

# "Traditional" Approach to Energy Bands in Solids

In P140A we discussed two pictures of energy bands in solids:

(1) Evolution from highly degenerate discrete atomic levels as nuclei pushed closer

(2) Second quantized approach  $H = -t \sum (c_e^\dagger c_{e+1} + c_{e+1}^\dagger c_e)$   
 $\rightarrow E(k) = -2t \cos k$

We now follow Kittel ch 7 by considering what periodic potential might do to change  $\psi = e^{i\vec{k}\cdot\vec{r}}$   $E = \hbar^2 k^2 / 2m$  of free particles.

\* Great quote by Felix Bloch from Kittel  $\rightarrow$   
How can  $e^-$  sneak by all the ions?  
 $\psi(r)$  differs from  $e^{i\vec{k}\cdot\vec{r}}$  by only a periodic modulation!

Key point: For some  $k$  the effect is strong enough, so

strong that the associated  $E(k)$  are no longer allowed  $\rightarrow$  Energy gaps

metals vs insulators

$\uparrow$  Hall coefficient  $\geq 0$

$\leftarrow$  Explain host of phenomena

# K7-2 PHYSICAL PICTURE

X rays scattering off nuclei  $\vec{k}' = \vec{k} + \vec{G}$  Bragg condition.  
 $e^{-} n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$

like-wise  $e^{-}$  are scattered off nuclei

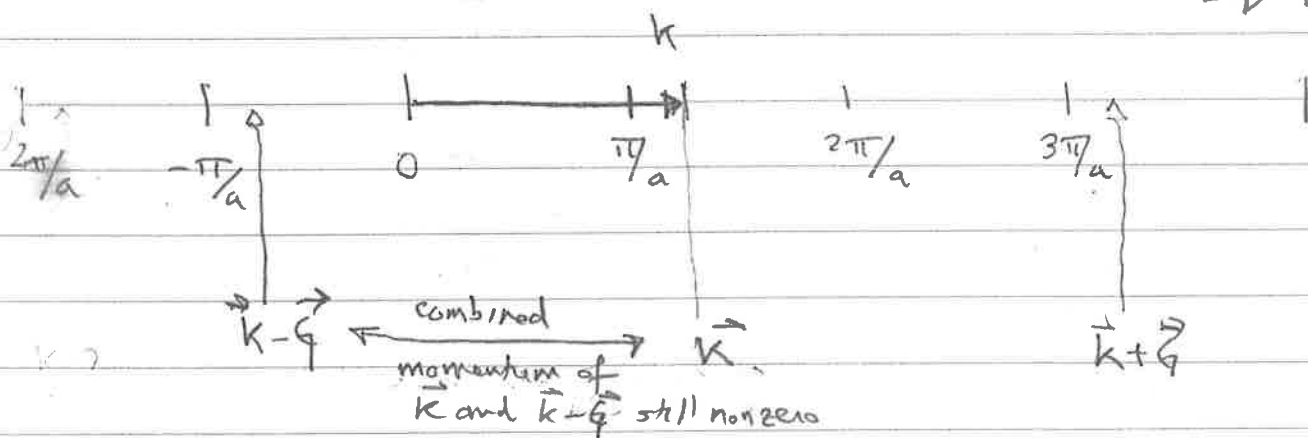
$d=1$ :



$$\left. \begin{aligned} \vec{R}_n &= n\vec{a} \\ \vec{G} &= \frac{2\pi}{a} m \end{aligned} \right\} e^{i\vec{G} \cdot \vec{R}_n} = 1$$

Suppose  $\vec{k} = \frac{\pi}{a} \cdot 1.2$

x rays constructive interference of all scatterings  $\Rightarrow$  Bragg peak



Something special might happen when  $k = \pi/a$  because then  $\vec{k} - \vec{G} = -\vec{k}$  and combined momentum of  $\vec{k}$  and  $\vec{k} - \vec{G}$  is zero  $\Rightarrow$  no flow of  $e^{-}$

Really looks a lot like x-ray problem  $\vec{k}$  lies on  $\perp$  bisector of  $\vec{G}$  vector

K7-3

$$-\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad \Psi_{n\ell m}(\vec{r})$$

BLOCH'S THM

$n \leftarrow$  "band"  
(orbital)  
index

The eigenstates of  $-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})$

where  $U(\vec{r}) = U(\vec{r} + \vec{R}) \quad \forall \vec{R} \in \text{Bravais lattice}$

have the form  $\Psi_{nk}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{nk}(\vec{r})$  H-atom

where  $u_{nk}(\vec{r} + \vec{R}) = u_{nk}(\vec{r})$

$$\Psi_{n\ell m}(\theta, \phi) = Y_{\ell m}(\theta, \phi) R_{n\ell}(r)$$

$\rightarrow$  (K7-3')

Proof #1 Define the translation operator  $T_{\vec{R}} f(\vec{r}) = f(\vec{r} + \vec{R})$

$T_{\vec{R}}$  commutes with  $H$  since

$$T_{\vec{R}} H \Psi = H(\vec{r} + \vec{R}) \Psi(\vec{r} + \vec{R}) = H(\vec{r}) \Psi(\vec{r} + \vec{R}) = H T_{\vec{R}} \Psi(\vec{r})$$

$T_{\vec{R}}$  also commutes with each other

$$\begin{aligned} T_{\vec{R}} T_{\vec{R}'} \Psi(\vec{r}) &= T_{\vec{R}} \Psi(\vec{r} + \vec{R}') = \Psi(\vec{r} + \vec{R}' + \vec{R}) = T_{\vec{R}'} \Psi(\vec{r} + \vec{R}) \\ &= T_{\vec{R}'} T_{\vec{R}} \Psi(\vec{r}) \end{aligned}$$

So can choose eigenstates of  $H$  to be eigenstates of  $T_{\vec{R}}$

$$T_{\vec{R}} H \Psi(\vec{r}) = \epsilon \Psi(\vec{r})$$

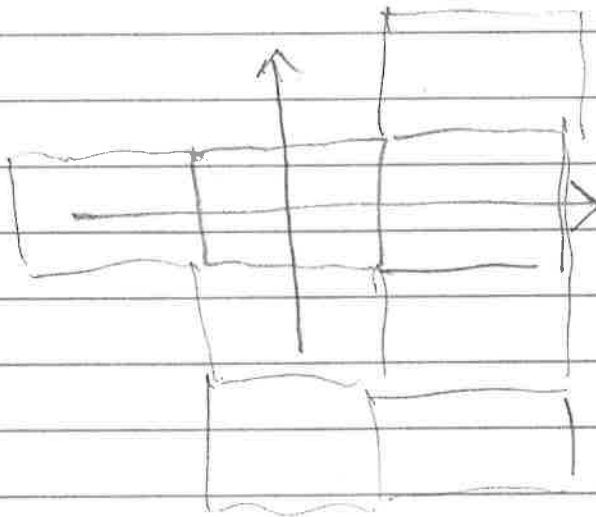
$$T_{\vec{R}} \Psi(\vec{r}) = c(\vec{R}) \Psi(\vec{r})$$

K7-3'

$$\begin{aligned}\psi_{nk}(\vec{r}+\vec{R}) &= e^{i\vec{k}(\vec{r}+\vec{R})} \psi_{nk}(\vec{r}+\vec{R}) \\ &= e^{i\vec{k}\cdot\vec{R}} e^{i\vec{k}\cdot\vec{r}} \psi_{nk}(\vec{r}) \\ &= e^{i\vec{k}\cdot\vec{R}} \psi_{nk}(\vec{r})\end{aligned}$$

$$\boxed{\psi_{nk}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_{nk}(\vec{r})}$$

Equivalent way of expressing Bloch's  $\psi_n$



WF looks  
same from unit  
cell to unit cell  
except  
phase  $e^{i\vec{k}\cdot\vec{R}}$

K7-4

The eigenvalues  $c(R)$  must obey  $c(R)c(R') = c(R+R')$

$$R = n_1 a_1 + n_2 a_2 + n_3 a_3$$

$$c(a_1) = e^{2\pi i x_1}$$

$$c(a_2) = e^{2\pi i x_2}$$

$$c(a_3) = e^{2\pi i x_3}$$

Because  $\langle \psi | \psi \rangle = 1 = \int d^3 r \psi^*(r) \psi(r)$

$$= \int d^3 r \psi^*(r+a_i) \psi(r+a_i)$$

$$= \int d^3 r c^*(a_i) \psi^*(r) c(a_i) \psi(r)$$

$$= c^*(a_i) c(a_i) \underbrace{\int d^3 r \psi^*(r) \psi(r)}_1$$

$$\Rightarrow |c|^2 = 1$$

$$c(R) = c(a_1)^{n_1} c(a_2)^{n_2} c(a_3)^{n_3}$$

$$= e^{2\pi i (x_1 n_1 + x_2 n_2 + x_3 n_3)}$$

But this is the same as saying

$$c(R) = e^{i \vec{k} \cdot \vec{R}}$$

with  $\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$  and  $\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

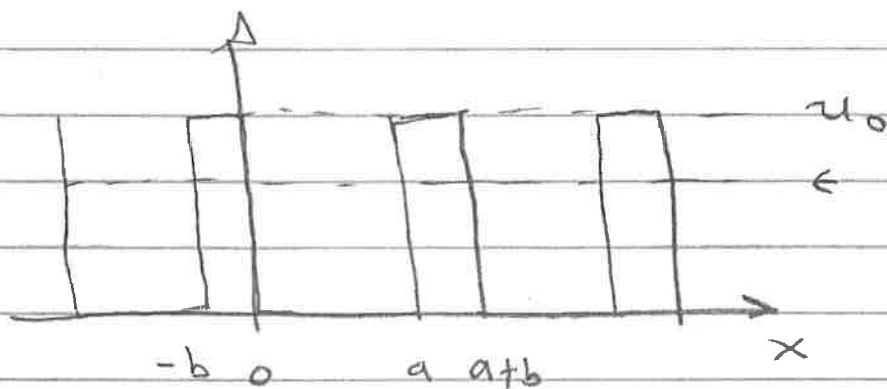
$$\therefore T_R \psi(\vec{r}) = \psi(\vec{r} + \vec{R}) = e^{i \vec{k} \cdot \vec{R}} \psi(\vec{r})$$

K7-5

Review  $\delta$  function first

Kronig-Penney Model

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



$$0 < x < a \quad \psi(x) = A e^{ikx} + B e^{-ikx} \quad \leftarrow = \frac{\hbar^2 k^2}{2m}$$

$$-b < x < 0 \quad \psi(x) = C e^{\alpha x} + D e^{-\alpha x}$$

$$U_0 - E = \frac{\hbar^2 \alpha^2}{2m}$$

$$\left( -\frac{\hbar^2 \alpha^2}{2m} + U_0 = E \right)$$

A, B, C, D determined by  $\psi$  and  $\frac{d\psi}{dx}$  continuous at  $x=0, x=a$

Bloch theorem  $\psi(a < x < a+b)$  related to  $\psi(-b < x < 0)$

$$\psi \left( \downarrow \right) = e^{ik(a+b)} \psi \left( \downarrow \right)$$

i.e.  $\hbar k$

$$x=0: \quad A + B = C + D$$

$$ik(A - B) = \alpha(C - D)$$

k7-6

$$x=a \quad Ae^{iKa} + Be^{-iKa} = C(e^{-Qb} + De^{-Qb}) e^{ik(a+b)}$$

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

Four eqns in four unknowns ABCD

if nonzero soln  $\det = 0$

$\Rightarrow$  quantization condition on energy

13.17 Sidewalk

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

Analog of  $K \tan Ka = Q$  but obviously a lot messier

↑  
Instead of discrete intersections (just one well)

there are ranges of  $K$  values that work.

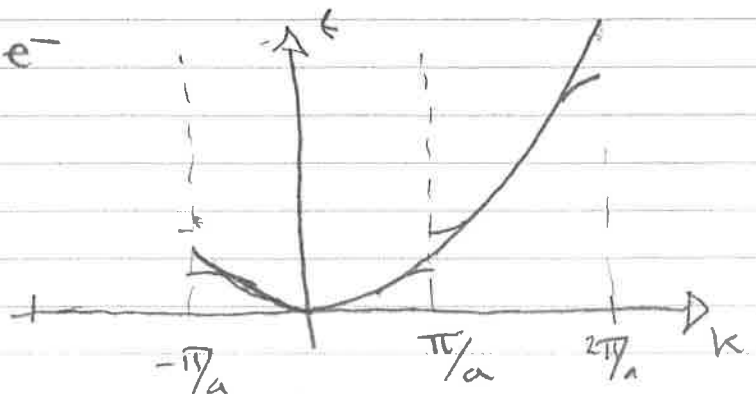
Hence ranges of energies and energy bands.

Actually quite messy to work out details.  $\Rightarrow$  HW.!

Easiest to understand gaps

Consider x ray, Bragg peak p k7-2

analogy here to  $e^-$



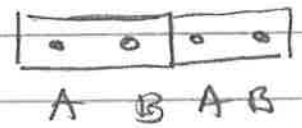
k7-7

Using our 2nd quantized approach we saw

how a periodic potential

$$E_A, E_B = E + \Delta(-1)^l = E + \Delta e^{i\pi l}$$

$\uparrow$     $\uparrow$   
 odd   even  
 $E - \Delta$     $E + \Delta$

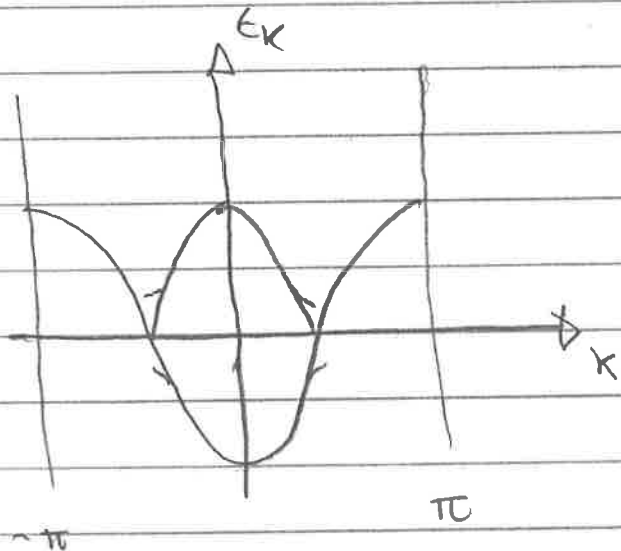


coupled  $k$  to  $k + \pi$  only, leading to a

simple  $2 \times 2$  matrix

$$\begin{pmatrix} E_k & \Delta \\ \Delta & E_{k+\pi} \end{pmatrix}$$

whose eigenvalues are  $\frac{1}{2} [E_k \pm \sqrt{E_k^2 + \Delta^2}]$



$\sim \Delta^2$  if  $E_k \gg \Delta$   
 $\sim \Delta$  if  $E_k$  small

We will now see how this "restricted coupling" of  $k$  only to a "small # of other  $k$  values" arises in Sch Eqn "first quantized QM"

$\Delta = 0.1$     $t = 1$

$k$	$E_k = -2t \cos k$	$E_k$
$\pi$	2.0000	2.0012
0	-2.0000	-2.0012
$\frac{\pi}{2}$	0.0000	0.05   -0.05

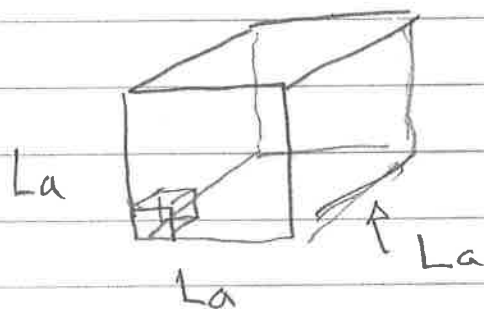
} 50x!



~~1/8~~ k7-8 Expand soln  $\psi(\vec{r})$  to sch Eqn in plane waves

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

chosen to obey periodic bc  
 $\psi(\vec{r})$  will be periodic over whole crystal:



$$N = L^3 \text{ atoms}$$

L atoms in each direction

La = size of crystal side

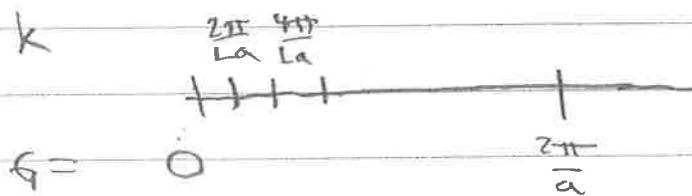
$$\psi(\vec{r} + La\hat{x}) = \psi(\vec{r})$$

This means  $k = \frac{2\pi}{La} \{1, 2, \dots, L\}$

Meanwhile the potential  $U(\vec{r})$  is periodic when we move from cell to cell inside the big crystal

$$U(\vec{r}) = \sum_{\vec{G}} u_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \quad \vec{G} = \frac{2\pi}{a} \{ \text{integer} \}$$

There are many, many more  $\vec{k}$  values than  $\vec{G}$



k7-9

$$U(\vec{r}) \text{ is real} \quad U_{-G} = U_G^*$$

Choose  $U_{G=0} = 0$  as origin of energy

$$\frac{\hat{p}^2}{2m} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi = \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} c_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

$$U\psi = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \sum_{\vec{k}} c_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

$$= \sum_{\vec{G}, \vec{k}} U_{\vec{G}} c_{\vec{k}} e^{i(\vec{G} + \vec{k}) \cdot \vec{r}} = \sum_{\vec{G}, \vec{k}'} U_{\vec{G}} c_{\vec{k}' - \vec{G}} e^{i\vec{k}' \cdot \vec{r}}$$

$$k' = G + k$$

$$k = k' - G$$

$$\left( \text{Rename } k' \rightarrow k \right) \rightarrow = \sum_{\vec{G}, \vec{k}} U_{\vec{G}} c_{\vec{k} - \vec{G}} e^{i\vec{k} \cdot \vec{r}}$$

The "Central Eqn"

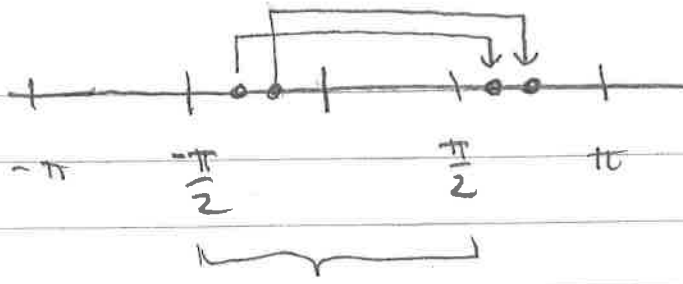
$$\left( \frac{\hbar^2 k^2}{2m} - E \right) c_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} c_{\vec{k} - \vec{G}} = 0$$

NOTE: Just as in second quantized

approach Each  $\vec{k}$  value (very dense) coupled

only to  $k+G$  sparse

K7-10



desireset  
of  $k$  values

→ 2x2 problem

100 Egn's  
in 100 unknowns

$$\begin{aligned} x_1 + x_2 &= 7 \\ x_1 - 3x_2 &= 9 \\ x_3 - x_4 &= 2 \\ 2x_3 + x_4 &= 1 \end{aligned}$$

Realspace looks like all  
100 coupled

↳  $k$  space realize only  
coupled in pairs ← our  $\epsilon_A \epsilon_B$  problem

only coupled  $k, k+\delta$  ← our Sch Eqn picture

Now SOLN IS NUMERICAL.

So if you look inside electronic structure (DFT)

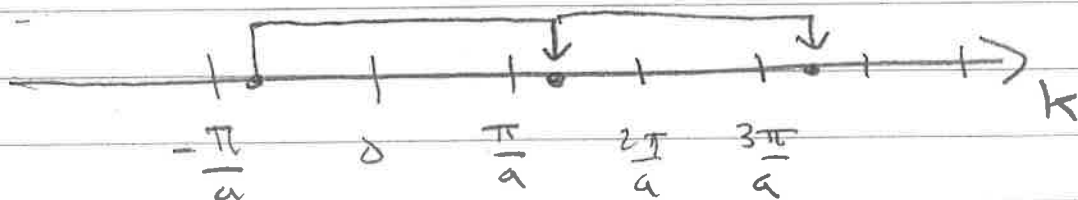
code.

(Kittel gives an example)

K7-11

So we need to look at  $k$  on  $(-\frac{\pi}{a}, \frac{\pi}{a})$

and then these  $k$  get coupled by  $\vec{G}$  to all other  $\vec{k}$  values:



First step in process is then to "fold" all

free energy bands back to  $(-\frac{\pi}{a}, \frac{\pi}{a})$  and then

consider what  $U_g$  does to them.

Let's describe that process for simple cubic lattice

(your HW is free)

K7-12

$$E(k_x, k_y, k_z) = \frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2$$

$$= \frac{\hbar^2}{2m} [(k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2]$$

Consider  $\vec{G} = 0$  and examine  $E$  along  $(k_x, 0, 0)$

$$\vec{G} = 0: E(k_x, 0, 0) = \frac{\hbar^2}{2m} k_x^2$$

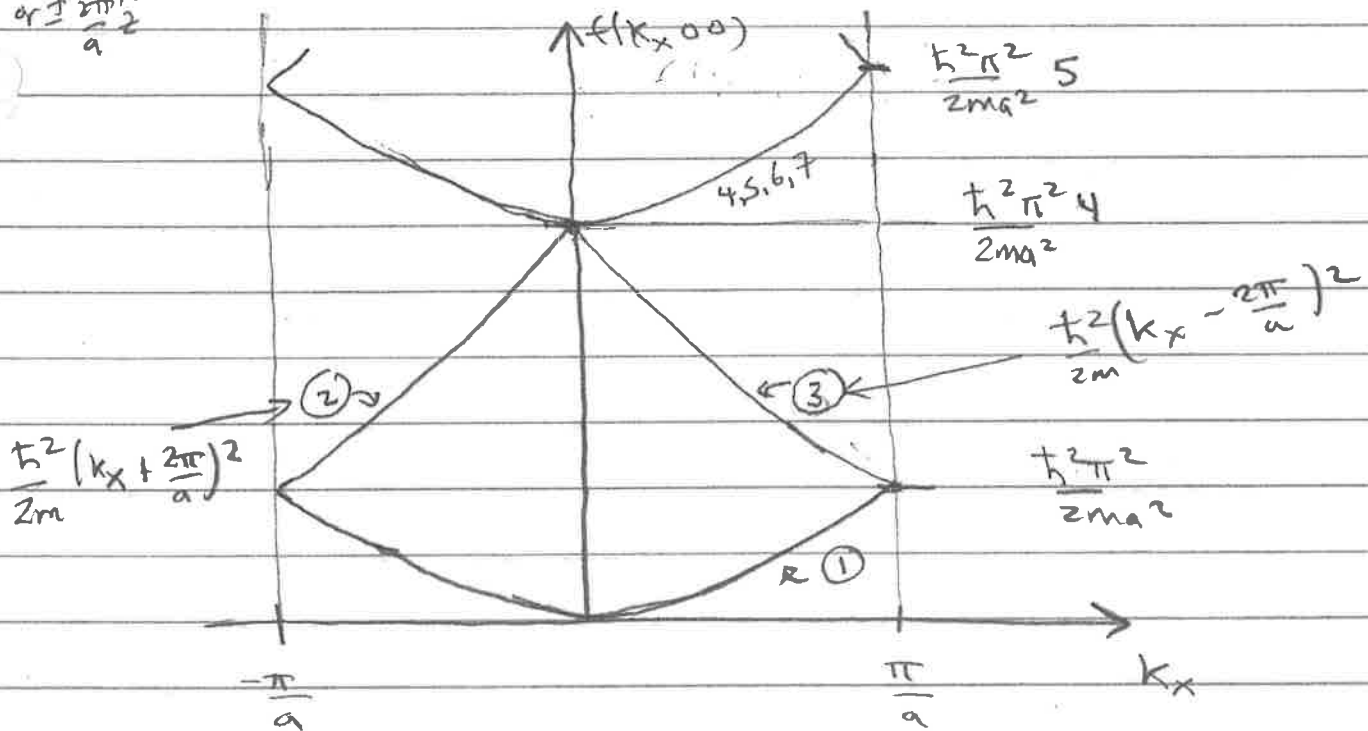
"band 1"

$$\vec{G} = \pm \frac{2\pi}{a} \hat{x}: E(k_x, 0, 0) = \frac{\hbar^2}{2m} \left(k_x \pm \frac{2\pi}{a}\right)^2$$

"bands 2, 3"

$$\vec{G} = \pm \frac{2\pi}{a} \hat{y} \text{ or } \pm \frac{2\pi}{a} \hat{z}: E(k_x, 0, 0) = \frac{\hbar^2}{2m} \left[k_x^2 + \left(\frac{2\pi}{a}\right)^2\right]$$

"bands 4, 5, 6, 7"



FSW-φ

# Why quantization?

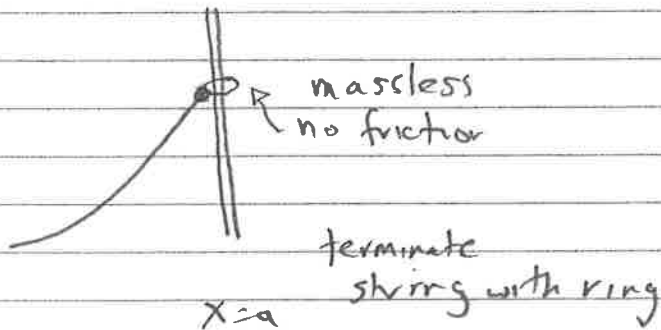
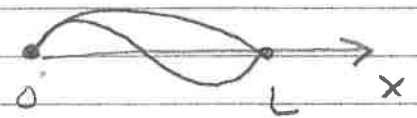
Vibrating string

wave eqn  $\frac{1}{v^2} \frac{d^2 y}{dt^2} = \frac{d^2 y}{dx^2}$

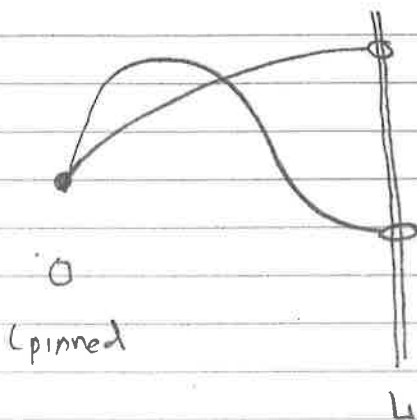
sols  $\sin(kx - kv t) = y(x, t)$  any k

But Boundary conditions  $y(x=0, t) = y(x=L, t) = 0$

forces quantized  $k = n\pi/L$

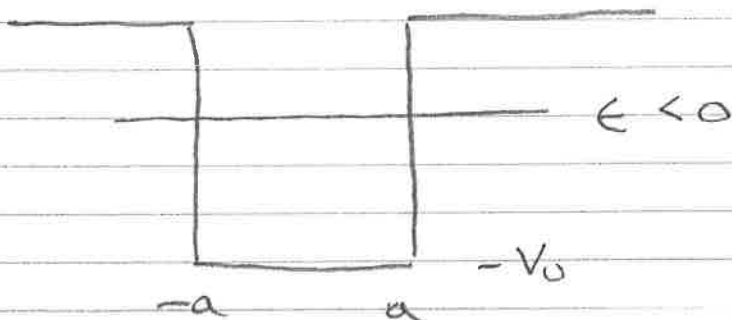


Boundary condition  $\left. \frac{\partial y}{\partial x} \right|_{x=a} = 0$



$k = \frac{\pi}{2L}, \frac{3\pi}{2L}, \dots$

## Finite Square well



$$E > -V_0$$

$$E + V_0 > 0$$

Outside well

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = \epsilon\psi$$

$$\uparrow$$

$$\epsilon < 0$$

 $x > 0$ 

$$\psi(x) = Ae^{-\alpha x}$$

$$\rightarrow \psi(x) = e^{\alpha x}, e^{-\alpha x}$$

$$\frac{\hbar^2 \alpha^2}{2m} = -\epsilon$$


Inside well

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - V_0\psi = \epsilon\psi$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = (V_0 + \epsilon)\psi \rightarrow \psi(x) = \sin kx \text{ or } \cos kx$$

$$\underbrace{\hspace{2cm}}_{> 0}$$

$$\frac{\hbar^2 k^2}{2m} = (V_0 + \epsilon)$$

Inside well wave like vibrating string 

But at well wall wave has specified slope, must

$$\text{match up } \frac{d\psi}{dx} = \frac{d}{dx} Ae^{-\alpha x} = -\alpha Ae^{-\alpha a}$$

This known slope forces  $k$  to be quantized (just like vibrating string!)

Look for even solns (since  $V(x) = V(-x)$   
solns will be even or odd)

$$P f(x) = f(-x) \quad \text{parity operator}$$

$$HP = PH$$

$$P^2 = I$$

even

$$Pv = \lambda v$$

$$P^2 v = \lambda^2 v = v$$

$$\lambda = \pm 1$$

even  
odd

$$\psi(x) = \begin{cases} Ae^{-\alpha x} & x > a \\ B \cos kx & x < a \end{cases} \quad \begin{cases} Ae^{-\alpha a} = B \cos ka \\ -\alpha Ae^{-\alpha a} = -k B \sin ka \end{cases}$$

Dividing  $k \tan ka = \alpha$

$$\text{Define } z = ka \quad z_0 = \frac{a}{\hbar} \sqrt{2mV_0}$$

$$\frac{\hbar^2 k^2}{2m} = (V_0 + \epsilon) = V_0 - \frac{\hbar^2 \alpha^2}{2m} \Rightarrow \frac{\hbar^2}{2m} (\alpha^2 + k^2) = V_0$$

$$\frac{\hbar^2 \alpha^2}{2m} = -\epsilon$$

$$\alpha^2 + k^2 = \frac{2mV_0}{\hbar^2} = \left(\frac{z_0}{a}\right)^2$$

$$\alpha^2 a^2 = z_0^2 - k^2 a^2 = z_0^2 - z^2$$

$$\tan ka = \frac{\alpha}{k} = \frac{\alpha a}{ka} = \frac{\sqrt{z_0^2 - z^2}}{z} = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$$

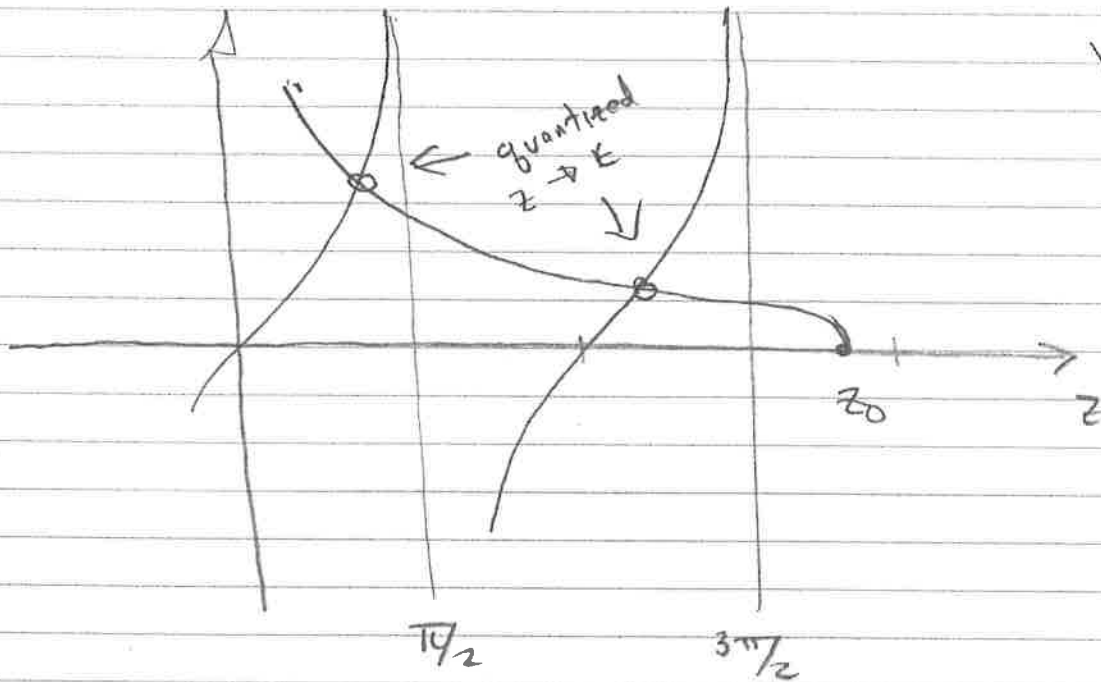
$\uparrow$   
 $\tan z$



FSW-3

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$$

$$z_0 = \frac{a}{\hbar} \sqrt{2mV_0}$$



$\sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$  ends  
when

$$\frac{z_0}{z} = 1$$
$$z = z_0$$