EEE6212
# "Semiconductor Materials" -Excitons & Free Carriers

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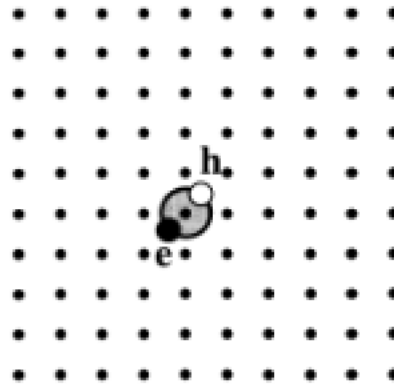Email - r.hogg@shef.ac.uk

Outline

- Coulomb attraction

- Free exciton binding energies, radius

- Absorption process and spectra

- Electric fields

- Increasing carrier densities

- Applications

- Frenkel excitons

- Summary

Coulomb Attraction
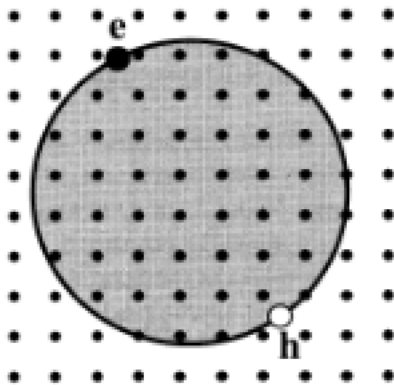
Free exciton   **Bound exciton**

Wannier-Mott   **Frenkel**

Absorption of a photon by an Interband transition

Electron and hole created in same spatial location

Oppositely charged particles – mutual attraction

Attractive interaction increases transition rate

May form a bound electron-hole pair analogous to hydrogen atom – an exciton

Free Exciton Binding Energy

$$E(n) = -\frac{\mu}{m_0}\frac{1}{\varepsilon_r^2}\frac{R_H}{n^2} = -\frac{R_x}{n^2}$$

$$\frac{1}{\mu} = \left(\frac{1}{m_e} + \frac{1}{m_h}\right)$$

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

Apply Bohr model to exciton to determine energies of bound states. Modified due to e-h pair having reduced effective mass, and being in high dielectric constant material

Bound states characterised by principal quantum number n

μ/m_0 - reduced electron-hole mass
R_H - Rydberg energy of H atom (13.6eV)
R_x - exciton Rydberg energy
ε_r – relative permittivity

Free Exciton Radius

$$r_n = \frac{m_0}{\mu}\varepsilon_r n^2 a_H = n^2 a_x$$

r_n - radius of electron-hole orbit
a_H - Bohr radius of hydrogen atom
(a_H=5.29 x10^{-11} m)
a_x – exciton Bohr radius

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

Ground-state, (n=1)
- Largest binding energy
- Smallest radius

Excited States (n>1)
- Less strongly bound, larger radius

Typical Materials

General trend – as E_g increases, so Rydberg energy increases and a_x decreases

To have a stable exciton at room temperature – one requirement is that we need $R_x \sim kT$

Only possible in wider band-gap materials

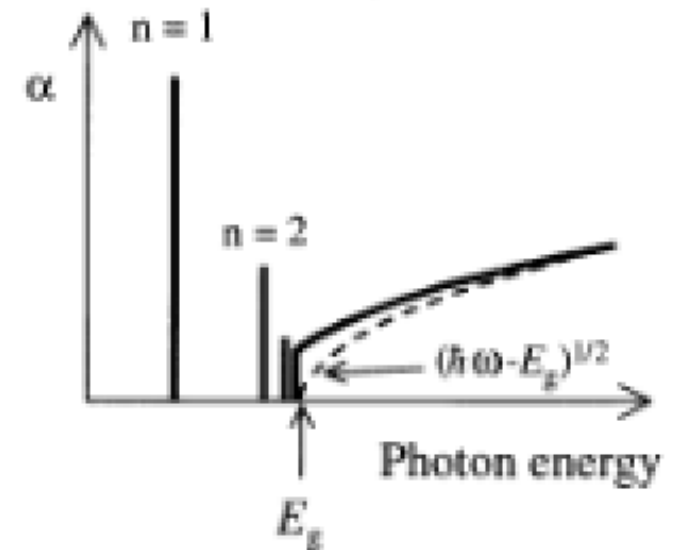| Crystal	E_g (eV)	R_X (meV)	a_X (nm)
GaN	3.5	23	3.1
ZnSe	2.8	20	4.5
CdS	2.6	28	2.7
ZnTe	2.4	13	5.5
CdSe	1.8	15	5.4
CdTe	1.6	12	6.7
GaAs	1.5	4.2	13
InP	1.4	4.8	12
GaSb	0.8	2.0	23
InSb	0.2	(0.4)	(100)

Interband Absorption
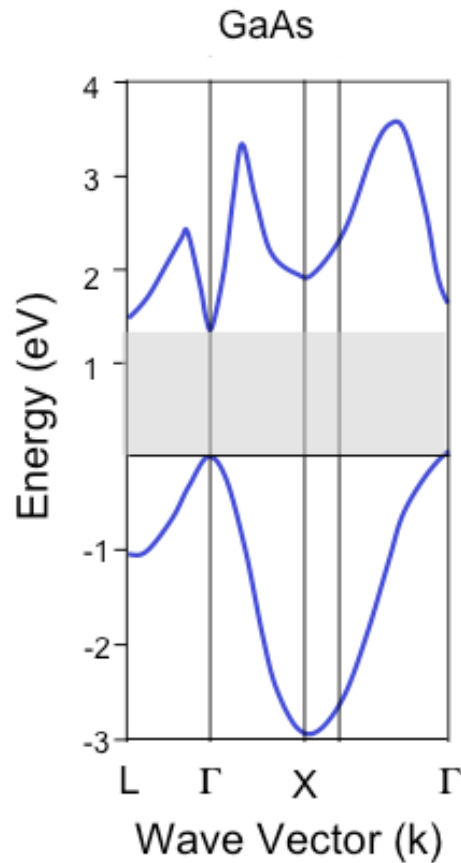
GaAs

Additional requirement is that electron and hole group velocities are the same

Only occurs at Γ-point

$V_g = 0$ for both

All other k – e and h have opposite group velocities

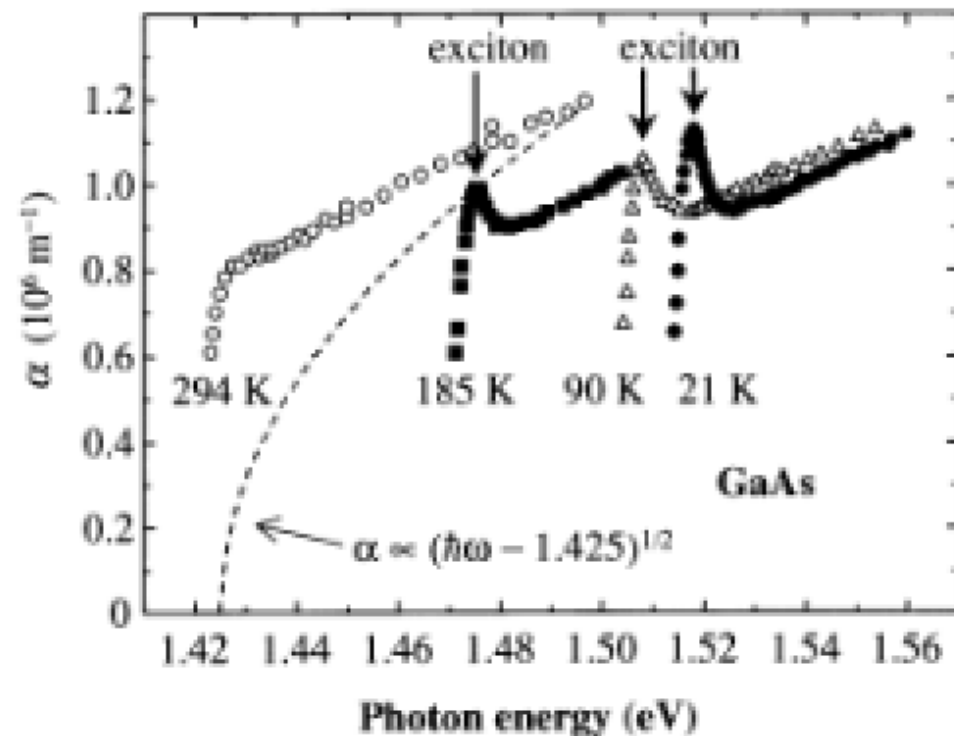$$v_g = \frac{1}{\hbar} \frac{\partial E}{\partial k}$$

Absorption Spectra - GaAs

$$E(n) = E_{gap} - \frac{R_x}{n^2}$$

Whilst excitonic absorption peak is lost if $kT \gg R_x$

Absorption is modified at room temperature
- Reduction in energy of onset of absorption
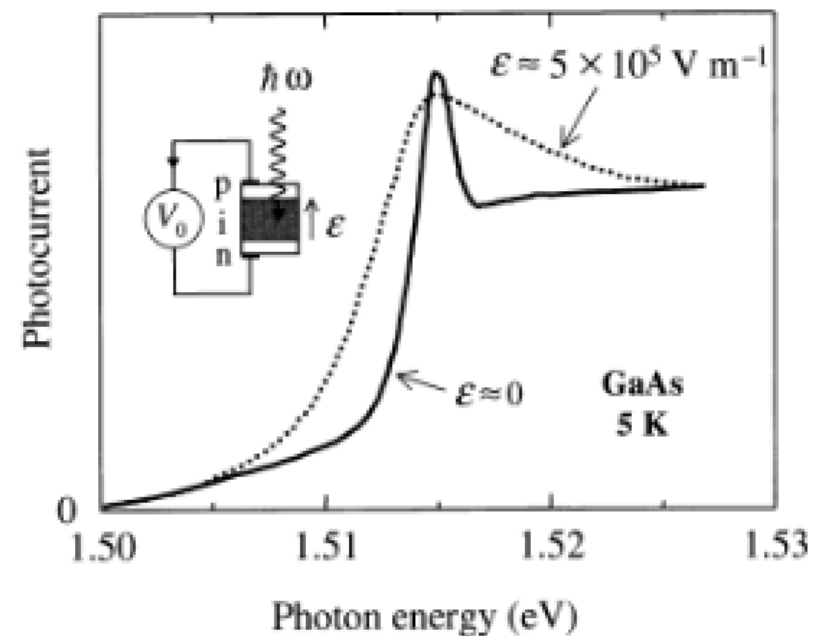- Higher absorption than predicted by 3D DOS

Electric Field – Field Ionisation

Electric field accelerates electron and hole in opposite directions

Ionisation field is approximated as-

$$\frac{2R_x}{ea_x}$$

~6x10^5 Vm^{-1}
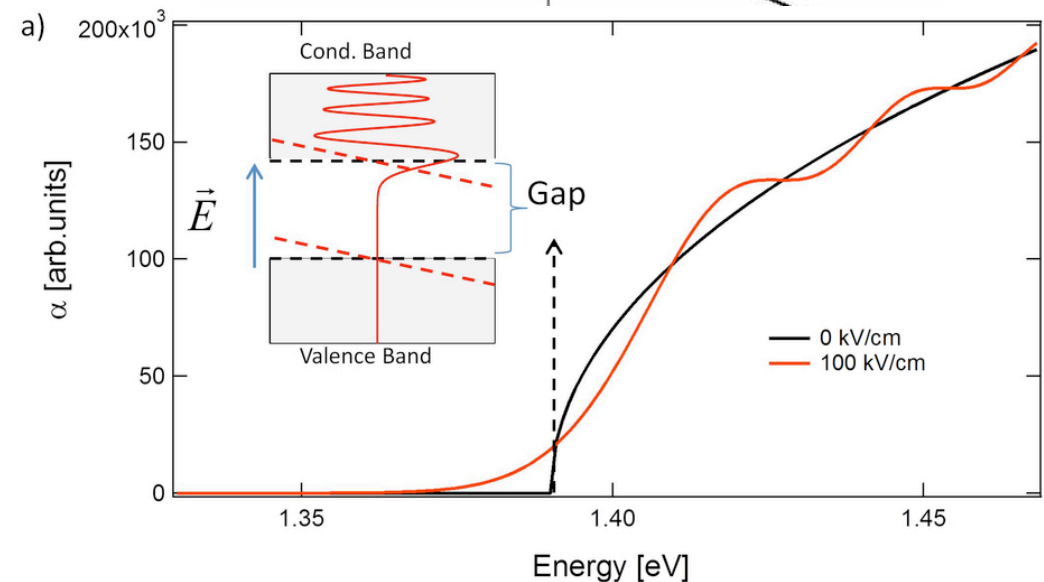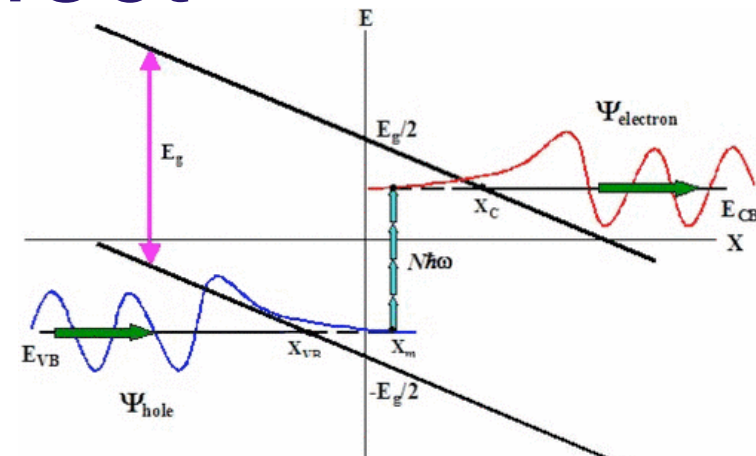
Occurs at very modest E-fields…..

Franz-Keldysh Effect

^At higher E-fields…..

Electron and hole wave-function take on Airy wavefunctions and "leak" into the band-gap

Observe absorption below the band-gap and oscillations above the band-gap

Mott Transition

The interaction of excitons can lead to additional effects – new effect depends upon ratio of R_x and kT

Exciton interaction occurs when number ~1/exciton volume – Mott density

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

- Creation of electron hole plasma – loss of excitonic effects
- Biexcitons….
- Bose-Einstein condensates
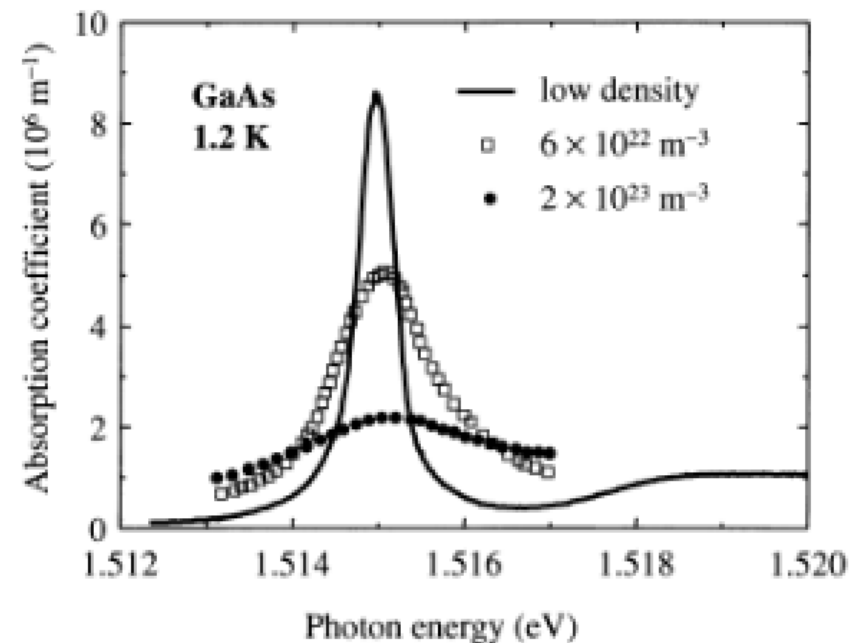
Higher Carrier Densities

- If electron and/or hole densities are high their own Coulomb potentials may begin to screen out the atomic potential

- The weakening of the atomic potential will tend to reduce the band-gap (c.f. reducing inter-atomic spacing)

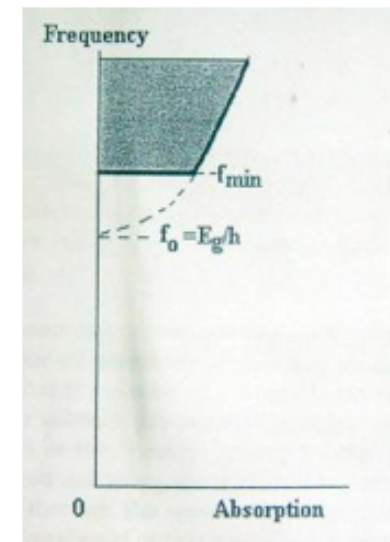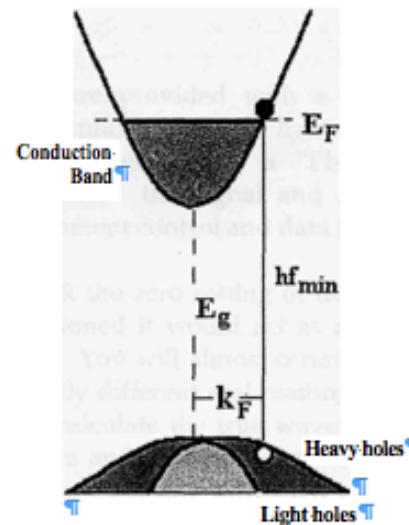- Band-gap shrinkage $\Delta E_g = -cN^{1/3}$,

$$c \approx 32 \text{ meV}/(10^{18} \text{ cm}^{-3})^{1/3}, \qquad (\text{bulk GaAs})$$

Moss-Burstein Shift

Degenerate semiconductors (E_f lies in the conduction or valence band)

Observe a shift in the onset of absorption due to the filling of states

Blocking of the absorption transitions due to the Pauli exclusion principle

$$hf_{min} = E_g + \frac{\hbar^2 k_F^2}{2}\left(\frac{1}{m_c} + \frac{1}{m_v}\right) = E_g + E_F\left(1 + \frac{m_c}{m_v}\right)$$

$$E_F = \frac{\hbar^2 k_F^2}{2m_c} = \frac{\hbar^2}{2m_c}\left(3\pi^2 n\right)^{2/3}$$

Frenkel Excitons

- Observed in large band-gap materials with small dielectric constants and large effective masses
- Predicted excitonic radius comparable to atomic spacing – large binding energies
- Bohr model breaks down
- Frenkel exciton akin to an excited state of the atom which "hops" from atom to atom
- Observed in rare gas crystals, alkali halides, some organic crystals
- Not covered further

Applications

- Bulk excitonic effects – limited to modification of absorption spectra in photo-diodes

- In quantum well structures – modulators
    - Direct absorption
    - Mach-Zehnder

- Lots of quantum information processing, quantum optics, non-linear optics application
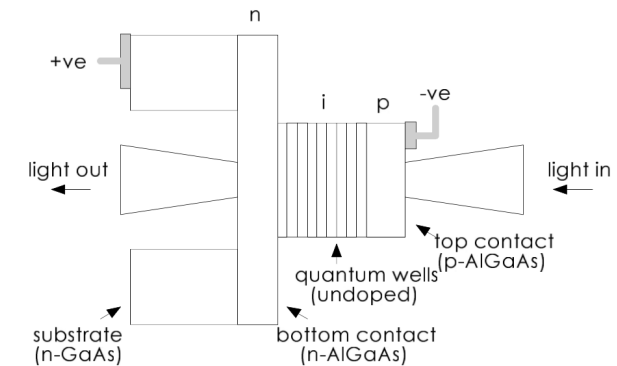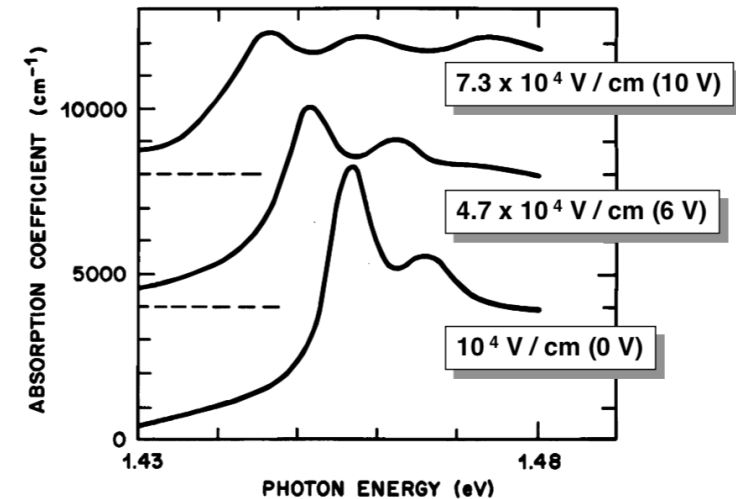
Summary

- Discussed Coulomb effects which give rise to excitons

- Explored Bohr treatment of free excitons

- Looked at absorption process, spectra and effect of electric field

- Discussed effects of high exciton and free carrier density

- Touched upon Frenkel excitons

- Discussed applications of these effects