6.730 Physics for Solid State Applications

Lecture 22:

Outline

- Review of Effective Mass Theorem
- Impurity States in Semiconductors
- Fermi Surfaces in Metals
- Fermi Level, Chemical Potential
  - Intrinsic Semiconductors
  - Extrinsic Semiconductors

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Summary Wavepacket properties

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

\[
\left( E_n(-i\nabla_r) + \hat{V}_{\text{ext}}(r) \right) G_n(r, t) = i\hbar \frac{\partial G_n(r, t)}{\partial t}
\]

or

\[
\left( E_n(k_o - i\nabla_r) + \hat{V}_{\text{ext}}(r) \right) F_n(r, t) = i\hbar \frac{\partial F_n(r, t)}{\partial t}
\]

\[
< r(t) >_G = \frac{< G_n(r(t)) | G_n(r(t)) >}{< G_n(r(t)) | G_n(r(t)) >} = < r(t) > \\
< p >_G = \frac{< G_n(r(t)) | \hat{p} G_n(r(t)) >}{< G_n(r(t)) | G_n(r(t)) >} \approx \hbar k_c
\]

Semiclassical Equations of Motion:

\[
\frac{d}{dt} < r(t) > = < \mathbf{v}_n(k) > = \frac{1}{\hbar} \nabla_k E_n(k)
\]

\[
F_{\text{ext}} = \hbar \frac{dk}{dt}
\]
Donor Impurity States
Example of Effective Mass Approximation

Replace silicon (IV) with group V atom...

\[ V(r) = \sum_{R_i} V_{Si}(r - R_i) + \left[ V_{As}(r) - V_{Si}(r) \right] \]

\[ \Phi_{ext}(r) = -\frac{e^2}{4\pi\epsilon_{Si}|r|} \]

Donor Impurity States
Example of Effective Mass Approximation

\[ E_N(k) = E_c + \frac{\hbar^2(k - k_d)^2}{2m^*} + \ldots \]

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

\[ F_N(r, t) = F_N(r)e^{-iE_d t/\hbar} \]

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

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

\[ E_l = E_d - E_c = -\frac{m^*e}{2(4\pi\epsilon)^2\hbar^2l^2} = -\frac{13.6}{l^2} \left( \frac{m^*e_0^2}{m_e c^2} \right) \text{eV} \]

with \( l = 1, 2, 3, 4, \ldots \)
Donor Impurity States
Example of Effective Mass Approximation

Hydrogenic wavefunction with an equivalent Bohr radius.

\[ F_1(r) = A e^{-r/r_0} \quad \text{where} \quad r_0 = \frac{\varepsilon \hbar^2}{m^* e^2} = \frac{\varepsilon m}{m^*} (0.53 \text{ A}) \]

Donor ionization energy...

\[ E_d = E_c - \frac{13.56 m^*}{l^2 e^2} \text{ eV} \]

There are an infinite number of donor energies, \( E_d \) is the lowest energy with \( l=1 \), and from Statistical Mechanics we will see it is the most important one...

Donor Impurity States
Example of Effective Mass Approximation

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

When there are \( N_d \) donor impurities...

\[ g(E) = g_{Si}(E) + N_d \sum_l g_l \delta(E - E_l) \]
Acceptor Impurity States
Example of Effective Mass Approximation

Replace silicon (IV) with group III atom...

\[ V(r) = \sum_{R_i} \frac{V_{S_i}(r - R_i)}{\text{periodic}} + \left| \frac{V_B(r) - V_{S_i}(r)}{\Phi_{\text{ext}}(r)} \right| \]

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

Another central potential problem...

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

\[ \left( E_v + \frac{\hbar^2 \nabla^2}{2m^*} + \frac{e^2}{4\pi\epsilon|\mathbf{r}|} \right) F_N(r,t) = \frac{i}{\hbar} \frac{\partial F_N(r,t)}{\partial t} \]

\[ G_N(r,t) = G_N(r)e^{-iE_at/\hbar} \]
Acceptor Impurity States
Example of Effective Mass Approximation

Hydrogenic wavefunction with an equivalent Bohr radius.

\[ F_1(r) = Ae^{-r/r_0} \]

where \[ r_0 = \frac{\hbar^2}{m^*e^2} = \frac{\epsilon m^*}{m^*} (0.53 \text{ Å}) \]

Acceptor ionization energy...

\[ E_a = E_v + \frac{13.56 m^*}{l^2 e^2 m} \text{ eV} \]

There are an infinite number of acceptor energies, \( E_A \) is the lowest energy with \( l=1 \), and from Statistical Mechanics we will see it is the most important one.

Finite Temperatures: Where in the world is the Fermi Energy?

\[ E_F(T) = \mu(T) \]

\[ n = \frac{N}{V} = \int_{-\infty}^{E_F} \frac{1}{1 + e^{(E - \mu)/k_BT}} \frac{d^3k}{(2\pi)^3} \]

\[ n = \int_{-\infty}^{E_F} \frac{1}{1 + e^{(E - \mu)/k_BT}} g(E) dE \]

\( \mu \) is found from the integral equation given that \( n \) is fixed.

1. A metal: If \( \mu \) is in the bands
2. A semiconductor: if \( \mu \) is in the gap and gap > kT
3. Semimetal: if \( m \) is in the gap and gap is of the order of kT
2D Monatomic Square Crystals

Dispersion Relations

\[ a = 5.5 \text{ A} \]

\( \Gamma \rightarrow W \rightarrow X \)

Conductor

Insulator

\( \text{Na} \)

\( \text{Al} \)

\( \text{Mg} \)

\( \text{Si} : [\text{Ne}] 3s^2 3p^2 \)

4 e- per silicon atom
2 silicon atoms per lattice site
total: 8 electrons at each site

Si: [Ne] 3s^2 3p^2

4 e- per silicon atom
2 silicon atoms per lattice site
total: 8 electrons at each site
For free electrons, energy surfaces are simple spheres (circles)...

Valence (# of electrons) determines radius of energy surface...

When \( k \) near to BZ boundary:

\[ E \text{ contours become distorted} \]

Periodic potential pulls on the spherical FS forming ‘necks’
Fermi Surfaces (3D)

\[ N_e = 1 \] monovalent metals, e.g. Na, Cu, with values ~ f.e. theory

other cases, e.g. Be \((N_e=2)\), Al \((N_e=3)\), there are serious differences

Periodic Table of the Fermi Surfaces of Elemental Solids

http://www.phys.ufl.edu/fermisurface

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Semiconductors: Silicon Bandstructure

The fermi “tails” are in the conduction and valence bands.

Density of State Effective Mass (3D)
Ellipsoidal Energy Surfaces

Silicon energy surfaces can often be approximate as near the top or bottom as

A. For each of the 6 conduction “pockets”

\[ E_N(k) = E_c + \frac{\hbar^2}{2} \left( \frac{(k_x - k_{x0})^2}{m_t} + \frac{(k_y - k_{y0})^2}{m_t} + \frac{(k_z - k_{z0})^2}{m_t} \right) \]

\[ g_c = \frac{\sqrt{2}}{\pi^2 \hbar^3} (m_{dc}^*)^{3/2} \sqrt{E - E_c} \]

where the density of states effective mass is

\[ m_{dc}^* = (m_t m_l m_l)^{1/3} \]

B. For each of the valence bands

\[ E_N(k) = E_v - \frac{\hbar^2}{2m_i} k^2 \]

\[ g_v = \frac{\sqrt{2}}{\pi^2 \hbar^3} (m_i^*)^{3/2} \sqrt{E_v - E} \]

for each of the valence bands.
To find the Fermi Level of the Semiconductor

The number of particles thermally excited to the conduction band \( n_c \) must equal the number of electron vacancies in the valence band \( p_v \) so that charge neutrality is preserved.

\[
n_c = \int_{-\infty}^{\infty} \frac{1}{1 + e^{(E - \mu)/k_B T}} 6g_c(E) \, dE
\]

\[
p_v = \int_{-\infty}^{\infty} \left[ 1 - \frac{1}{1 + e^{(E - \mu)/k_B T}} \right] \left( \sum_i g_{vi}(E) \right) \, dE
\]

Solving for \( n_c = p_v \) give the fermi level (chemical potential) \( \mu(T) \)

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Counting and Fermi Integrals

3-D Conduction Electron Density

\[
n = \int_{E_c}^{\infty} 6g_c(E)f(E) \, dE \quad \quad g_c(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}
\]

\[
n = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \int_{E_c}^{\infty} \frac{\sqrt{E}}{1 + \exp \left( \frac{E - \mu}{k_B T} \right)} \, dE
\]

\[
= \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \int_{E_c}^{\infty} \frac{\sqrt{y} k_B T}{1 + ey - v} \, k_B T dy
\]

\[
y = \frac{E - \mu}{k_B T}
\]

\[
v = \frac{\mu - E_c}{k_B T}
\]

\[
n = \frac{2}{\sqrt{\pi}} N_c \, F_1/2 \left( \frac{\mu - E_c}{k_B T} \right)
\]
Counting and Fermi Integrals

3-D vacancy Density

\[ p = \int_{-\infty}^{E_v} \left( \sum_i g_{ii}(E) \right) (1 - f(E)) \, dE \]

\[ p_{hh} = \frac{2}{\sqrt{\pi}} \left( \frac{m_{hh}^* k_B T}{2 \pi \hbar^2} \right)^{3/2} F_{1/2} \left( \frac{E_v - \mu}{k_B T} \right) \]

\[ m_{hh}^* \text{GaAs} = 0.51 \, m \quad \quad m_{lh}^* \text{GaAs} = 0.087 \, m \]

\[ \frac{p_{lh}}{p_{hh}} = \left( \frac{m_{hh}^*}{m_{lh}^*} \right)^{3/2} \approx \left( \frac{0.51}{0.087} \right)^{3/2} = 13.7 \]

\[ p = \frac{2}{\sqrt{\pi}} \left( \frac{m_{hh}^* k_B T}{2 \pi \hbar^2} \right)^{3/2} F_{1/2} \left( \frac{E_v - \mu}{k_B T} \right) \negation{(m_{hh}^*)^{3/2}} = (m_{hh}^*)^{3/2} + (m_{lh}^*)^{3/2} \]

\[ p = \frac{2}{\sqrt{\pi}} N_v F_{1/2} \left( \frac{E_v - \mu}{k_B T} \right) \]

Boltzmann Approximation

Boltzmann Approximation:

\[ F_{1/2}(v) \approx \frac{\sqrt{\pi}}{2} e^v \]

\[ n_o = \frac{2}{\sqrt{\pi}} N_c F_{1/2} \left( \frac{E_F - E_c}{k_B T} \right) \to N_c \exp \left( \frac{-(E_c - E_{F_0})}{k_B T} \right) \]

\[ p_o = \frac{2}{\sqrt{\pi}} N_v F_{1/2} \left( \frac{E_v - E_{F_0}}{k_B T} \right) \to N_v \exp \left( \frac{-(E_{F_0} - E_v)}{k_B T} \right) \]

Intrinsic carrier concentration with \( n = p \)

\[ n_o p_o = N_c N_v \exp \left( \frac{-(E_c - E_v)}{k_B T} \right) = N_c N_v \exp \left( \frac{-E_g}{k_B T} \right) = \overline{n_i}^2 \]

Intrinsic Fermi level

\[ E_{F_0} = E_i = \frac{E_c'}{2} + \frac{k_B T}{2} \ln \frac{N_v}{N_c} \]
Electronic Specific Heat of the Semiconductor

The particles thermally excited to the conduction band \( n_C \) must gain an energy of about \( E - E_c \):

\[
\Delta E = \int_{-\infty}^{\infty} \frac{1}{1 + e^{(E - \mu)/k_B T}} 6g_c(E) (E - E_c) \, dE
\]

\[
\Delta E \approx n_i(T) E_g = \frac{\sqrt{2}}{\pi} N_c(T) e^{-E_g/2k_B T} E_g
\]

\[
C_v \approx \frac{\sqrt{2}}{\pi} N_c(T) \frac{E_g^2}{2k_B T^2} e^{-E_g/2k_B T}
\]

Electronic Specific heat decreases exponentially fast with T at low T; in contrast, a metal decreases linearly with T.

Doped Semiconductors

The fermi level is again found from Charge Neutrality

\[
p - n + N_D^+ - N_A^+ = 0
\]

Density of “ionized” donors \( N_D^+ \) \quad Density of “ionized” acceptors \( N_A^+ \)

Use the fact that even for doped materials, in the Boltzmann limit,

\[
n = \frac{2}{\sqrt{\pi}} N_c F_{1/2} \left( \frac{E_F - E_c}{k_B T} \right) \rightarrow N_c \exp \left( \frac{-(E_c - E_F)}{k_B T} \right)
\]

\[
p = \frac{2}{\sqrt{\pi}} N_v F_{1/2} \left( \frac{E_v - E_F}{k_B T} \right) \rightarrow N_v \exp \left( \frac{-(E_F - E_v)}{k_B T} \right)
\]

\[
np = N_c N_v \exp \left( \frac{-(E_c - E_v)}{k_B T} \right) = N_c N_v \exp \left( \frac{-E_g}{k_B T} \right) = n_i^2
\]
Extrinsic Semiconductors

For high temperatures where all the donors and acceptors are ionixed,

\[ \frac{n_i^2}{n} - n + N_D - N_A = 0 \]

Therefore, in the Boltzman (extrinsic) limit,

\[ n = \frac{N_D - N_A}{2} + \left[ \left( \frac{N_D - N_A}{2} \right)^2 + n_i^2 \right]^{1/2} \]

For n doped materials, \( N_D \gg N_A \) and \( N_D \gg n_i \),

\[ n \approx N_D \quad \text{and} \quad p = \frac{n_i^2}{N_D} \]

We also find that \( E_F = E_i + k_B T \ln \frac{N_D}{n_i} \).

http://www.physics.fsu.edu/courses/Spring04/phz3400/notes/semicon1.pdf
Approximations for Fermi Integrals
3-D Carrier Densities

\[ N_o = \frac{2}{\sqrt{\pi}} N_c F_{1/2} \left( \frac{E_{F_o} - E_c}{k_B T} \right) = \frac{2}{\sqrt{\pi}} N_c F_{1/2}(v) \]

where

\[ v = \frac{E_{F_o} - E_c}{k_B T} \]

Sommerfeld Approximation:

\[ F_{1/2}(v) \approx \frac{2}{3} v^{3/2} \left[ a_1 + a_2 v^{-2} + \ldots \right] \]

\[ a_1 = 1 \quad a_2 = \frac{\pi^2}{8} \approx 1.2337 \]

Unger Approximation:

\[ F_{1/2}(v) \approx \frac{\sqrt{\pi}}{2} z \left[ a_1 + a_2 z + \ldots \right] \quad \text{where} \quad z = \ln \left( 1 + e^v \right) \]

\[ a_1 = 1 \quad a_2 = \frac{1}{2} \left( 1 - \frac{1}{\sqrt{2}} \right) \approx 0.14645 \]
Approximations for Inverse Fermi Integrals

\[ r = \frac{N}{N_c} \quad v = \frac{E_{F_0} - E_c}{k_B T} \]

**Inverse First-order Sommerfeld Approximation:**

\[ v \approx \left( \frac{3\sqrt{\pi}}{4} r \right)^{3/2} \quad v > 2C \quad \text{for 0.04 error} \]

**Inverse Second-order Unger Approximation:**

\[ v \approx \ln(\exp\left(\frac{1}{2a_2} (\sqrt{1 + 4a_2 r} - 1)\right) - 1) \]

- \[ a_2 = 0.146545 \quad v < 2.8 \quad \text{for 0.04 error} \]
- \[ a_2 = 0.15 \quad v < 7.4 \]