6.730 Physics for Solid State Applications

Lecture 18: Nearly Free Electron Bands (Part II)

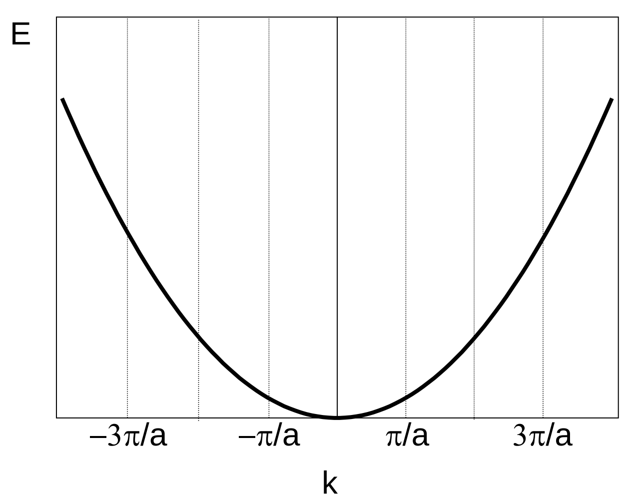
Outline

- Free Electron Bands
- Nearly Free Electron Bands
- Approximate Solution of Nearly Free Electron Bands
- Bloch's Theorem
- Properties of Bloch Functions

March 15, 2004

Free Electron Dispersion Relation

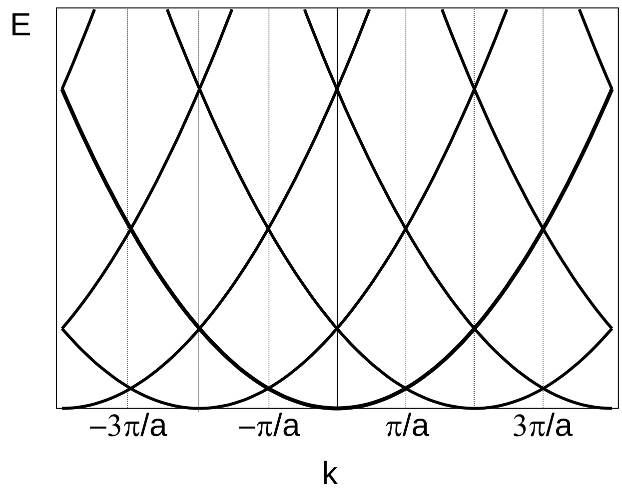
$$E = \frac{\hbar^2 k^2}{2m}$$



Nearly Free Electron Dispersion Relation

For weak lattice potentials, E vs k is still approximately correct... $E = \frac{\hbar^2 k^2}{2m}$

Dispersion relation must be periodic.... $E(k) = E(k + K_i)$



Nearly Free Electron Dispersion Relation

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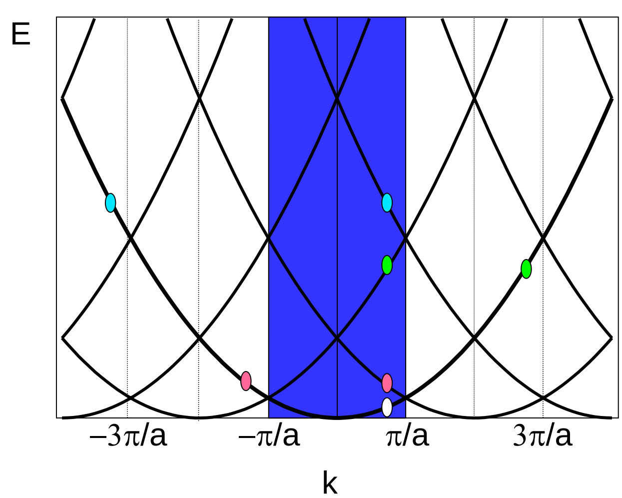
Expect all solutions to be represented within the Brillouin Zone (reduced zone)



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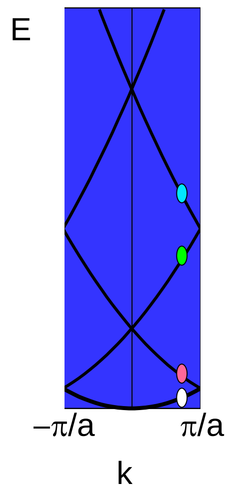

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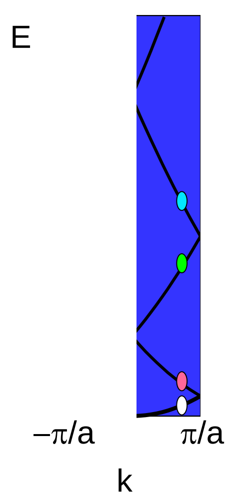
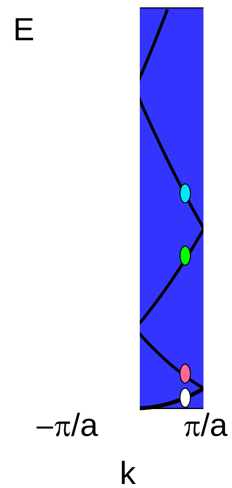
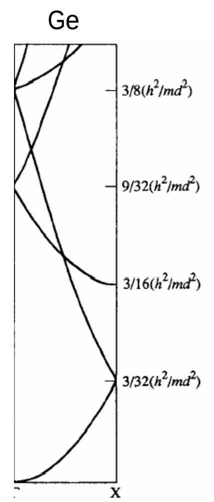


Nearly Free Electron Dispersion Relation

Extension to 3-D requires, translation by reciprocal lattice vectors in all directions... $E(\mathbf{k}) = \mathbf{E}(\mathbf{k} + \mathbf{K_i})$





Nearly Free Electron Dispersion Relation

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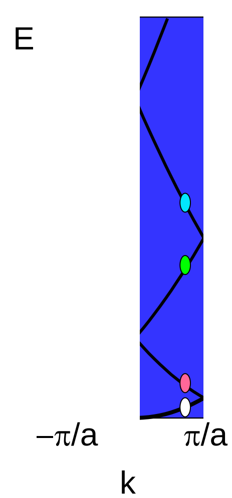
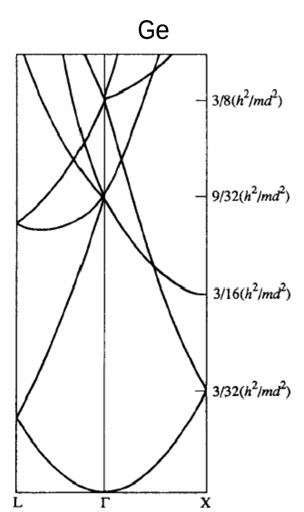




Finite Basis Set Expansion with Plane Waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

Fourier series expansion of Bloch function

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\{\mathbf{K_i}\}} u_{\mathbf{k}}[\mathbf{K_i}] e^{i\mathbf{K_i}\cdot\mathbf{r}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\{\mathbf{K_i}\}} u_{\mathbf{k}}[\mathbf{K_i}] \left(\frac{1}{\sqrt{V_{\text{box}}}} e^{i(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}} \right)$$

Basis functions in expansion are...

$$\phi_{\ell}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}}$$

Finite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

$$H_{m,n} = \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_n})^2 \delta_{\mathbf{K_m},\mathbf{K_n}} + \mathbf{V}[\mathbf{K_m}-\mathbf{K_n}]$$

Fourier Series coefficients for the lattice potential...

$$V[\mathbf{K_m}-\mathbf{K_n}] = \frac{1}{\mathbf{V}_{\text{WSC}}} \int_{\mathbf{V}_{\text{WSC}}} e^{-i(\mathbf{K_m}-\mathbf{K_n})\cdot\mathbf{r}} \mathbf{V}(\mathbf{r}) d^3\mathbf{r}$$

$$E_n(\mathbf{k}) \begin{pmatrix} u_{\mathbf{k,n}}[\mathbf{K_0}] \\ u_{\mathbf{k,n}}[\mathbf{K_1}] \\ u_{\mathbf{k,n}}[\mathbf{K_2}] \\ u_{\mathbf{k,n}}[\mathbf{K_3}] \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_0})^2+\mathbf{V}[0] & V[\mathbf{K_0}-\mathbf{K_1}] & V[\mathbf{K_0}-\mathbf{K_2}] & V[\mathbf{K_0}-\mathbf{K_3}] \\ V[\mathbf{K_1}-\mathbf{K_0}] & \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_1})^2+\mathbf{V}[0] & V[\mathbf{K_1}-\mathbf{K_2}] & V[\mathbf{K_1}-\mathbf{K_3}] \\ V[\mathbf{K_2}-\mathbf{K_0}] & V[\mathbf{K_2}-\mathbf{K_1}] & \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_2})^2+\mathbf{V}[0] & V[\mathbf{K_2}-\mathbf{K_3}] \\ V[\mathbf{K_3}-\mathbf{K_0}] & V[\mathbf{K_3}-\mathbf{K_1}] & V[\mathbf{K_3}-\mathbf{K_2}] & \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K_3})^2+\mathbf{V}[0] \end{pmatrix} \begin{pmatrix} u_{\mathbf{k,n}}[\mathbf{K_0}] \\ u_{\mathbf{k,n}}[\mathbf{K_1}] \\ u_{\mathbf{k,n}}[\mathbf{K_2}] \\ u_{\mathbf{k,n}}[\mathbf{K_3}] \end{pmatrix}$$

Infinite Basis Set Expansion with Plane Waves

Hamiltonian Matrix

$$
\begin{bmatrix}
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\lambda(k+K_{-3})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} & V_{-7} \\
V_1 & \lambda(k+K_{-2})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} & V_{-6} \\
V_2 & V_1 & \lambda(k+K_{-1})^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} & V_{-5} \\
V_3 & V_2 & V_1 & \lambda(k+K_0)^2+V_0 & V_{-1} & V_{-2} & V_{-3} & V_{-4} \\
V_4 & V_3 & V_2 & V_1 & \lambda(k+K_1)^2+V_0 & V_{-1} & V_{-2} & V_{-3} \\
V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_2)^2+V_0 & V_{-1} & V_{-2} \\
V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_3)^2+V_0 & V_{-1} \\
V_7 & V_6 & V_5 & V_4 & V_3 & V_2 & V_1 & \lambda(k+K_4)^2+V_0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots
\end{bmatrix}
\begin{pmatrix} \vdots \\ u_{\mathrm{k,n}}[\mathrm{K}_{-3}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-2}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-1}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{0}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{1}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{2}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{3}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{4}] \\ \vdots \end{pmatrix}
= E_n(\mathbf{k})
\begin{pmatrix} \vdots \\ u_{\mathrm{k,n}}[\mathrm{K}_{-3}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-2}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{-1}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{0}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{1}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{2}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{3}] \\ u_{\mathrm{k,n}}[\mathrm{K}_{4}] \\ \vdots \end{pmatrix}
$$

$$\psi_{\mathbf{k,n}}(\mathbf{r}) = \sum_{\{\mathbf{K_i}\}} \mathbf{u_{k,n}}[\mathbf{K_i}] \left(\frac{\mathbf{1}}{\sqrt{V_{\text{box}}}} \mathbf{e}^{\mathbf{i}(\mathbf{k}+\mathbf{K_i})\cdot\mathbf{r}} \right)$$

$$a_{\mathbf{k,n}}(\mathbf{q}) = \sum_{\mathbf{K_i}} \frac{\mathbf{1}}{\sqrt{V_{\text{box}}}} \mathbf{u_{k,n}}[\mathbf{K_i}] \delta(\mathbf{q} - (\mathbf{k}+\mathbf{K_i}))$$

LCAO and Nearly Free Electron Bandstructure

$$\psi_i(r) = \sum_{\alpha} \sum_{\mathbf{R}_n} c_{i,\alpha[\mathbf{R}_n]} \phi_\alpha(r - \mathbf{R}_n) \qquad \psi(r) = \sum_{\mathbf{R}} c_{\mathbf{k}} e^{i\mathbf{kr}}$$

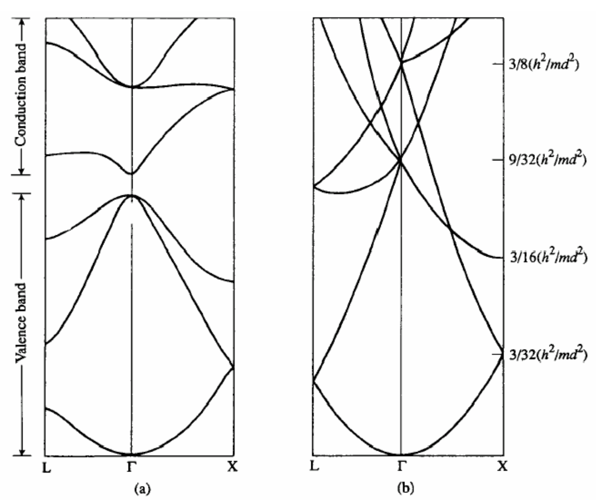


Fig. 7.6 Comparison between the LCAO bands for Ge, computed with an sp^3 basis, and the free electron bands. From Harrison (1980).

Why Is Lattice Potential Important Near Crossing Points ?

Let's consider lattice potential to be a perturbation on free electrons....

$$E_n^{(2)} \approx E_n^0 + V_{nn} + \sum_{p \neq n} \frac{|V_{np}|^2}{E_n^0 - E_p^0} \qquad \text{provided} \quad E_n^0 \neq E_p^0$$

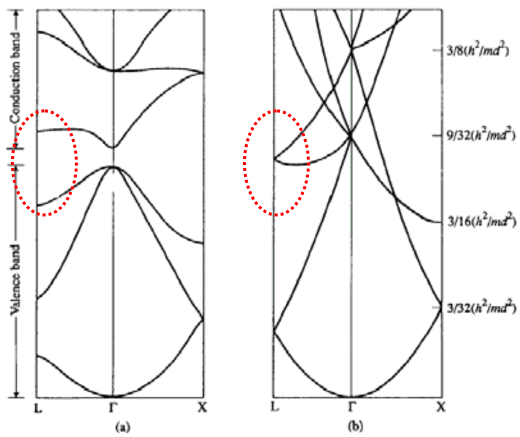


Fig. 7.6 Comparison between the LCAO bands for Ge, computed with an sp[3] basis, and the free electron bands. From Harrison (1980).

$$\phi_{\mathbf{k}}^0(\mathbf{r}) \sim |\mathbf{k}> = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$E^0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

Periodic Perturbation of Free Electron Bands

$$\phi_{\mathbf{k}}^0(\mathbf{r}) \sim |\mathbf{k}> = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \text{and} \qquad E^0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

Energy up to second-order in perturbation expansion....

$$E^{(2)}(\mathbf{k}) = E^0(\mathbf{k}) + <\mathbf{k}|V(\mathbf{r})|\mathbf{k}> + \sum_{k' \neq k} \frac{|<\mathbf{k}|V(\mathbf{r})|\mathbf{k}'>|^2}{E^0(\mathbf{k}) - E^0(\mathbf{k}')}$$

Matrix elements for periodic potential...

$$<\mathbf{k}|V(\mathbf{r})|\mathbf{k}'> = \int_V \frac{1}{\sqrt{V}} e^{-i\mathbf{k}'\cdot\mathbf{r}} \left(\sum_{\mathbf{K}_\ell} V[\mathbf{K}_\ell] e^{i\mathbf{K}_\ell\cdot\mathbf{r}} \right) \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \, d^3\mathbf{r}$$

$$= \begin{cases} V[\mathbf{K}_\ell] & \text{if} \quad \mathbf{k}' = \mathbf{k} + \mathbf{K}_\ell \\ 0 & \text{otherwise} \end{cases}$$

Periodic Perturbation of Free Electron Bands

$$E^{(2)}(\mathbf{k}) = E^0(\mathbf{k}) + V[0] + \sum_{\mathbf{K}_\ell \neq 0} \frac{|V[\mathbf{K}_\ell]|^2}{E^0(\mathbf{k}) - E^0(\mathbf{k}+\mathbf{K}_\ell)}$$

If the potential is sufficiently weak, this is a small perturbation on the free electron bands, unless $E^0(\mathbf{k}) = E^0(\mathbf{k}+\mathbf{K}_\ell)$

Since these are free electron energies, we can relate this easily to the wave vectors…

$$\frac{\hbar^2}{2m}k^2 = \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K}_\ell)^2$$

$$\mathbf{k}\cdot\mathbf{K}_\ell = \frac{1}{2}\mathbf{K}_\ell^2$$, when k is at edge of B-Z

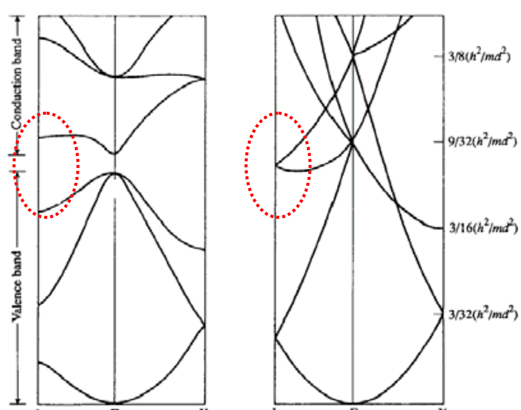
Periodic Perturbation of Free Electron Bands

If only two bands cross…

$$E^0(\mathbf{k}) = E^0(\mathbf{k}+\mathbf{G})$$

$$\phi_1(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\phi_2(\mathbf{r}) = e^{i(\mathbf{k}+G)\cdot\mathbf{r}}$$



$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\begin{pmatrix} E^0(\mathbf{k}) + V[0] & V[\mathbf{G}] \\ V[-\mathbf{G}] & E^0(\mathbf{k}+\mathbf{G}) + V[0] \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Periodic Perturbation of Free Electron Bands

Solutions

$$\begin{pmatrix} E^0(\mathbf{k}) + V[0] & V[\mathbf{G}] \\ V[-\mathbf{G}] & E^0(\mathbf{k}+\mathbf{G}) + V[0] \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Eigen-values...

$$E^{\pm}(\mathbf{k}) = \mathbf{E}^{(0)}(\mathbf{k}) + \mathbf{V}[\mathbf{0}] \pm \mathbf{V}[\mathbf{G}]$$

Eigen-vectors...

$$\chi^+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \chi^- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\chi^+ = \frac{1}{\sqrt{2}}(e^{i\mathbf{k}\cdot\mathbf{r}} + e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}) = \frac{2}{\sqrt{2}} e^{i(\mathbf{k}+\mathbf{G}/2)\cdot\mathbf{r}} \left[\cos\frac{1}{2}\mathbf{G}\cdot\mathbf{r}\right]$$

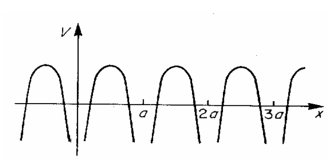
$$\chi^- = \frac{1}{\sqrt{2}}(e^{i\mathbf{k}\cdot\mathbf{r}} - e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}) = -\frac{2i}{\sqrt{2}} e^{i(\mathbf{k}+\mathbf{G}/2)\cdot\mathbf{r}} \left[\sin(\frac{1}{2}\mathbf{G}\cdot\mathbf{r})\right]$$

Periodic Perturbation of Free Electron Bands

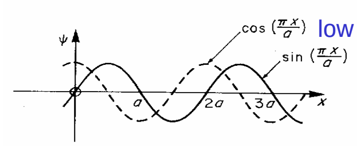
Solutions

$$E^+ = E^{(0)}(\mathbf{k}) + \mathbf{V}[\mathbf{0}] + \mathbf{V}[\mathbf{G}] \quad \text{and} \quad |\chi^+|^2 = 2\cos^2\frac{1}{2}\mathbf{G}\cdot\mathbf{r}$$

$$E^- = E^{(0)}(\mathbf{k}) + \mathbf{V}[\mathbf{0}] - \mathbf{V}[\mathbf{G}] \quad \text{and} \quad |\chi^+|^2 = 2\sin\frac{1}{2}\mathbf{G}\cdot\mathbf{r}$$



$\mathbf{V}[\mathbf{G}] < 0$



low energy solution

high energy solution

Plots are for a potential of the form... $V(x) \approx -\cos(\frac{2\pi}{a})$

Bloch's Theorem

'When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal….
By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation'

F. BLOCH

For wavefunctions that are eigenenergy states in a periodic potential...

$$\psi_{\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{\mathbf{ik\cdot r}}\tilde{\mathbf{u}}_{\mathbf{k}}(\mathbf{r})$$

or

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \mathrm{e}^{\mathbf{ik\cdot R}}\psi_{\mathbf{k}}(\mathbf{R})$$

Proof of Bloch's Theorem

Step 1: Translation operator commutes with Hamiltonain...
so they share the same eigenstates.

$$T_{\mathbf{R}}\psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{R})$$

Translation and periodic Hamiltonian commute...

$$T_{\mathbf{R}}H(\mathbf{r})\psi(\mathbf{r}) = \mathbf{H}(\mathbf{r}+\mathbf{R})\psi(\mathbf{r}+\mathbf{R}) = \mathbf{H}(\mathbf{r})\psi(\mathbf{r}+\mathbf{R}) = \mathbf{H}(\mathbf{r})\mathbf{T}_{\mathbf{R}}\psi(\mathbf{r})$$

Therefore,

$$H\psi(\mathbf{r}) = \mathbf{E}\psi(\mathbf{r})$$

$$T_{\mathbf{R}}\psi(\mathbf{r}) = \mathbf{c}(\mathbf{R})\psi(\mathbf{r})$$

Step 2: Translations along different vectors add...
so the eigenvalues of translation operator are exponentials

$$T_{\mathbf{R}}T_{\mathbf{R}'}\psi(\mathbf{r}) = \mathbf{c}(\mathbf{R})\mathbf{T}_{\mathbf{R}'}\psi(\mathbf{r}) = \mathbf{c}(\mathbf{R})\mathbf{c}(\mathbf{R}')\psi(\mathbf{r})$$

$$T_{\mathbf{R}}T_{\mathbf{R}'}\psi(\mathbf{r}) = \mathbf{T}_{\mathbf{R}+\mathbf{R}'}\psi(\mathbf{r}) = \mathbf{c}(\mathbf{R}+\mathbf{R}')\psi(\mathbf{r})$$

$$\Rightarrow$$

$$c(\mathbf{R}+\mathbf{R}') = \mathbf{c}(\mathbf{R})\mathbf{c}(\mathbf{R}')$$

$$c(\mathbf{R}) = \mathrm{e}^{\mathbf{ik\cdot R}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \mathrm{e}^{\mathbf{ik\cdot R}}\psi_{\mathbf{k}}(\mathbf{R})$$

Normalization of Bloch Functions

Conventional (A&M) choice of Bloch amplitude...

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\tilde{u}_{\mathbf{k}}(\mathbf{r})$$

6.730 choice of Bloch amplitude...

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

Normalization of Bloch amplitude...

$$1 = \int_0^{V_{\text{box}}} \Psi^*_{\mathbf{k}}(\mathbf{r})\Psi_{\mathbf{k}}(\mathbf{r})\, d^3\mathbf{r}$$

$$= \frac{1}{V_{\text{box}}} \int_{V_{\text{box}}} u^*_{\mathbf{k}}(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})\, d^3\mathbf{r}$$

$$= \frac{1}{V_{\text{WSC}}} \int_{V_{\text{WSC}}} u^*_{\mathbf{k}}(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r})\, d^3\mathbf{r}$$

Momentum and Crystal Momentum

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_{\text{box}}}} \sum_{\{\mathbf{K}_i\}} u_{n,\mathbf{k}}[\mathbf{K}_i] e^{i(\mathbf{k}+\mathbf{K}_i)\cdot\mathbf{r}}$$

where the Bloch amplitude is normalized... $\sum_{\mathbf{K}_i} |u_{n,\mathbf{k}}[\mathbf{K}_i]|^2 = 1$

$$< \mathbf{p} > = < \psi_{n,\mathbf{k}}(\mathbf{r}) | \frac{\hbar}{i}\nabla | \psi_{n,\mathbf{k}}(\mathbf{r}) >$$

$$= \sum_{\mathbf{K}_i} \hbar(\mathbf{k}+\mathbf{K}_i)|u_{n,\mathbf{k}}[\mathbf{K}_i]|^2$$

$$= \hbar\mathbf{k}|u_{n,\mathbf{k}}[0]|^2 + \sum_{\mathbf{K}_i\neq 0} \hbar(\mathbf{k}+\mathbf{K}_i)|u_{n,\mathbf{k}}[\mathbf{K}_i]|^2 \neq \hbar\mathbf{k}$$

Physical momentum is <u>not</u> equal to crystal momentum

So how do we figure out the velocity and trajectory in real space of electrons ?