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Electrical Properties of Matter

Potential experienced by e^- in passing through crystal (Assumption)

(1) Perfectly periodic with the period of lattice

(2) Arise from periodic distribution of +ve charge associated with ion cores situated on lattice + constant (average) contribution due to all other free e's of the crystal

1-D represent. of potential experienced by an e^- in perfectly periodic lattice of const. a, shows a sharp fall when e^- approaches a +ve charged nucleus

(3) Ion cores are considered at rest

(4) Total wave function for the system is obtained from a combination of wave functions each one of which involves the coordinates of one e^-

A Field experienced by a particular e^- is assumed to be resultant of the field due to fixed nuclei & avg field due to charge distribution of all other e's

Result: (1) Existence of allowed ~~band~~ energy bands separated by a forbidden gap

(2) E(K) are periodic in K (energy function of e's)

(3) In free e's theory $E = \frac{\hbar^2 k^2}{2m}$ → No upper lt to energy & K but here band gap exists.

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Bloch Theorem

1) One Dimensional Schr. eqn for e^- moving in const potential V_0

$$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

Soltns of above (plane wave) $\rightarrow \psi(x)\, e^{iKx}$

Also $(E - V_0) = \frac{\hbar^2 K^2}{2m} = p^2/2m = E_{Kin}$

2) for e^- in 1-D for periodic potential $V(x)$, Sch eqn $\Rightarrow$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi = 0 \longrightarrow \text{eq } (t)$$

3) $V(x) = V(x+a) \longrightarrow$ Periodic Potential & period $= a =$ lattice const

This property is known as Bloch Theorem / Floquet's theorem.

$\downarrow$ solution of Sch. eqn in (2) are plane waves modulated by a function $U_K(x)$ having same periodicity as that of lattice const

$$\psi(x) = e^{iKx}\, U_K(x) \longrightarrow \text{eq } (p)$$

$$U_K(x) = U_K(x+a) \longrightarrow \text{eq } (2)$$

Here $\psi_K(x) \longrightarrow$ Bloch functions

4) <u>Proof</u> $\Rightarrow$

let $g(x)$, $f(x) \rightarrow$ Two real & independent solutions of eqn in (2)

General solution $\Rightarrow$ $\psi(x) = A f(x) + B g(x)$

$$\left.\begin{aligned} V(x) &= V(x+a) \\ g(x) &= g(x+a) \\ f(x) &= f(x+a) \end{aligned}\right] \rightarrow \text{Also soltn of eqn in (2)}$$

But eqn in (2) ~~must~~ can't have more than 2 independent soltn

Hence $g(x+a)$, $f(x+a)$ must be expressible in terms of $g(x)$, $f(x)$

$$\left.\begin{aligned} f(x+a) &= \alpha_1 f(x) + \alpha_2 g(x) \\ g(x+a) &= \beta_1 f(x) + \beta_2 g(x) \end{aligned}\right] \rightarrow \text{eq } (*)$$

$\alpha_1, \alpha_2, \beta_1, \beta_2 \longrightarrow$ Real functns of energy E.

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5) Another general soln of eqn in (2) —

$$\psi(x+a) = A f(x+a) + B g(x+a)$$
$$= A(\alpha_1 f(x) + \alpha_2 g(x)) + B(\beta_1 f(x) + \beta_2 g(x))$$
$$= (A\alpha_1 + B\beta_1) f(x) + (A\alpha_2 + B\beta_2) g(x)$$
$$= f(x)\lambda A + \lambda B g(x) = \lambda (A f(x) + B g(x))$$

$\lambda \to$ Constt.

Also, $\boxed{\psi(x+a) = \lambda \psi(x)}$ eq (v)

~~Also~~ $\cancel{\psi(x+a) = \lambda \psi(x)}$

We assumed
$A\alpha_1 + B\beta_1 = \lambda A$
$A\alpha_2 + B\beta_2 = \lambda B$ $\to$ (xx)

From (xx)
$$A(\alpha_1 - \lambda) + B\beta_1 = 0$$
$$A\alpha_2 + B(\beta_2 - \lambda) = 0$$

Eqns (xx) yields non-zero values for A, B only if determinant of coefficients vanishes,
$$\begin{vmatrix} \alpha_1 - \lambda & \beta_1 \\ \alpha_2 & \beta_2 - \lambda \end{vmatrix} = 0$$
$$\lambda^2 - (\alpha_1 + \beta_2)\lambda + (\alpha_1\beta_2 - \alpha_2\beta_1) = 0$$

We now show, $\alpha_1\beta_2 - \alpha_2\beta_1 = 1$

As $g(x)$, $f(x)$ are real & independent soltns of eqn in (2), —
$$\frac{d^2 g(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V(x)) g(x) = 0 \quad \times f(x)$$
$$\frac{d^2 f(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V(x)) f(x) = 0 \quad \times g(x)$$

& subtract we get,
$$f(x)\frac{d^2 g(x)}{dx^2} - g(x)\frac{d^2 f(x)}{dx^2} = 0$$

or
$$\frac{d}{dx}\left[f(x)\frac{dg(x)}{dx} - g(x)\frac{df(x)}{dx}\right] = 0$$
$$\underbrace{f(x)\frac{dg(x)}{dx} - g(x)\frac{df(x)}{dx}}_{W(x) = \text{Wronskian}} = \text{Constt.}$$

$W(x) \rightarrow$ Wronskian of the solns. Similarly from eq (x) we get

$$f(x+a)\frac{d}{dx}g(x+a) - g(x+a)\frac{d}{dx}f(x+a) = (\alpha_1\beta_2 - \alpha_2\beta_1)\left(f(x)g'(x) - g(x)f'(x)\right)$$

$$W(x+a) = (\alpha_1\beta_2 - \alpha_2\beta_1)\,W(x)$$

$$\rightarrow \boxed{\alpha_1\beta_2 - \alpha_2\beta_1 = 1} \rightarrow \text{Proved}$$

How?? Multiply eq (x) by $g(x+a)$ & $f(x+a)$ and then subtract them.

$$f(x+a)\frac{d}{dx}g(x+a) = (\alpha_1 f_x + \alpha_2 g_x)\frac{d}{dx}(\beta_1 f_x + \beta_2 g_x)$$

$$= (\alpha_1 f_x + \alpha_2 g_x)(\beta_1 f'_x + \beta_2 g'_x)$$

$$-g(x+a)\frac{d}{dx}f(x+a) = -(\beta_1 f_x + \beta_2 g_x)(\alpha_1 f'_x + \alpha_2 g'_x)$$

$$f_{x+a}\,g'_{x+a} - g_{x+a}\,f'_{x+a} = (\alpha_1 f_x + \alpha_2 g_x)(\beta_1 f'_x + \beta_2 g'_x) - (\beta_1 f_x + \beta_2 g_x)(\alpha_1 f'_x + \alpha_2 g'_x)$$

$$= \cancel{\alpha_1\beta_1 f'_x \alpha_1}$$

$$= \alpha_1\beta_1 \cancel{f_x f'_x} + \alpha_1\beta_2 f_x g'_x + \alpha_2\beta_1 g_x f'_x + \cancel{\alpha_2\beta_2 g_x g'_x}$$

$$- \beta_1\alpha_1 \cancel{f_x f'_x} - \beta_1\alpha_2 f_x g'_x - \beta_2\alpha_1 g_x f'_x - \cancel{\beta_2\alpha_2 g_x g'_x}$$

$$= \alpha_1\beta_2(f_x g'_x - g_x f'_x) + \alpha_2\beta_1(g_x f'_x - f_x g'_x)$$

$$= (\alpha_1\beta_2 - \alpha_2\beta_1)(f_x g'_x - g_x f'_x)$$

$$RHS = \underbrace{(\alpha_1\beta_2 - \alpha_2\beta_1)}_{(\alpha_1\beta_2 - \alpha_2\beta_1)}\underbrace{\left(f(x)\frac{d}{dx}g(x) - g(x)\frac{d}{dx}f(x)\right)}_{W(x)}$$

$$LHS = \underbrace{\left(f(x+a)\frac{d}{dx}g(x+a) - g(x+a)\frac{d}{dx}f(x+a)\right)}_{W(x+a)}$$

So $W(x+a) = \underbrace{(\alpha_1\beta_2 - \alpha_2\beta_1)}_{\text{Should be unity}}\,W(x)$

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Hence $\boxed{\lambda^2 - (\alpha_1+\beta_2)\lambda + 1 = 0}$

$(\alpha_1+\beta_2)^2 < 4$ $\quad$ $(\alpha_1+\beta_2)^2 > 4$

Case - I. $\lambda^2 - (\alpha_1+\beta_2)\lambda + 1 = 0 \longrightarrow$ It has two roots

Sum of roots $= \lambda_1 + \lambda_2 = \frac{-b}{a} = \alpha_1 + \beta_2$

Product " " $= \lambda_1\lambda_2 = c/a = \frac{1}{1} = 1$

But $\lambda_1, \lambda_2 \rightarrow$ complex roots & $\lambda_1\lambda_2 = 1$ so they must be complex conjugates of each other

$\Rightarrow \quad \lambda_1 = e^{iKa}$

$\lambda_2 = e^{-iKa}$

$\Rightarrow \left.\begin{array}{l} \psi_1(x+a) = e^{iKa}\psi_1(x) \\ \psi_2(x+a) = e^{-iKa}\psi_2(x) \end{array}\right\} \rightarrow$ Bloch function or $\boxed{\psi(x+a) = e^{\pm iKa}\psi(x)}$ eq (r)

Replace $x \rightarrow x+a$ in Bloch function in eq (p)

and $\psi(x+a) = e^{\pm iK(x+a)} u_K(x+a)$

using eq (q), $\psi(x+a) = e^{\pm iK(x+a)} u_K(x)$

$= e^{\pm iKa} e^{\pm iKx} u_K(x)$

$\boxed{\psi(x+a) = e^{\pm iKa}\psi(x)}$ eq (s)

eq (r) & eq (s) are same

Hence $\psi(x)$ represent a solution to eq (t) having same property as eq (u) with $\lambda = e^{\pm iKa}$

Hence Bloch function of type of eq (p) represents soln to such eq in, proves Bloch theorem

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Case-II : $\lambda_1, \lambda_2 \rightarrow$ Real roots

such that $\lambda_1 = e^{\mu a}$, $\lambda_2 = e^{-\mu a}$ $\mu \rightarrow$ Real

Corresponding soltns to sch. eqn are —

$$\psi_1(x) = e^{\mu x} u(x)$$
$$\psi_2(x) = e^{-\mu x} u(x)$$

- Mathematically ψ_1, ψ_2 are valid but these soltns are not acceptable e^- wave functions as these are not bounded
- Ratio $\dfrac{\psi(x+na)}{\psi(x)} \rightarrow \infty$ as n approaches $\pm\infty$
- Allowed roots $\rightarrow$ Allowed energy regions
  Disallowed roots $\rightarrow$ forbidden energy regions
- Energy spectrum of an e^- in periodic potential consists of allowed & forbidden energy regions / bands.
- 3-D $\rightarrow$ $\psi_K(\vec{r}) = e^{i\vec{K}\cdot\vec{r}} u_K(\vec{r})$
  Bloch th.
- If lattice potential vanishes $\rightarrow u_K(\vec{r}) = $ Const.
  & $\psi_K(\vec{r}) = e^{i\vec{K}\cdot\vec{r}}$

(7)

KRONIG-PENNY MODEL

1-D Periodic Potential used by Kronig & Penney for e^- moving in lattice

K P Model → P.E. of an e^- in a linear array of +ve nuclei has the form of a periodic array of square wells with period $(a+b)$

$0 < x < a \longrightarrow P.E. = 0$ (e^- is independent of nucleus)

$-b < x < 0 \longrightarrow P.E = V_0$

This model is highly artificial is very useful as it illustrates the imp. characteristics of e^- in periodic lattice in a very simple way.

* Wave-functns →

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-0)\psi = 0 \quad , 0<x<a$$

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

* let $\alpha^2 = \frac{2mE}{\hbar^2}$, $\beta^2 = \frac{2m(V_0-E)}{\hbar^2}$

$$\boxed{\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0} \quad 0<x<a \quad \text{and} \quad \boxed{\frac{d^2\psi}{dx^2} - \beta^2\psi = 0} \quad -b<x<0 \longrightarrow \text{eqn } (1)$$

* Since potential is periodic wave functions must be of form Bloch function: $\psi(x) = e^{ikx}\, U_k(x)$

$$\boxed{U_k(x) = U_k(x + (a+b))}$$

$$\frac{d\psi(x)}{dx} = ik e^{ikx} U_k(x) + e^{ikx}\frac{dU_k(x)}{dx}$$

$$\frac{d^2\psi(x)}{dx^2} = (ik)^2 e^{ikx} U_k(x) + ik e^{ikx}\frac{dU_k(x)}{dx} + (ik) e^{ikx}\frac{dU_k}{dx} + e^{ikx}\frac{d^2U_k(x)}{dx^2}$$

$$\boxed{\frac{d^2\psi(x)}{dx^2} = -k^2 e^{ikx} U_k(x) + 2ik e^{ikx}\frac{dU_k}{dx} + e^{ikx}\frac{d^2U_k(x)}{dx^2}}$$

(8)

Substitute $\frac{d^2\psi(x)}{dx^2}$, $\psi(x)$ in eqn (1)

$$\left(-k^2 e^{ikx} u_k(x) + 2ik e^{ikx}\frac{du_k}{dx} + e^{ikx}\frac{d^2u_k(x)}{dx^2}\right) + \alpha^2\left(e^{ikx}u_k(x)\right) = 0$$

$$\Rightarrow \frac{d^2u_k(x)}{dx^2} + 2ik\frac{du_k}{dx} + (\alpha^2 - k^2)u_k(x) = 0 \longrightarrow \text{eq (i)}'$$

$$\& \Rightarrow \frac{d^2u_k(x)}{dx} + 2ik\frac{du_k}{dx} + (-\beta^2 - k^2)u_k(x) = 0 \longrightarrow \text{eq (ii)}'$$

Put $u_k(x) = u_1$ for $0<x<a$
$= u_2$ for $-b<x<0$

$$\Rightarrow u_1'' + 2iku_1' + (\alpha^2 - k^2)u_1 = 0 \qquad 0<x<a$$
$$u_2'' + 2iku_2' - (\beta^2 + k^2)u_2 = 0 \qquad -b<x<0$$

Solutions to these eqns are

$$u_1 = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x} \qquad 0<x<a$$
$$u_2 = Ce^{(\beta-ik)x} + De^{-(\beta+ik)x} \qquad -b<x<0$$

Bdry Condtns: continuous $u_1(0) = u_2(0)$, $\left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0}$

periodicity $u_1(a) = u_2(-b)$, $\left(\frac{du_1}{dx}\right)_{x=a} = \left(\frac{du_2}{dx}\right)_{x=-b}$

Applying these condtns $\longrightarrow$

$$A + B = C + D$$

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

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

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

Non-zero solutn exist only if

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ i(\alpha-K) & -i(\alpha+K) & \beta-iK & -(\beta+iK) \\ e^{i(\alpha-K)a} & e^{-i(\alpha+K)a} & e^{-(\beta-iK)b} & e^{(\beta+iK)b} \\ i(\alpha-K)e^{i(\alpha-K)a} & -i(\alpha+K)e^{-i(\alpha+K)a} & (\beta-iK)e^{-(\beta-iK)b} & -(\beta+iK)e^{(\beta+iK)b} \end{vmatrix} = 0$$

$$\Rightarrow \frac{\beta^2+\alpha^2}{2\beta\alpha}\sinh\beta b \sin\alpha a + \cosh\beta b \cos\alpha a = \cos K(a+b) \rightarrow eq\ (2)$$

To further simplify Kronig & Penney considered the case when $V_0 \rightarrow \infty$, $b \rightarrow 0$, $V_0 b \rightarrow$ finite

Potential barrier remains delta $\Rightarrow$ fonctn $\rightarrow$ Known as barrier strength

As $b \rightarrow 0 \Rightarrow \sinh\beta b \rightarrow \beta b$

$\cosh\beta b \rightarrow 1$

so,

Adding α^2 & β^2 we get

$$\beta^2+\alpha^2 = \cancel{\frac{2mE}{\hbar^2}} + \frac{2mV_0}{\hbar^2} - \cancel{\frac{2mE}{\hbar^2}}$$

$$\beta^2+\alpha^2 = \frac{2mV_0}{\hbar^2}$$

$$\frac{\beta^2+\alpha^2}{2} = \frac{mV_0}{\hbar^2}$$

$$\frac{\beta^2+\alpha^2}{2\alpha\beta} = \frac{mV_0}{\beta\hbar^2} \quad \text{--- (3)}$$

Similarly from eq (2) we get

$$\frac{\beta^2+\alpha^2}{2\alpha\beta}\cdot(\beta b)\cdot\sin\alpha a + 1\cdot\cos\alpha a = \cos Ka \rightarrow (4)$$

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$\Rightarrow$ from (3), (4) we get $\rightarrow$

$$\left(\frac{mV_0}{\alpha\beta\hbar^2}\right)\beta b \sin\alpha a + \cos\alpha a = \cos ka$$

Put $P = \frac{mV_0 ba}{\hbar^2}$

$$\left(\frac{P}{ba}\right)\frac{1}{\alpha\beta}\beta b \sin\alpha a + \cos\alpha a = \cos ka$$

$$\Rightarrow \quad P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka \longrightarrow \text{eq } (5)$$

Solid lines $\rightarrow$ Allowed energy regions
Broken lines $\rightarrow$ forbidden energy regions

Conclusion

1. Energy spectrum of e^-s $\rightarrow$ Alternate regions of allowed energy bands & forbidden energy bands
2. Width of allowed energy bands $\uparrow$ with $\uparrow$ value of αa or energy
3. Width of particular allowed energy bands $\downarrow$ with $P \uparrow$
   or $\uparrow$ in Binding energy of e^- the width $\downarrow$

$P \rightarrow \infty \Rightarrow$ Allowed energy bands compresses into energy levels & line spectrum is resulted.

& eq (5) has solution only if —

$n \rightarrow$ Integer and $E = \frac{\alpha^2 \hbar^2}{2m} = \frac{\pi^2 \hbar^2}{2ma^2} n^2$

* Above E $\rightarrow$ Energy levels of a particle in const potential box of atomic dimensions.

* Large P $\Rightarrow$ Tunnelling becomes difficult
* $P \rightarrow 0$ $\Rightarrow$ $\cos\alpha a = \cos ka$

$$\alpha = k$$

$$E = \frac{k^2 \hbar^2}{2m} \longrightarrow \text{free } e^- \text{ case}$$

At zero binding energy e^- becomes free

≡ Allowed

Rest portion $\rightarrow$ forbidden energy zone

Above graph

Extreme left $\Rightarrow P = 0 \Rightarrow$ Energy Spect. is quasi continuous

Extreme right $\Rightarrow P = \infty \Rightarrow$ " " " line spectrum

For any other value of P $\rightarrow$ position & width obtained by drawing a vertical line