EE 232 Lightwave Devices
Lecture 19: Excitons

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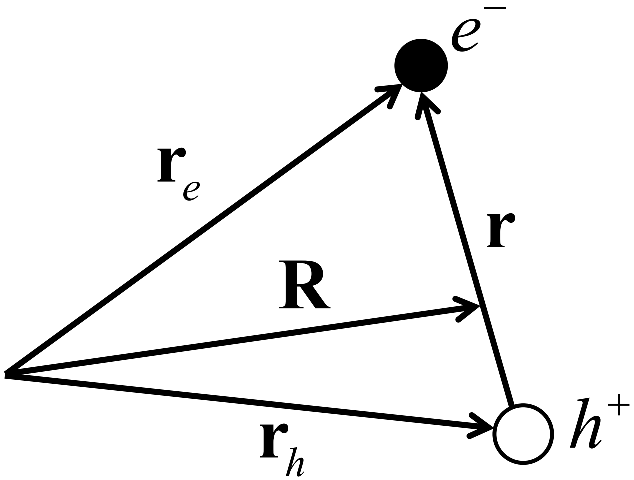
Two-particle effective mass equations

- So far, we have ignored any attraction between the negative electron and positive hole. In reality, the Coulombic attraction results in new bound electron-hole states, or excitons.
- Like many two-body problem in physics, we can break up the problem into one describing the center of mass motion of the two-particle system and the internal motion of the individual particles.

$$\left[-\frac{\hbar^2}{2(m_e^* + m_h^*)}\nabla_R^2 - E_R\right] G(\mathbf{R}) = 0$$ (motion of a "free" particle)

$$\left[\frac{\hbar^2}{2m_r^*}\nabla_r^2 - \frac{q^2}{4\pi\epsilon|\mathbf{r}|} - E_r\right]\phi(\mathbf{r}) = 0$$ (relative motion of the "hydrogen-like" molecule)



$$\Phi(\mathbf{R},\mathbf{r}) = G(\mathbf{R})\phi(\mathbf{r})$$ (two-particle envelope wave-function)

$$E_X = E_g + E_r + E_R$$ (total energy)

Bohr Hydrogen Model

- Electron orbit around nucleus with quantized angular momentum

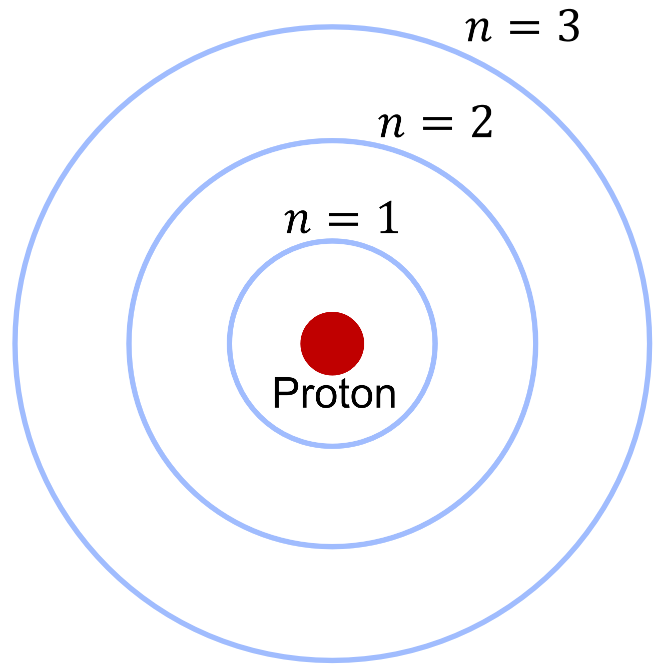
$$mv \cdot r = n\hbar$$

- Electron energy levels are quantized:

$$E_n = -\frac{m_e q^4}{2(4\pi\varepsilon_0)^2 \hbar^2} \frac{1}{n^2} = -\frac{R_y}{n^2}$$

$$R_y = 13.6 \text{ eV}$$

- Orbit radius = $n^2 a_H$
  - $a_H = 0.0529\ nm$: Bohr radius

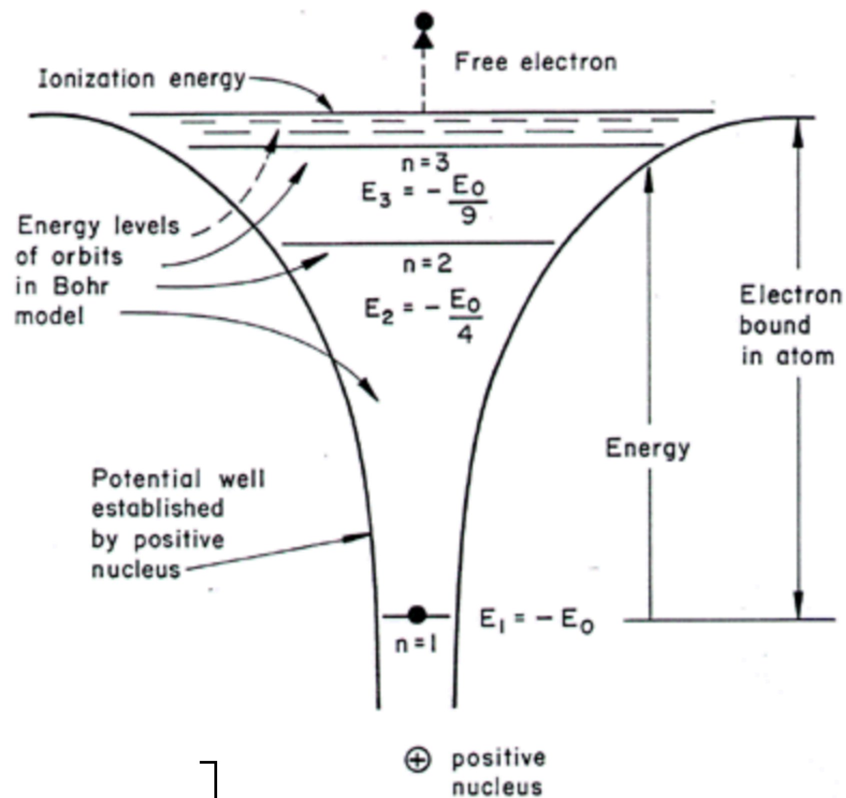


Solution of Schrodinger Eq.

$$E_n = -\frac{1}{n^2} R_y$$

$$R_y = \frac{\hbar^2}{2m_r}\frac{1}{a_0^2}$$

$$a_H = \frac{4\pi\varepsilon\hbar^2}{q^2 m_r} \text{ : Bohr radius}$$



Wavefunctions at origin:

Bound State: $$\left|\psi_{n00}(\mathbf{r}=0)\right|^2 = \frac{1}{\pi a_0^3 n^3}$$

Continuum: $$\left|\psi_{E00}(\mathbf{r}=0)\right|^2 = \frac{1}{R_y a_0^3 4\pi}\left[\frac{e^{\pi/ka_0}}{\sinh\left(\frac{\pi}{ka_0}\right)}\right]$$

Ref: Chuang, Section 3.4

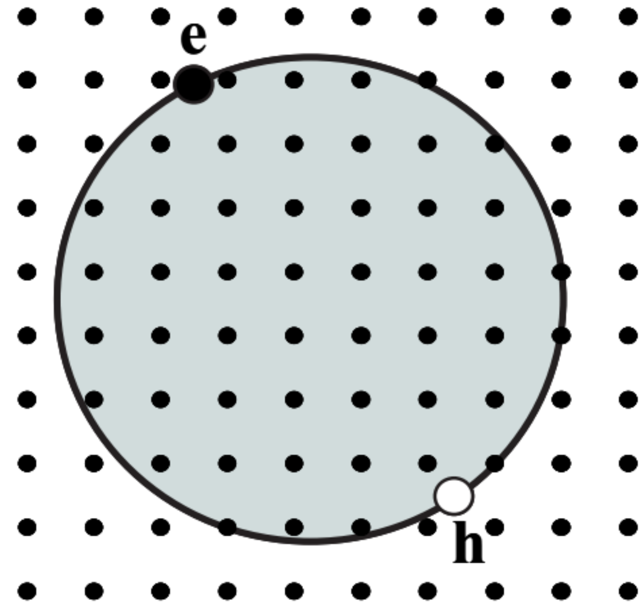
Exciton energy

Exciton "kinetic" energy

$$E_R = \frac{\hbar^2 |\mathbf{K}|^2}{2M}$$

$$\mathbf{K} = \mathbf{k}_e + \mathbf{k}_h$$

Exciton center of mass moves through the crystal as plane wave



Exciton binding (internal) energy

$$E_r = -\left(\frac{1}{(4\pi\epsilon_0\epsilon_r)^2} \frac{q^4 m_r^*}{2\hbar^2} \right) \frac{1}{n^2}$$

$$= -\frac{m_r^*}{m_0} \frac{1}{\epsilon_r^2} \frac{R_y}{n^2} = -\frac{R_X}{n^2}$$

R_y : Rydberg energy (13.6 eV)

R_X : Exciton Rydberg energy

Exciton radius

$$\boxed{r_n = \frac{m_0}{m_r^*} \epsilon_r n^2 a_H = n^2 a_X}$$

a_H : Bohr radius (5.29×10^{-11})

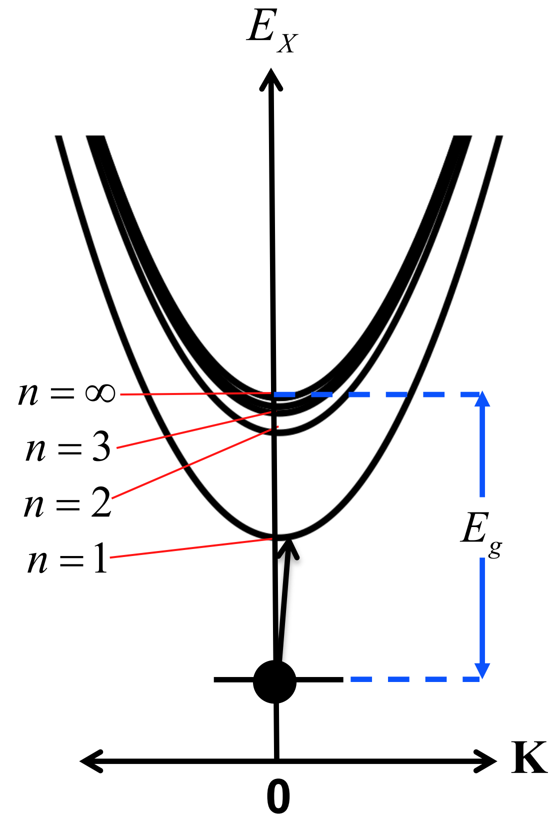
Exciton energy

$$E_X = E_g - \frac{R_X}{n^2} + \frac{\hbar^2 |\mathbf{K}|^2}{2M}$$

$$\boxed{E_X \simeq E_g - \frac{R_X}{n^2}} \quad \text{since } |\mathbf{K}| = |\mathbf{k}_{optical}| \text{ is small}$$

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)

Exciton binding energy for common semiconductors



Black dot represents the ground state (electron in valence band).

Photon with $\hbar\omega = E_g - R_X / n^2$ creates an electron-hole bound pair with energy and K-vector on one of the curves
(see Blood Appendix C)

Absorption with inclusion of excitonic effect

$$\alpha(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 2\sum_n \left|\phi_n(r=0)\right|^2 \delta(E_r + E_g - \hbar\omega)$$ (Assume here that $f_v = 1$)

This is a more general expression for absorption that can account for both free carrier and excitonic absorption.
First, let us check that we recover our result for free carrier absorption

e.g. Bulk (without excitonic effect)

$$\phi_n(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}_x+\mathbf{k}_y+\mathbf{k}_z)\cdot\mathbf{r}} \rightarrow \phi_n(0) = \frac{1}{\sqrt{V}}$$

$$E_n = \frac{\hbar^2 k^2}{2m_r^*}$$

$$k_x = n_x \frac{2\pi}{L_x} \quad k_y = n_y \frac{2\pi}{L_y} \quad k_z = n_z \frac{2\pi}{L_z}$$

$$\alpha(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \frac{2}{V} \sum_n \delta(E_r + E_g - \hbar\omega)$$

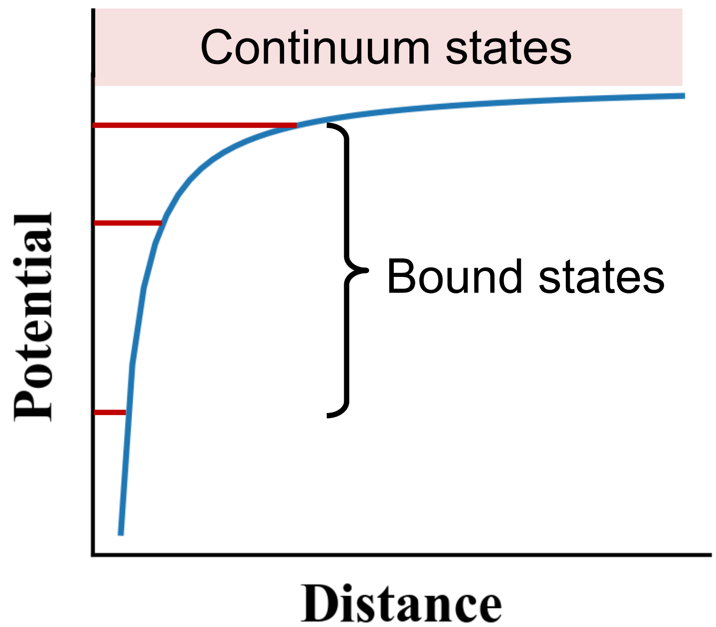
Sum over all states

$$= C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \int \rho_r(E_n)\delta(E_r + E_g - \hbar\omega)dE$$

$$\boxed{= C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \rho_r(\hbar\omega - E_g)}$$

Refer to Chuang Ch. 14 for details of the derivation

Absorption with inclusion of excitonic effect



$$|\phi(0)|^2 = \text{Bound states} + \text{continuum states}$$

$$|\phi_B(0)|^2 = \frac{1}{\pi a_X^3 n^3}$$ (Bound states)

$$|\phi_C(0)|^2 = \frac{1}{R_X a_x^3 4\pi}\left[\frac{e^{\pi/\sqrt{E_r/R_X}}}{\sinh(\pi/\sqrt{E_r/R_X})}\right]$$

(Continuum states)

(See Chuang Ch. 3)

Absorption with inclusion of excitonic effect

Bound states

$$\alpha_B(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \sum_n \frac{2}{\pi a_X^3 n^3}\delta(-R_x/n^2 + E_g - \hbar\omega)$$

$$\boxed{\alpha_B(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \sum_n \frac{2}{R_x \pi a_X^3 n^3}\delta(\epsilon + 1/n^2)}$$

$$\epsilon = (\hbar\omega - E_g)/R_X$$

Continuum states

$$\alpha_C(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \int \frac{dE}{R_X a_x^3 2\pi}\left[\frac{e^{\pi/\sqrt{E_r/R_X}}}{\sinh(\pi/\sqrt{E_r/R_X})}\right]\delta(E_r + E_g - \hbar\omega)$$

$$\alpha_C(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \frac{1}{2\pi^2}\left(\frac{2m_r^*}{\hbar^2}\right)^{3/2}\sqrt{\hbar\omega - E_g}\, S_{3D}(\epsilon)$$

$$\boxed{\alpha_c(\hbar\omega) = \alpha_{free}(\hbar\omega) S_{3D}(\epsilon)}$$

$$\epsilon = (\hbar\omega - E_g)/R_X \quad \text{and} \quad S_{3D}(\epsilon) = \frac{2\pi/\sqrt{\epsilon}}{1 - e^{-2\pi/\sqrt{\epsilon}}}$$

We see that the continuum absorption is bulk absorption multiplied by the Sommerfeld enhancement factor. Evidently, the electrostatic attraction between electron and hole increases the transition strength.

Summary - Absorption with excitonic effects for bulk semiconductor

Exciton Energy $$E_X = E_g - \frac{R_X}{n^2}$$

Absorption

Bound states $$\alpha_B(\hbar\omega) = C_0 \left| \hat{e} \cdot \mathbf{p}_{cv} \right|^2 \sum_n \frac{2}{R_x \pi a_X^3 n^3} \delta(\epsilon + 1/n^2)$$

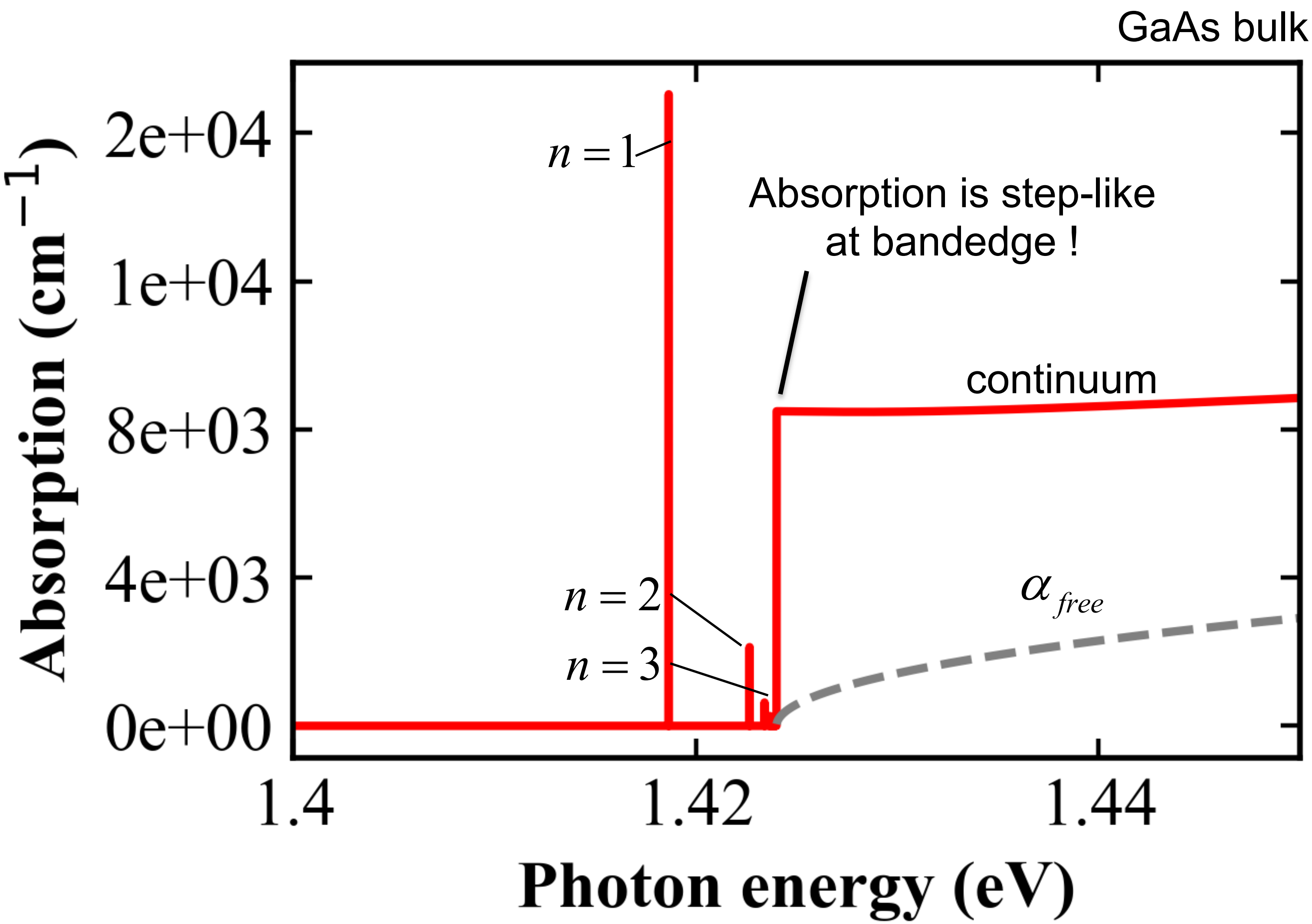
Continuum states $$\alpha_C(\hbar\omega) = \alpha_{free}(\hbar\omega) S_{3D}(\epsilon)$$

Total absorption $$\alpha(\hbar\omega) = \alpha_B(\hbar\omega) + \alpha_C(\hbar\omega)$$

$$\alpha(\hbar\omega) = C_0 \left| \hat{e} \cdot \mathbf{p}_{cv} \right|^2 \sum_n \frac{2}{R_x \pi a_X^3 n^3} \delta(\epsilon + 1/n^2) + \alpha_{free}(\hbar\omega) S_{3D}(\epsilon)$$

$$\epsilon = (\hbar\omega - E_g)/R_X \qquad S_{3D}(\epsilon) = \frac{2\pi/\sqrt{\epsilon}}{1 - e^{-2\pi/\sqrt{\epsilon}}}$$

Summary - Absorption with excitonic effects for bulk semiconductor



Linewidth broadening not included

Experimental data - Bulk semiconductor

M.D. Sturge. Phys. Rev. 127, 768 (1963).

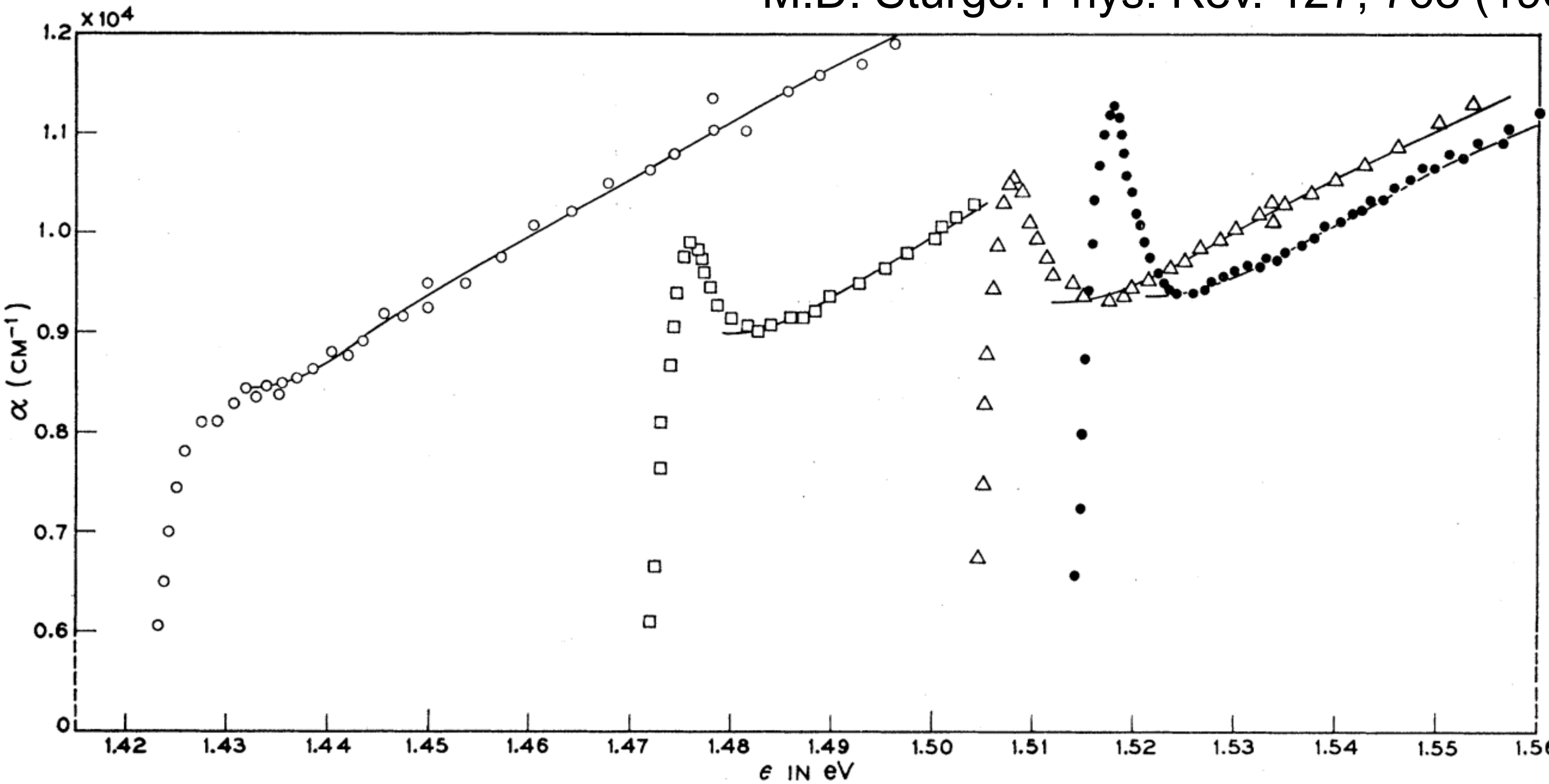
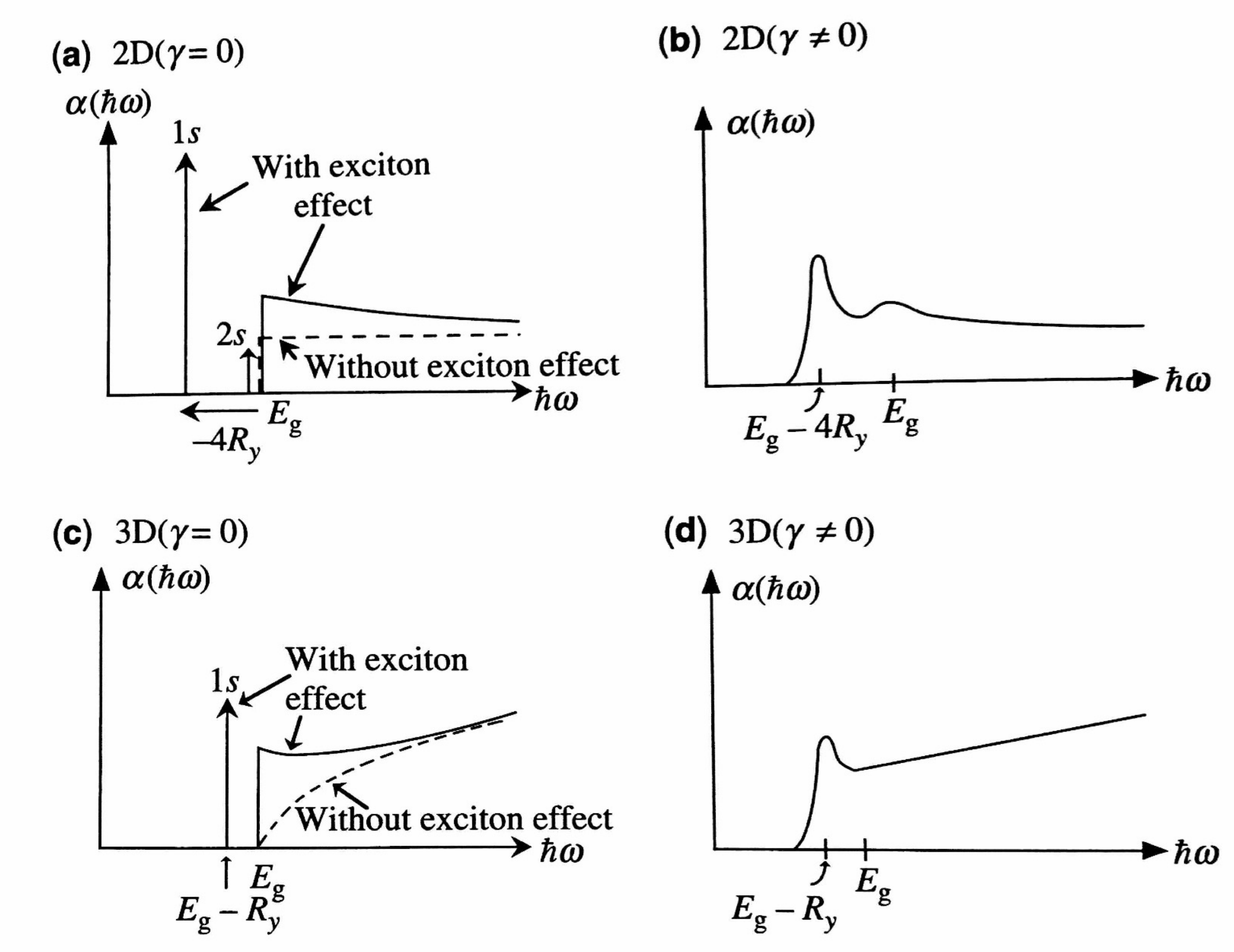
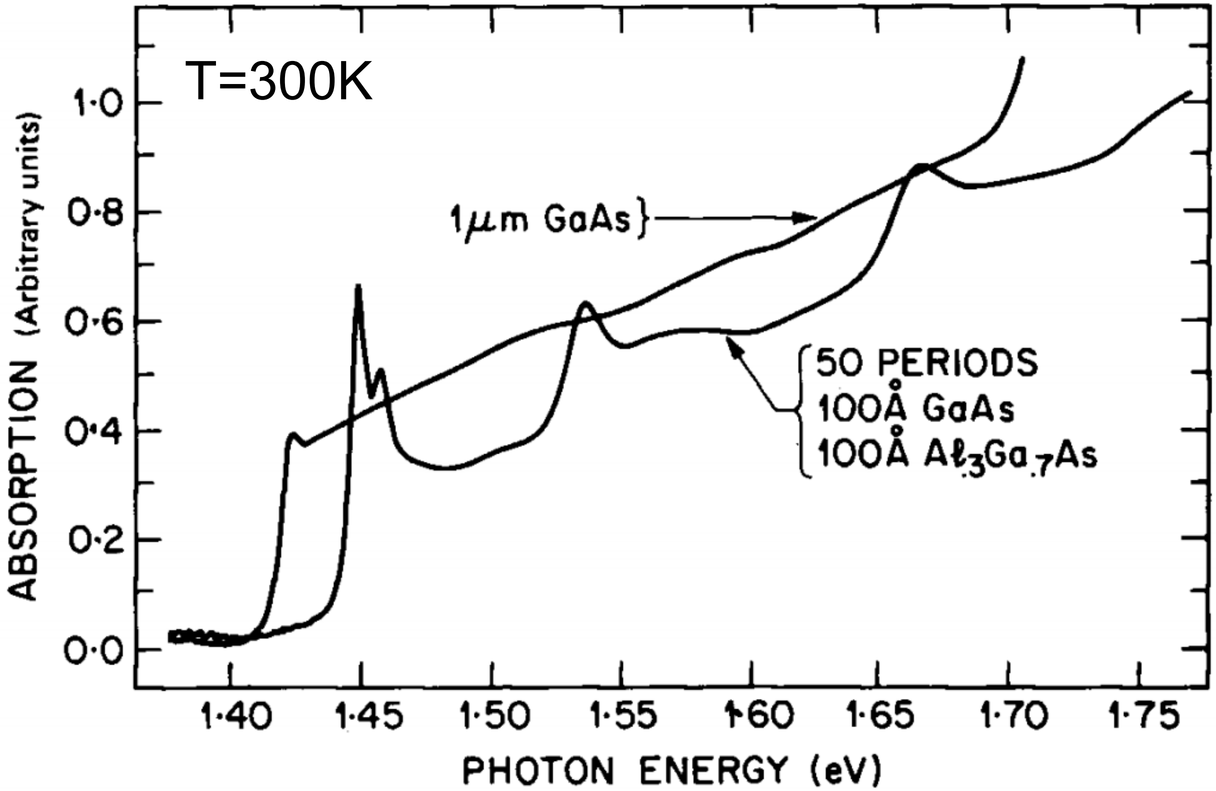


FIG 3 Exciton absorption in GaAs; ○ 294°K, □ 186°K, Δ90°K, ● 21°K.

Excitonic effects in bulk and quantum wells



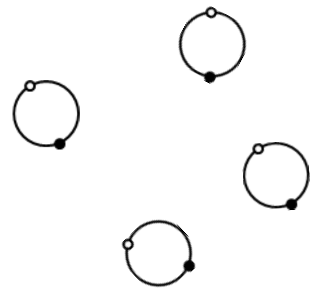
Experimental data - Quantum well



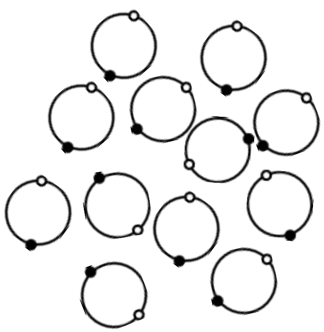
We observe exciton peaks due to bound states and enhancement of the absorption in the continuum. Exciton peak observed near the beginning of each subband transition. Quantization gives higher binding energy allowing for clear observation of exciton peaks even at room temperature. (See Chuang Ch 14 for more details)

Source: S. Schmitt-Rink et al. Advances in Physics, 38:2, 89-188

Excitons at high carrier injection



Low-density
separation > a_X



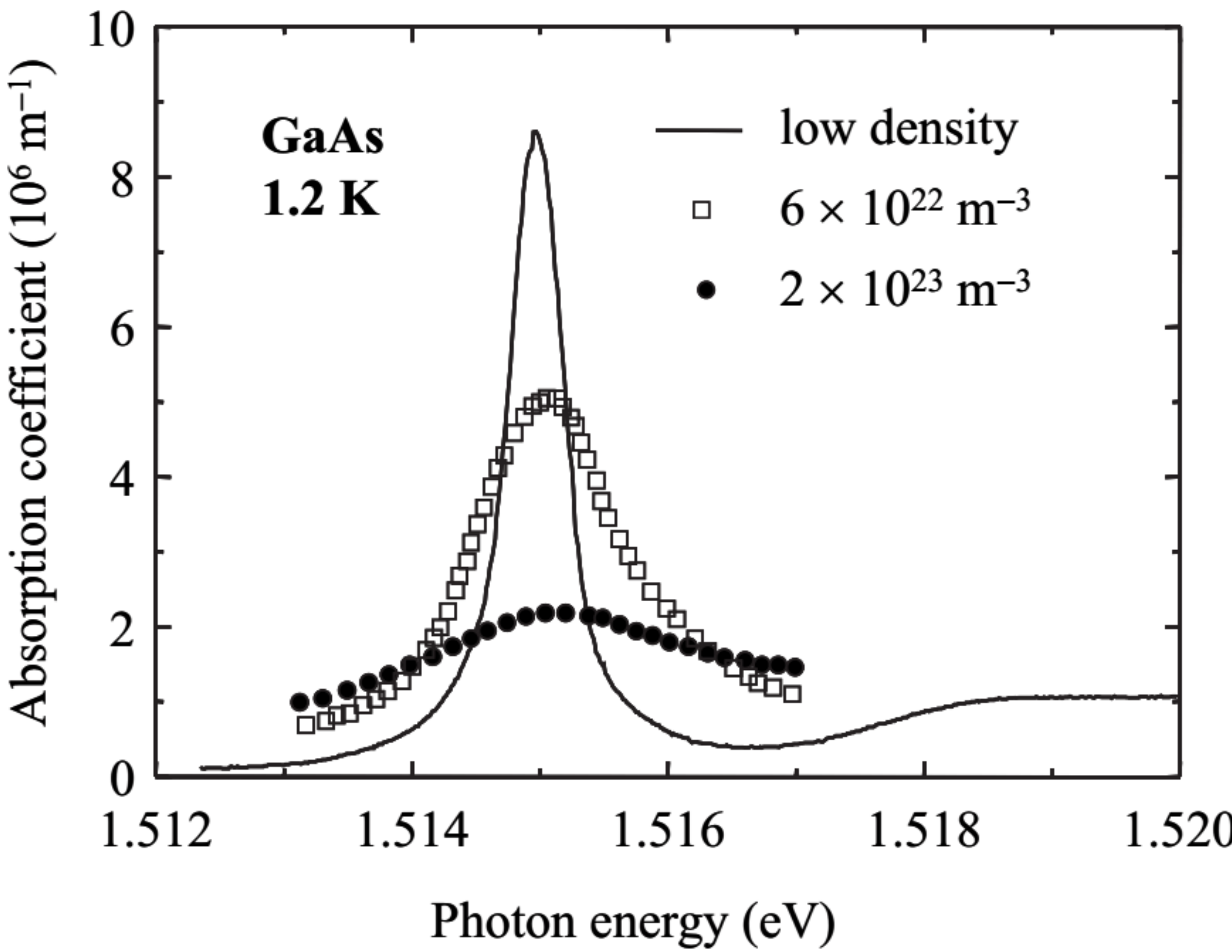
High-density
separation ~ a_X

- At high carrier injection, the Coulombic potential is "screened-out" and excitons do not form.
- The exciton density at which excitons begin to dissociate is called the Mott density.

$$N_{Mott} \approx \frac{1}{\text{Exciton volume}} = \frac{1}{\frac{4}{3}\pi a_X^3}$$

- For GaAs, this estimation gives $N_{Mott} \approx 10^{17}\ cm^{-3}$. Photonic devices are often operated with carrier density exceeding the Mott density.
- In this case, the exciton effects (Coulombic enhancements) may be reduced.

Excitons at high carrier injection

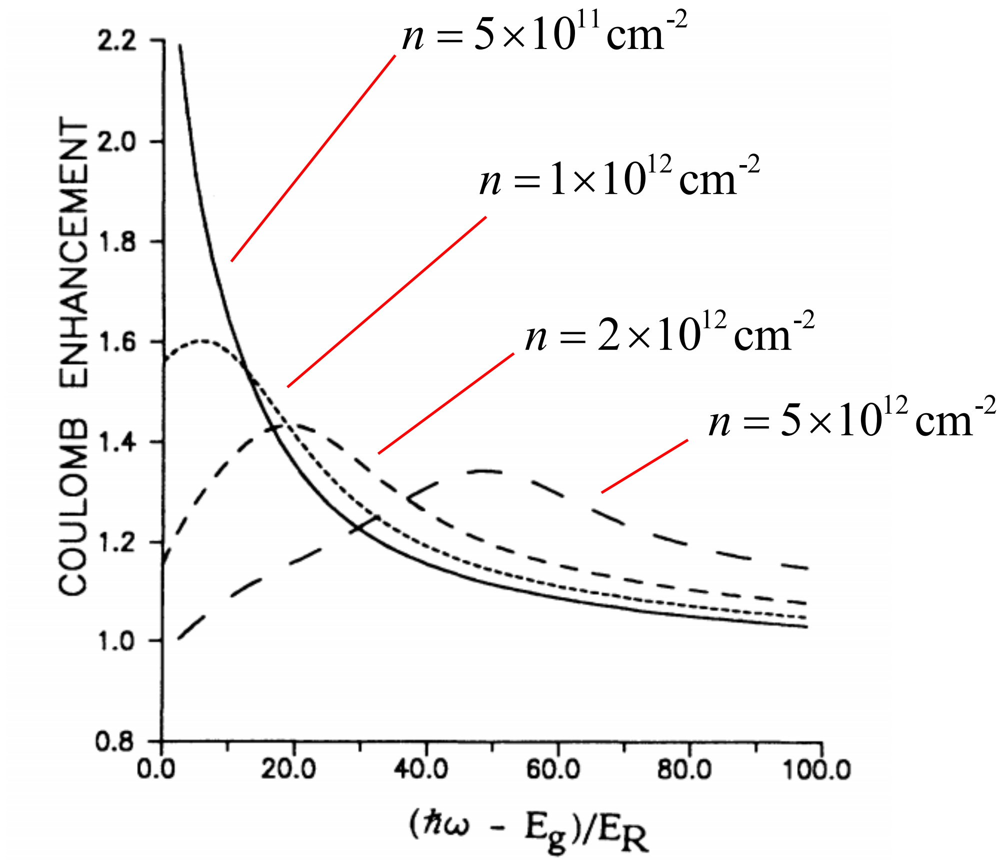


Absorption from n=1 exciton state decreases with increased carrier injection

Fox. Optical Properties of Solids.

Excitons at high carrier injection

Coulomb enhancement of optical transition probability for GaAs quantum well (T=300K)



To a reasonable first approximation, Coulombic enhancement can be ignored under typical operating conditions for a semiconductor laser at room temperature.

Haug and Koch. Phys. Rev. A 39, 1887 (1989).

Appendix: Absorption with inclusion of excitonic continuum states

$$\alpha_C(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \int \frac{dE}{R_X a_x^3 2\pi} \left[\frac{e^{\pi/\sqrt{E_r/R_X}}}{\sinh(\pi/\sqrt{E_r/R_X})} \right] \delta(E_r + E_g - \hbar\omega)$$

Let $\epsilon = (\hbar\omega - E_g)/R_X$

$$\alpha_C(\epsilon) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \int \frac{dE}{R_X a_x^3 2\pi} \left[\frac{e^{\pi/\sqrt{E_r/R_X}}}{\sinh(\pi/\sqrt{E_r/R_X})} \right] \delta(E_r/R_x + \epsilon)$$

$$\alpha_C(\epsilon) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \frac{\sqrt{\epsilon}}{R_X a_x^3 2\pi^2} \left[\frac{(\pi/\sqrt{\epsilon}) e^{\pi/\sqrt{\epsilon}}}{\sinh(\pi/\sqrt{\epsilon})} \right]$$

$$= C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \frac{\sqrt{\epsilon}}{R_X a_x^3 2\pi^2} \left[\frac{2\pi/\sqrt{\epsilon}}{1 - e^{-2\pi/\sqrt{\epsilon}}} \right]$$

$$\alpha_C(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \frac{\sqrt{\epsilon}}{R_X a_x^3 2\pi^2} S_{3D}(\epsilon)$$

where $\epsilon = (\hbar\omega - E_g)/R_X$ and $S_{3D} = \dfrac{2\pi/\sqrt{\epsilon}}{1 - e^{-2\pi/\sqrt{\epsilon}}}$ is the Sommerfeld enhancement factor

Appendix: Absorption with inclusion of excitonic continuum states (contd)

Continuum states (cont'd)

$$\alpha_c(\hbar\omega) = C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \frac{\sqrt{\hbar\omega - E_g}}{\left(\dfrac{q^4 m_r^*}{(4\pi\epsilon_0\epsilon_r)^2 2\hbar^2}\right)^{3/2}\left(\dfrac{4\pi\epsilon_0\epsilon_r\hbar^2}{q^2 m_r^*}\right)^3 2\pi^2} S_{3D}(\epsilon)$$

$$= C_0 \left|\hat{e}\cdot\mathbf{p}_{cv}\right|^2 \frac{1}{2\pi^2}\left(\frac{2m_r^*}{\hbar^2}\right)^{3/2}\sqrt{\hbar\omega - E_g}\, S_{3D}(\epsilon)$$

$$= \boxed{\alpha_{free}(\hbar\omega) S_{3D}(\epsilon)}$$