# 6.730 Physics for Solid State Applications

## Lecture 19: Properties of Bloch Functions

<u>Outline</u>

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

March 17, 2004

## 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...

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

or

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

## 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

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

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

$$\Rightarrow$$

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

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

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

## 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...

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

Normalization of Bloch amplitude...

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

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

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

## 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 ?

## <u>Momentum Operator</u>

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

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

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

$$= e^{i\mathbf{k}\cdot\mathbf{r}}\left(\hbar\mathbf{k} + \frac{\hbar}{i}\nabla\right)\tilde{u}_{n,\mathbf{k}}(\mathbf{r})$$

$$\hat{\mathbf{p}}^2\,\psi_{n,\mathbf{k}} = \hat{\mathbf{p}}\cdot\left\{\hat{\mathbf{p}}\,\psi_{n,\mathbf{k}}\right\} = \hat{\mathbf{p}}\cdot\left\{e^{i\mathbf{k}\cdot\mathbf{r}}\left(\hbar\mathbf{k} + \frac{\hbar}{i}\nabla\right)\tilde{u}_{n,\mathbf{k}}(\mathbf{r})\right\}$$

$$= e^{i\mathbf{k}\cdot\mathbf{r}}\left\{\left(\hbar\mathbf{k} + \frac{\hbar}{i}\nabla\right)\cdot\left(\hbar\mathbf{k} + \frac{\hbar}{i}\nabla\right)\tilde{u}_{n,\mathbf{k}}(\mathbf{r})\right\}$$

$$= e^{i\mathbf{k}\cdot\mathbf{r}}\left\{\left(\hbar\mathbf{k} + \frac{\hbar}{i}\nabla\right)^2\tilde{u}_{n,\mathbf{k}}(\mathbf{r})\right\}$$

# Hamiltonian for $u_{n,k}(r)$

$$\frac{\hat{\mathbf{p}}^2}{2m}\psi_{n,\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}\left\{\frac{1}{2m}\left(\hbar\mathbf{k} + \frac{\hbar}{i}\nabla\right)^2 \tilde{u}_{n,\mathbf{k}}(\mathbf{r})\right\}$$

$$V(\mathbf{r})\,\psi_{n,\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}\left\{V(\mathbf{r})\,\tilde{u}_{n,\mathbf{k}}(\mathbf{r})\right\}$$

$$E_{\mathbf{k}}\,\psi_{n,\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}\left\{E_{\mathbf{k}}\,\tilde{u}_{n,\mathbf{k}}(\mathbf{r})\right\}$$

Add the above to obtain

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

Therefore,

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

## 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

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

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

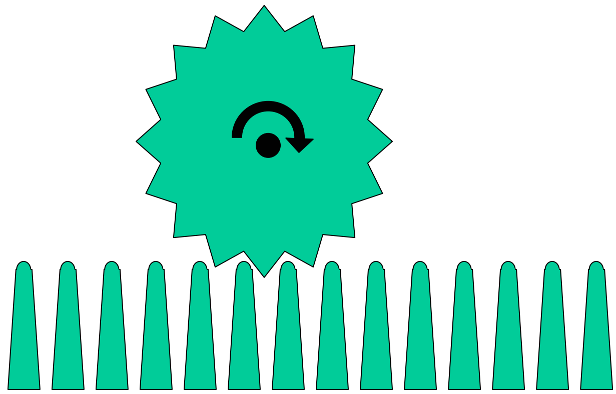
$$\frac{\partial E_n}{\partial k_i} = \int dr\, \psi_{nk}^* \frac{\hbar^2}{m} \left( \frac{1}{i} \nabla \right)_i \psi_{nk}$$

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

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

## Electron Wavepacket in Periodic Potential

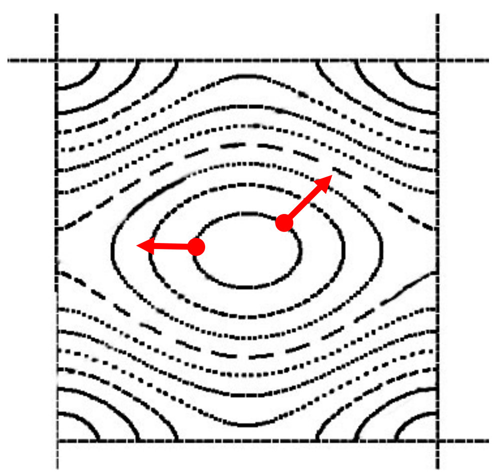
Wavepacket in a dispersive media... $\mathbf{v_g} = \nabla_{\mathbf{k}}\omega(\mathbf{k})$



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

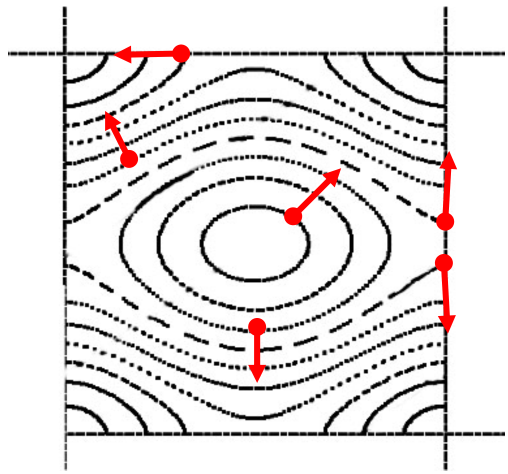
$$< \mathbf{v_n}(\mathbf{k}) > = \frac{1}{\hbar}\nabla_{\mathbf{k}}\mathbf{E_n}(\mathbf{k})$$



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

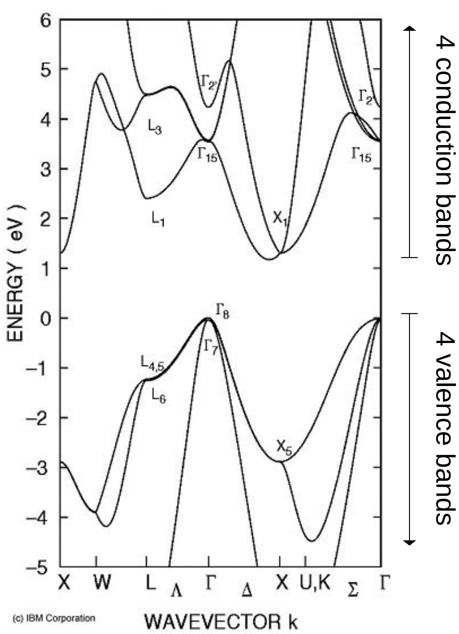
## Energy Surface for 2-D Crystal

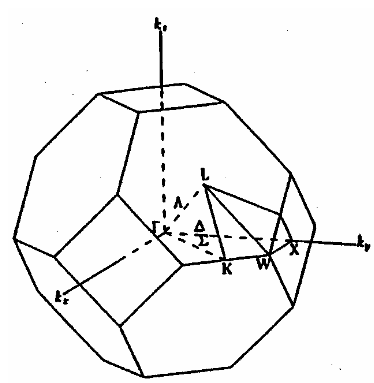
$$< \mathbf{v_n(k)} >= \frac{1}{\hbar}\nabla_{\mathbf{k}}\mathbf{E_n(k)}$$



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

## Silicon Bandstructure



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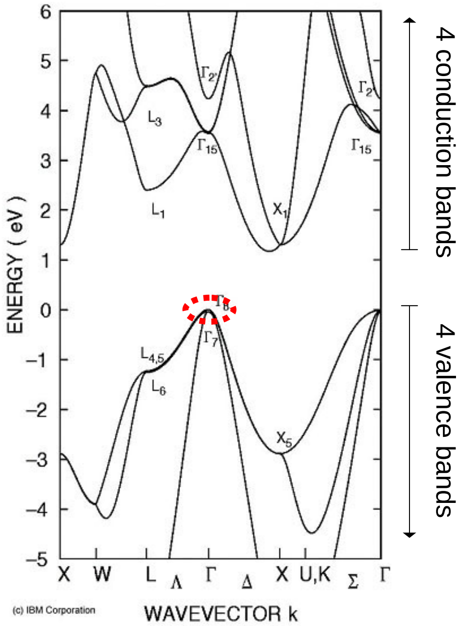


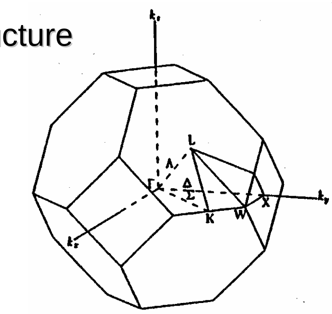

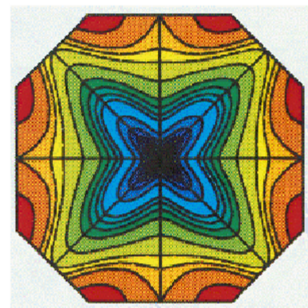

http://csmr.ca.sandia.gov/workshops/nacdm2002/viewgraphs/Conor_Rafferty_NACDM2002.pdf

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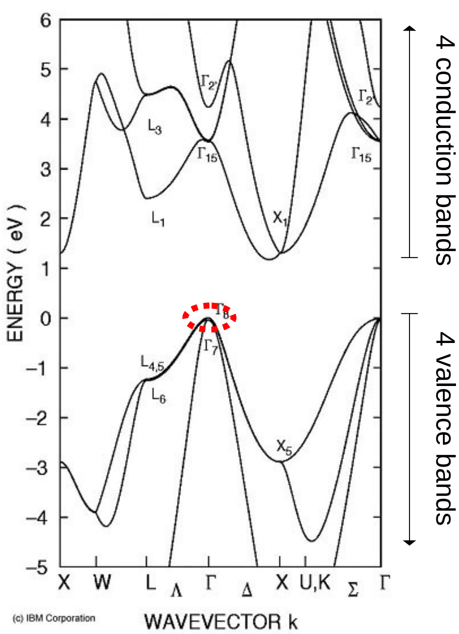


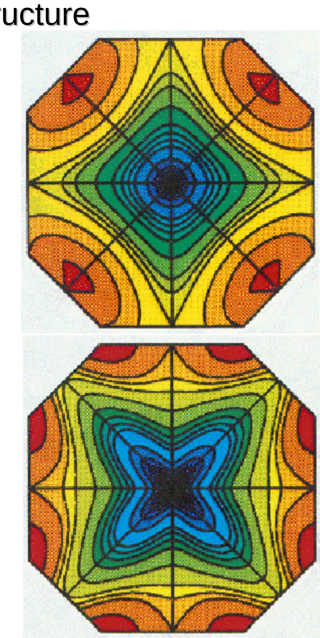

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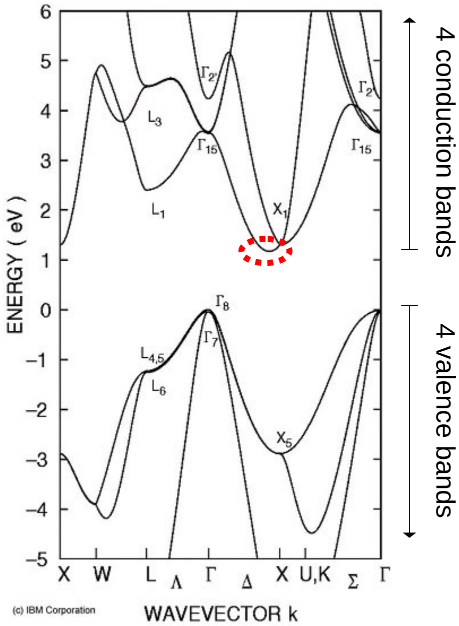


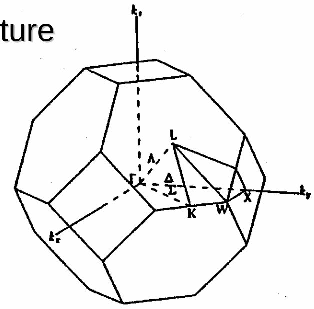


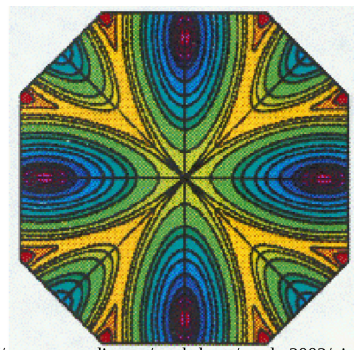

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## Semiclassical Equation of Motion

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...

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

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

Equation of motion for translation operator becomes...

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

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

Can evaluate the commutation relation in the position basis...

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

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

## 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...

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

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

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

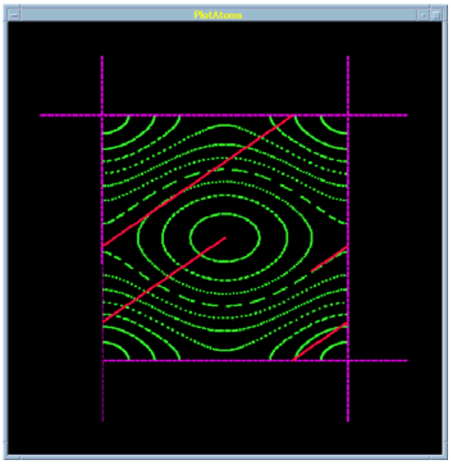
$$k = \frac{eE}{\hbar}t + k_0$$

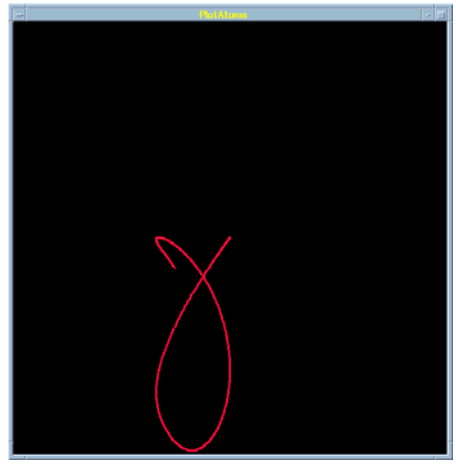
$$eE = \hbar\frac{dk}{dt}$$

$$\boxed{\mathbf{F}_{\mathrm{ext}} = \hbar\frac{\mathbf{dk}}{\mathbf{dt}}}$$

# Electron Motion in a Uniform Electric Field

2-D Crystal





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