

"When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal... By straight Fourier analysis I found to my delight that the wave function differed from the plane wave of free electrons only by a periodic modulation." - F. Bloch

## Band Theory I

(2)

The free electron model of metals gives us an understanding — qualitative, and in some cases, quantitative — of the bulk modulus, heat capacity, thermal and electrical conductivity, etc. of metals. Not only macroscopic properties, but also the properties of metallic nanostructures, are explained. However, many large questions remain unexplained, such as the distinction between metals, insulators, and semiconductors, positive values of the Hall coefficient, and the relation of

conduction electrons to the valence electrons of free atoms. (3)

Electron waves, like X-rays, are diffracted by the periodic potential of a lattice of ions.

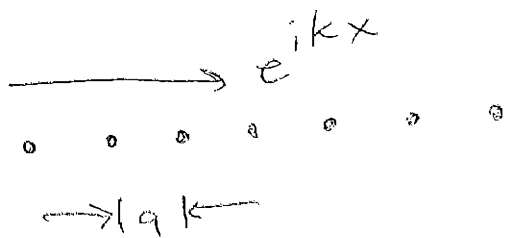
As a result, for certain bands of energy, propagating electron waves exist, while other energies are forbidden (band gaps), and still other specific energy values correspond to standing waves, rather than

propagating waves. By properly including electron diffraction, we can resolve the questions

left unanswered by the 4  
free electron model.

## Origin of the energy gap

Consider an electron of wave number  $k$  propagating through a 1D lattice of lattice constant  $a$ :



The condition for scattering is

$$k' = k + G, \quad G = \frac{2\pi n}{a}, \quad n \in \mathbb{Z}$$

i.e.,  $G$  is a reciprocal lattice vector. Thus an electron of

wave number  $k = \frac{\pi}{a}$

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will be scattered to  $k' = -\frac{\pi}{a}$   
and vice versa. Since these

two states are degenerate  
in energy, the lattice potential  
will break this degeneracy,

so the true eigenstates  
will be linear combinations

of  $e^{\pm i\frac{\pi x}{a}}$ . Since the

electron is continuously scattered  
back and forth between  $k = \pm \frac{\pi}{a}$ ,

it is physically reasonable

to assume the eigenstates

will be not plane waves, but

standing waves.

$$\psi_+(x) = e^{i\frac{\pi x}{a}} + e^{-i\frac{\pi x}{a}} = 2\cos\frac{\pi x}{a}$$

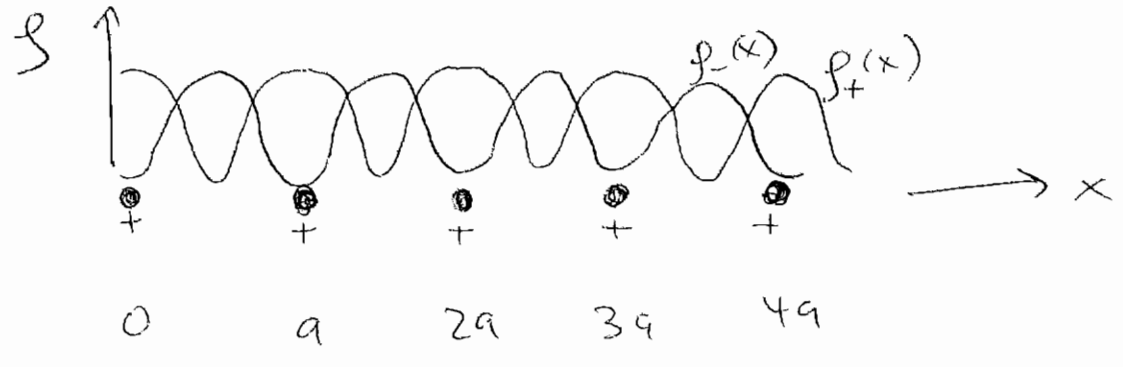
$$\psi_-(x) = e^{i\frac{\pi x}{a}} - e^{-i\frac{\pi x}{a}} = 2i\sin\frac{\pi x}{a}$$

The electron charge density in the two states is

$$\rho_{\pm}(x) = |\psi_{\pm}(x)|^2$$

$$\rho_+(x) \propto \cos^2\frac{\pi x}{a}$$

$$\rho_-(x) \propto \sin^2\frac{\pi x}{a}$$



You see that the electron density is large near the ions in the state  $\psi_+(x)$ , and small in between, while the opposite is true of  $\psi_-(x)$ .

Since electrons are negatively charged, the standing wave  $\psi_+(x)$ , which concentrates electrons near the positive ions, will be lowered in energy compared to a plane wave (with uniform charge density), while  $\psi_-(x)$  will be raised in energy. The

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potential) an electron feels  
as it propagates through the  
lattice is periodic:

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$$U(x) = \sum_G U_G e^{iGx}$$

$$= U_0 + U_1 \cos \frac{2\pi x}{a} + U_2 \cos \frac{4\pi x}{a}$$

+ ...

In general, the Fourier components  
of  $U$  drop off rapidly, so  
 $U_1$  will give the dominant  
effect. Normalizing  $\psi_{\pm}(x)$

to a crystal of length  $L = Na$ ,

$$\text{one has } \psi_{\pm}(x) = \sqrt{\frac{2}{L}} \left( e^{i\pi x/a} \pm e^{-i\pi x/a} \right).$$



The energy shift of the  $\lfloor 9$   
state  $\psi_{\pm}(x)$  is

$$\begin{aligned}\Delta E_{\pm} &= \int_0^L dx U(x) |\psi_{\pm}(x)|^2 \\ &\approx \int_0^L dx U_1 \cos \frac{2\pi x}{a} |\psi_{\pm}(x)|^2\end{aligned}$$

The energy gap is

$$\begin{aligned}E_g &= \Delta E_- - \Delta E_+ \\ &= \frac{2}{L} \int_0^L dx U_1 \cos \frac{2\pi x}{a} \left( \sin^2 \frac{2\pi x}{a} - \cos^2 \frac{2\pi x}{a} \right) \\ &= -\frac{2}{L} \int_0^L dx U_1 \cos^2 \frac{2\pi x}{a} = -U_1\end{aligned}$$

We expect  $U_1 < 0$ ,  
since the potential should  
be a minimum at  $x = 0, \pm a, \pm 2a, \dots$

Thus  $E_g = |U_1|$ . Qualitatively,  
we now understand why an  
energy gap opens at the  
Brillouin zone boundary,  $k = \pm \frac{\pi}{a}$ .

Let us now treat the  
problem more rigorously.

Schrödinger equation for an  
electron in a periodic potential

An electron propagating through a crystal will see a potential  $U(\vec{x})$  due to the ions and the other electrons. This potential will have the periodicity of the Bravais lattice

$$U(\vec{x} + \vec{R}) = U(\vec{x}) \quad \forall \vec{R} \in BL.$$

$$\Rightarrow U(\vec{x}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G} \cdot \vec{x}}$$

The Schrödinger equation for the electron is

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{x}) \right] \psi(\vec{x}) = E \psi(\vec{x})$$

$\psi(\vec{x})$  may be expressed as a Fourier

Series over all wavevectors  
satisfying the appropriate boundary  
conditions:

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$$\Psi(\vec{x}) = \sum_{\vec{k}} C(\vec{k}) e^{i\vec{k} \cdot \vec{x}}$$

[note that  $\vec{k}$  is not in general a reciprocal  
lattice vector.]

Substituting  $\Psi(\vec{x})$  into the Schrödinger  
equation, one obtains

$$\frac{\hbar^2}{2m} \sum_{\vec{k}} k^2 C(\vec{k}) e^{i\vec{k} \cdot \vec{x}} + \sum_{\vec{G}} \sum_{\vec{k}} U_{\vec{G}} C(\vec{k}) e^{i(\vec{k} + \vec{G}) \cdot \vec{x}} = E \sum_{\vec{k}} C(\vec{k}) e^{i\vec{k} \cdot \vec{x}}$$

Each Fourier component must have the  
same coefficient on both sides  
of the equation, thus:

$$\left(\frac{\hbar^2 k^2}{2m} - \varepsilon\right) C(\mathbf{k}) + \sum_{\vec{G}} U_{\vec{G}} C(\mathbf{k} - \vec{G}) = 0$$

"central equation" = Fourier transform of Schrödinger equation

From the central equation, we see that the electronic eigenstates are superpositions of several different momentum states, separated by reciprocal lattice vectors:

$$\psi_{\mathbf{k}}(\vec{x}) = \sum_{\vec{G}} C(\mathbf{k} - \vec{G}) e^{i(\mathbf{k} - \vec{G}) \cdot \vec{x}}$$

This reflects the fact that electron waves are diffracted by the lattice. If we inject an electron of definite momentum  $\vec{k}$  into the crystal, it will be

scattered to  $\vec{k} + \vec{G}$   $\forall \vec{G} \in RL$ . (14)

The eigenstates are thus superpositions of several plane waves, and no longer have a well defined momentum. That momentum is no longer a good quantum number reflects the breaking of translational invariance by the crystal potential.

### Bloch's theorem

$$\Psi_{\vec{k}}(\vec{x}) = e^{i\vec{k} \cdot \vec{x}} \phi_{\vec{k}}(\vec{x}),$$

where  $\phi_{\vec{k}}(\vec{x} + \vec{R}) = \phi_{\vec{k}}(\vec{x}) \quad \forall \vec{R} \in BL$

Proof:

$$\begin{aligned}\psi_{\vec{k}}(\vec{x}) &= e^{i\vec{k}\cdot\vec{x}} \sum_{\vec{G}} c(\vec{k}-\vec{G}) e^{-i\vec{G}\cdot\vec{x}} \\ &\equiv e^{i\vec{k}\cdot\vec{x}} \phi_{\vec{k}}(\vec{x})\end{aligned}$$

$$\begin{aligned}\phi_{\vec{k}}(\vec{x}+\vec{R}) &= \left( \sum_{\vec{G}} c(\vec{k}-\vec{G}) e^{-i\vec{G}\cdot\vec{x}} \right) e^{-i\vec{G}\cdot\vec{R}} \\ &= \phi_{\vec{k}}(\vec{x}) \quad \text{since } e^{i\vec{G}\cdot\vec{R}} = 1\end{aligned}$$

Q.E.D.

Thus, the wavefunction indeed has the form of a plane wave modulated by a periodic function.

### Crystal momentum

What is the significance of the

wavevector  $\vec{k}$  used to label  
the Bloch wavefunctions?

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- Under a lattice translation

$\vec{x} \rightarrow \vec{x} + \vec{R}$ , one has

$$\psi_{\vec{k}}(\vec{x} + \vec{R}) = e^{i\vec{k} \cdot (\vec{R} + \vec{x})} \phi_{\vec{k}}(\vec{x} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{\vec{k}}(\vec{x}).$$

Thus  $e^{i\vec{k} \cdot \vec{R}}$  is still the  
eigenvalue of the translation operator

$$T(\vec{R}) : T(\vec{R}) \psi_{\vec{k}}(\vec{x}) = \psi_{\vec{k}}(\vec{x} + \vec{R}) \\ = e^{i\vec{k} \cdot \vec{R}} \psi_{\vec{k}}(\vec{x}).$$

However, only translations by a  
Bravais lattice vector represent  
symmetries of the system.

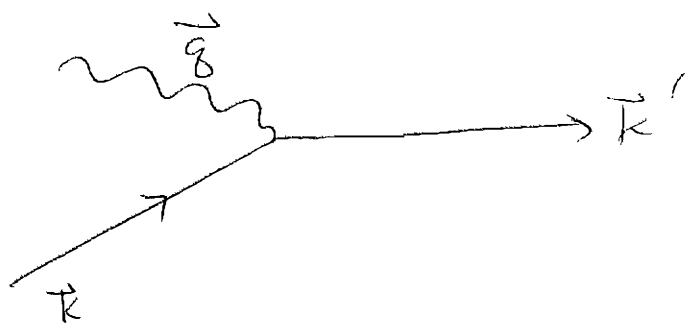
- Since  $\vec{k}$  is only defined modulo  
a reciprocal lattice vector, it is



conventional to restrict  $\vec{k}$  to the first Brillouin zone, as we did for phonons.

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The conservation law for scattering of electrons from phonons is:



$$\vec{k} + \vec{q} = \vec{k}' + \vec{G}$$

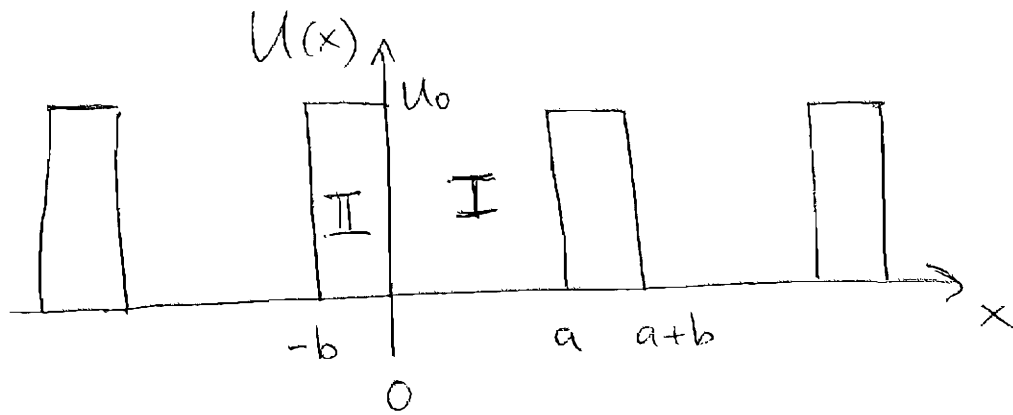
Thus  $\hbar\vec{k}$  is referred to as the "crystal momentum."

Kronig-Penney Model

consider the following potential

in one dimension:

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The period of the potential is  $a+b$ .

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + U(x) \psi(x) = \epsilon \psi(x)$$

In region I,

$$\psi_{\text{I}}(x) = A e^{iKx} + B e^{-iKx}$$

In region II, if  $\epsilon < U_0$ ,

$$\psi_{\text{II}}(x) = C e^{\alpha x} + D e^{-\alpha x},$$

$$\text{with } \frac{\hbar^2 \alpha^2}{2m} = U_0 - \epsilon.$$

Bloch's theorem implies

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$$\psi(a) = e^{ik(a+b)} \psi(-b),$$

which defines the Bloch wavevector  $k$ . Also

$$\psi'(a) = e^{ik(a+b)} \psi'(-b).$$

We also have

$$\psi_{\text{I}}(0) = \psi_{\text{II}}(0) \quad \psi'_{\text{I}}(0) = \psi'_{\text{II}}(0).$$

Thus we have 4 equations for the 4 unknowns  $A, B, C,$  and  $D$ :

$$1) \quad A + B = C + D$$

$$2) \quad ik(A - B) = Q(C - D)$$

$$3) \quad Ae^{iKa} + Be^{-iKa} = (Ce^{-Qb} + De^{Qb})e^{ik(a+b)} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} 20$$

$$4) \quad iK(Ae^{iKa} - Be^{-iKa}) = Q(Ce^{-Qb} - De^{Qb})e^{ik(a+b)}$$

These 4 equations have a solution only if the determinant of coefficients vanishes, which leads to the equation

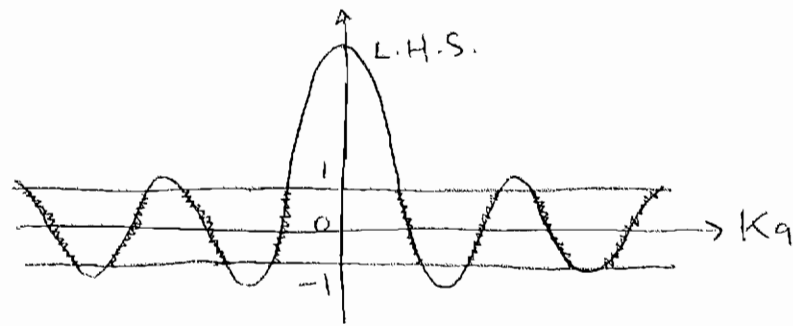
$$\frac{Q^2 - K^2}{2QK} \sinh Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a+b).$$

Since  $|\cos k(a+b)| \leq 1$ , any energy

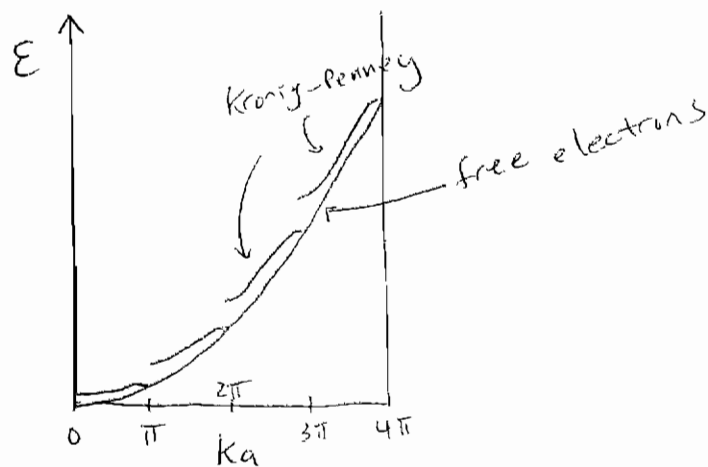
$$E = \frac{\hbar^2 K^2}{2m} = U_0 - \frac{\hbar^2 Q^2}{2m} \quad \text{for which}$$

the left side of the equation

in the box is greater than  $\pm 1$  or less than  $-1$  is forbidden.



Allowed values of  $ka$  : ~~.....~~



Note the energy gaps at

$$ka = \pi, 2\pi, 3\pi, \dots$$