# In This Lecture:

➢ **Excitons** in bulk

Excitonic Effects & Modulation of Optical Properties [SI Units]

➤Excitons are important from physical & technological points of view

➤There is an unimpeded steady increase of their importance

➤A very academic subject (say, biexcitons) becomes engineers' tool

in a few years!

➤Excitons are quite stable and can have a relatively long lifetime (ps to ns)

➤Excitons are the main mechanism for light emission in se/c's at low T

(where kT is less than the exciton binding energy), replaced by the free e-h

recombination at higher temperatures.

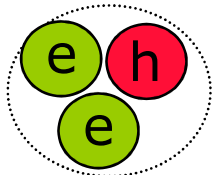➤The subject gained further importance with 2D materials (next lecture)

The Exciton Family

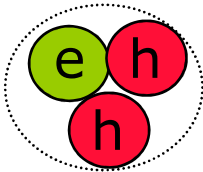Binding energy decreases
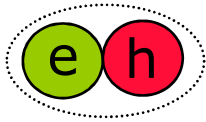
Exciton (X): a bound e-h pair
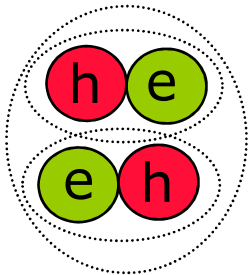
Biexciton (XX): a bound exciton pair

-ve Trion (X$^-$): a negatively charged exciton

+ve Trion (X$^+$): a positively charged exciton

*Sometimes a [huge] magnetic field is used to observe trions*

Two types of Excitons

Wannier (Mott) Exciton

Extends over many unit cells
Near band edge (CBM-VBM) treatment
EFA is applicaple, at least qualitatively

Frenkel Exciton

Localized to a few unit cell hence, delocalized
in k-space (requires full-band treatment)
for low-dielectric constant mat'ls where
screening is weak (organic molecules)

Ref: Singh
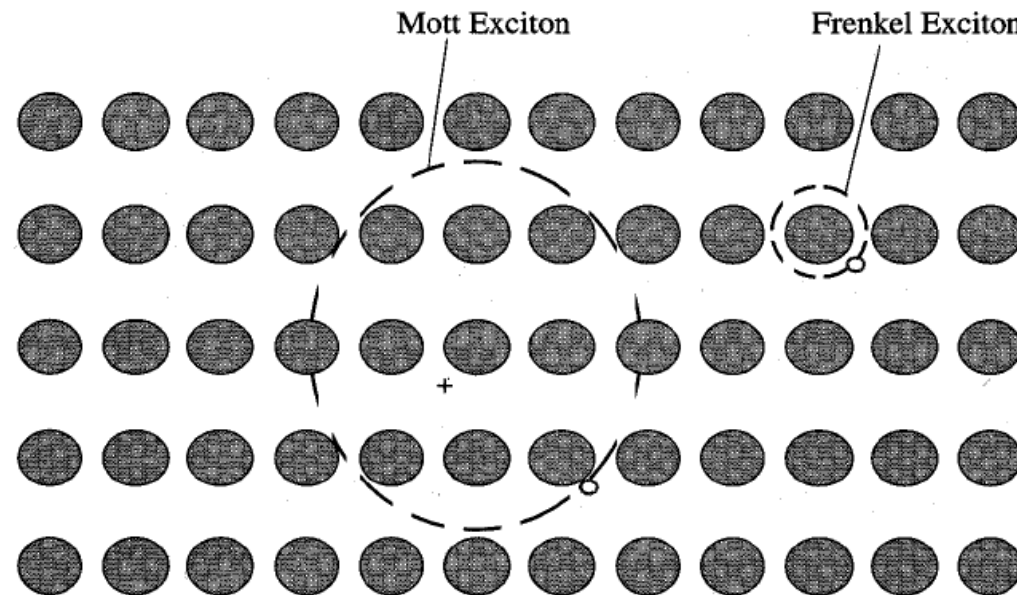
Excitons in Bulk

We shall be dealing with Wannier excitons in bulk [and in 2D] within EFA

For a qualitative feeling start with parabolic CB/VB

$$\left[-\frac{\hbar^2}{2m_e^*}\nabla_e^2 - \frac{\hbar^2}{2m_h^*}\nabla_h^2 - \frac{e^2}{4\pi\epsilon |\boldsymbol{r}_e - \boldsymbol{r}_h|} \right] \psi_{\text{ex}} = E\psi_{\text{ex}}$$

Two-body problem; introduce center of mass and relative variables:

$$\boldsymbol{R} = \frac{m_e^* \boldsymbol{r}_e + m_h^* \boldsymbol{r}_h}{m_e^* + m_h^*} \qquad \boldsymbol{r} = \boldsymbol{r}_e - \boldsymbol{r}_h$$

$$\boldsymbol{K} = \boldsymbol{k}_e - \boldsymbol{k}_h \qquad \boldsymbol{k} = \frac{m_e^* \boldsymbol{k}_e + m_h^* \boldsymbol{k}_h}{m_e^* + m_h^*}$$

The Hamiltonian then becomes:

center of mass   relative motion of e-h pair   reduced mass:

$$H = \frac{\hbar^2 K^2}{2(m_e^* + m_h^*)} + \left\{ \frac{\hbar^2 k^2}{2m_r^*} - \frac{e^2}{4\pi\epsilon |\boldsymbol{r}|} \right\} \qquad \frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

Effective in X condensation   Effective in X binding

Ref: Singh

Center of mass solution: $\psi_{cm} = e^{i\mathbf{K}\cdot\mathbf{R}}$ use $\mathbf{K}_{ex} = \mathbf{K}$

Relative motion part (EFA): $\left(\dfrac{\hbar^2 k^2}{2m_r^*} - \dfrac{e^2}{4\pi\epsilon\,|r|}\right) F(\mathbf{r}) = E F(\mathbf{r})$

The form of the complete solution including the cell-periodic parts:

$$\psi_{n\mathbf{K}_{ex}} = e^{i\mathbf{K}_{ex}\cdot\mathbf{R}}\, F_n(\mathbf{r})\, \phi_c(\mathbf{r}_e)\, \phi_v(\mathbf{r}_h)$$

Band edge
cell-periodic fn's

Bound-state
envelope fn
quantum label

Excitonic energy levels: $E_{n\mathbf{K}_{ex}} = E_n + \dfrac{\hbar^2}{2(m_e^* + m_h^*)} K_{ex}^2$

Kinetic en. of
center of mass

From analogy with
the hydrogen atom $E_n = -\dfrac{m_r^* e^4}{2(4\pi\epsilon)^2 \hbar^2}\dfrac{1}{n^2}$

R_{ex}: Excitonic Rydberg
for most se/c 2-25 meV

Ref: Singh

"Free states"

$E_{2K_{ex}}$

$E_{1K_{ex}}$

e and h wf's are still modified by the Coulomb attraction

E_{ex}

E_g

E_2

E_1

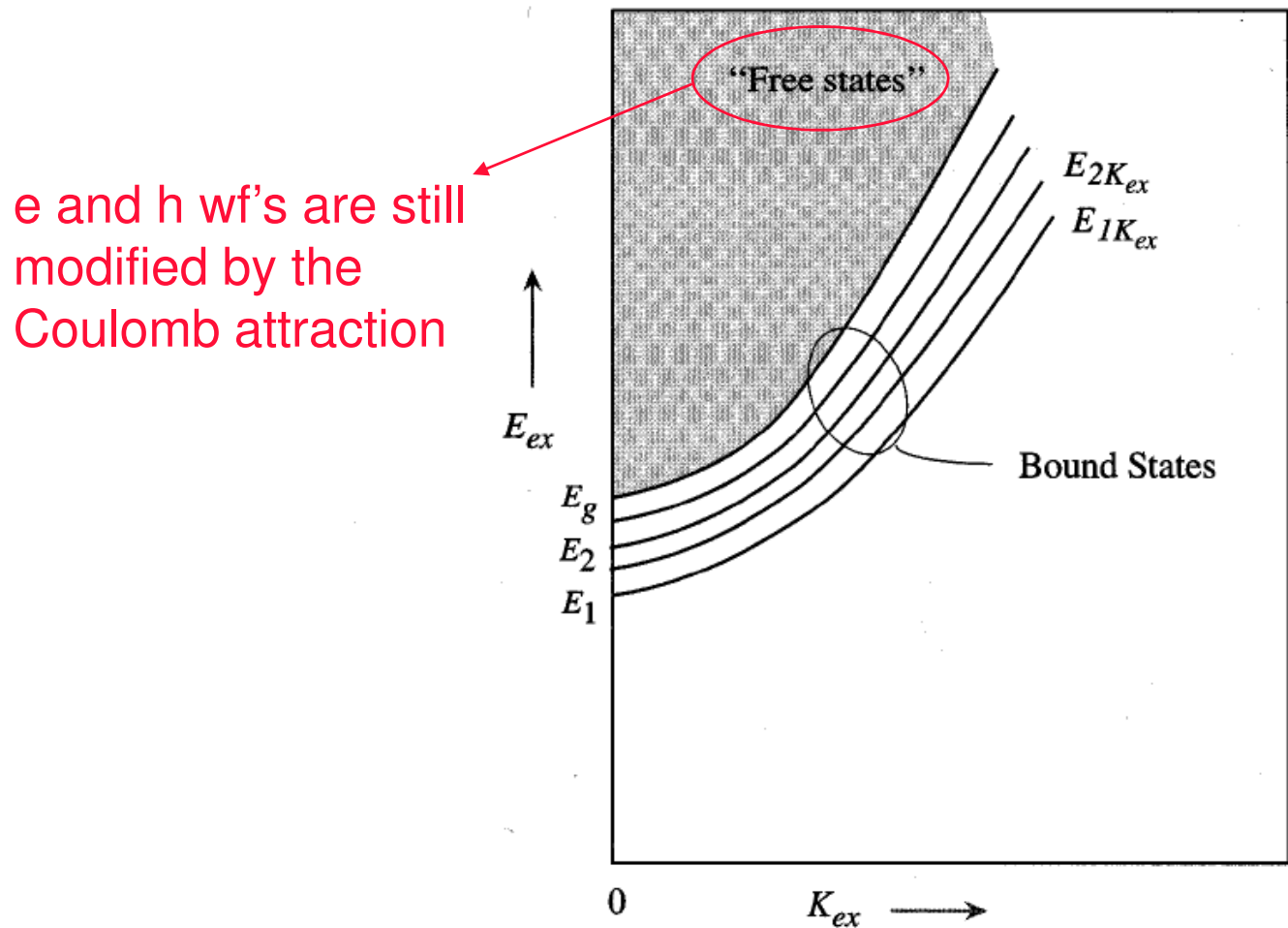Bound States

0

$K_{ex} \longrightarrow$

Figure 10.3: Dispersion curves for the electron-hole system in the exciton framework.

X and XX binding energies

Biexciton (XX) dispersion relation: $E_{XX}(K_{ex}) = 2\left(E_g - E_X^b\right) - E_{XX}^b + \dfrac{\hbar^2 K_{ex}^2}{4M_{ex}}$

Ref: Singh

A Bit More Refined Formulation:

Now, switch from the electron-hole picture to electron picture (either in CB or VB)

The Hamiltonian is given by:

$$H_e = H_0 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon |r_i - r_j|}$$
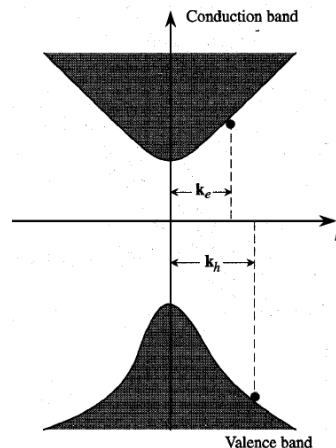
one-electron part

Exchange and correlation interactions are neglected

Due to invariance of the Hamiltonian under DLV translation:

$$\psi_{ex}(r_1 + R, r_2 + R, r_3 + R, \ldots) = e^{iK_{ex} \cdot R} \psi_{ex}(r_1, r_2, r_3, \ldots)$$

Expand the X state in terms of the basis fn's: $\Phi_{c,k_e,S_e;v,k_h,S_h}$

e labels   h labels

Figure 10.4: Schematic picture of an exciton in the Bloch representation. The state $\Phi_{c,k_e,S_e;v,k_h,S_h}$ represents an extra electron of wave vector k_e and spin S_e in the conduction band and a hole of wave vector k_h and spin S_h in the valence band.

Ref: Singh

However, we need to represent the center of mass wavevector of $\mathbf{K}_{ex}$ which requires the expansion to be written as:

$$\psi_{ex}^{n\ell m} = \sum_{\mathbf{k}} A_{n\ell m}(\mathbf{k}) \, \Phi_{c,\mathbf{k}+\mathbf{K}_{ex}/2,S_e;v,\mathbf{k}-\mathbf{K}_{ex}/2,S_h}^{n\ell m}$$

X quantum labels
principal/angular/magnetic

expansion
coefficients

Now switch to real-space via Fourier transforming variables & eq's

Real-space envelope fn: $F_{n\ell m}(\mathbf{r}) = \sum_{\mathbf{k}} A_{n\ell m}(\mathbf{k}) \, e^{i\mathbf{k}\cdot\mathbf{r}}$

Hamiltonian for the envelope part becomes:

$$\left[E_{cv}(-i\nabla, \mathbf{K}_{ex}) - \frac{e^2}{4\pi\epsilon r} \right] F_{n\ell m}(\mathbf{r}) = E_{ex} F_{n\ell m}(\mathbf{r})$$

Expand $E_{cv}(-i\nabla, \mathbf{K}_{ex}) = E_c\left(\mathbf{k} + \dfrac{\mathbf{K}_{ex}}{2}\right) - E_v\left(\mathbf{k} - \dfrac{\mathbf{K}_{ex}}{2}\right)$

in powers of $\mathbf{k} \to -i\nabla$

Ref: Singh

Recall the solution for simple parabolic (uncoupled) bands

$$E_n^{ex} = E_g - \frac{m_r^* e^4}{2\hbar^2 (4\pi\epsilon)^2} \frac{1}{n^2}$$

$$= E_g - \underbrace{\frac{R_{ex}}{n^2}}_{\text{X binding energy}}$$

Exciton Rydberg (3D)

For ε that goes in R_{ex}, use the static dielectric constant at low carrier densities
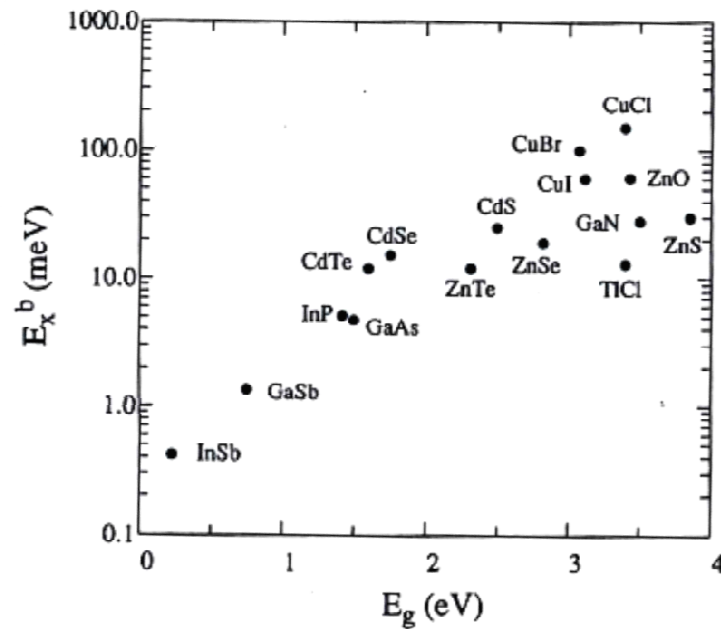
Under the same parabolic band assumption and static screening, the X envelope fn is that of the H atom, but with ε and m_r:

$$F_{100}(\mathbf{r}) = \frac{1}{\sqrt{\pi a_{ex}^3}} e^{-r/a_{ex}} \qquad \text{where} \quad a_{ex} = \frac{\varepsilon m_0}{\varepsilon_0 m_r^*} a_B \longrightarrow \text{Bohr radius } 0.529 \text{ Å}$$

Excitonic Bohr radius (3D)
gives an estimate of X wf spread
and the validity of EFA

Ref: Singh

Measured Bulk Exciton Binding Energy vs Gap Energy


Ref: Klingshirn

Excitonic Absorption in Bulk: X-polaritons

As the X is an e-h pair, it constitutes an electric dipole which can efficiently couple to electromagnetic wave, forming the new quasi-particle: so-called **exciton-polaritons**
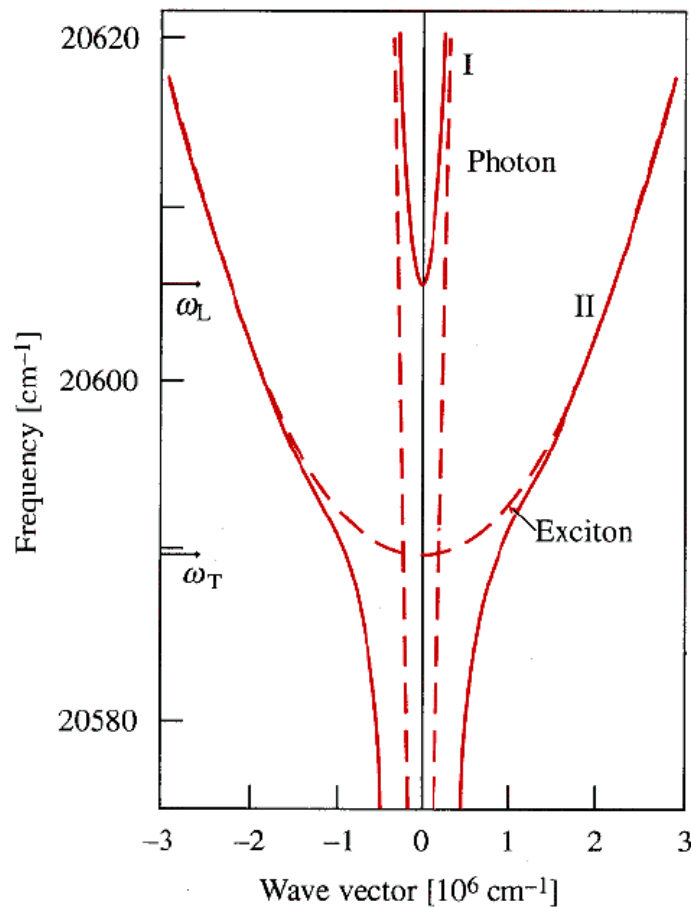
Fig. 6.22. Dispersion curves of a "bare" photon, a "bare" exciton (*dashed curves*) and an exciton-polariton (*solid curves* labeled I and II) for the A exciton in CdS. The curves labeled I and II are usually referred to as the "upper" and "lower" branches of the polariton [6.43]

Ref: Yu-Cardona
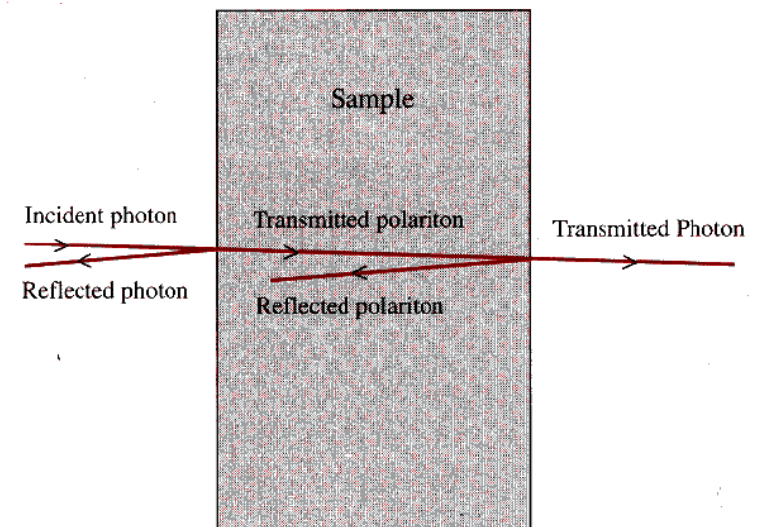
Exciton-polaritons (cont'd)

➤ As Xs travel in the se/c they radiate EM waves, in turn, EM waves excite Xs

➤ In principle, there is no way to separate the X from the EM wave, hence X-polaritons!

➤ Within this picture, <u>no optical absorption inside such a medium would take place</u>

➤ However, there are scattering mechanisms which can take away energy from the
X-polaritons; especially via the phonon-X coupling

➤ Hence, we shall assume that X damping constant is larger than the X-photon
interaction. In this approximation, one can replace polaritons by the "bare" Xs and
photons. Whenever photon→ X, it will lose its energy completely inside the
medium via X damping processes

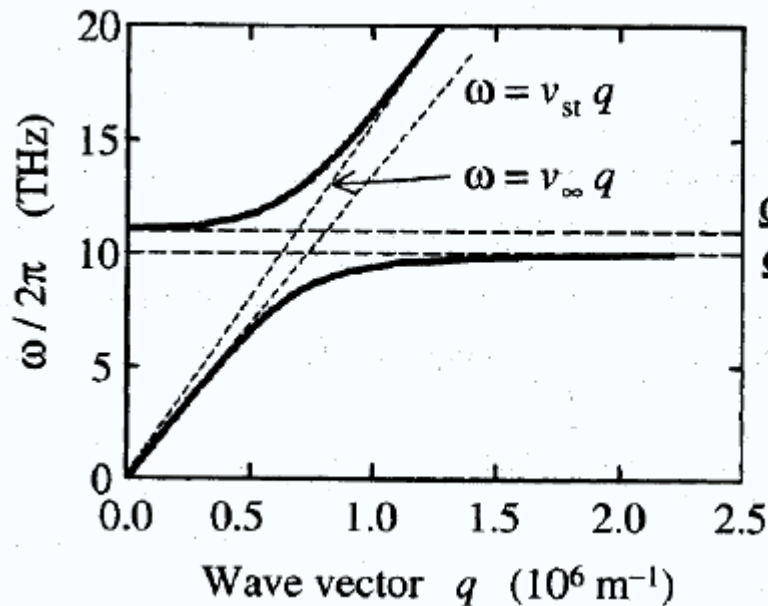*In this regime one can ignore the X-polariton effects altogether!*

Phonon-Polaritons (a digression)

For completeness it is good to know that another kind of polariton can also be formed with the coupling of photons to polar phonon branches in ionic se/c's.
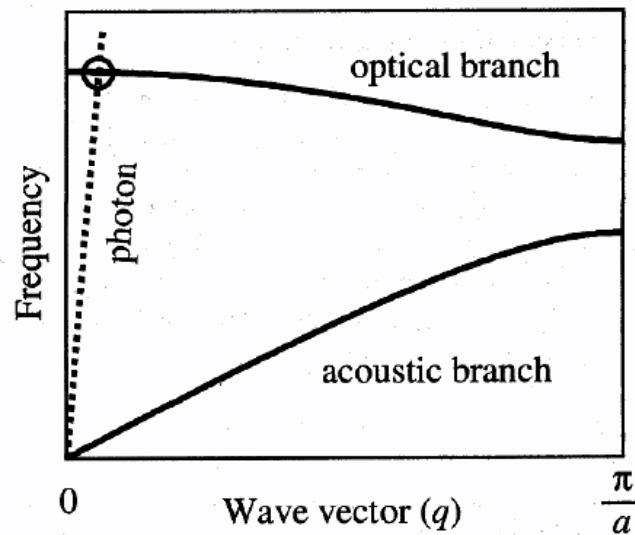
Transverse and Longitudinal phonon polarizations exist (not shown).

Fig. 10.2 Dispersion curves for the acoustic and optical phonon branches in a typical crystal with a lattice constant of a. The dispersion of the photon modes in the crystal is shown by the dotted line.

Ref: Fox

Fig. 10.6 Polariton dispersion predicted from eqn 10.19 with ϵ_r given by eqn 10.16. The curves are calculated for a crystal with $\nu_{TO} = 10$ THz, $\epsilon_{st} = 12.1$ and $\epsilon_\infty = 10$. The asymptotic velocities ν_{st} and ν_∞ are equal to $c/\sqrt{\epsilon_{st}}$ and $c/\sqrt{\epsilon_\infty}$ respectively.

$\Omega_{LO}/2\pi$ $\left.\begin{array}{c}\end{array}\right\}$ $\varepsilon_{eff} < 0$ **All incident**
$\Omega_{TO}/2\pi$ $\left.\begin{array}{c}\end{array}\right\}$ **EM waves reflected**

LO phonons do not show any dispersion because they do not couple to (<u>transverse</u>) EM waves

Experiment:
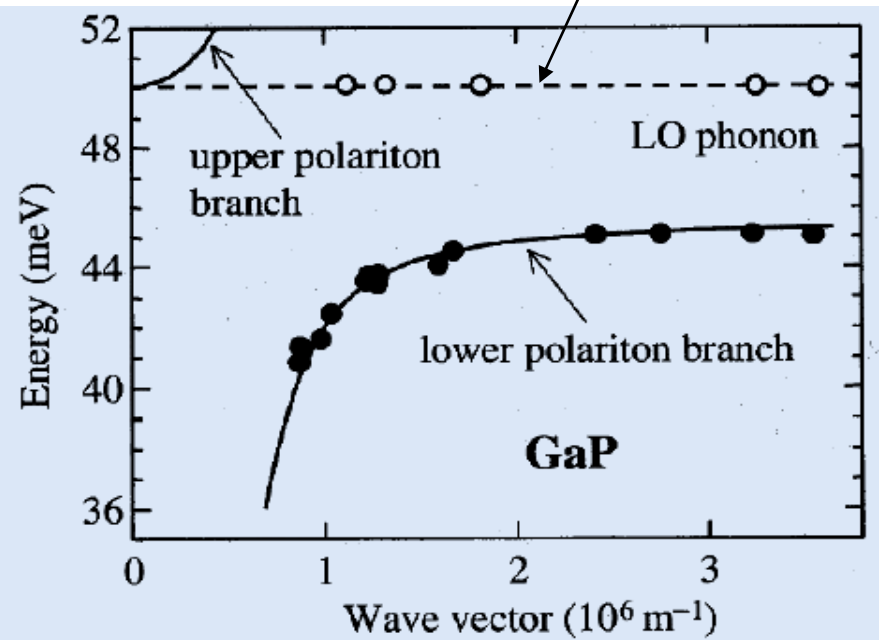
Fig. 10.7 Dispersion of the TO and LO phonons in GaP measured by Raman scattering. The solid lines are the predictions of the polariton model with $h\nu_{TO} = 45.5$ meV, $\epsilon_\infty = 9.1$ and $\epsilon_{st} = 11.0$. After [3], copy-

Ref: Fox

Excitonic Absorption in Bulk

The bulk optical absorption profile will be modified due to the presence of X as:

➤ Just below the band gap: sharp absorption lines

➤ Just above the band gap: strong enhancement of absorption (esp. in 3D)

Recall the bulk absorption coef. w/o X:

$$\alpha(\hbar\omega) = \frac{\pi e^2}{m_0^2 c n_r \epsilon_0} \frac{\hbar}{\hbar\omega} \int \frac{2\, d^3 k}{(8\pi^3)} |a \cdot p_{\text{if}}(k)|^2 \; \delta(E_c(k) - E_v(k) - \hbar\omega)$$

For allowed transitions we can assume that p_{if} is independent of k:

$$
\begin{aligned}
\alpha(\hbar\omega) &= 0 && \text{if } \hbar\omega < E_g \\
&= \frac{\pi e^2}{m^2 c n_r \epsilon_0} \frac{\hbar}{\hbar\omega} |a \cdot p_{\text{if}}|^2 \cdot N_{\text{cv}}(\hbar\omega) && \text{if } \hbar\omega \geq E_g
\end{aligned}
$$

JDOS: dictates the energy dependence

Ref: Singh

For the contribution of X, consider a transition from the ground-state (all e's In the VB) to the excited X state; using Fermi's golden rule:

$$W(\psi_0 \rightarrow \psi_{K_{ex}}) = \frac{2\pi}{\hbar} \left(\frac{eA}{m_0}\right)^2 \delta_{K_{ex}} \left| \sum_k A(k)\, a \cdot p_{cv}(k) \right|^2 \delta(E_{ex} - E_0 - \hbar\omega)$$

X expansion coefficients   ground-state energy

Again assume that p_{cv} is independent of k:

$$W(\psi_0 \rightarrow \psi_{K_{ex}}) = \frac{2\pi}{\hbar} \left(\frac{eA}{m_0}\right)^2 \delta_{K_{ex}} |a \cdot p_{if}(0)|^2 \left| \sum_k A(k) \right|^2 \delta(E_{ex} - E_0 - \hbar\omega)$$

Recall Fourier transform relation:

$$F_{n\ell m}(r) = \sum_k A_{n\ell m}(k)\, e^{ik\cdot r} \left. \right\} \qquad F_{n\ell m}(0) = \sum_k A_{n\ell m}(k)$$

Recall from H-atom problem that $F_{nlm}(0)$ is nonzero only for *s*-type states, and in general,

$$F_{n\ell m}(0) = \frac{1}{\sqrt{\pi a_{ex}^3 n^3}}\, \delta_{\ell,0}\delta_{m,0}$$

Ref: Singh

Thus the absorption rate is given by

$$W(\psi_0 \to \psi_{\mathbf{K}_{ex}}) = \frac{2\pi}{\hbar} \left(\frac{eA_0}{m_0}\right)^2 \delta_{\mathbf{K}_{ex}} |\mathbf{a} \cdot \mathbf{p}_{if}(0)|^2 \frac{\delta(E_{ex}^n - E_0 - \hbar\omega)}{\pi a_{ex}^3 n^3}$$

The transition strength decreases as $1/n^3$
$2s$, $3s$,… progressively much weaker than $1s$

If we compare with the ordinary
Interband expression, we realize that

$$N_{cv}(\hbar\omega) \to \frac{\delta(E_{ex}^n - E_0 - \hbar\omega)}{\pi a_{ex}^3 n^3}$$

Include a Gaussian broadening:

$$\delta(\hbar\omega - E) \to \frac{1}{\sqrt{1.44\pi}\,\sigma} \exp\left(\frac{-(\hbar\omega - E)^2}{1.44\,\sigma^2}\right)$$

Then, for the ground-state $n=1$ X, the absorption coefficient becomes

$$\alpha(\hbar\omega) = \frac{\pi e^2 \hbar}{2 n_r \epsilon_0 c m_0 (\hbar\omega)} \frac{2|p_{cv}|^2}{m_0} \left(a_p\right) \left(\frac{1}{\sqrt{1.44\pi}} \frac{1}{\sigma} \frac{1}{\pi a_{ex}^3} \exp\left(\frac{-(\hbar\omega - E_{ex})^2}{1.44\sigma^2}\right)\right)$$

polarization projection;
2/3 for unpolarized light

Ref: Singh

What about just at the band edge?

As one approaches the band edge, the X lines become closer and closer

$$E_n^{ex} = E_g - \frac{R_{ex}}{n^2}$$

even though each transition becomes weaker and weaker; hence, the absorption over an infinitesimal energy range reaches a finite value. In fact, the concept the DOS of $K_{ex}=0$ states becomes a meaningful concept. Using the above expression, the DOS becomes:

$$D_{ex}(E) = 2\frac{\partial n}{\partial E}$$

instead of k

$$= \frac{n^3}{R_{ex}}$$

Optically active states

E_g

0 K_{ex}
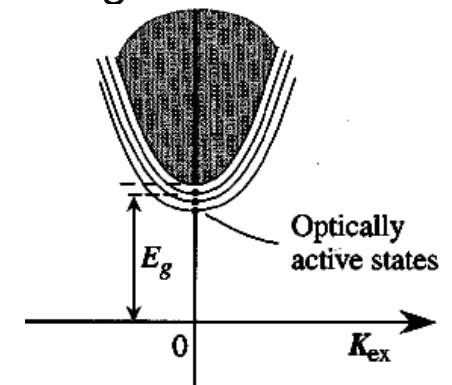
So, extend the transition rate expression by including a final density of excitonic states

$$W(\psi_0 \rightarrow \psi_{ex}) = \frac{2\pi}{\hbar}\left(\frac{eA_0}{m_0}\right)^2 \delta_{\mathbf{K}_{ex}} |a \cdot p_{if}(0)|^2 \left|\sum_n \sum_k A(k)\right|^2 \delta\left(E_{ex}^n - E_0 - \hbar\omega\right)$$

$$= \frac{2\pi}{\hbar}\left(\frac{eA_0}{m_0}\right)^2 |a \cdot p_{if}(0)|^2 \frac{1}{\pi a_{ex}^3}\frac{1}{R_{ex}}$$

Ref: Singh

Near the band edge the absorption coef. becomes

$$\alpha_{ex}(\hbar\omega \approx E_g) = \alpha_F \cdot \frac{2\pi\, R_{ex}^{1/2}}{(\hbar\omega - E_g)^{1/2}}$$

w/o X coef.
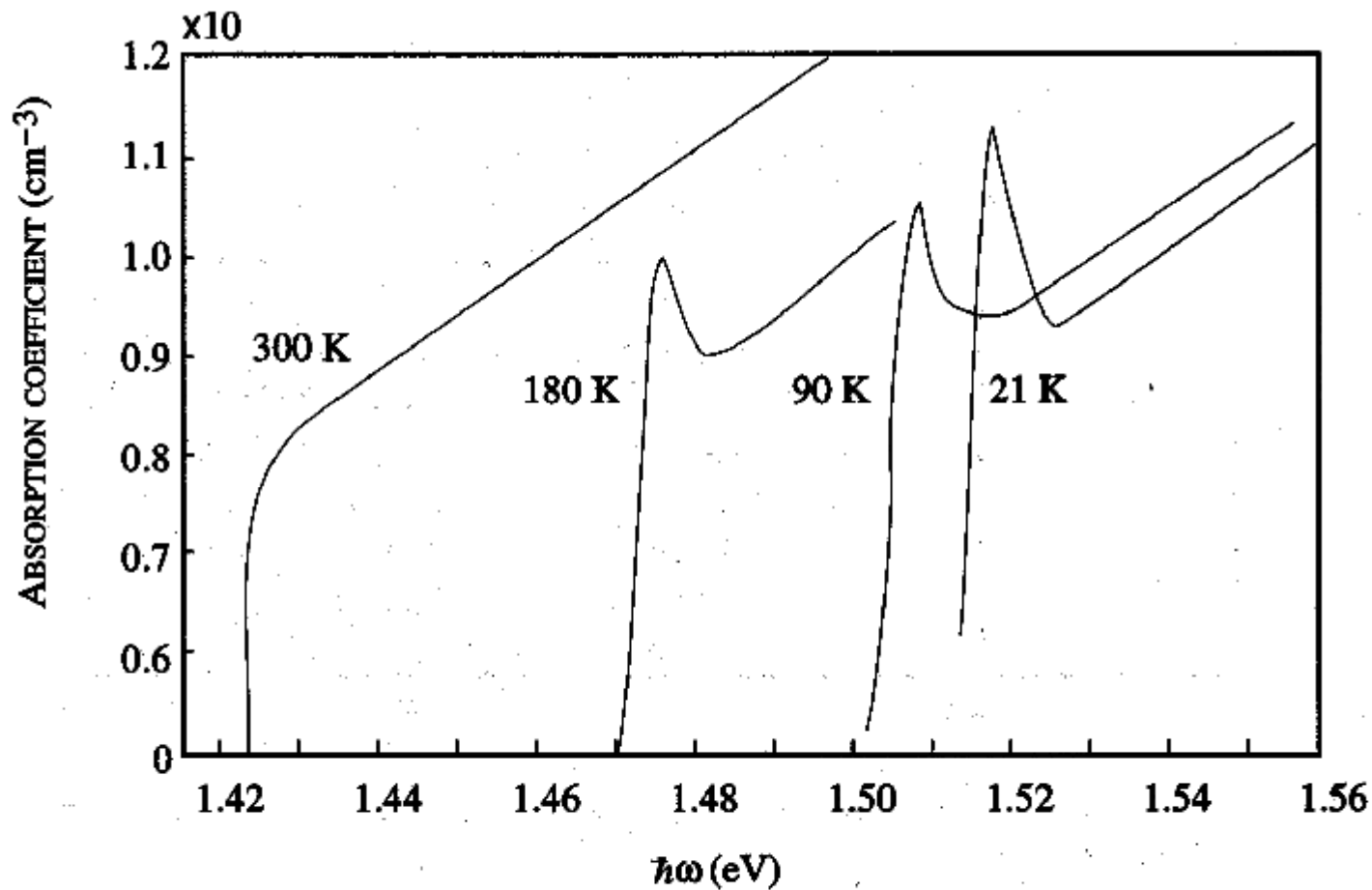
Most important effect is that
it goes to a constant at the band edge

Biexciton &
trions visible in
low-dimensions
(not in bulk)
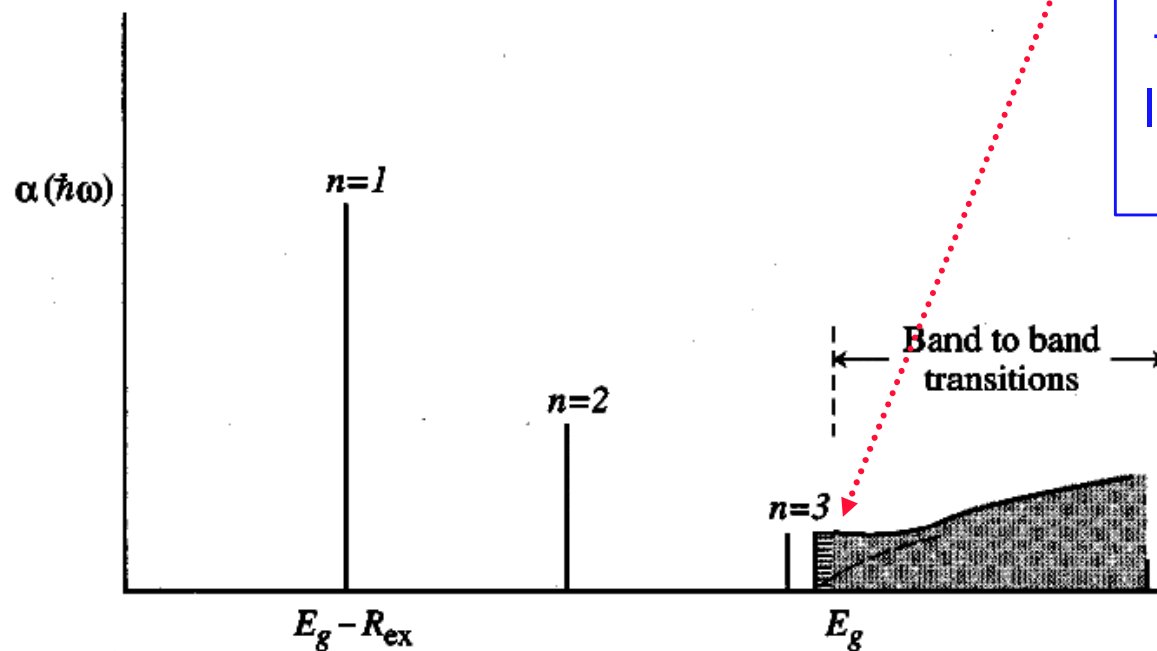
Figure 10.6: A schematic picture of the absorption spectra with (solid line) and without (dashed line) excitonic effects.

Ref: Singh

Effect of Temperature

Figure 10.7: Typical optical transitions GaAs. As can be seen, the excitonic peak essentially merges with the band-to-band absorption onset at room temperature. (see M.D. Sturge, *Physical Review*, **127**, 768 (1962).)

Ref: Singh