

LECTURE #20NEARLY FREE ELECTRONS

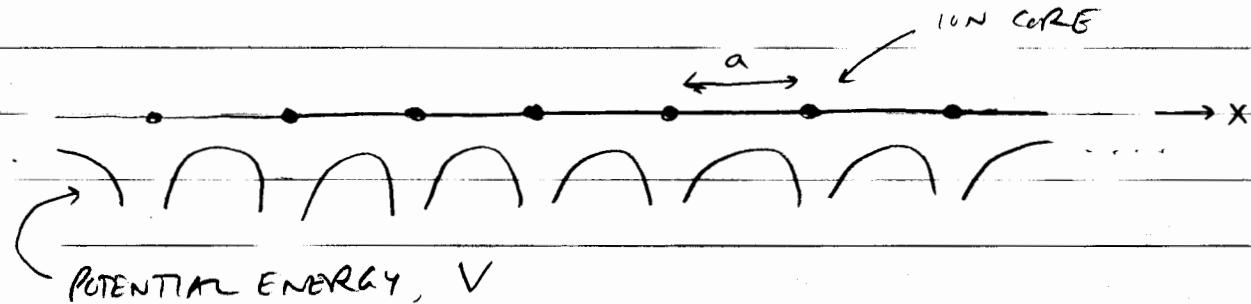
"WHEN I STARTED TO THINK ABOUT IT, I FELT THAT THE MAIN PROBLEM WAS TO EXPLAIN HOW THE ELECTRONS COULD SNEAK BY ALL THE IONS IN A METAL... By STRAIGHTFORWARD FOURIER ANALYSIS, I FOUND TO MY DELIGHT THAT THE WAVE DIFFERRED FROM THE PLANE WAVE OF FREE ELECTRONS ONLY BY A PERIODIC MODULATION."

- F. BLOCH

\* THE WEAK PERIODIC POTENTIAL IN CRYSTALS LEADS TO SUBTLE BUT IMPORTANT MODIFICATIONS TO THE FREE ELECTRON MODEL.

\* THESE SUBTLE DIFFERENCES WILL EXPLAIN WHY THE ELECTRICAL RESISTIVITY OF A METAL CAN BE  $\sim 10^{-10} \Omega\text{-cm}$  WHILE A GOOD INSULATOR HAS AN ELECTRICAL RESISTIVITY AS HIGH AS  $\sim 10^{22} \Omega\text{-cm}$ .

FIRST CONSIDER THE PERIODIC CRYSTAL POTENTIAL QUANTITATIVELY IN 1-D:



A FREE ELECTRON IS DESCRIBED AS A PLANE WAVE,  
WHICH WILL UNDERGO BRAGG REFLECTION WHEN  
 $K = \pm n\pi/a$ ,  $n = 1, 2, \dots$

AT THE BRAGG CONDITION, PROPAGATING WAVE  
SOLUTIONS ARE NO LONGER PERMITTED



### GENERATION OF A STANDING WAVE

ASSUME  $K = \pi/a \Rightarrow 2$  WAYS TO FORM A STANDING  
WAVE FROM TRAVELING WAVE SOLUTIONS

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

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

THE  $e^-$  CHARGE DENSITY IS:

$$\rho(+) \propto |\Psi(+)|^2 \propto \cos^2(\pi x/a)$$

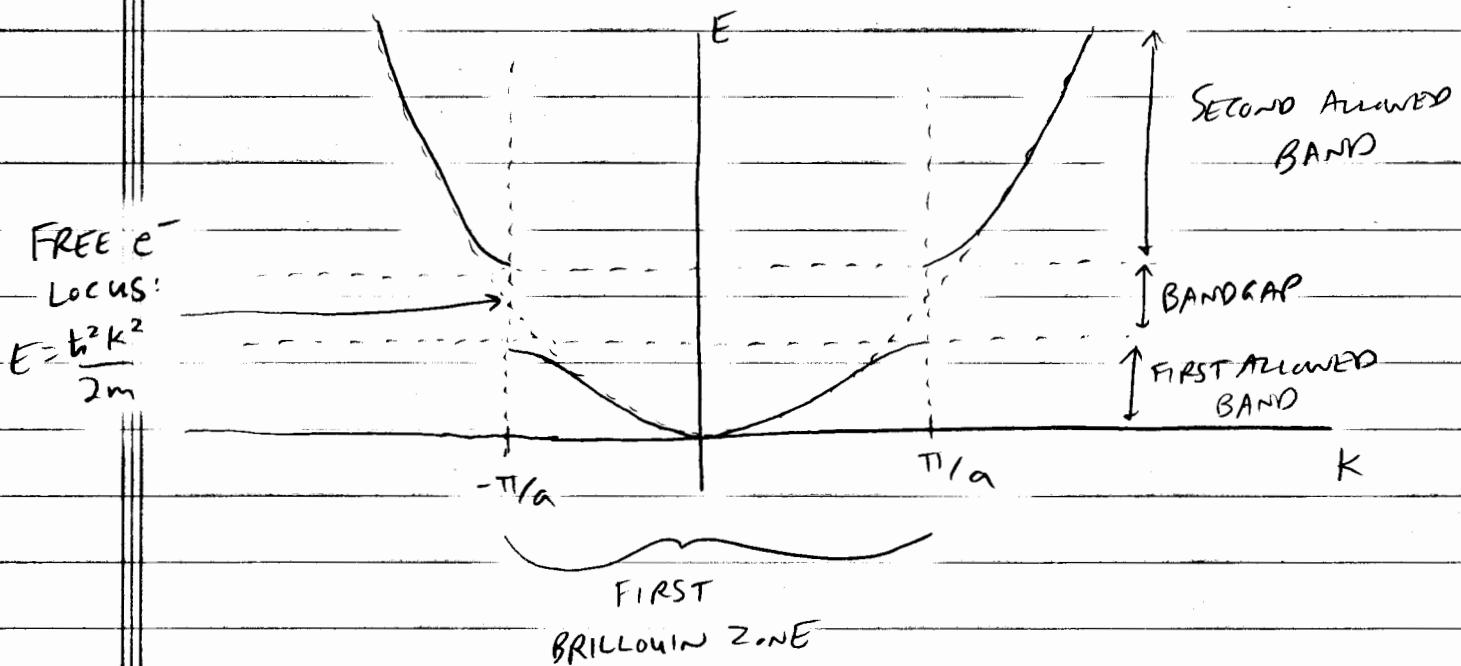
$$\rho(-) \propto |\Psi(-)|^2 \propto \sin^2(\pi x/a)$$

SEE FIGURE 3

$\rho(+)$   $\Rightarrow$  MAXIMA OVER IONS  $\Rightarrow$  LOW ENERGY

$\rho(-)$   $\Rightarrow$  MINIMA OVER IONS  $\Rightarrow$  HIGH ENERGY

$\Rightarrow$  BRAGG REFLECTION IMPLIES THE OPENING OF AN ENERGY GAP AT  $K = \pm n\pi/a$ ,  $n = 1, 2, \dots$

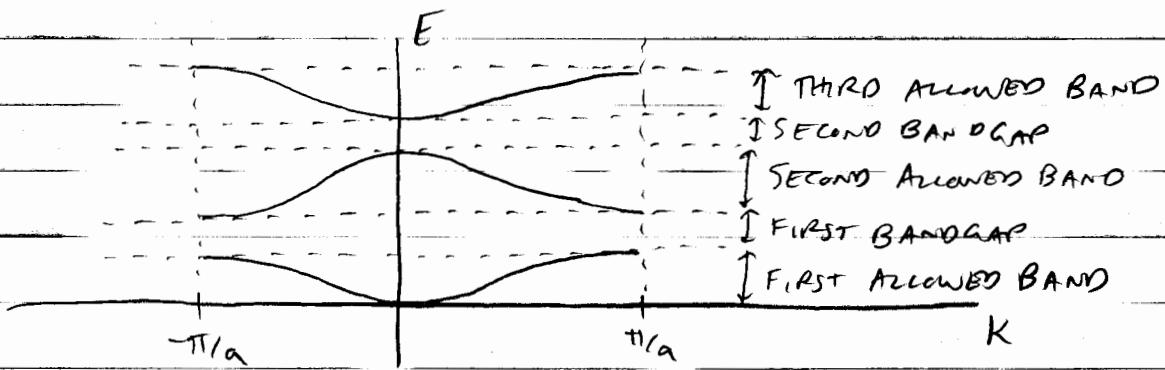


NOTE: OTHER ENERGY GAPS WILL OCCUR FOR INTEGER MULTIPLES OF  $\pi/a$  IN K-SPACE.

NOTE: SINCE THE LATTICE IS PERIODIC, K-SPACE IS PERIODIC  $\Rightarrow K + 2\pi/a$  IS EFFECTIVELY EQUIVALENT TO  $K$



THE E-K DIAGRAM CAN BE COLLAPSED TO THE FIRST BRILLOUIN ZONE (REDUCED ZONE SCHEME)



## BLOCH WAVES:

BLOCH PROPOSED THAT, IN WEAK PERIODIC POTENTIALS,  
THE SCHRODINGER EQUATION GIVES:

$$\psi(\vec{r}) = u(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad \text{"Bloch waves"}$$

WHERE  $u(\vec{r}) = u(\vec{r} + \vec{a})$ ,  $\vec{a}$  = LATTICE VECTOR

$$\Rightarrow \psi(\vec{r} + \vec{a}) = u(\vec{r} + \vec{a}) e^{i\vec{k} \cdot (\vec{r} + \vec{a})} = u(\vec{r}) e^{i\vec{k} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{a}}$$

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

$\Rightarrow$  WE ONLY NEED TO SOLVE THE SCH-EQ. WITHIN  
ONE PERIOD OF THE PERIODIC POTENTIAL SINCE THE  
RECURSIVE APPLICATION OF THE PREVIOUS EQUATION  
GENERATES THE SOLUTION EVERYWHERE ELSE

## 1-D PROOF OF BLOCH'S THEOREM :

DEFINE THE DISPLACEMENT OPERATOR:  $Df(x) = f(x+a)$

FOR A PERIODIC POTENTIAL  $V(x) = V(x+na)$ ,  $n=0, \pm 1, \pm 2, \dots$

$$[D, H]F = D \left[ -\frac{\hbar^2}{2m} \frac{d^2 f}{dx^2} + V(x) f(x) \right] - H D f(x)$$

$$= -\frac{\hbar^2}{2m} \frac{d^2 f(x+a)}{dx^2} + V(x+a) f(x+a) - H f(x+a)$$

$$= -\frac{\hbar^2}{2m} \frac{d^2 f(x+a)}{dx^2} + V(x) f(x+a) - H f(x+a)$$

$$= H f(x+a) - H f(x+a) = 0$$

$$\therefore [D, H] = 0$$

$\Rightarrow$  SIMULTANEOUS EIGENFUNCTIONS EXIST FOR H AND D

i.e.,  $H\psi = E\psi$  AND  $D\psi = \lambda\psi$

$\therefore D\psi = \psi(x+a) = \lambda\psi(x)$ ,  $\lambda = \text{COMPLEX CONSTANT}$

OF COURSE, NO SOLID IS INFINITELY PERIODIC.

HOWEVER, N IS LARGE ( $\approx 10^{23}$ ), WHICH SUGGESTS THE FOLLOWING MOVE TO SALVAGE BLOCH'S THEOREM:

MODEL THE SOLID AS N LATTICE POINTS ON A RING WITH CIRCUMFERENCE  $Na$

$$\Rightarrow \psi(x+Na) = \psi(x) = \lambda^N \psi(x)$$

$$\therefore \lambda^N = 1 = e^{i2\pi n} \Rightarrow \lambda = e^{i2\pi n/N}$$

$$\therefore \psi(x+a) = e^{i2\pi n/N} \psi(x) = e^{ik_a} \psi(x)$$

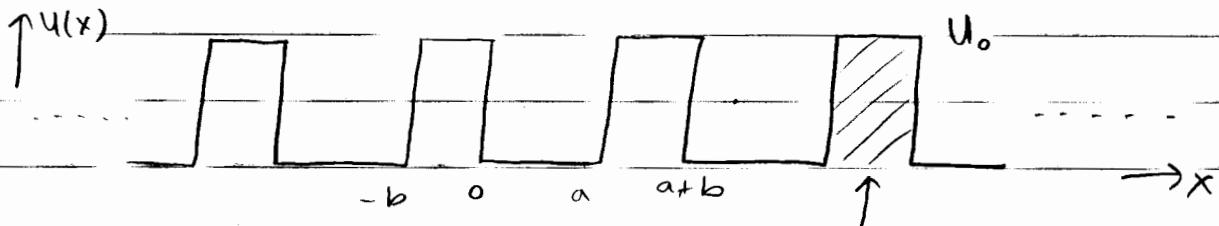
WHERE  $k = \frac{2\pi n}{Na} \Rightarrow k \text{ IS REAL}$

BLOCH  
THEOREM  
IN 1-D

NOTE: SINCE  $K$  IS REAL,

$$|\psi(x+a)|^2 = |\psi(x)|^2 \quad (\text{AS EXPECTED})$$

### KRÖNIG-PENNEY MODEL : BASIC 1-D TREATMENT



$U(x)$  = CRYSTAL POTENTIAL

AREA =  $U_0 b$  = CONSTANT

ASSUME  $0 < E < U_0$ :

(EVEN FOR A  $\delta$  FUNCTION)

IN THE POTENTIAL WELLS (e.g.,  $0 < x < a$ ),  $U(x) = 0$

$$\therefore \psi(x) = Ae^{ikx} + Be^{-ikx}, \quad E = \frac{\hbar^2 K^2}{2m}$$

IN THE POTENTIAL BARRIERS (e.g.,  $-b < x < 0$ ),  $U(x) = U_0$

$$\therefore \psi(x) = Ce^{Qx} + De^{-Qx}, \quad U_0 - E = \frac{\hbar^2 Q^2}{2m}$$

BLOCH PERIODICITY CONDITION:

$$\psi(a < x < a+b) = \psi(-b < x < 0) e^{ik(a+b)}$$

COMBINE THE BLOCH PERIODICITY CONDITION

WITH THE CONTINUITY REQUIREMENTS FOR

$\psi$  AND  $d\psi/dx$ :

AT  $x=0$ :

$$\gamma \text{ continuous: } A + B = C + D$$

$$\frac{d\gamma}{dx} \text{ continuous: } iK(A - B) = Q(C - D)$$

AT  $x=a$  (COMPARE  $\gamma(a)$  WITH  $\gamma(-b)$  USING BLOCH PERIODICITY CONDITION):

$$\gamma \text{ continuous: } Ae^{ik_a} + Be^{-ik_a} = (Ce^{-Qb} + De^{Qb})e^{ik(a+b)}$$

$$\frac{d\gamma}{dx} \text{ continuous: } iK(Ae^{ik_a} - Be^{-ik_a}) = Q(Ce^{-Qb} - De^{Qb})e^{ik(a+b)}$$

THESE 4 EQUATIONS WILL ONLY HAVE A SOLUTION IF THE DETERMINANT OF THE COEFFICIENTS OF  $A, B, C$ , AND  $D$  IS EQUAL TO ZERO.

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

KITTEL: "IT IS RATHER TEDIOUS TO OBTAIN THIS EQUATION"

TO SIMPLIFY THE ANALYSIS, LET THE BARRIERS REDUCE TO  $\delta$  FUNCTIONS:

i.e.,  $b \rightarrow 0$  AND  $U_0 \rightarrow \infty$  SUCH THAT  $\frac{Q^2 b a}{2} = P$  IS FINITE

CONSIDER EACH TERM OF THE ABOVE EQUATION SEPARATELY:

$$\lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} Q = \lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} \frac{\sqrt{2m(U_0 - E)}}{\hbar} = \infty$$

HOWEVER, SINCE  $P = \frac{Q^2 ab}{2}$  IS FINITE,

$$\lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} Qb = \lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} \frac{2P}{Qa} = 0$$

$$\lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} \cosh Qb \cos Ka = \cosh(\alpha) \cos Ka = \cos Ka$$

$$\lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} \frac{-K^2}{2QK} \sinh Qb \sinh Ka = \frac{-K}{2Q} \sinh(\alpha) \sinh Ka = 0$$

$$\lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} \cos K(a+b) = \cos ka$$

$$\lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} \frac{Q^2}{2QK} \sinh Qb \sinh Ka = \frac{P}{QKab} \sinh Qb \sinh Ka = \frac{\sinh(\alpha)}{0} = \frac{0}{0}$$

$\Rightarrow$  INDETERMINANT  $\Rightarrow$  L'Hopital's Rule  $\Rightarrow$  DIFFERENTIATE w.R.T.  $Qb$

$$\therefore \lim_{\substack{U_0 \rightarrow \infty \\ b \rightarrow 0}} \frac{P}{Ka} \cosh Qb \sinh Ka = \frac{P}{Ka} \cosh(\alpha) \sinh Ka = \frac{P}{Ka} \sinh Ka$$

PUTTING IT ALL TOGETHER:

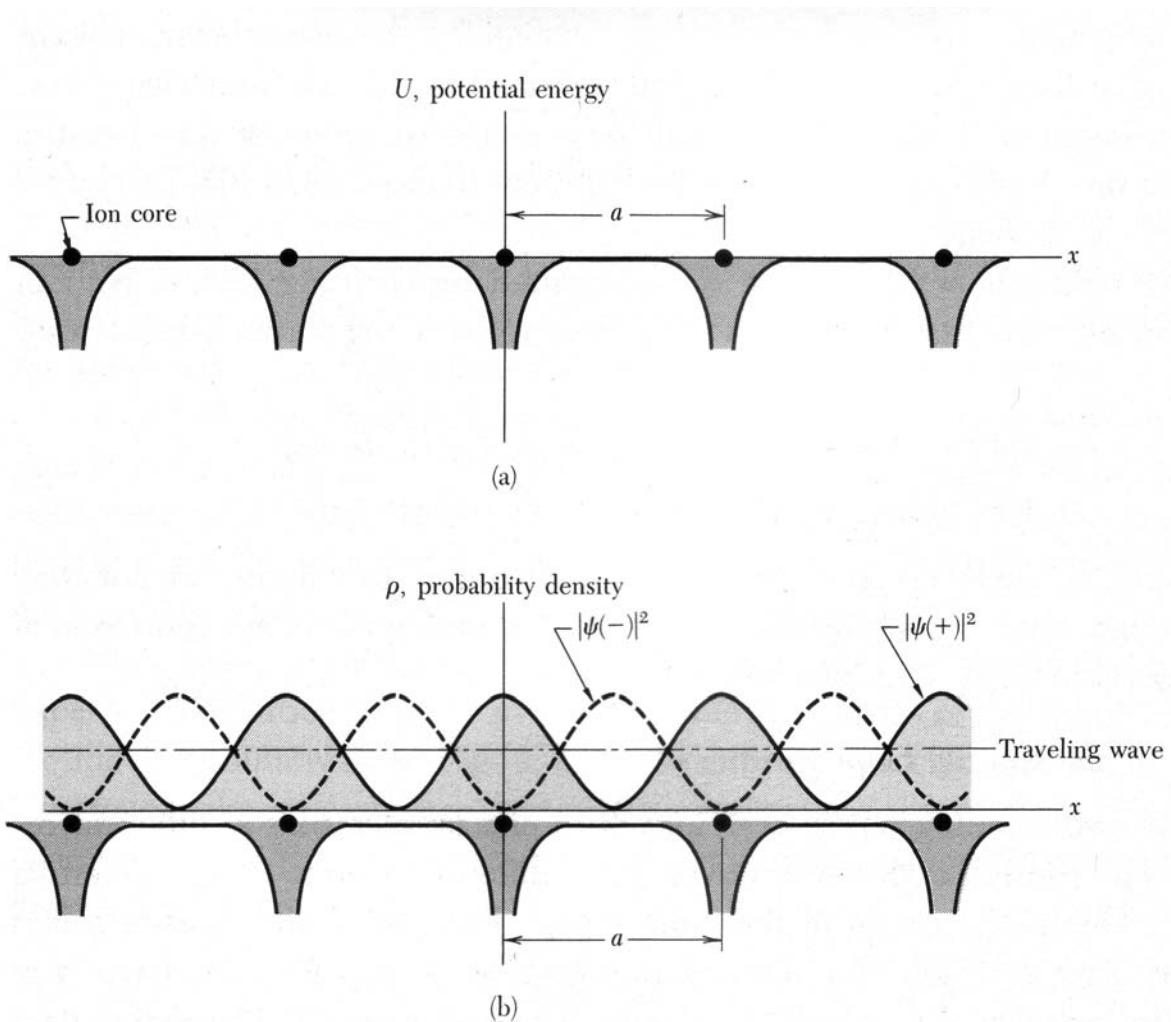
$$\boxed{\frac{P}{Ka} \sinh Ka + \cos Ka = \cos ka}$$

SINCE  $|\cos ka| \leq 1$ , ONLY CERTAIN BANDS OF  $K$

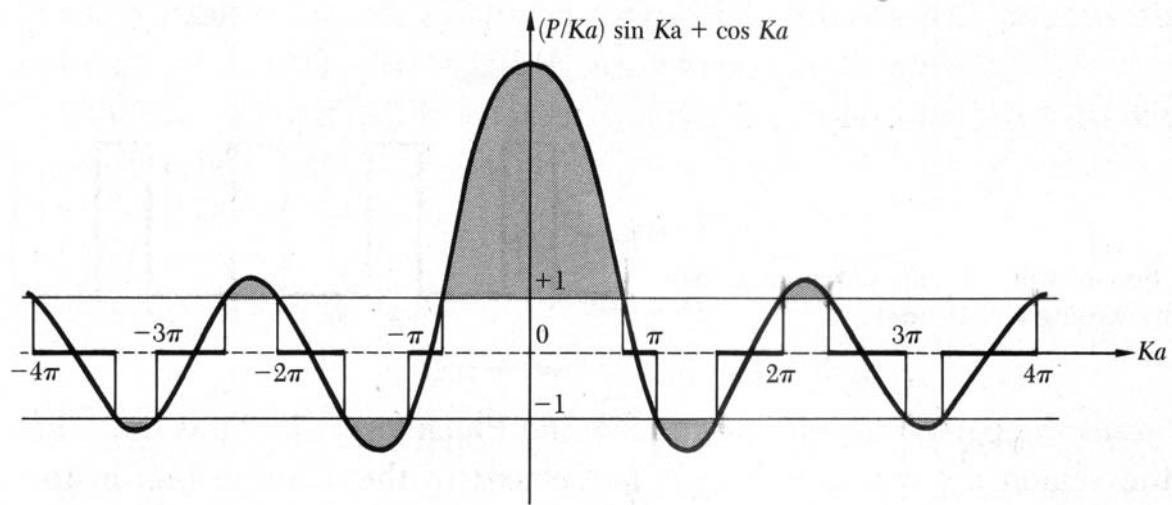
(AND THEREFORE  $E = \hbar^2 K^2 / 2m$ ) ARE ALLOWED.

SEE FIGURES 5 AND 6

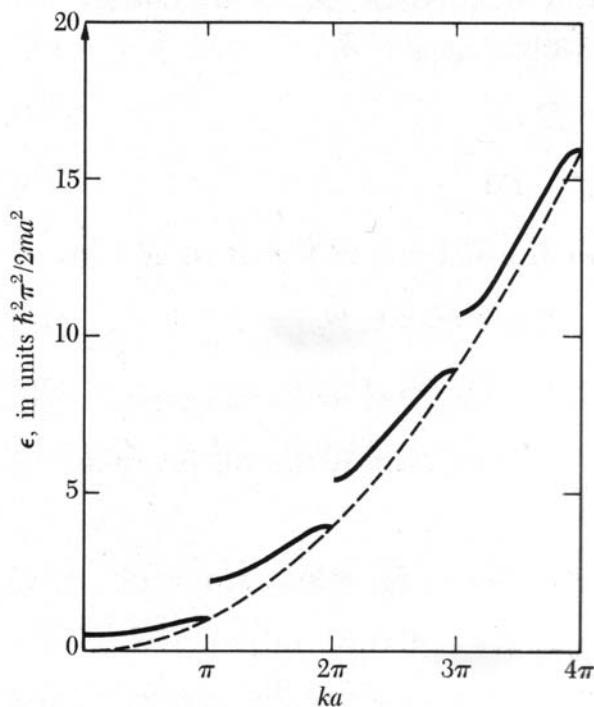
\* KRONIG-PENNEY LEADS TO THE SAME QUALITATIVE RESULT AS OUR PREVIOUS BRAGG REFLECTION ARGUMENT.



**Figure 3** (a) Variation of potential energy of a conduction electron in the field of the ion cores of a linear lattice. (b) Distribution of probability density  $\rho$  in the lattice for  $|\psi(-)|^2 \propto \sin^2 \pi x/a$ ;  $|\psi(+)|^2 \propto \cos^2 \pi x/a$ ; and for a traveling wave. The wavefunction  $\psi(+)$  piles up electronic charge on the cores of the positive ions, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave. The wavefunction  $\psi(-)$  piles up charge in the region between the ions, thereby raising the potential energy in comparison with that seen by a traveling wave. This figure is the key to understanding the origin of the energy gap.



**Figure 5** Plot of the function  $(P/Ka) \sin Ka + \cos Ka$ , for  $P = 3\pi/2$ . The allowed values of the energy  $\epsilon$  are given by those ranges of  $Ka = (2m\epsilon/\hbar^2)a$  for which the function lies between  $\pm 1$ . For other values of the energy there are no traveling wave or Bloch-like solutions to the wave equation, so that forbidden gaps in the energy spectrum are formed.



**Figure 6** Plot of energy vs. wavenumber for the Kronig-Penney potential, with  $P = 3\pi/2$ . Notice the energy gaps at  $ka = \pi, 2\pi, 3\pi \dots$