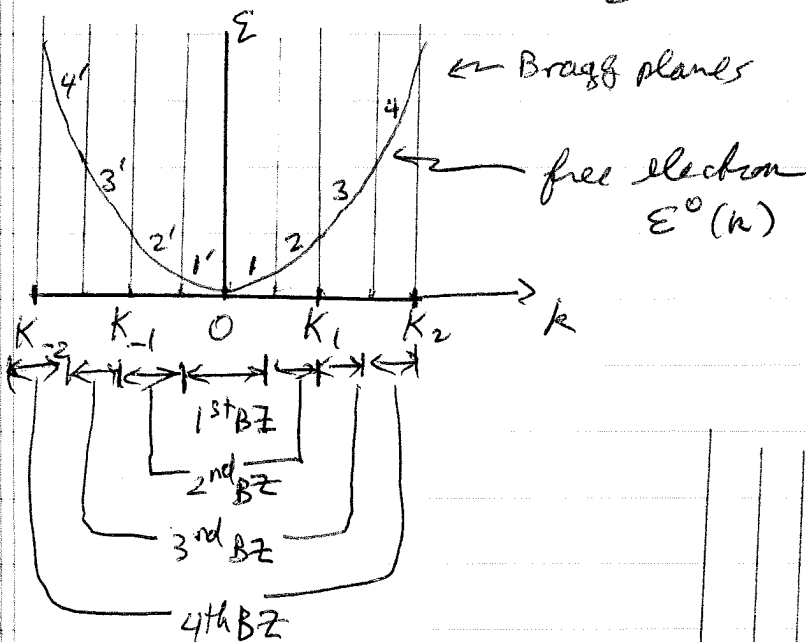
write 
$$E^0(\vec{k}) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (\vec{g} + \vec{K})^2}{2m} = E_n(\vec{g})$$

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

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

Ex: in a 1D B.L. of lattice constant  $a$   
R.L. vectors are  $k_n = \left(\frac{2\pi}{a}\right)n$ ,  $n = 0, \pm 1, \pm 2, \dots$

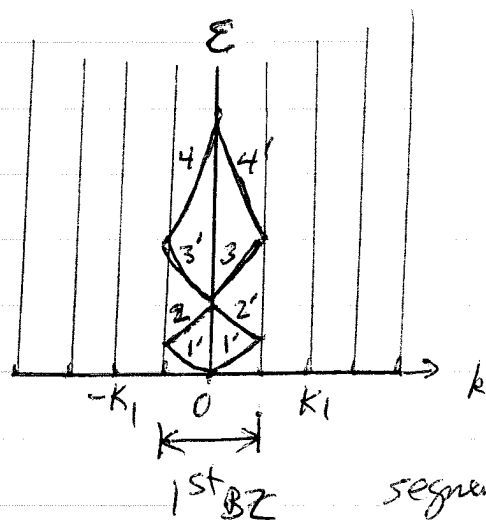
Bragg planes at  $k = \frac{K_n}{2} = \left(\frac{\pi}{a}\right)n$



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 correspondingly 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:

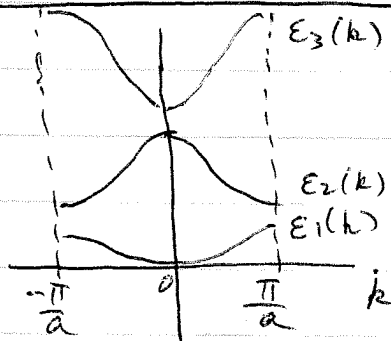
① Because  $\vec{k}$  enters the matrix equation as a parameter via the terms  $E_{\vec{k}+\vec{K}}$ , we expect that the eigenvalues  $E_n(\vec{k})$  are smooth continuous functions of  $\vec{k}$ .

② Because  $E_n(\vec{k})$  is periodic in  $\vec{k}$ ,  $E_n(\vec{k}+\vec{K}) = E_n(\vec{k})$ , we ~~repeat~~ 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.

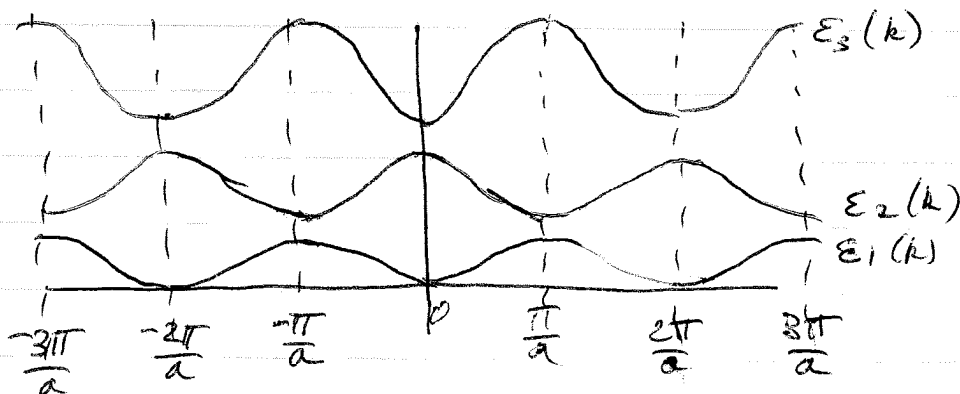
③ Since  $\psi_{kn}(\vec{r}) = \sum_{\vec{k}} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} c_{\vec{k}-\vec{k}'}$  is no longer a pure plane wave,  $\psi_{kn}$  is NOT an eigenstate of momentum. This is reasonable since with the periodic potential turned on the system no longer has translational invariance. However the system does have invariance in translations by B.L. vectors  $\vec{K}$ . This is why  $\psi_{kn}$  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 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  $n$

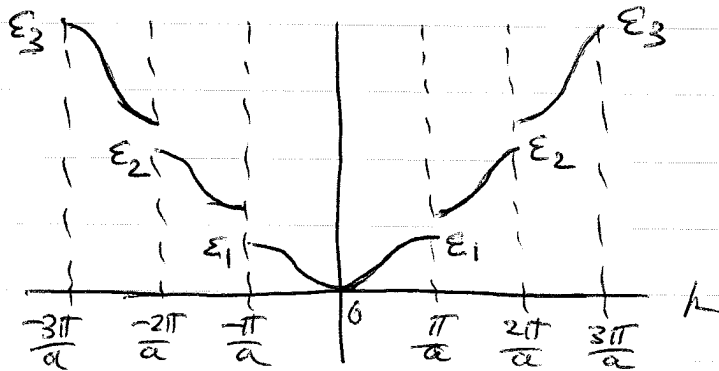


Repeated Zone scheme: show all values of  $\vec{k}$ , with  $E_n(\vec{k})$  periodic in  $\vec{k}$





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



Note: However one represents the band structure,  
 each band contains only  $N$  <sup>distinct</sup> ~~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  $\downarrow$ )  
 $N = \#$  <sup>primitive cells</sup> ~~cells~~ 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

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

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

$\uparrow$  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  $\tau$ . The reason Drude's picture does not hold is because of the wave nature of the electron and its <sup>phase</sup> coherent scattering off the ions.

A nonperturbative proof for

$$\vec{V}_{\vec{k}} = \frac{1}{\hbar} \frac{\partial \epsilon_{\vec{k}}}{\partial \vec{k}}$$

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

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

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  $\Omega$  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  $\Omega$  we get

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

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

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