Optical Properties of Solids: Lecture 10

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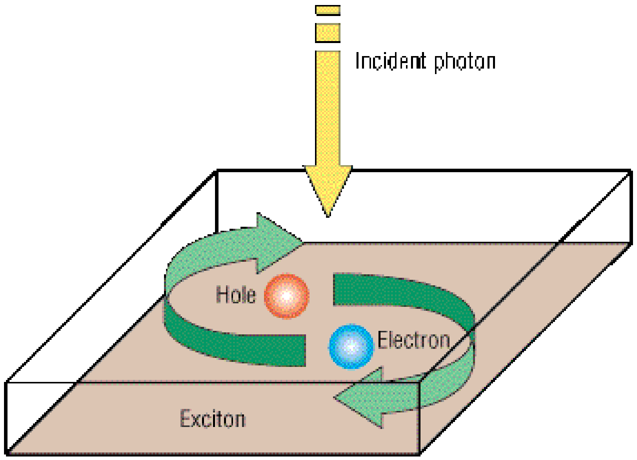
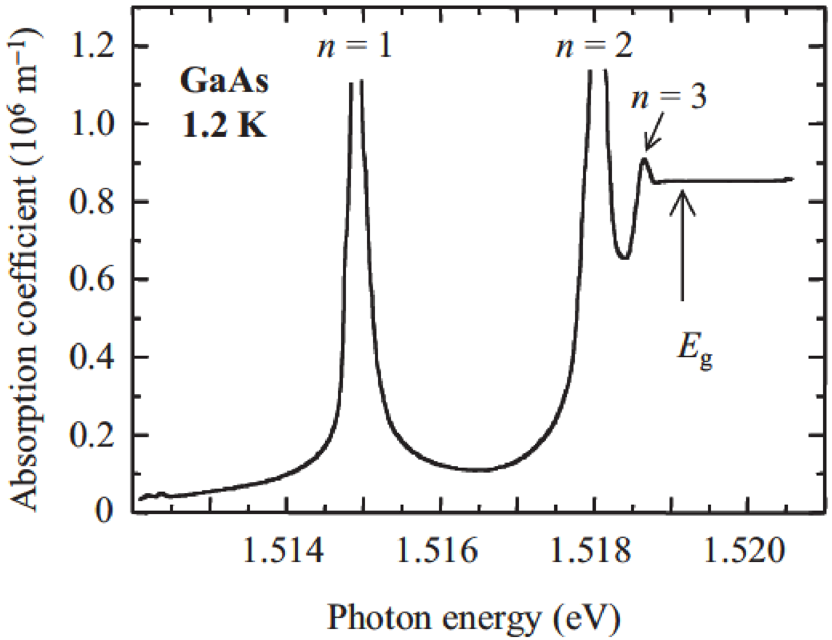
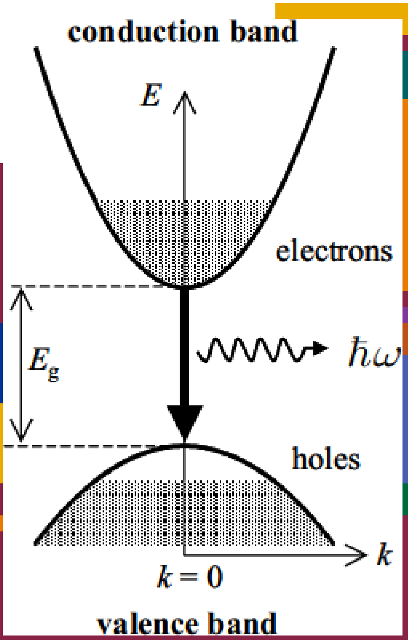
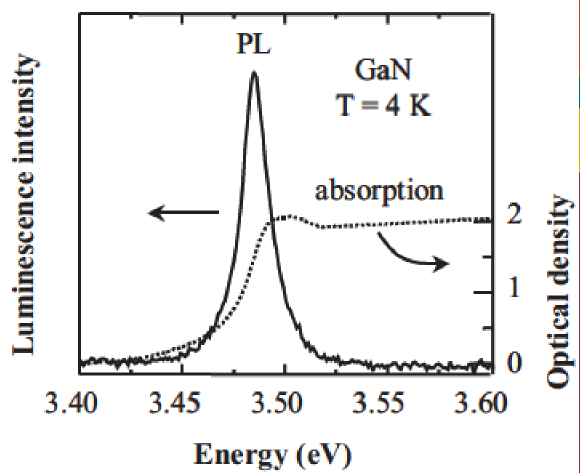
Optical Properties of Solids: Lecture 10

Excitons (Wannier-Mott, Frenkel)
Ionization of excitons
Excitons in low dimensions









References: Band Structure and Optical Properties

Solid-State Theory and Semiconductor Band Structures:

- Mark Fox, Optical Properties of Solids (Chapter 4)
- Ashcroft and Mermin, Solid-State Physics
- Yu and Cardona, Fundamentals of Semiconductors
- Dresselhaus/Dresselhaus/Cronin/Gomes, Solid State Properties
- Cohen and Chelikowsky, Electronic Structure and Optical Properties
- Klingshirn, Semiconductor Optics
- Grundmann, Physics of Semiconductors
- Ioffe Institute web site: NSM Archive
  http://www.ioffe.ru/SVA/NSM/Semicond/index.html

Outline

Wannier-Mott and Frenkel Excitons

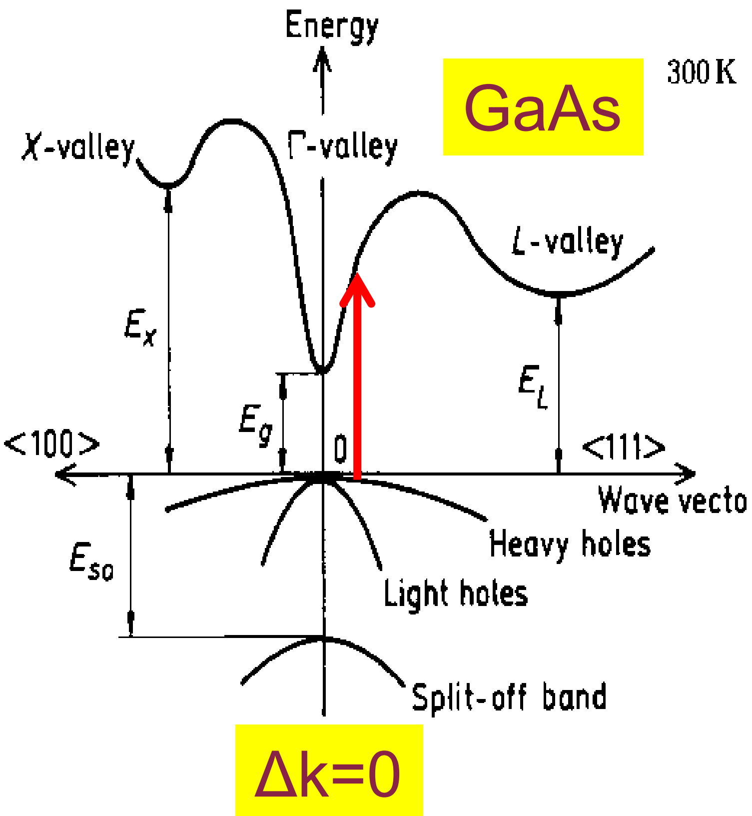
Bohr model for excitons (Elliott/Tanguy theory)

Examples: GaAs, ZnO, LiF, solid rare gases

Ionization of excitons (thermal, high field, high density)

Excitons in low-dimensional semiconductors

Uncorrelated single-electron energy



Direct transition:

Initial and final electron state have **same** wave vector.

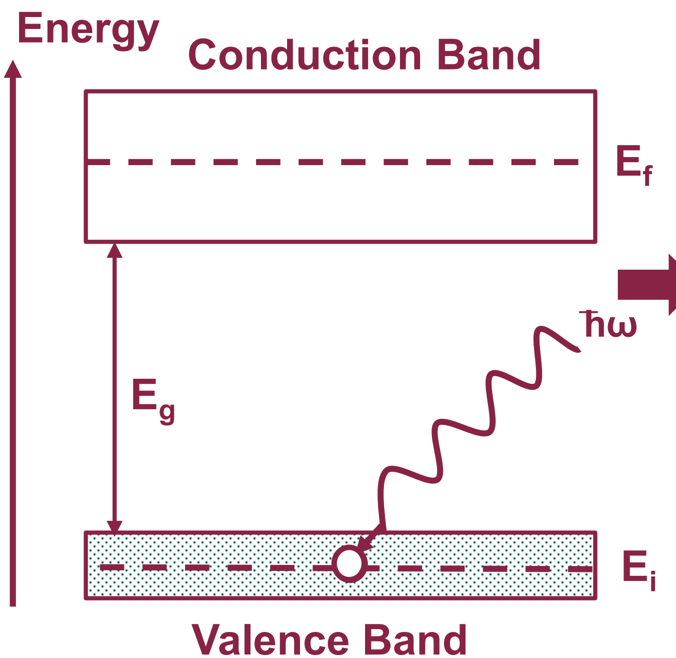
- A **photon** is absorbed.
- A negatively charged electron is removed from the VB, leaving a positively charged **hole**.
- The negatively charged **electron** is placed in the CB.
- Energy conservation: $\hbar\omega = E_f - E_i$

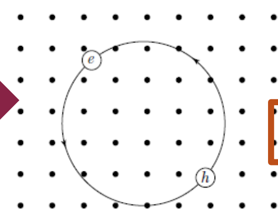
This IGNORES the Coulomb force between the electron and hole.

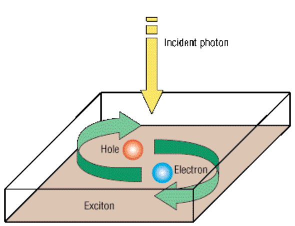
Use **BOHR** model.

Exciton concept

Exciton: bound electron – hole pair



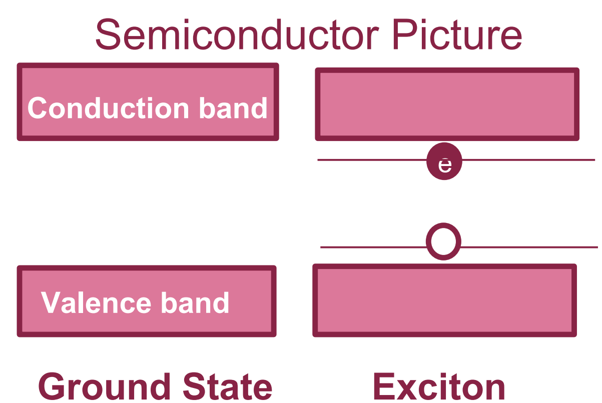




Excitons in semiconductors

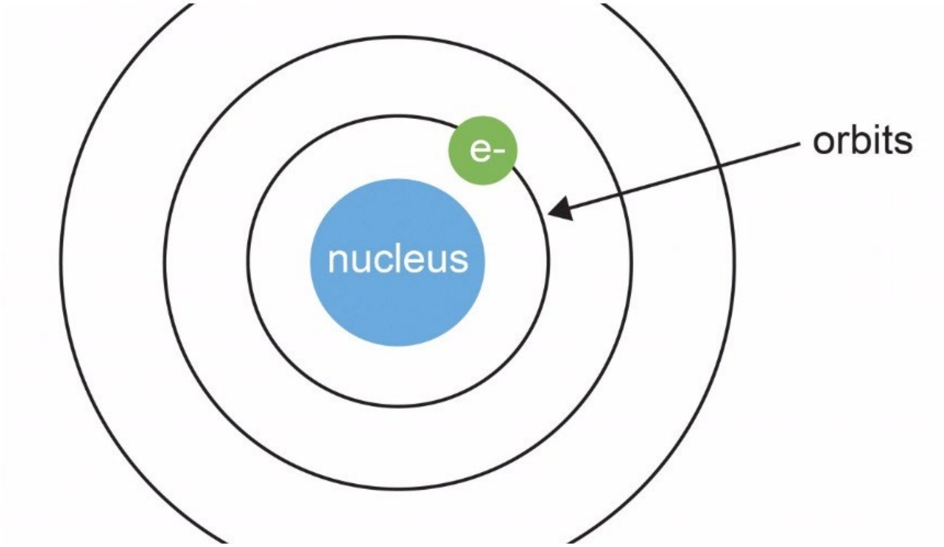
	Excitonic Radius(Å)	Lattice Constant(Å)	Excitonic Binding Energy (meV)
GaAs	130	5.6532	4.2
$SrTiO_3$	62.5	3.9050	20
GaP	50	5.4505	21
ZnO	20	a=3.2500, c=5.2040	60

- Large radius
- Radius is larger than atomic spacing
- Weakly bound



NM STATE

Bohr model for free excitons



Electron and hole form a bound state with binding energy.

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

R_H=13.6 eV Rydberg energy.
QM mechanical treatment easy.

1. Reduced electron/hole mass (**optical mass**)

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

2. **Screening** with static dielectric constant ε_r.

3. **Exciton radius**:

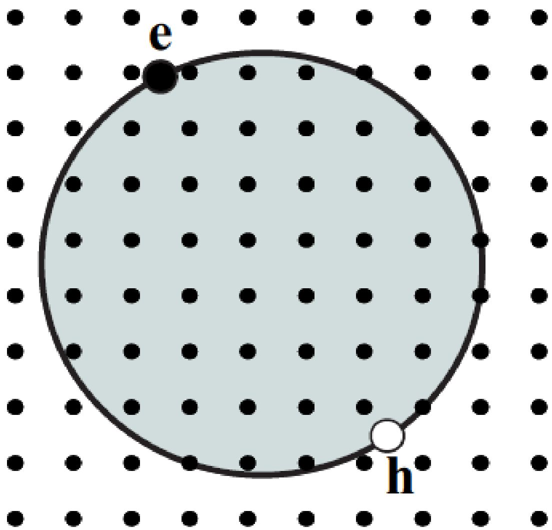
$$r_n = \frac{m_0}{\mu}\varepsilon_r n^2 a_H$$

a_H=0.53 Å

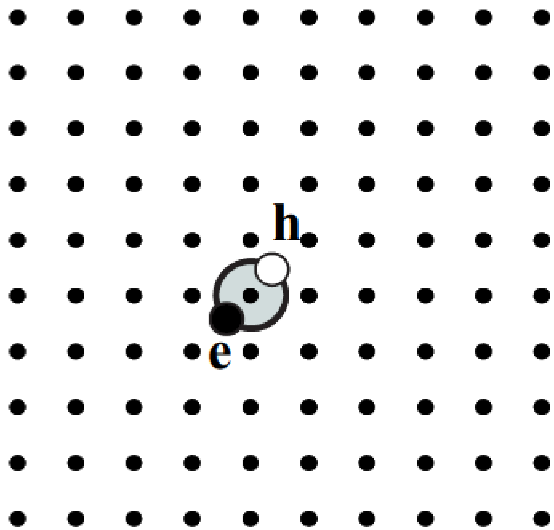
4. Excitons **stable** if E_X>>kT.
5. Exciton **momentum** is zero.

Wannier-Mott and Frenkel excitons

How does the (excitonic) Bohr radius compare with the lattice constant?



(a) Free exciton



(b) Tightly bound exciton

localized

Wannier-Mott exciton
(semiconductors)
~1-10 meV

Frenkel exciton
(insulators)
100-1000 meV

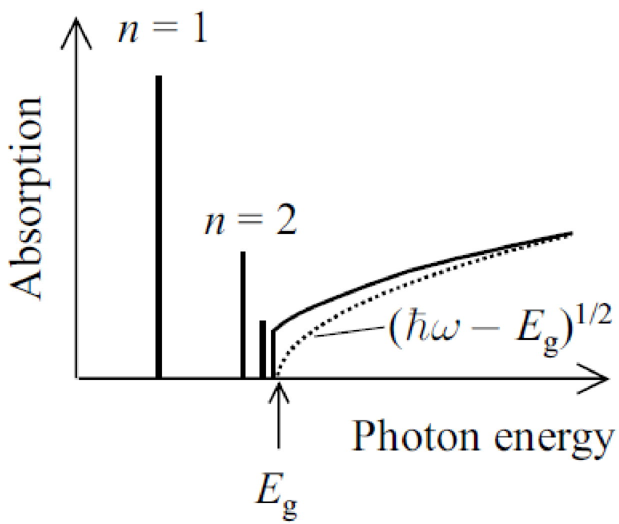
Fox, Chapter 4
Yu & Cardona

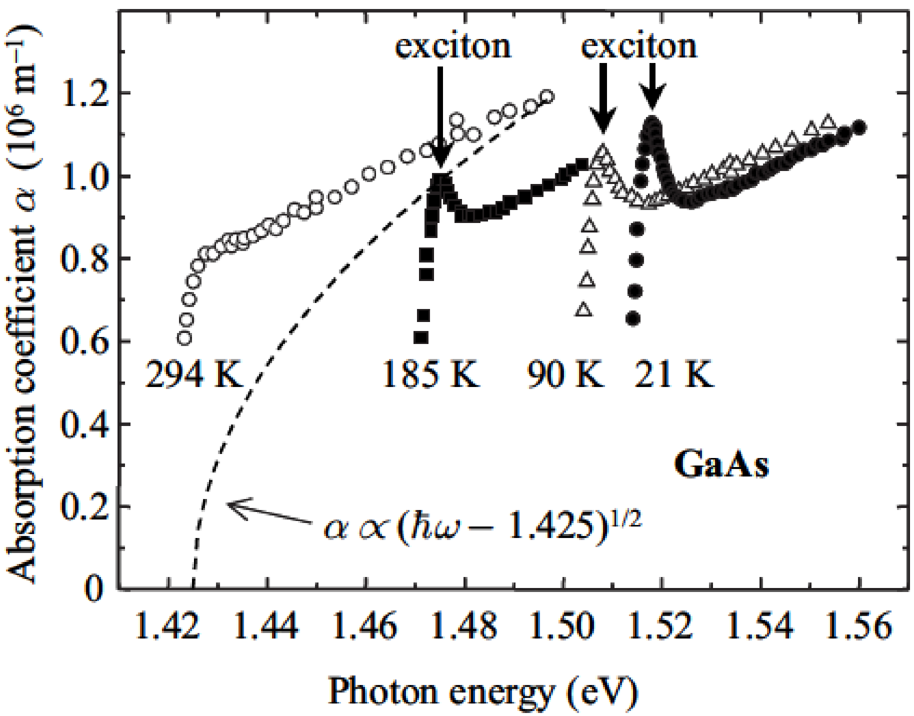
Free exciton examples

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)

- Effective mass increases like the band gap.
- Narrow-gap semiconductors have weak excitons.
- Insulators (GaN, ZnO, SiC) have strongly bound excitons.

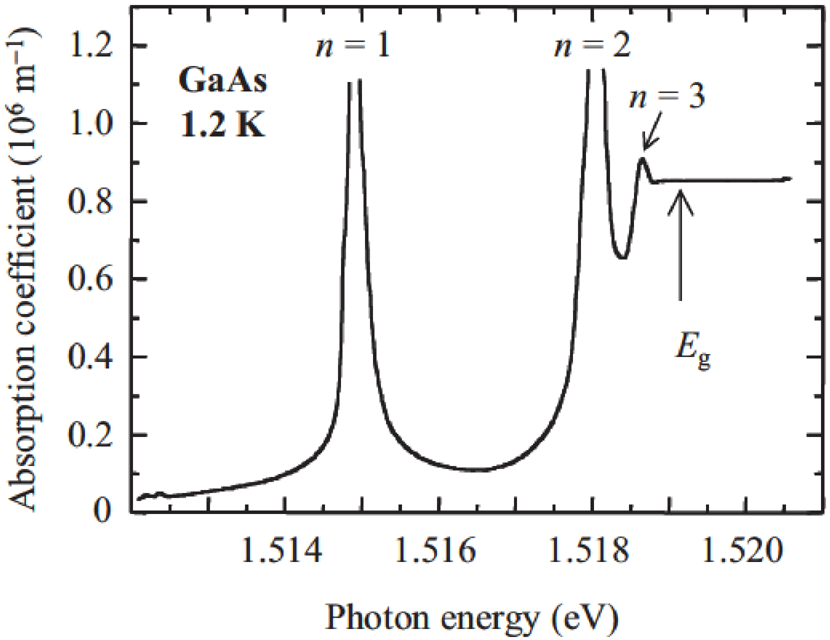
- Discrete series of exciton states
- (unbound) exciton continuum Sommerfeld enhancement.



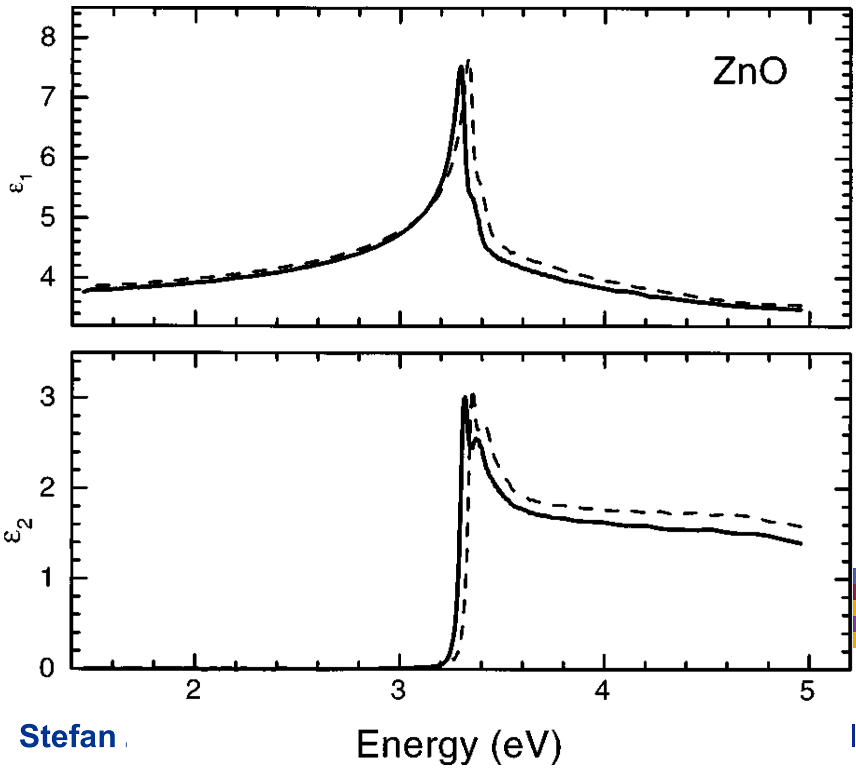


Fox, Chapter 4
Yu & Cardona

Free exciton examples



Several discrete states can be seen in pure GaAs at very low T.

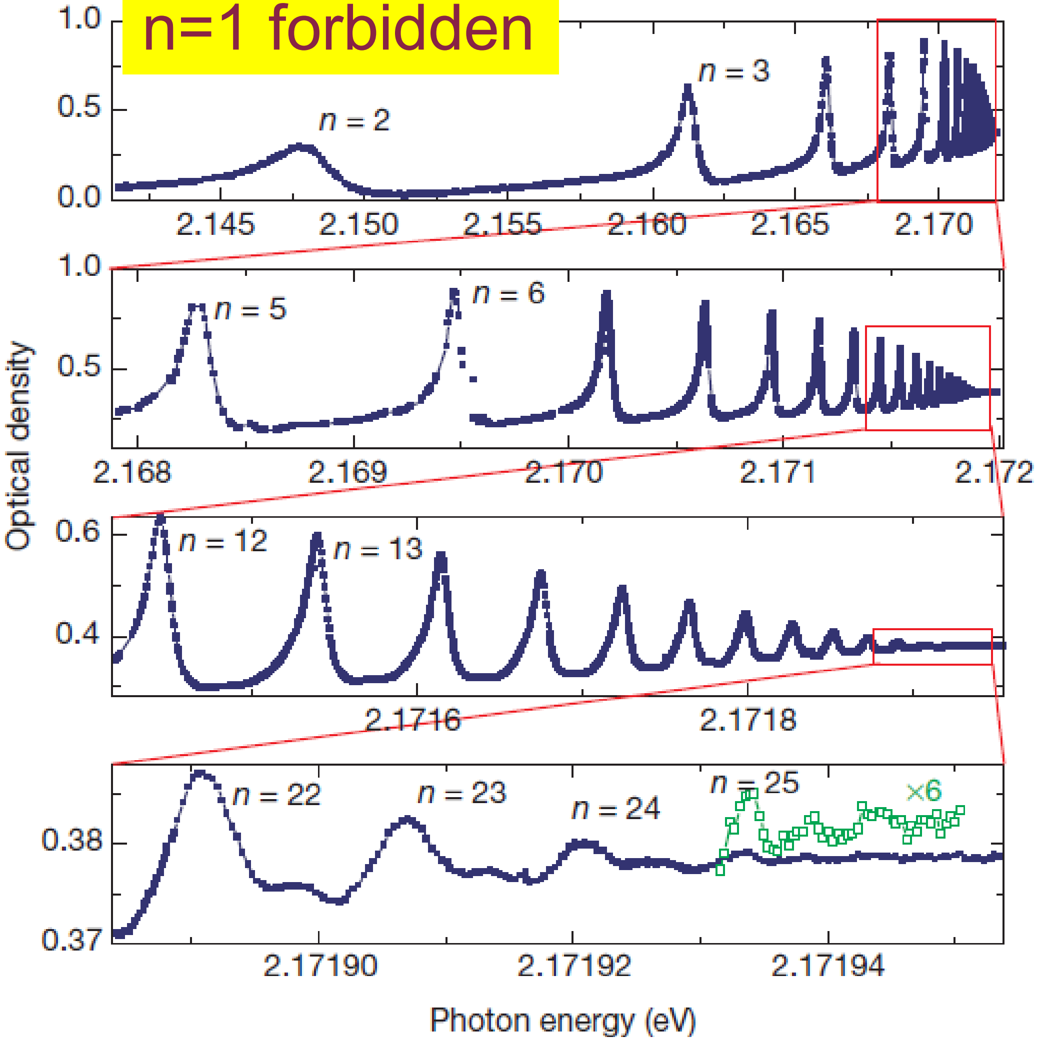


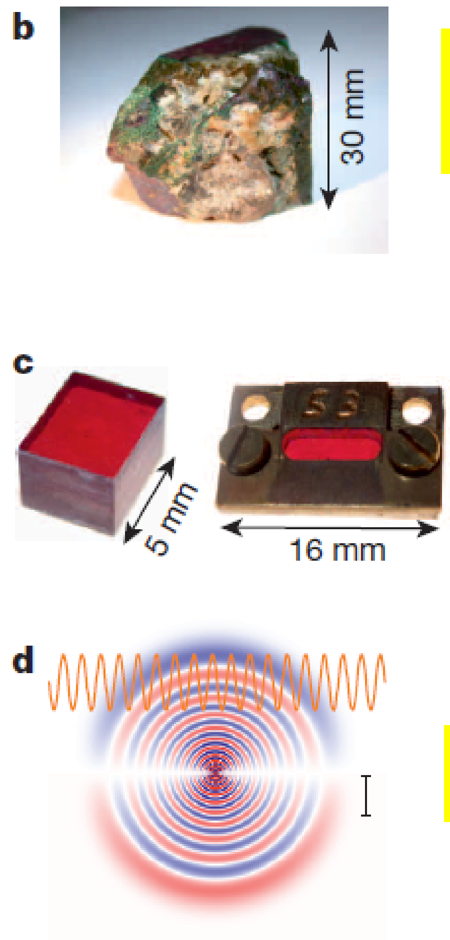
ZnO has a very strong exciton.
II/VI material, very polar.
Uniaxial (solid-dashed lines).
Strong exciton-phonon coupling.
Exciton-phonon complex.

Fox, Chapter 4
Jellison, PRB **58**, 3586 (1998).

Giant Rydberg excitons in Cu_2O

n=1 forbidden





$$E(n) = -\frac{R_X}{n^2}$$

n=25

Band-band optical dipole transition forbidden by parity

Kazimierczuk, Nature **514**, 343 (2014)

Excitonic effects are weak if band gap is small

InSb:

E_g=0.2 eV

E_X=0.4 meV

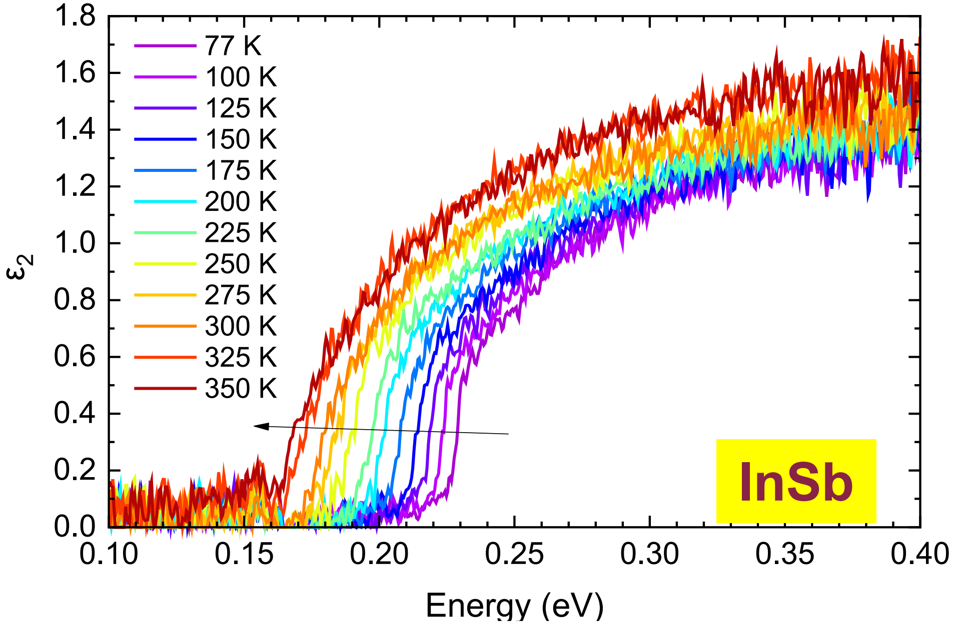
a_X=100 nm

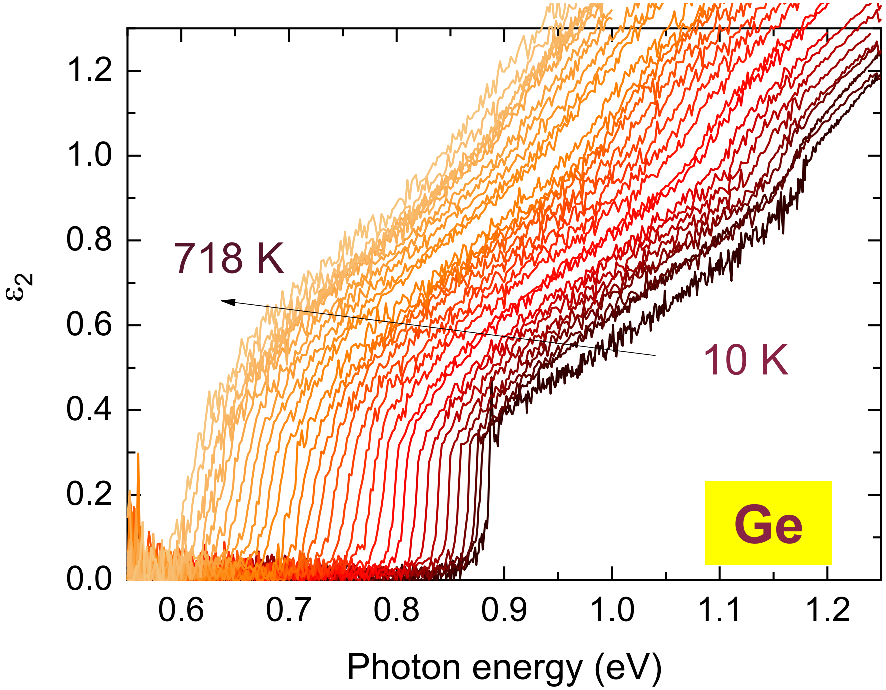
Ge:

E_g=0.9 eV

E_X=1.7 meV

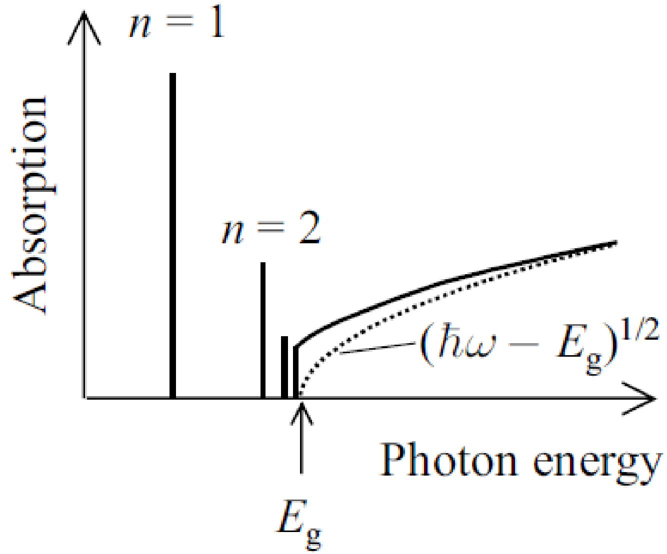
a_X=24 nm





Emminger, Zamarripa, ICSE 2019

Sommerfeld enhancement



Excitonic Rydberg energy $$R_X = \frac{\mu}{m_0 \varepsilon_r^2} R_H$$

Discrete states $$E_n = E_g - \frac{1}{n^2} R_X$$

Discrete absorption

$$\varepsilon_2(E) = \frac{8\pi |P|^2 \mu^3}{\omega^2 (4\pi\varepsilon_0)^3 \varepsilon_r^3} \sum_{n=1}^{\infty} \frac{1}{n^3} \delta(E - E_n)$$

Continuum absorption

$$\varepsilon_2(E) = \frac{2|P|^2 (2\mu)^{3/2} \sqrt{E - E_0}}{\omega^2} \frac{\xi e^{\xi}}{\sinh \xi}$$

$$\xi = \pi \sqrt{R_X / E - E_0}$$

Use Bohr wave functions to calculate ε_2.
Toyozawa discusses broadening.

R. J. Elliott, Phys. Rev. **108**, 1384 (1957)
Yu & Cardona

Tanguy: Kramers-Kronig transform of Elliott formula

exciton bound states and continuum:

$$\varepsilon(E) = \frac{A\sqrt{R_X}}{(E+i\Gamma)^2}\{g[\xi(E+i\Gamma)] + g[\xi(-E-i\Gamma)] - 2g[\xi(0)]\}$$

$$g(\xi) = 2\ln(\xi) - 2\pi\cot(\pi\xi) - 2\psi(\xi) - \frac{1}{\xi}$$

Sommerfeld enhancement (excitonic effects)

Electron-hole absorption

$$\psi(z) = \frac{d\ln\Gamma(z)}{dz}$$

Digamma function

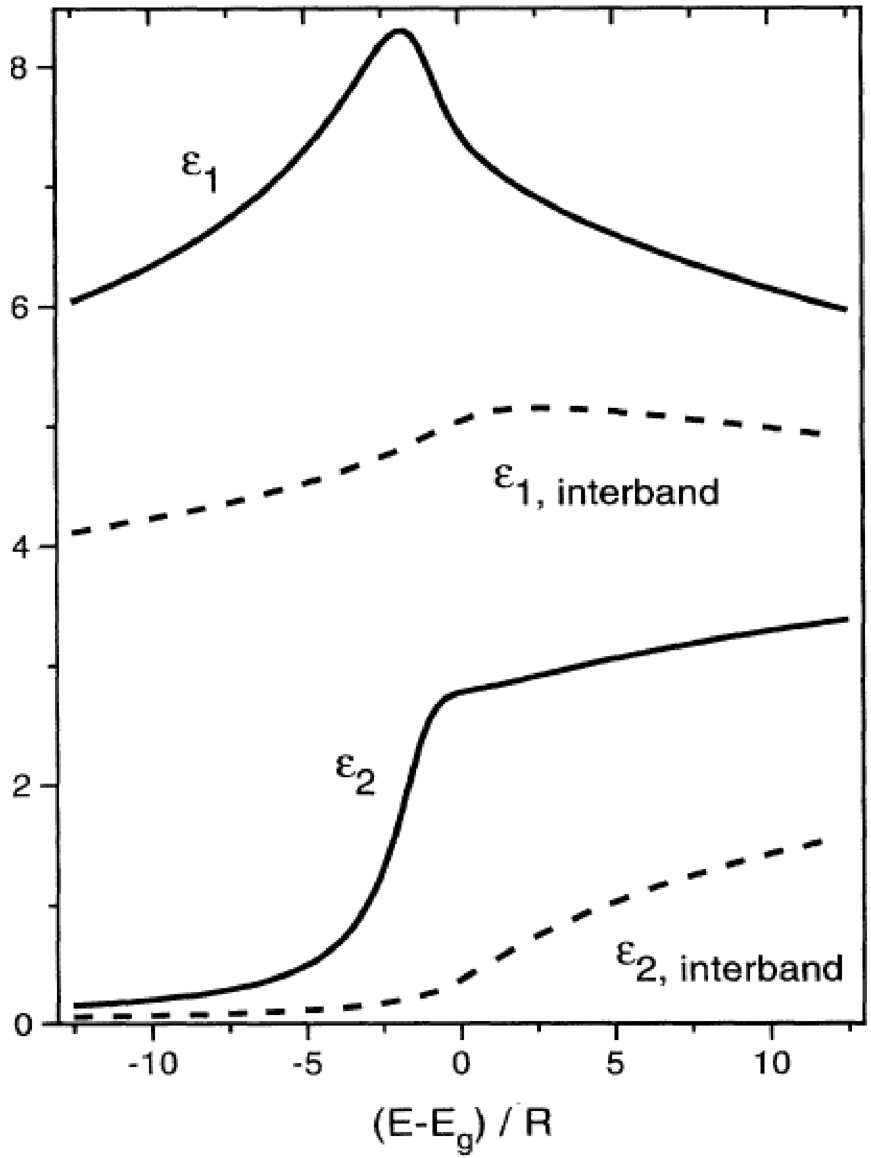
$$\xi(z) = \sqrt{R_X/_{E_0 - z}}$$

Amplitude pre-factor

$$A = \frac{\hbar^2 e^2}{2\pi\varepsilon_0 m_0^2}\left(\frac{2\mu}{\hbar^2}\right)^{3/2}|P|^2$$

R. J. Elliott, Phys. Rev. **108**, 1384 (1957)
C. Tanguy, Phys. Rev. Lett. **75**, 4090 (1995)

Tanguy: Kramers-Kronig transform of Elliott formula



Exciton bound states have disappeared due to broadening.

Significant Sommerfeld enhancement of the excitonic continuum.

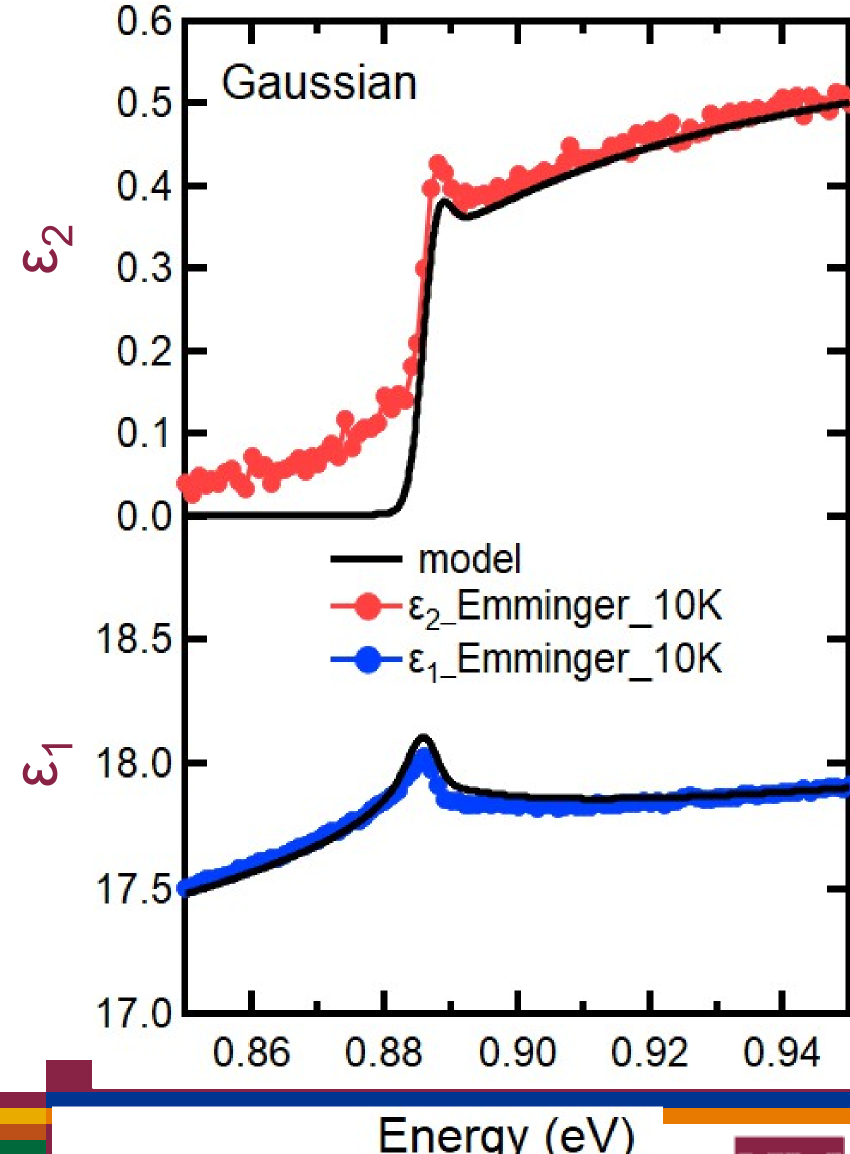
ε_1 peaks below E_g due to excitonic effects.

E_g=1.42 eV,
R_X=4 meV, Γ=6 meV

R. J. Elliott, Phys. Rev. **108**, 1384 (1957)
C. Tanguy, Phys. Rev. Lett. **75**, 4090 (1995)

Tanguy model applied to Ge

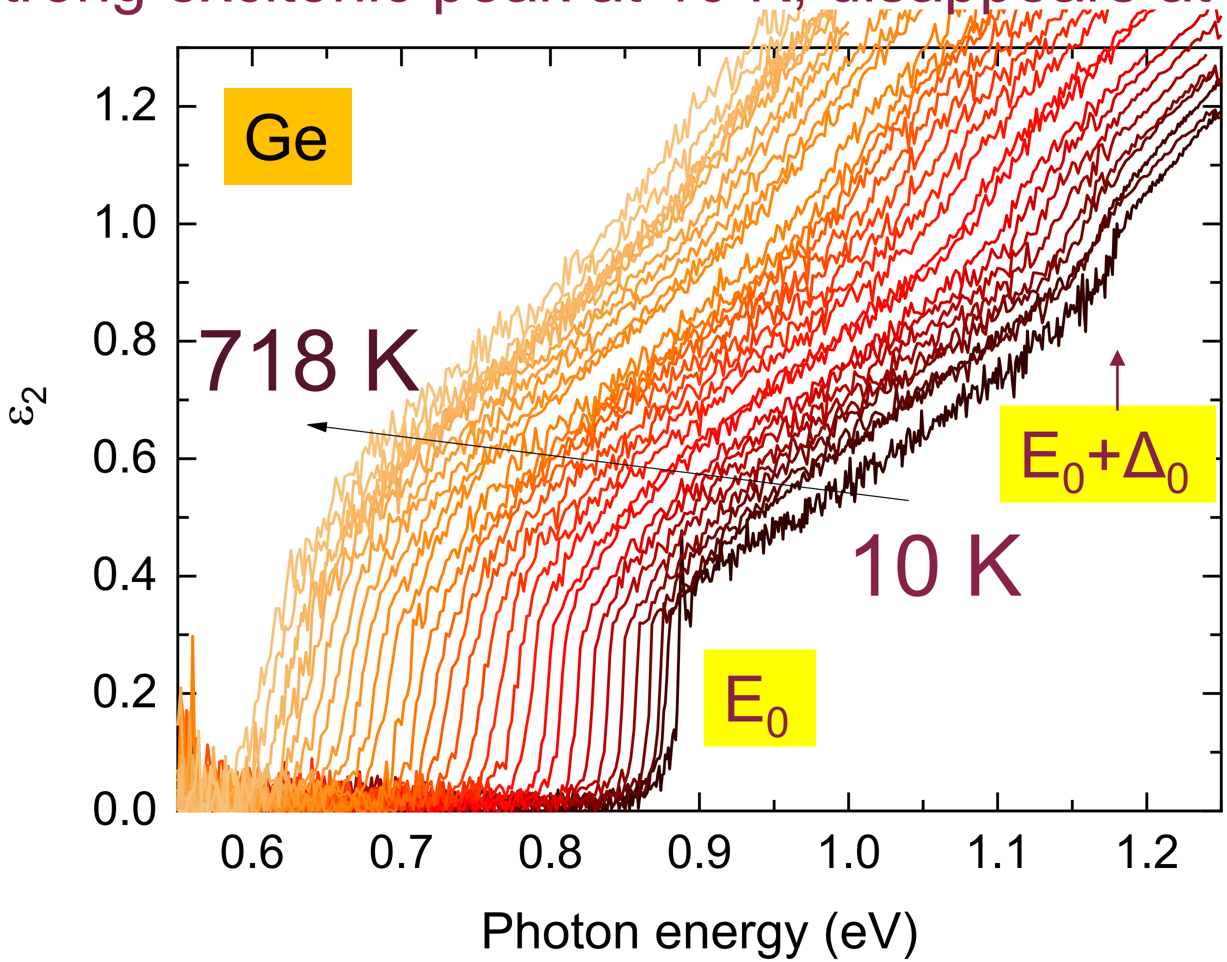
- Fixed parameters:
  - Electron and hole masses
  - Excitonic binding energy R_i
- Adjustable parameters:
  - Linear background A_1 and B_1 (contribution from E_1)
  - Broadening Γ: 2.3 meV
  - Band gap E_0
  - Amplitude A (similar to P)



Carola Emminger, ICSE 2019

Thermal ionization of excitons

Strong excitonic peak at 10 K, disappears at high T.



$E_X(hh)$=1.7 meV

k_B=0.086 meV/K

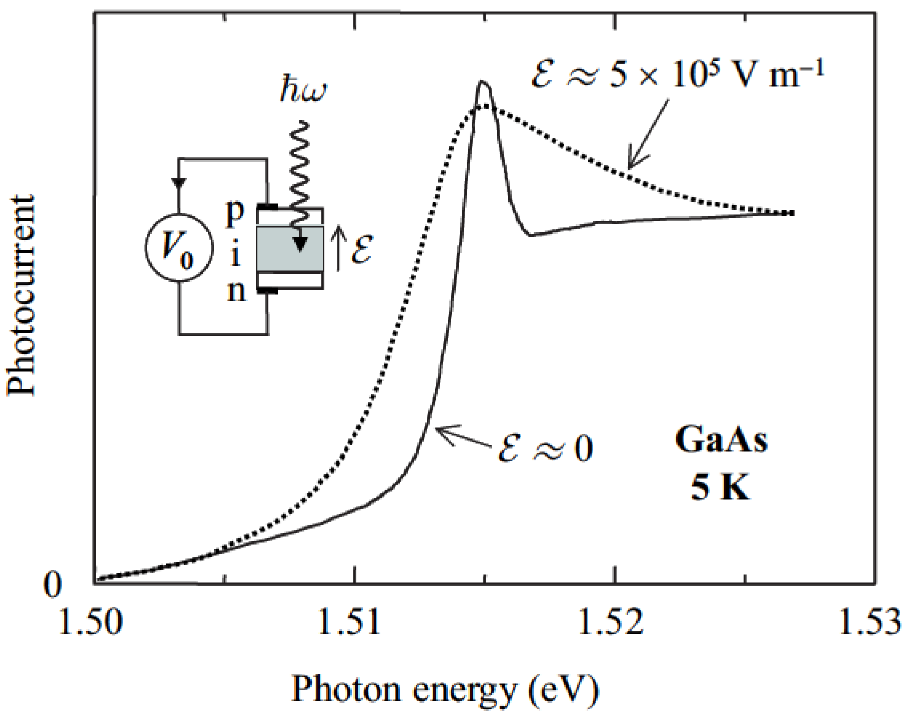
T_C=20 K

Carola Emminger, ICSE 2019

Excitons in electric fields

Excitons are unstable at high temperature, if $kT >> E_X$.

They are also unstable in a high electric field.



Energy of dipole in electric field

$$U = \vec{p} \cdot \vec{E} = 2a_x eE = R_X$$

Critical field

$$E_c = \frac{R_X}{2a_X e}$$

GaAs:

R_X=1.5 meV

a_X=13 nm

E_c=60 kV/m

Field ionization

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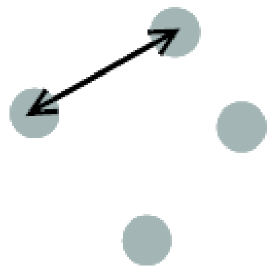
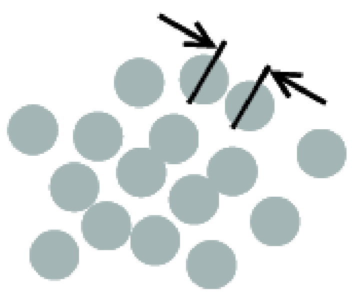
Condensation of excitons at high density

Exciton gas



(a) Low density
Separation $\gg$ diameter

Electron-hole liquid



(b) High density
Separation $\approx$ diameter

Mott transition (insulator-metal) when electron separation equals exciton radius.

Electron separation d for density N

$$d = \sqrt[3]{\frac{3}{4\pi N}}$$

$$r_s = \frac{d}{a_X}$$ dimensionless

Mott transition occurs at r_s near 1.
GaAs: $n=10^{17}$ cm^{-3}.

Biexciton, triexciton molecule formation.
Electron-hole droplets.
Bose-Einstein condensation.

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Excitons in doped or excited semiconductors

Need to include exciton screening due to doping.
Yukawa potential: Schrödinger equation not solvable.
Use Hulthen potential as an approximation

$$k = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r}$$

Coulomb $V(r) = -k\frac{1}{r}$

Yukawa $V(r) = -k\frac{\exp(-r/\lambda_\mathrm{D})}{r}$

$$\lambda_D = \sqrt{\frac{\varepsilon_r\varepsilon_0 k_B T}{ne^2}}$$

Hulthen $V(r) = -k\frac{2/ga_X}{\exp\left(\frac{2r}{ga_X}\right) - 1}$

$$g = \frac{\lambda_D}{a_X}$$

Unscreened: g=∞
Fully screened: g=0
Mott criterion: g=1

Hulthen exciton

C. Tanguy, Phys. Rev. **60,** 10660 (1999)
Banyai & Koch, Z. Phys. B **63**, 283 (1986).

Tanguy: Dielectric function of screened excitons

Bound exciton states:

$$A = \frac{\hbar^2 e^2}{2\pi\varepsilon_0 m_0^2}\left(\frac{2\mu}{\hbar^2}\right)^{3/2}|P|^2$$

$$\varepsilon_2(\omega) = \frac{2\pi A\sqrt{R_X}}{E^2}\sum_{n=1}^{n^2<g} 2R_X \frac{1}{n}\left(\frac{1}{n^2}-\frac{n^2}{g^2}\right)\delta\left[E-E_g+\frac{R}{n^2}\left(1-\frac{n^2}{g}\right)^2\right]$$

exciton continuum:

$$k = \pi\sqrt{{(E-E_0)}/{R_X}}$$

$$\varepsilon_2(\omega) = \frac{2\pi A\sqrt{R_X}}{E^2}\frac{\sinh \pi g k}{\cosh(\pi g k)-\cosh\left(\pi g\sqrt{k^2-\frac{4}{g}}\right)}\theta(E-E_g)$$

Need to introduce Lorentzian broadening and perform KK transform.

C. Tanguy, Phys. Rev. B **60**, 10660 (1999)

NM STATE

Tanguy: Dielectric function of screened excitons

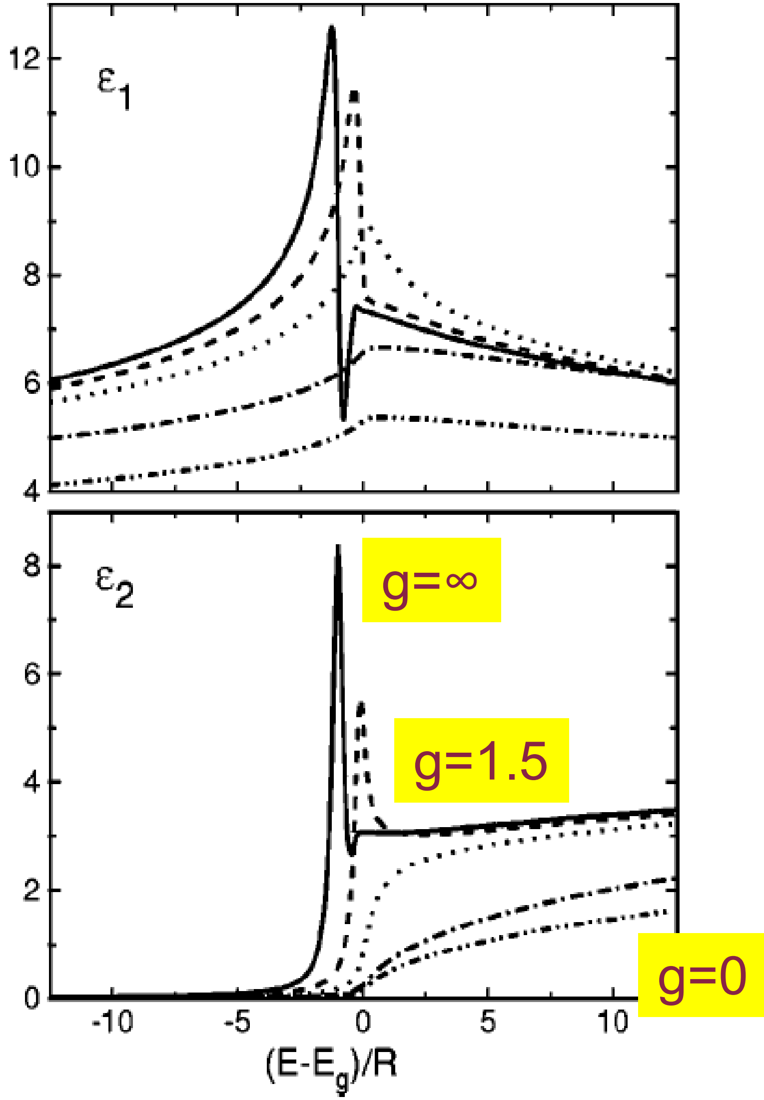
$$\varepsilon(E)=\frac{A\sqrt{R_X}}{(E+i\Gamma)^2}\{g[\xi(E+i\Gamma)]+g[\xi(-E-i\Gamma)]-2g[\xi(0)]\}$$

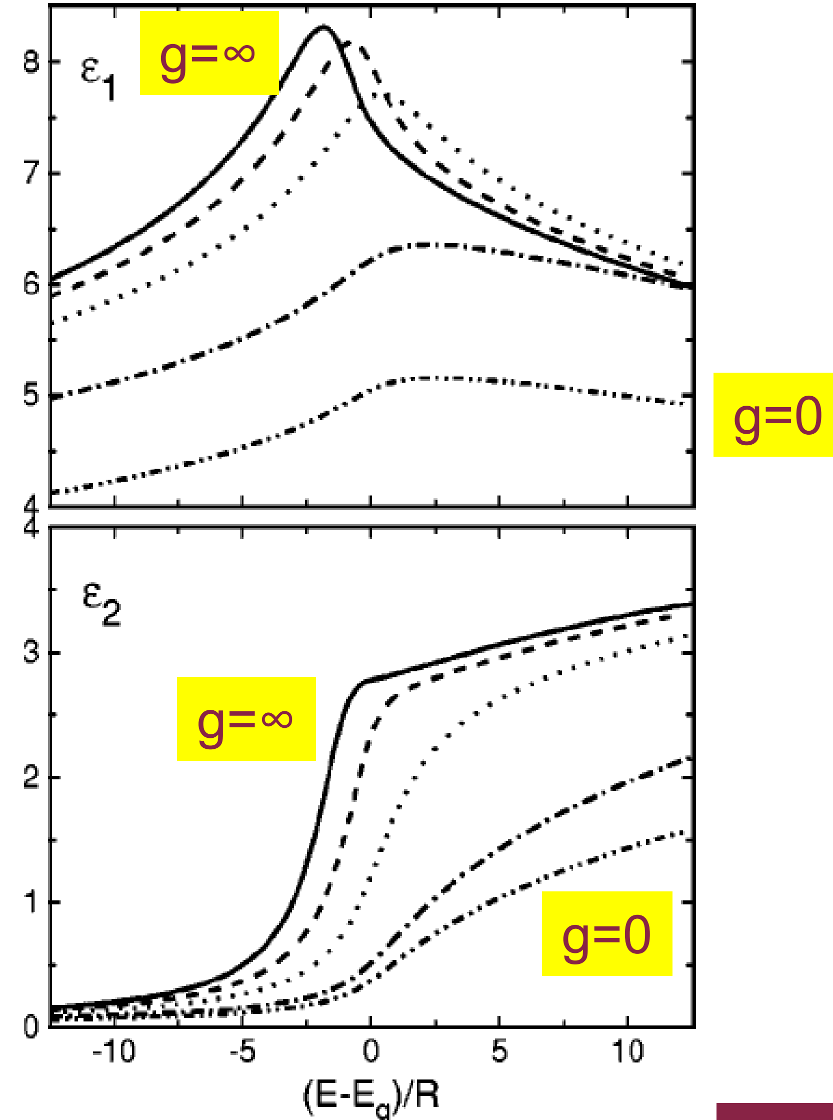
$$g(\xi)=-2\psi\left(\frac{g}{\xi}\right)-\frac{\xi}{g}-2\psi(1-\xi)-\frac{1}{\xi}$$

$$\xi(z)=\frac{2}{\sqrt{\frac{E_g-z}{R_X}}+\sqrt{\frac{E_g-z}{R_X}+\frac{4}{g}}}$$

C. Tanguy, Phys. Rev. B **60**, 10660 (1999)

Tanguy: Dielectric function of screened excitons



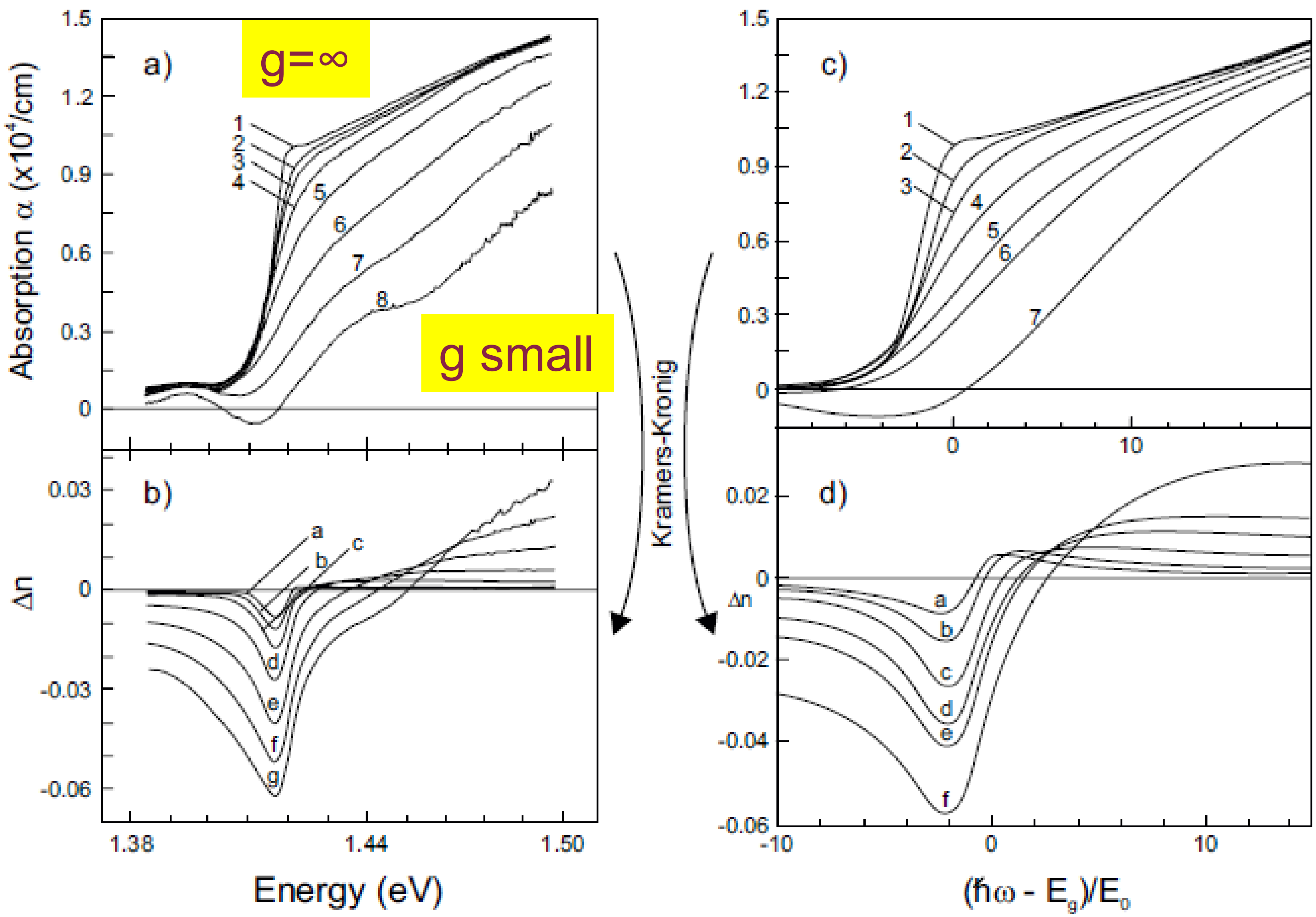


Small broadening

Large broadening

C. Tanguy, Phys. Rev. B **60**, 10660 (1999)

Excitons in laser-excited GaAs



GaAs
300 K

High laser excitation

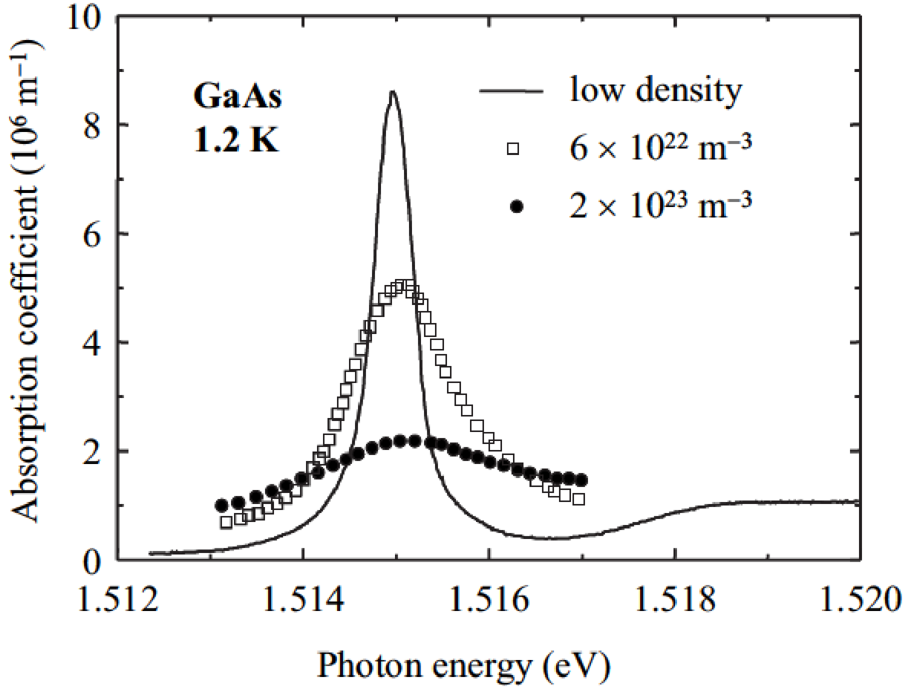
Hulthen exciton

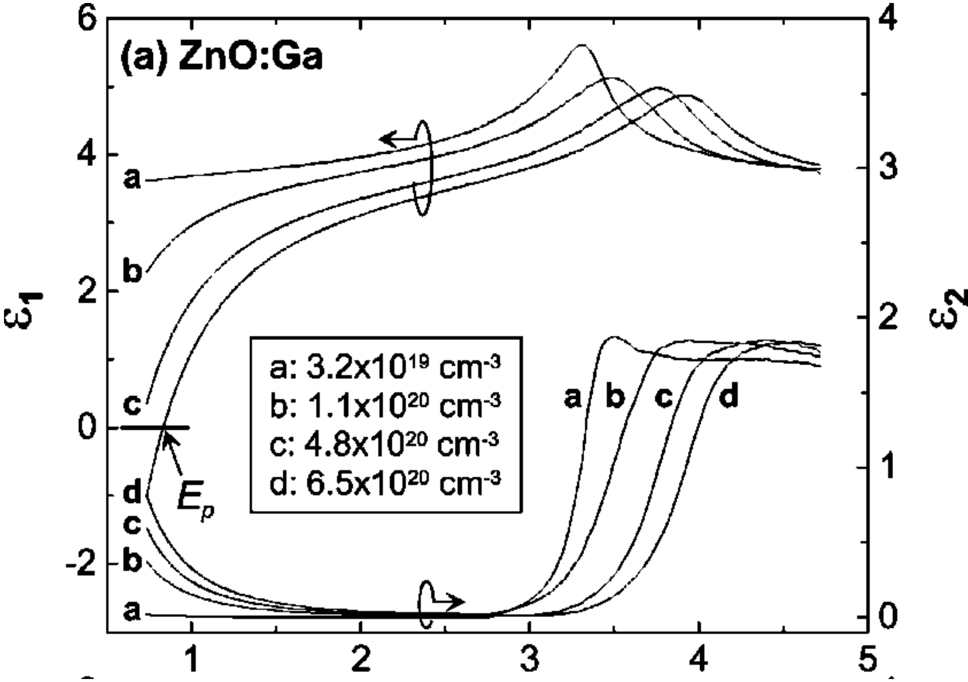
Haug and Koch, Quantum Theory of Optical and Electronic Properties of Semiconductors
Y. H. Lee, Phys. Rev. Lett **57**, 2446 (1986)

Excitons in doped or excited semiconductors

High laser excitation

High doping



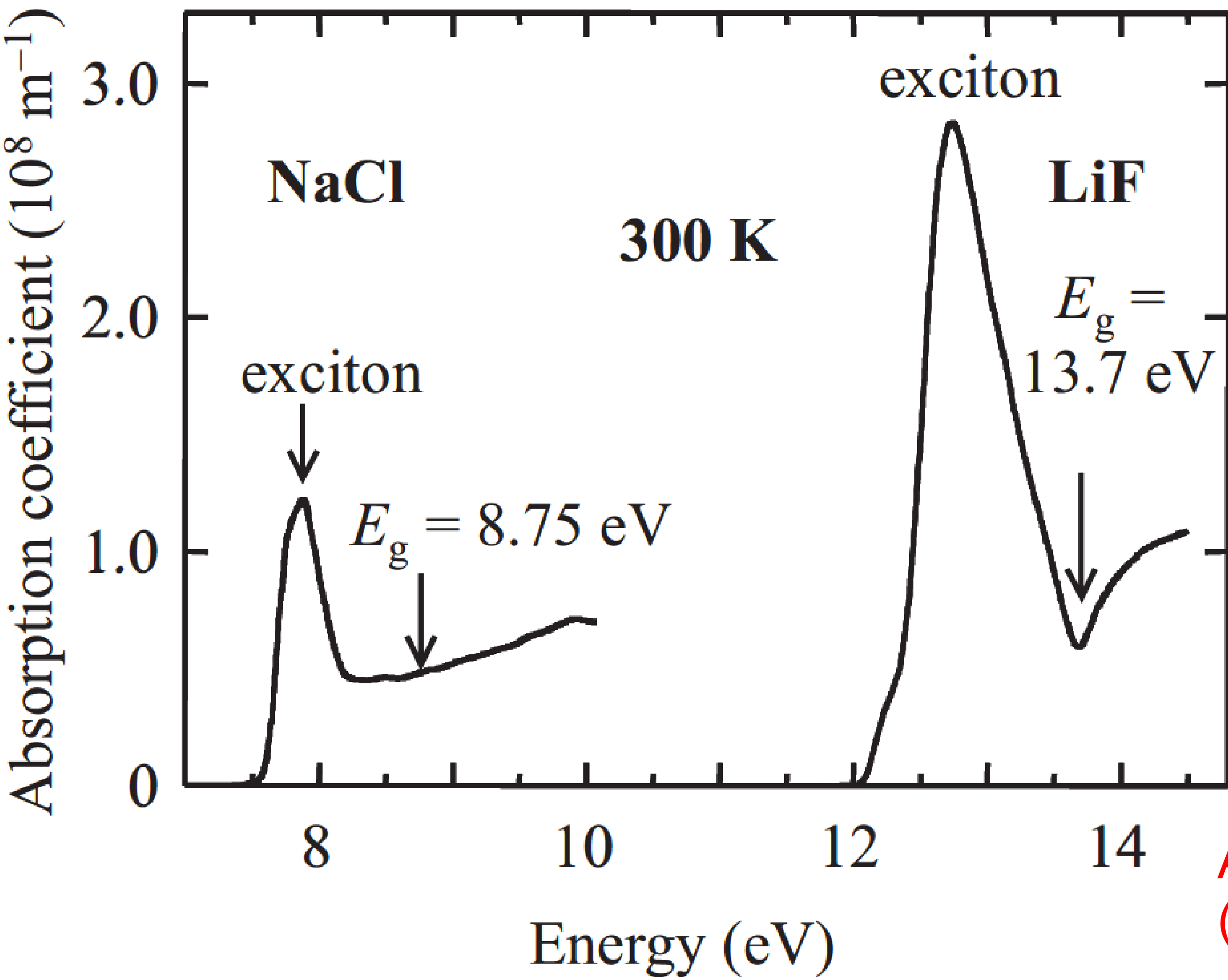


Non-linear effect.

Fox, Chapter 4

Fujiwara, Phys. Rev. B **71**, 075109 (2005)

Frenkel excitons in alkali halides



Crystal	E_g	E_1	E_b
KI	6.3	5.9	0.4
KBr	7.4	6.7	0.7
KCl	8.7	7.8	0.9
KF	10.8	9.9	0.9
NaI	5.9	5.6	0.3
NaBr	7.1	6.7	0.4
NaCl	8.8	7.9	0.9
NaF	11.5	10.7	0.8
CsF	9.8	9.3	0.5
RbF	10.3	9.5	0.8
LiF	13.7	12.8	1.9

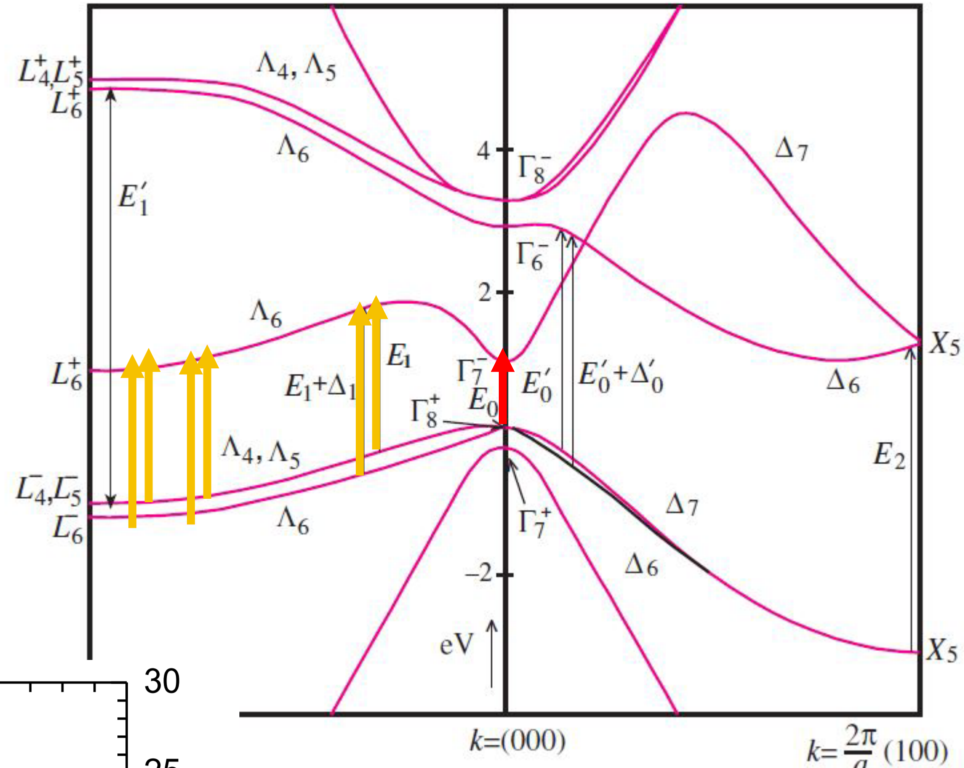
Also in rare gas crystals (Ne, Ar, Kr, Xe: 1–4 eV)

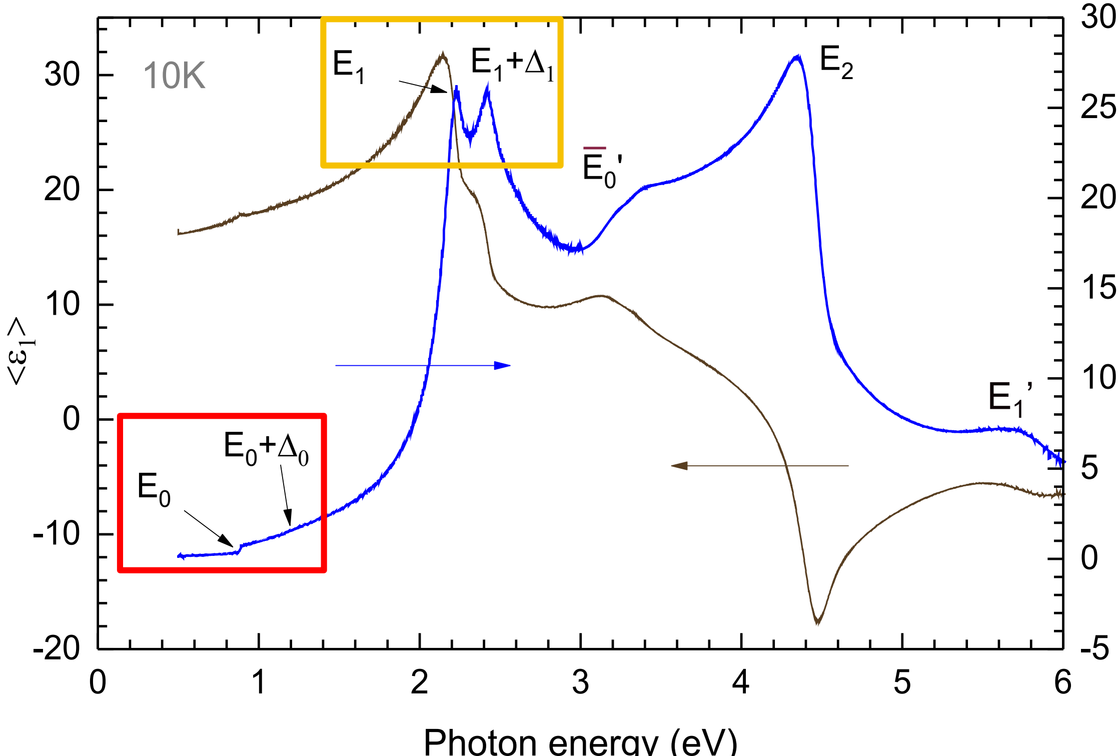
Fox, Chapter 4

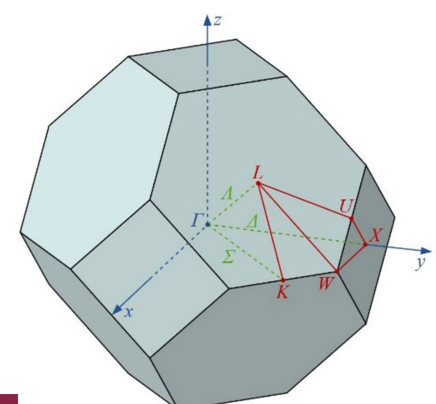
Critical Points in Germanium

- Structures in the dielectric function due to interband transitions
- Joint density of states
- Van Hove singularities

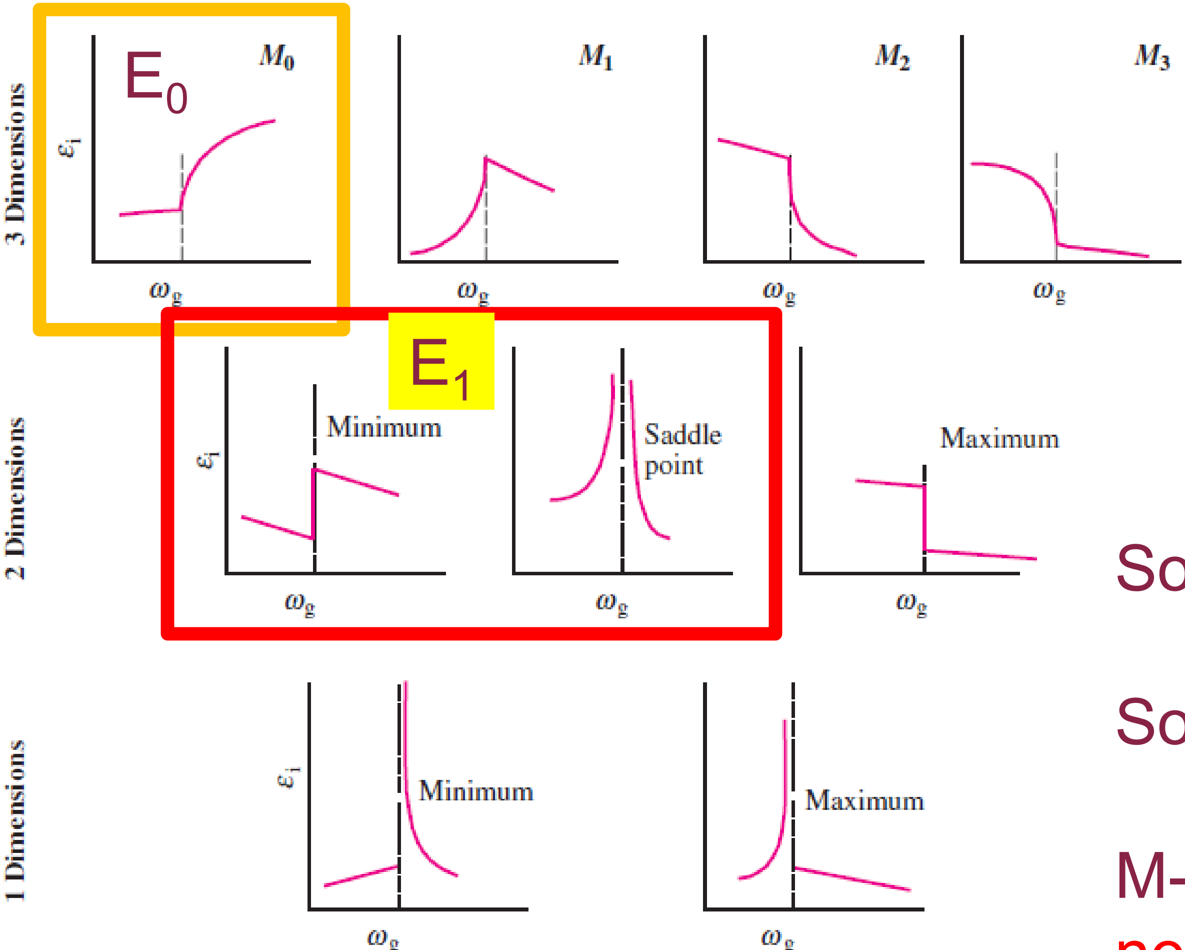
$$D_j(E_{CV}) = \frac{1}{4\pi^3}\int \frac{dS_k}{|\nabla_k(E_{CV})|}$$







Critical Points



$$E_{fi}(\vec{k}) = E_{fi}(\vec{k}_0) + \sum_{i=1}^{3} a_i (k_i - k_{0i})^2$$

Some a_i small or zero: 1D, 2D, 3D

Some a_i positive, some negative

M-subscript: Number of negative mass parameters

	Type	D_j $E < E_0$	D_j $E > E_0$
Three dimensions	M_0	0	$(E - E_0)^{1/2}$
	M_1	$C - (E_0 - E)^{1/2}$	C
	M_2	C	$C - (E - E_0)^{1/2}$
	M_3	$(E_0 - E)^{1/2}$	0
Two dimensions	M_0	0	C
	M_1	$-\ln(E_0 - E)$	$-\ln(E - E_0)$
	M_2	C	0
One dimension	M_0	0	$(E - E_0)^{-1/2}$
	M_1	$(E_0 - E)^{-1/2}$	0

Yu&Cardona
Dresselhaus, Chapter 17

Two-dimensional Bohr problem

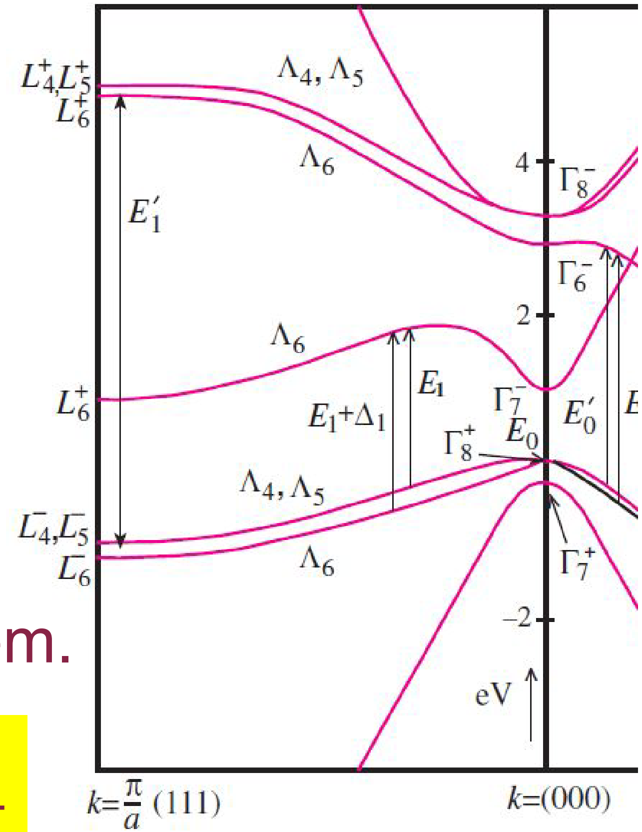
$$H=-\frac{\hbar^2}{2\mu_\perp}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)-\frac{\hbar^2}{2\mu_\parallel}\frac{\partial^2}{\partial z^2}-\frac{e^2}{\varepsilon_r r}$$

Assume that $\mu_{||}$ is infinite (separate term).

Use cylindrical coordinates.

Separate radial and polar variables.

Similar Laguerre solution as 3D Bohr problem.



$$a_X=\frac{4\pi\varepsilon_0\varepsilon_r\hbar^2 m_0}{\mu e^2}$$

$$R_X=\frac{\mu e^4}{2\hbar^2 m_0(4\pi\varepsilon_0\varepsilon_r)^2}$$

$$E_n=-\frac{R_X}{\left(n-\frac{1}{2}\right)^2},\qquad n=1,2,\ldots$$

Half-integral quantum numbers

M. Shinada and S. Sugano, J. Phys. Soc. Jpn. **21**, 1936 (1966).

Two-dimensional saddle-point excitons

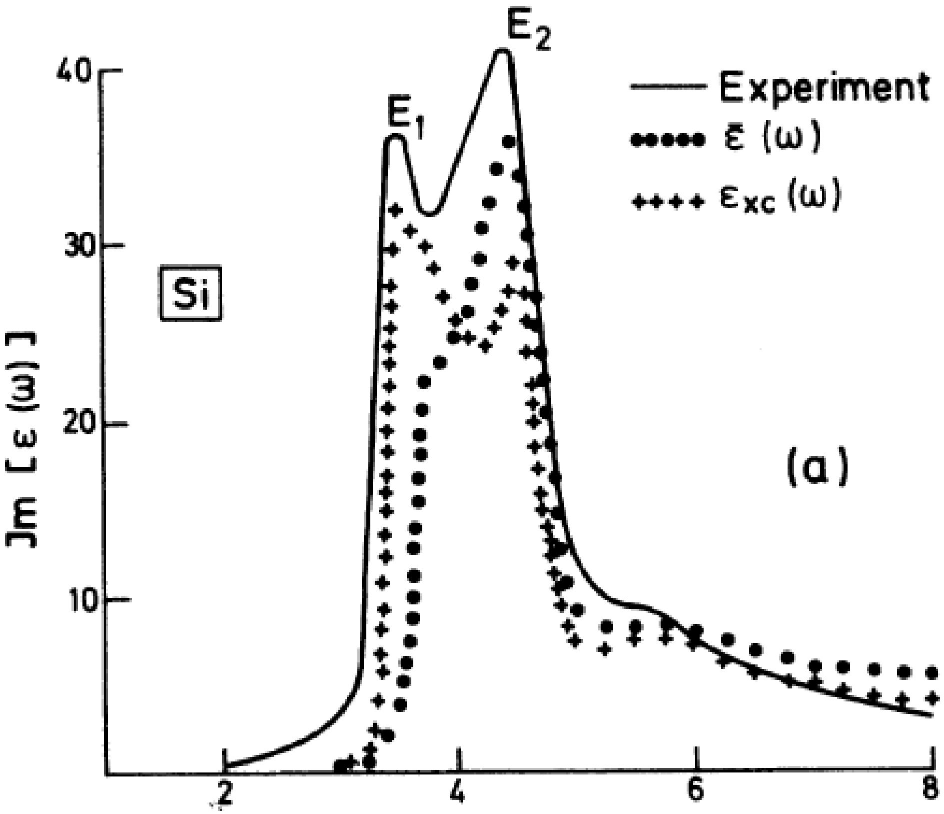
$$\varepsilon(E) = \frac{A}{(E+i\Gamma)^2}\{g[\xi(E+i\Gamma)] + g[\xi(-E-i\Gamma)] - 2g[\xi(0)]\}$$

$$g(\xi) = 2\ln(\xi) - 2\psi(\frac{1}{2} - \xi)$$

$$\psi(z) = \frac{d\ln\Gamma(z)}{dz}$$

$$\xi(z) = \sqrt{R_X/_{E_0 - z}}$$

$$A = \frac{\mu e^2}{\pi\varepsilon_0 m_0^2}|P|^2$$



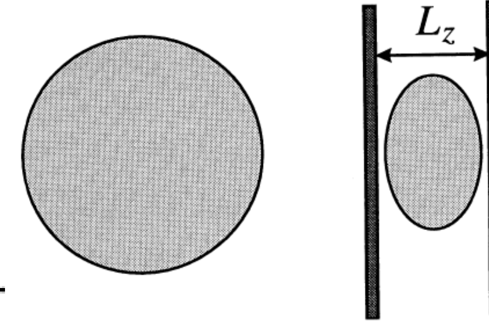
B. Velicky and J. Sak, phys. status solidi **16**, 147 (1966)
C. Tanguy, Solid State Commun. **98**, 65 (1996)
W. Hanke and L.J. Sham, Phys. Rev. B **21**, 4656 (1980)

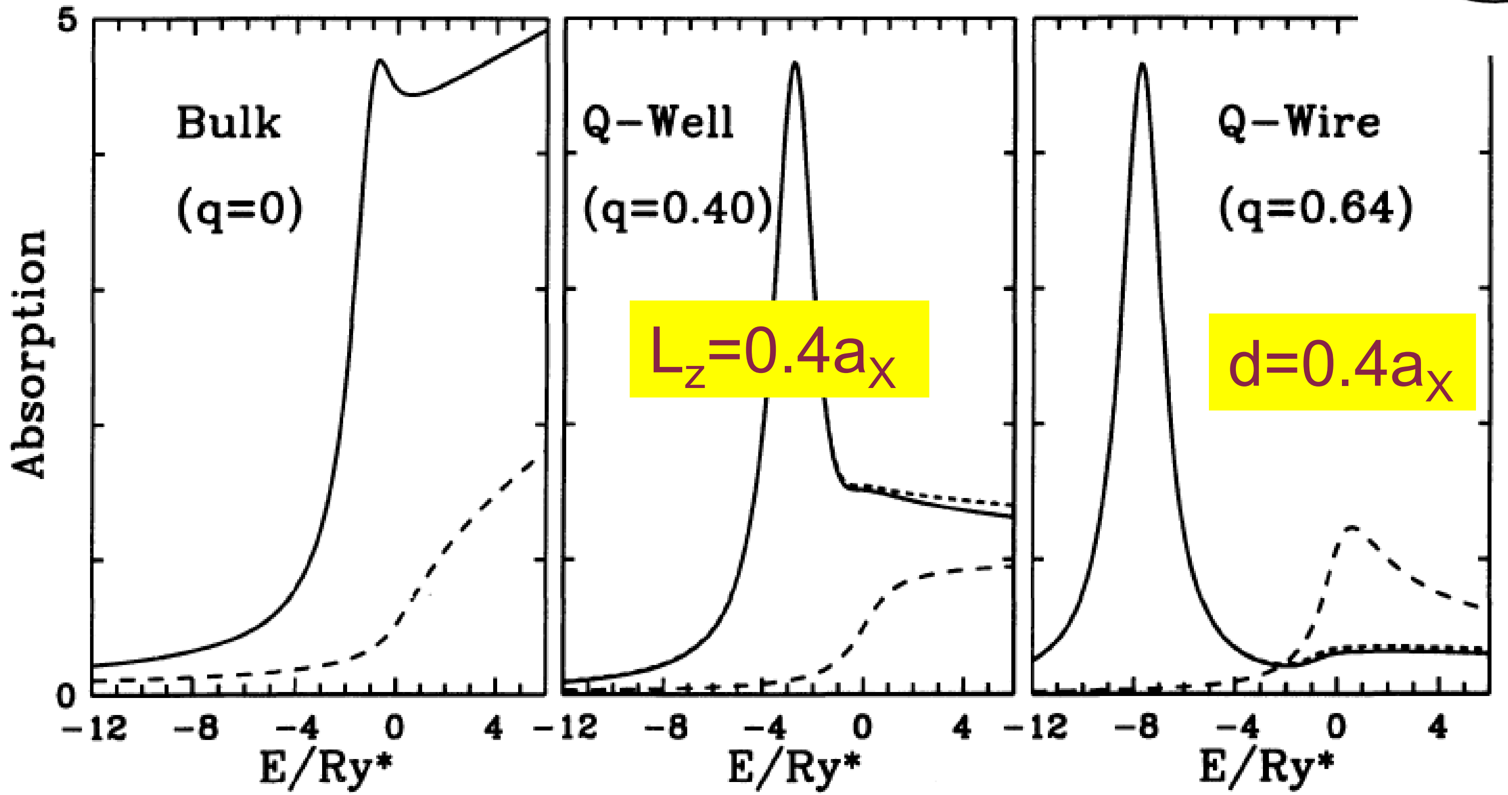
Excitons in Quantum Structures

$$E_n = -\frac{R_X}{(n-q)^2}$$

q=0.5 2D

q=0 3D





Electron-hole overlap is enhanced in quantum structures.

Excitonic effects (shift and enhancement) are stronger.

R. Zimmermann, Jpn. J. Appl. Phys. **34**, 228 (1995)

Summary

- Exciton: electron-hole pair bound by the Coulomb force.
- Excitonic effects enhance band gap absorption.
- Excitons can be ionized by electric fields, high temperature, or high carrier density.
- Excitonic effects stronger in low-dimensional materials.

What's next ???

11: Applications I

What would you like to see ?
Please send email to zollner@fzu.cz

Quantum structures (2D, 1D, 0D)

Defects

12: Applications II

Properties of thin films,
stress/strain, deformation potentials