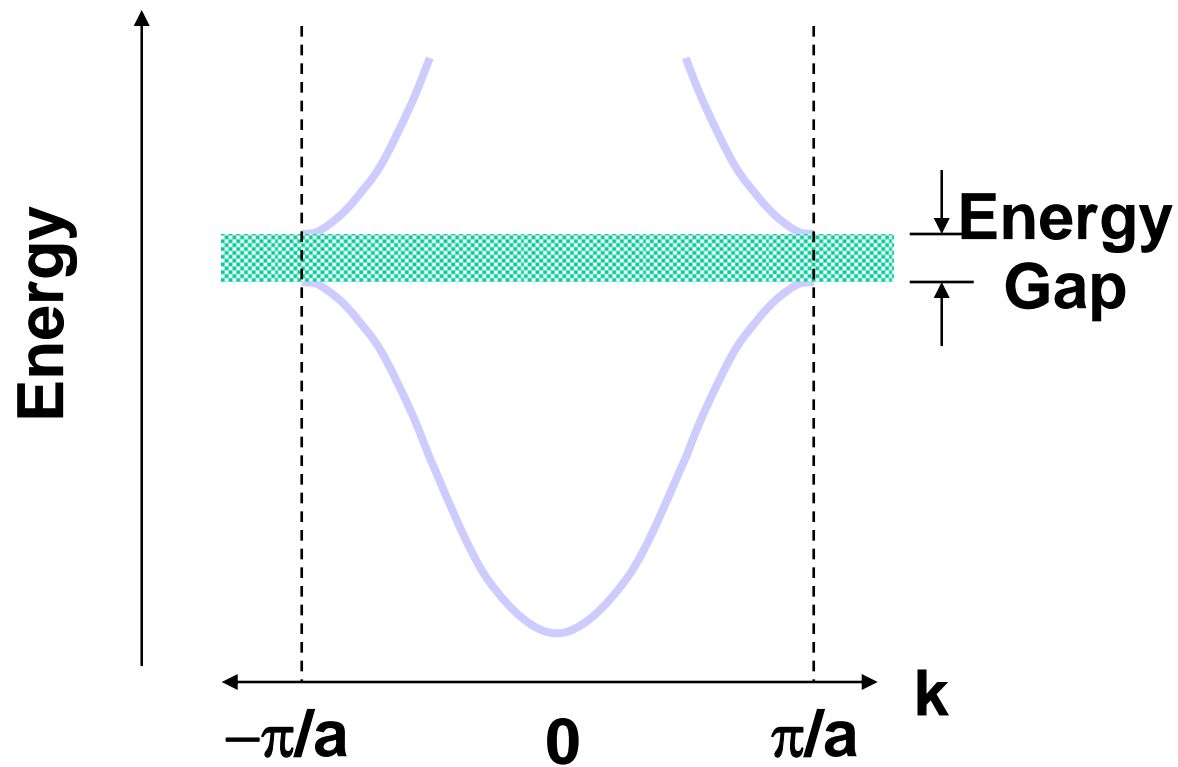


Energy Bands for Electrons in Crystals (Kittel Ch. 7)



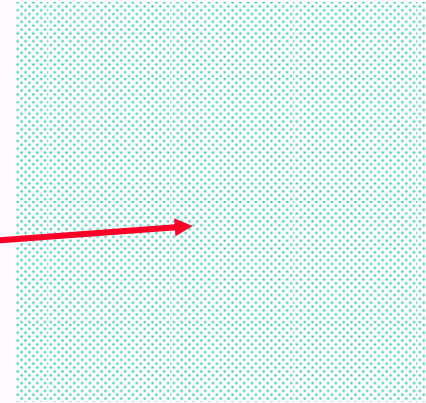
- Recall nature of free electron gas
 - Free electrons in box of size $L \times L \times L$
(artificial but useful)
 - Solved Schrodinger Equation
 - States classified by k with $E(k) = (\hbar^2/2m) k^2$
 - Periodic boundary conditions convenient:
Leads to $k_x = 2n\pi/L$, etc.
 - Pauli Exclusion Principle, Fermi Statistics
 - Simplest model for metals
- Why are some materials **insulators**, some **metals**?

- Recall nature of free electron gas
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 - Pauli Exclusion Principle, Fermi Statistics
 - Simplest model for metals
- Why are some materials **insulators**, some **metals**?
 - First step - NEARLY free electrons in a crystal
 - Simple picture of how **Bragg diffraction** leads to **standing waves** at the Brillouin Zone Boundary and to **energy gaps**

Understanding Electrons in Crystals

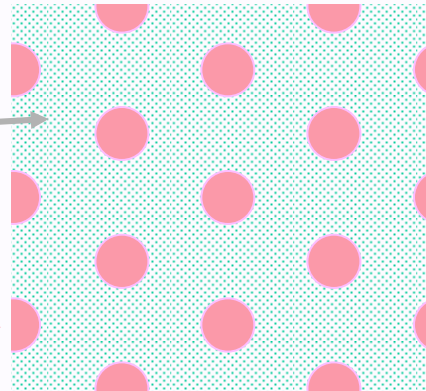
- **Electron Gas**

Simplest possible model for a metal - electrons are completely “free of the nuclei” - nuclei are replaced by a smooth background --
“Electrons in a box”



- **Real Crystal -**

Potential variation with the **periodicity of the crystal**



Attractive (negative) potential around each nucleus

Schrodinger Equation

- Basic equation of Quantum Mechanics

$$\left[- \left(\hbar^2/2m \right) \Delta^2 + V(\underline{\mathbf{r}}) \right] \Psi (\underline{\mathbf{r}}) = E \Psi (\underline{\mathbf{r}})$$

where

m = mass of particle

$V(\underline{\mathbf{r}})$ = potential energy at point $\underline{\mathbf{r}}$

$\Delta^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$

E = eigenvalue = energy of quantum state

$\Psi (\underline{\mathbf{r}})$ = wavefunction

$n (\underline{\mathbf{r}}) = | \Psi (\underline{\mathbf{r}}) |^2 =$ probability density

- Key Point for electrons in a crystal: The potential $V(\underline{\mathbf{r}})$ has the periodicity of the crystal

Schrodinger Equation

- How can we solve the Schrodinger Eq.

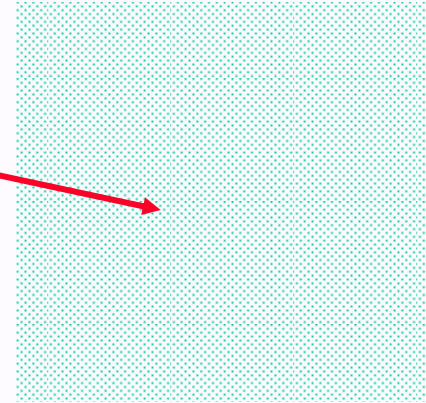
$$\left[- \left(\hbar^2 / 2m \right) \Delta^2 + V(\underline{r}) \right] \Psi(\underline{r}) = E \Psi(\underline{r})$$

where $V(\underline{r})$ has the periodicity of the crystal?

- **Difficult problem** - This is the basis of current research in the theory of electrons in crystals
- We will consider **simple cases** as an introduction
 - Nearly Free Electrons
 - Kronig-Penney Model

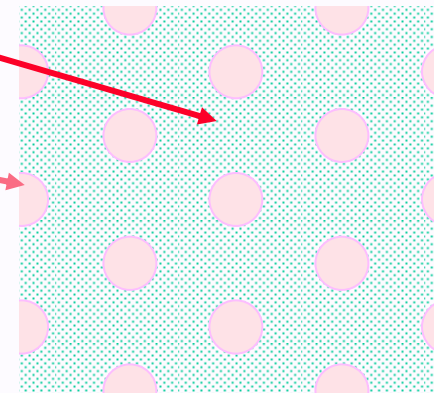
Next Step for Understanding Electrons in Crystals

- **Simplest extension of the Electron Gas model**



- **Nearly Free electron Gas -**
Very small potential variation
with the periodicity of the crystal

Very weak potentials
with crystal periodicity



- **We will first consider electrons in one dimension**

Consider 1 dimensional example

- If the electrons can move **freely** on a line from 0 to L
0 (with no potential),



we have seen **before** that :

- Schrodinger Eq. In 1D with $V = 0$
- $(\hbar^2/2m) d^2/dx^2 \Psi(x) = E \Psi(x)$
- Solution with $\Psi(x) = 0$ at $x = 0, L$
 $\Psi(x) = 2^{1/2} L^{-1/2} \sin(kx)$, $k = n \pi/L$, $n = 1, 2, \dots$

Fixed Boundary Condition

or

$$\Psi(x) = L^{-1/2} \exp(ikx), k = \pm n (2\pi/L), n = 0, 1, \dots$$

Periodic Boundary Condition

- $E(k) = (\hbar^2/2m) k^2$

Electrons on a line

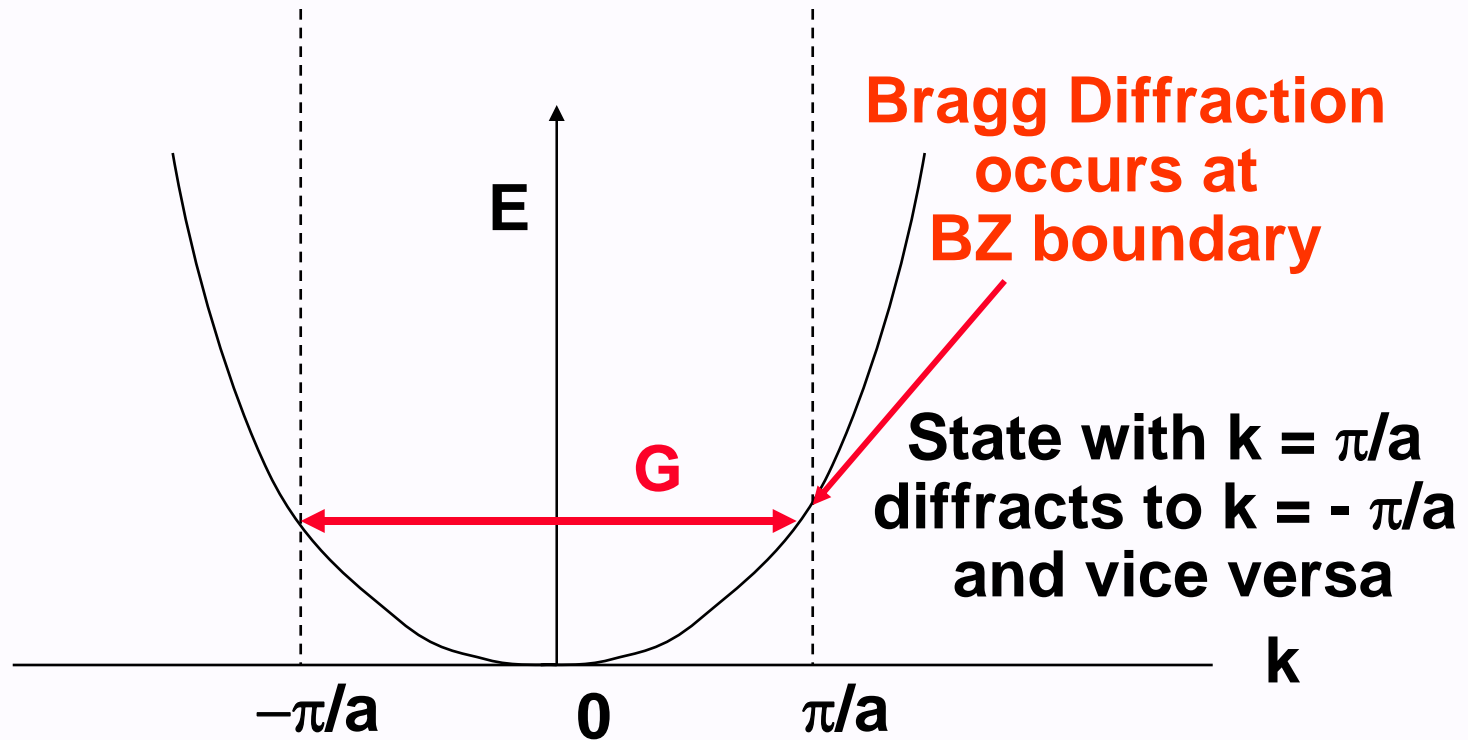
- For electrons in a box, the energy is just the kinetic energy

$$E(k) = \left(\hbar^2/2m \right) k^2$$

- Values of k fixed by the box, $k = \pm n (2\pi/L)$, $n = 0, 1, \dots$
- Crystal: $L = N_{\text{cell}} a$
- The maximum (Fermi) wavevector is determined by the number of free electrons
- $N_{\text{elec}}/2 = 2n_F + 1$, thus $n_F \sim N_{\text{elec}}/4$
- $k = \pm n (2\pi/N_{\text{cell}} a)$, $n = 0, 1, \dots N_{\text{elec}}/4$
- define number of electrons per cell N
- $k_F = N/2 (\pi/a)$

Electrons on a line with potential $V(x)$

- What happens if there is a potential $V(x)$ that has the periodicity a of the crystal?
- An electron wave with wavevector k can suffer Bragg diffraction to $k \pm G$, with G any reciprocal lattice vector

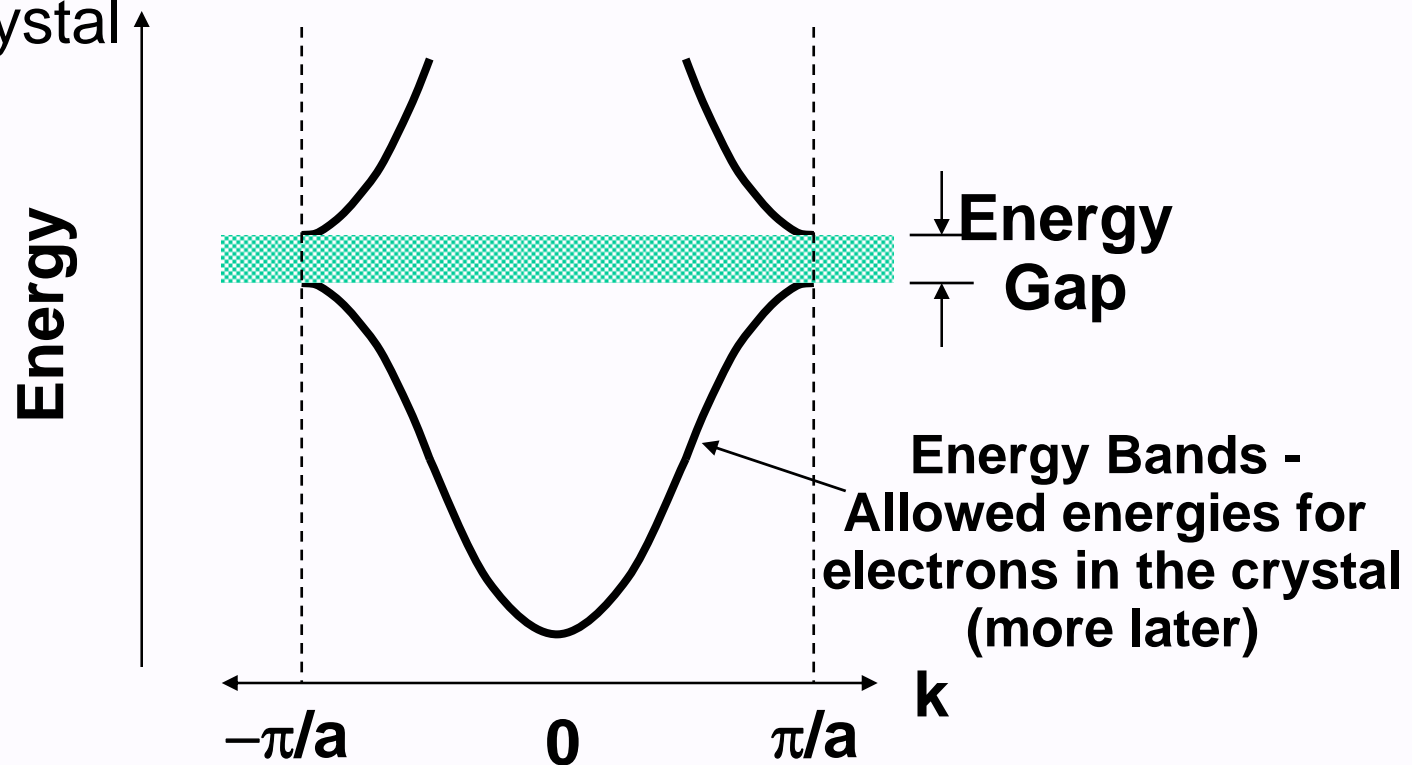


Electrons on a line with potential $V(x)$

- Result:

Standing wave at zone boundary

Energy gap where there are no waves that can travel in crystal



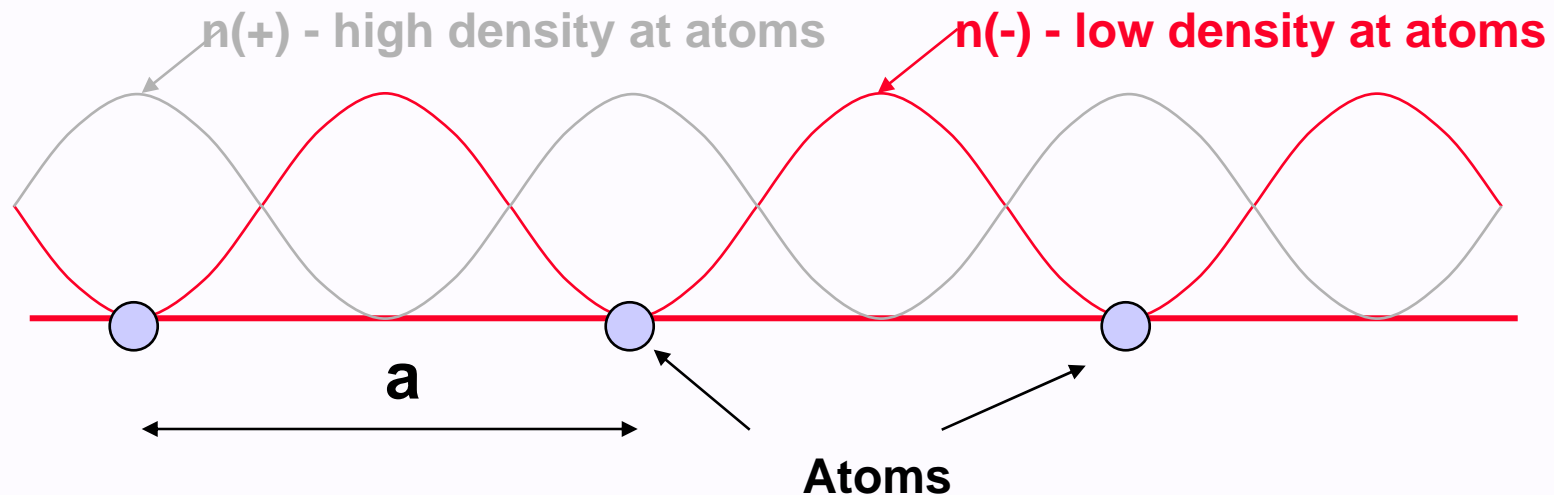
Interpretation of Standing waves at Brillouin Zone boundary

- Bragg scattering at $k = \pi/a$ leads to two possible combinations of the right and left going waves:

$$\Psi(+)= (2L)^{-1/2} [\exp(i\pi x/a) + \exp(-i\pi x/a)] = 2^{1/2} L^{-1/2} \cos(\pi x/a)$$

$$\Psi(-)= (2L)^{-1/2} [\exp(i\pi x/a) - \exp(-i\pi x/a)] = 2^{1/2} i L^{-1/2} \sin(\pi x/a)$$

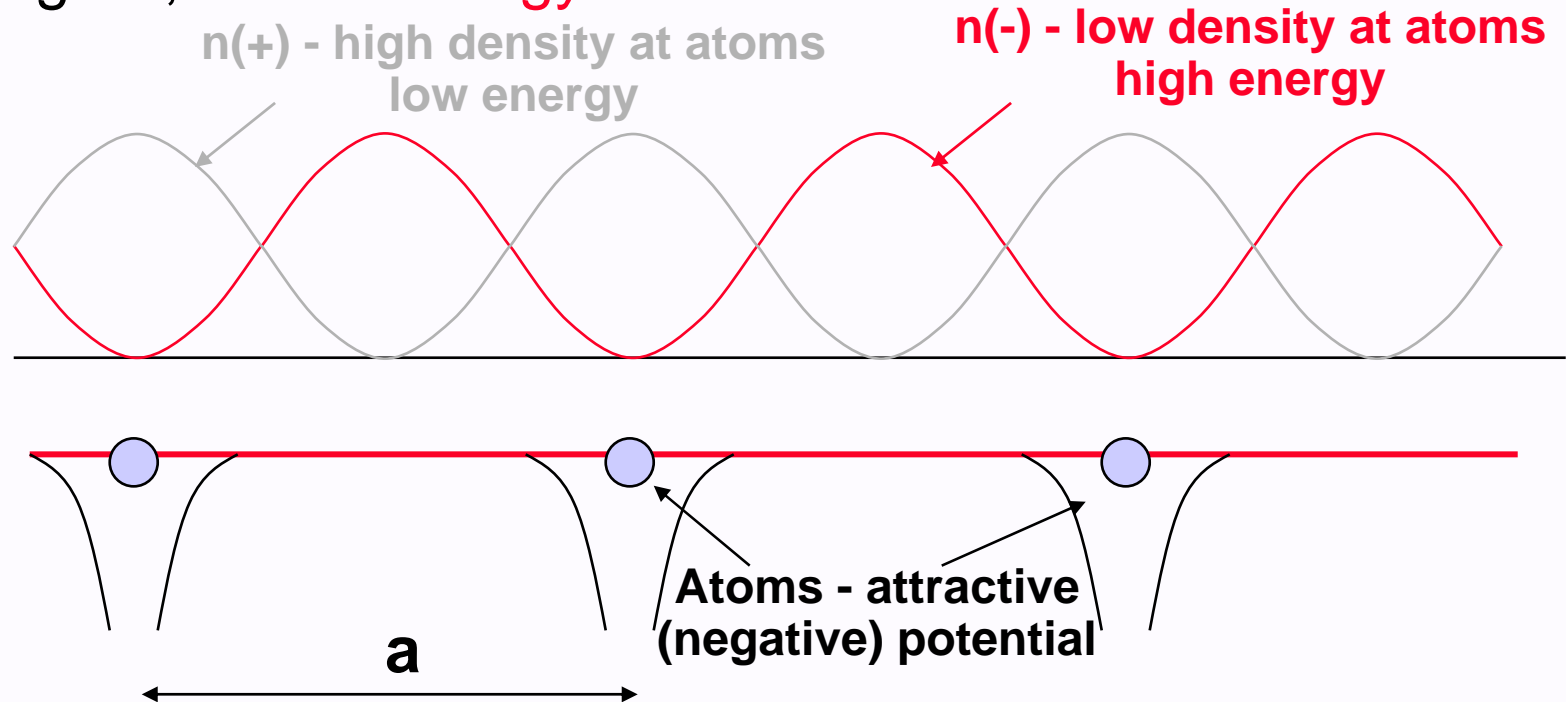
with density $n(+)= 2/L \cos^2(\pi x/a)$; $n(-)= 2/L \sin^2(\pi x/a)$



Energy difference between solutions

$$n(+)=2/L \cos^2(\pi x/a); n(-)=2/L \sin^2(\pi x/a)$$

for $n(+)$ the electrons are piled up on the positive ions, the magnitude of the **negative** potential energy is higher, so **the energy is lower**

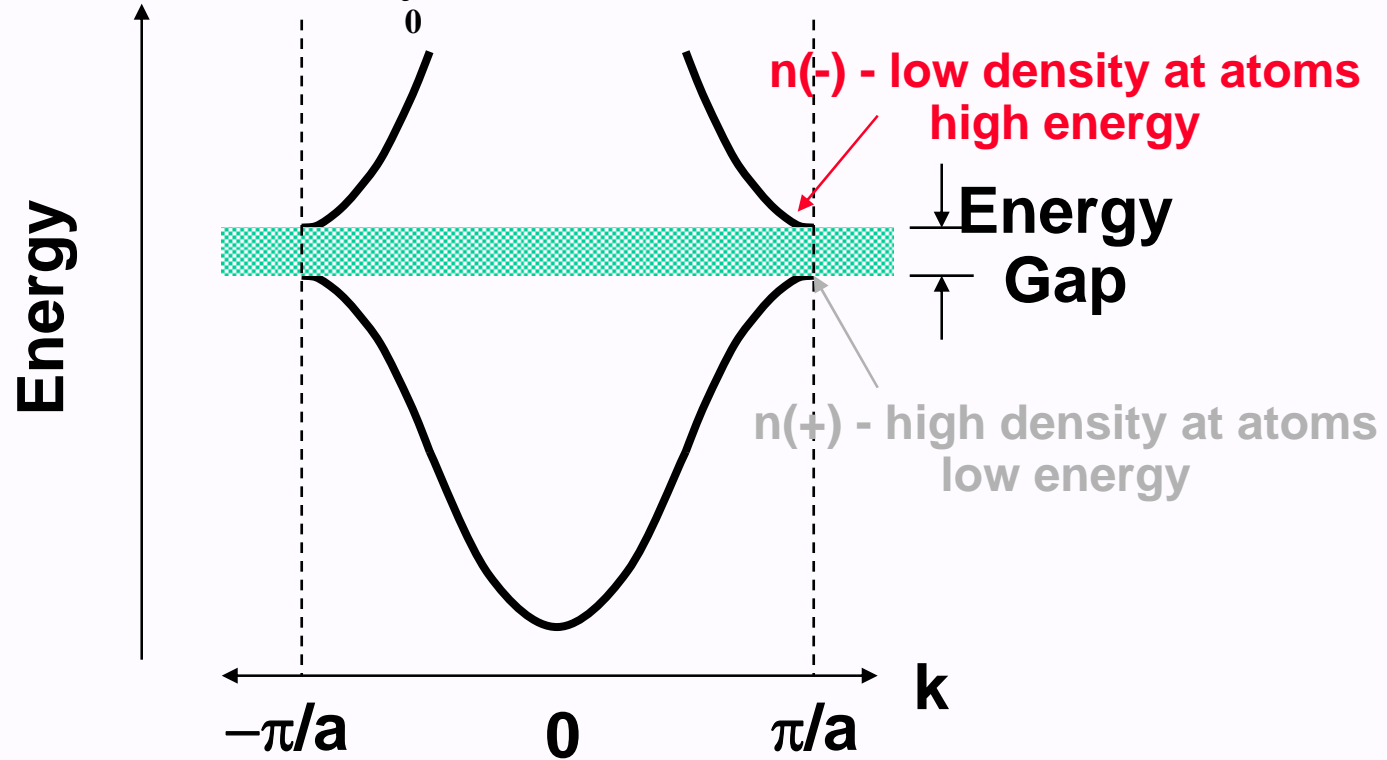


Electrons on a line with potential

$$V(x) = V \cos(2\pi x/a)$$

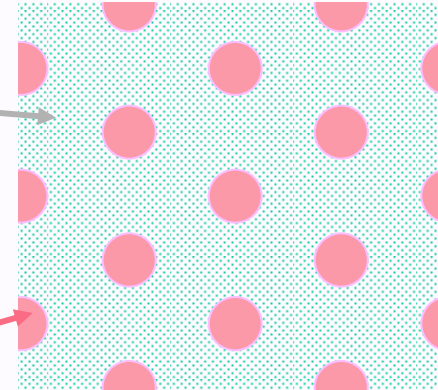
Energy gap -- energies at which no waves can travel through crystal

$$E_g = \int_0^L dx V(x) (n(+) - n(-)) = V$$



Understanding Electrons in Crystals

- Real Crystal -
Potential variation with
the **periodicity of the crystal**



Attractive (negative) potential
around each nucleus

- Potential leads to:
**Electron bands - $E(k)$ different from free
electron bands**
Band Gaps

Ex. In a 1D crystal $k_F = N/2 (\pi/a)$, where $N = \#$ of electrons per cell.
How many electron bands are expected for $N=1,2,3,\dots$?

Representing V as a periodic function

- We have seen (Kittel Ch 2) that any periodic function can be written as Fourier series

$$f(\underline{\mathbf{r}}) = \sum_{\underline{\mathbf{G}}} f_{\underline{\mathbf{G}}} \exp(i \underline{\mathbf{G}} \cdot \underline{\mathbf{r}})$$

where the $\underline{\mathbf{G}}$'s are reciprocal lattice vectors

$$\underline{\mathbf{G}}(m_1, m_2, \dots) = m_1 \underline{\mathbf{b}}_1 + m_2 \underline{\mathbf{b}}_2 + m_3 \underline{\mathbf{b}}_3$$

- Check: A periodic function satisfies

$$f(\underline{\mathbf{r}}) = f(\underline{\mathbf{r}} + \underline{\mathbf{T}}) \text{ where } \underline{\mathbf{T}} \text{ is any translation}$$

$$\underline{\mathbf{T}}(n_1, n_2, \dots) = n_1 \underline{\mathbf{a}}_1 + n_2 \underline{\mathbf{a}}_2 + n_3 \underline{\mathbf{a}}_3$$

the n 's are integers

- Thus $V(\underline{\mathbf{r}}) = \sum_{\underline{\mathbf{G}}} V_{\underline{\mathbf{G}}} \exp(i \underline{\mathbf{G}} \cdot \underline{\mathbf{r}})$
- And $V(\underline{\mathbf{r}}) = \text{real} \Rightarrow V_{\underline{\mathbf{G}}} = V_{-\underline{\mathbf{G}}}^*$ or if the crystal is symmetric $V_{\underline{\mathbf{G}}} = V_{-\underline{\mathbf{G}}}$

Schrodinger Equation - Again

- In a periodic crystal

$$\left[- \left(\hbar^2/2m \right) \Delta^2 + \sum_{\underline{\mathbf{G}}} V_{\underline{\mathbf{G}}} \exp(i \underline{\mathbf{G}} \cdot \underline{\mathbf{r}}) \right] \Psi (\underline{\mathbf{r}}) = E \Psi (\underline{\mathbf{r}})$$

- Now assume $\Psi (\underline{\mathbf{r}}) = \sum_{\underline{\mathbf{k}}} c_{\underline{\mathbf{k}}} \exp(i \underline{\mathbf{k}} \cdot \underline{\mathbf{r}})$

- Note we do NOT assume Ψ has the periodicity of the lattice! It is a superposition of waves!

- What is $\underline{\mathbf{k}}$?

Just as before for electrons in a box, we assume

$\Psi (\underline{\mathbf{r}})$ is periodic in a large box (L x L x L) which leads to

$$k_x = \pm n_x (2\pi/L), n = 0, 1, \dots \quad | \underline{\mathbf{k}} | = n (2\pi/L)$$

Schrodinger Equation - Continued

- Then the Schrodinger Eq. becomes:

$$\sum_{\underline{k}} c_{\underline{k}} \lambda_{\underline{k}} \exp(i \underline{k} \cdot \underline{r}) + \sum_{\underline{k}} c_{\underline{k}} \sum_{\underline{G}} V_{\underline{G}} \exp(i (\underline{k} + \underline{G}) \cdot \underline{r})] \\ = E \sum_{\underline{k}} c_{\underline{k}} \exp(i \underline{k} \cdot \underline{r})$$

where $\lambda_{\underline{k}} = (\hbar/2m) |\underline{k}|^2$

- Introduce $\underline{k}' = \underline{k} + \underline{G}$ then relabel \underline{k}' as \underline{k}

$$\sum_{\underline{k}} \{ [\lambda_{\underline{k}} - E] c_{\underline{k}} + \sum_{\underline{G}} V_{\underline{G}} c_{\underline{k}-\underline{G}} \} \exp(i \underline{k} \cdot \underline{r}) = 0$$

- Equating terms with the same \underline{r} dependence on the two sides on the equation, we find the “Central Equation”

$$[\lambda_{\underline{k}} - E] c_{\underline{k}} + \sum_{\underline{G}} V_{\underline{G}} c_{\underline{k}-\underline{G}} = 0$$

“Central Equation” for electron bands

- What is the interpretation of the equation:

$$[\lambda_{\underline{k}} - E] c_{\underline{k}} + \sum_{\underline{G}} V_{\underline{G}} c_{\underline{k}-\underline{G}} = 0$$

- If $V_{\underline{G}} = 0$ (no potential - free electrons) then each \underline{k} is independent and each wavefunction is

$$\Psi_{\underline{k}}(\underline{r}) = c_{\underline{k}} \exp(i \underline{k} \cdot \underline{r}) ; E = \lambda_{\underline{k}} = (\hbar^2/2m) |\underline{k}|^2$$

- If $V_{\underline{G}} \neq 0$, then each \underline{k} is mixed with $\underline{k} - \underline{G}$ where \underline{G} is any reciprocal lattice vector -- the solution is

$$\Psi_{\underline{k}}(\underline{r}) = \sum_{\underline{G}} c_{\underline{k}-\underline{G}} \exp(i (\underline{k} - \underline{G}) \cdot \underline{r})$$

←
Yet to be determined

Bloch Theorem

- One of the most important equations of the course!
- In a general crystal, the wave function for an electron has the form:

$$\Psi_{\underline{k}}(\underline{r}) = \sum_{\underline{G}} c_{\underline{k}-\underline{G}} \exp(i(\underline{k} - \underline{G}) \cdot \underline{r})$$

which can be written

$$\Psi_{\underline{k}}(\underline{r}) = \exp(i \underline{k} \cdot \underline{r}) u_{\underline{k}}(\underline{r})$$

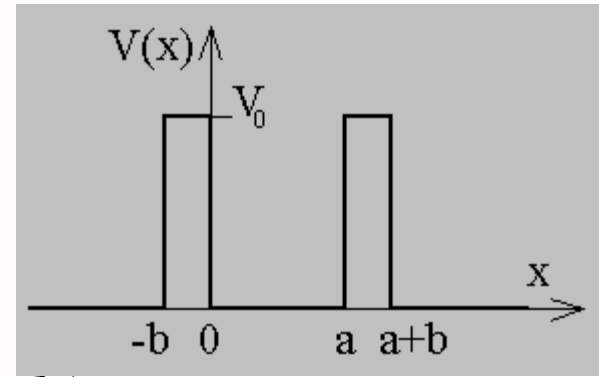
where $u_{\underline{k}}(\underline{r})$ is the periodic function with the periodicity of the crystal lattice

$$u_{\underline{k}}(\underline{r}) = \sum_{\underline{G}} c_{\underline{k}-\underline{G}} \exp(-i \underline{G} \cdot \underline{r})$$

Kronig-Penney model

square well potential

$$U(x) = \begin{cases} 0 & \text{for } n(a+b) < x < (n+1)a + nb \\ U_0 & \text{for } (n+1)a + nb < x < (n+1)(a+b) \end{cases}$$



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

Combination of traveling waves where $U=0$, exponential penetration into the $U=U_0$ region

$$\psi(x) = \begin{cases} A \exp(iKx) + B \exp(-iKx) & \text{for } 0 < x < a \\ C \exp(Qx) + D \exp(-Qx) & \text{for } a < x < a+b \end{cases}$$

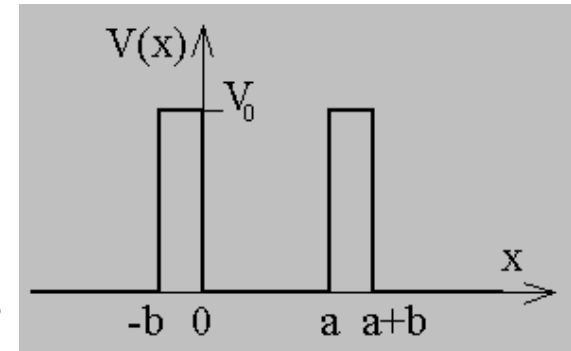
The solution must satisfy the Bloch theorem

$$\Psi_{\underline{k}}(x) = \exp(i\mathbf{k}(a+b)) \Psi_{\underline{k}}(x-a-b)$$

Periodicity of the lattice, \mathbf{k} is like a reciprocal vector

Kronig-Penney model

$$\psi(x) = \begin{cases} A \exp(iKx) + B \exp(-iKx) & \text{for } 0 < x < a \\ C \exp(Qx) + D \exp(-Qx) & \text{for } a < x < a + b \end{cases}$$



$$\Psi(a) = \exp(ik(a+b)) \Psi(-b)$$

boundary conditions: $\Psi(x)$, $d\Psi(x)/dx$ continuous

$$x=0: A+B = C+D, \quad iK(A-B) = Q(C-D)$$

$$x=a: A \exp(iKa) + B \exp(-iKa) = [C \exp(-Qb) + D \exp(Qb)] \exp(ik(a+b))$$

$$iK[A \exp(iKa) - B \exp(-iKa)] = Q [C \exp(-Qb) - D \exp(Qb)] \exp(ik(a+b))$$

Solution if determinant vanishes – relationship between a , b , Q , K , k

Kronig-Penney model - limiting case

Assume $b=0$, $U_0 \sim \infty$, $Q^2ba/2=P$

$$(P/Ka) \sin Ka + \cos Ka = \cos ka$$

Solution only when l.h.s. < 1

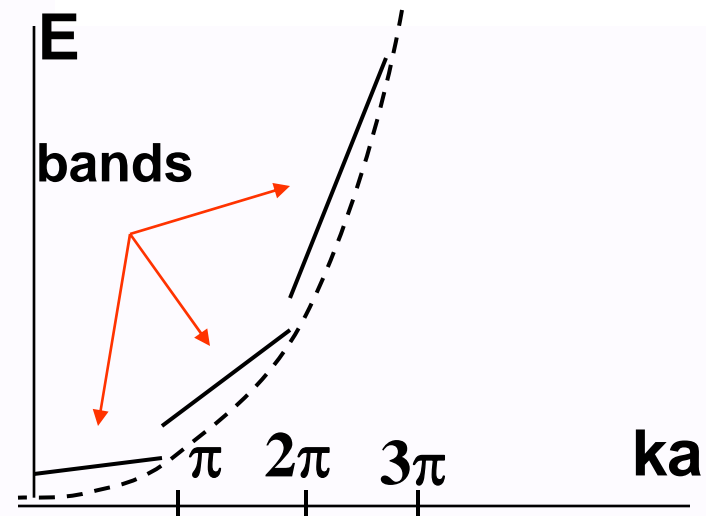
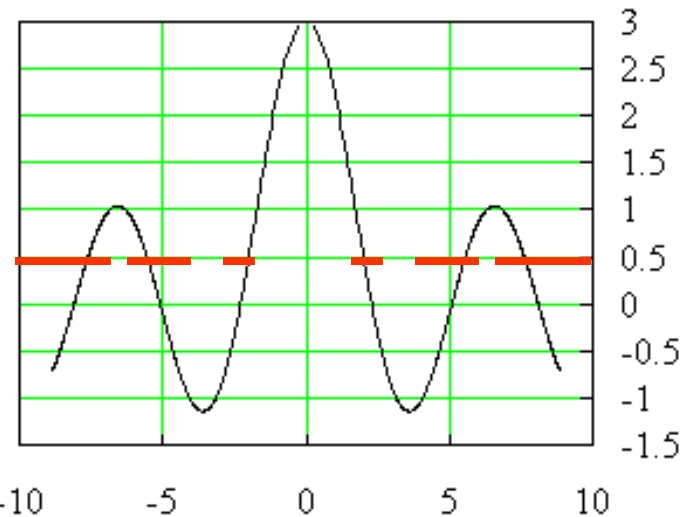
energy gaps at $k=0, \pm \pi/a, \dots$

$$E(k) = \left(\frac{\hbar^2}{2m} \right) K^2$$

Since K depends on P

E is plotted vs. ka

E is not $\sim k^2$



Bloch Theorem - II

- The general form is

$$\Psi_{\underline{k}}^n(\underline{r}) = \exp(i \underline{k} \cdot \underline{r}) u_{\underline{k}}^n(\underline{r})$$

where $u_{\underline{k}}^n(\underline{r})$ is a periodic function. Here n labels different bands

- Key Points:

- 1) Each state is labeled by a wave vector \underline{k}
- 2) \underline{k} can be restricted to the first Brillouin Zone
This may be seen since

$$\begin{aligned}\Psi_{\underline{k}+\underline{G}'}(\underline{r}) &= \exp(i(\underline{k} + \underline{G}') \cdot \underline{r}) u_{\underline{k}+\underline{G}'}(\underline{r}) \\ &= \exp(i \underline{k} \cdot \underline{r}) u'_{\underline{k}}(\underline{r})\end{aligned}$$

where $u'_{\underline{k}}(\underline{r}) = \exp(i \underline{G}' \cdot \underline{r}) u_{\underline{k}+\underline{G}'}(\underline{r})$ is just another periodic function

Bloch Theorem - III

- Thus a wavefunction in a crystal can always be written

$$\Psi_{\underline{k}}^n(\underline{r}) = \exp(i \underline{k} \cdot \underline{r}) u_{\underline{k}}^n(\underline{r})$$

where:

$u_{\underline{k}}^n(\underline{r})$ is a periodic function

n labels different bands

\underline{k} is restricted to the first Brillouin Zone

- In the limit of a large system

k becomes continuous

n is discrete index: $n = 1, 2, 3, \dots$

The total number of $\underline{\mathbf{k}}$ values

- We can use the idea of periodic boundary conditions on a box of size $L \times L \times L$ - same as for phonons, electrons in a box,...
- Volume per $\underline{\mathbf{k}}$ point = $(2\pi/L)^3$
- Total number of $\underline{\mathbf{k}}$ points in Brillouin zone
$$N_{\text{k-point}} = V_{\text{BZ}} / (2\pi/L)^3 = (2\pi/a)^3 (L/2\pi)^3 = (L/a)^3 = N_{\text{cell}}$$

Each primitive cell contributes exactly one independent value of $\underline{\mathbf{k}}$ to each energy band.

Taking the two spin orientations into account, there are $2N_{\text{cell}}$ independent orbitals in each energy band.

Solving the “Central Equation”

- Simple cases where we can solve

$$[\lambda_{\underline{k}} - E] c_{\underline{k}} + \sum_{\underline{G}} V_{\underline{G}} c_{\underline{k}-\underline{G}} = 0$$

- If $V_{\underline{G}}$ is weak, then we can solve the nearly free electron problem (and find the solution we saw earlier in the chapter).
- For \underline{k} near BZ boundary, the wave $\exp(i \underline{k} \cdot \underline{r})$ is mixed strongly with $\exp(i (\underline{k} - \underline{G}) \cdot \underline{r})$, where \underline{G} is the *single* vector that leads to $|\underline{k}| \sim |\underline{k} - \underline{G}|$
- Let $V = V_{\underline{G}} = V_{-\underline{G}}$ for that \underline{G}

Solving the Central Equation

- Leads to two coupled equations

$$[\lambda_{\underline{k}} - E] c_{\underline{k}} + V c_{\underline{k}-\underline{G}} = 0$$

$$[\lambda_{\underline{k}-\underline{G}} - E] c_{\underline{k}-\underline{G}} + V c_{\underline{k}} = 0$$

- or
$$\begin{vmatrix} [\lambda_{\underline{k}} - E] & V \\ V & [\lambda_{\underline{k}-\underline{G}} - E] \end{vmatrix} = 0$$

- Solution

$$E = (1/2) (\lambda_{\underline{k}} + \lambda_{\underline{k}-\underline{G}}) \pm [(1/4) (\lambda_{\underline{k}} - \lambda_{\underline{k}-\underline{G}})^2 + V^2]^{1/2}$$

and

$$c_{\underline{k}-\underline{G}} = [(-\lambda_{\underline{k}} + E)/V] c_{\underline{k}}$$

Solutions in 1D

$$E = (1/2) (\lambda_{\underline{k}} + \lambda_{\underline{k}-\underline{G}}) \pm [(1/4) (\lambda_{\underline{k}} - \lambda_{\underline{k}-\underline{G}})^2 + V^2]^{1/2}$$

$$c_{\underline{k}-\underline{G}} = [(-\lambda_{\underline{k}} + E)/V] c_{\underline{k}}$$

BZ boundary: $\underline{k} = \pi/a \underline{i}$, $\underline{k}-\underline{G} = -\pi/a \underline{i}$ (unit vector)

$$\lambda_{\underline{k}} = \lambda_{\underline{k}-\underline{G}} = \lambda,$$

$$E_- = \lambda - V, \quad E_+ = \lambda + V$$

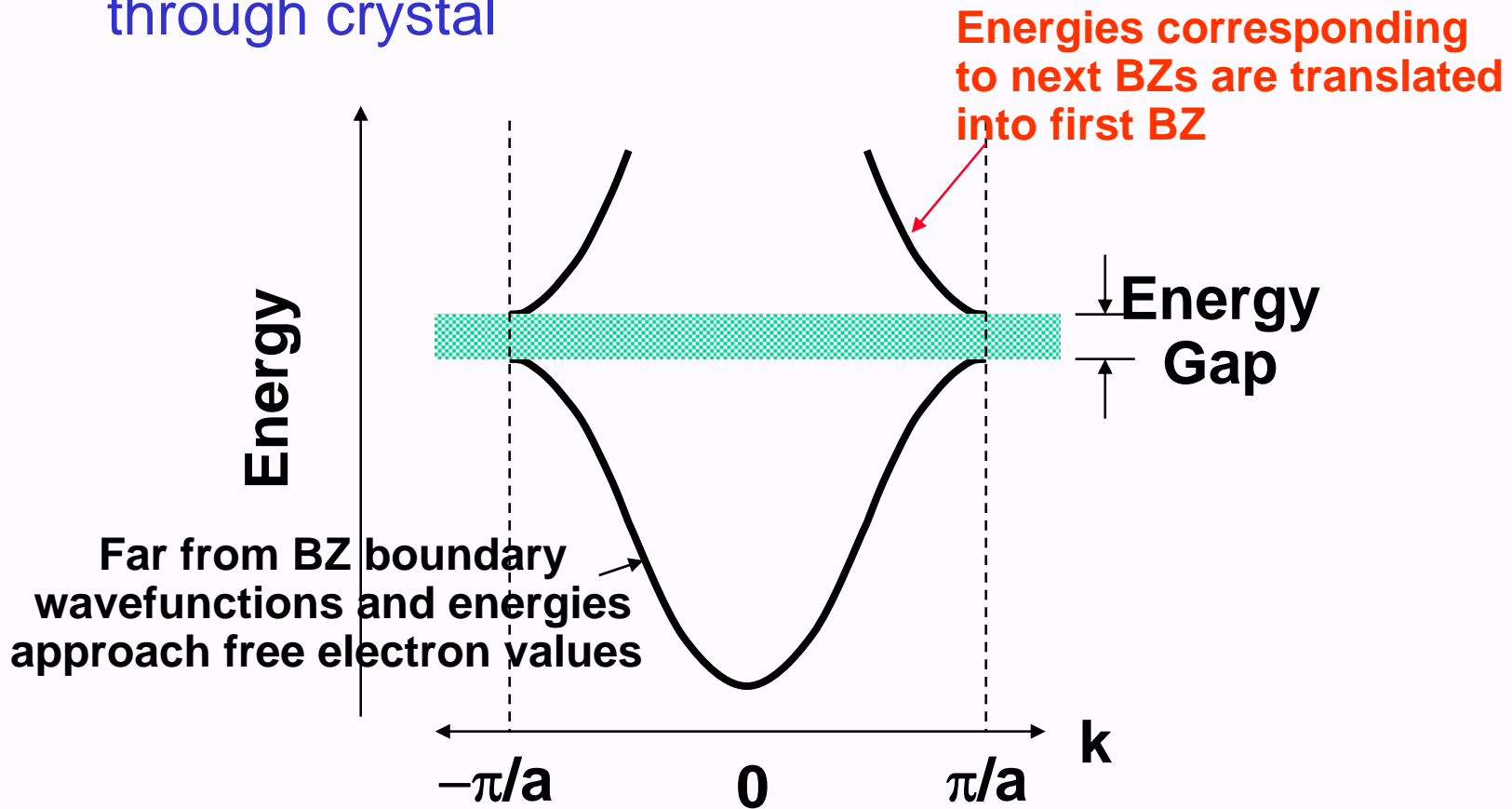
$$c_{\underline{k}-\underline{G}} = \pm c_{\underline{k}}$$

$$\Psi (+) = c_{\underline{k}} [\exp(i \pi x/a) + \exp(-i \pi x/a)]$$

$$\Psi (-) = c_{\underline{k}} [\exp(i \pi x/a) - \exp(-i \pi x/a)]$$

Nearly Free Electrons on a line

- Bands changed greatly only at zone boundary
Energy gap -- energies at which no waves can travel through crystal



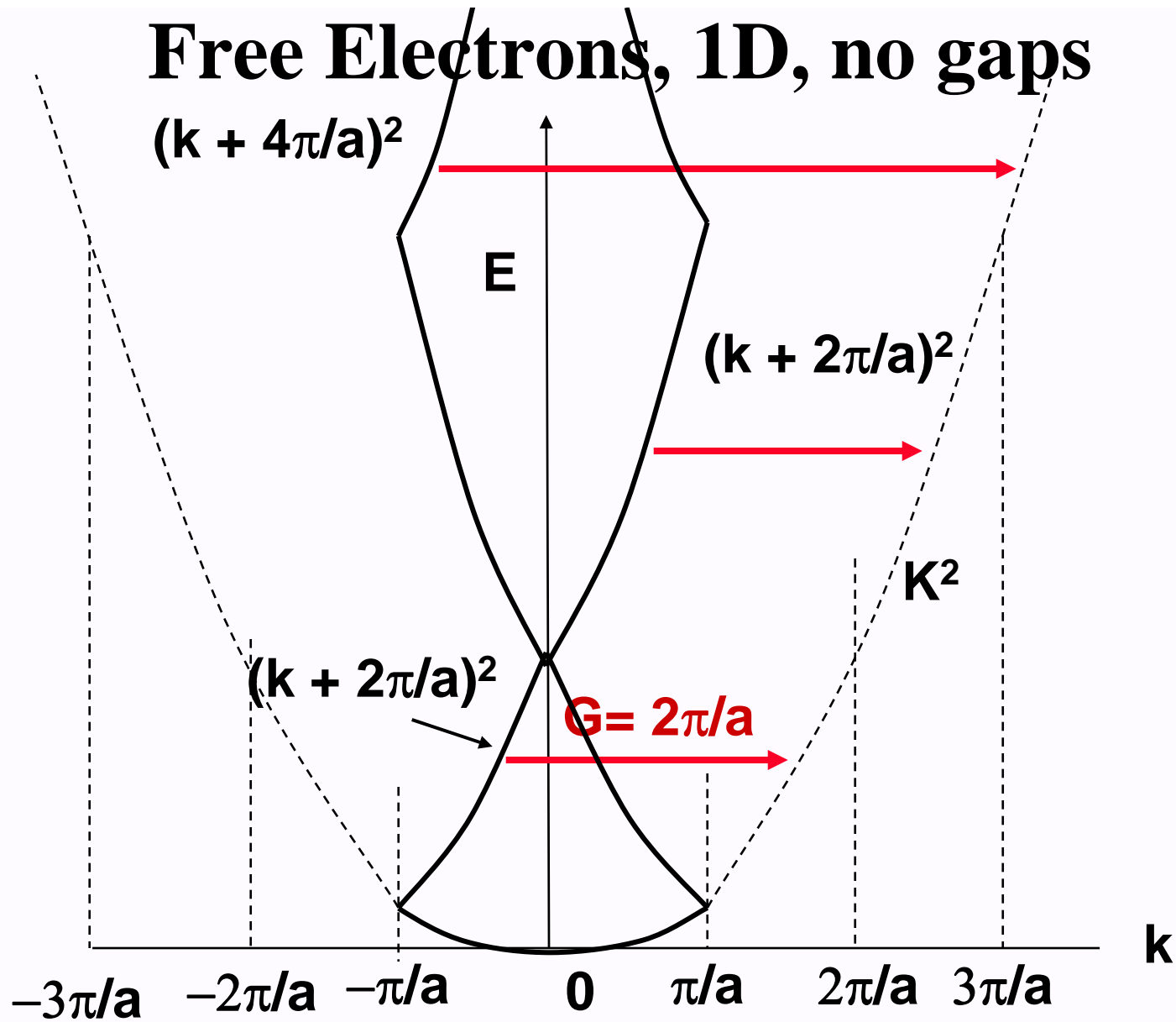
How to apply this idea in general

- First find free electron bands **plotted in BZ**
- The energy is **ALWAYS** $E(\mathbf{K}) = (\hbar^2/2m) K^2$ but now we “reduce” \mathbf{K} to first BZ, i.e., **we find \mathbf{G} such that $\mathbf{K} = \mathbf{k} + \mathbf{G}$** , and \mathbf{k} is in the first BZ
- $\mathbf{G}(m_1, m_2, \dots) = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3$
- $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$

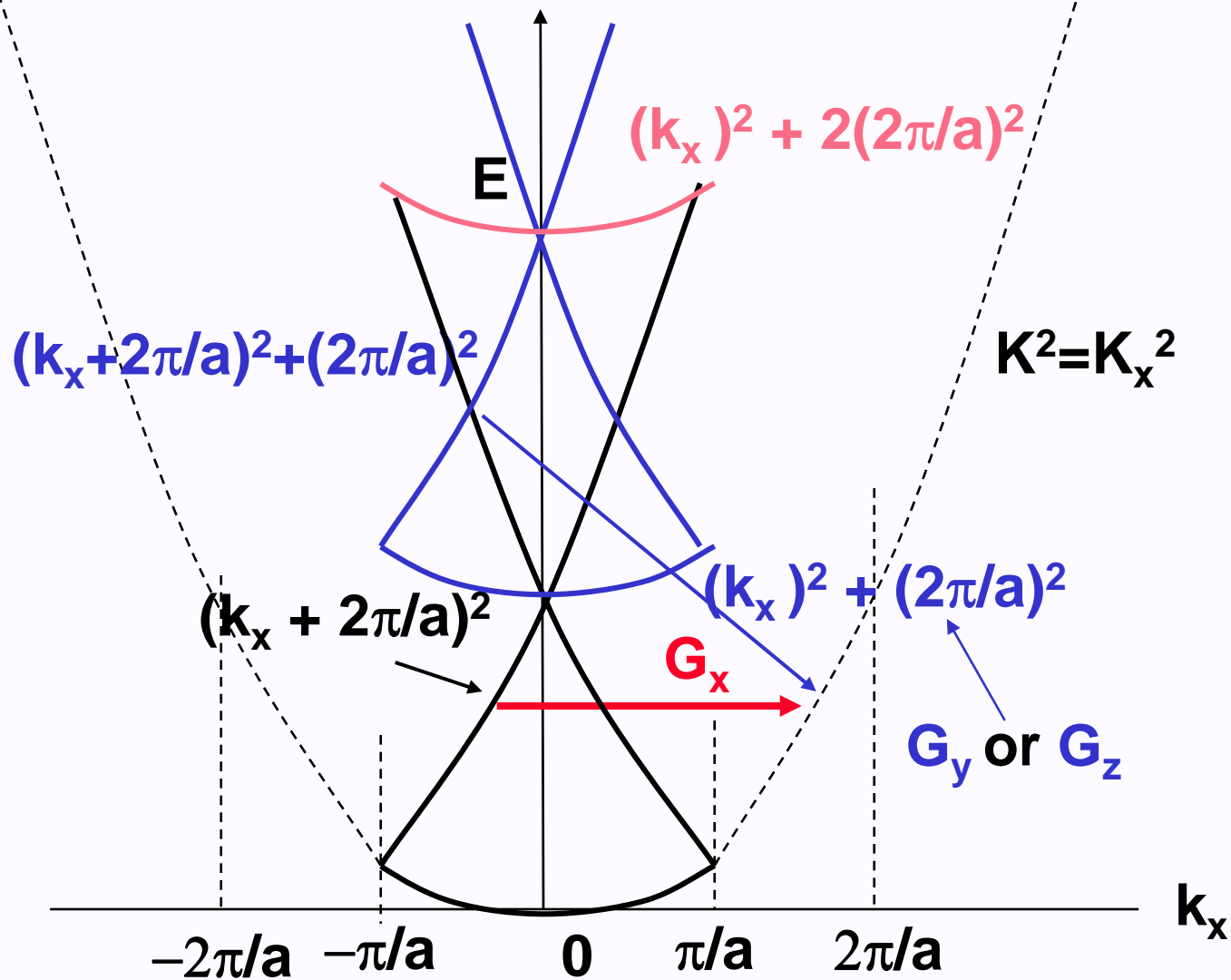
$$E(\mathbf{k}) = \frac{\hbar^2}{2m} (\vec{k} + \vec{G})^2 = \frac{\hbar^2}{2m} \left((k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2 \right)$$

- Then add effects of potential – energy gaps

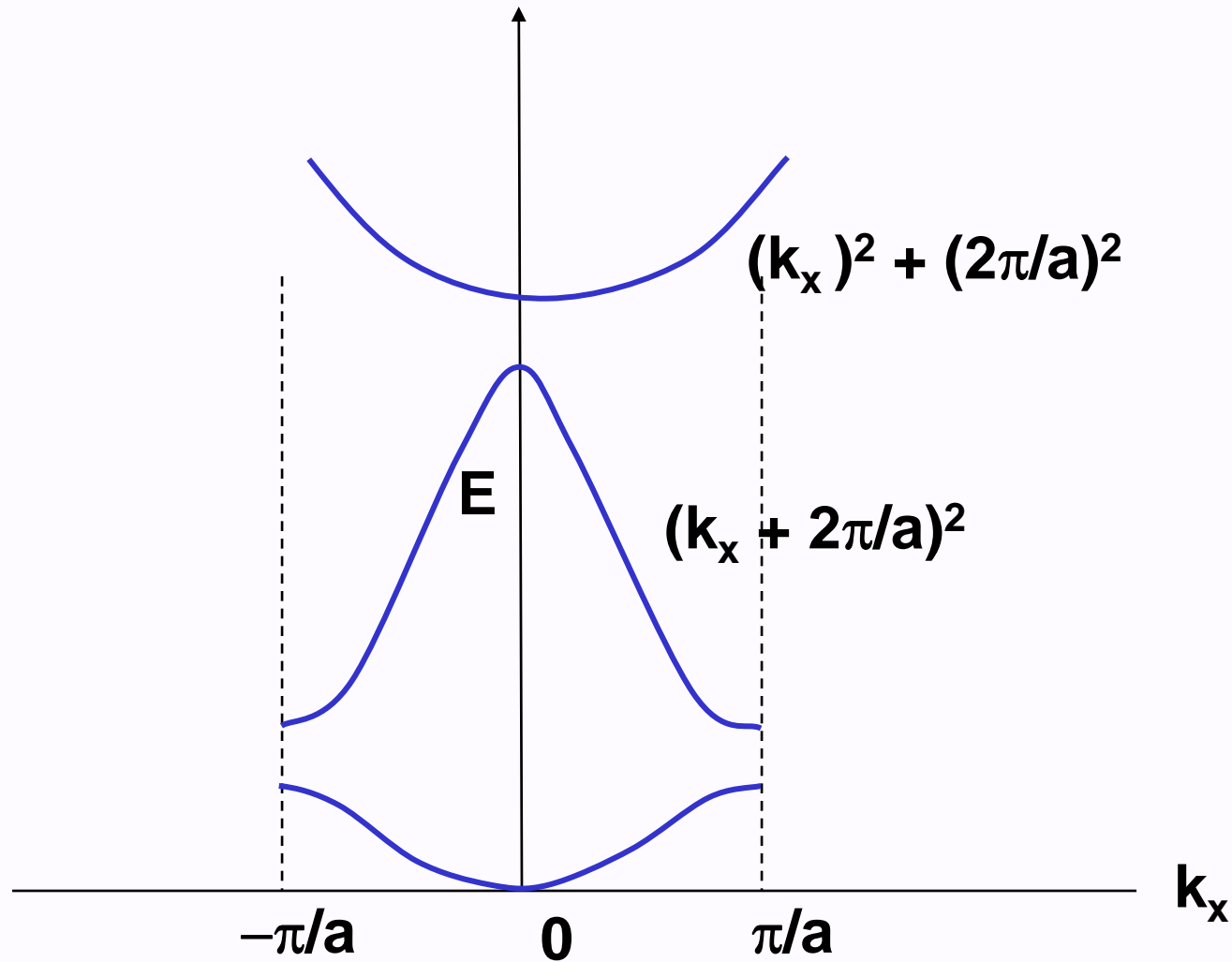
Free Electrons, 1D, no gaps



Free Electrons, 3D, simple cubic, $\mathbf{K}=(K_x,0,0)$

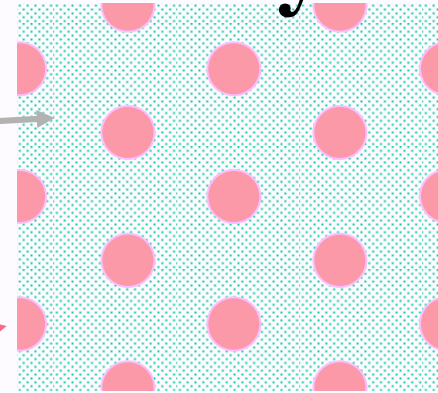


Nearly Free Electrons, 3D, schematic



Understanding Electrons in Crystals

- Real Crystal - Potential variation with the **periodicity of the crystal**



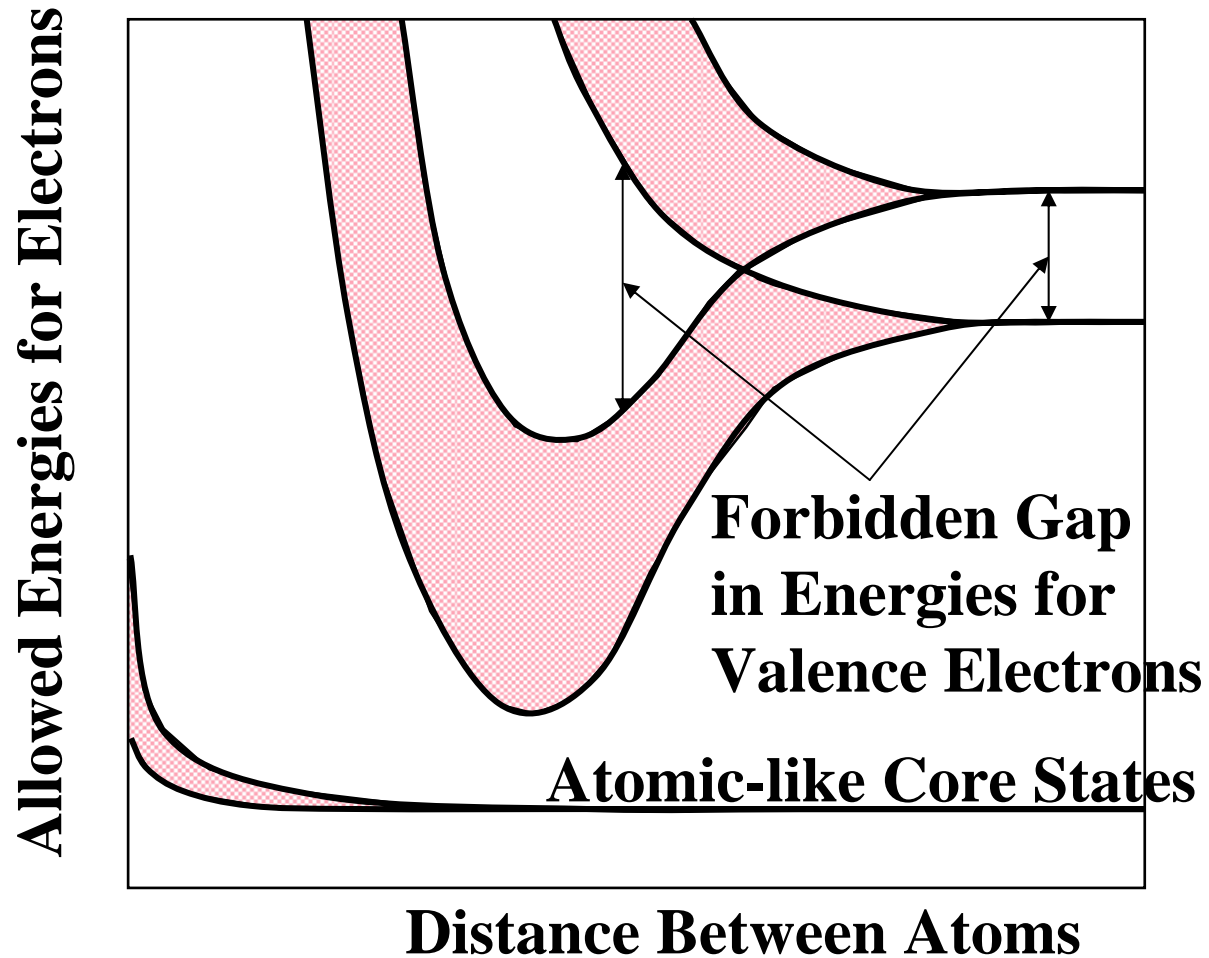
Attractive (negative) potential around each nucleus

The nearly free electron cases show the general form of bands:

Continuous bands of allowed states

Gaps where there are no states for the particular k points

Qualitative Picture of Electron Energy Bands and Gaps in Solids

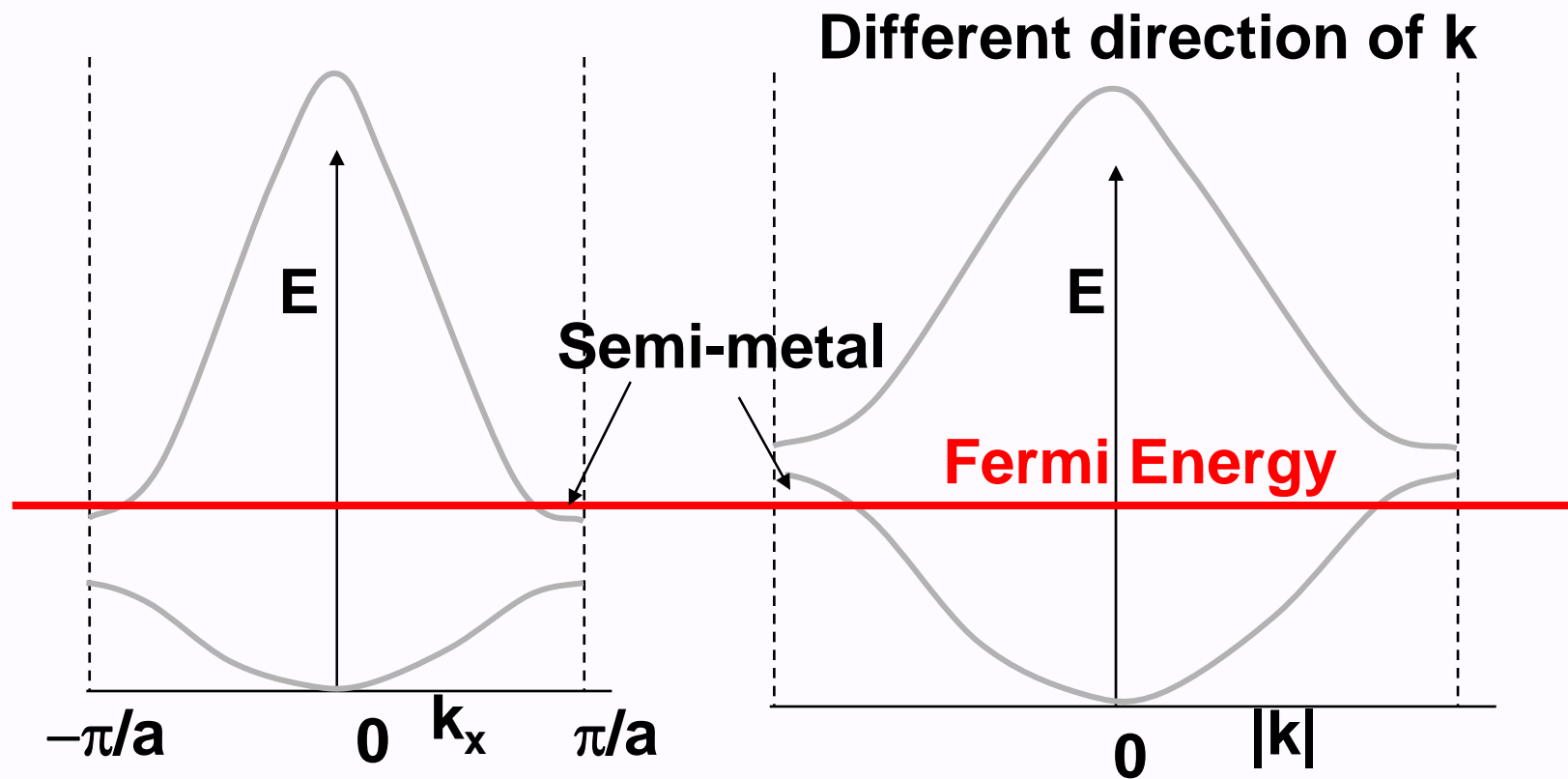


Metals vs Insulators

- A band holds two electrons per each cell
- Therefore a crystal with an **odd** number of electrons per cell **MUST*** be a **metal!**
 - Partially filled bands lead to Fermi energy and “Fermi surface” in k space
 - Conductivity** because states can change and scatter when electric field is applied
- A crystal with an **even** number of electrons per cell **MAY** be an **insulator!**
 - Electrons “frozen”
 - Gap in energy for any excitations of electrons**

Metals vs Insulators

- In 1d an **even** number of electrons per cell always leads to an **insulator**!
- In higher d, it depends on size of gaps



Summary

- Solving the “Central Equation” in Fourier space

Bloch Theorem

Bloch states for electrons in crystals

- Nearly Free Electrons
 - General Rules
 - First Free electron bands
 - Then add effects of small potential
- Energy Bands and Band Gaps -- basis for understanding metals vs. insulators
- Read Kittel Ch 7