# 6.730 Physics for Solid State Applications

## Lecture 20: Impurity States

### Outline

- Semiclassical Equations of Motion
- Review of Last Time: Effective Mass Hamiltonian
- Example: Impurity States

# 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…

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

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

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

# Semiclassical Equation of Motion

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

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 $T_R$…

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

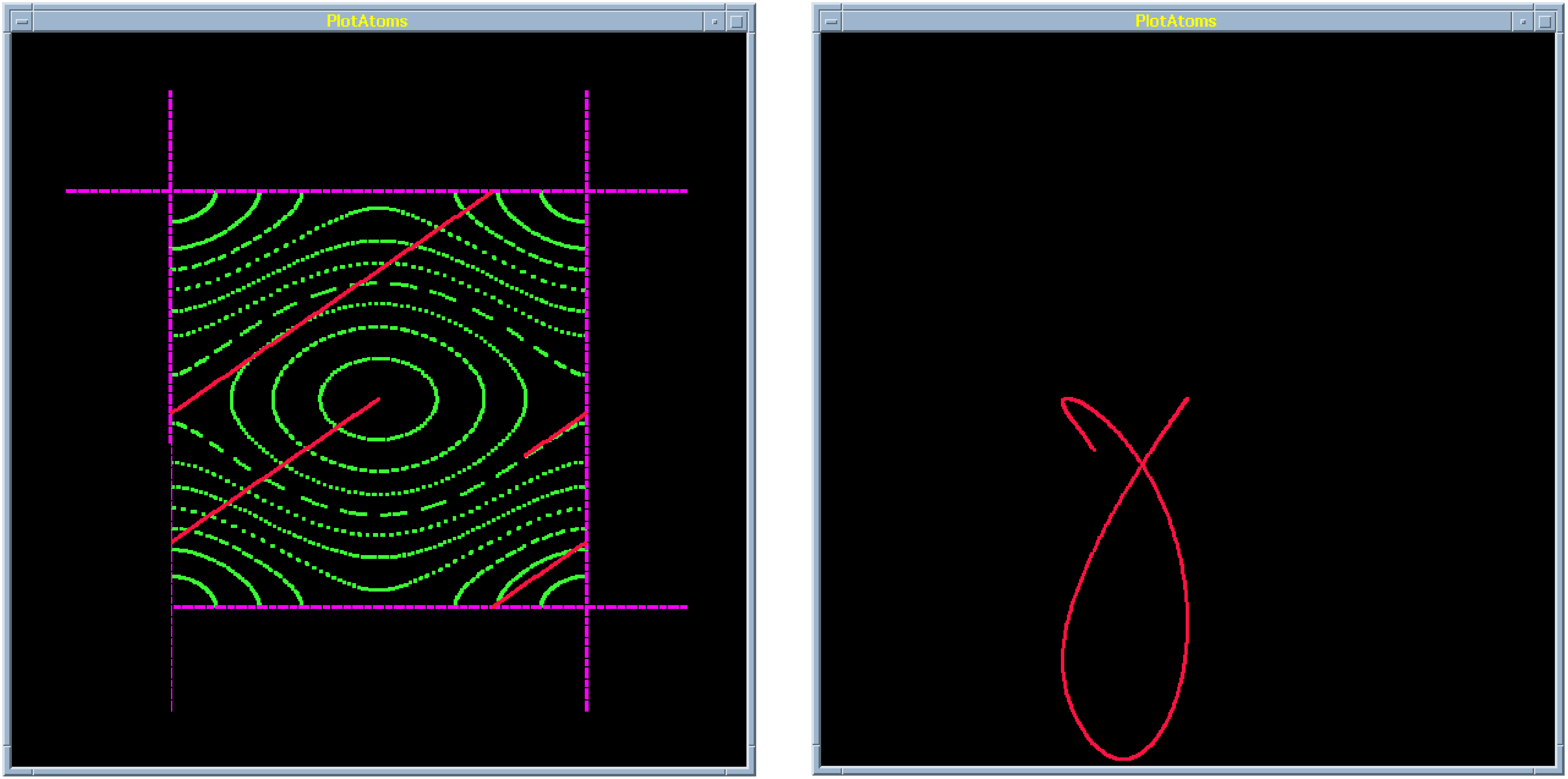
$$k = \frac{eE}{\hbar}t + k_0$$

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

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

# Electron Motion in a Uniform Electric Field

## 2-D Crystal




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

# Properties of the Translation Operator

Definition of the translation operator…

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

Bloch functions are eigenfunctions of the lattice translation operator…

$$\hat{T}_{\mathbf{R}}\psi(\mathbf{r}) = \mathbf{c}(\mathbf{R})\psi(\mathbf{r})$$

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

Lattice translation operator commutes with the lattice Hamiltonian ($V_{ext}$=0)

$$[\hat{T}_{\mathbf{R}}, H(\mathbf{r})] = \mathbf{0}$$

The translation operator commutes with other translation operators…

$$[\hat{T}_{\mathbf{R}_1}, \hat{T}_{\mathbf{R}_2}] = 0$$

# Properties of the Translation Operator

Lets see what the action of the following operator is…

$$\left[e^{-R\frac{\partial}{\partial x}}\right] f(x) = \left(1 - R\frac{\partial}{\partial x} + \frac{1}{2!}R^2\frac{\partial^2}{\partial x^2} - \frac{1}{3!}R^3\frac{\partial^3}{\partial x^3} + \cdots\right) f(x)$$

$$= f(x) - Rf'(x) + \frac{1}{2!}R^2 f''(x) - \frac{1}{3!}R^3 f'''(x) + \cdots$$

$$= f(x - R)$$

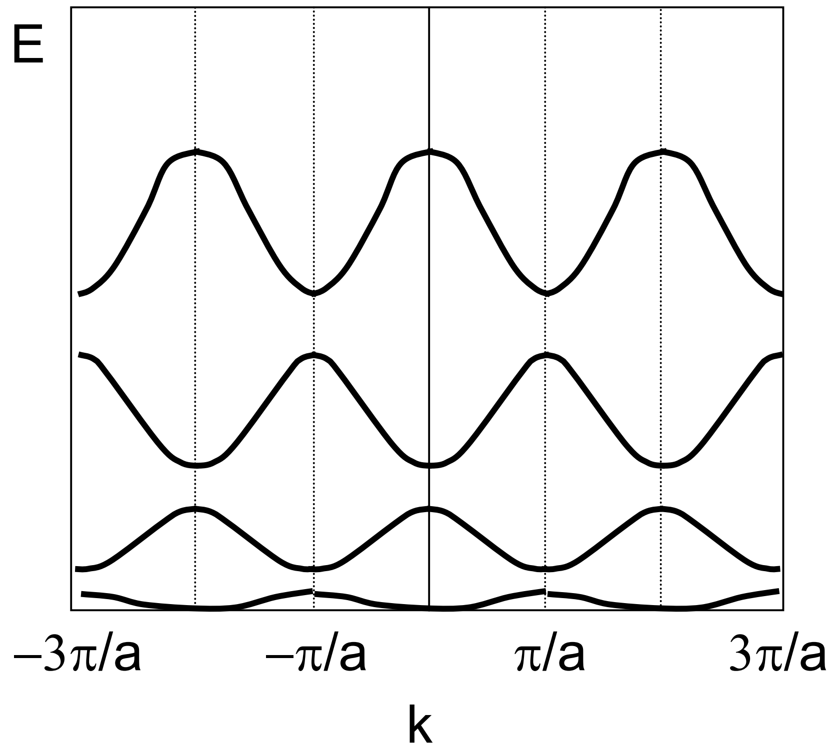
This is just the translation operator…

$$e^{-\mathbf{R}\cdot\nabla_{\mathbf{r}}} f(\mathbf{r}) = f(\mathbf{r} - \mathbf{R})$$

$$T_{-\mathbf{R}} f(\mathbf{r}) = e^{-\mathbf{R}\cdot\nabla_{\mathbf{r}}} f(\mathbf{r})$$

# Another Look at Electronic Bandstructure

$$E_n(k) = E_n(k + K_i)$$




As we will see, it is often convenient to represent the bandstructure by its inverse Fourier series expansion…

$$E_n(k) = \sum_{\ell} E_n(R_\ell) e^{ik \cdot R_\ell}$$

# Wavefunction of Electronic Wavepacket

The eigenfunction for $k \sim k_0$ are approximately…

$$\psi_{n,k}(r) = e^{ik\cdot r} u_{n,k}(r) \approx e^{i(k-k_0)\cdot r} \psi_{n,k_0}(r)$$

A wavepacket can therefore be constructed from Bloch states as follows…

$$\psi'_n(r,t) = \sum_k c_n(k,t) \psi_{n,k}(r)$$

$$\psi'_n(r,t) = \underbrace{G_n(r,t)}_{\text{envelope function}} \quad \underbrace{u_{n,k_0}(r)}_{\text{Bloch amplitude}}$$

Since we construct wavepacket from a small set of k's…

$$\Delta k \ll \frac{2\pi}{a} \quad \text{and} \quad \Delta r \gg a$$

…the envelope function must vary slowly…wavepacket must be large…

$$\Delta r \gg a$$

# Summary of Last Time

Without explicitly knowing the Bloch functions, we can solve for the envelope functions…

$$\left(\hat{H}_0 + \hat{V}_{ext}(r)\right) G_n(r,t) = i\hbar \frac{\partial G_n(r,t)}{\partial t}$$

Bandstructure shows up in here… $\hat{H}_0 = \sum_{\ell} E_n(R_\ell)\, \hat{T}_{R_\ell}$

The envelope functions are sufficient to determine the expectation of position and crystal momentum for the system…

$$< r(t) >_G = \frac{< G_n(r,t)|r|G_n(r,t) >}{< G_n(r,t)|G_n(r,t) >} = < r(t) >$$

$$< p >_G = \frac{< G_n(r,t)|\hat{p}|G_(r,t) >}{< G_n(r,t)|G_n(r,t) >} \approx \hbar k_0$$

# Using Bandstructure in Effective Mass Hamiltonian

$$\left(\hat{H}_0 + \hat{V}_{ext}(r)\right)\, G_n(r,t) = i\hbar\,\frac{\partial G_n(r,t)}{\partial t}$$

where $\hat{H}_0 = \sum_\ell E_n(R_\ell)\,\hat{T}_{R_\ell}$

Bandstructure shows up in here…

$$E_n(k) = \sum_\ell E_n(R_\ell) e^{ik\cdot R_\ell}$$

$$\hat{H}_0 = \sum_\ell E_n(R_\ell)\,\hat{T}_{R_\ell}$$

$$= \sum_\ell E_n(R_\ell)\, e^{R_\ell\cdot\nabla_r}$$

For example…

$$E_N(k) = \left(\frac{\hbar^2}{2m^*}\right) k^2$$

$$\hat{H}_0 = -\left(\frac{\hbar^2}{2m^*}\right)\nabla_r^2$$

# Donor Impurity States
## Example of Effective Mass Approximation

Replace silicon (IV) with group V atom…

$$V(\mathbf{r}) = \sum_{\mathbf{R}_\ell} \underbrace{V_{\mathsf{Si}}(\mathbf{r} - \mathbf{R}_\ell)}_{\text{periodic}} + \underbrace{\left[V_{\mathsf{As}}(\mathbf{r}) - V_{\mathsf{Si}}(\mathbf{r})\right]}_{\Phi_{\text{ext}}(\mathbf{r})}$$

$$\Phi_{\text{ext}}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_{\mathsf{Si}}}\frac{1}{|\mathbf{r}|}$$

# Donor Impurity States
## Example of Effective Mass Approximation

$$E_N(k) = E_c + \frac{\hbar^2 k^2}{2m^*} + \ldots$$

$$\left(-\frac{\hbar^2\nabla^2}{2m^*} + E_c - \frac{e^2}{4\pi\epsilon|\mathbf{r}|}\right) G_N(r,t) = -\frac{\hbar}{i}\frac{\partial G_N(r,t)}{\partial t}$$

$$G_N(r,t) = G_N(r)e^{-iE_d t/\hbar}$$

This is a central potential problem, like the hydrogen atom…

$$\left(-\frac{\hbar^2\nabla^2}{2m^*} - \frac{e^2}{4\pi\epsilon|r|}\right) G_N(r) = (E_d - E_c)G_N(r)$$

$$E_l = E_d - E_c = -\frac{m^* e}{2(4\pi\epsilon)^2\hbar^2 l^2} = -\frac{13.6}{l^2}\left(\frac{m^*}{m}\frac{\epsilon_0^2}{\epsilon^2}\right) \text{ eV}$$

with $l = 1, 2, 3, 4, \ldots$

# Donor Impurity States

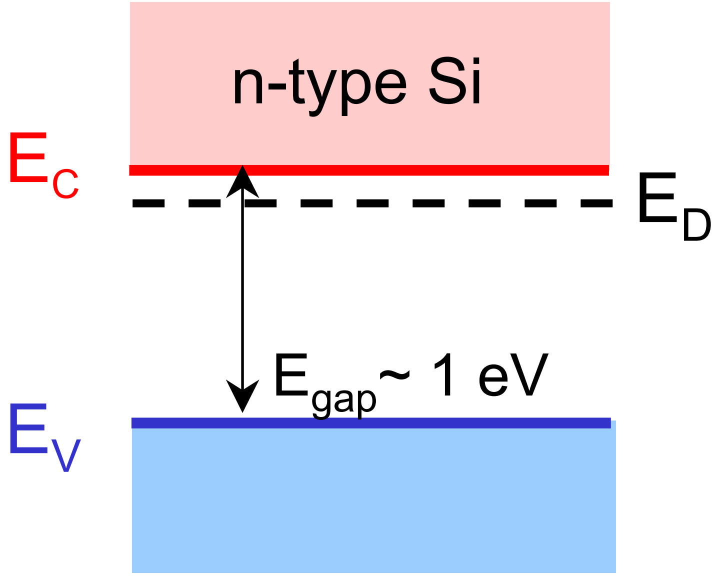
## Example of Effective Mass Approximation

Hydrogenic wavefunction with an equivalent Bohr radius..

$$G_1(r) = Ae^{-r/r_0} \quad \text{where} \quad r_0 = \frac{\epsilon\hbar^2}{m^* e^2} = \epsilon\frac{m}{m^*}(0.53\,\text{A})$$

Donor ionization energy…

$$E_d = E_c - \frac{13.56}{l^2\epsilon^2}\frac{m^*}{m}\ \text{eV}$$

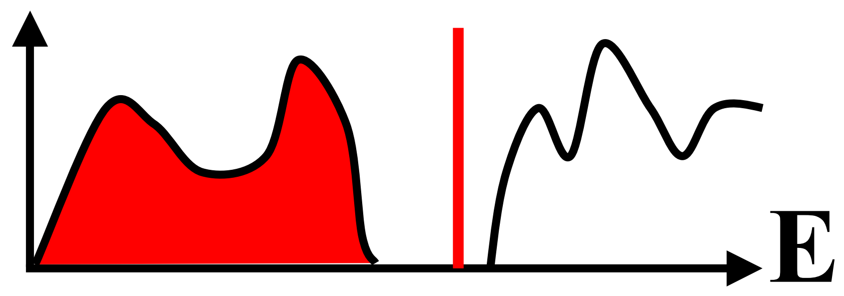


# Donor Impurity States
## Example of Effective Mass Approximation

$$g(E) = g_{\mathrm{Si}}(E) + \sum_l g_l \delta(E - E_l)$$

When there are $N_d$ donor impurities…

$$g(E) = g_{\mathrm{Si}}(E) + N_d \sum_l g_l \delta(E - E_l)$$



# Acceptor Impurity States
## Example of Effective Mass Approximation

Replace silicon (IV) with group III atom…

$$V(\mathbf{r}) = \sum_{\mathbf{R}_\ell} \underbrace{V_{\mathsf{Si}}(\mathbf{r} - \mathbf{R}_\ell)}_{\text{periodic}} + \underbrace{\left[V_{\mathsf{B}}(\mathbf{r}) - V_{\mathsf{Si}}(\mathbf{r})\right]}_{\Phi_{\text{ext}}(\mathbf{r})}$$

$$\Phi_{\text{ext}}(r) = \frac{e^2}{4\pi\epsilon}\frac{1}{|r|}$$

# Acceptor Impurity States

## Example of Effective Mass Approximation

$$E(k) = E_v - \frac{\hbar^2 k^2}{2m^*} + \ldots$$

$$\left(E_v + \frac{\hbar^2\nabla^2}{2m^*} + \frac{e^2}{4\pi\epsilon|r|}\right) G_N(r,t) = -\frac{\hbar}{i}\frac{\partial G_N(r,t)}{\partial t}$$

$$G_N(r,t) = G_N(r) e^{-iE_a t/\hbar}$$

Another central potential problem…

$$\left(-\frac{\hbar^2\nabla^2}{2m^*} - \frac{e^2}{4\pi\epsilon|r|}\right) G_N(r) = (E_v - E_a) G_N(r)$$

$$E_l = E_v - E_a = -\frac{m^* e}{2(4\pi\epsilon)^2\hbar^2 l^2} = -\frac{13.6}{l^2}\left(\frac{m^*}{m}\frac{\epsilon_0^2}{\epsilon^2}\right) \text{ eV}$$

with $l = 1, 2, 3, 4, \ldots$

# Acceptor Impurity States

## Example of Effective Mass Approximation

Hydrogenic wavefunction with an equivalent Bohr radius..

$$G_1(r) = Ae^{-r/r_0} \qquad \text{where} \qquad r_0 = \frac{\epsilon \hbar^2}{m^* e^2} = \epsilon \frac{m}{m^*}(0.53\,\text{Å})$$

Acceptor ionization energy…

$$E_a = E_v + \frac{13.56}{l^2 \epsilon^2}\frac{m^*}{m}\ \text{eV}$$