Energy Band Theory of Solids

in free electron model of metals assumes the conduction electrons to move freely in a region of constant potential or zero potential without interacting with the crystal lattice

this model explains certain properties of metals, such as conductivity, sp heat, etc but fails to explain other properties of solids in general, hence it needs to modified

- In fact an electron in a solid moves in a region of periodic varying potential, caused by positive ion cores situated at the lattice points, plus the average effect of all other free electrons
- This results in the diffraction of electrons by the lattice
- When the de Broglie wavelength of the electrons corresponds to a periodicity in the spacing of the ions
  -the electron interacts strongly with the lattice
  -and undergoes bragg reflection

We solve the Schrödinger equation for an electron in a crystal lattice to find the allowed energies.

--Let us consider a one dimensional crystal lattice, actual potential as shown in figure

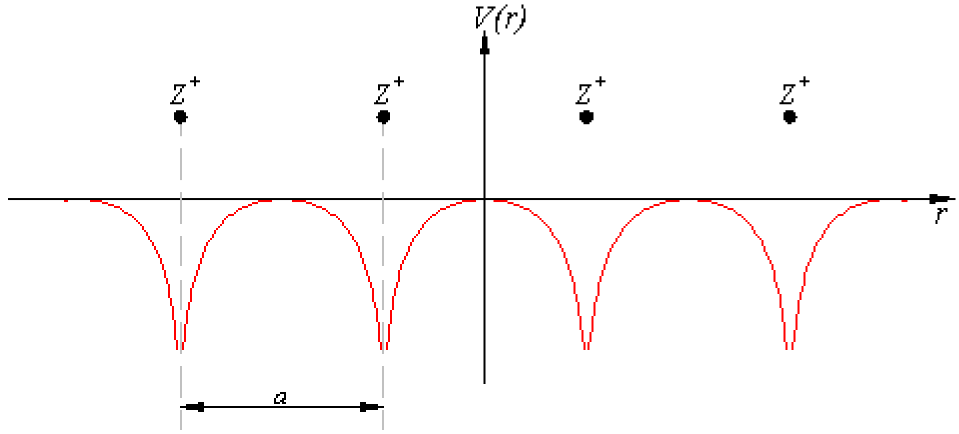
--kronig penny suggested a simplified model potential consisting of an infinite row of rectangular potential wells separated by barriers of width b

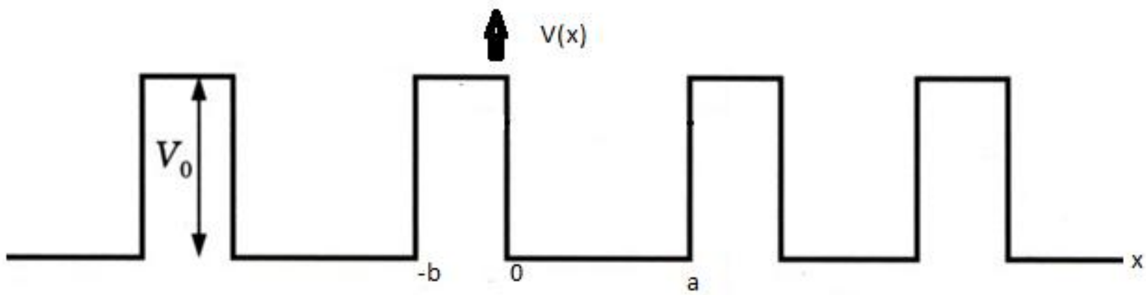
--with the space periodicity a

-- each well represents a potential produced by ions

Plane wave function $\psi_k(x) = e^{ikx}$ is modified by the periodic potential to be of the form $\psi_k(x) = u_k(x)e^{ikx}$.

Where $u_k(x) = u_k(x+a)$ (Bloch Function)





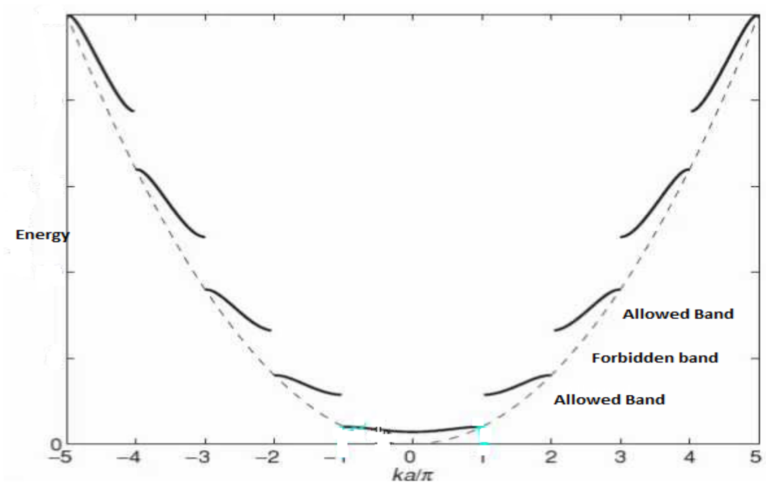
On solving Schrodinger equation of the electron for the Kronig Penney potential under the condition that ψ and $d\psi / dx$ must be continuous at the boundaries of the well, a complicated expression for the allowed energies in terms of k of the electron is obtained which shows that the gap in the energy occur at values given by

$$k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm\frac{3\pi}{a}, ...$$

Figure shows the relationship between energy ε and wave number k for a one dimensional lattice. The dashed curve is the free electron parabola (when there no potential, KE $=p^2/2m$, or

$$E = \frac{h^2}{2m}k^2$$

At the above value of k we get energy gap, whereas for values of k not near these values the energy are much like that of free electron. The origin of the allowed energy bands are forbidden gaps are seen in figure.



The occurrence of gaps can be understood in terms of Bragg reflection. The Bragg's condition is

$$2a\sin\theta = n\lambda$$

Where a is the spacing between the ions of the lattice. Since we are considering the lattice in one dimension only, the above equation becomes

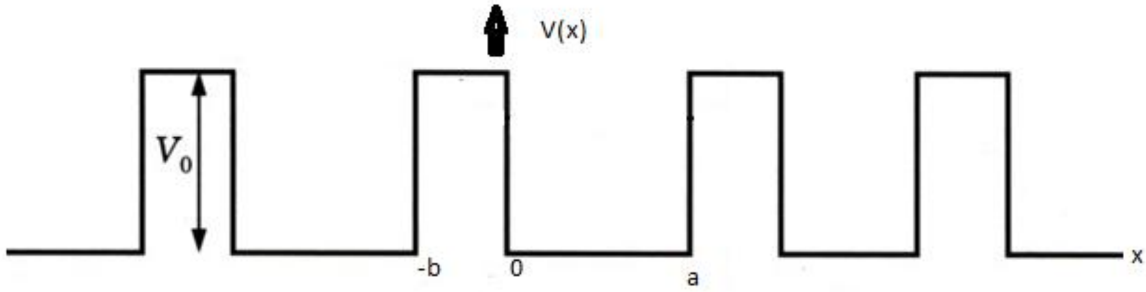
$$2a = n\lambda$$

Or $2a = n\lambda 2\pi / 2\pi$

Or, $k = n\dfrac{\pi}{a} = \pm\dfrac{\pi}{a}, \pm\dfrac{2\pi}{a}, \pm\dfrac{3\pi}{a}.....$

These are just the values of k at which the gaps in the $\varepsilon - k$ curve occur. The waves corresponding to values of k not satisfying the above condition travel almost freely and those satisfying the condition are reflected resulting in standing waves.

The wave function associated with Kronig Penney model may be calculated on solving Schrodinger wave equation. We have S E



$H\psi = E\psi$

Or, $\frac{d^2\psi}{dx^2} + \frac{2m}{h^2}E\psi = 0$ for 0 < x < a

Or we can write $\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0$ (1)

Where the value of $\alpha^2 = \frac{2mE}{h^2}$

Also, $\frac{d^2\psi}{dx^2} + \frac{2m}{h^2}(E - V_0)\psi = 0$ for -b < x < 0

Or we can write $\frac{d^2\psi}{dx^2} - \beta^2\psi = 0$ (2)

Where $\beta^2 = \frac{2m}{h^2}(V_0 - E)$

As the potential is periodic, the wave function must have the Bloch form

$\psi(x) = e^{ikx}u(x)$ (3)

Where $\mathrm{u}(x) = \mathrm{u}(\mathrm{x}+\mathrm{a})$

If $\mathrm{u}_1(x)$ and $\mathrm{u}_2(x)$ represent the value of $u(x)$

-in two different regions

Then above equations may be written as

Differentiating eq (3)

$$\frac{d\psi}{dx} = ike^{ikx}u(x) + \mathrm{e}^{ikx}\frac{du_1}{dx}$$

Again differentiating

$$\frac{d^2\psi}{dx^2} = ikike^{ikx}u_1(x) + \mathrm{ike}^{ikx}\frac{du_1}{dx} + ik\,\mathrm{e}^{ikx}\frac{du_1}{dx} + e^{ikx}\frac{d^2u_1}{dx^2}$$

Or, $\dfrac{d^2\psi}{dx^2} = -k^2e^{ikx}u_1(x) + 2\,\mathrm{ike}^{ikx}\dfrac{du_1}{dx} + e^{ikx}\dfrac{d^2u_1}{dx^2}$

Putting these values in eq (1)

$$-k^2e^{ikx}u_1(x) + 2\,\mathrm{ike}^{ikx}\frac{du_1}{dx} + e^{ikx}\frac{d^2u_1}{dx^2} + \alpha^2e^{ikx}u_1 = 0$$

Or simplifying, we get

$$\frac{d^2u_1}{dx^2} + 2\,\mathrm{ik}\frac{du_1}{dx} - (k^2 - \alpha^2)u_1 = 0 \qquad (4)$$

Similarly, we get

$$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (\beta^2 + k^2)\,\mathrm{u}_2 = 0 \qquad (5)$$

The solution of these equations may be written as

$$u_1 = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x} \qquad (6)$$

$$u_2 = Ce^{(\beta-ik)x} + De^{-(\beta+ik)x} \qquad (7)$$

Here A B C D are constant to be determined by the boundary conditions.

ψ and $d\psi / dx$ to be continuous throughout the crystal.

$$u_1(x)\big|_0 = u_2(x)\big|_0 \qquad (8)$$

$$du_1 / dx\big|_{x=0} = du_2 / dx\big|_{x=0} \qquad (9)$$

And $u_1(x)\big|_{x=a} = u_2(x)\big|_{x=-b}$ (10)

$du_1/dx\big|_{x=a} = du_2/dx\big|_{x=-b}$ (11)

Now applying the boundary conditions we get the following relations

$$A + B = C + D \quad (12)$$

$$Ai(\alpha - k) - Bi(\alpha + k) = C(\beta - ik) - D(\beta + ik)$$

(13) $Ae^{i(\alpha-k)a} + Be^{-i(\alpha+k)a} = Ce^{-(\beta-ik)b} + De^{(\beta+ik)b}$ (14)

$$Ai(\alpha - k)e^{i(\alpha-k)a} - Bi(\alpha + k)e^{-i(\alpha+k)a} = C(\beta - ik)e^{-(\beta-ik)b} - D(\beta + ik)e^{(\beta+ik)b} \quad (15)$$

Determinant coefficient must be zero For non vanishing solution

On simplifying these equation one can get

$$\cos k(a+b) = \left[\frac{\beta^2 - \alpha^2}{2\alpha\beta}\right]\sin\alpha a \sinh\beta b + \cos\alpha a \cosh\beta b$$

This equation is quite complicated; however we must draw some conclusions

To solve above equation, Kronig Penney supposed that the potential energy is zero at lattice sites and equal V_0 inside. Also assumed that, as the height of the potential barrier V_0 tends to infinity and the width of the barrier b tends to zero so that the product V_0 b remains finite. Under these assumptions

$$\sinh\beta b \to \beta b$$

$$\cosh\beta b \to 1 \text{ as } b \to 0$$

Therefore

$$\cos ka = \left[\frac{\beta^2 - \alpha^2}{2\alpha\beta}\right]\beta b \sin\alpha a + \cos\alpha a$$

Hence on solving we get

$$\cos ka = \left[\frac{mV_0}{\alpha\beta h^2}\right]\beta b \sin \alpha a + \cos \alpha a$$

$$\cos ka = \left[\frac{mV_0 b}{\alpha h^2}\right]\sin \alpha a + \cos \alpha a$$

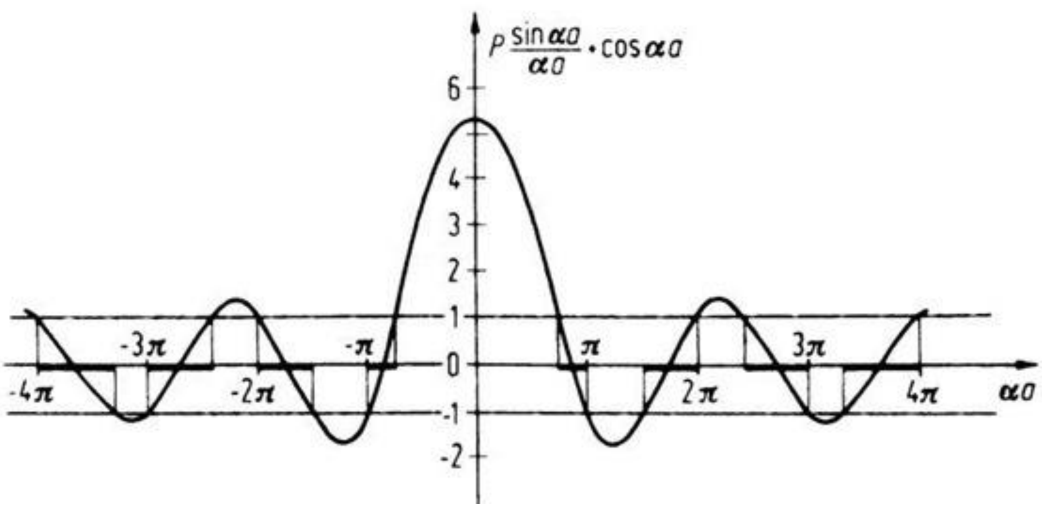
Or, $\cos ka = \left[\frac{mV_0 ba}{\alpha a h^2}\right]\sin \alpha a + \cos \alpha a$

Or, $\cos ka = \left[\frac{mV_0 ba}{h^2}\right]\frac{\sin \alpha a}{\alpha a} + \cos \alpha a$

Or, $\cos ka = P(\sin \alpha a / \alpha a) + \cos \alpha a$

Where

$$P = \left[\frac{mV_0 ba}{h^2}\right]$$



This is the condition for the solutions of the wave equation to exist. As you see that this is satisfied only for those value of αa for which its left hand side lies between +1 and -1. It is because its right hand side must lie in range. Such values of αa represent the wave like solution and are reachable. On the other hand, the other values of αa will be inaccessible. The significances of this can be agreed very well by the figure. The part of vertical axis lying between the horizontal lines represents the range acceptable. Since α^2 is proportional to the energy so αa will be measure of energy. It is clear that the region for αa where the value of $P \sin \alpha a / \alpha a + \cos \alpha a$ does not lie between -1 and +1. Therefore, these values of αa and henceforth of energy E, there is no solution. Such region of energy is disallowed and is named forbidden bands. This analysis led to the following

The energy spectrum of the electron consists of alternate regions of allowed energy that is continuous band and forbidden energy band. Usually these bands are referred as allowed and forbidden energy bands.

1. As the value of αa increases the width of the allowed energy bands increases.
2. The quantity P, which is noted as a measure of potential barrier strength. If P is large, means the potential barrier V_0 b is large. For the infinite deep well the electron can be considered as confined into a single potential well. It is applied to the crystals where the electrons are very tightly bound with their nuclei.
3. In second case, when P is small, the barrier strength is small that is $P \to 0$, the electron can be considered to be moving freely through the potential well. It is the case of crystal where the electron is almost free of their nuclei.
4. Hence we conclude that the width of particular allowed band decreases as P increases. As $P \to \infty$, the allowed bands are compressed into energy levels and the energy spectrum is thus a line spectrum. Whereas $P \to 0$, we have the free electron model of the energy spectrum. It is known as continuous. In between these limits, the position and the width of the allowed and forbidden bands for any value of P are obtained.
5. To calculate the energy spectrum in extreme cases ($P \to \infty$), then we have

$\sin \alpha a / \alpha a$ tends to zero

or

$$\sin \alpha a = 0 = \sin n\pi$$

$$\alpha a = n\pi$$

Or we can write $\frac{2mE}{h^2} a^2 = n^2 \pi^2$

Or you can write, $E = \frac{\pi^2 h^2}{2ma^2} n^2$

It is the physically expected result because the large P makes the tunneling through the barrier nearly unlikely.

In second case when $P \to 0$

We get $\cos \alpha a = \cos ka$

Which implies $\alpha = k$

Or, $\alpha^2 = k^2$

Which gives $E = \frac{h^2 k^2}{2m}$, this is equivalent to the case of free particle.

This shows that the allowed energy states of electrons are continuous.

Ex: Show that for the Kronig Penney potential with $P \leq 1$, the energy of the lowest energy band at k=0 is given by $E = \dfrac{h^2 P}{4\pi^2 m a^2}$

Solution: for k=0 $P \sin \alpha a / \alpha a + \cos \alpha a = \cos ka$ becomes

$P \sin \alpha a / \alpha a + \cos \alpha a = 1$

Or we may write

$P / \alpha a = 1 - \cos \alpha a / \sin \alpha a$

On expanding sine and cosine function

Where $\cos \alpha a \simeq 1 - \dfrac{\alpha^2 a^2}{2}$

And $\sin \alpha a \simeq \alpha a$

So we can write $P / \alpha a = \dfrac{\alpha^2 a^2}{2}$

We know $\dfrac{8\pi^2 m E}{h^2} = \alpha^2$

Hence we get $P = \dfrac{8\pi^2 m E}{h^2} (a^2 / 2)^2$

Or $E = \dfrac{h^2 P}{4\pi^2 m a^2}$