Band Theory of Solids

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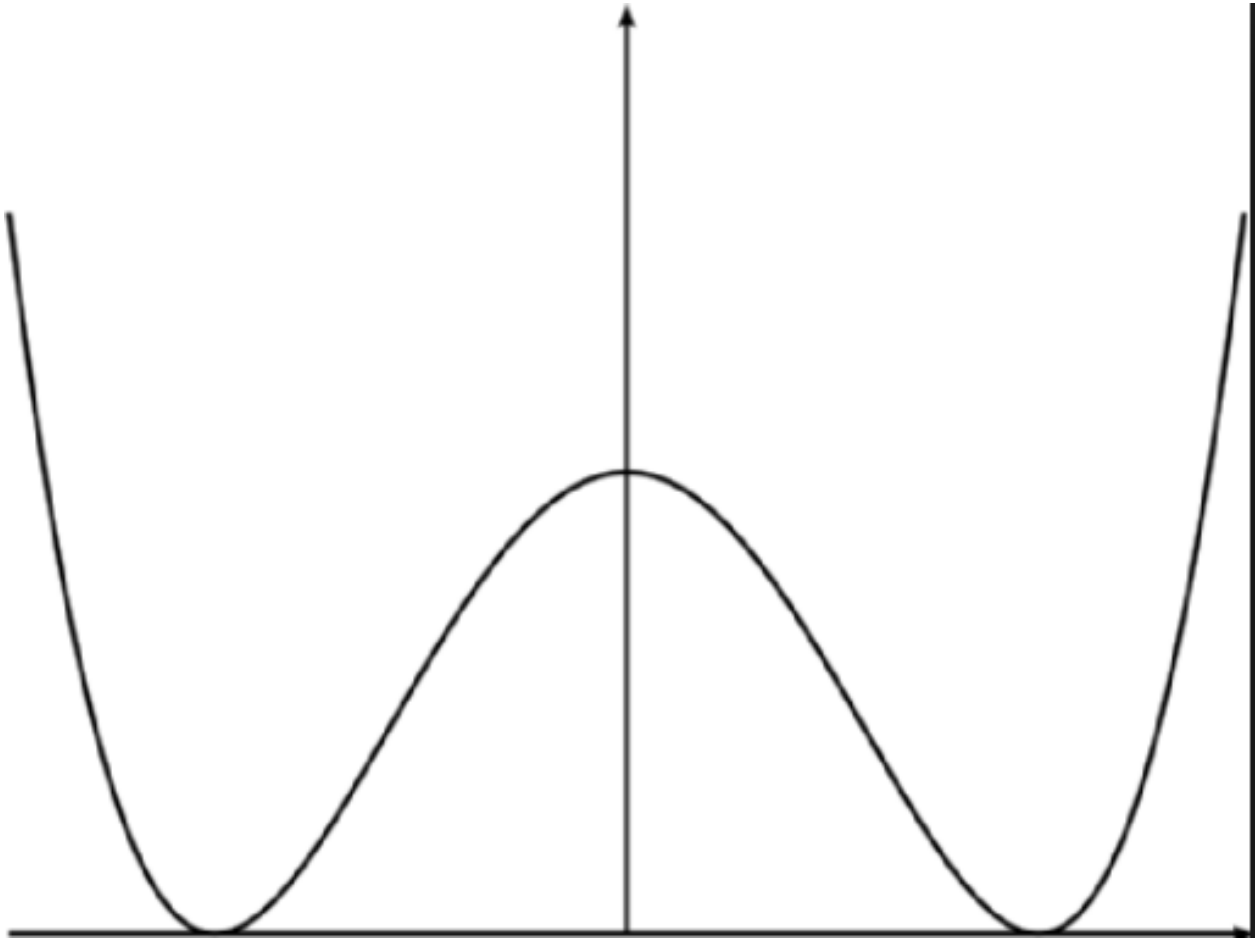
Free Electron Gas Model of Metals

- In the last two classes, we considered "Free Electron Gas" model of metals in two versions: (a) in the form of a classical gas (Drude model) and (b) in the form of a fermion gas (Sommerfeld model)
- Predictions of Drude model are qualitatively correct but a lot of details are wrong. For example the elctronic contribution to the specific heat of the solid is too high and the temperature dependence of the resistivity is wrong.
- Sommerfeld model got the electronic specific heat correct. With the assumption that it is the defects in the lattice which are responsible for the resistivity, we also get the correct magnitude for the conductivity and also the correct temperature dependence. However, Sommerfeld model also predicts that the Hall coefficient should always be negative. Experiment finds positive values for some materials.
- Most importantly, none these models address the very important question: What is the property of the solid which makes it a conductor or an insulator?

Band Theory

- To overcome these shortcomings, another model of solids was constructed. It is a quantum mechanical model which takes into account the symmetries of the lattice.
- This model is called Band Theory of solids. Based on the properties of the bands, we can classify a solid as a metal or as an insulator or sometimes as a semiconductor.
- This model retains the original picture of the free electron gas model: That the solid consists of massive ions at the lattice points and the electrons move around in the lattice.
- The symmetries of the lattice impose certain conditions on the allowed wave functions and the energy levels of the electrons.
- The energy levels of the electrons fall within certain well defined allowed ranges (bands) and these bands are separated by forbidden energy levels (band gaps).
- The relationship between the bands and the band gaps determine whether a solid is a conductor or a semiconductor or an insulator.

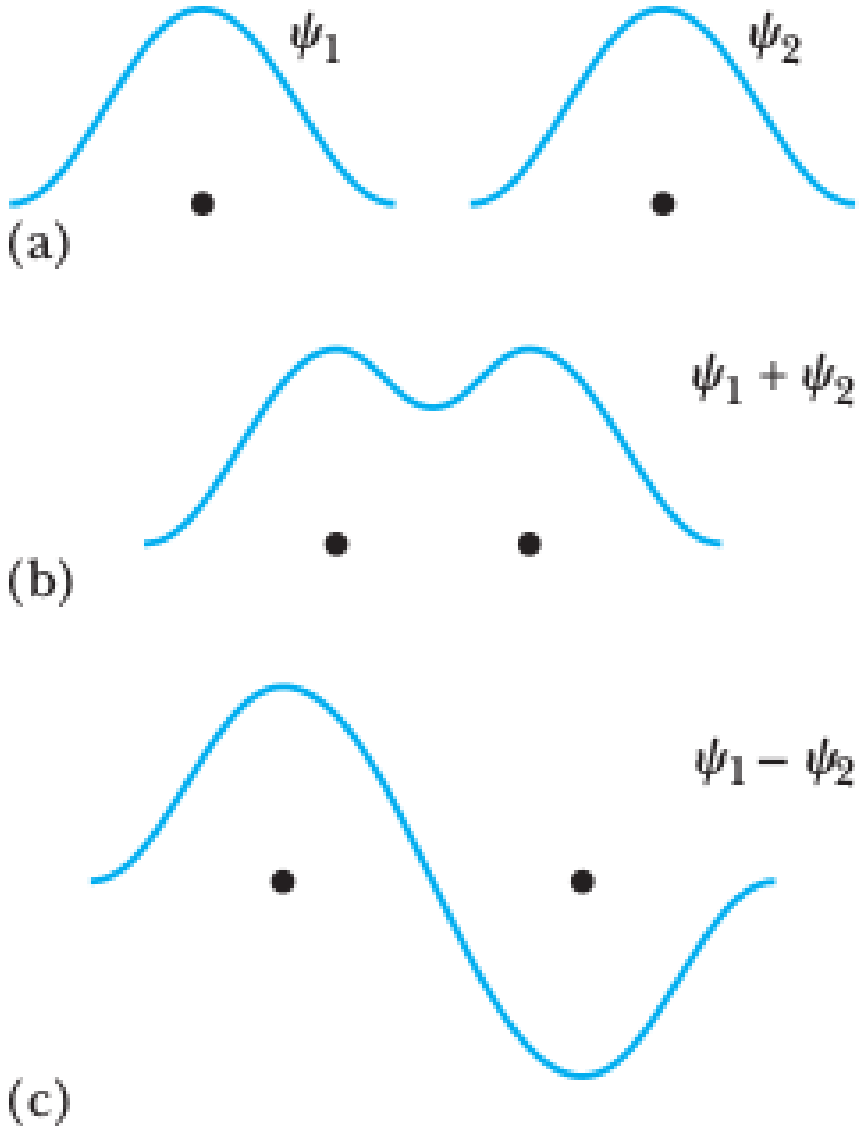
Symmetric Double Well Potential



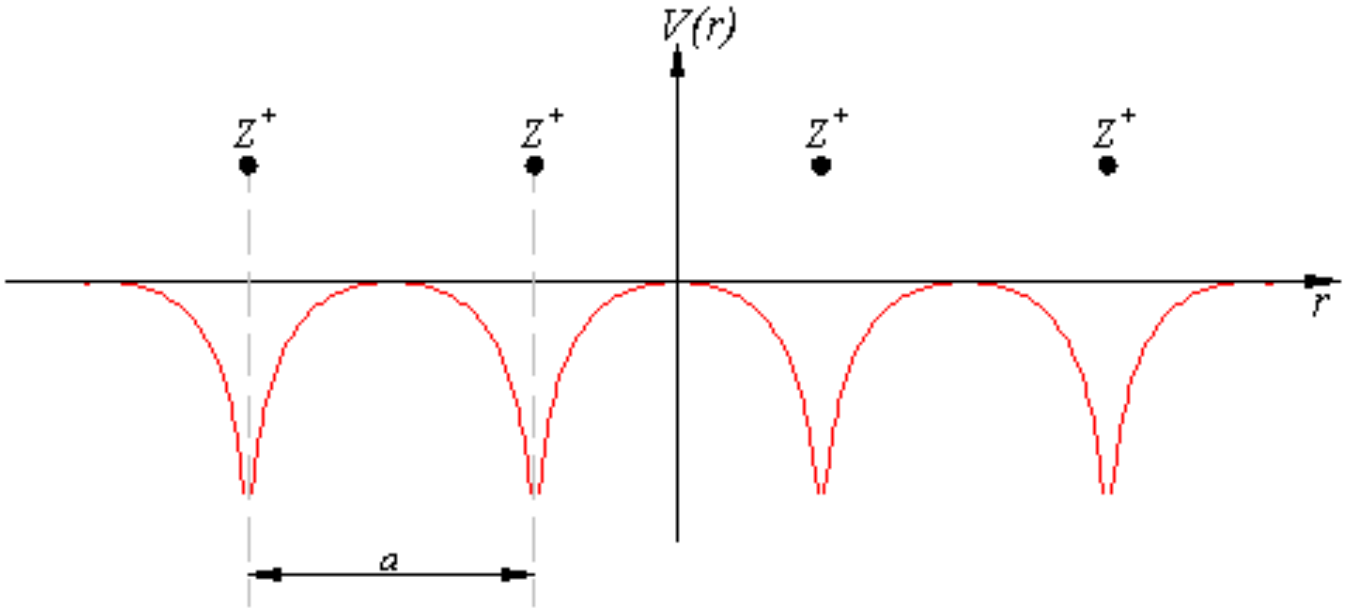
Level Splitting in Symmetric Double Well

- Suppose we solve the Schroedinger's equation for the double well potential.
- Exact solution is quite complicated. But we suppose that the two wells are well separated so that they can be treated independently.
- Then there is a ground state ψ_L for the left well and another ground state ψ_R for the right well. The energies for these ground states are exactly the same.
- Since the potential barrier between the two minima is finite, there is a possibility for ψ_L to tunnel through and become ψ_R and similarly for ψ_R to tunnel through and become ψ_L.
- It can be shown that we will have two non-degenerate states $(\psi_L + \psi_R)/\sqrt{2}$ and $(\psi_L - \psi_R)/\sqrt{2}$ with energies $E_0 \mp \Gamma$ where Γ is the tunnelling rate, expressed in energy units.

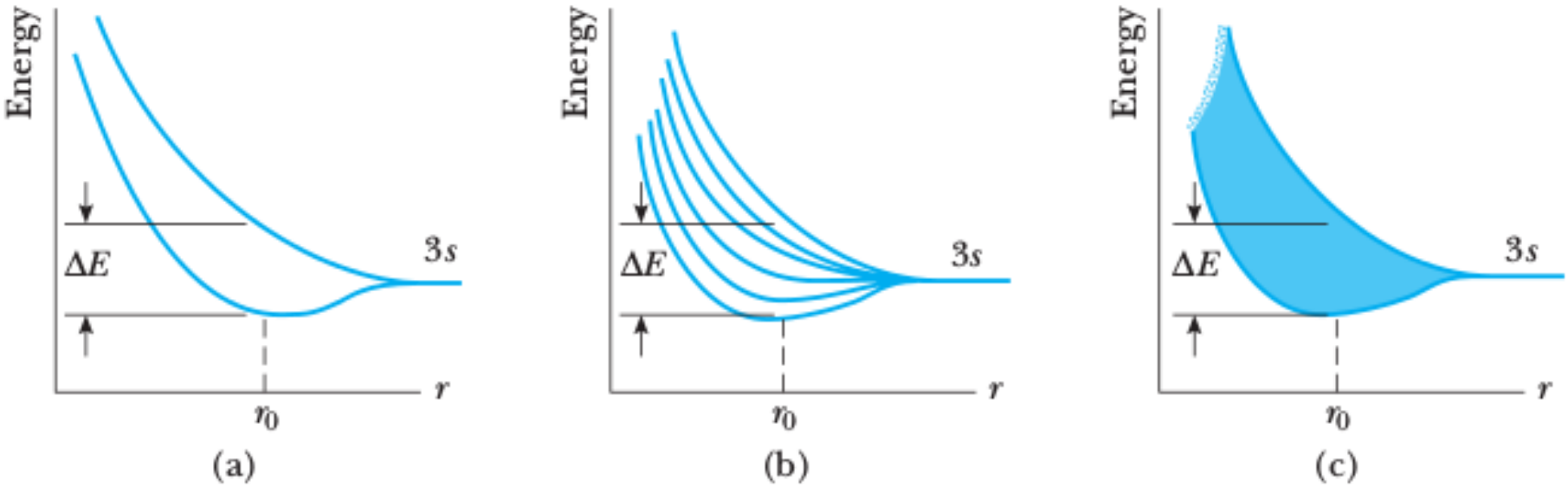
Lowest Energy Wavefunctions of Symmetric Double Well



Potential for a One-Dimensional Solid



Energy Bands for a One-Dimensional Solid



Bloch Wave

- Felix Bloch proved an important theorem regarding the wave function for a periodic potential $V(x + na) = V(x)$, where n is an integer.
- Based on Fourier analysis, he argued that the wave function of an electron moving in a one dimensional periodic potential must have the form

$$\psi(x) = u(x)e^{ikx}, \text{ where } u(x + na) = u(x).$$

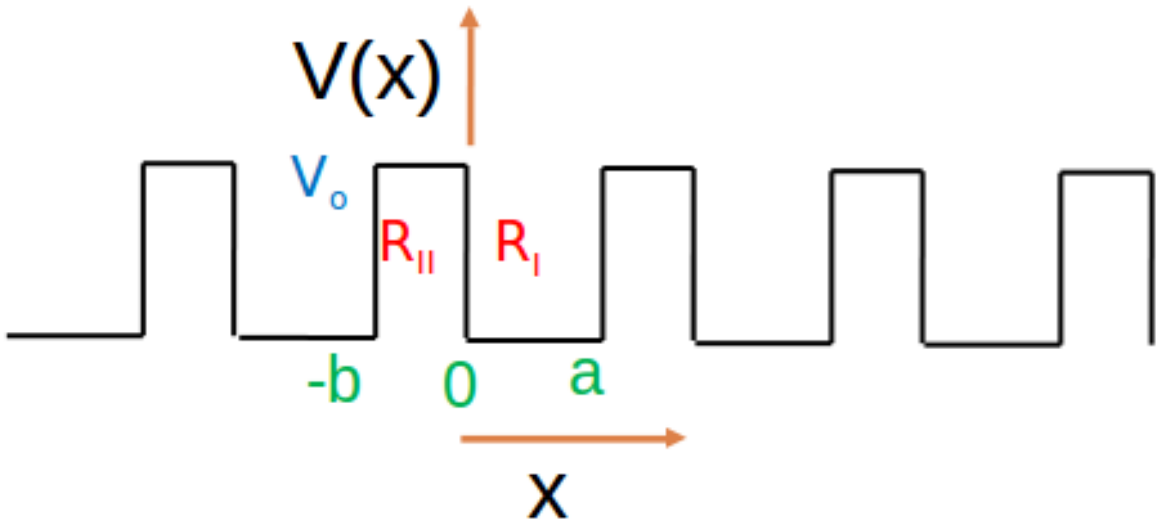
  That is, the function $u(x)$ has the same symmetry as the potential.
- Explicit form of $u(x)$ depends on the explicit form of the potential.
- Another form of stating the Bloch wave function is

$$\psi(x + na) = \psi(x)e^{ikna}.$$

One Dimensional Potential for Kronig-Penney Model

Let us consider a simple explicit periodic potential and apply Bloch's theorem.

Kronig- Penny Model



$V = 0$ for $0 \leq x < a$ R_I

$V = V_o$ for $-b \leq x < 0;\ V_o > 0$ R_{II}

Kronig-Penney Model

- The time independent Schroedinger equation is

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

- In the region $0 < x < a$, the solution has the form

$$\psi(x) = Ae^{iKx} + Be^{-iKx},$$

with $E = \hbar^2 K^2/2m$.

- In the region $-b < x < 0$, we have a potential barrier. We assume that the height of the barrier is such that the solution in this region is has exponential dependence,

$$\psi(x) = Ce^{Qx} + De^{-Qx}.$$

Since the height of the barrier is not specified, we do not know what Q is.

- Later we will make an approximation which makes the height of the barrier irrelevant.

Kronig-Penney Model

- We want $\psi(x)$ to be a Bloch wave. That is we impose the condition

$$\psi(a < x < 2a + b) = \psi(-b < x < a)e^{ik(a+b)},$$

where k is the wave number of Bloch wave. It is, as yet, not related to the energy of the electron.

- We require $\psi(x)$ and $d\psi/dx$ to be to continuous at $x = 0$ and $x = a$. The $x = 0$ conditions are trivial.

$$\begin{aligned} A + B &= C + D \\ iK(A - B) &= Q(C - D). \end{aligned}$$

- To obtain the continuity conditions at $x = a$, we need to use Bloch wave condition above to obtain the $\psi(x)$ for $x = a + \epsilon$. This gives

$$\begin{aligned} Ae^{iKa} + Be^{-iKa} &= \left[Ce^{-Qb} + De^{Qb}\right] e^{ik(a+b)} \\ iK\left[Ae^{iKa} - Be^{-iKa}\right] &= Q\left[Ce^{-Qb} - De^{Qb}\right] e^{ik(a+b)}. \end{aligned}$$

Kronig-Penney Model

- The four boundary conditions are four linear equations in the four unknown constants A, B, C and D. They can be written such that the RHS of all equations is zero.
- Hence we get non-zero values for A, B, C and D only if the determinant of the matrix of their coefficients vanishes.
- The calculation of this determinant is fairly tedious. We just quote the result,

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

This equation is the energy quantization condition (similar to what we obtained in for finite potential well).

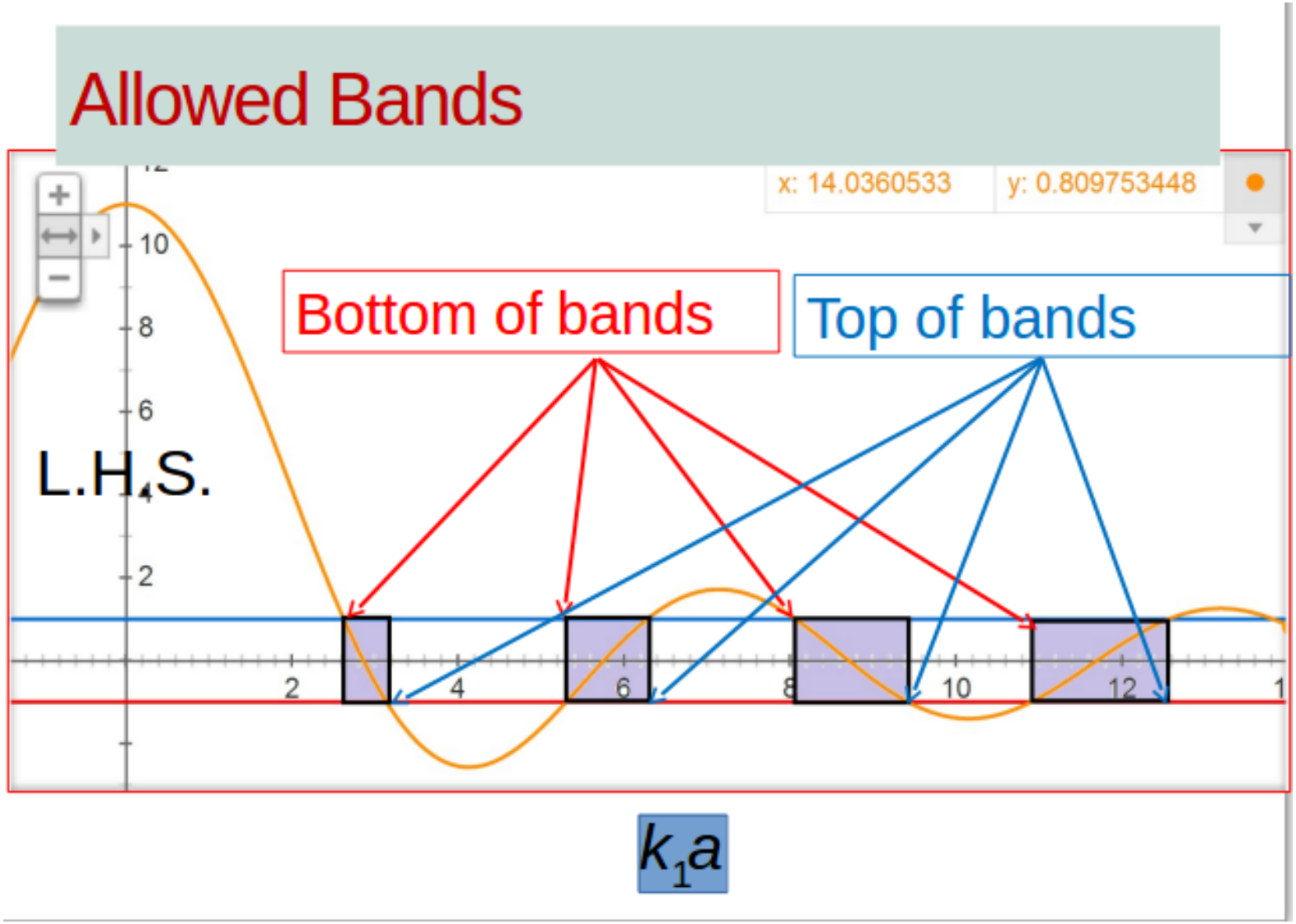
Kronig-Penney Model

- We simplify this equation by assuming a tall and thin barrier. Mathematically, we take the limits $b \to 0$, $V_0 \to \infty$ such that $Q^2ab/2 = P$ is a finite quantity.
- P characterizes the strength of the barrier. The larger the value of P the stronger the barrier and the smaller the tunneling probability.
- In the above limit, $Q \gg K$ and $Qb \ll 1$ and the energy quantization condition reduces to

$$\frac{P}{Ka}\sin(Ka) + \cos(Ka) = \cos(ka).$$

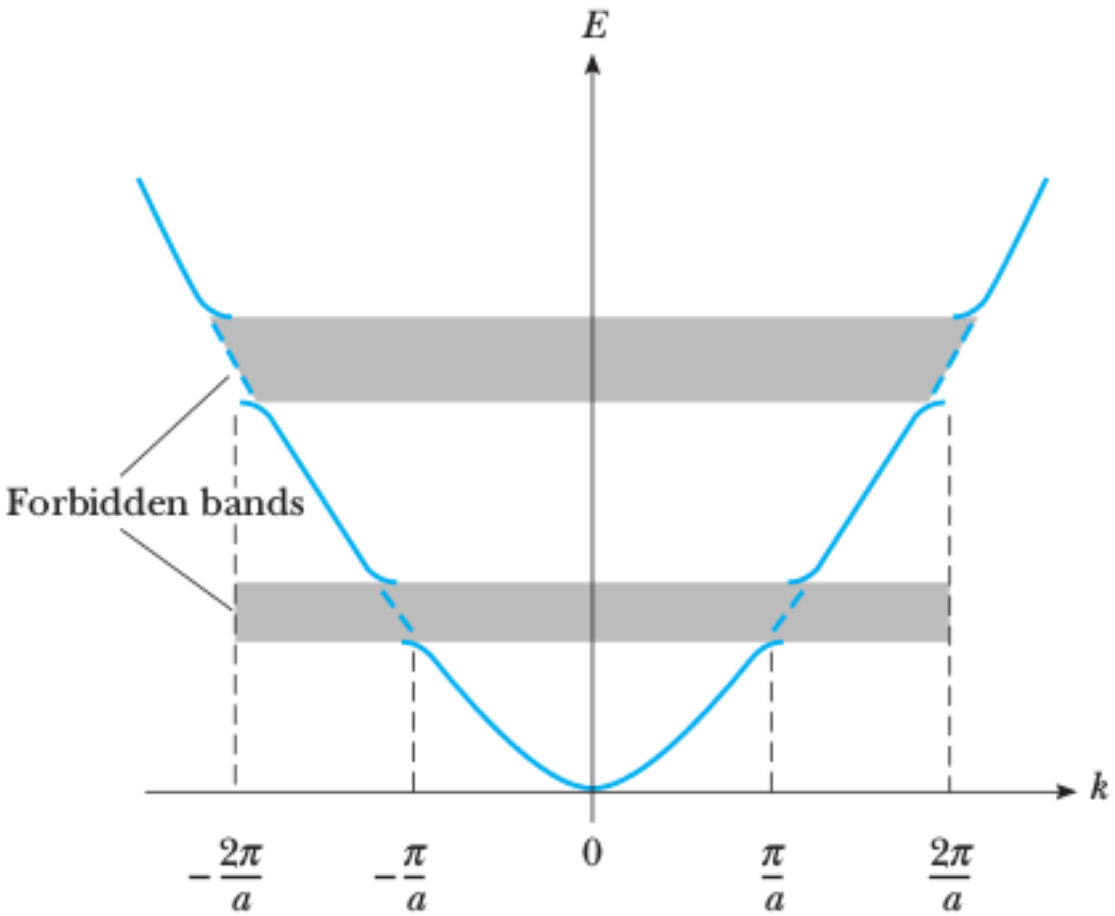
- For a given value of P, we can plot the LHS as a function of Ka.
- For certain values of (Ka), the LHS can be more than 1 or less than -1. For those values it is impossible satisfy the energy quantization condition because the $|\cos(ka)| \leq 1$.
- The corresponding energies $E = \hbar^2K^2/2m$ are forbidden.

Plot of Energy Quantization Condition of K-P model



Kronig-Penney Model

Let us consider the plot of energy vs k (wave number of Bloch wave)



Effective Electron Mass

- The function $E(k)$ can be complicated for a Bloch wave. Quite often it is parametrized as

$$E(k) = E_0 \left[1 - \cos(ka)\right]$$

  $E(k) \sim k^2$ for small k.
- For a plane wave we have $E = \hbar^2 k^2 / 2m$. This implies

$$\begin{aligned} \frac{1}{\hbar}\frac{dE}{dk} &= \frac{p}{m} = v \\ \frac{1}{\hbar^2}\frac{d^2E}{dk^2} &= \frac{1}{m} \end{aligned}$$

Effective Electron Mass

- Given the $E(k)$ relation for an electron in a Bloch wave, we define an effective speed and an effective mass through the equations

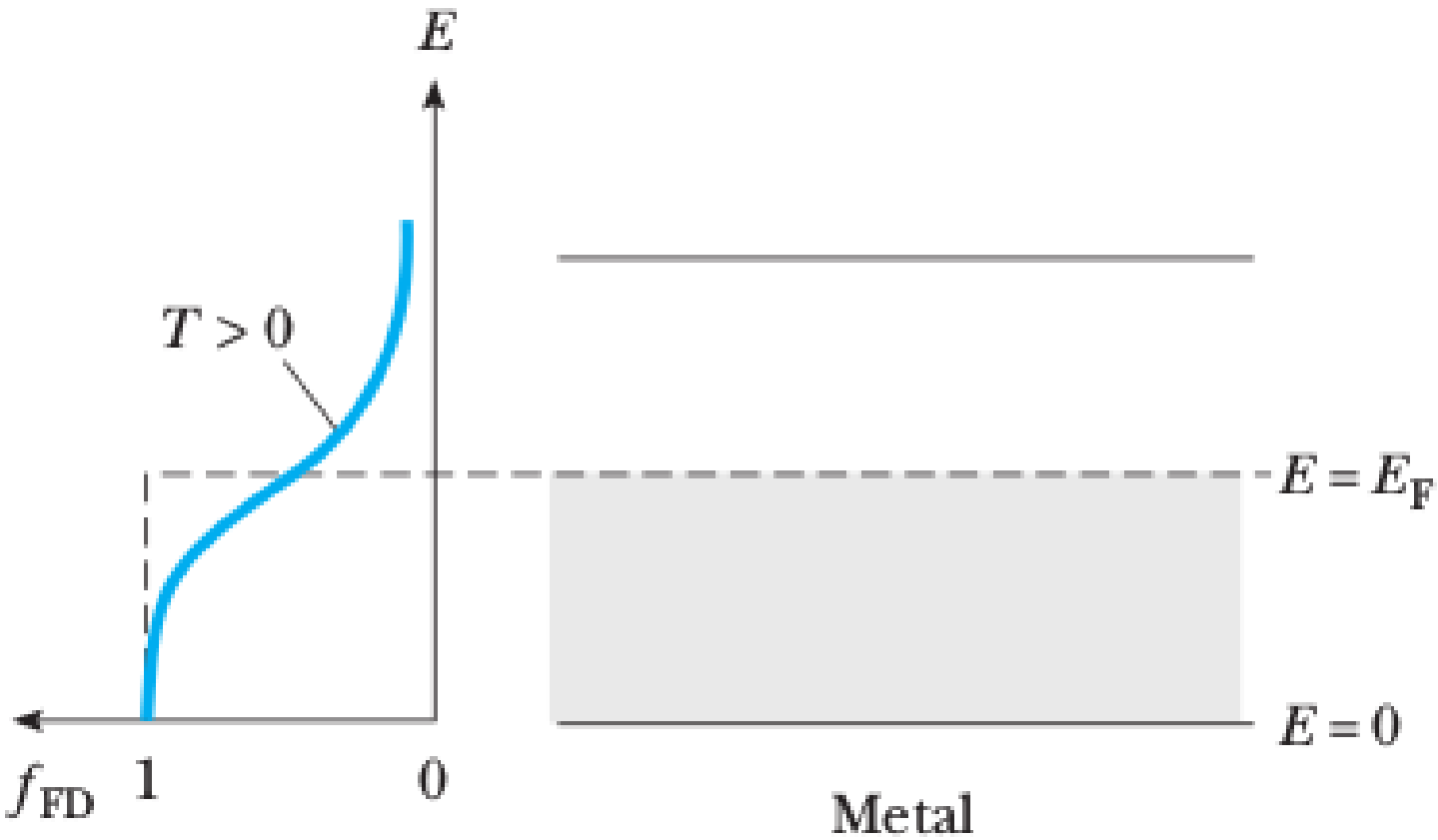
$$\begin{aligned} \frac{1}{\hbar}\frac{dE}{dk} &= v^* \\ \frac{1}{\hbar^2}\frac{d^2E}{dk^2} &= \frac{1}{m^*} \end{aligned}$$

- This mass is positive for values of k near the bottom of the band and is negative for values of k near the top of the bond.
- This occurs because $E(k)$ curve is concave (i.e. curves upwards) at the bottom of the band but it is convex (i.e. curves downwards) at the top of the band.

Energy Band in Conductors

- We look at the lowest energy band that contains these free electrons. If all the energy levels in this band are NOT filled, then the material is called conductor and the energy band is called conduction band.
- These electrons are free to move around the material. If an electron is disturbed, it can move to a neighbouring quantum state because such states are empty.
- If an external electric field is applied they will move in the direction opposite to the electric field and give rise to an electric current.
- Thus in metals, the charge carriers are always electrons and the Hall coefficient is always negative.
- The conductivity of a material depends on the fraction of the energy levels in the conduction band that are filled.

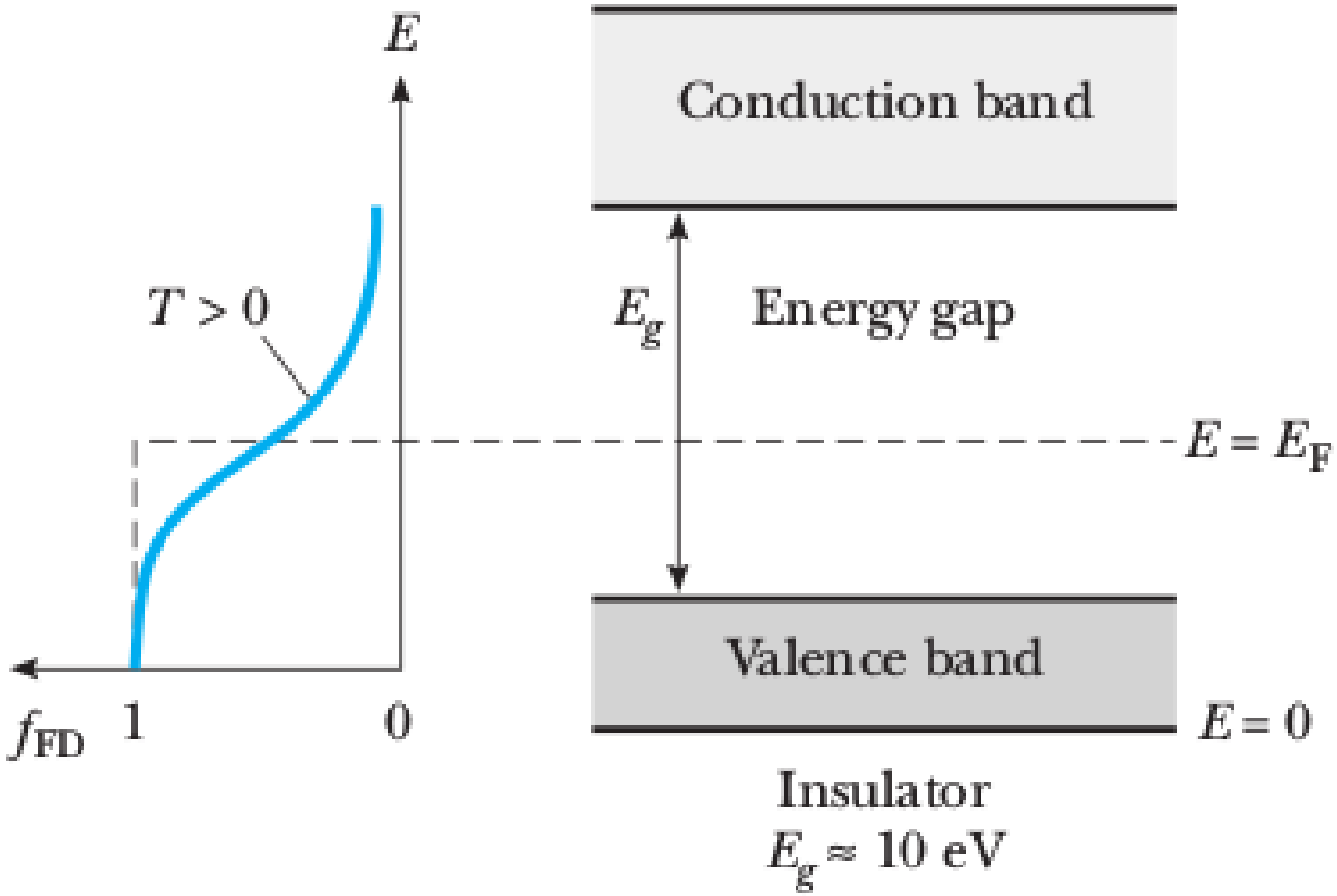
Fermi Energy for Conductors



Valence Band and Conduction Band in Insulators

- If all the energy levels in the lowest energy band are filled, then the material is an insulator and the lowest energy band is called valence band and the allowed energy band above it is called conduction band.
- If an electron in the valence band is disturbed, it can not move into a neighbouring quantum state because all the neighbouring states are filled.
- Pauli's exclusion principle forbids the movement of the electrons within the valence band.
- If an electron can promoted to the conduction band, it is free to move. For insulators, $E_g \simeq 10$ eV. So the probability of the electrons acquiring thermal energy to go upto conduction band is negligible.
- So an insulator does not conduct at all.

Fermi Energy for Insulators



Valence Band and Conduction Band in Semiconductors

- Sometimes, a material is an insulator at low temperatures but is a conductor at high temperatures. For these materials, the energy band gap $E_g \simeq 1$ eV and there is a non-negligible probability for the thermal energy to move some of the electrons from the valence band to the conduction band.
- Semiconductors are the most famous examples of such materials.
- How good a conductor it becomes depends on (a) the temperature and (b) the energy band gap between the valence and conduction bands.

Fermi Energy in Band Theory

- In discussing the Fermi-Dirac distribution, we introduced the concept of Fermi energy. Then it was defined to be the highest energy state that was filled at $T = 0$.
- Later, when we considered the F-D distribution for $T \neq 0$, we defined E_F to be the energy where $f_{\mathrm{FD}} = 1/2$. We use this definition in band theory.
- For conductors, the E_F is the highest energy level that is occupied at $T = 0$.
- For insulators, E_F is defined to be midway between the top of the valence band and the bottom of the conduction band. It is in the forbidden region (within the band gap).
- The definition is a bit artificial but it is useful definition which lends itself to appropriate modifications when we consider situations where some of the electrons are transferred from the valence band to the conduction band.