

ME597/PHYS57000

Fall Semester 2009

Lecture 02

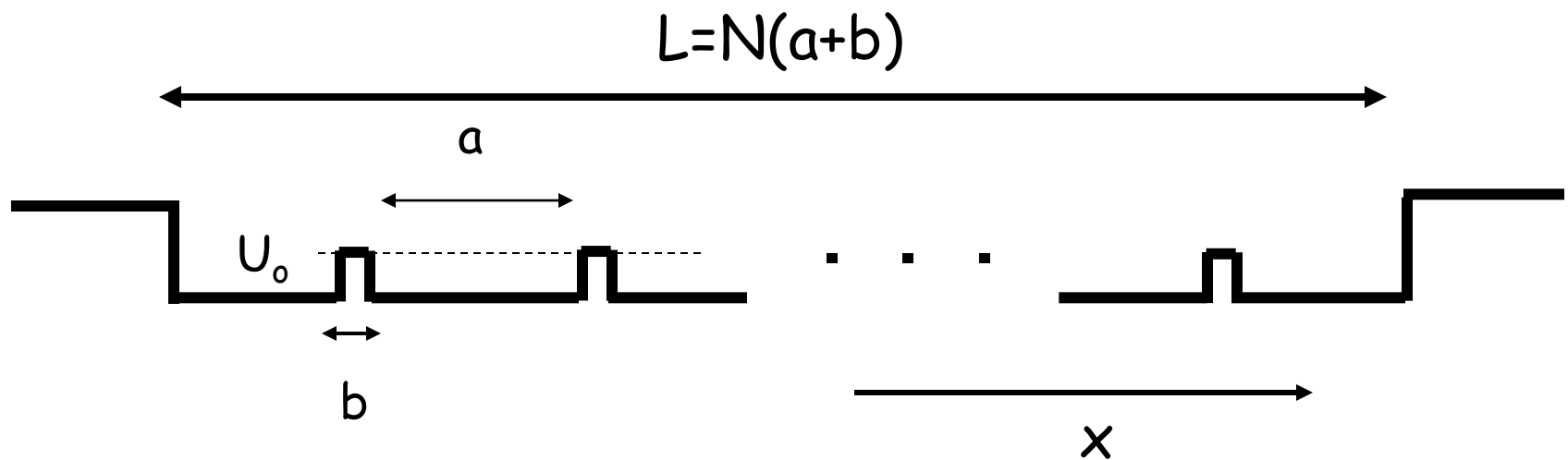
Electron States in Solids - Bloch Functions

Kronig-Penney Model

Density of States

What happens when the  
electron-ion interaction is more  
realistically approximated?  
the 1D Kronig-Penney Model

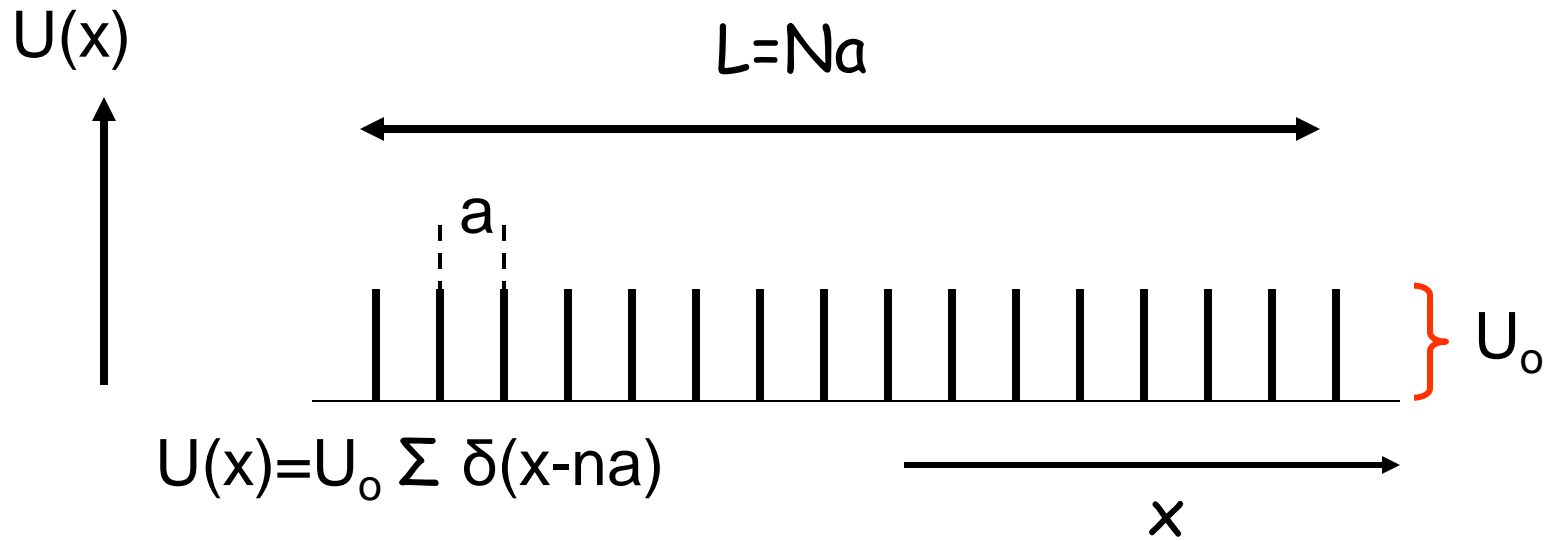
Model A:



Note that  $U(x) = U(x+a+b)$

# The periodic delta function Kronig Penney Model (1930)

Model B:



$$U(x) = U_0 \sum \delta(x - na)$$

Note that  $U(x) = U(x+a)$

Model C:

Etc...

# Any Unifying Principles?

Whenever  $U(x)$  is periodic, the resulting Schrödinger equation belongs to a class of differential equations known as Hill's equation.

Mathematicians have shown that solutions to Hill's equation must obey Floquet's theorem (aka as Bloch's theorem) which states that solutions  $\Psi$  must be of the form:

$$\Psi_k(x) = u_k(x)e^{ikx}$$

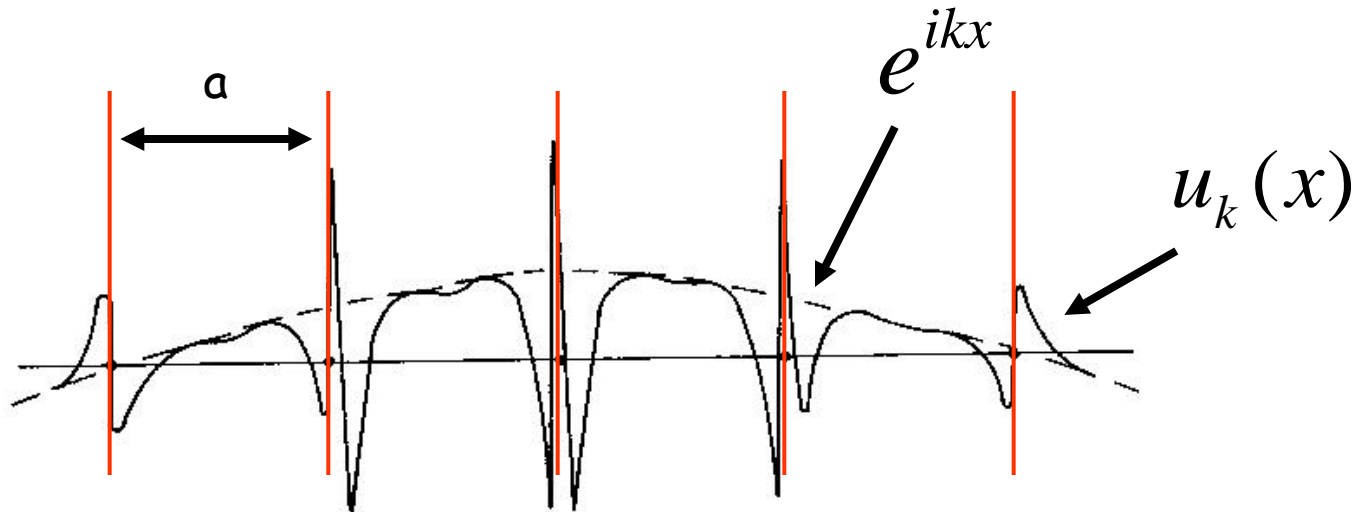
where  $u_k(x)$  is some function (that depends on  $k$ ) which must have the same periodicity as the lattice.

$u_k(x)$  are known as Bloch functions

# What's it Mean?

- Bloch's theorem states that no matter what the form of the periodic potential, the solutions must have certain properties that satisfy very general conditions.
- Consider  $u_k(x)$  as a "correction factor" to generate solutions for periodic potentials starting from the trivial  $e^{ikx}$  solutions for constant potential. The  $u_k(x)$  are related to atomic wavefunctions.
- $k$  is an index that distinguishes the various solutions

# Plot of $\Psi_k(x)$



**Figure 3-44** A wave-function for an electron in the 3s band of metallic sodium as a function of position, for the eigen-energy which corresponds with  $k = \pi/4a$ . After J. C. Slater, Rev. Mod. Phys. 6, 209 (1934). The dashed curve shows the simple plane wave which approximates the wave-function fairly well in the regions of space outside the atomic cores.

Under these circumstances, what is the relationship between  $E$  and  $k$ ??

# What determines "Bloch form" for $\Psi$ ?

Due to the translation symmetry of  $U(x)$ ,  
an electron has same probability to be at equivalent points in the lattice.

This means  $\Psi(x+a)$  should be somehow related to  $\Psi(x)$ .

Accordingly,  $|\Psi(x+ma)|^2 = |\Psi(x)|^2 \quad m = 1, 2, 3 \dots N$

This means  $\Psi(x+a) = J\Psi(x)$  where  $J$  is some function to be determined.

It follows that  $\Psi(x+ma)$  should be related to  $\Psi(x)$

as  $J^m\Psi(x) = \Psi(x+ma)$

Accordingly, for  $N$  unit cells in a 1D crystal, then

$\Psi(x+Na)$  would satisfy  $J^N\Psi(x) = \Psi(x+Na)$

What are the implications for  $J$ ?

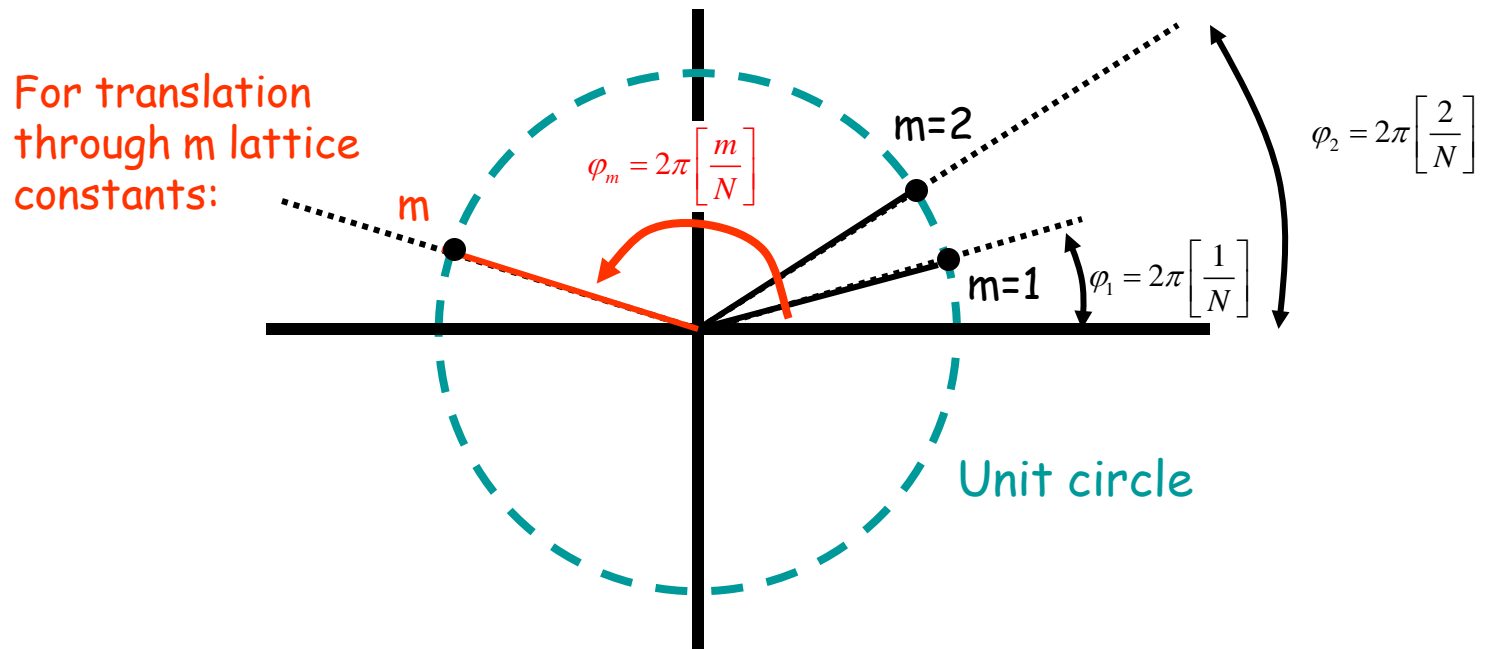


Implication is that  $J$  must be one of  $N$  roots of unity, i.e.

$$J = 1 = e^{2\pi i \left(\frac{m}{N}\right)} ; 1 \leq m \leq N$$

where

$$e^{2\pi i \left(\frac{m}{N}\right)} = \cos \left[ 2\pi \left(\frac{m}{N}\right) \right] + i \sin \left[ 2\pi \left(\frac{m}{N}\right) \right]$$



# The Bloch form

These translational requirements for  $\Psi$  can be met if we write

$$\Psi(x) = u_m(x) e^{2\pi i \frac{m}{Na} x}$$

provided  $u_m(x)$  has same periodicity as  $U(x)$ .

By specifying  $m$ , we specify how many complete cycles the exponential completes in a distance  $L$ , since for a given  $m$ ,

$$e^{2\pi i \frac{m}{Na} x}$$

oscillates through  $m$  complete cycles as  $x$  goes from 0 to  $Na$ .

Writing  $K = \frac{2\pi m}{Na}$ , we then have  $\Psi(x) = u_K(x) e^{iKx}$ .

## A few consequences

The effect of a translation:

$$\Psi(x + ma) = e^{iKa} \Psi(x) \quad \text{with} \quad K = \frac{2\pi m}{Na}$$

Since  $\Psi(x) = u_K(x)e^{iKx}$ ,  $\Psi(0) = u_K(0)$  (remember this!)

## Another way of saying the same thing

If we assume the solutions are of the form  $\Psi(x) = u_K(x)e^{iKx}$

AND we require that  $\Psi(x+L) = u_K(x+L)e^{iK(x+L)} = \Psi(x)$

(i.e., wavefunction solutions repeat after  $L=Na$ ),

then it follows that

(i)  $u_K(x) = u_K(x+L)$ , and

(ii)  $e^{iKL} = 1$

When does  $e^{iKL} = 1$ ?

only when  $KL = 2\pi m$ ;  $m$ =integer

$$K = 2\pi \frac{m}{L} = \frac{2\pi}{a} \frac{m}{N}$$

Either argment implies that if we choose to write

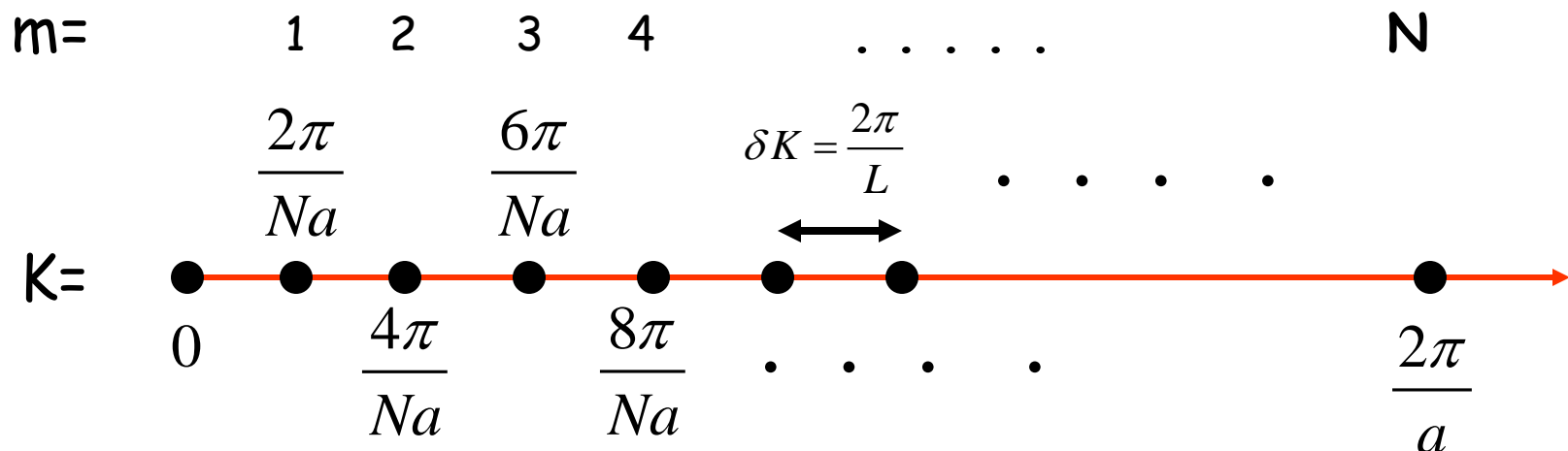
$$K \text{ as } \frac{2\pi m}{Na} \text{ or } \frac{2\pi m}{L}; \quad m = 1, 2, \dots, N$$

then we can write

$$\Psi(x) = u_K(x)e^{iKx}$$

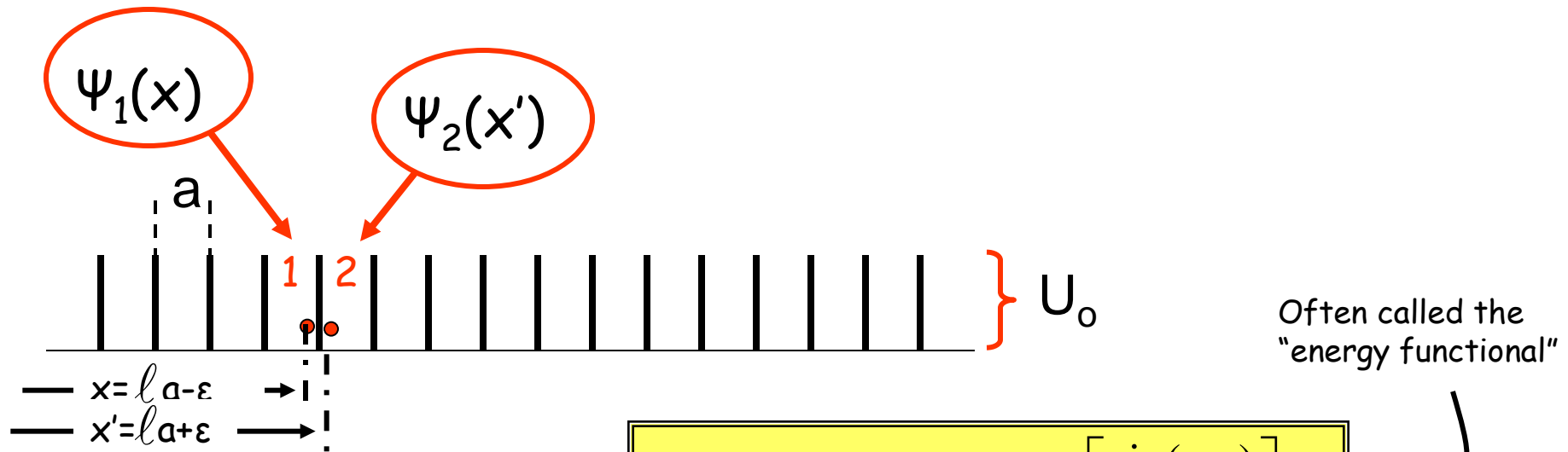
and Bloch's theorem will be explicitly satisfied.

The bottom line is that  $K$  now has DISCRETE values



If  $K$  has DISCRETE values, then so will  $E(K)$ !

# Apply these general ideas to Kronig-Penney delta function model



Require that

$$\Psi_1(x) = \Psi_2(x')$$

and require that

$$\left[ \frac{d\Psi_1}{dx} \right]_{x=la-\epsilon} = \left[ \frac{d\Psi_2}{dx} \right]_{x'=la+\epsilon}$$

$$\cos(Ka) = \cos(\alpha a) + P \left[ \frac{\sin(\alpha a)}{\alpha a} \right]$$

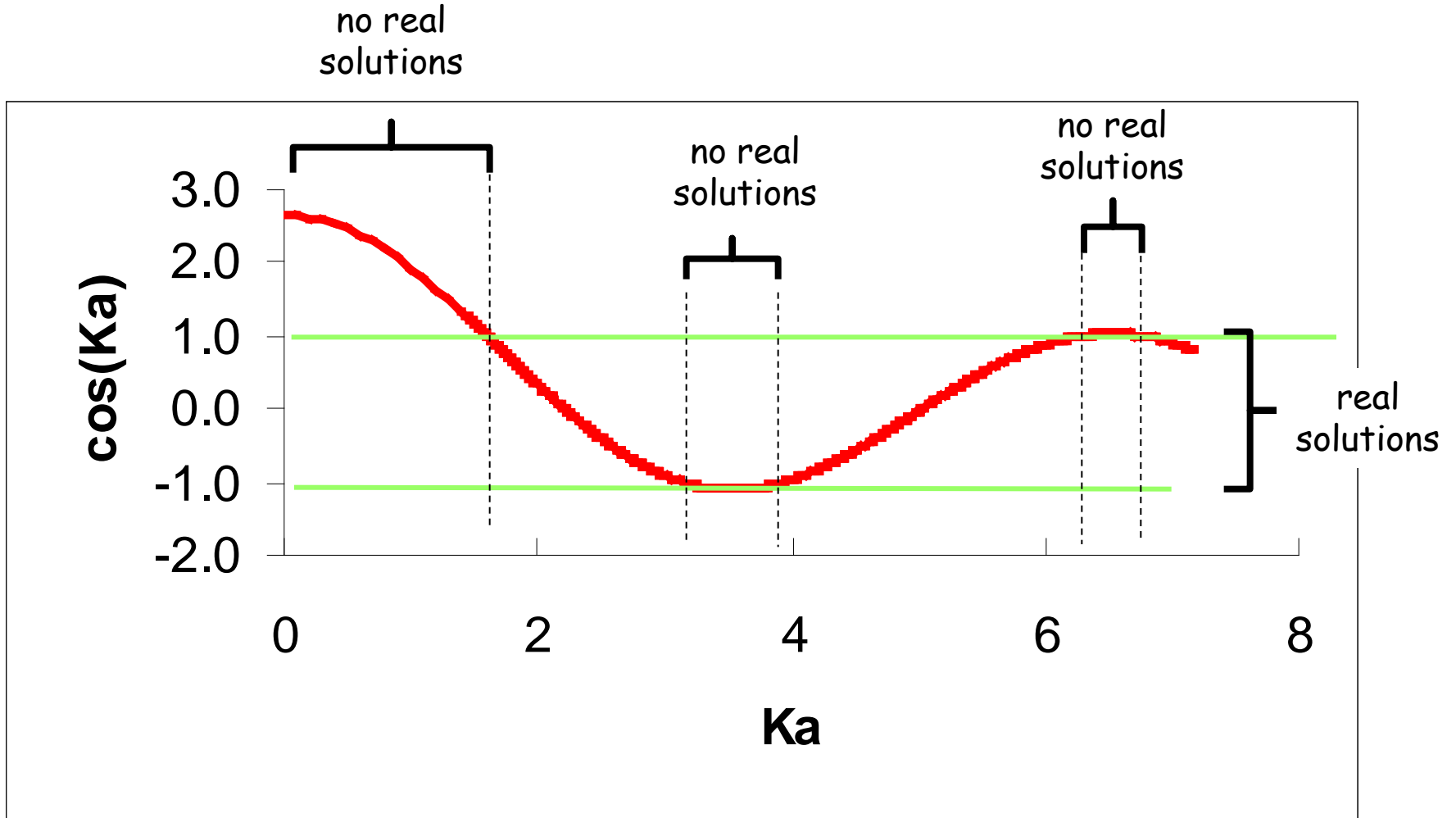
$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} \text{ and } P = \lim_{\substack{b \rightarrow 0 \\ U_0 \rightarrow \infty}} [bU_0] \frac{ma}{\hbar^2}$$

b is width of barrier (see earlier slide)

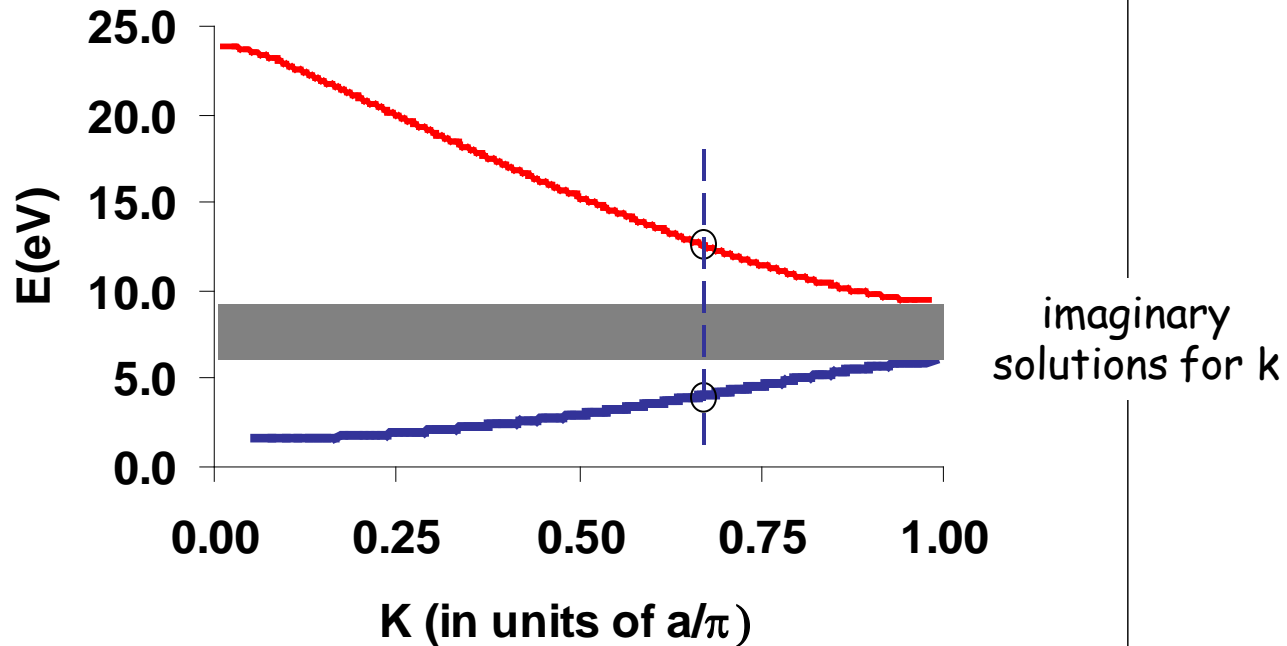
when  $P \rightarrow 0, K$  (free electron case)

when  $P \rightarrow \infty, E_n = n^2 \frac{\pi^2 \hbar^2}{2ma^2}$  (bound electron case)

# Plotting it out



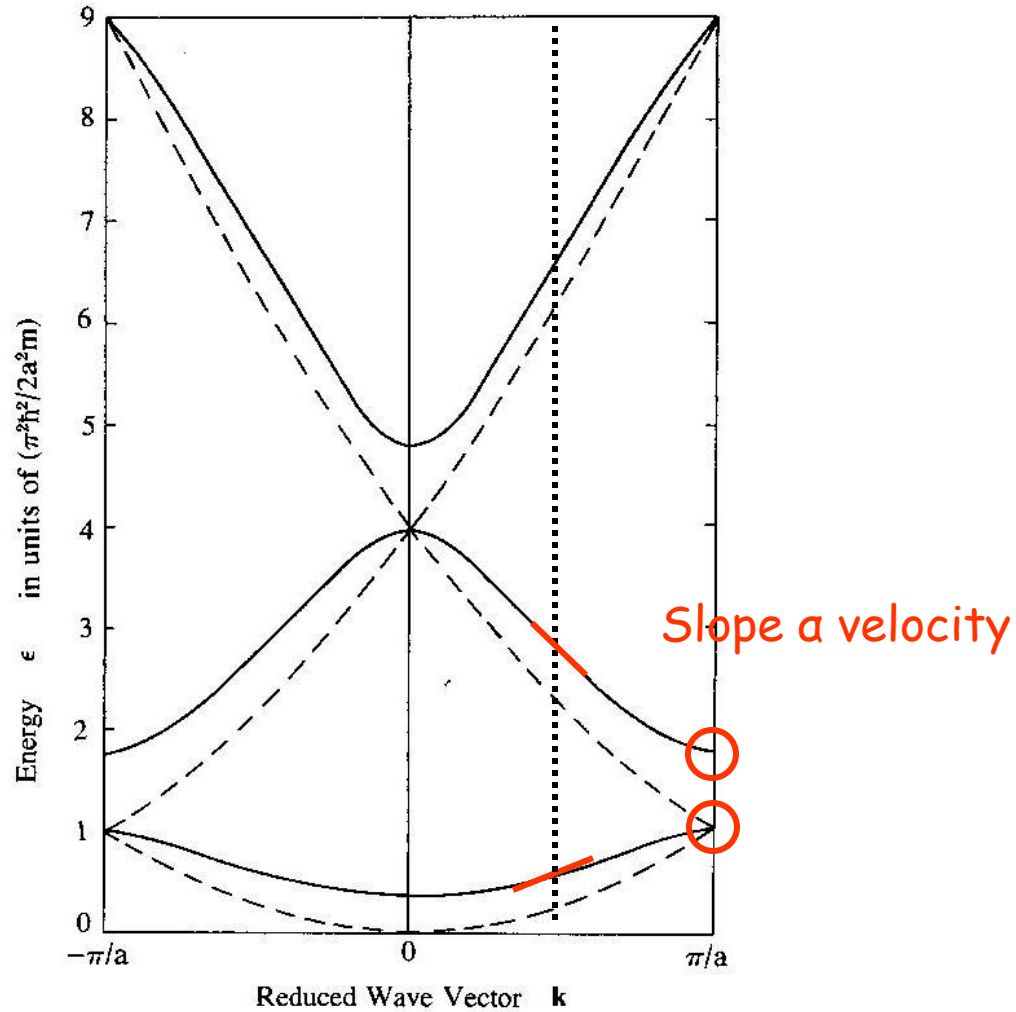
## Delta-function Kronig Penny P=1.65; first two bands



- $E$  is no longer single valued with  $K$
- Energy gaps appear - no solutions for real  $K$
- $E$  vs.  $K$  no longer free electron-like



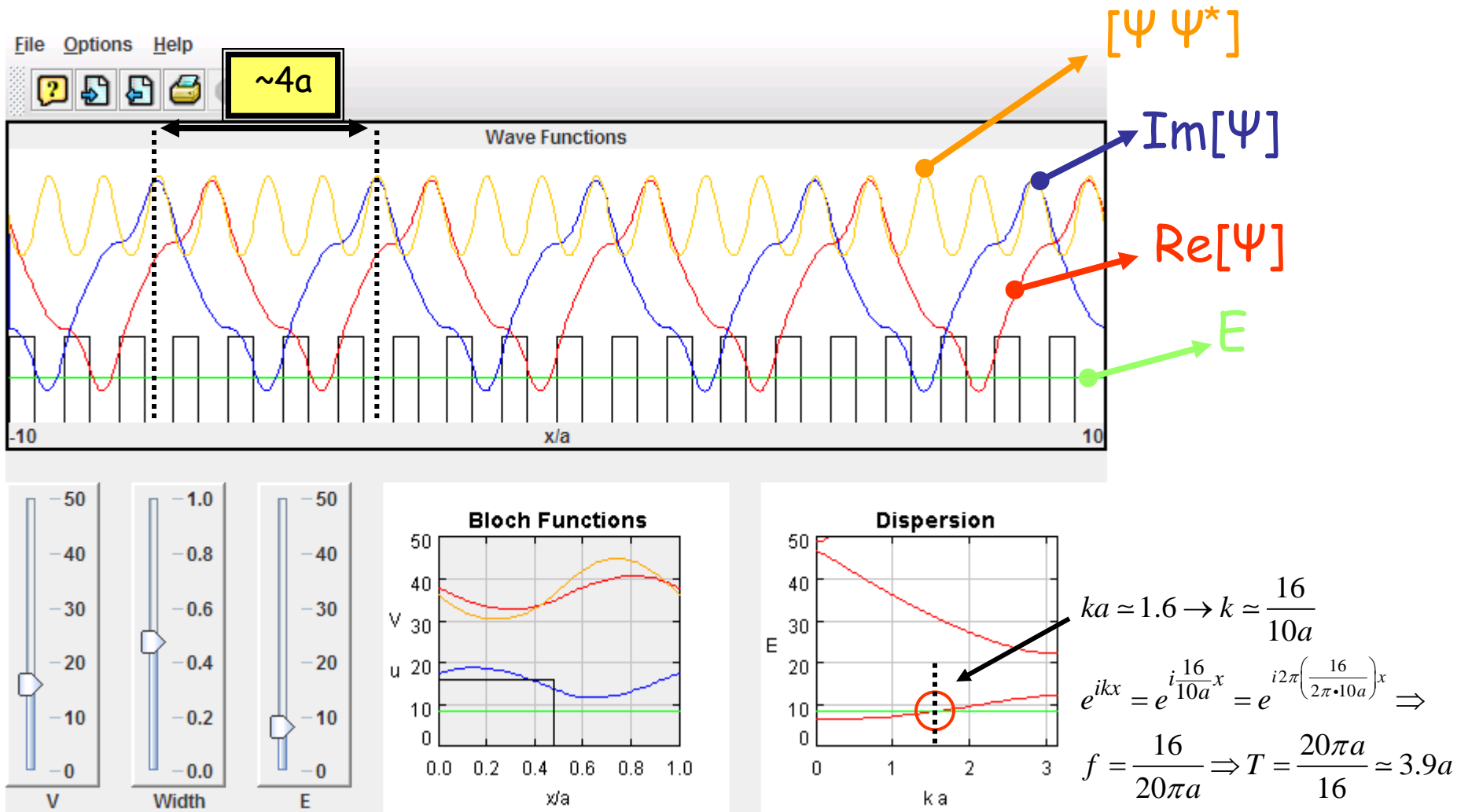
# Compare to free-electron case



**Figure 3-27** A reduced-zone representation of energy versus wave-vector for the Kronig-Penney model when  $P = 2$  (as was chosen in Figure 3-26). The corresponding curves for  $P = 0$  (free electrons) are shown as dashed curves.

Check out the Kronig Penney applet at

<http://fermi.la.asu.edu/schmidt/applets/kp/plugkp.html>



$$ka \approx 1.6 \rightarrow k \approx \frac{16}{10a}$$

$$e^{ikx} = e^{i\frac{16}{10a}x} = e^{i2\pi\left(\frac{16}{2\pi \cdot 10a}\right)x} \Rightarrow$$

$$f = \frac{16}{20\pi a} \Rightarrow T = \frac{20\pi a}{16} \approx 3.9a$$

# Applet notes

The real part of  $\Psi$  is in red, and the imaginary part is in blue. The magnitude is plotted in orange. The potential is shown in black.

The "Bloch Functions" plot shows the periodic Bloch functions. The color code is identical to the top plot.

To emphasize "atomic" like nature of Bloch functions, choose energy near bottom of square well.

# Finally, where are the electrons?

- position:  $\Psi(x)\Psi^*(x)\Delta x$
- charge:  $-e\Psi(x)\Psi^*(x)\Delta x$
- energy: **define density of states**

In 3D:

Number of energy states per unit volume in the energy interval  $\Delta E$

$$n(E) \Delta E = g(E) f(E) \Delta E$$

Number of particles per unit volume with energy between  $E$  and  $E + \Delta E$

Fermi-Dirac Probability that an electron is actually in the energy state  $E$

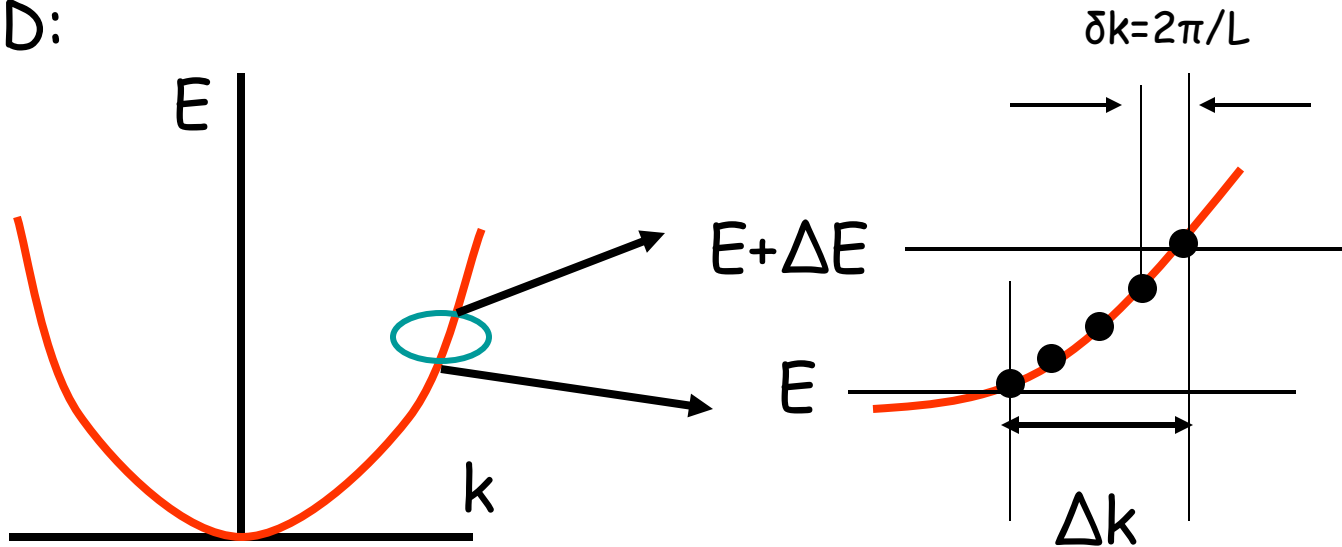
In 2D,  $V \rightarrow$  Area  
In 1D,  $V \rightarrow$  Length

From  $n(E)$ , define the Density of States (DOS):  
Number of electron states per unit volume per unit energy at energy  $E$

$$\rho(E) = \lim_{\Delta E \rightarrow 0} \frac{n(E + \Delta E) - n(E)}{\Delta E} \equiv \frac{d n}{d E}$$

Given  $E(k)$ , what is  $n(E)$ ?

In 1D:

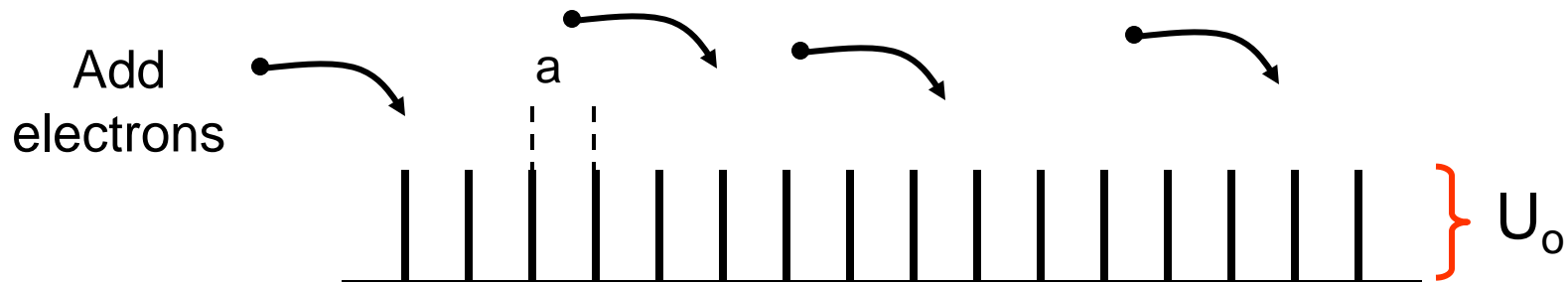


$$\Delta n = \text{No. of states} = 2 \times \frac{\Delta k}{\delta k} = 2 \times \left( \frac{1}{2\pi/L} \right) \frac{\Delta k}{\Delta E} \Delta E$$

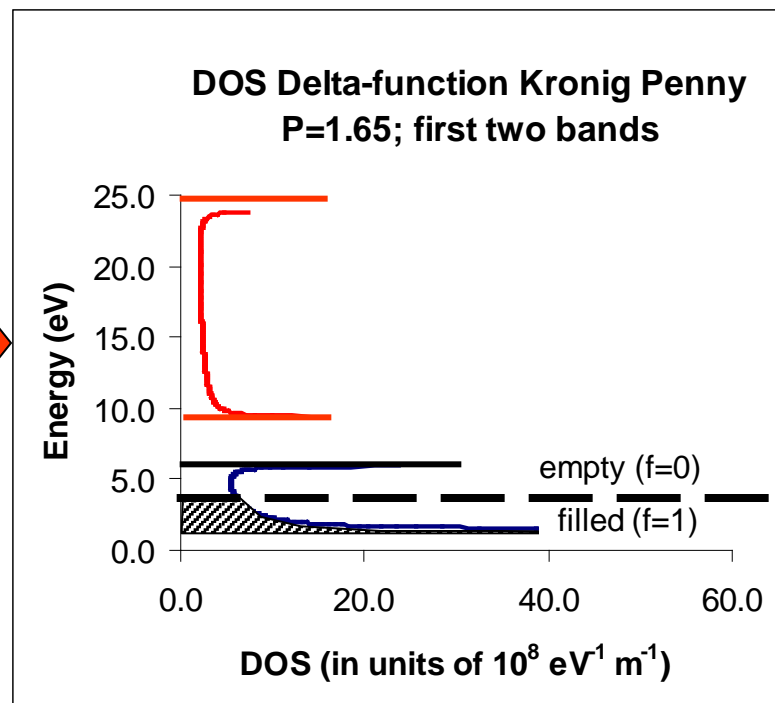
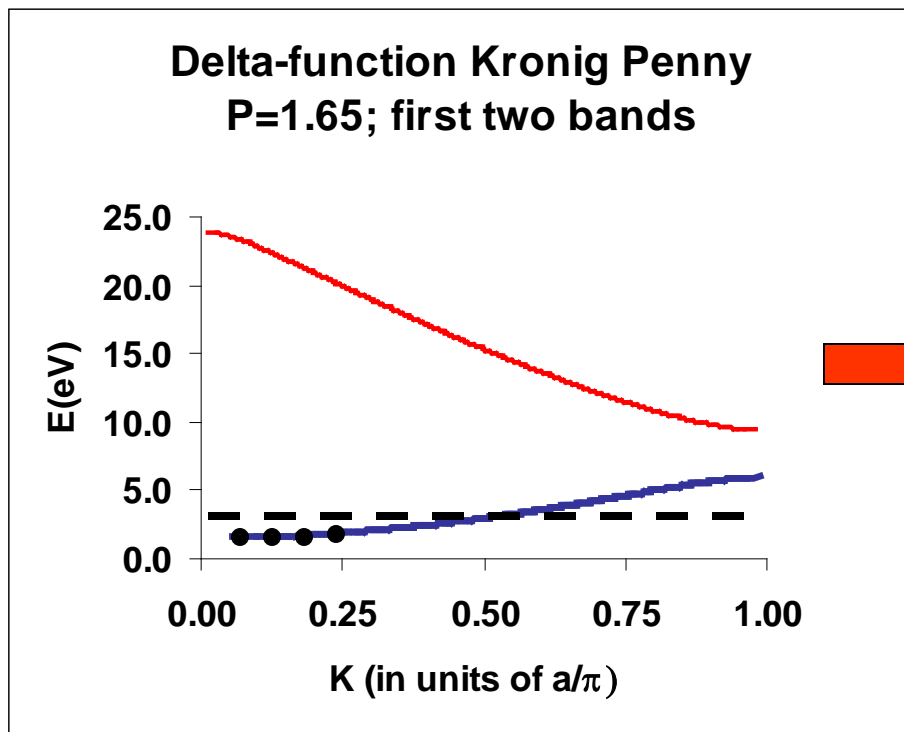
$$= \frac{L \Delta k}{\pi \Delta E} \Delta E$$

$$\lim_{\Delta E \rightarrow 0} \left( \frac{1}{L} \frac{\Delta n}{\Delta E} \right) = \frac{1}{L} \frac{dn}{dE} \equiv \rho(E) = \frac{1}{\pi} \frac{dk}{dE}$$

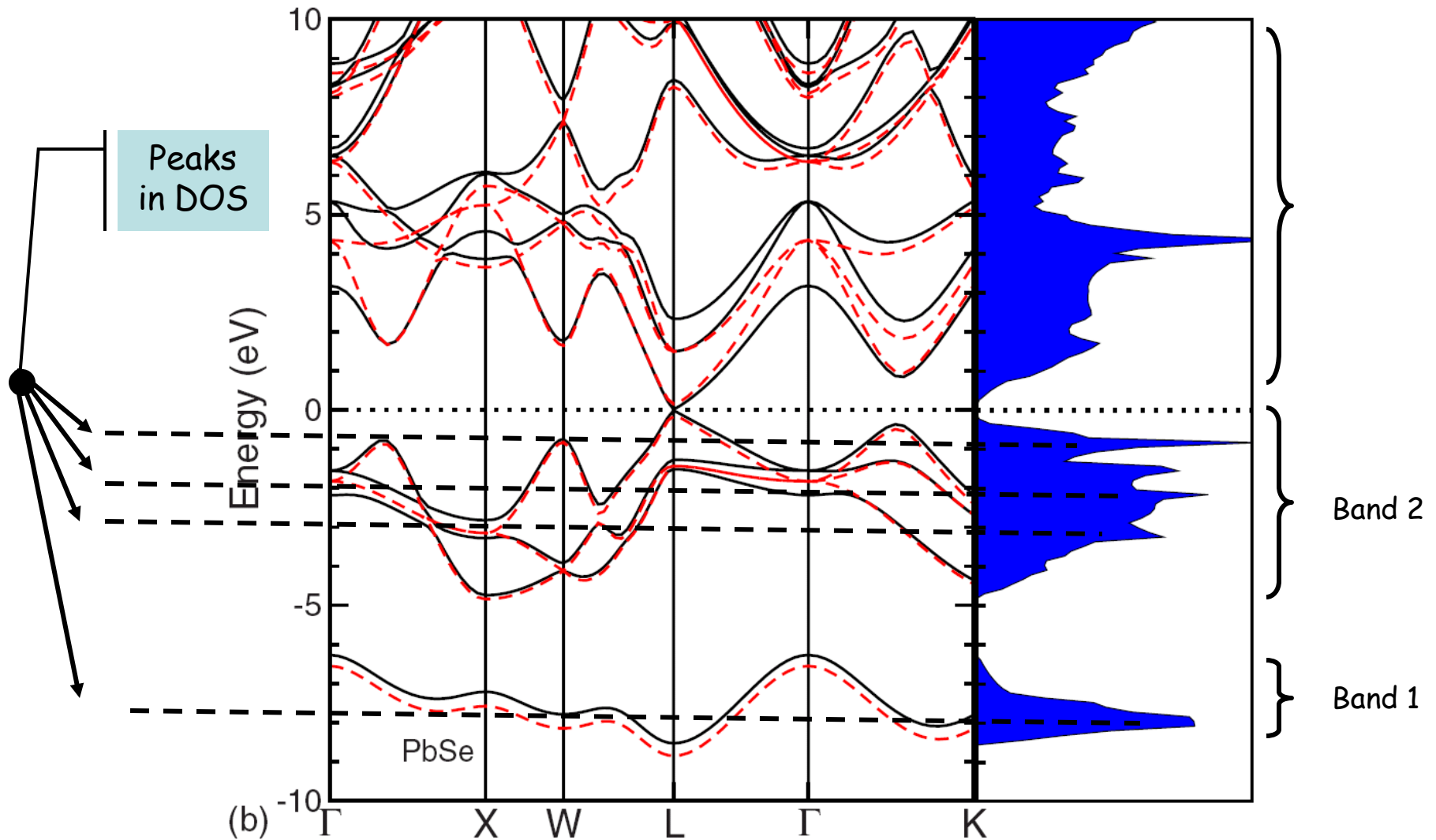
Units:  $\text{m}^{-1}\text{J}^{-1}$



$$\text{in 1D } \rho(E) = \frac{1}{\pi} \frac{dK}{dE} = \frac{1}{\pi} \left[ \frac{1}{dE/dK} \right]$$



# An example of a 3D band structure and DOS (PbSe)



# For idealized isotropic systems

**TABLE A.1. Properties of Coordinate and  $k$ -Space in One, Two and Three Dimensions**

Coordinate Region	$k$ -Space Unit Cell	Fermi Region	Value of $k^2$	Dimensions
Length $L$	$2\pi/L$	$2k_F$	$k_X^2$	1
Area $A = L^2$	$(2\pi/L)^2$	$\pi k_F^2$	$k_X^2 + k_Y^2$	2
Volume $V = L^3$	$(2\pi/L)^3$	$4\pi k_F^3/3$	$k_X^2 + k_Y^2 + k_Z^2$	3

**TABLE A.2. Number of electrons  $N(E)$  and Density of States  $D(E) = dN(E)/dE$  as Function of Energy  $E$  for Electrons Delocalized in One, Two, and Three Spatial Dimensions, Where  $A = L^2$  and  $V = L^3$**

Number of Electrons $N(E)$	Density of States $D(E)$	Delocalization Dimensions
$N(E) = \frac{4k_F}{2\pi/L} = \frac{2L}{\pi} \left[ \frac{2m}{\hbar^2} \right]^{1/2} E^{1/2}$	$D(E) = \frac{L}{\pi} \left[ \frac{2m}{\hbar^2} \right]^{1/2} E^{-1/2}$	1
$N(E) = \frac{2\pi k_F^2}{(2\pi/L)^2} = \frac{A}{2\pi} \left[ \frac{2m}{\hbar^2} \right] E$	$D(E) = \frac{A}{2\pi} \left[ \frac{2m}{\hbar^2} \right]$	2
$N(E) = \frac{2(4\pi k_F^3/3)}{(2\pi/L)^3} = \frac{V}{3\pi} \left[ \frac{2m}{\hbar^2} \right]^{3/2} E^{3/2}$	$D(E) = \frac{V}{2\pi^2} \left[ \frac{2m}{\hbar^2} \right]^{3/2} E^{1/2}$	3