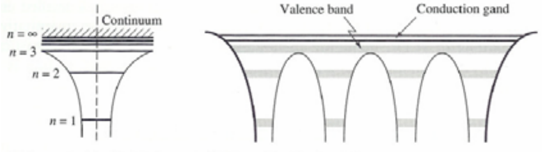
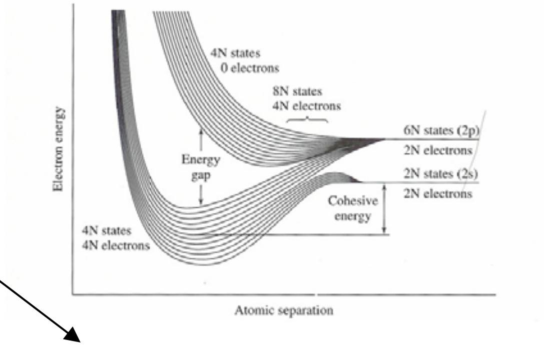
Lecture 16: Free Electrons (Optical Properties)

Electron bands originate from atomic levels:



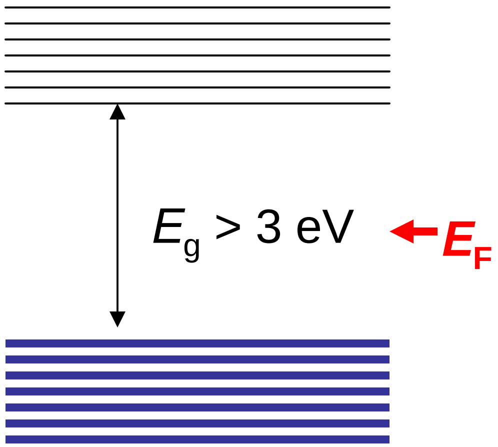
(a) Energy levels of isolated atom

(b) Energy bands of crystals



Three band structure scenario

Dielectrics



CB

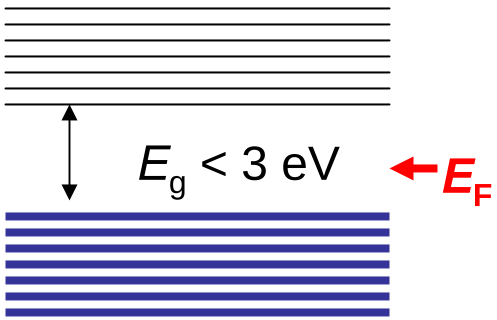
$E_g > 3$ eV

E_F

VB

CB: A lot of available states, no electrons
VB: A lot of electrons, no states available

Semiconductors



CB

$E_g < 3$ eV

E_F

VB

CB: A lot of available states, no electrons at T = 0
VB: A lot of electrons, no states available

Metals

CB

E_F

CB: A lot of electrons and available states ⇒ free electron model with strong conductivity

Materials

Application of the Lorentz oscillator model to free electron systems:

- Metals
- Doped semiconductors

Plasma reflectivity

Combination:

- Lorentz model of dipole oscillator (No restoring force in plasma)
- Drude model of free electron conductivity (τ - scattering time)

Oscillation of a free electron induced by AC electric field E(t) of EM wave:

$$m_0 \frac{d^2 x}{dt^2} + m_0 \gamma \frac{dx}{dt} = -eE(t) = -eE_0 e^{-i\omega t}$$

$$x = x_0 e^{-i\omega t}$$

$$x(t) = \frac{eE(t)}{m_0(\omega^2 + i\gamma\omega)}$$

Damping term

$1/\gamma = \tau$ - mean scattering time

Macroscopic polarization: $P = N(-e)x(t)$

$$D = \varepsilon_r \varepsilon_0 E = \varepsilon_0 E + P = \varepsilon_0 E - \frac{Ne^2 E}{m_0(\omega^2 + i\gamma\omega)}$$

$$\varepsilon_r(\omega) = 1 - \frac{Ne^2}{\varepsilon_0 m_0(\omega^2 + i\gamma\omega)}$$

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)}$$

$$\omega_p = \left(\frac{Ne^2}{\varepsilon_0 m_0}\right)^{\frac{1}{2}}$$

Formally follows from
bound *e*-resonace:

$$\varepsilon_r = 1 + \frac{Ne^2}{\varepsilon_0 m_0} \frac{1}{(\omega_j^2 - \omega^2 - i\gamma\omega)}$$

Under $\omega_j = 0$ - No restoring force

ω_p – plasma frequency

In the limit $\gamma \Rightarrow 0$

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

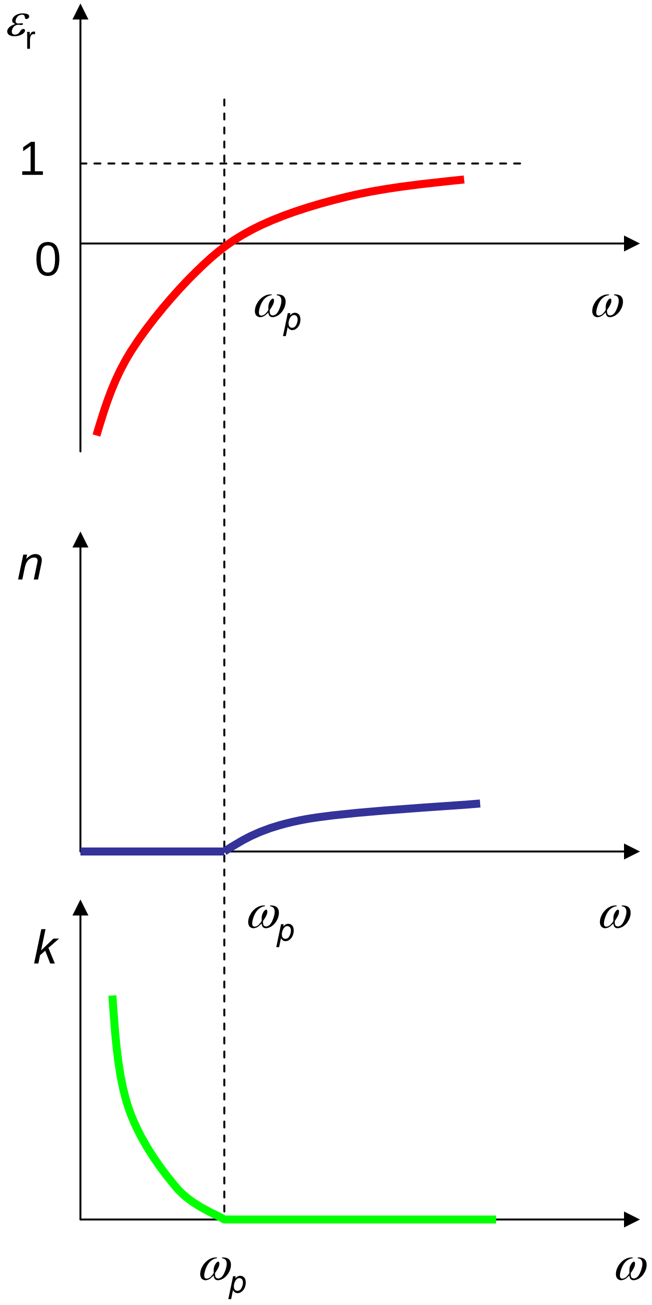
$$\varepsilon_1 = 1 - \frac{\omega_p^2}{\omega^2}$$

$$\varepsilon_2 = 0$$

$$n = \frac{1}{\sqrt{2}}\left[\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}}\right]^{\frac{1}{2}} = \frac{1}{\sqrt{2}}\left[\varepsilon_1 + |\varepsilon_1|\right]^{\frac{1}{2}}$$

$$k = \frac{1}{\sqrt{2}}\left[-\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{\frac{1}{2}}\right]^{\frac{1}{2}} = \frac{1}{\sqrt{2}}\left[-\varepsilon_1 + |\varepsilon_1|\right]^{\frac{1}{2}}$$

$$\boxed{\begin{aligned} &\omega < \omega_p \Rightarrow n = 0, k = \sqrt{|\varepsilon_1|} \\ &\omega > \omega_p \Rightarrow n = \sqrt{|\varepsilon_1|}, k = 0 \end{aligned}}$$



$n = 0$ what's going on?

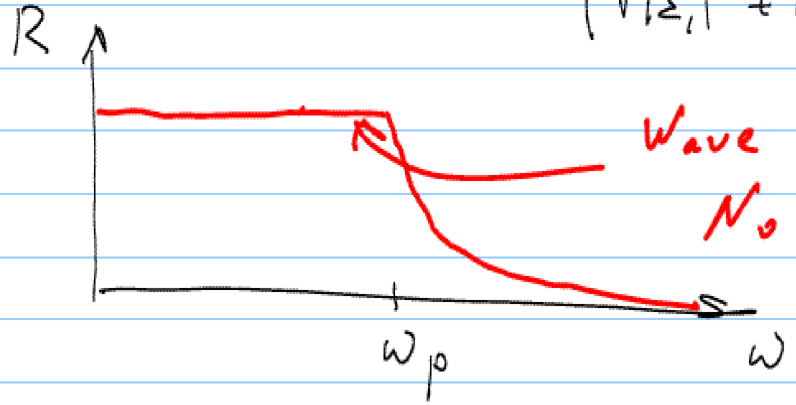
$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

$\omega < \omega_p$ $\begin{cases} n = 0 \\ k = \sqrt{|\varepsilon_1|} \end{cases}$

$\omega > \omega_p$ $\begin{cases} n = \sqrt{|\varepsilon_1|} \\ k = 0 \end{cases}$

$\omega < \omega_p \Rightarrow R = 1$!!!

$$\omega > \omega_p \Rightarrow R = \frac{\left(\sqrt{|\varepsilon_1|} - 1\right)^2}{\left(\sqrt{|\varepsilon_1|} + 1\right)^2}$$



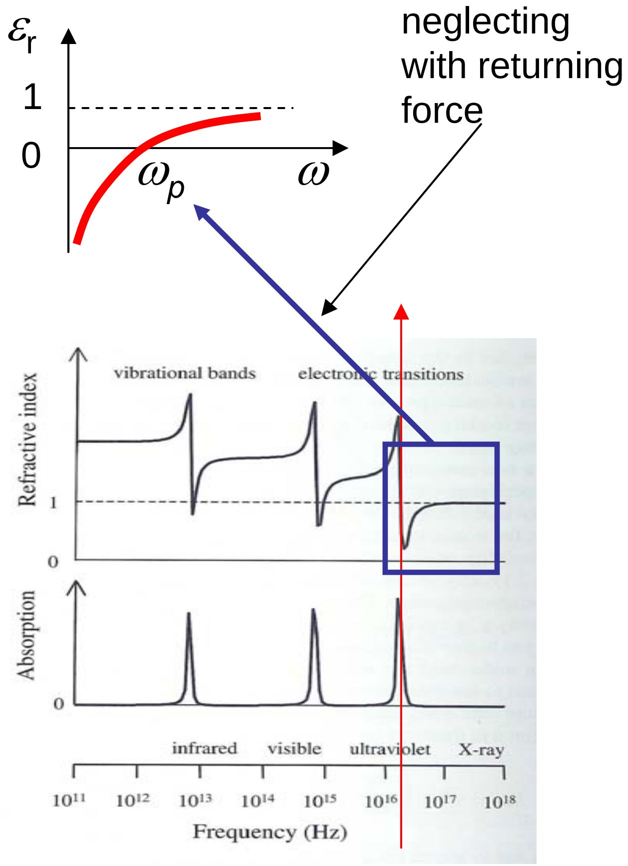
Wave is reflected $\omega < \omega_p$
No propagation

Lecture 17: Free Electrons (Optical Properties)

Main Effects in relation to Plasma Reflectivity Model

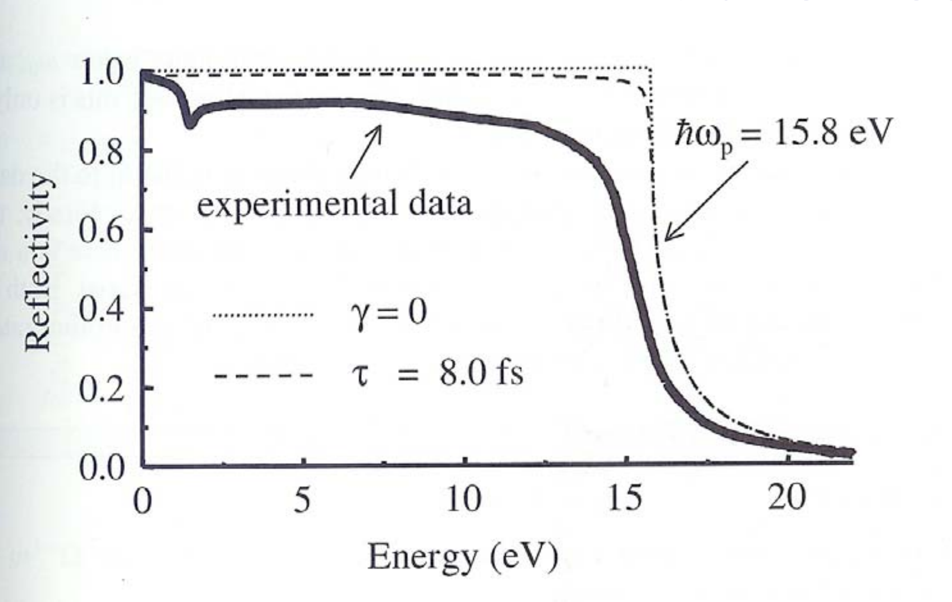
1. **High reflectivity in visible and NI regimes combined with high transmission in UV**
   - Plasma model without damping force,
     High *R* for $\omega < \omega_{p,}$, high *T* for $\omega > \omega_p$
2. **Skin Effect at low frequencies**
   - Plasma model with damping force,
     Absorption for $\omega < 1/\tau$, τ - scattering time
3. **Interband transitions in metals**
   - Quantum process in *E*-*k* band diagram, superimposed on the plasma model
4. **Free carrier absorption in semiconductors**
   - Shift of ω_p to much lower frequencies,
     Plasma model with damping forω > ω_p
5. **Plasmons**
   - Plasma model at $\omega = \omega_p$ where $\varepsilon_r = 0$,
     Restoring force due to macroscopic polarization

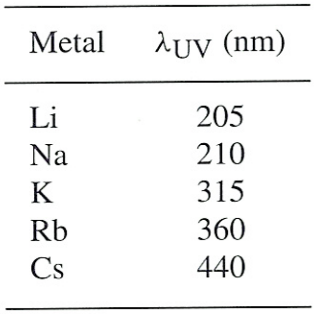
Plasma model in relation to dipole oscillator model



neglecting with returning force

High reflectivity in visible and NI regimes combined with high transmission in UV





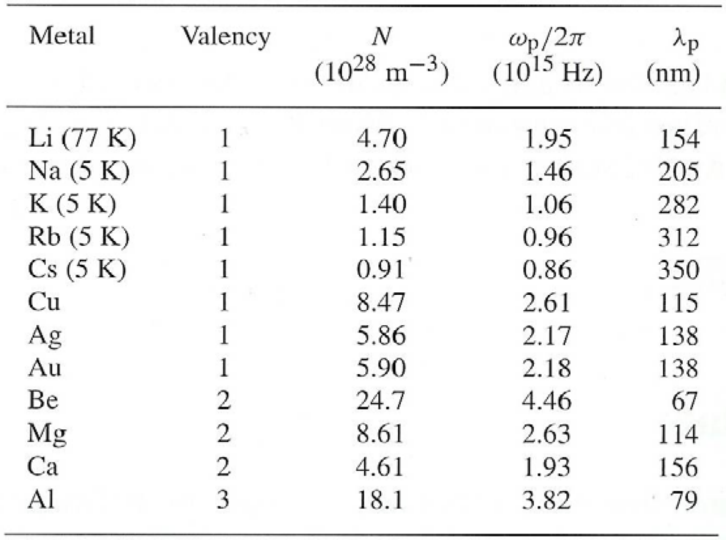
Metal	λ_{UV} (nm)
Li	205
Na	210
K	315
Rb	360
Cs	440

Aluminium

$h\nu_p = \hbar\omega_p = 15.8$ eV

$\sigma = 3.6\ 10^7\ \Omega^{-1}\ m^{-1}$

$\tau = 1/\gamma = m_0\sigma/(Ne^2)$ – determines the absorption at low ω, as we will see below, σ - DC conductivity



Metal	Valency	N $(10^{28}\ \mathrm{m}^{-3})$	$\omega_p/2\pi$ $(10^{15}\ \mathrm{Hz})$	λ_p (nm)
Li (77 K)	1	4.70	1.95	154
Na (5 K)	1	2.65	1.46	205
K (5 K)	1	1.40	1.06	282
Rb (5 K)	1	1.15	0.96	312
Cs (5 K)	1	0.91	0.86	350
Cu	1	8.47	2.61	115
Ag	1	5.86	2.17	138
Au	1	5.90	2.18	138
Be	2	24.7	4.46	67
Mg	2	8.61	2.63	114
Ca	2	4.61	1.93	156
Al	3	18.1	3.82	79

Skin Effect at low frequencies

Eqn. of motion with damping force

$$m_e \frac{dv}{dt} + \frac{m_e}{\tau} v = -eE \qquad \gamma = \frac{1}{\tau}$$

τ – mean time between scattering events

expects solutions $v(t) = \tilde{v}_0 \cdot e^{-i\omega t}$

$E(t) = E_0 e^{-i\omega t}$

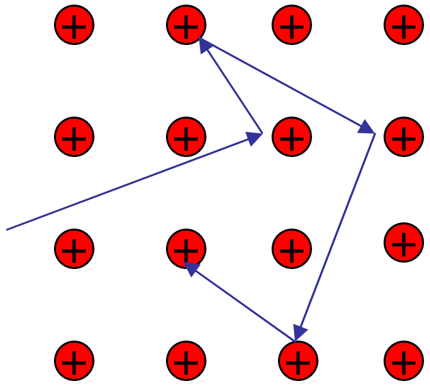
$p = mv$

$$\frac{dp}{dt} + \frac{p}{\tau} = -eE$$

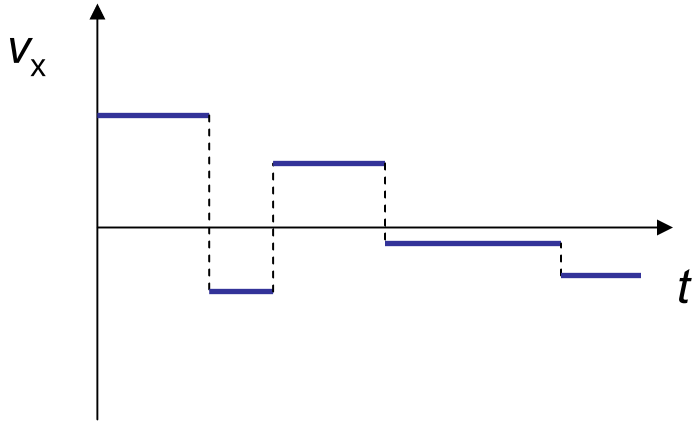
$$v(t) = -\frac{e\tau}{m_e} \frac{1}{1-i\omega\tau} E(t)$$

Model of conduction

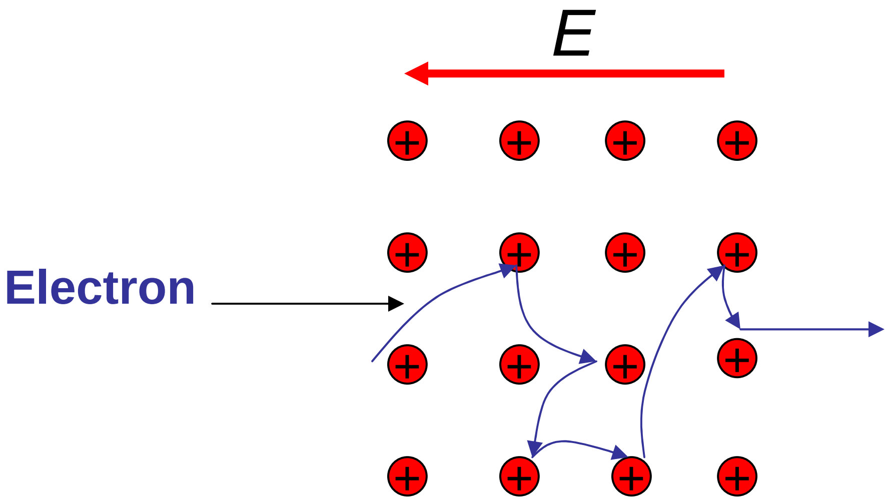
$E = 0$



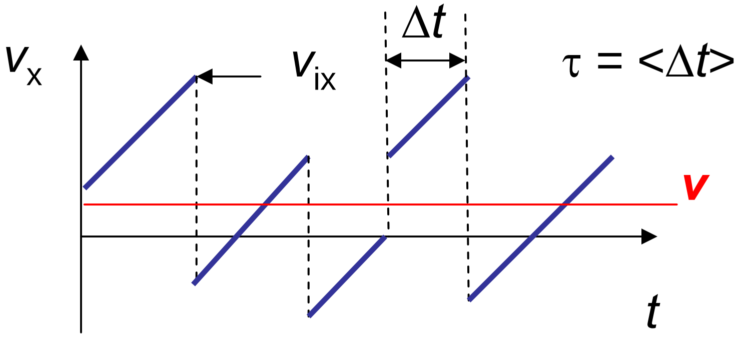
Frequent collisions, but no net displacement



$v = \langle v_x \rangle = 0$



Net displacement superimposed on the random thermal motion



$v = \langle v_x \rangle = \langle v_{ix} \rangle + (eE/m)\langle \Delta t \rangle = (e\tau/m)E$

$i = eNAv = (Ne^2\tau/m)AE \Rightarrow j = i/A = \sigma E$

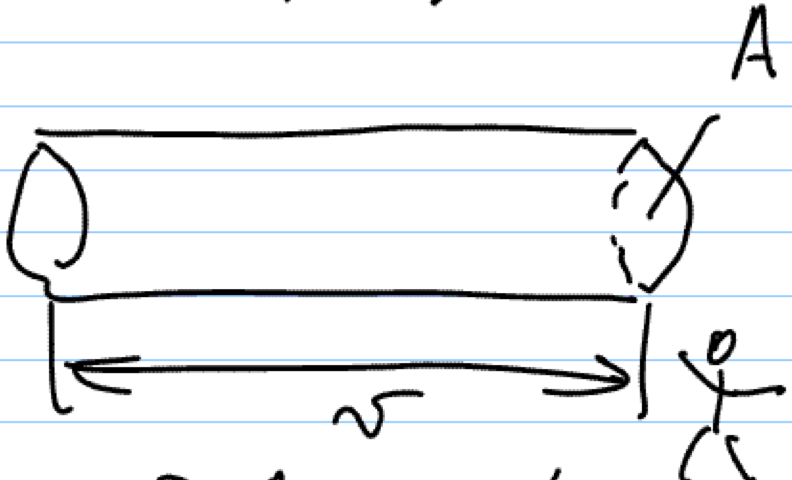
where $\boxed{\sigma = Ne^2\tau/m}$

Drude conductivity model;

$i = eNAv$

v - drift velocity

$v = \langle v \rangle$



$v \cdot A = \Delta V$

$$\langle v \rangle = \overbrace{\langle v_i \rangle}^{=0} + \frac{eE}{m}\langle \Delta t \rangle = \frac{eE}{m}\tau, \quad \boxed{\tau = \langle \Delta t \rangle}$$

Substitute v;

$$i = \frac{e^2 N A E \tau}{m} \Rightarrow$$

$$j = \frac{i}{A} = \frac{e^2 N \tau}{m} E =$$

$$= \sigma E$$

$$\sigma = \frac{e^2 N \tau}{m} = \sigma_{DC} \, , \qquad \boxed{R = \rho \frac{L}{A} = \frac{1}{\sigma} \frac{L}{A}}$$

$$I = \frac{V}{R} = \frac{V \cdot \sigma \cdot A}{L}$$

$$I = j \cdot A = N \cdot v \cdot (-e) \cdot A$$

$$\frac{\underbrace{V \cdot}_{E} \sigma \cdot \cancel{A}}{\underbrace{L}_{}} = - N \cdot v \cdot e \cdot \cancel{A}$$

$$\sigma \cdot E = - N \cdot v \cdot e$$

$$\sigma = - \frac{N \cdot e \cdot v}{E} .$$

$$v(\omega, t) = - \frac{e\tau}{m_e} \frac{1}{1 - i\omega\tau} E$$

$$\sigma(\omega) = \frac{\sigma_0}{(1 - i\omega\tau)}, \qquad \sigma_0 = \frac{Ne^2\tau}{m_e}$$

As we showed previously: $\varepsilon_r(\omega) = 1 - \frac{Ne^2}{m_e\varepsilon_0}\frac{1}{\omega^2 + i\frac{\omega}{\tau}} \Rightarrow$

$$\varepsilon_r(\omega) = 1 - \frac{\sigma_0}{\tau\varepsilon_0}\frac{1}{\omega^2 + i\frac{\omega}{\tau}}$$

substituting $\sigma_0 = \sigma(\omega)(1 - i\omega\tau)$

$$\boxed{\varepsilon_r(\omega) = 1 + i\frac{\sigma(\omega)}{\varepsilon_0\omega}}$$

Thus optical measurements of $\varepsilon_r(\omega)$ are equivalent to AC conductivity measuments of $\sigma(\omega)$

Additional link: $\omega_p^2 = \frac{Ne^2}{m_e\varepsilon_0}$

$$\left.\begin{aligned}\omega_p^2 &= \frac{Ne^2}{m_e\varepsilon_0}\\ \sigma_0 &= \frac{Ne^2\tau}{m_e}\end{aligned}\right| \Rightarrow \omega_p^2\tau = \frac{\sigma_0}{\varepsilon_0}$$

From general Eq for ε_r:

$$\varepsilon_r = 1 - \frac{Ne^2}{\varepsilon_0 m_e} \frac{1}{(\omega^2 + i\frac{\omega}{\tau})}$$ using $\varepsilon_r = \varepsilon_1 + i\varepsilon_2$

$$\left\{ \begin{aligned} \varepsilon_1 &= 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \\ \varepsilon_2 &= \frac{\omega_p^2 \tau}{\omega (1 + \omega^2 \tau^2)} \end{aligned} \right.$$

Since $\frac{1}{\tau}$ (typically) $\sim 10^{14} - 10^{15}$ Hz

Whereas $\omega_p \sim 10^{15} - 10^{16}$ Hz

Consider $\boxed{\omega \ll \frac{1}{\tau} \ll \omega_p}$

Means $\omega \tau \ll 1$

$$\varepsilon_1 \sim -\omega_p^2 \tau^2$$

$$\varepsilon_2 \sim \frac{\omega_p^2 \tau}{\omega} \implies |\varepsilon_2| \gg |\varepsilon_1|$$

Using expressions for n and k:

$$n \sim \sqrt{\frac{\varepsilon_2}{2}} \qquad n \simeq K$$

$$K \sim \sqrt{\frac{\varepsilon_2}{2}}$$

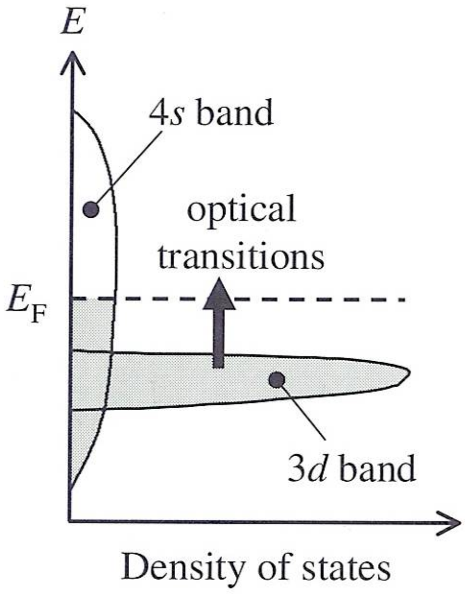
Since real absorption $\alpha = \frac{2\omega k}{c}$, where $c^2 = \frac{1}{\varepsilon_0 \mu_0}$ we have

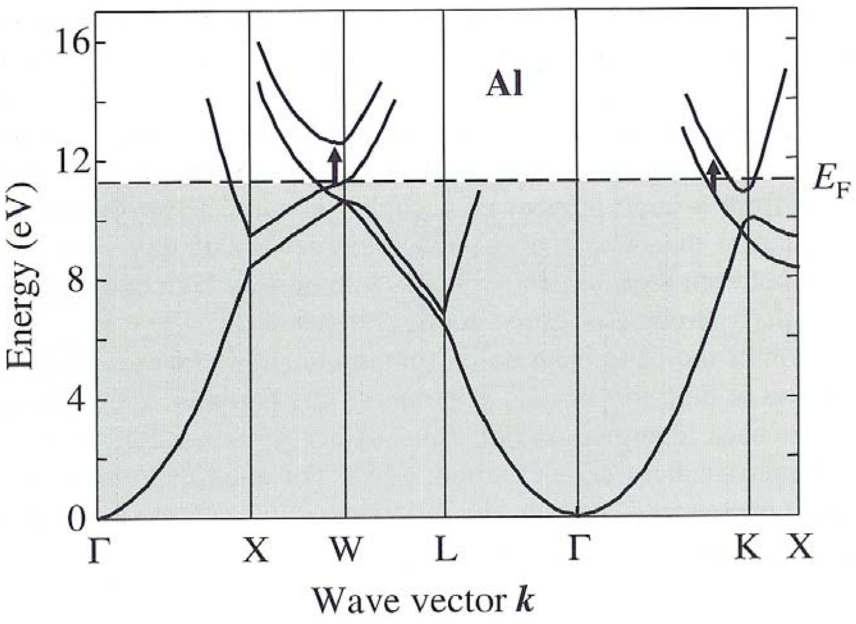
$$\alpha = \frac{2\omega K}{c} = \frac{2\omega}{c}\sqrt{\frac{\omega_p^2 \tau}{2\omega}} = \sqrt{\frac{2\omega\omega_p^2 \cdot \tau}{c^2}} =$$

$= \sqrt{2\sigma_0 \omega \mu_0}$ – Skin Effect, The power attenuates as $\exp(-2z/\delta)$ where $\delta = \frac{2}{\alpha} = \sqrt{2/\sigma_0 \omega \mu_0}$ – Skin Depth.

Interband transitions in metals

Explains color of such metals as gold and copper

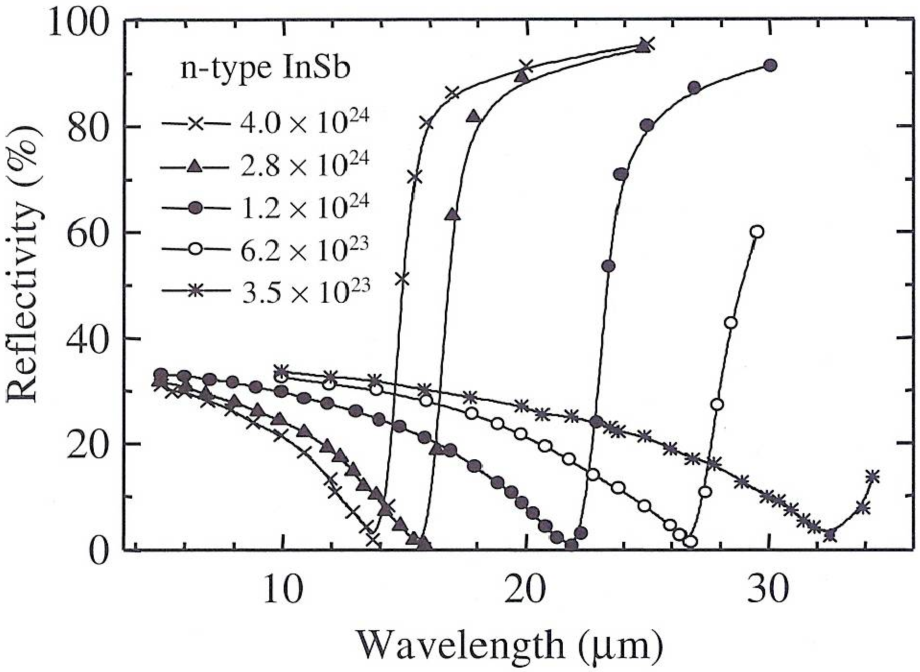




- Inner *d* orbitals form narrow bands below E_F
- Transition to half-full *s* band gives an absorption

- Very high density of states for parallel bands
- Hence reflectivity dip at 1.5 eV

Free carrier absorption and reflectivity in semiconductors



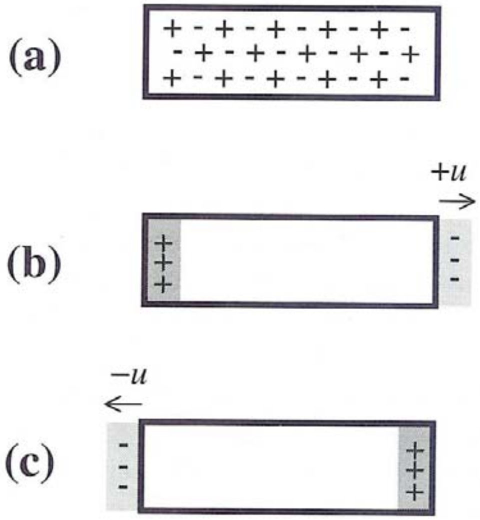
Plasma frequency is reduced due to $\varepsilon_r > 1$ and $m^* > m_0$:

$$\omega_p = (Ne^2/\varepsilon_0\varepsilon_r m^*)^{1/2}$$

- Control plasma frequency by varying the doping density
- Plasma edge in the infrared

Plasmons

Longitudinal oscillations of the electron plasma at ω_p where $\varepsilon_r = 0$



$$Nm_0 \frac{d^2u}{dt^2} = -NeE = -\left(\frac{N^2e^2}{\varepsilon_0}\right)u$$

$$\frac{d^2u}{dt^2} + \left(\frac{Ne^2}{\varepsilon_0 m_0}\right)u = 0$$

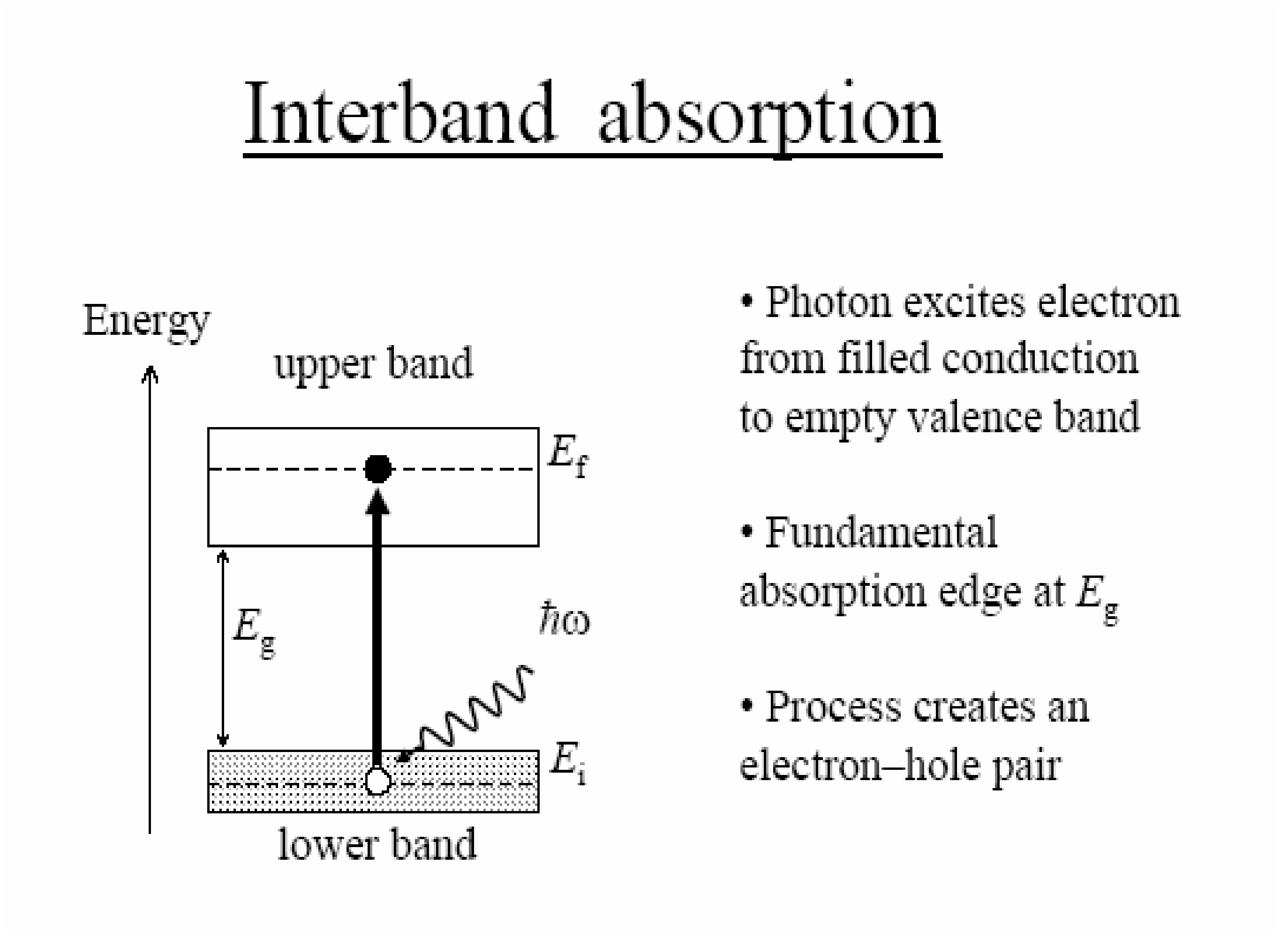
$$\omega_0 = \left(Ne^2 / \varepsilon_0 m_0\right)^{\frac{1}{2}}$$

Metals: $\hbar\omega_p$ ~3-20 eV

Doped demiconductors: $\hbar\omega_p$ ~ 10 meV

Measure by Raman Scattering: $\hbar\omega_{out} = \hbar\omega_{in} \pm n\hbar\omega_p$

Lectures 18: Interband Absorption



Interband absorption

- Photon excites electron from filled conduction to empty valence band

- Fundamental absorption edge at E_g

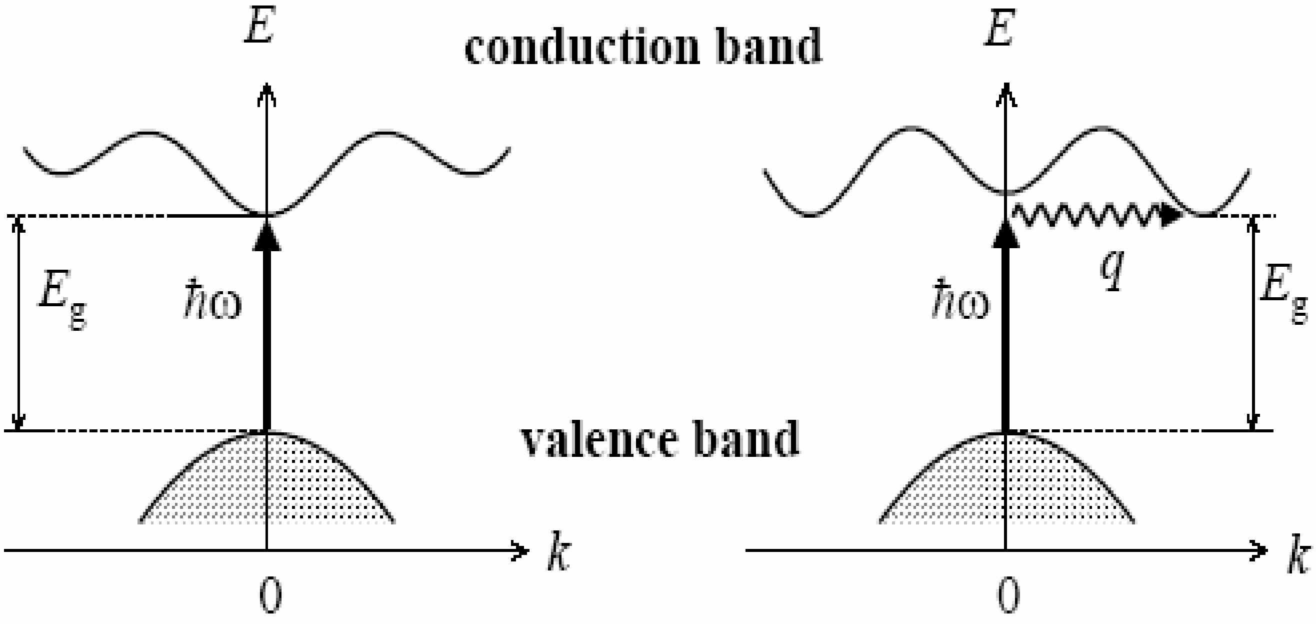
- Process creates an electron–hole pair

Direct and Indirect Absorption

(a) Direct band gap:
C.B. minimum at $k = 0$

Figure 3.2

(b) Indirect band gap
C.B. minimum at $k \neq 0$



- $k_{\text{photon}} = 2\pi/\lambda \sim 10^7\ \text{m}^{-1}$ negligible compared to B.Z. size $\pi/a \sim 10^{11}\ \text{m}^{-1}$
- Transitions appear as vertical lines on $E - k$ diagrams
- Phonon needed to conserve momentum for indirect gap materials
- Indirect absorption 2nd order process, therefore low probability

The Transition Rate for Direct Absorption

Transition Rate:

$$W_{i\to f} = \frac{2\pi}{\hbar}|M|^2 g(\hbar\omega)$$

The matrix element *M*

Density of states g

$$M = \int \psi_f^*(\mathbf{r})H'(\mathbf{r})\psi_i(\mathbf{r})\,d^3\mathbf{r}$$

The first-order energy shift for a given state is the expectation value of the perturbing potential

$$H' = -p_e \cdot \mathbf{E}_{photon}$$

Quantum perturbation

$$E_{photon}(\mathbf{r}) = \mathbf{E}_0 e^{\pm i\mathbf{k}\mathbf{r}}$$

$$H'(\mathbf{r}) = e\mathbf{E}_0 r e^{\pm i\mathbf{k}\mathbf{r}}$$

$$\psi_i(r) = \frac{1}{\sqrt{V}}u_i(\mathbf{r})e^{\pm i\mathbf{k}_i\mathbf{r}}$$

$$\psi_f(r) = \frac{1}{\sqrt{V}}u_f(\mathbf{r})e^{\pm i\mathbf{k}_f\mathbf{r}}$$

Continuing

$$M = \frac{e}{V}\int u_f^*(\mathbf{r})e^{-i\mathbf{k}_f\mathbf{r}}(\mathbf{E}_0 \cdot \mathbf{r}e^{\pm i\mathbf{k}\mathbf{r}})u_i(\mathbf{r})e^{-i\mathbf{k}_i\mathbf{r}}d^3\mathbf{r}$$

$\hbar\mathbf{k_f} - \hbar\mathbf{k_i} = \pm\hbar\mathbf{k}$ → Required for the integral to be non zero

$|M| \sim \int\limits_{unit\_cell} u_i^*(\mathbf{r})xu_f(\mathbf{r})d^3\mathbf{r}$ → For *x*-polarized light

M – electric dipole moment of the transition

$$\mathbf{k_f} = \mathbf{k_i}$$

$g(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}}E^{\frac{1}{2}}$ → Obtained previously in 3-D case,

m^* instead of *m*

Atomic Physics of Semiconductors

- $\Delta m = -1, 0, +1$
- **$\Delta l = \pm 1$**
- $\Delta m_s = 0$

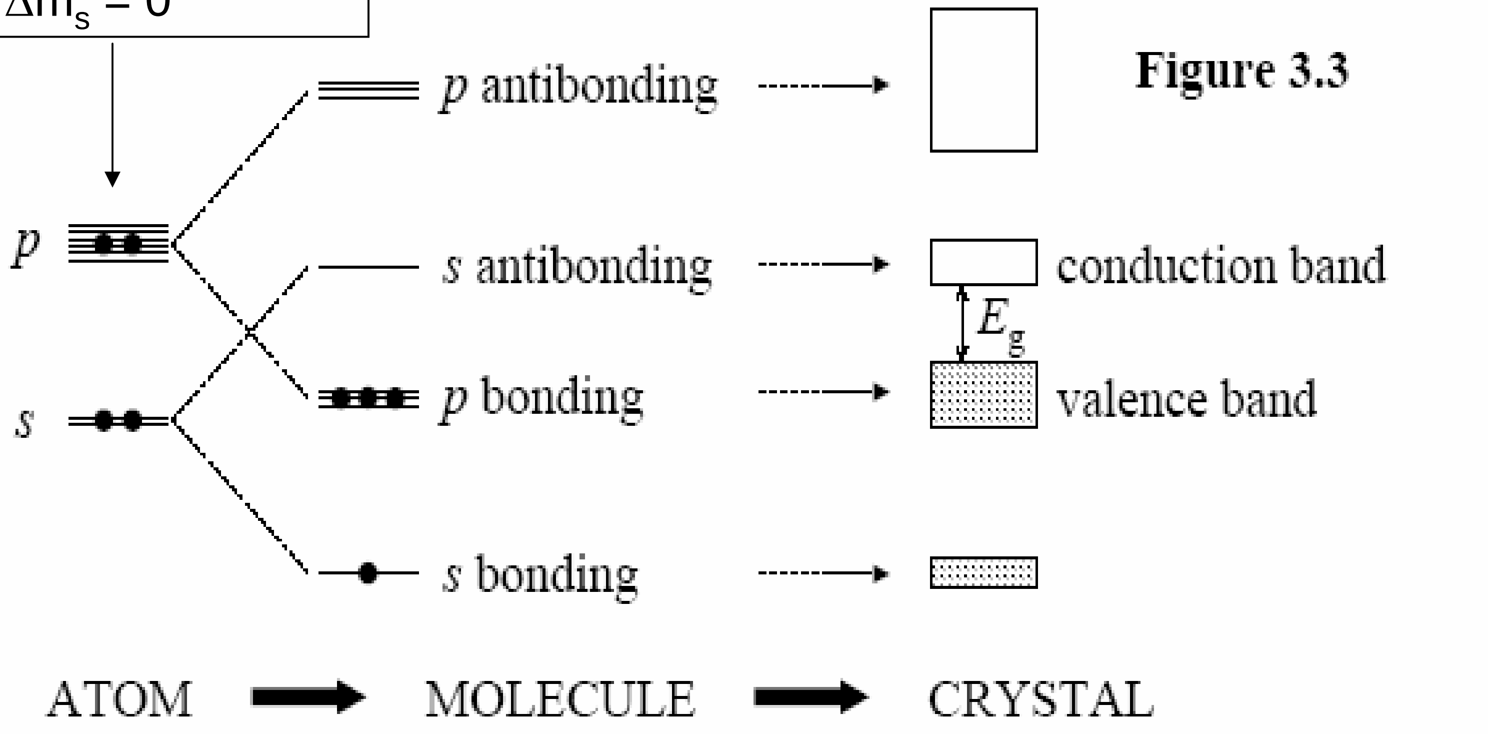


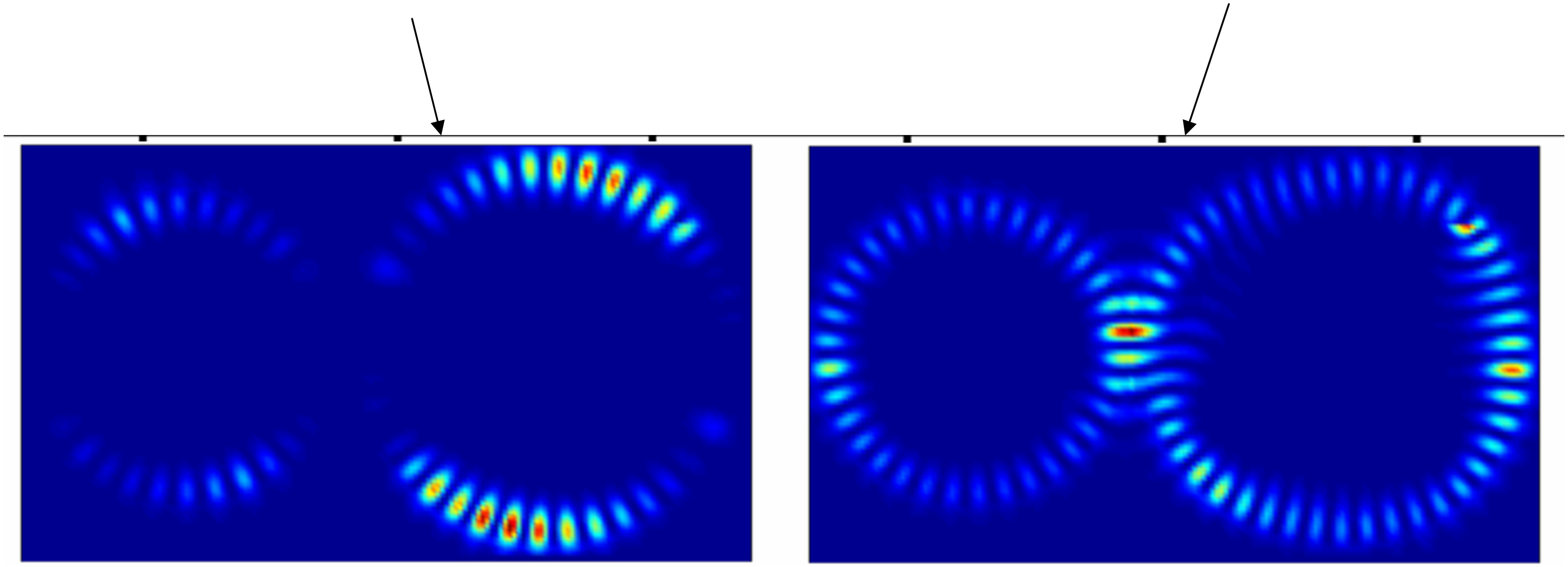
Figure 3.3

- Four valence electrons per atom: Group IV (C, Si, Ge),
- III-V compounds (GaAs, InAs, InSb, GaN ….)
- II-VI compounds (ZnS, ZnSe, CdSe, HgTe, ….)
- V.B. → C.B. is $p \rightarrow s$, hence allowed transition

Ge: $4s^2 4p^2$

Bonding and Antibonding Modes in Bispherical “Atoms”

Illustrated by coupled Whispering Gallery Modes in Dielectric Bispheres



Antibonding

Bonding

- Due to different fractions in high (dielectric spheres) and low (air) index media these modes have different energy ⇒ anticrossing splitting

Lectures 19: Interband Absorption (Continue)

GaAs Band Structure

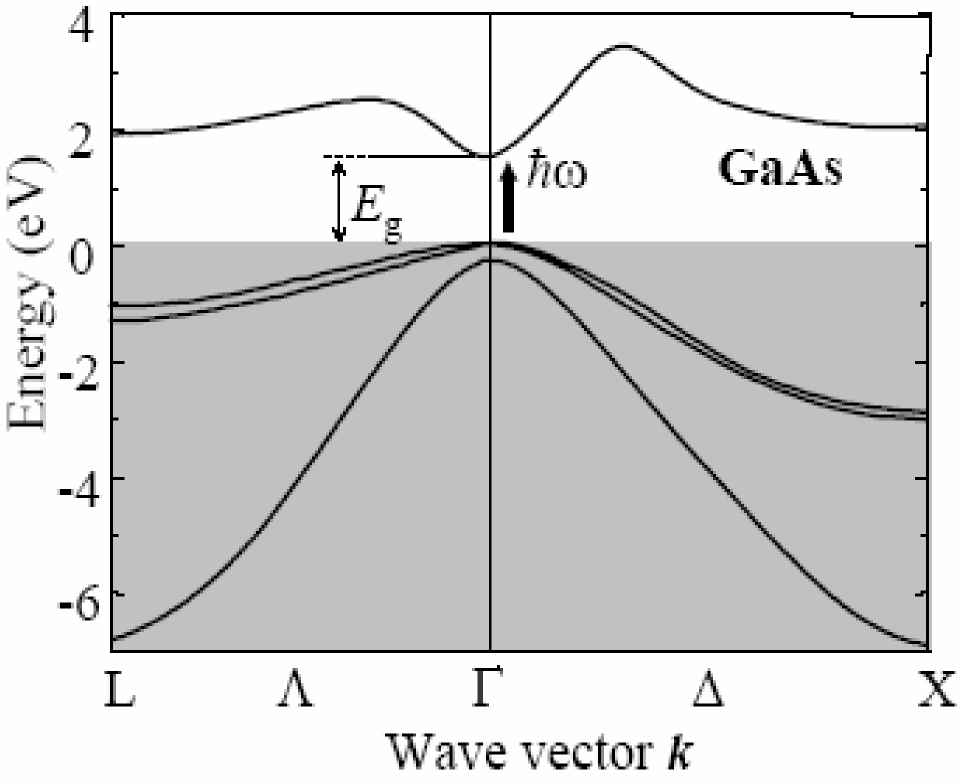


Figure 3.4

- Direct gap at 1.5 eV
- Very important optoelectronic material
- Strong absorption for $\hbar\omega > E_g$

Four-Band Model

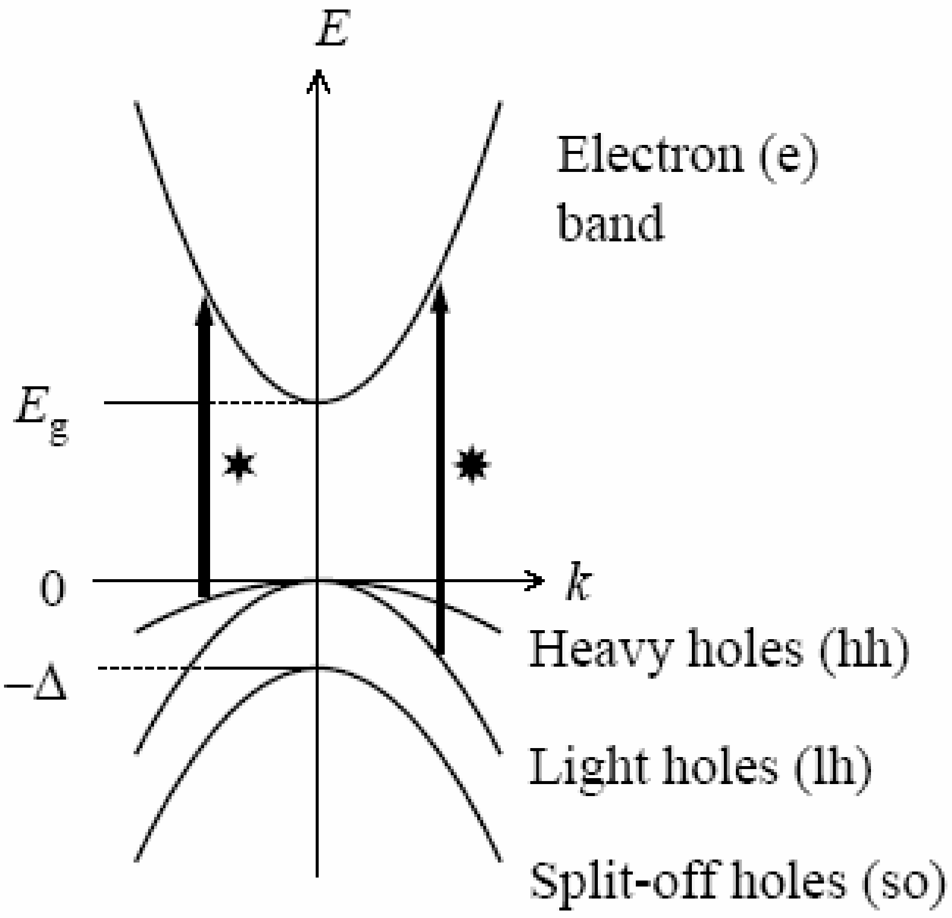


Figure 3.5

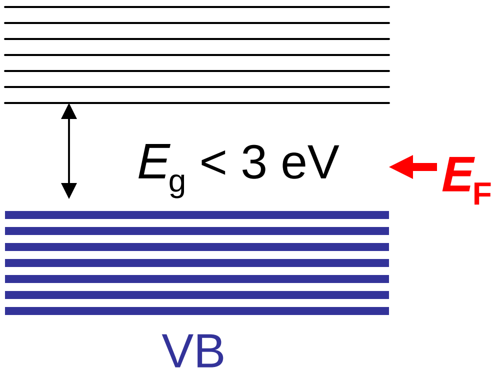
- Simplified band structure first proposed by Kane (1957)
- valid near $k = 0$

✶ Heavy hole transition

✸ Light hole transition

- Split-off hole transitions also possible

Joint Density of States



$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

$$\hbar\omega = E_g + \frac{\hbar^2 k^2}{2m_e^*} + \frac{\hbar^2 k^2}{2m_h^*} = E_g + \frac{\hbar^2 k^2}{2\mu}$$

$$For\_\hbar\omega < E_g,\_g(\hbar\omega) = 0$$

$$For\_\hbar\omega > E_g,\_g(\hbar\omega) = \frac{1}{2\pi}\left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}\left(\hbar\omega - E_g\right)^{\frac{1}{2}}$$

InAs Band Edge Absorption

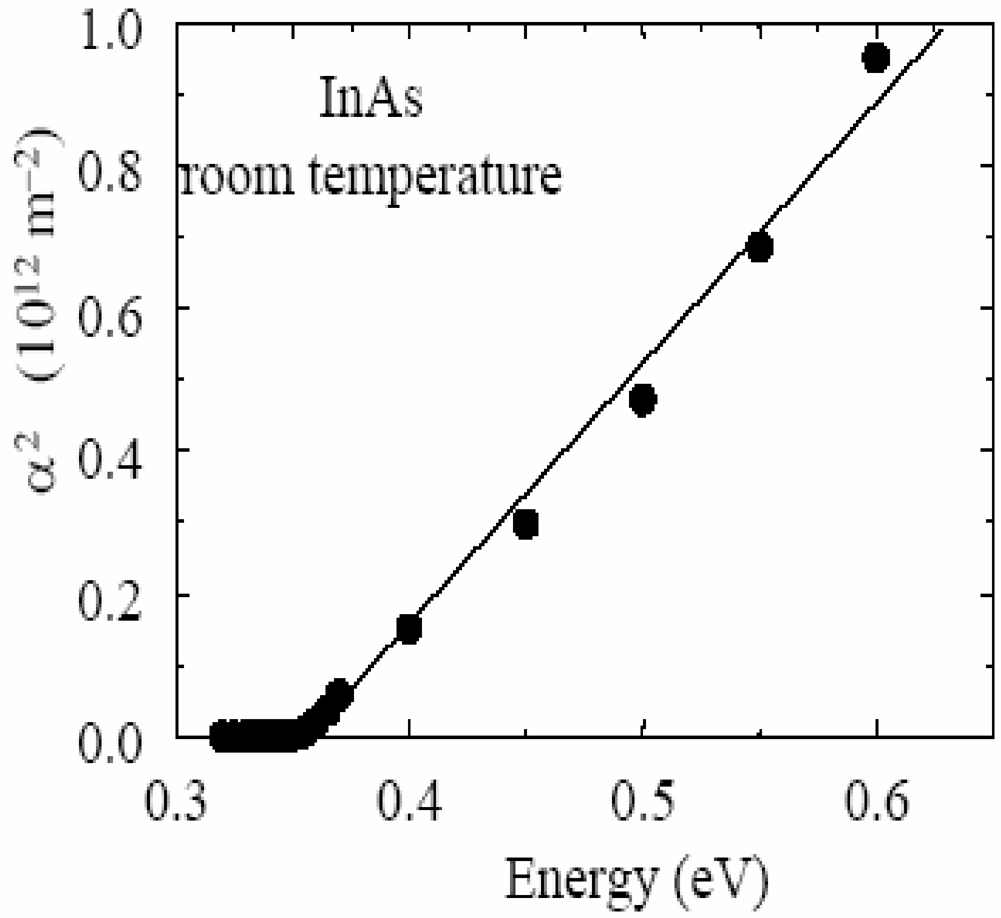


Figure 3.6

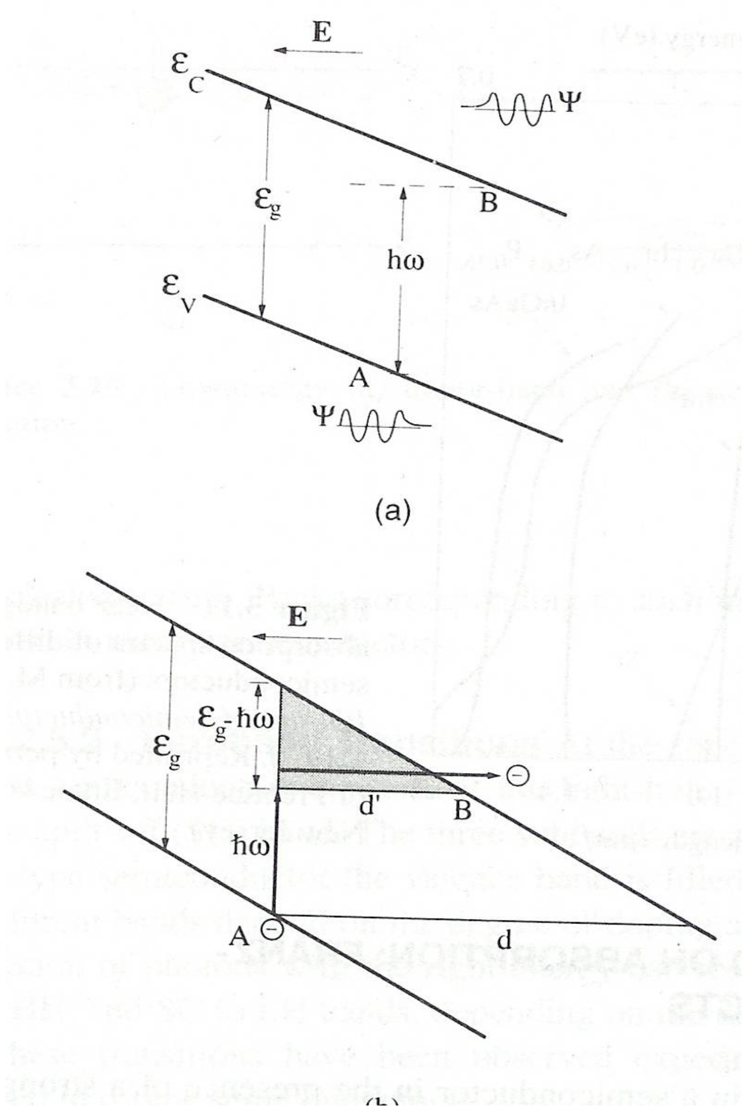
InAs is a direct gap III–V semiconductor with $E_g = 0.35$ eV

$\hbar\omega < E_g$: $\alpha = 0$

$\hbar\omega > E_g$:

$\alpha \propto (\hbar\omega - E_g)^{1/2}$

The Franz-Keldysh Effect



First effect

- At the classical turning points *A* and *B*, ψ change from oscillatory to decaying: $\psi \sim u_k e^{ikx}$, where *k* is imaginary

- With increase of *E* the distance *AB* decreases and the overlap of ψ increases

- In the absence of photons $AB = d = E_g/qE$

- For $h\nu < E_g$ $AB = d' = (E_g - h\nu)/qE$ – tunneling barrier is reduced ⇒ absorption

- The frequency dependence of α is given:

$$\alpha(\hbar\omega) \sim \exp\left(-\frac{4\sqrt{2m_e^*}}{3|e|\hbar E_{el}}\left(E_g - \hbar\omega\right)^{\frac{3}{2}}\right)$$

- Transmission coefficient through a triangular barrier

Second Effect →

- For $h\nu > E_g$ α displays Franz-Keldysh oscillations

Magneto-Absorption in Germanium

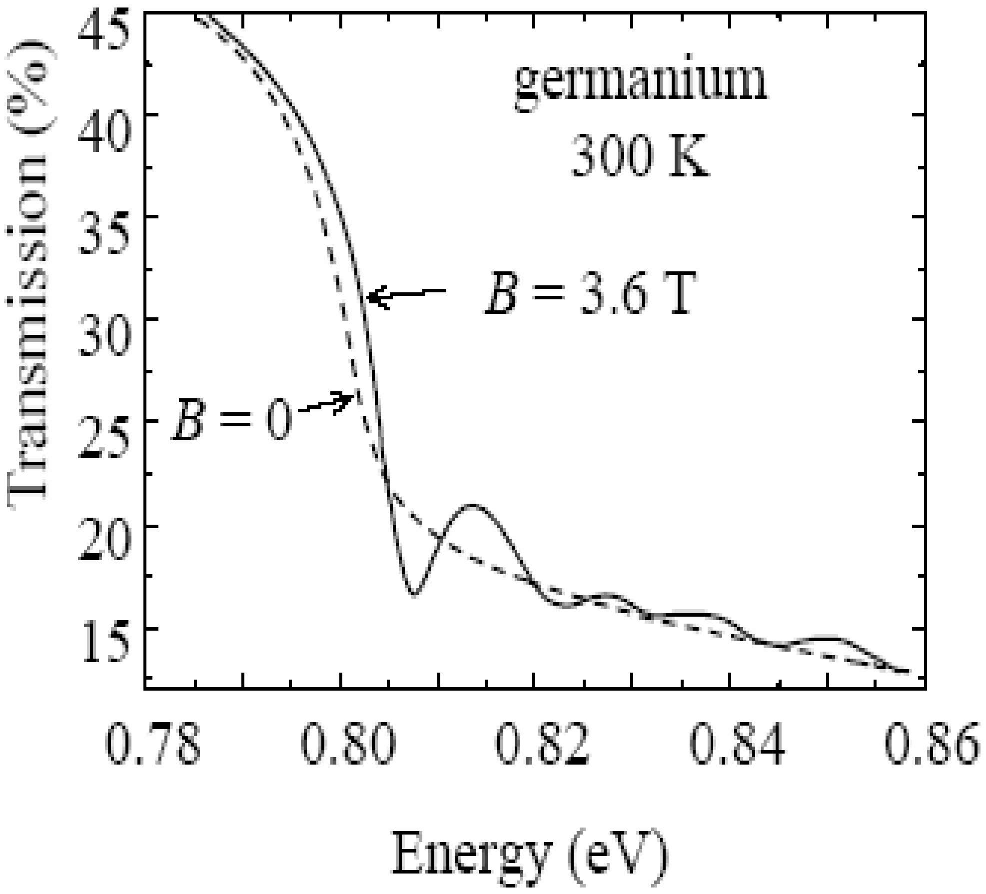


Figure 3.7

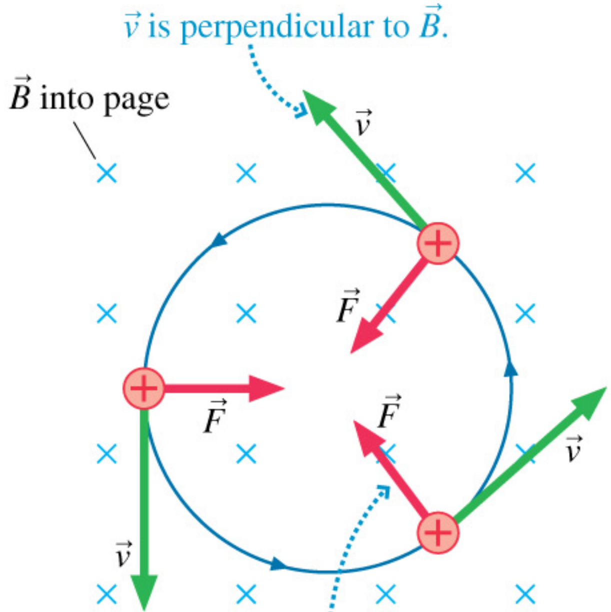
- direct gap at 0.80 eV
- B-Field quantizes motion in direction perpendicular to B
- Landau level absorption when

$$\hbar\omega = E_g + (n+\tfrac{1}{2})\,\hbar\omega_c$$

$\omega_c = eB / m_e$

(cyclotron frequency)

Cyclotron Motion



The magnetic force is always perpendicular to $\vec{v}$, causing the particle to move in a circle.

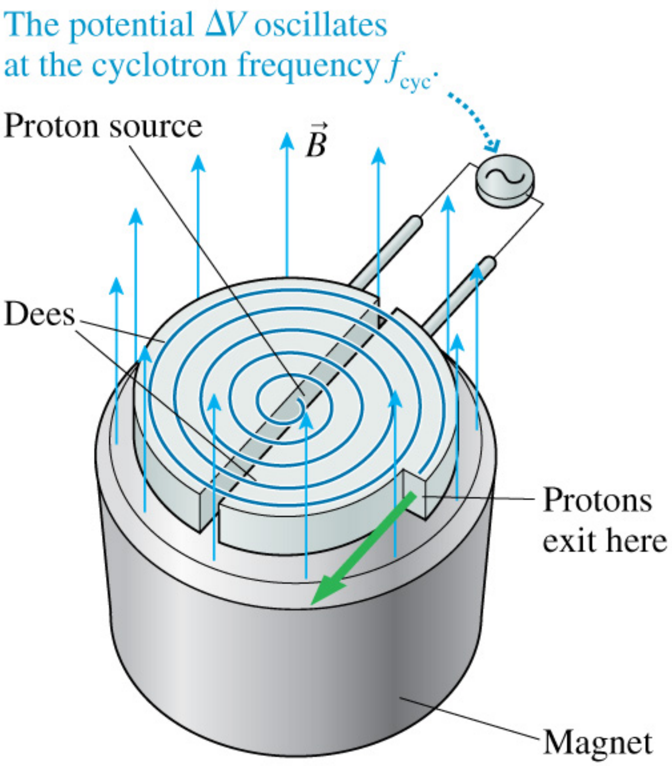
$F = qvB = ma_r = mv^2/r$

$r_{cyc} = mv/(qB)$

$f_{cyc} = v/2\pi r = qB/(2\pi m)$

$\omega_{cyc} = qB/m$

Application in particle physics:



- ω_{cyc} is independent of the particle speed

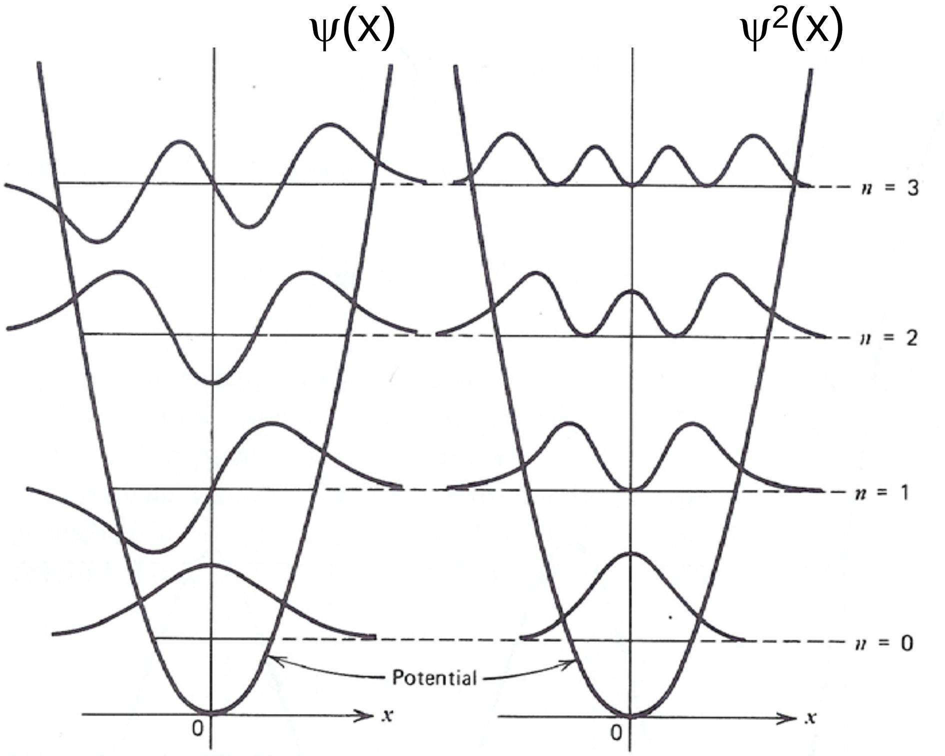
- Each time traversing the gap the particle gains kinetic energy $e\Delta V$

Magneto-Optics in Semiconductors

In quantum physics the energy is quantized. In can be shown that this problem can be formally reduced to a **harmonic oscillator potential:** $U = kx^2/2 \Rightarrow$

$E_n = (n+1/2)\hbar\omega_c$ - Landau Levels

The ground state $E_0 = \hbar\omega_c/2$ is explained by the uncertainty principle: $\Delta p \Delta x \sim \hbar$



$H = p^2/2m + kx^2/2$

Band Edge Absorption in a Magnetic Field

$$E_n^e(k_z) = E_g + \left(n + \frac{1}{2}\right)\frac{e\hbar B}{m_e^*} + \frac{\hbar^2 k_z^2}{2m_e^*}$$

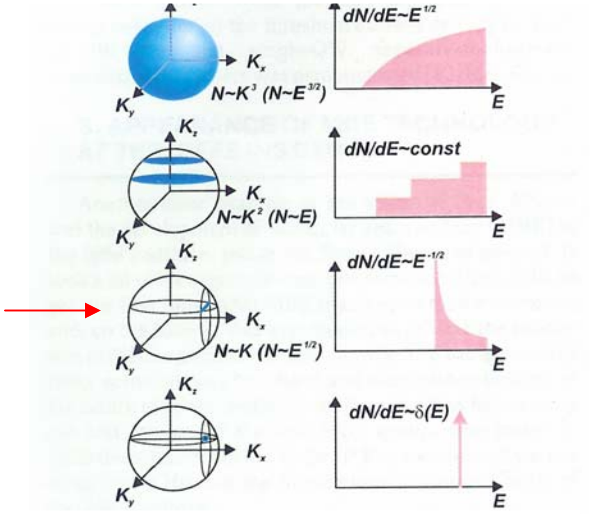
$$E_n^h(k_z) = -\left(n + \frac{1}{2}\right)\frac{e\hbar B}{m_h^*} - \frac{\hbar^2 k_z^2}{2m_e^*}$$

It can be shown that the Landau level number *n* does not change in transition:

$$\hbar\omega = E_n^e(k_z) - E_n^h(k_z) = E_g + \left(n + \frac{1}{2}\right)\frac{e\hbar B}{\mu} + \frac{\hbar^2 k_z^2}{2\mu}$$

$$\hbar\omega = E_g + \left(n + \frac{1}{2}\right)\frac{e\hbar B}{\mu}$$

In a 1-D system the density of states is peaked at k_z=0 →



Explains a series of equally spaced peaks

Blue shift of the absorption edge by $\hbar eB/2\mu$

Lectures 20: Interband Absorption (Continue)

Direct Versus Indirect Absorption

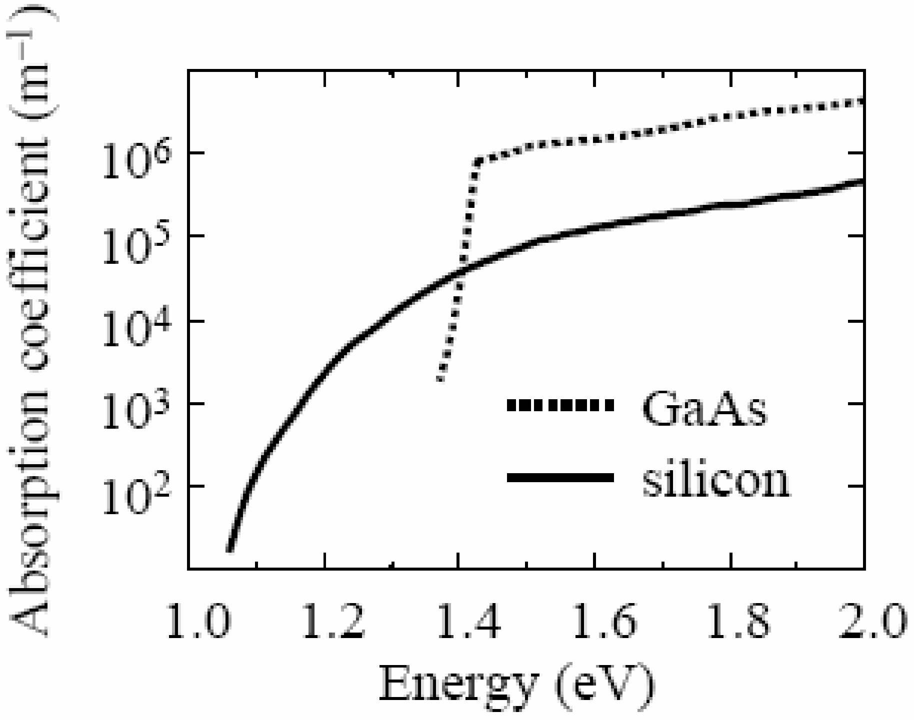


Figure 3.8

- Direct absorption is much stronger than indirect absorption
- Silicon has **indirect** gap at 1.1 eV
- GaAs has **direct** gap at 1.4 eV

Indirect transitions:

$E_f = E_i + \hbar\omega \pm \hbar\Omega$ ← Energy conservation

$\hbar k_f = \hbar k_i \pm \hbar q$ ← Momentum conservation

Initial state: (E_i, k_i)
Final state: (E_f, k_f)

Germanium Band Structure

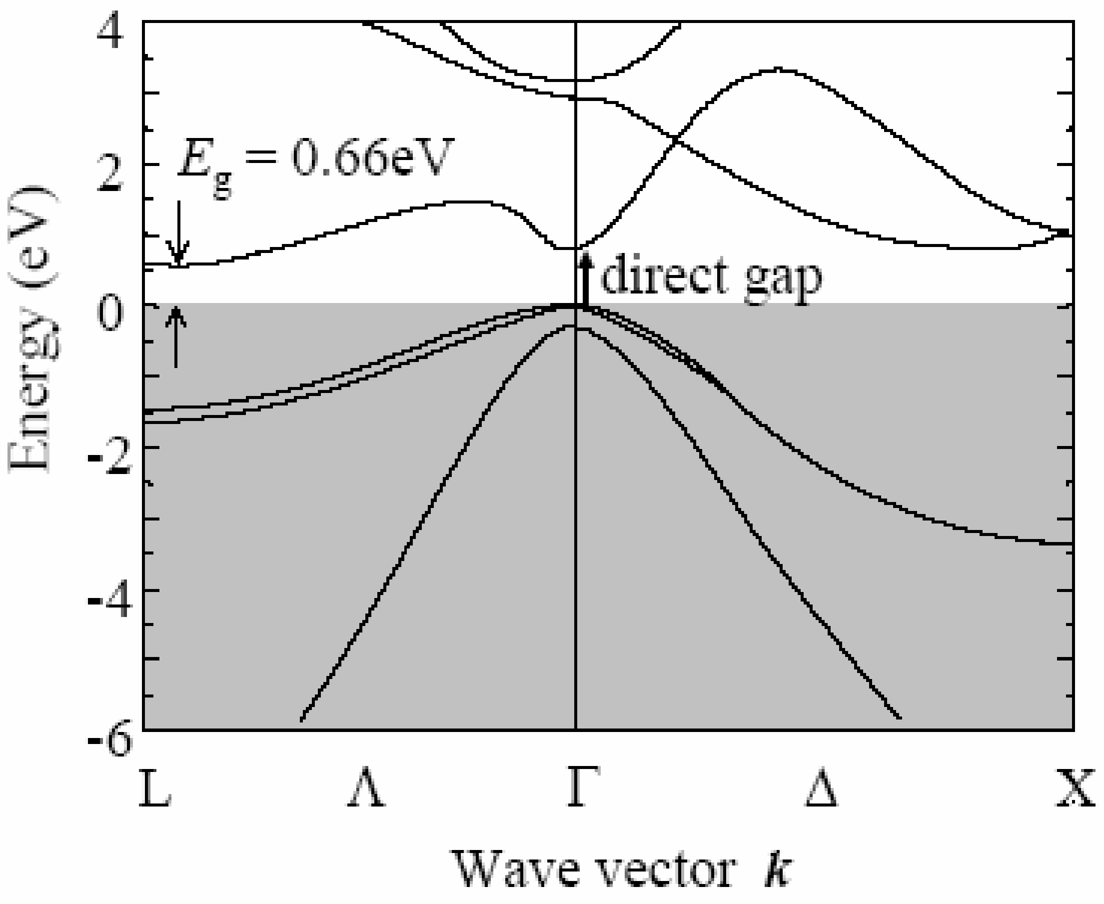


Figure 3.9

- Indirect gap at 0.66 eV
- Direct gap at 0.80 eV

Germanium Band Edge Absorption

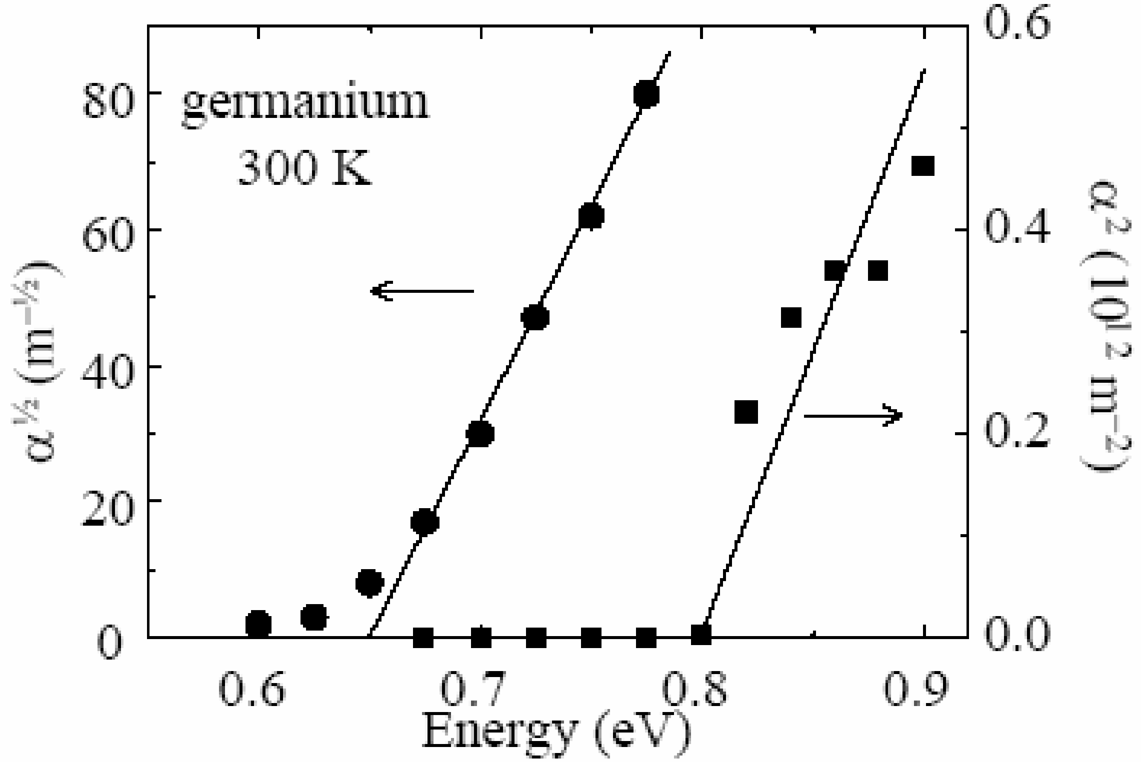


Figure 3.10

$E_g^{ind} = 0.66$ eV

$E_g^{dir} = 0.80$ eV

- indirect absorption: $\alpha \propto (\hbar\omega - E_g^{ind} \pm \hbar\Omega_{phonon})^2$
- direct absorption: $\alpha \propto (\hbar\omega - E_g^{dir})^{1/2}$

Silicon Absorption

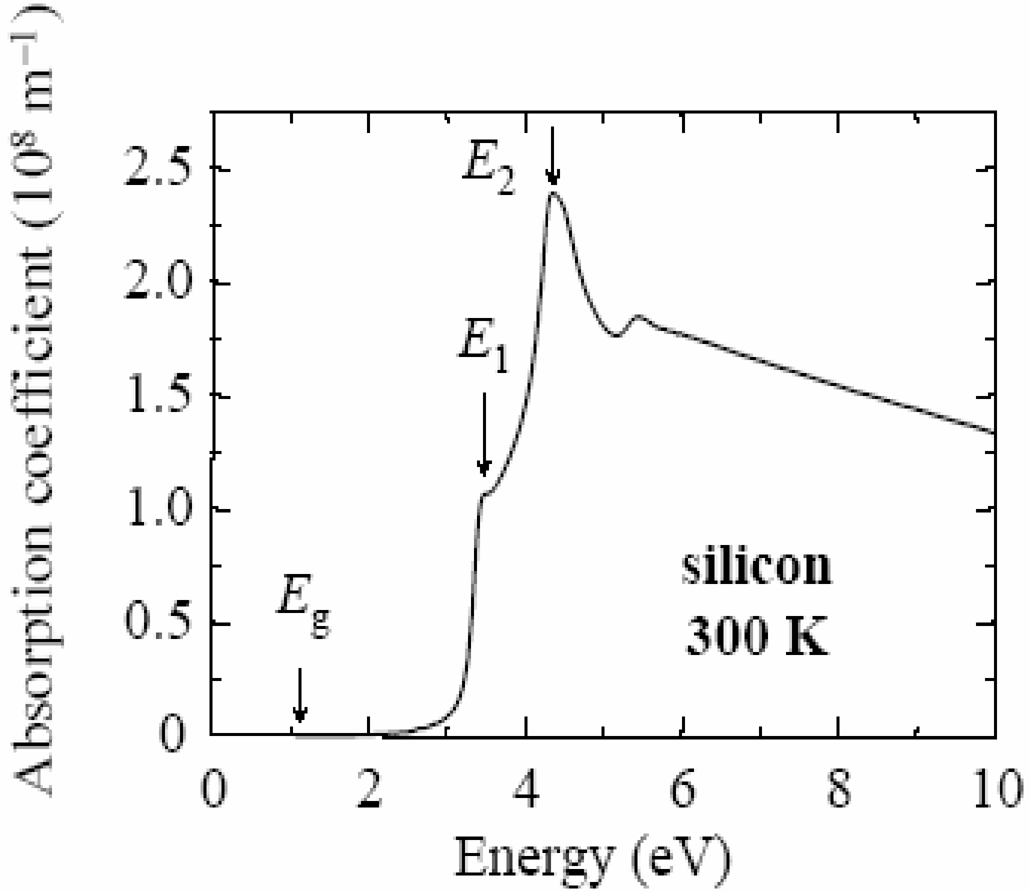


Figure 3.11

- Indirect band gap at 1.1 eV
- **Critical** points at E_1 (3.2 eV) and E_2 (4.3 eV)

Band Structure

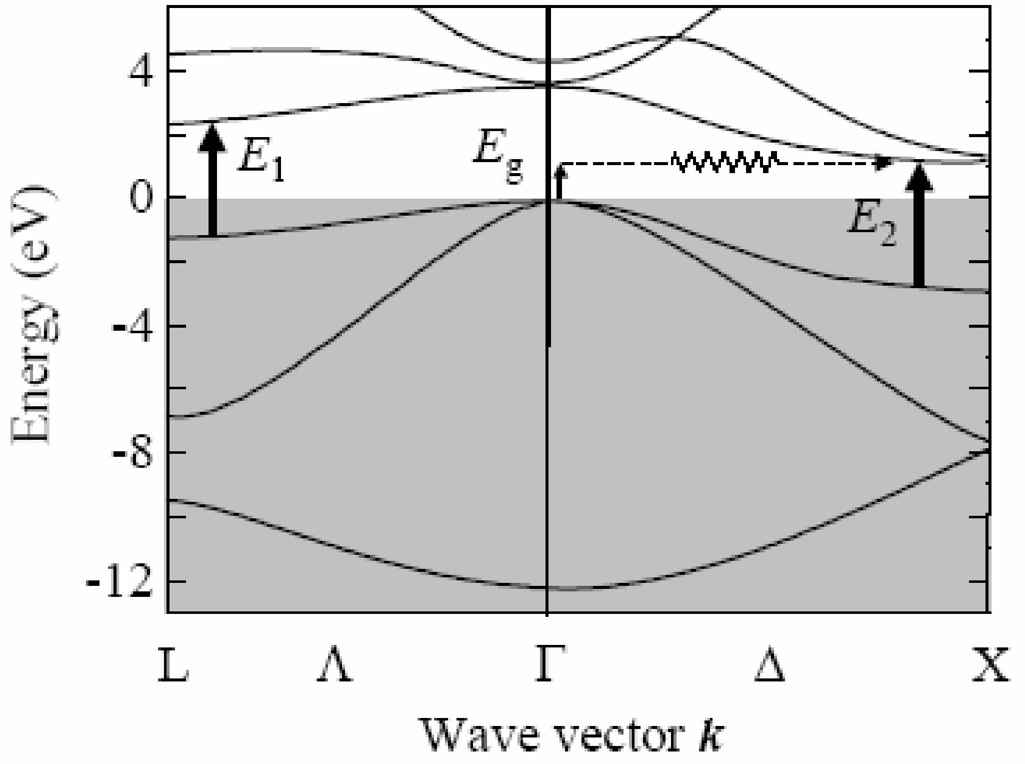
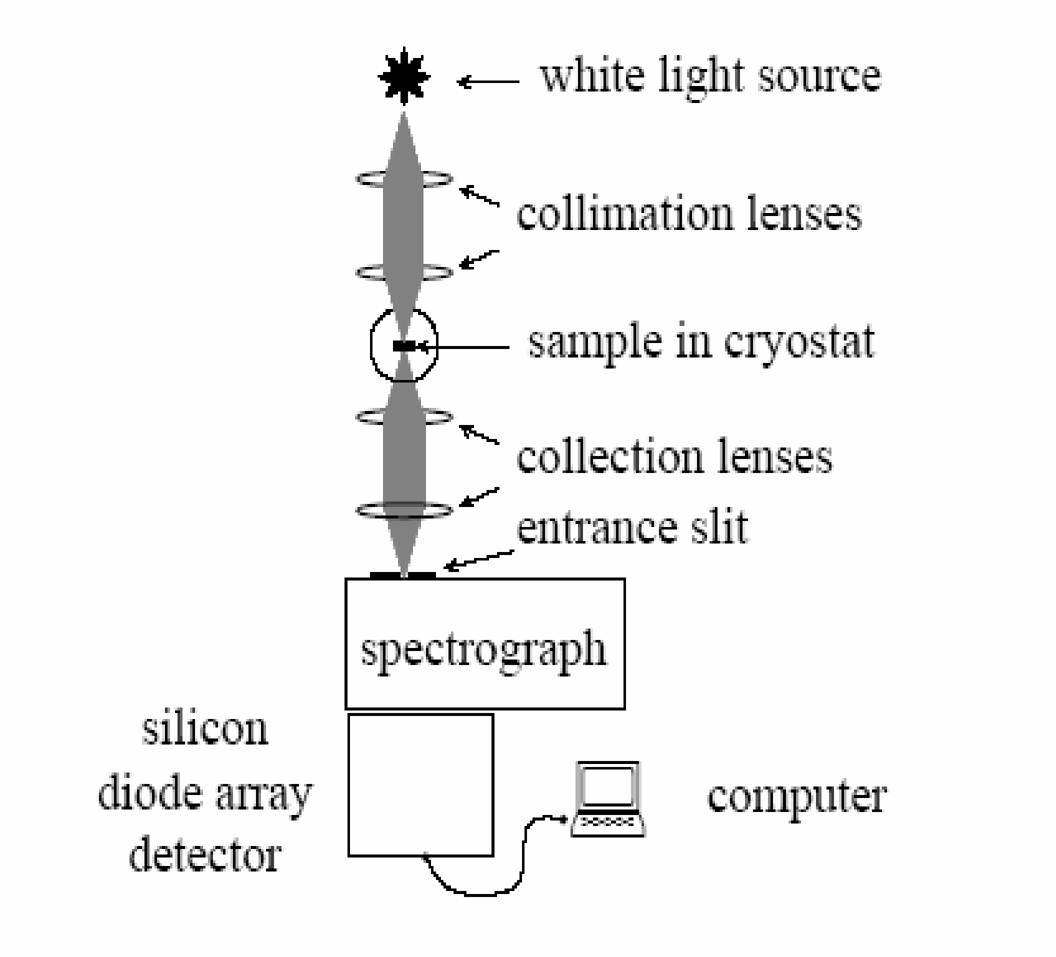


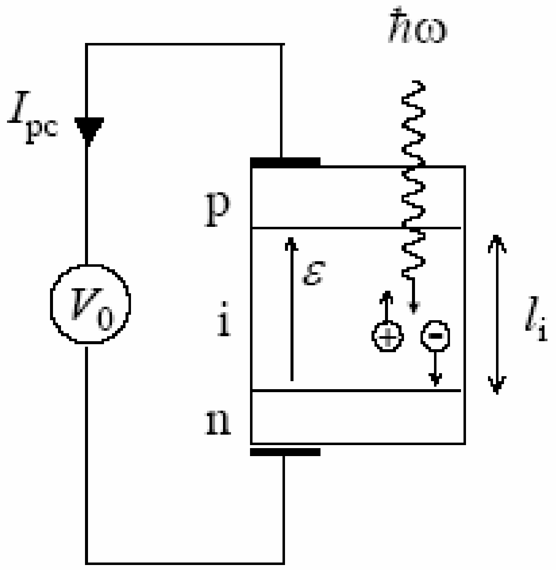
Figure 3.12

- density of states $g(E) \propto 2\, g(k)\, (\mathrm{d}E/\mathrm{d}k)^{-1}$
- **Critical points** (van Hove singularities) whenever $\mathrm{d}E/\mathrm{d}k = 0$
- occurs when conduction and valence bands are parallel to each other: "Parallel band effect"

Absorption Spectroscopy



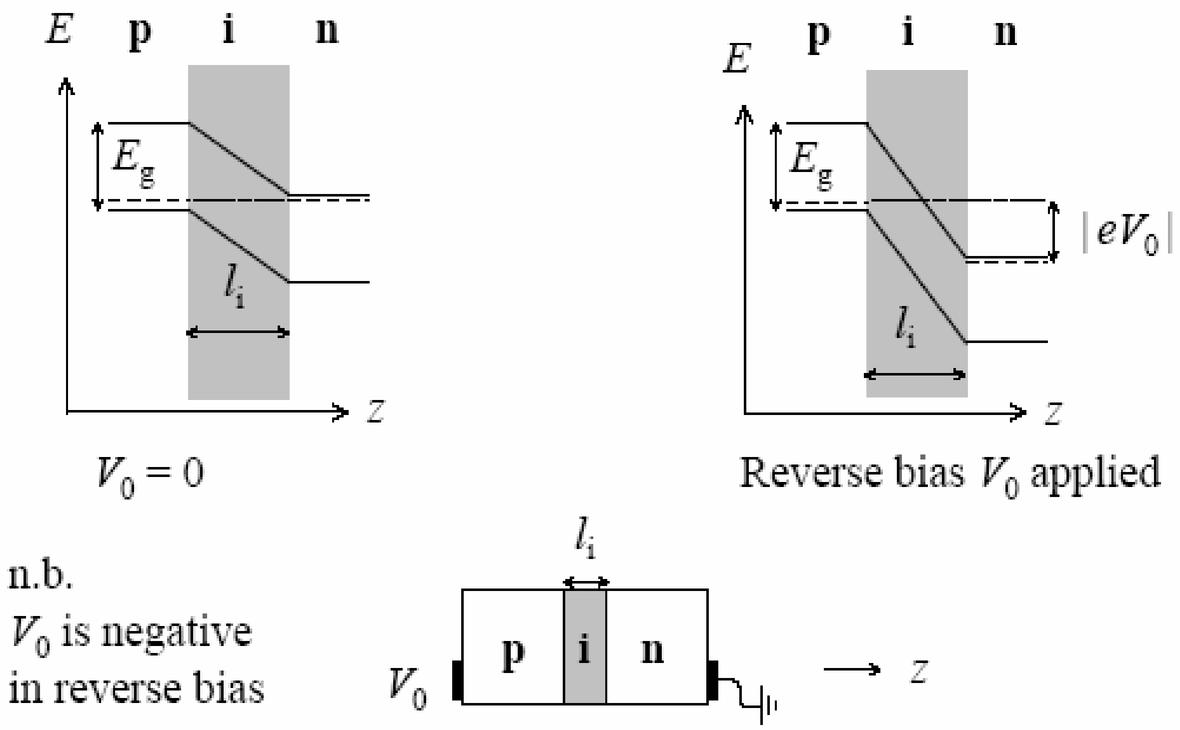
Photodetectors



Examples:
- photodiodes
- solar cells ($V_0 = 0$)

- Embed absorbing region within p-n junction to form **p-i-n diode**
- Apply reverse bias V_0 (i.e. V_0 negative)
- Electric field $\mathcal{E} = (V_{bi} - V_0) / l_i$
- V_{bi} = built-in voltage $\approx E_g / e$
- Photons absorbed if $\hbar\omega > E_g$
- Creates electron-hole pairs in i-region
- Carriers swept out by $\mathcal{E}$ field into external circuit to generate **photocurrent** I_{pc}

p-i-n Diodes



$V_0 = 0$

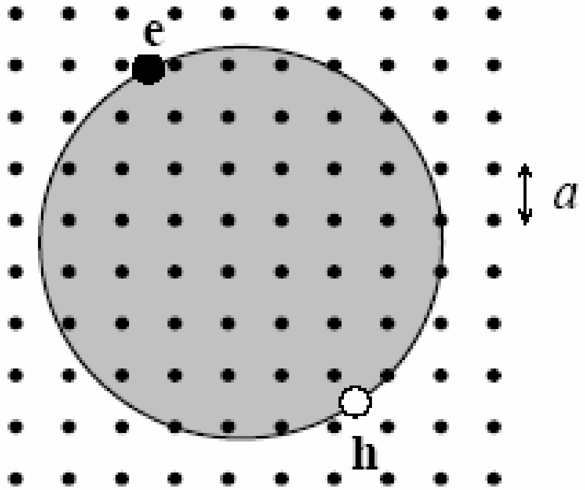
Reverse bias V_0 applied

n.b.
V_0 is negative
in reverse bias

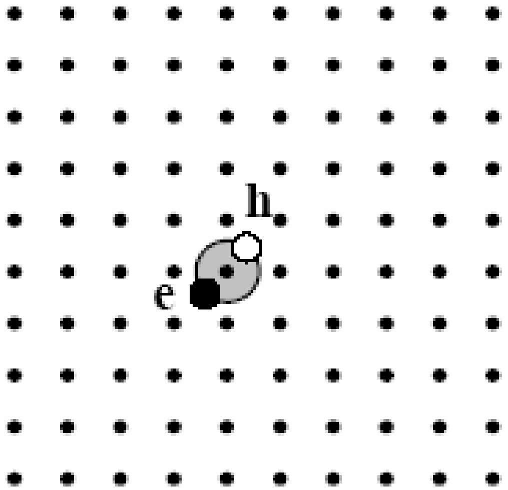
Lectures 21: Excitons

Theory: Frenkel 1931 (Ioffe Institute) – exciton is small and tightly bound
Mott and Wannier – exciton is large and weakly bound

Experimental discovery (1951) of hydrogen-like exciton optical spectrum in semiconductor crystals of cuprous oxide, E.F. Gross (Ioffe Institute)



Free (Wannier)
radius >> a
small binding energy
moves freely through crystal



Tightly-bound (Frenkel)
radius ~ a
large binding energy
localized on one lattice site

An electron and a hole may be bounded together by their attractive coulomb interaction, just as an electron is bound to a proton to form a hydrogen atom.

Properties

- An exciton can move through the crystal and transport energy

- It does not transport charge because it is electrically neutral

- Excitons can be formed by photon absorption at any critical point, for if $\nabla_{\mathbf{k}}\mathcal{E}_v = \nabla_{\mathbf{k}}\mathcal{E}_c$ the group velocities for electrons and holes are equal and they can be bounded.

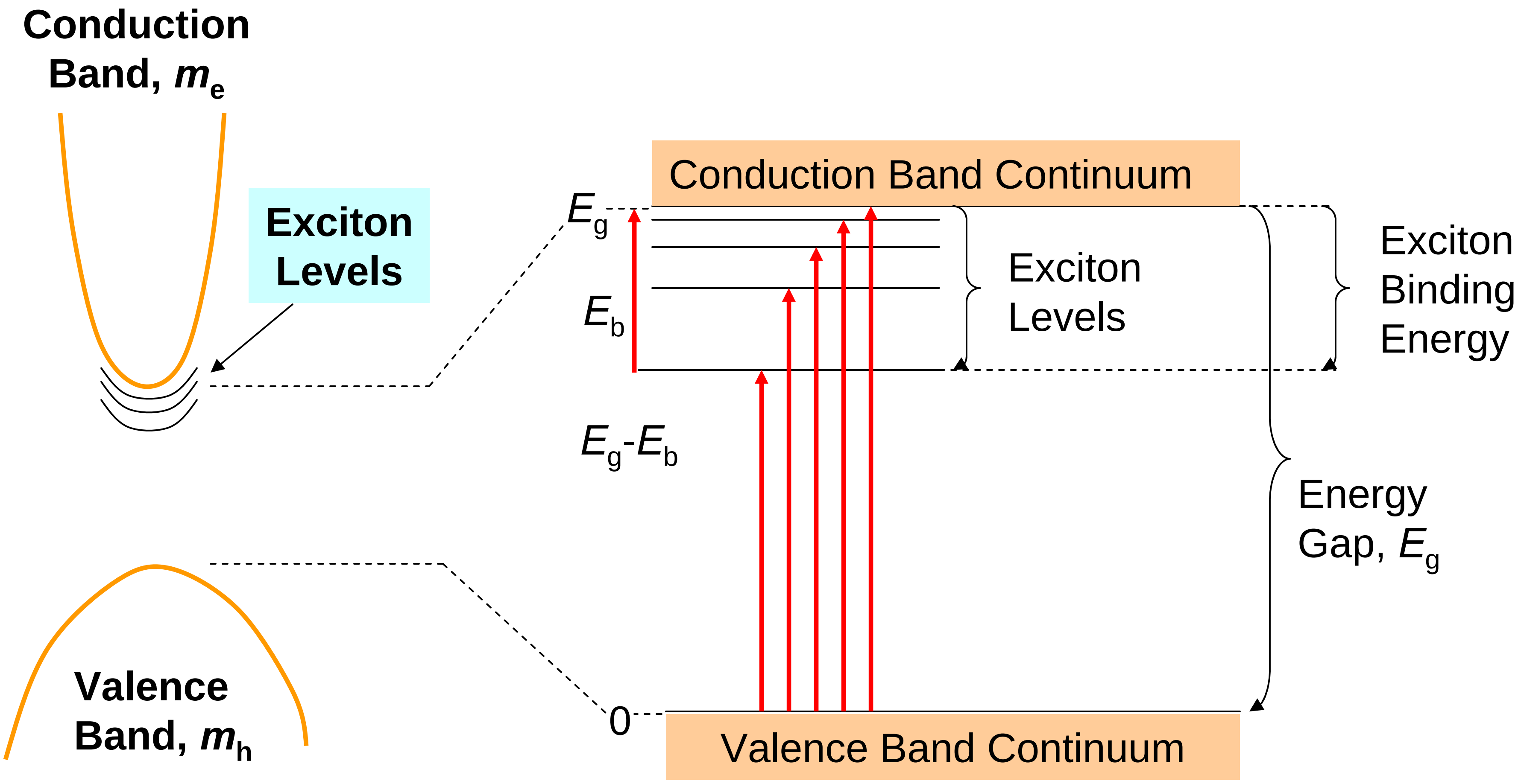
- In direct band gap semiconductors the excitons can be formed at ***k*** = 0 corresponding to energy E_g

- When the band gap is indirect, excitons near the direct gap can be unstable with respect to decay into a free electron and free hole.

- The energy of the exciton formation in a direct transition at k = 0 is R_x less the binding energy due to the Coulomb interaction:

$$E_n = E_g - R_x / n^2 \text{, where } R_x \text{ – exciton binding energy}$$

Exciton Levels



- An excition can have translational kinetic energy

- Excitions can recombine rediatively

- Energy levels of an exciton created in a direct process

Bohr model of hydrogenic atoms

Bohr Postulates:

1. Angular momentum is quantized (stationary orbits):
   $mvr = nh/2\pi$ (1)
2. Transitions at $h\nu = E - E'$

Let us consider nuclear charge Ze, electron $-e$, radius r.

Coulomb Force = Centrifugal Force

$$(CGS)\_\text{units}:$$

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}\_\text{Combined}\_\text{with}\_(1):$$

$$r = \frac{1}{4\pi^2}\frac{n^2h^2}{Ze^2m}\_\text{and}\_v = \frac{2\pi Ze^2}{hn}$$

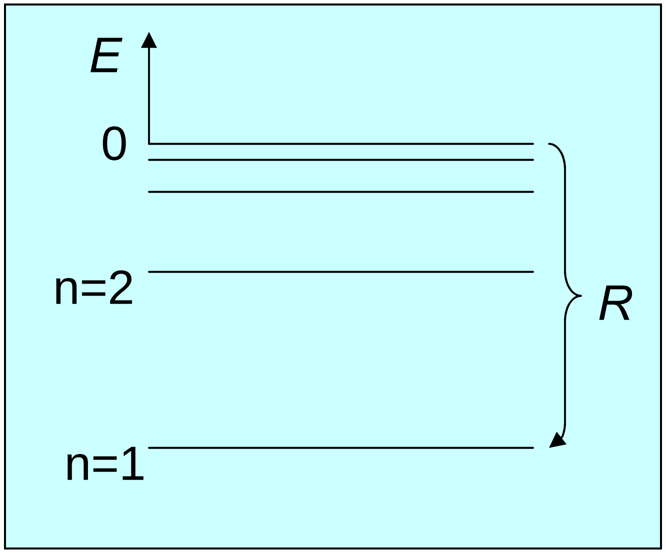
$$\text{The}\_\text{energy}:\_E = \frac{1}{2}mv^2 - \frac{Ze^2}{r} = -\frac{2\pi^2e^4Z^2m}{h^2n^2}$$

Weakly Bound (Wannier-Mott) Excitons

For $Z = 1$

$$R = \frac{e^4 m_0}{2\hbar^2} = 13.6eV - Rydberg\_Const$$

$$a = \frac{\hbar^2}{m_0 e^2} = 5.29 \cdot 10^{-9} cm \approx 0.5\text{A}$$



For an exciton in a solid the “Rydberg Constant” can be calculated taking into account polarization of lattice (ε_r) and effective mass (μ). Such a “Rydberg Constant” is the exciton binding energy R_x.

$$R_x = R\frac{\mu}{m_0 \varepsilon_r^2}$$

$$a_x = a\frac{\varepsilon_r m_0}{\mu}$$

For Ge, Si and $A^{III}B^{V}$ (GaAs) and $A^{II}B^{VI}$ semiconductors:

$\mu = m_e m_h/(m_e + m_h) \sim m_e \sim 0.1 m_0$, $\varepsilon_r \sim 10$ $\Rightarrow$

$R_x \sim 10$ meV << E_g , $a_x \sim 10$ nm >> Lattice Constant

More detailed data on R_x and a_x

Crystal	E_g (eV)	R_X (meV)	a_X (nm)
GaN	3.5	23	3.1
ZnSe	2.8	20	4.5
CdS	2.6	28	2.7
ZnTe	2.4	13	5.5
CdSe	1.8	15	5.4
CdTe	1.6	12	6.7
GaAs	1.5	4.2	13
InP	1.4	4.8	12
GaSb	0.8	2.0	23
InSb	0.2	(0.4)	(100)

E_g ↑

- As E_g increases R_x increases and a_x decreases
- This can be explained by decreasing ε_r and increasing μ for larger E_g
- R_x is smaller than kT at room temperature for all semiconductors
- In insulators $E_g \geq 5$ eV a_x is comparable to the lattice constant $\Rightarrow$ Wannier-Mott model is no longer valid

Frenkel Excitons

- A Frenkel exciton is essentially an excited state of a single atom, but the excitation can hop from one atom to another by virtue of the coupling between neighbors.
- Can be present in extremely wide band gap materials.
- Stable at room temperature

Phenomenological Treatment Based on interaction constant (T), see Kittel

$$\psi_g = u_1 u_2 \cdots u_{N-1} u_N$$

Consider a crystal of N ***noninteracting*** atoms

$$\varphi_j = u_1 u_2 \cdots u_{j-1} v_j u_{j+1} \cdots u_N$$

Describe a single excited atom and N-1 atoms

$$H\varphi_j = E\varphi_j + T(\varphi_{j-1} + \varphi_{j+1})$$

If there is an interaction between excited atom and its close neighbors when *T* measures the rate of transfer of the excitation. Here *E* is the free atom excitation energy.

$$\psi_k = \sum_j \exp(ijka)\varphi_j$$

If *T* = 0 when the solution is φ_j.
If *T* ≠ 0 when use a Bloch form…

$$H\psi_k = \sum_j e^{ijka} H\varphi_j = \sum_j e^{ijka}\left[E\varphi_j + T(\varphi_{j-1} + \varphi_{j+1})\right]$$

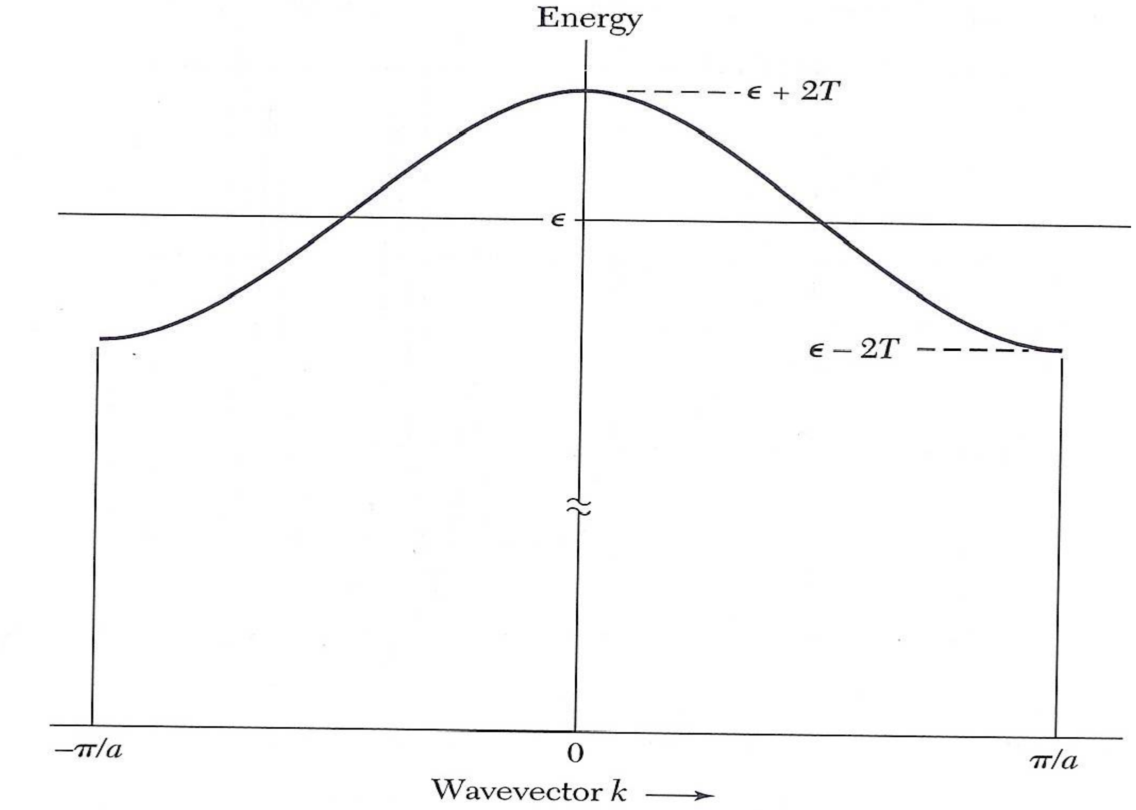
Let *H* operate on ψ_k

Rearrange the right-hand side to obtain:

$$H\psi_k = \sum_j e^{ijka}\left[E + T(e^{ika} + e^{-ika})\right]\varphi_j = (E + 2T\cos ka)\psi_k$$

$$E_k = E + 2T\cos ka \longleftarrow$$ So, the energy eigenvalues are found

$$k = 2\pi s / Na,\_\, s = -\frac{1}{2}N, -\frac{1}{2}N + 1, \cdots \frac{1}{2}N - 1$$



Large E_g:

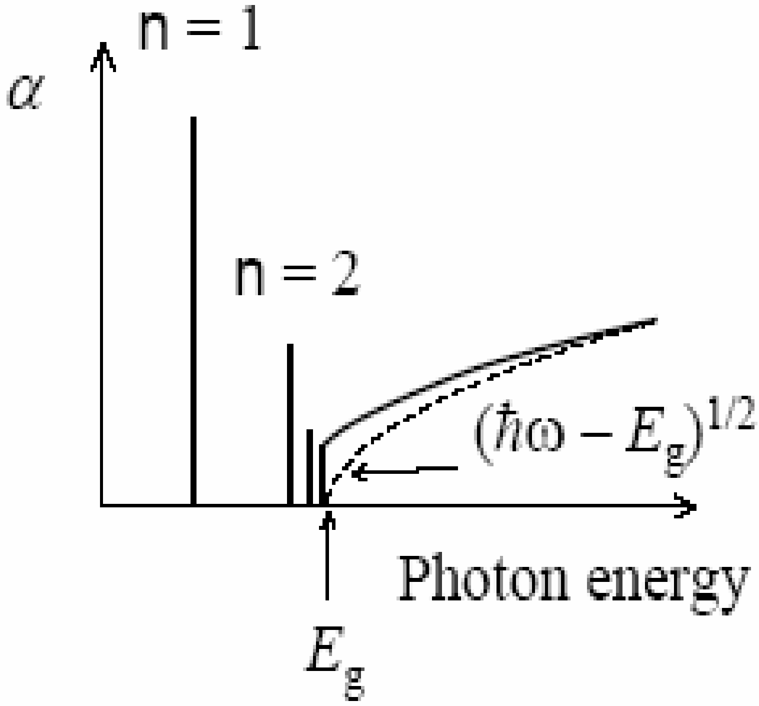
Rare Gas Crystals
Ne, Ar, Kr, Xe

Alkali halides:
KI, KBr, KCl , KF
NaI,…

Molecular thin films and
organic crystals

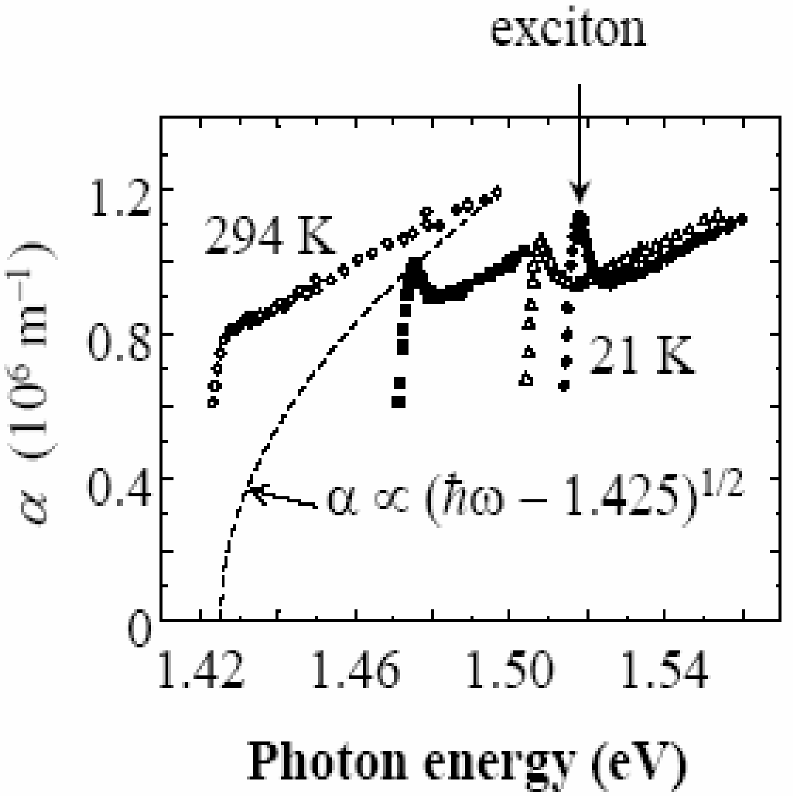
Lectures 22: Excitons

Free Exciton Absorption

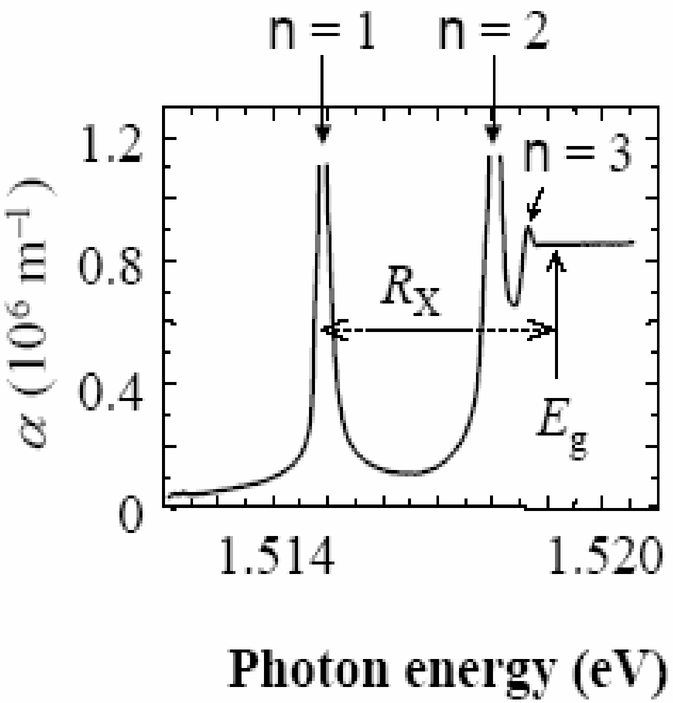


- Hydrogenic series of lines satisfying : $\hbar\omega = E_g - R_X / n^2$
- enhanced absorption for $\hbar\omega > E_g$
- only observed when $T \leq (R_X / k_B)$

Excitons in Bulk GaAs



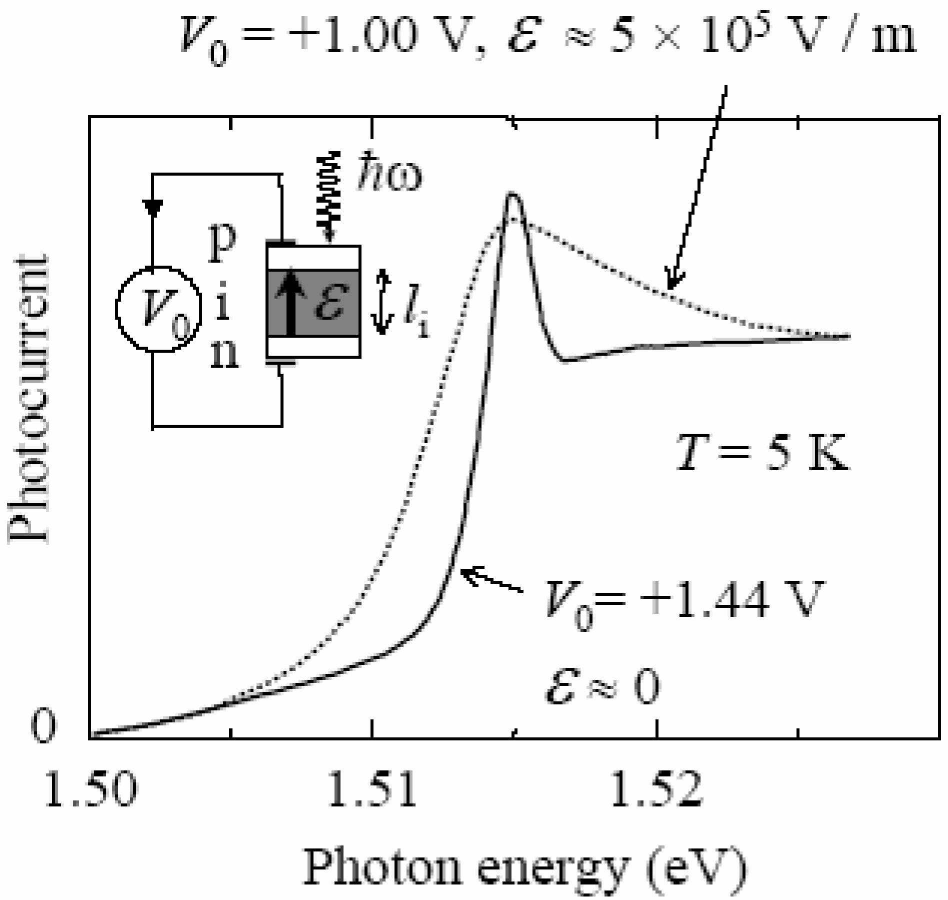
- standard purity sample
- $T = 21$ K – 294 K

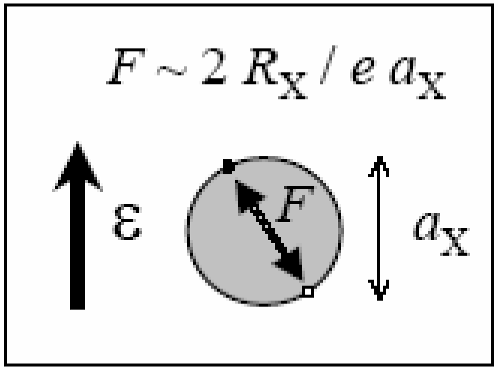


- ultra pure sample
- $T = 1.2$ K
- $R_X = 4.2$ meV

The dominating mechanisms of exciton broadening are impurity scattering (low T) and scattering on LO phonons (high T). Since E_{LO} = 35 meV>>kT the occupancy of LO phonons is small ⇒ collisional broadening is small even at high temperatures.

Field Ionization in GaAs





ionized if $\varepsilon > F$

GaAs parameters :

$R_X \sim 4.2$ meV

$a_X \sim 13$ nm

$l_i = 1$ μm (typical)

$F \sim 6 \times 10^5$ V / m

$\varepsilon \sim 1.5 \times 10^6$ V / m

for $V_0 = 0$!

Excitonic effects do not play a large part in the physics of bulk semiconductor diodes. The dominant effect is Franz-Keldysh effect. This however is not true for QWs!

Magnetic Fields

$$\hbar\omega_c = \hbar\frac{eB}{\mu}$$

ω_c – exciton cyclotron frequency
μ - reduced electron-hole effective mass

Weak Field Limit

$R_X \gg \hbar\omega_c$

The magnetic field is a perturbation on excitons.

For a ground state (n=1) it will be a diamagnetic shift:

$$\delta E = \frac{e^2}{12\mu} r_n^2 B^2$$

Induced magnetic moment

Strong Field Limit

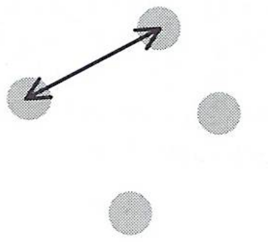
$R_X \ll \hbar\omega_c$

Landay Levels for individual electron and holes

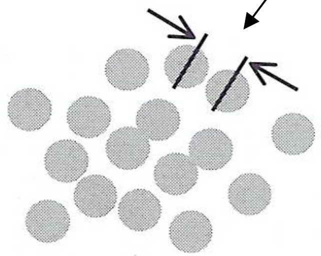
Coulomb interaction is a small perturbation

In GaAs the transition occurs at T ~ 2T for n=1

Free Excitons at High Densities



(a) Low density
Separation » diameter



(b) High density
Separation ≈ diameter

Exciton-Exciton interaction

- Exciton-exciton interactions are controlled by their concentration

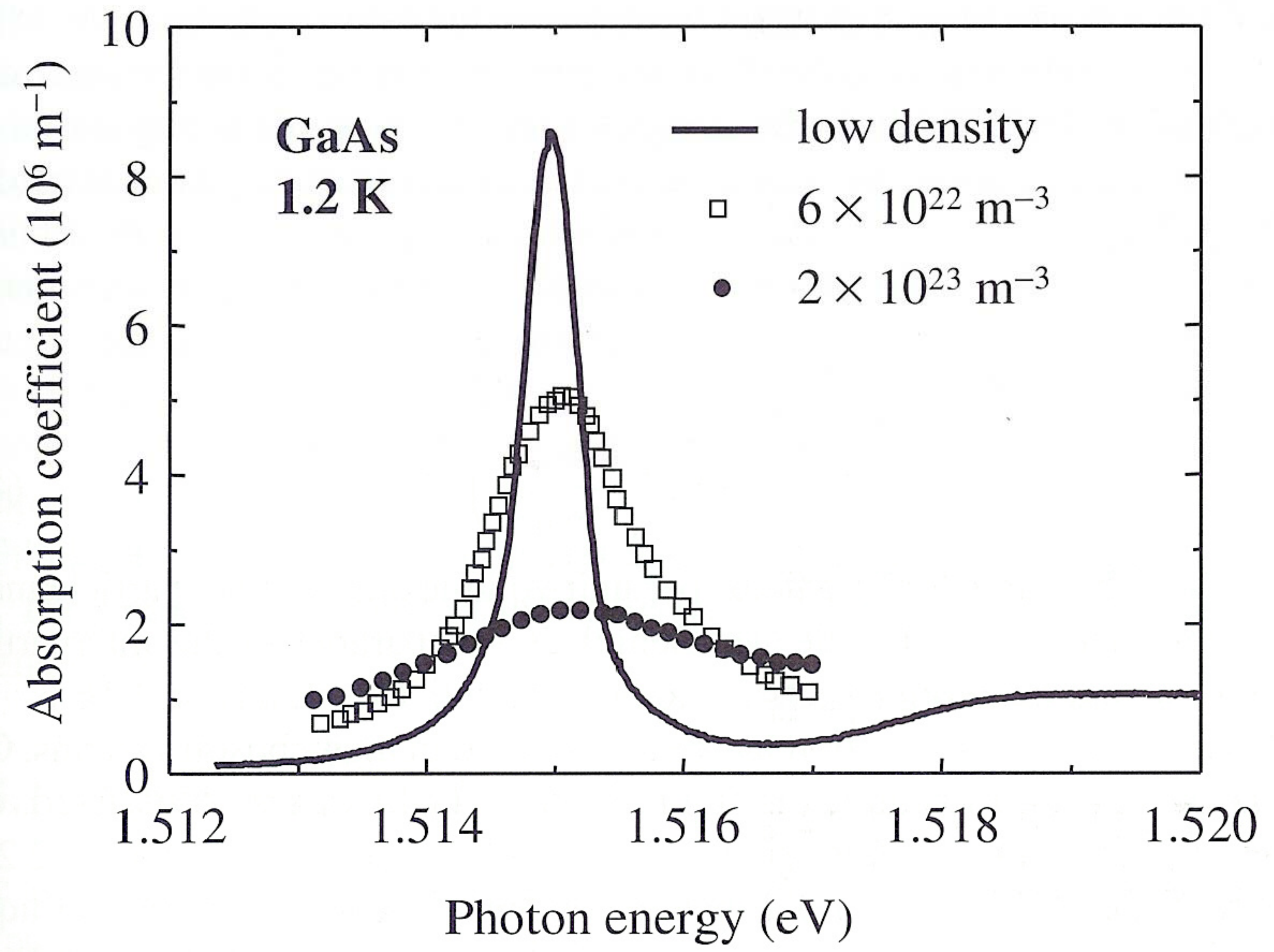
- The excitons wavefunction overlap occurs when their separation is equal to a_x. Mott density:

$$N_{Mott} \approx \frac{1}{\frac{4}{3}\pi r_n^3}$$

r_n – radius for the excitons in the n-th quantum state.

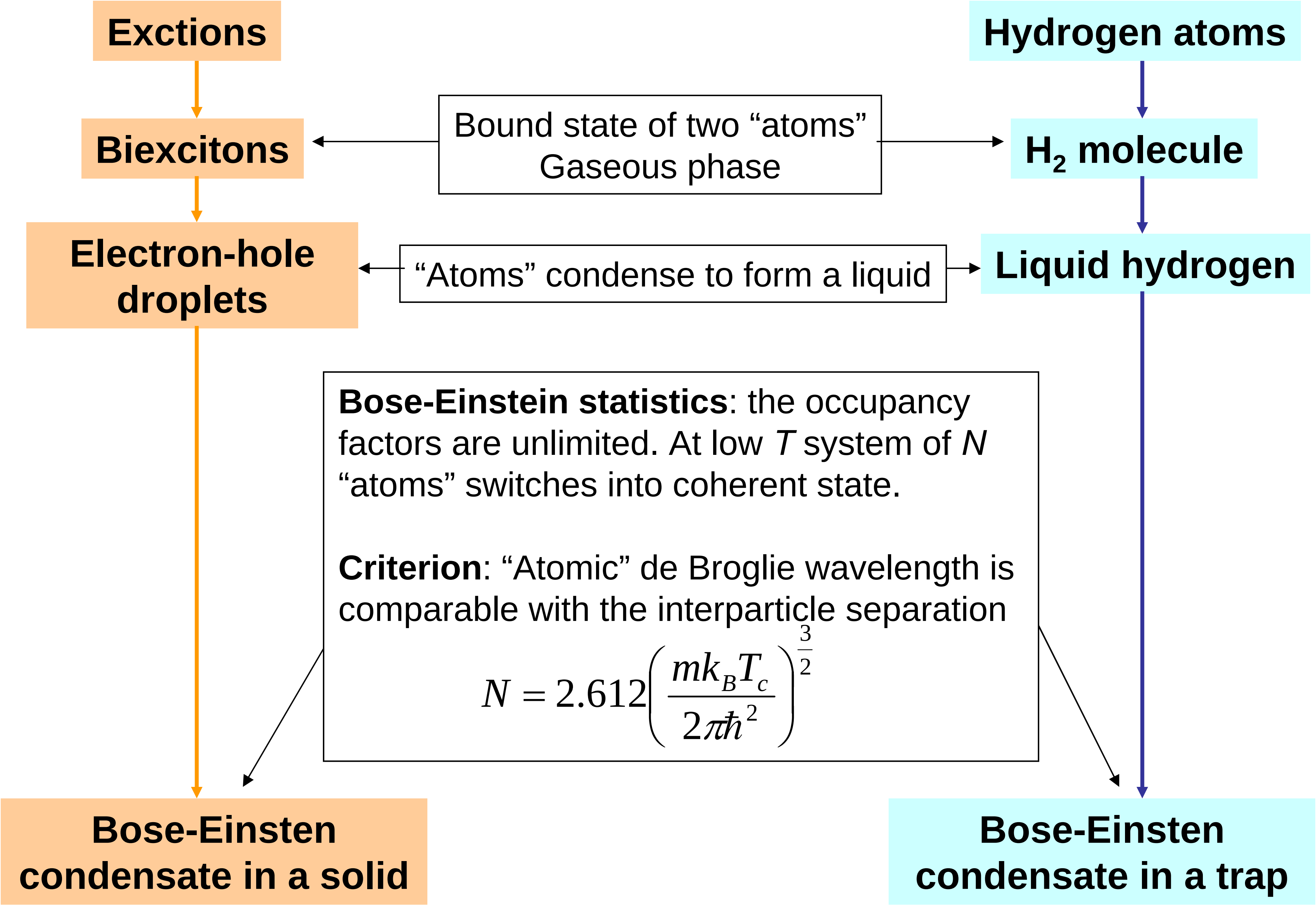
For excitons in GaAs for the n=1 states $N_{Mott} = 1.1\times 10^{23}\ \mathrm{m}^{-3}$

Screening by an electron-hole plasma



Electron-hole pairs generated either directly or in the cause of excitons collisions screen the excitons ⇒ broadening and weakening of the excitonic feature

Excitons against hydrogen atoms



Exctions

Biexcitons

Electron-hole droplets

Bose-Einsten condensate in a solid

Hydrogen atoms

H_2 molecule

Liquid hydrogen

Bose-Einsten condensate in a trap

Bound state of two “atoms”
Gaseous phase

“Atoms” condense to form a liquid

Bose-Einstein statistics: the occupancy factors are unlimited. At low *T* system of *N* “atoms” switches into coherent state.

Criterion: “Atomic” de Broglie wavelength is comparable with the interparticle separation

$$N = 2.612\left(\frac{mk_BT_c}{2\pi\hbar^2}\right)^{\frac{3}{2}}$$