# 6.730 Physics for Solid State Applications

## Lecture 18: Properties of Bloch Functions

### Outline

- Momentum and Crystal Momentum
- k.p Hamiltonian
- Velocity of Electrons in Bloch States

# 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…

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

or

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

# 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

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

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

$\Rightarrow$

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

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

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

# Normalization of Bloch Functions

Conventional (A&M) choice of Bloch amplitude…

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

6.730 choice of Bloch amplitude…

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

Normalization of Bloch amplitude…

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

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

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

# Momentum and Crystal Momentum

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

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

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

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

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

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 ?

# Momentum and Crystal Momentum

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

$$\hat{\mathbf{p}}\,\psi_{n,\mathbf{k}} = \frac{\hbar}{i}\nabla\psi_{n,\mathbf{k}} = \frac{\hbar}{i}\nabla\left(\frac{1}{\sqrt{V_{\text{box}}}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(r)\right)$$

$$= \hbar\mathbf{k}\psi_{\mathbf{n},\mathbf{k}} + \frac{1}{\sqrt{V_{\text{box}}}} \mathbf{e}^{\mathbf{ik}\cdot\mathbf{r}} \frac{\mathbf{\hbar}}{\mathbf{i}} \nabla \mathbf{u}_{\mathbf{n},\mathbf{k}}(\mathbf{r})$$

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

$$\hat{\mathbf{p}}\,\psi_{n,\mathbf{k}} = \hbar\mathbf{k}\psi_{\mathbf{n},\mathbf{k}} + \mathbf{e}^{\mathbf{ik}\cdot\mathbf{r}} \frac{\mathbf{\hbar}}{\mathbf{i}} \nabla \tilde{\mathbf{u}}_{\mathbf{n},\mathbf{k}}(\mathbf{r})$$

# Momentum and Crystal Momentum

$$\hat{\mathbf{p}}\,\psi_{n,k} = \hbar k \psi_{n,k} + e^{ik\cdot r}\frac{\hbar}{i}\nabla \tilde{u}_{n,k}(r)$$

canceling exponentials from both sides

$$\hat{\mathbf{p}}\,\tilde{u}_{n,k}(r) = \hbar k \tilde{u}_{n,k}(r) + \frac{\hbar}{i}\nabla \tilde{u}_{n,k}(r)$$

A useful identity, for the action of the momentum operator on the Bloch amplitude....

$$\hat{\mathbf{p}}\,\tilde{u}_{n,\mathbf{k}}(r) = \hbar\left(k + \frac{1}{i}\nabla\right)\tilde{u}_{n,k}(r)$$

Leads us to, the action of the Hamiltonian on the Bloch amplitude....

$$H_k \tilde{u}_k(r) = \left(\frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + k\right)^2 + V(r)\right)\tilde{u}_k(r)$$

$$= E_k \tilde{u}_k(\mathbf{r})$$

# k.p Hamiltonian
(in our case q.p)

$$H_k \tilde{u}_k(r) = \left( \frac{\hbar^2}{2m} \left( \frac{1}{i} \nabla + k \right)^2 + V(r) \right) \tilde{u}_k(r)$$

If we know energies as k we can extend this to calculate energies at k+q for small q…

$$H_{k+q} = \frac{\hbar^2}{2m} \left( \frac{1}{i} \nabla + k + q \right)^2 + V(r)$$

$$H_{k+q} = H_k + \frac{\hbar^2}{m} q \cdot \left( \frac{1}{i} \nabla + k \right) + \frac{\hbar^2}{2m} q^2$$

# k.p Hamiltonian

$$H_{k+q} = H_k + \frac{\hbar^2}{m} q \cdot \left( \frac{1}{i} \nabla + k \right) + \frac{\hbar^2}{2m} q^2$$

Taylor Series expansion of energies...

$$E_n(k+q) = E_n(k) + \sum_i \frac{\partial E_n}{\partial k_i} q_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 E_n}{\partial k_i \partial k_j} q_i q_j + O(q^3)$$

Matching terms to first order in q...

$$\sum_i \frac{\partial E_n}{\partial k_i} q_i = \sum_i \int dr\, \tilde{u}^*_{nk} \frac{\hbar^2}{m} q_i \left( \frac{1}{i} \nabla + k \right)_i \tilde{u}_{nk}$$

# Velocity of an Electron in a Bloch Eigenstate

$$\sum_i \frac{\partial E_n}{\partial k_i} q_i = \sum_i \int dr\, \tilde{u}^*_{nk} \frac{\hbar^2}{m} q_i \left(\frac{1}{i}\nabla + k\right)_i \tilde{u}_{nk}$$

$$\frac{\partial E_n}{\partial k_i} = \int dr\, \tilde{u}^*_{nk} \frac{\hbar^2}{m} \left(\frac{1}{i}\nabla + k\right)_i \tilde{u}_{nk}$$

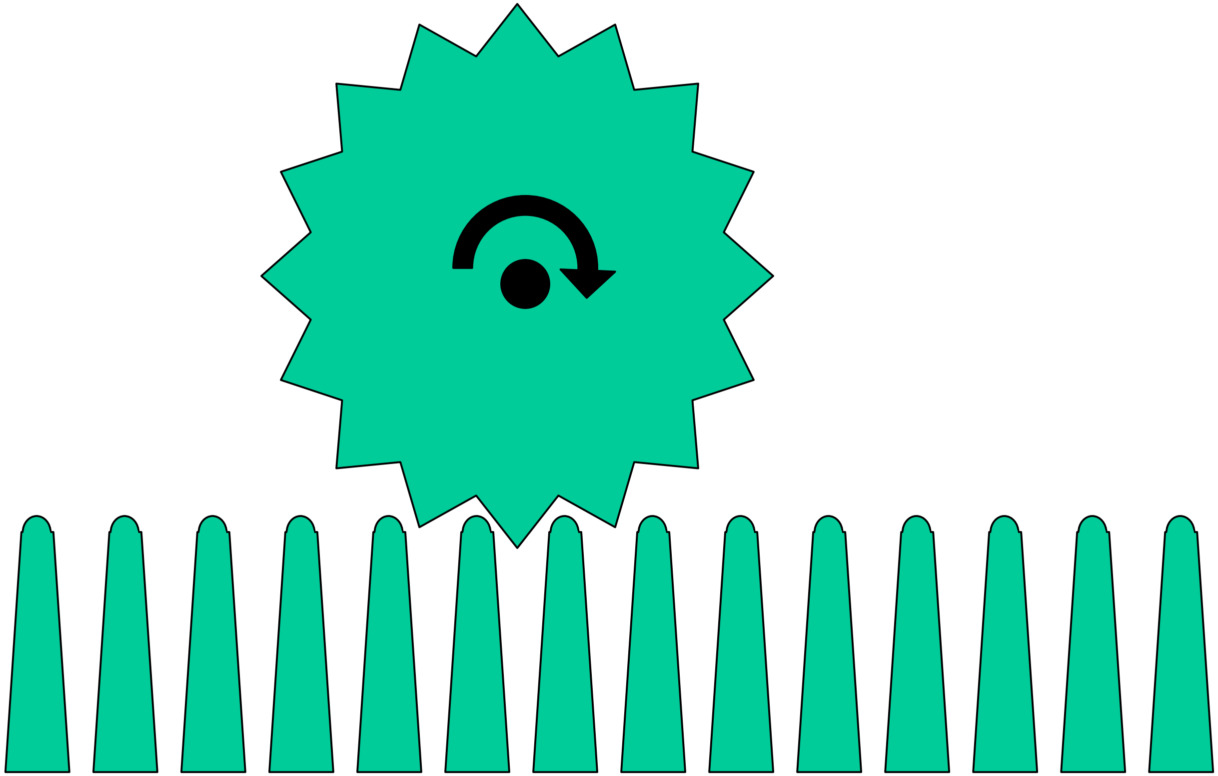
$$\frac{\partial E_n}{\partial k_i} = \int dr\, \psi^*_{nk} \frac{\hbar^2}{m} \left(\frac{1}{i}\nabla\right)_i \psi_{nk}$$

$$\frac{\partial E_n}{\partial k_i} = \int dr\, \psi^*_{nk} \frac{\hbar}{m} \widehat{p}_i \, \psi_{nk} = \frac{\hbar}{m} < \widehat{p}_i >$$

$$< \mathbf{v_n(k)} >= \frac{< \mathbf{p} >}{\mathbf{m}} = \frac{\mathbf{1}}{\boldsymbol{\hbar}} \nabla_{\mathbf{k}} \mathbf{E_n(k)}$$

# Electron Wavepacket in Periodic Potential

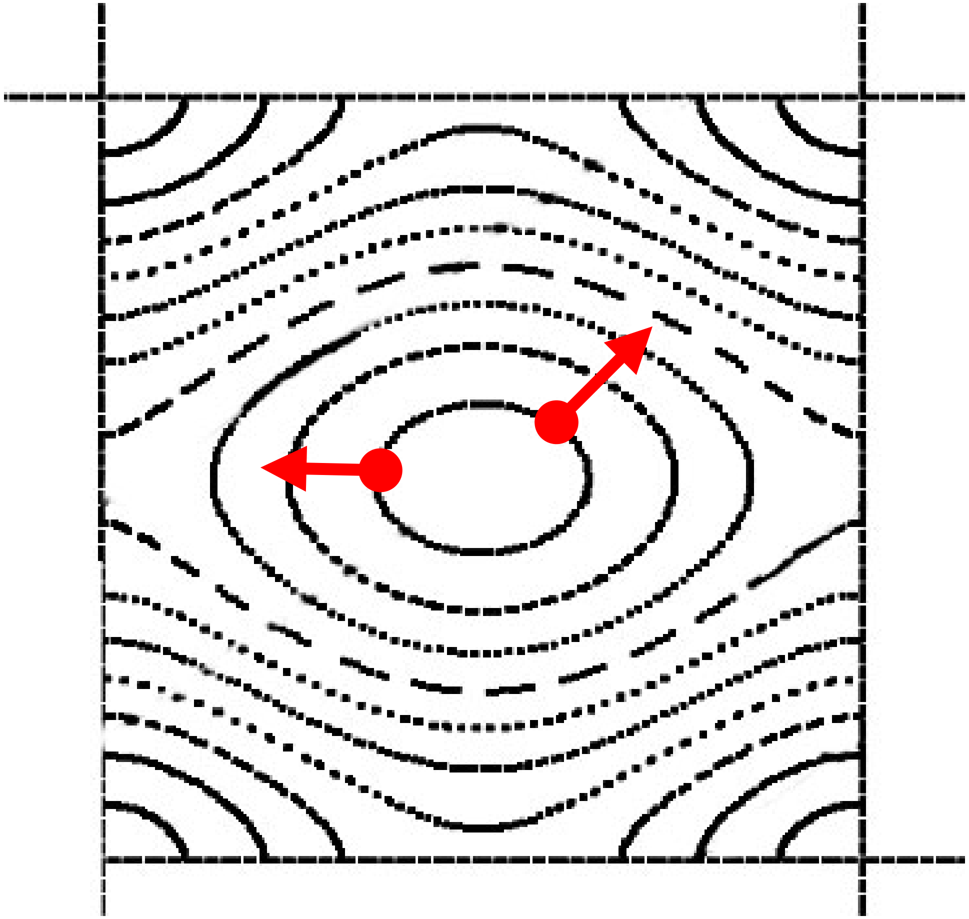
Wavepacket in a dispersive media… $\mathbf{v_g} = \nabla_{\mathbf{k}}\omega(\mathbf{k})$



So long as the wavefunction has the same short range periodicity as the underlying potential, the electron can experience smooth uniform motion at a constant velocity.

# Energy Surface for 2-D Crystal

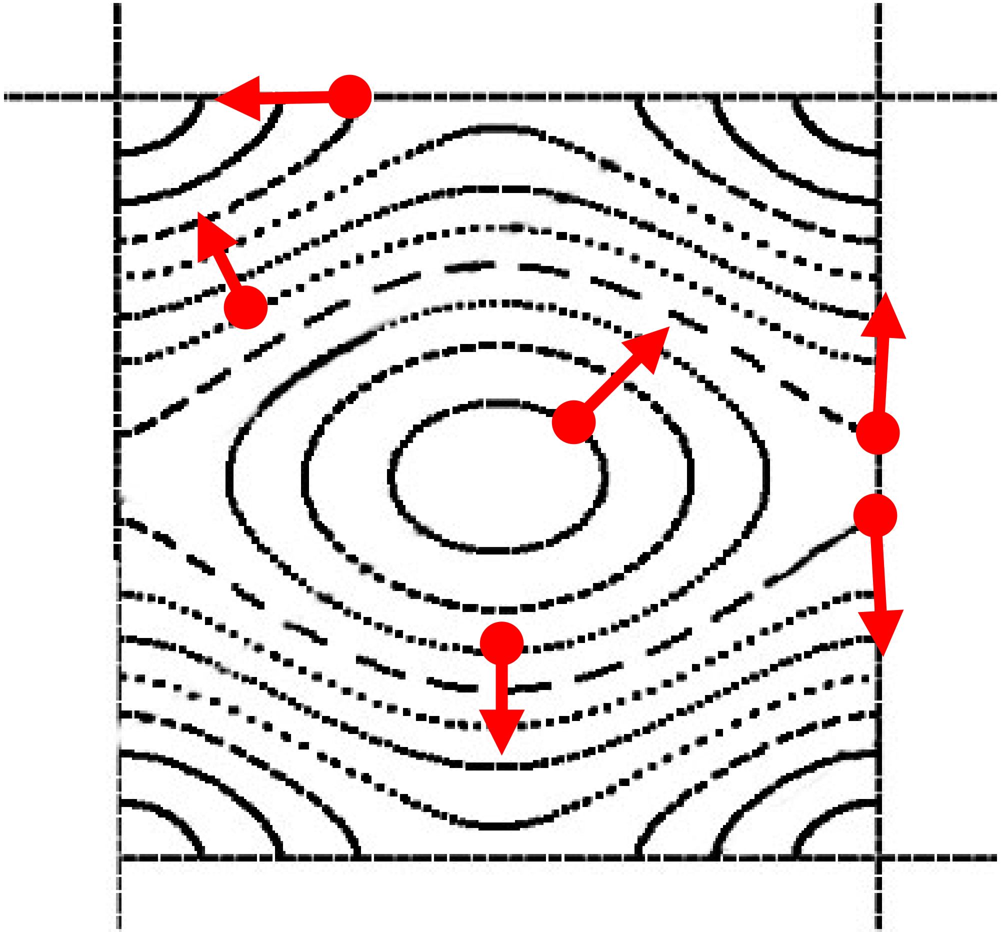
$$< \mathbf{v_n(k)} >= \frac{1}{\hbar}\nabla_{\mathbf{k}}\mathbf{E_n(k)}$$



In 2-D, circular energy contours result in $< \mathbf{v_n(k)} >$ parallel to $\mathbf{k}$

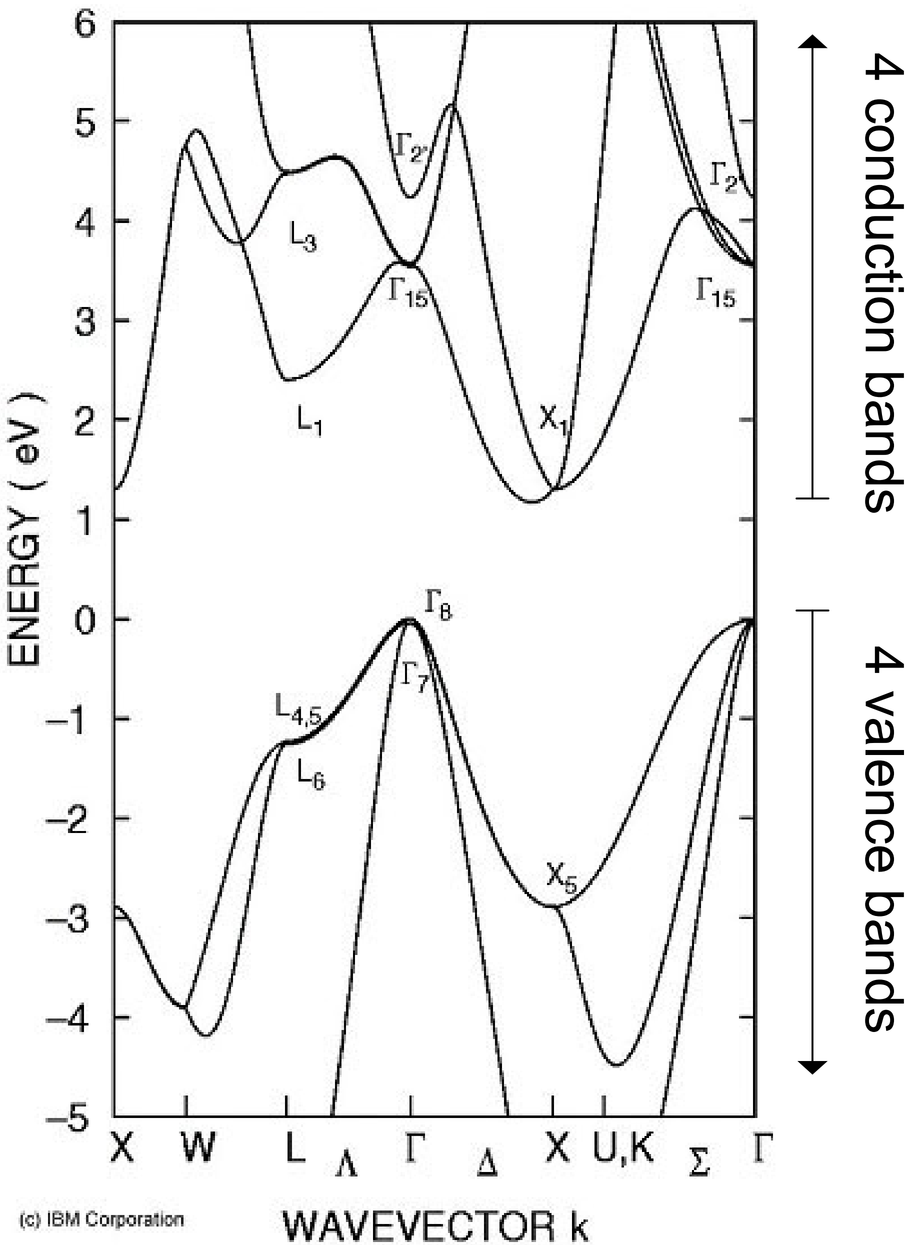
# Energy Surface for 2-D Crystal

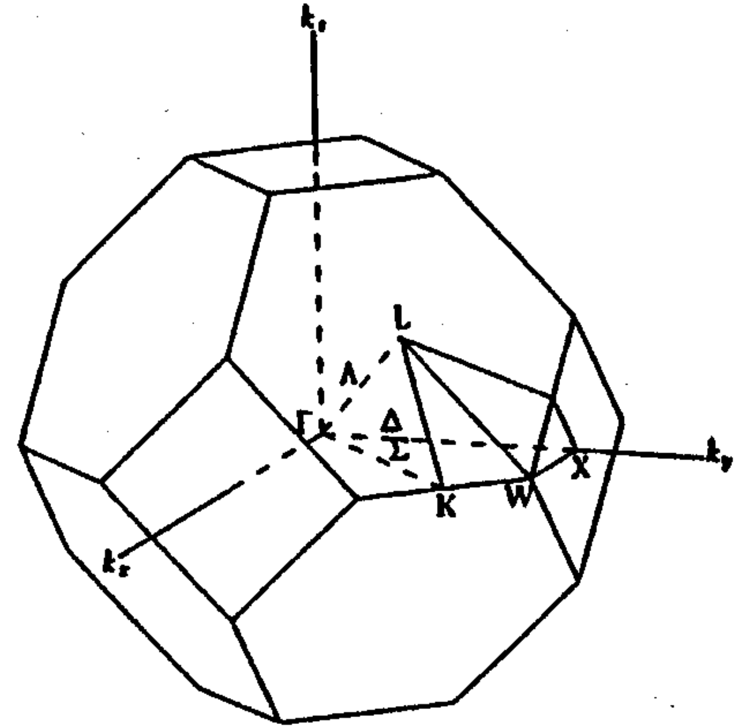
$$< \mathbf{v_n(k)} > = \frac{1}{\hbar} \nabla_{\mathbf{k}} \mathbf{E_n(k)}$$



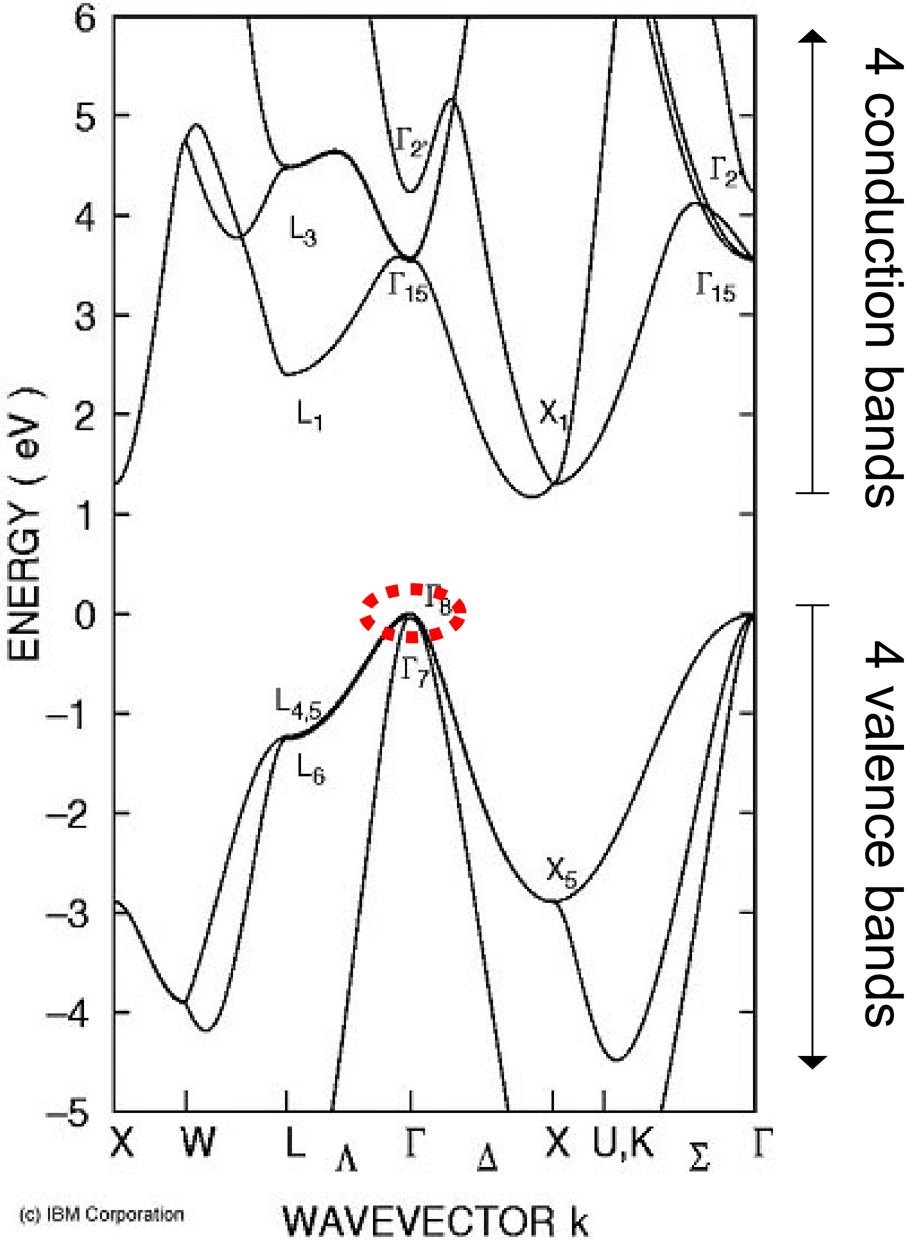
In general, for higher lying energies $< \mathbf{v_n(k)} >$ is not parallel to $\mathbf{k}$

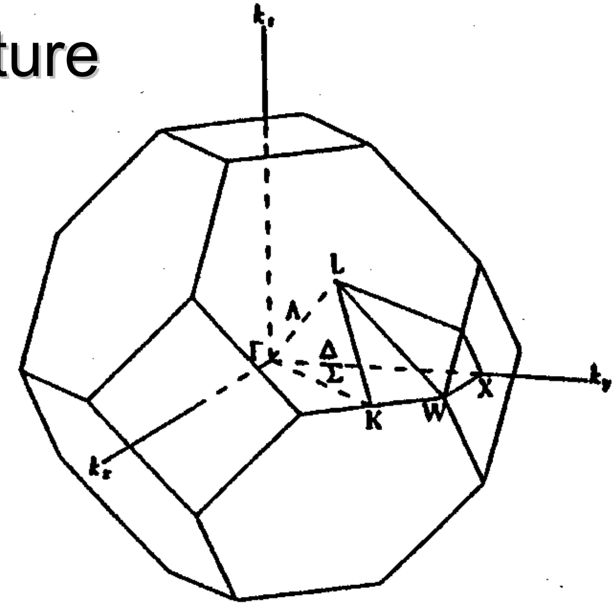
# Silicon Bandstructure



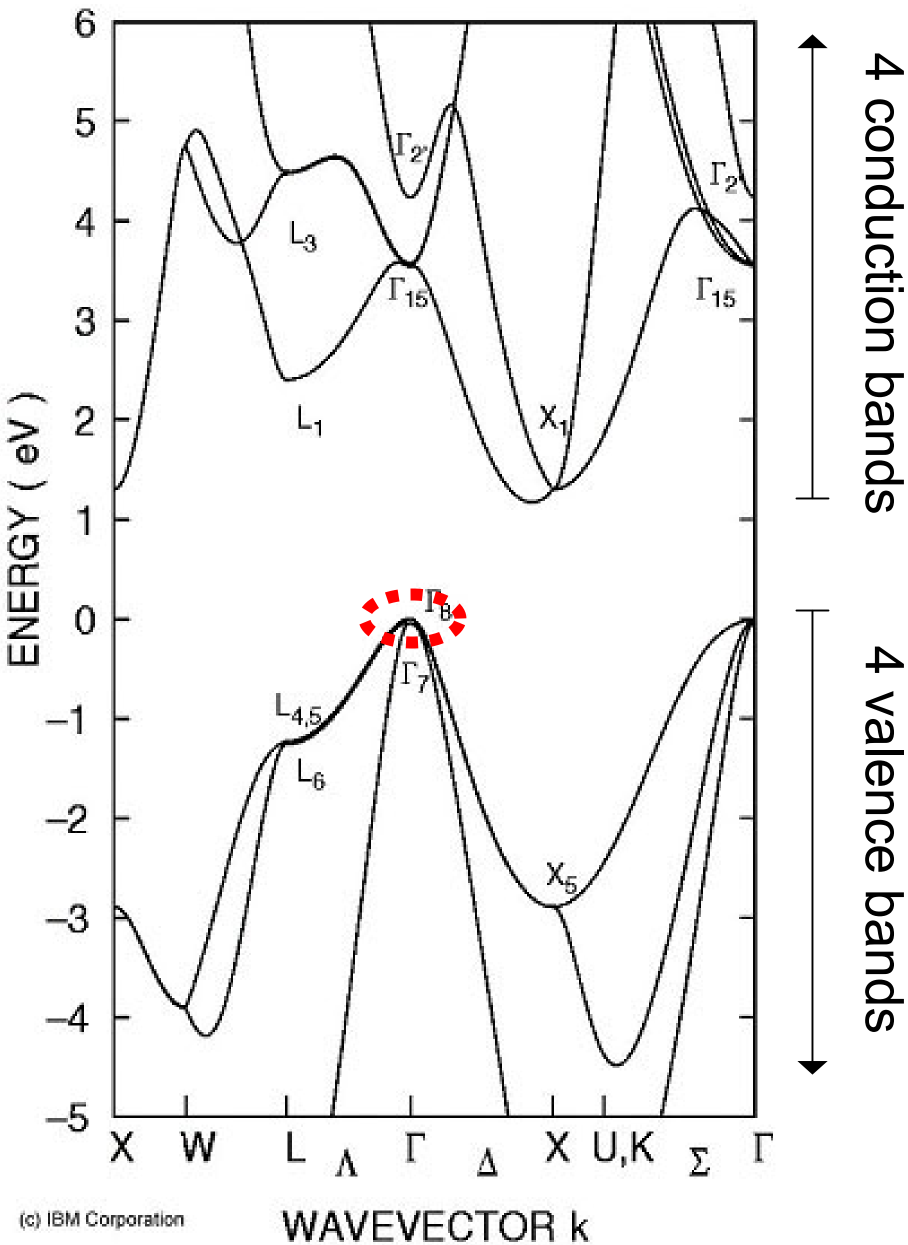



# Silicon Bandstructure

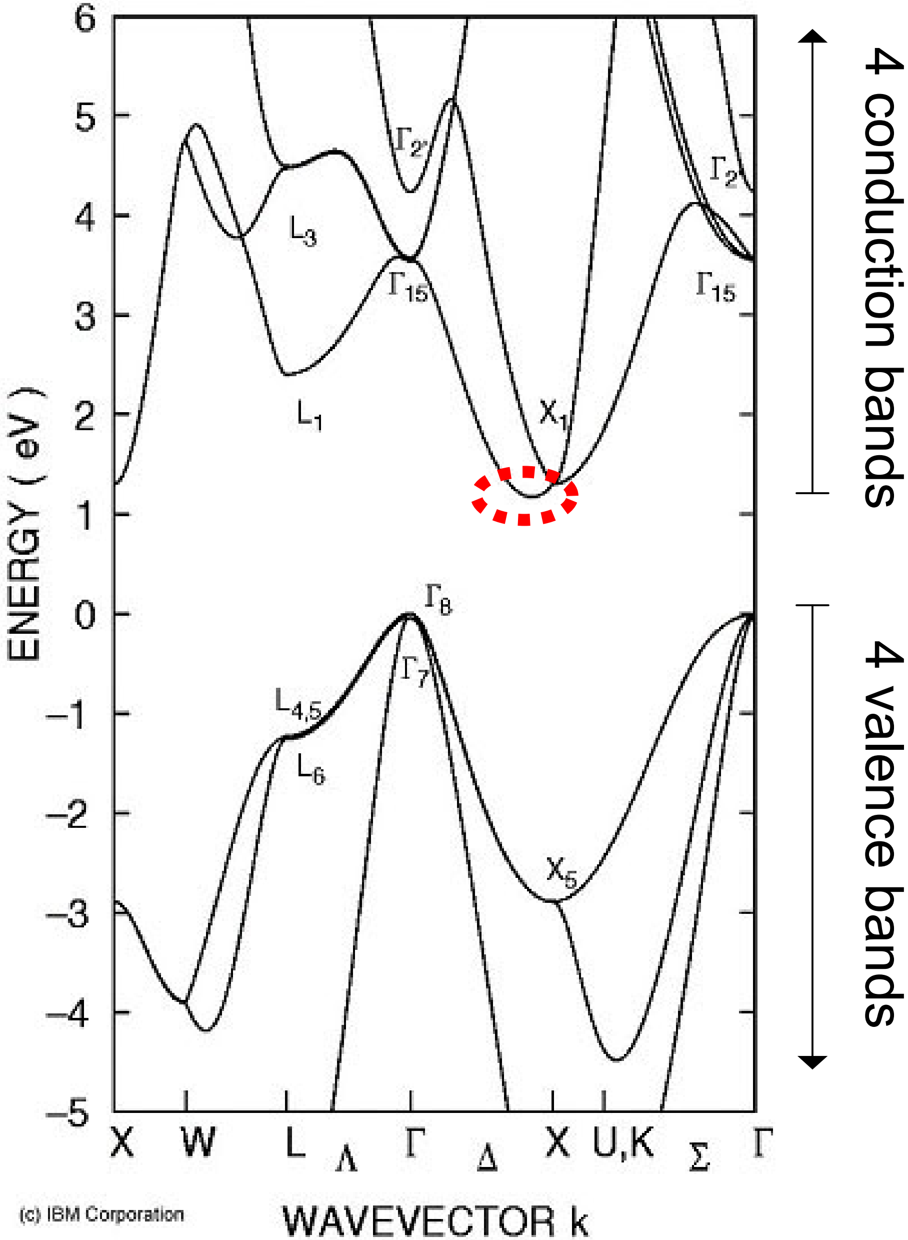


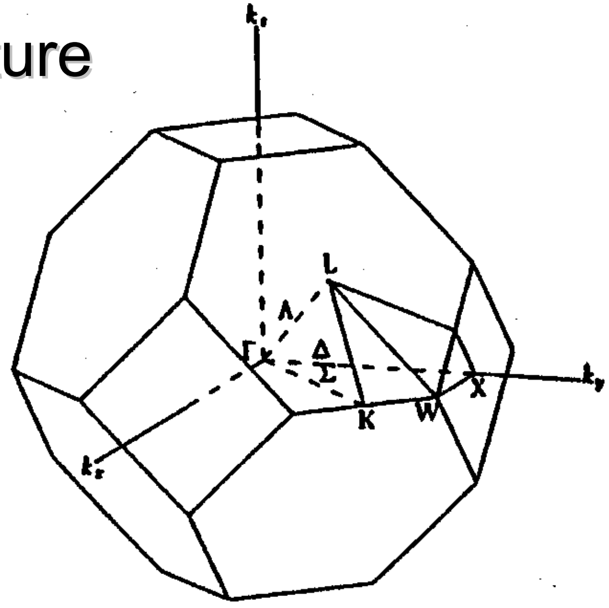



# Silicon Bandstructure



# Silicon Bandstructure



# Semiclassical Equation of Motion

Ehrenfest's Theorem:

$$\frac{d < \hat{A} >}{dt} = \frac{i}{\hbar}\langle[\hat{H}, \hat{A}]\rangle$$

Consider some external force that perturbs the electron in the lattice…

$$\hat{H} = \hat{H}_0 + \hat{V}_{ext}$$

An elegant derivation can be made if we consider the equation of motion for the lattice translation operator $T_R\psi(r) = \psi(r + R)$

$$\frac{d < \hat{T}_R >}{dt} = \frac{i}{\hbar}\langle[\hat{H}_0 + \hat{V}_{ext}, \hat{T}_R]\rangle$$

Since the lattice translation and Hamiltonian commute with each other…

$$\frac{d < \hat{T}_R >}{dt} = \frac{i}{\hbar}\langle[\hat{V}_{ext}, \hat{T}_R]\rangle$$

# Semiclassical Equation of Motion

Lets consider a specific external force…an external uniform electric field…

$$\widehat{H} = \widehat{H}_0 + \widehat{V}_{ext}$$

$$= \widehat{H}_0 + eE\widehat{r}$$

Equation of motion for translation operator becomes…

$$\frac{d < \widehat{T}_R >}{dt} = \frac{i}{\hbar}\langle[\widehat{V}_{ext}, \widehat{T}_R]\rangle$$

$$= eE\frac{i}{\hbar}\langle[\widehat{r}, \widehat{T}_R]\rangle$$

Can evaluate the commutation relation in the position basis…

$$[\widehat{r}, \widehat{T}_R]|r_0 >= \left(\widehat{r}\widehat{T}_R - \widehat{T}_R\widehat{r}\right)|r_0 >= \widehat{r}|r_0 + R > -\widehat{T}_R r_0|r_0 >$$

$$= (r_0 + R)|r_0 + R > -r_0|r_0 + R >= R|r_0 + R >= R\widehat{T}_R|r_0 >$$

# Semiclassical Equation of Motion

$$[\hat{r}, \hat{T}_R] = R\,\hat{T}_R$$

Plugging in this commutation relation into the equation of motion…

$$\frac{d < \hat{T}_R >}{dt} = eE\frac{i}{\hbar}\langle[\hat{r}, \hat{T}_R]\rangle$$

$$= eER\,\frac{i}{\hbar}\langle\hat{T}_R\rangle$$

Solving the simple differential equation…

$$\langle\hat{T}_R\rangle = e^{ieE\,R\,t/\hbar}$$

From Bloch's Thm. We know the eigenvalues of $T_R$…

$$T_R\psi(r) = e^{ikR}\psi(r) \qquad \langle\hat{T}_R\rangle = e^{ik\,R}$$

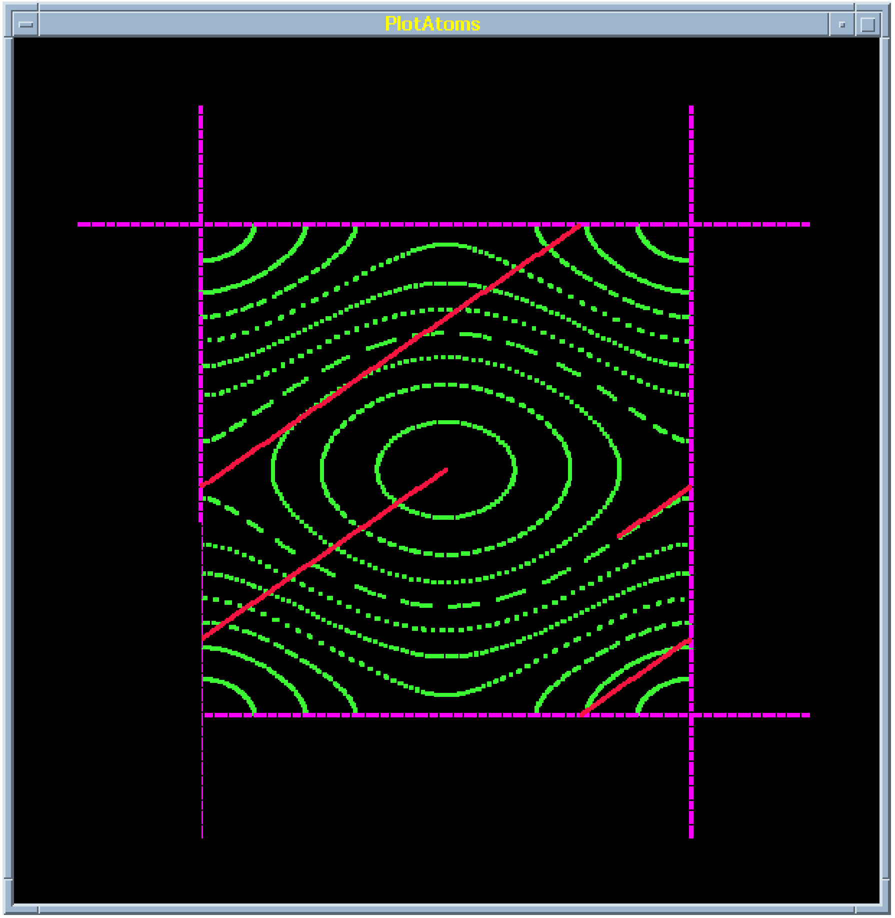
$$k = \frac{eE}{\hbar}t + k_0$$

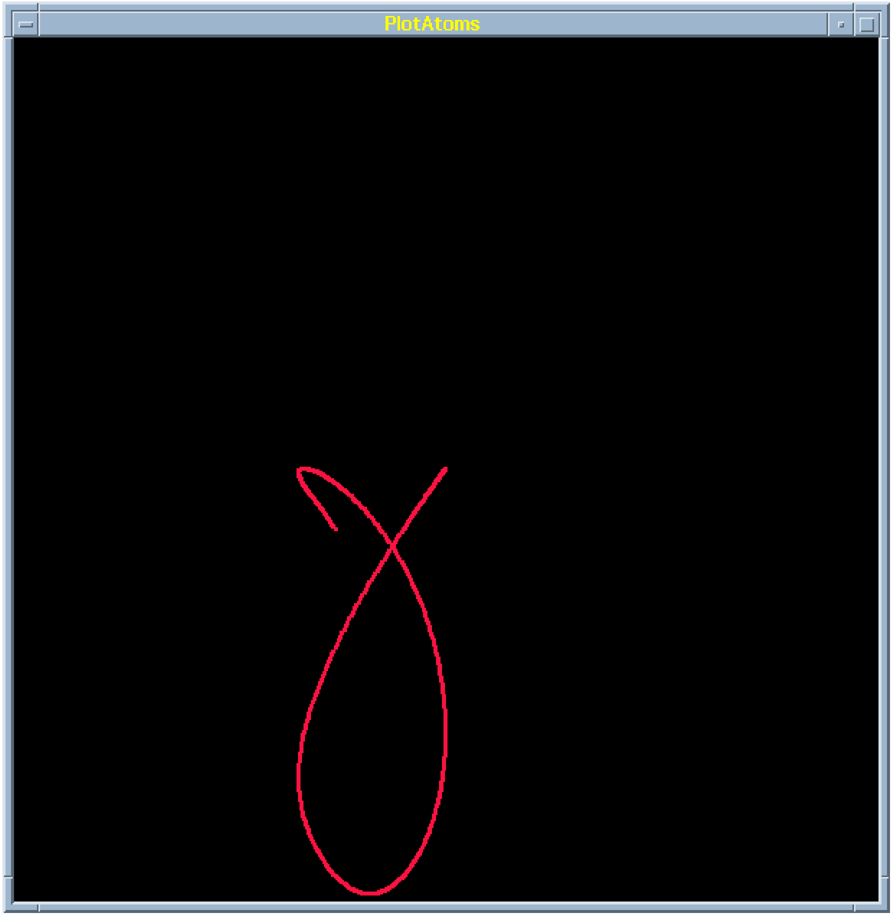
$$eE = \hbar\frac{dk}{dt}$$

$$\mathbf{F_{ext}} = \hbar\frac{\mathbf{dk}}{\mathbf{dt}}$$

# Electron Motion in a Uniform Electric Field

## 2-D Crystal




http://www.physics.cornell.edu/sss/ziman/ziman.html