Lecture 9

Reading Material

Reading:

Finish Chapter 7 Solymar and Walsh

Effective Mass

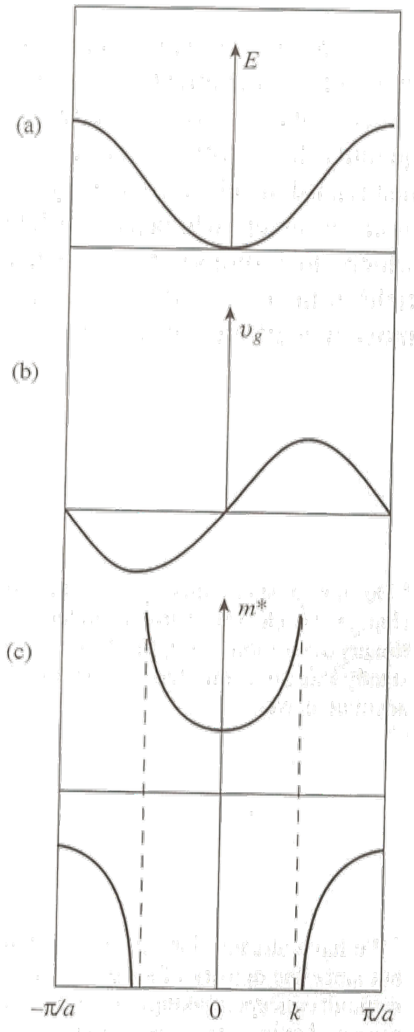
- In a one dimensional lattice, the effective mass can be written as

$$m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$$

$$= \hbar^2 \left(\frac{\partial^2 \left(E_1 - 2A\cos(ka) \right)}{\partial k^2} \right)^{-1}$$

$$= \frac{\hbar^2}{2Aa^2} \sec(ka)$$

- Plots of E vs. ν_g and m^* are shown to the right. Note that as an electron is moved from rest to higher and higher velocities its mass increases, reaching infinite mass at k=π/2a



Effective Mass

- For a 3D crystal, we can extend these results to propagation in x, y or z

$$\begin{pmatrix} m_x^* \\ m_y^* \\ m_z^* \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{2A_x a^2}\sec(k_x a) \\ \frac{\hbar^2}{2A_y b^2}\sec(k_y b) \\ \frac{\hbar^2}{2A_z c^2}\sec(k_z c) \end{pmatrix}$$

- An even in arbitrary directions, e.g. the xy plane

$$m_{xy}^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k_x \partial k_y} \right)^{-1}$$

Effective Number of Free Electrons

- In order to derive a formula for the effective number of free electrons, lets take the one dimensional case and use an approach similar to what we used in the effective mass case. The acceleration of the electron can be given by

$$a_e = \frac{d\upsilon_g}{dt} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2} qF_e$$

- Summing over all electrons in occupied states and considering the rate of change of electric current in response to an applied electric field

$$\frac{dI}{dt} = \sum \frac{d\left(q\upsilon_g\right)}{dt}$$

$$= \frac{1}{\hbar^2} q^2 F_e \sum \frac{\partial^2 E}{\partial k^2}$$, and considering the limit where the density of states in the range dk is dk/π

$$= \frac{1}{\hbar^2} q^2 F_e \frac{1}{\pi} \int \frac{\partial^2 E}{\partial k^2} dk$$

Effective Number of Free Electrons

- Assuming N non-interacting electrons

$$\frac{dI}{dt} = \frac{q^2 F_e}{m} N$$

- Solving for N and using the electron acceleration result, at T=0 we can define the effective number of free electrons

$$N_{eff} = \frac{dI}{dt}\frac{m}{q^2 F_e}$$

$$= \frac{1}{\pi}\frac{m}{\hbar^2}\int \frac{d^2 E}{dk^2} dk$$

Effective Number of Free Electrons

- At T=0, all states up to some energy E_a are filled and all states above are empty. If E_a is inside the energy band, the we integrate from $k=-k_a$ to $k=k_a$.

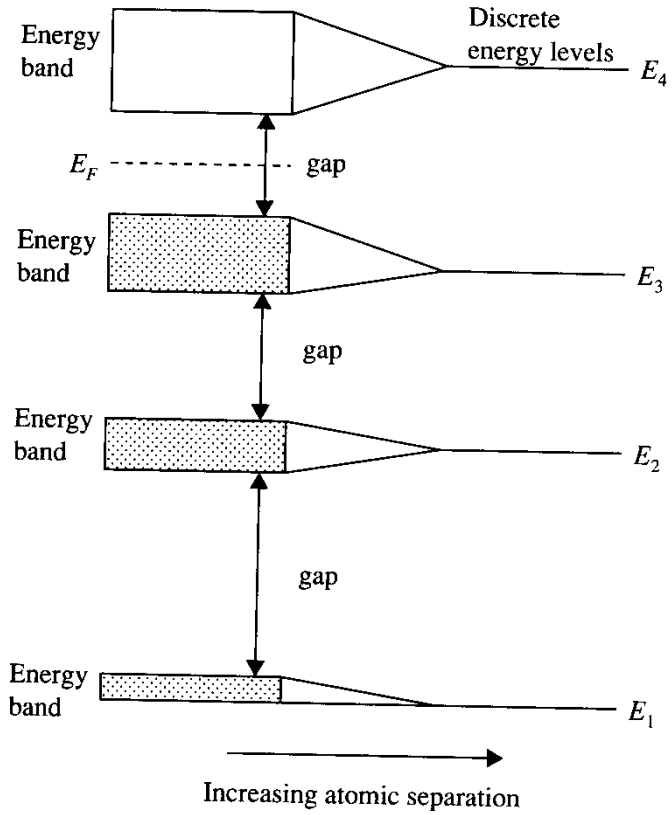
$$N_{eff} = \frac{1}{\pi}\frac{m}{\hbar^2}\left\{\left(\frac{dE}{dk}\right)_{k=k_a} - \left(\frac{dE}{dk}\right)_{k=-k_a}\right\}$$

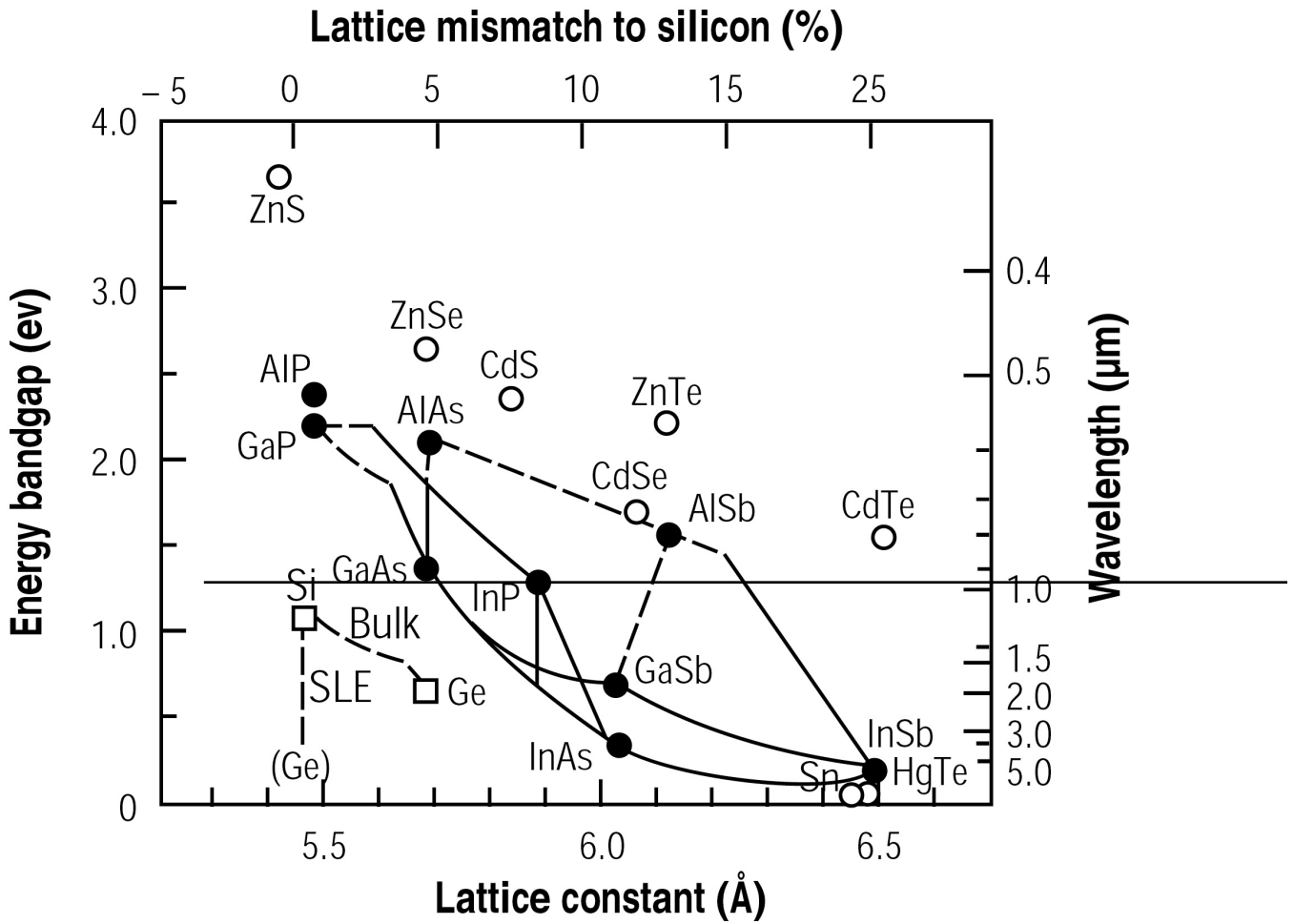
$$= \frac{2}{\pi}\frac{m}{\hbar^2}\left(\frac{dE}{dk}\right)_{k=k_a}$$

- Which tells us that the effective number of electrons that can contribute to electrical conduction depends on the slope of the E-k curve. At high energy levels in the banbd, dE/dk tends to zero and the number of effective electrons for a full band is zero.

Origin of SC Bandgap

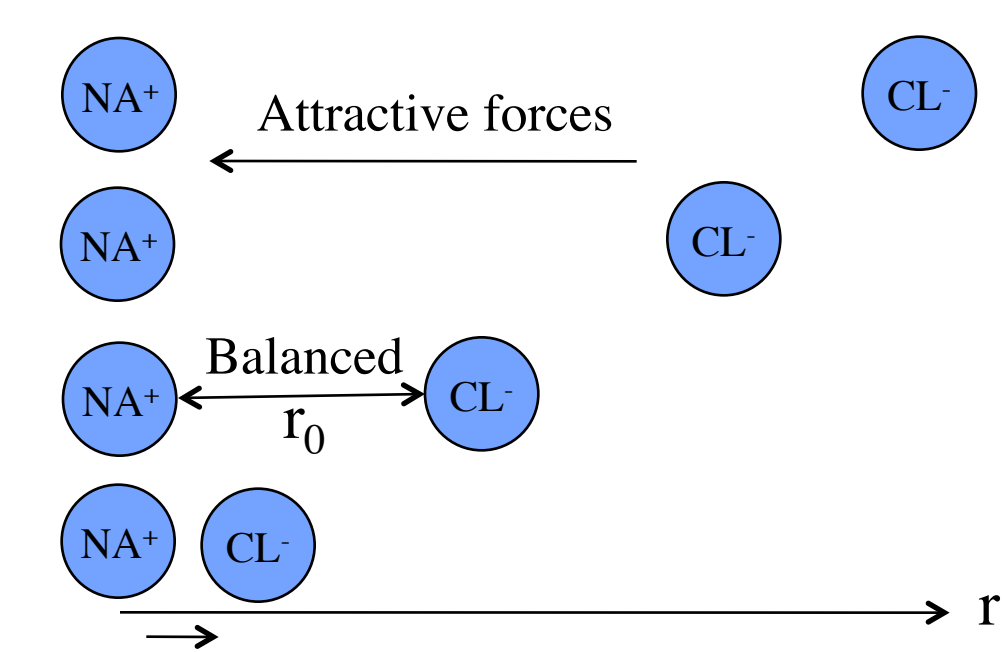
- The discrete energy states of electrons in an atom are broadened from the individual atom states into energy bands as the atoms are brought closer together to form a crystal.
- When the bandgap energy is on the order of 2eV, room temperature thermal energy can break covalent bonds and accelerate ionized electrons into empty states in the crystal where they can conduct electrically -> Semiconductors

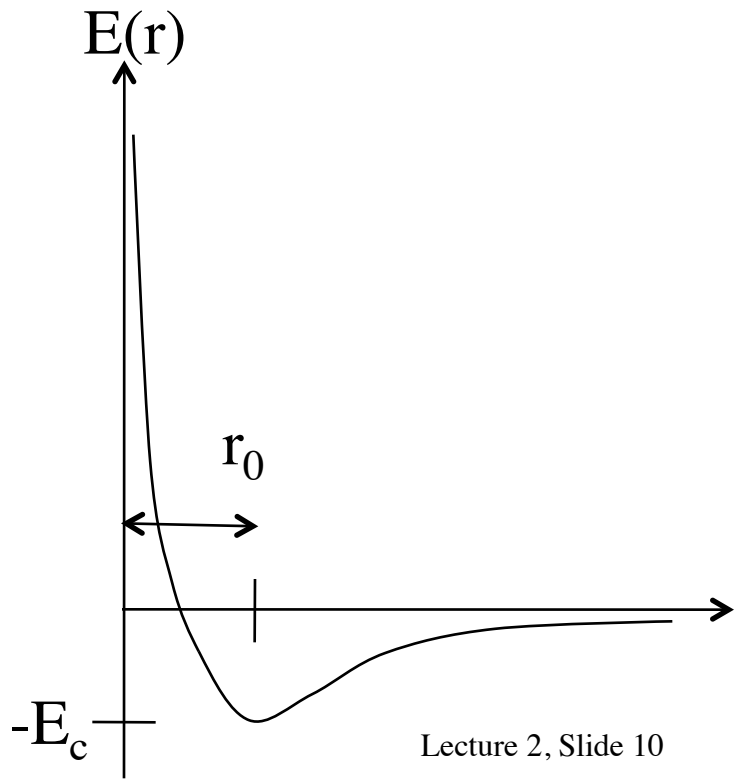



Lattice mismatch to silicon (%)
– 5
0
5
10
15
25
4.0
3.0
2.0
1.0
0
Energy bandgap (ev)
ZnS
ZnSe
CdS
ZnTe
AlP
AlAs
GaP
CdSe
AlSb
CdTe
Si
GaAs
InP
Bulk
SLE
Ge
GaSb
(Ge)
InAs
InSb
Sn
HgTe
0.4
0.5
1.0
1.5
2.0
3.0
5.0
Wavelength (μm)
5.5
6.0
6.5
Lattice constant (Å)

Equilibrium

- Equilibrium
  - Where is the minimum energy distance for two oppositely charged particles?





Bulk Elastic Constant of a Solid

- If each atom distance compresses Δr, then the total change in linear dimension is $(a/r_0)\,\Delta r$ and each face compresses by $(1/2)\,(a/r_0)\,\Delta r$ and the total work done to compress the material is

$$\text{Total Work Done on Material} = \frac{6}{2} T a^2 \left(\frac{a}{2r_0}\right) \Delta r$$

- From the Taylor expansion we can equate the total energy increase and the work done to solve for T

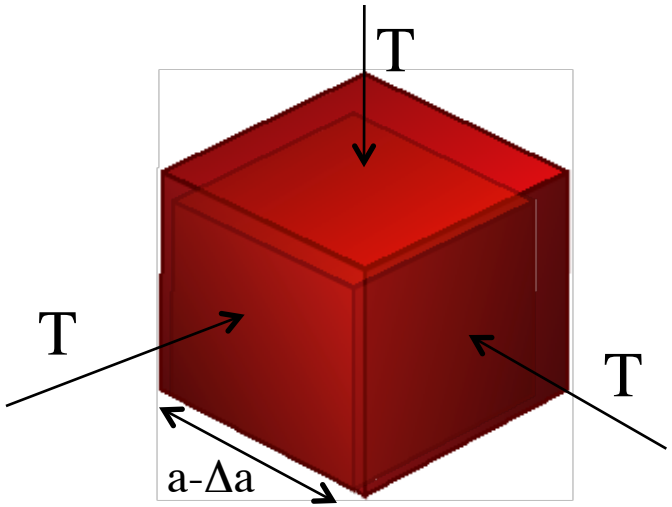
$$\mathrm{T} = \frac{1}{3r_0}\left(\frac{\partial^2 E}{\partial r^2}\right)_{r=r_0} \frac{\Delta r}{r_0}$$

- The bulk elastic modulus c is defined as

$$\mathrm{T} = c\left(\frac{\Delta a^3}{a^3}\right) \cong c\left(\frac{3\Delta a}{a}\right) = c\left(\frac{3\Delta r}{r_0}\right)$$

Hook's Law $\Rightarrow$

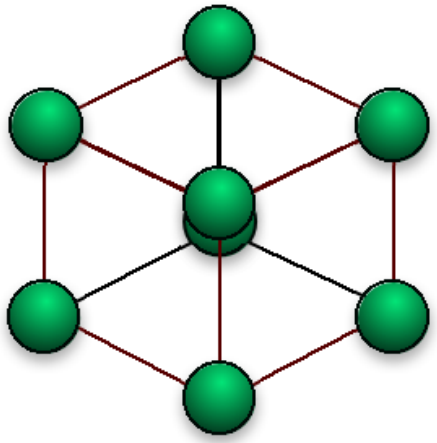
$$c = \frac{1}{9r_0}\left(\frac{\partial^2 E}{\partial r^2}\right)_{r=r_0}$$



Ionic Bonds

- How much energy would it take to take this crystal apart?
  - This is the ***Cohesive Energy*** E_c
  - Summing the electrostatic forces of the crystal
    - 6 Cl ions bonded to each Na ion at distance *a*
    - 12 Na ions bonded to each Na ion at a distance *a sqrt(2)*
    - 8 Cl ions bonded to each Na ion at a distance *a sqrt(3)*
    - Keep going ……

Cubic Lattice Crystal



$$6\left(-\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a}\right)$$

$$12\left(\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a\sqrt{2}}\right)$$

$$E_c = 6\left(-\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a}\right) + 12\left(\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a\sqrt{2}}\right) - 8\left(\frac{q^2}{4\pi\varepsilon_0}\frac{1}{a\sqrt{3}}\right) + \cdots$$

M is the *Madelung* Constant

$$E_c = -\frac{q^2}{4\pi\varepsilon_0}\left(\frac{6}{a} - \frac{12}{a\sqrt{2}} + \frac{8}{a\sqrt{3}} + \cdots\right)$$

$$E_c = -M\frac{q^2}{4\pi\varepsilon_0 a}$$

Metallic Bonds

- A metal can be thought of as a lattice of thermally vibrating atoms with a sea of free, conducting electrons scattering off each other and the fixed atoms.
- But these electrons are confined for the most part to the metal and we have to do some work to remove them from the metal
- The metallic bond is similar to the ionic bond in that electrostatic forces generated by the moving electrons play a key role in keeping the lattice together

Covalent Bond

- In general the Covalent bond is very strong
  - Electrons are not easily removed (bond broken) or free to conduct
  - Insulator
- In some material systems (compound) the covalent bond is more easily broken and the electrons freed by breaking this bond can conduct
  - Semiconductor

Van der Waals Forces

- What happens when we have an electrically neutral atom (not ionized) and there is no attraction to neighboring electrons?
- How do neutral atoms form bonds?
- The electron position density function fluctuates in time, forming a displacement between the electron and nucleus
  - This is called an oscillating dipole
- One dipole will generate a field (static or dynamic) that will distort nearby atoms into becoming dipoles (like oppose, opposites attract).
- Tendency on average is for attraction or the Van der Waals Force.

Feynman's Coupled Mode Approach

- Richard Feynman, Physicist, Nobel Laureate (see Feynman Lectures on Physics, Addison Wesley Longman, ISBN-13: 978-0201021158)
  - Developed an approach that can be used to describe all physical systems that are coupled
  - Sometimes called coupled mode theory
  - Other examples besides pendulums include electrical oscillators, atoms, acoustics and vibrational systems, etc.
  - Step 1: Write a model for each part of the system by itself
  - Step 2: Introduce a coupling factor in each equation that describes how each part of the system interacts with the other parts of the system
  - This couple can be in time, space, time and space or other manner

Coupled Schrodinger's Equations

- Lets consider the simplest case where there are two solutions j=1 and j=2.
- Our two Diff. equations will look like

$$i\hbar\frac{d(\omega_1(t))}{dt} = H_{11}\omega_1(t) + H_{12}\omega_2(t)$$

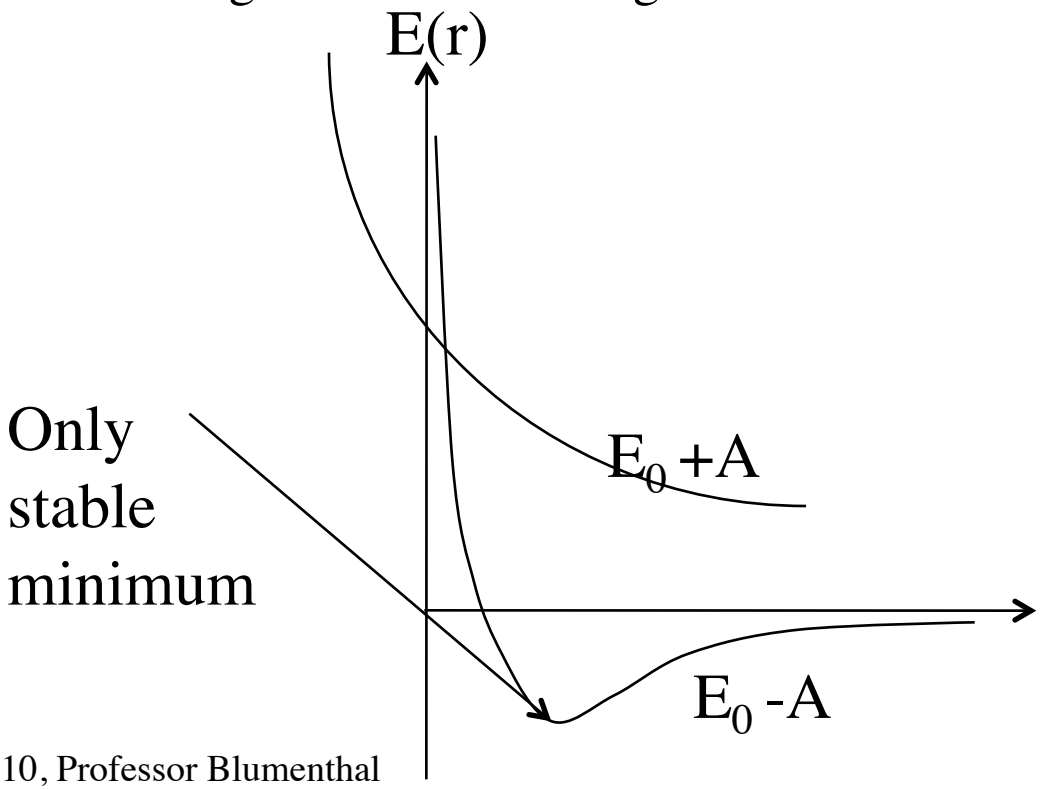
$$i\hbar\frac{d(\omega_2(t))}{dt} = H_{21}\omega_1(t) + H_{22}\omega_2(t)$$

Coupling Term

Coupling Term

Coupled States

- As the two are brought together from infinity, only one solution has attractive and repulsive forces balance out to a stable solution.
- In the time dynamic solution, the electron can jump from one nucleus to the other and a sharing can occur forming a bond.



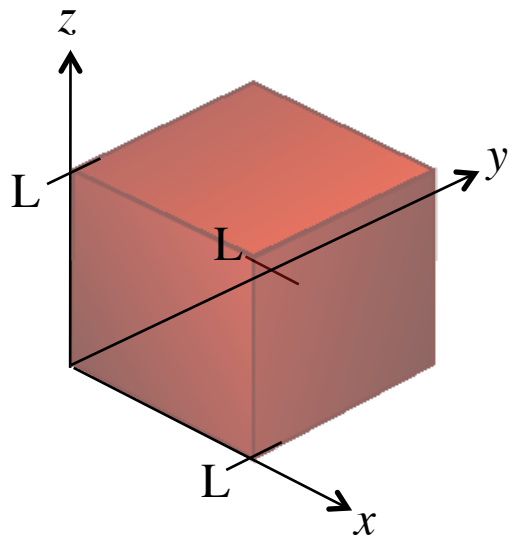
The Free Electron Model of Metals

- Now lets look at a cube with sides L that contains the electrons. The electron energy can be written as

$$E = \frac{\hbar^2}{2m}(\kappa_x^2 + \kappa_y^2 + \kappa_z^2)$$

$$= \frac{\hbar^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

$$n_x, n_y, n_z = 1,2,3\ldots$$



Fermi-Dirac Statistics

Region I: E_F-E >> k_BT

$$F(E) \approx 1 - \exp\left[\frac{E - E_F}{\kappa_B T}\right] \approx 1$$

Approximately Unity

Region II: E_F-E >> k_BT

$$0 \le F(E) \le 1$$

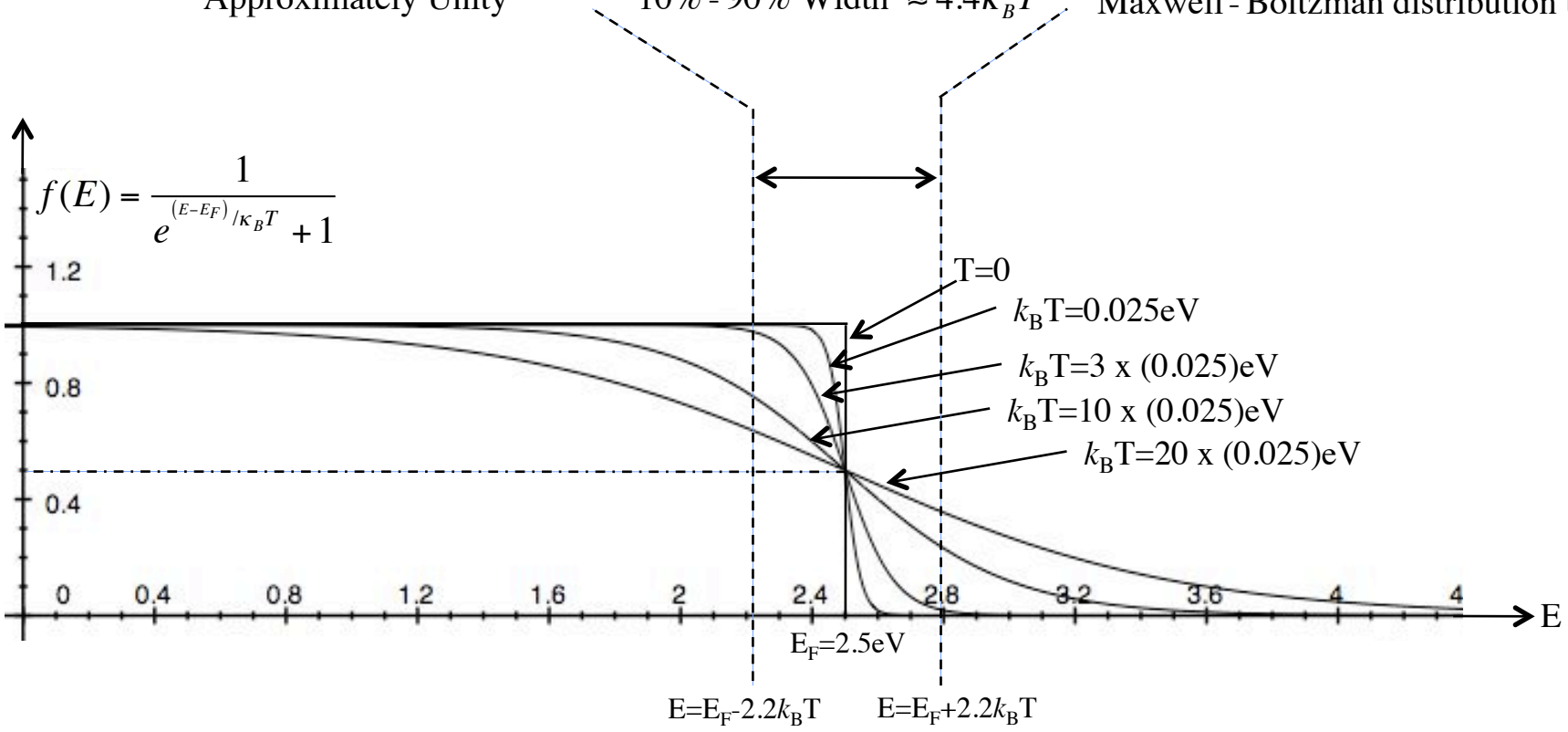
Slope is function of T

10% - 90% Width $\approx 4.4\kappa_B T$

Region III: E_F-E >> k_BT

$$F(E) \approx \exp\left[-\frac{E - E_F}{\kappa_B T}\right]$$

Maxwell - Boltzman distribution tail



Specific Heat of Electrons

- Assume that all electrons with energy

$$E_F - 2.2k_BT \le E \le E_F$$

contribute to the specific heat and can be treated as classical electrons (i.e. there are plenty of available states to excite them into)

- Assume each classical electron has an average energy $3/2k_BT$, then the average energy of the electrons that can contribute too the SH and the resulting specific heat of these electrons is given by

$$\langle E \rangle = \frac{3}{2}\kappa_B T \frac{2.2\kappa_B T}{E_F}$$

$$c_V = \frac{d\langle E \rangle}{dT} = \frac{d}{dT}\left[\frac{3}{2}\kappa_B T \frac{2.2\kappa_B T}{E_F}\right] = 6.6\kappa_B^2 \frac{T}{E_F}$$

Thermionic Emission

- Solving the integrals for Gaussians

$$N(\rho_x)d\rho_x = \left(\frac{4\pi m k_B T}{h^3}\right)\exp\left(\frac{E_F}{k_B T}\right)\exp\left(-\frac{\rho_x^2}{2mk_B T}\right)d\rho_x$$

- Then solving for the current density assuming r is independent of momentum direction (an approximation)

$$J = \frac{q}{m}\int_{\rho_{x0}}^{\infty}\left[1-r(\rho_x)\right]\rho_x N(\rho_x)d\rho_x$$

$$= \frac{q}{m}\int_{\rho_{x0}}^{\infty}\left[1-r\right]N(\rho_x)d\rho_x = \frac{q}{m}\left[1-r\right]\exp\left(\frac{E_F}{k_B T}\right)\int_{\rho_{x0}}^{\infty}\exp\left(-\frac{\rho_x^2}{2mk_B T}\right)d\rho_x$$

$$= \frac{4\pi q m k_B^2}{h^3}(1-r)T^2\exp\left(-\phi \big/ k_B T\right)$$

Thermionic Emission

- Note the dependence on temperature and the value of the work function. A_0 is constant. There is an exponential dependence on temperature.
- In reality, electrons that escape the metal will have several mechanisms to be attracted back (e.g. electrostatic forces from positively charged surface) so we need to replenish the electrons with an external circuit. Putting the metal in a vacuum will also improve emission.

Image Effect for modeling Schottky Effect

- Now we have to sum the applied field with the mirror charge field

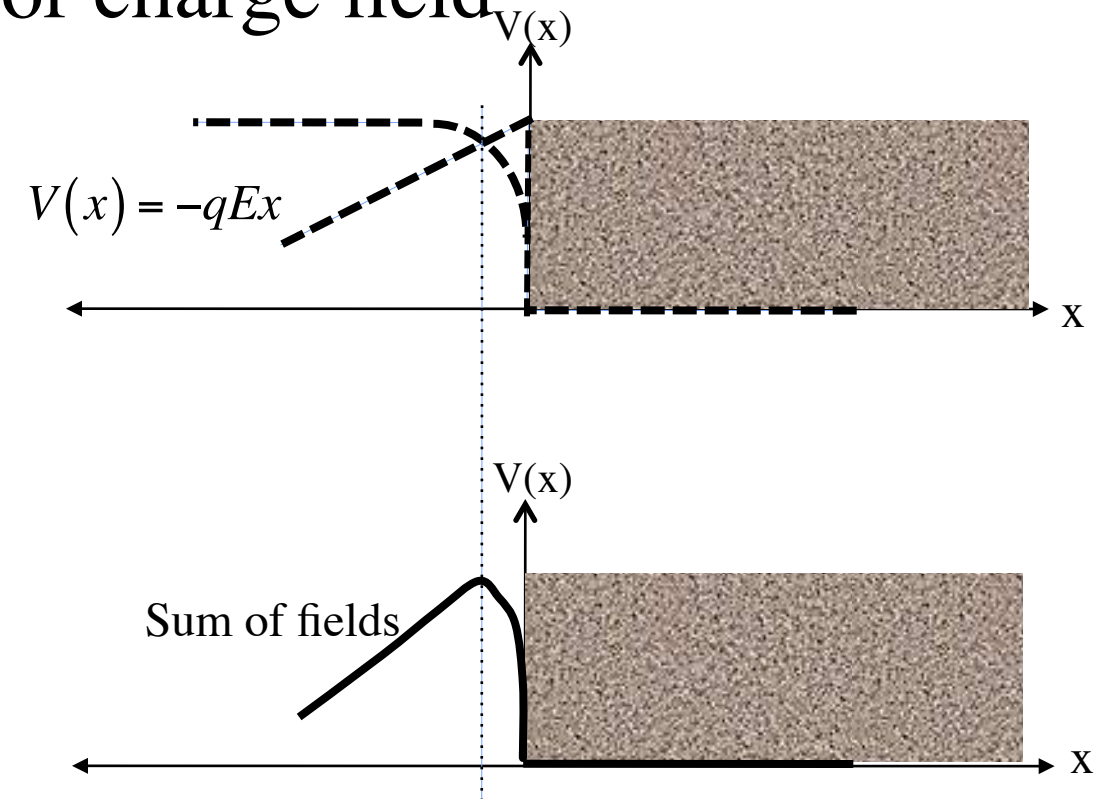


Image Effect for modeling Schottky Effect

- The maximum is obtained by differentiating the potential and setting equal to zero

$$\frac{d}{dx}\left(\left(\frac{q^2}{16\pi\varepsilon_0 x} - qEx\right)\right) = 0$$

$$V_{Max} = -q\left(\frac{qE}{4\pi\varepsilon_0}\right)^{1/2}$$

- This reduces the work function we talked about before to an effective work function

$$\phi_{eff} = \phi - q\left(\frac{qE}{4\pi\varepsilon_0}\right)^{1/2}$$

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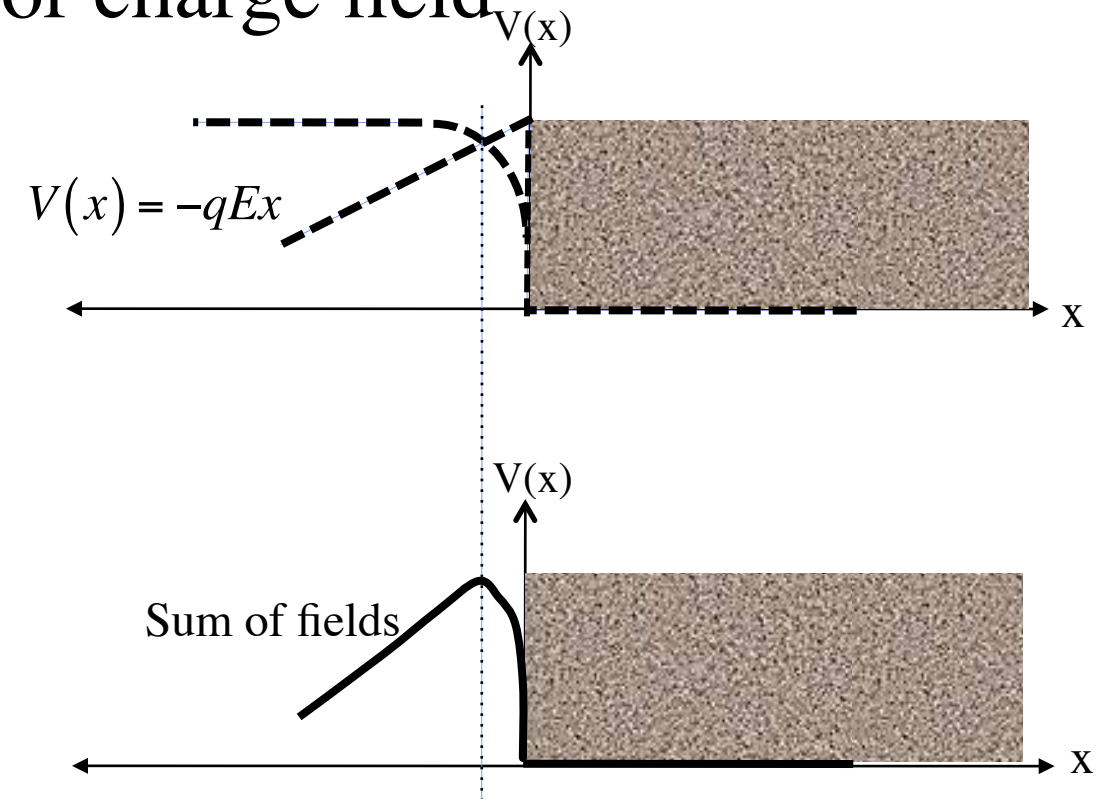

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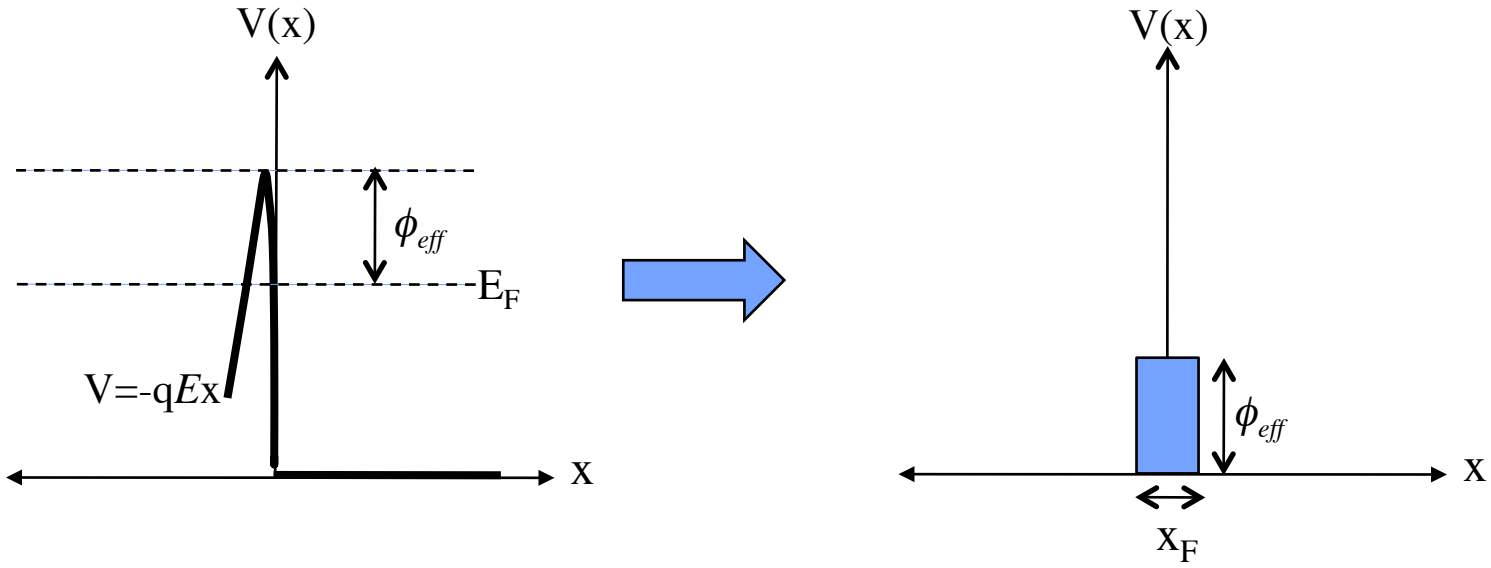
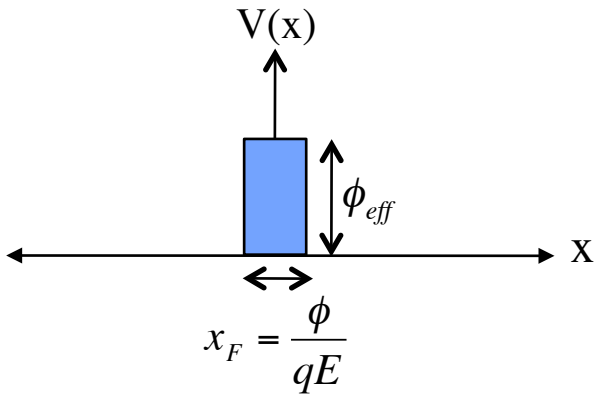
Field Emission

- The narrowed barrier can be modeled as an effective barrier of height ϕ_{eff} and width x_F.



Field Emission

- The width of the barrier is $x_F = \dfrac{\phi}{qE}$
- The tunneling current may be approximated by



$$J \approx \exp\left(-\frac{\left(2\phi_{eff}\right)^{1/2}}{\hbar} x_F\right) = xp\left(-\frac{\left(2\phi_{eff}\right)^{1/2}}{\hbar}\frac{\phi}{qE}\right)$$

$$\approx \exp\left(-\frac{(2m)^{1/2}}{\hbar e}\frac{\left(\phi_{eff}\right)^{1/2}\phi}{E}\right)$$

Function of E not T

The Photoelectric Effect

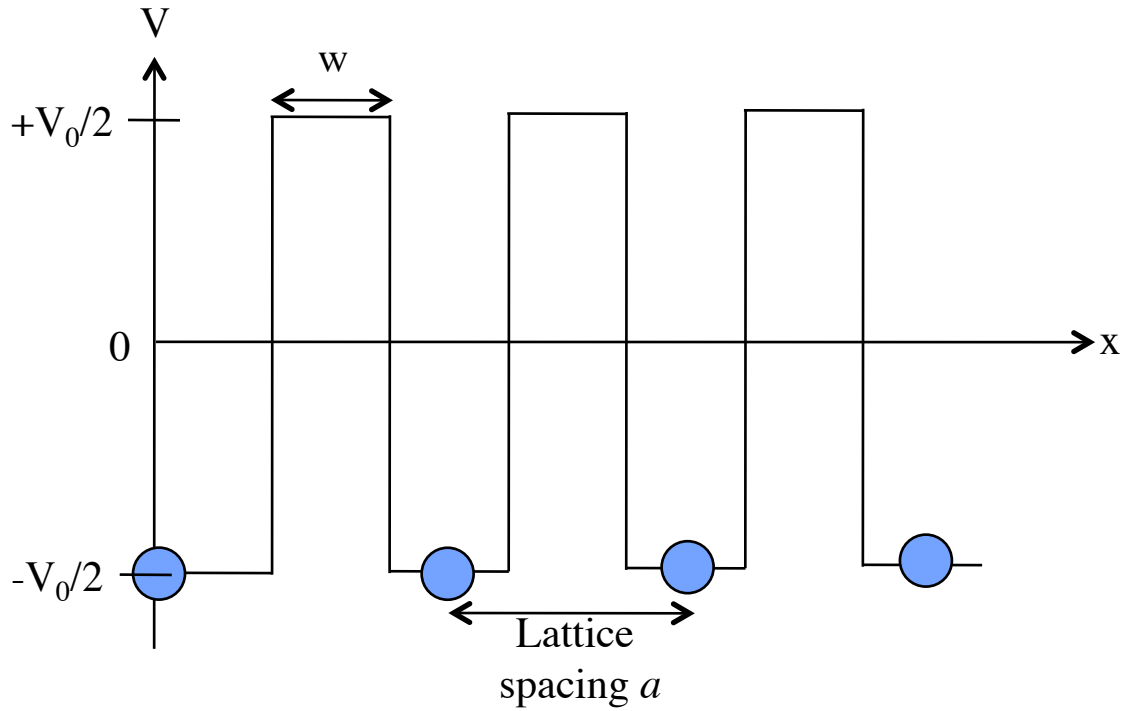
- Electrons can also be removed (emitted) from the surface of a metal by an incident electromagentic wave – the "photoelectric effect"
- A photon of frequency ω carriers energy

$$E_P = \hbar\omega$$

- If the photon energy is greater than or equal to the work (or effective) function, then an electron can be emitted from the metal.

The Kronig-Penney Model

- Consider first the one dimensional case which has the following features
  - The potential has the same period as the lattice
  - The potential is lower near the lattice ions and higher in between the lattice ions.



The Kronig-Penney Model

- Note that as we vary P, the height and therefore the slopes of the oscillating curve change.
- As P is increased the slope of the right hand side increases within the [-1,+1] region and the forbidden bands increase width and allowed bands decrease in width
- Lets look at some limits in P to understand its physical significance
  - (i) $P \to \infty$

    $\sin(\alpha a) \to 0$

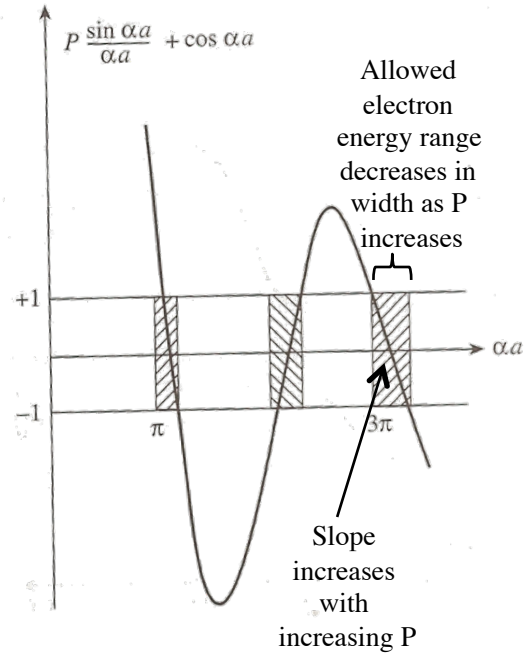
    $E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2$

    Which is the energy level of a potential well of width a. P is like the height of the potential barrier, infinite in this case, and each electron is confined independent to each other
  - (ii) $P \to 0$

    $\cos(\alpha a) = \cos(ka)$

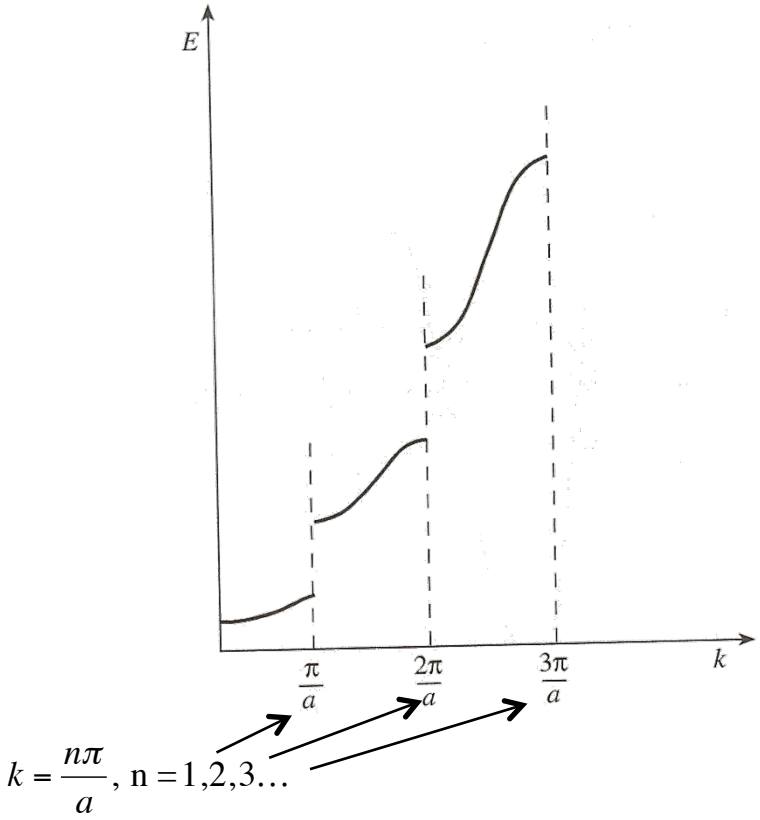
    $E = \frac{\pi^2 \hbar^2}{2m}$

    Which is the energy level of a free electron. P is then indicative of a zero height barrier and the electrons are not confined.



The Kronig-Penney Model

- At the boundary of each allowed band where cos(ka) = ±1, the momentum takes on discrete values and there is a discontinuity in energy at these boundaries as shown in the figure below.



The Ziman Model

- Assuming the same potential as in the Kronig-Penney Model with *2w=a*

$$V_{\pm} = \frac{1}{a}\int_0^a \begin{pmatrix} 2\cos^2 kx \\ 2\sin^2 kx \end{pmatrix} V(x)dx$$

$$= \frac{1}{a}\int_0^a \begin{pmatrix} 1+\cos 2kx \\ 1-\cos 2kx \end{pmatrix} V(x)dx$$

$$= \pm\frac{1}{a}\int_0^a \cos 2kx V(x)dx$$

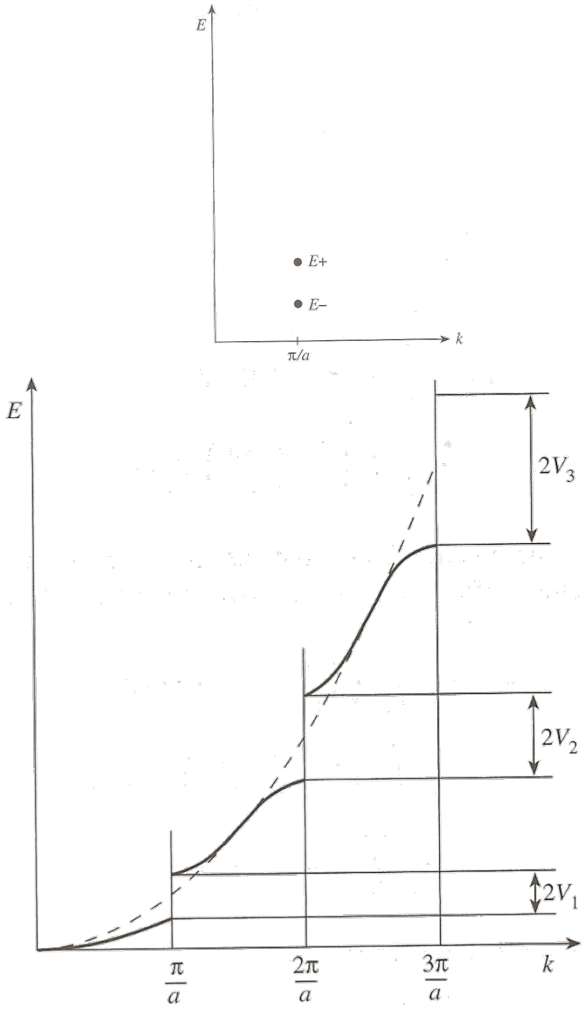
$$= \pm V_n$$

- The kinetic energies of the wave functions are the same and the total energy is the sum of the kinetic and potential energies

$$E_{\pm} = \frac{\hbar^2 k^2}{2m} \pm V_n$$

$$E_{+} = \frac{\hbar^2 k^2}{2m} + V_1$$

$$E_{-} = \frac{\hbar^2 k^2}{2m} - V$$



The Feynman Model

- Assuming a time varying solution for ω_j of the form $\omega_j = K_j e^{-iEt/\hbar}$ we can rewrite the coupled DE for atom *j* as

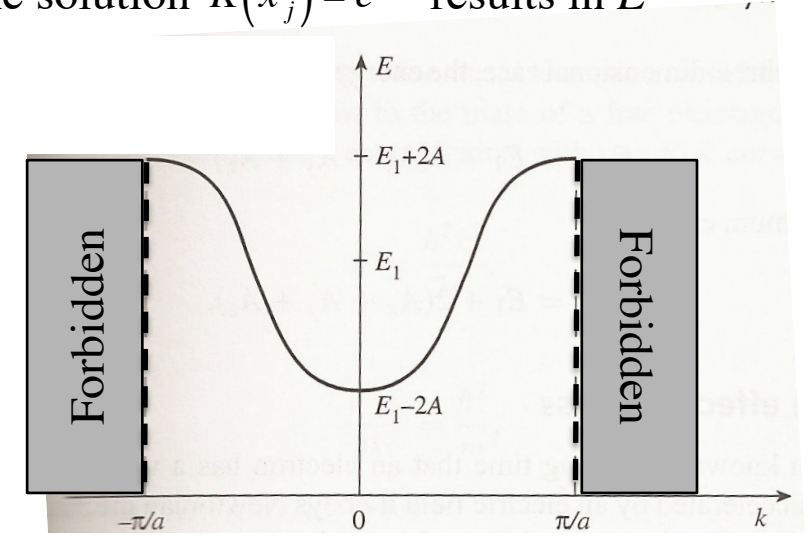
$$EK_j = E_1 K_j - A\left(K_{j-1} + K_{j+1}\right)$$

- Writing the amplitude as a function of their lattice position (x-coordinate) we end up with the difference equation

$$EK\left(x_j\right) = E_1 K\left(x_j\right) - A\left(K\left(x_j + a\right) + K\left(x_j - a\right)\right)$$

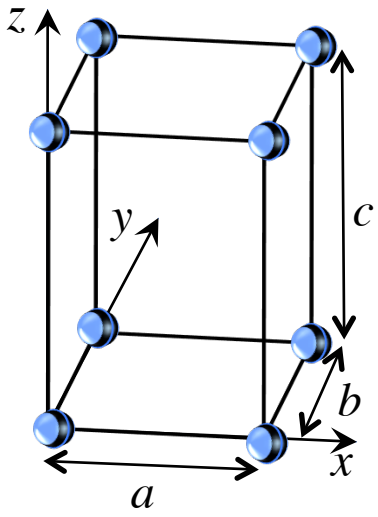
- Solving the difference equation assuming the solution $K\left(x_j\right) = e^{ikx_j}$ results in E

$$\begin{aligned} Ee^{ikx_j} &= E_1 e^{ikx_j} - A\left(e^{ik(x_j+a)} + e^{ik(x_j-a)}\right) \\ &= E_1 e^{ikx_j} - Ae^{ikx_j}\left(e^{ika} + e^{-ika}\right) \\ &= e^{ikx_j}\left(E_1 - A\left(e^{ika} + e^{-ika}\right)\right) \\ E &= \left(E_1 - A\left(e^{ika} + e^{-ika}\right)\right) \\ E &= E_1 - 2A\cos(ka) \end{aligned}$$



3D Extension of The Feynman Model

- We can simply extend the Feynman Model to three dimensions (not as easily done for the other models we looked at)



$$i\hbar\frac{\partial\omega(x,y,z,t)}{\partial t} = E_1\omega(x,y,z,t)$$
$$-A_x\omega(x+a,y,z,t) - A_x\omega(x-a,y,z,t)$$
$$-A_y\omega(x,y+b,z,t) - A_y\omega(x,y-b,z,t)$$
$$-A_z\omega(x,y,z+c,t) - A_z\omega(x,y,z-c,t)$$

- With solution

$$\omega(x,y,z,t) = e^{-iEt/\hbar}e^{i\left[k_x x + k_y y + k_z z\right]}$$
$$E = E_1 - 2A_x\cos(k_x a) - 2A_y\cos(k_y b) - 2A_z\cos(k_z c)$$