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

- **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 applicable, 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

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

\[
\begin{align*}
R &= \frac{m_e r_e + m_h r_h}{m_e + m_h} \\
K &= k_e - k_h
\end{align*}
\]

The Hamiltonian then becomes:

\[
H = \frac{\hbar^2 K^2}{2(m_e^* + m_h^*)} + \left\{ \frac{\hbar^2 k^2}{2m^*_r} - \frac{e^2}{4\pi\varepsilon |r|} \right\}
\]

Reduced mass:

\[
\frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_h}
\]

Effective in X condensation
Effective in X binding

Ref: Singh
Center of mass solution: \[ \psi_{\text{cm}} = e^{iK \cdot R} \] use \[ K_{\text{ex}} = K \]

Relative motion part (EFA): \[ \left( \frac{\hbar^2 k^2}{2m^*_r} - \frac{e^2}{4\pi\varepsilon |r|} \right) F(r) = EF(r) \]

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

\[
\psi_{nK_{\text{ex}}} = e^{iK_{\text{ex}} \cdot R} F_n(r) \phi_c(r_e) \phi_v(r_h)
\]

- Bound-state envelope fn
- quantum label

- Band edge
- cell-periodic fn's

Excitonic energy levels:

\[
E_{nK_{\text{ex}}} = E_n + \frac{\hbar^2}{2(m^*_e + m^*_h)} K_{\text{ex}}^2
\]

From analogy with the hydrogen atom

\[
E_n = -\frac{m^*_r e^4}{2(4\pi\varepsilon)^2 \hbar^2} \frac{1}{n^2}
\]

- Kinetic en. of center of mass

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

Ref: Singh
e and h wf’s are still modified by the Coulomb attraction

Biexciton (XX) dispersion relation: 

\[ E_{XX}(K_{ex}) = 2\left(E_g - E_X^b\right) - E_{XX}^b + \frac{\hbar^2 K_{ex}^2}{4M_{ex}} \]

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:

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

Due to invariance of the Hamiltonian under DLV translation:

$$\psi_{ex}(r_1 + R, r_2 + R, r_3 + R, \ldots) = e^{i\mathbf{K}_{ex} \cdot \mathbf{R}} \psi_{ex}(r_1, r_2, r_3, \ldots)$$

Expand the X state in terms of the basis fn’s:

$$\Phi_{c, k_e, S_e; v, k_h, S_h}$$

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.
However, we need to represent the center of mass wavevector of $K_{ex}$ which requires the expansion to be written as:

$$
\psi_{ex}^{nlm} = \sum_{k} A_{nlm}(k) \Phi_{c,k+k_{ex}/2,S_e;v,k-K_{ex}/2,S_h}^{nlm}
$$

X quantum labels principal/angular/magnetic expansion coefficients

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

Real-space envelope fn: $$F_{nlm}(r) = \sum_{k} A_{nlm}(k) e^{ik \cdot r}$$

Hamiltonian for the envelope part becomes:

$$\left[ E_{cv}(-i\nabla, K_{ex}) - \frac{e^2}{4\pi \epsilon \rho} \right] F_{nlm}(r) = E_{ex} F_{nlm}(r)$$

Expand $$E_{cv}(-i\nabla, K_{ex}) = E_c(k + \frac{K_{ex}}{2}) - E_v(k - \frac{K_{ex}}{2})$$

in powers of $k \rightarrow -i\nabla$

Ref: Singh
Recall the solution for simple parabolic (uncoupled) bands

\[ E_{n}^{ex} = E_{g} - \frac{m_{r}^{*}e^{4}}{2\hbar^{2}(4\pi\varepsilon)^{2}} \left( \frac{1}{n^{2}} \right) \]

For \( \varepsilon \) 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 \( \varepsilon \) and \( m_{r}^{*} \):

\[ r_{0}^{*} \]

\[ a_{ex} = \frac{\varepsilon m_{0}^{*}}{\varepsilon_{0} m_{r}^{*}} a_{B} \]

Bohr radius 0.529 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, no optical absorption inside such a medium would take place.
- 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.

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
ε_{eff} < 0  All incident EM waves reflected

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

Experiment:

**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 ω_{TO} = 10 THz, ε_{st} = 12.1 and ε_{∞} = 10. The asymptotic velocities v_{st} and v_{∞} are equal to c/\sqrt{ε_{st}} and c/\sqrt{ε_{∞}} respectively.

**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, ε_{∞} = 9.1 and ε_{st} = 11.0. After [3], copy.
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:

\[
\alpha(\hbar\omega) = \frac{\pi e^2}{m_0^2 c n_r \varepsilon_0} \frac{\hbar}{\hbar \omega} \int \frac{2 \, d^3 k}{(8\pi^3)} |a \cdot p_{if}(k)|^2 \delta(E_c(k) - E_v(k) - \hbar\omega)
\]

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

\[
\alpha(\hbar\omega) = \begin{cases} 0 & \text{if } \hbar\omega < E_g \\ \frac{\pi e^2}{m^2 c n_r \varepsilon_0} \frac{\hbar}{\hbar \omega} |a \cdot p_{if}|^2 \cdot N_{cv}(\hbar\omega) & \text{if } \hbar\omega \geq E_g \end{cases}
\]

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:

\[ W(\psi_0 \rightarrow \psi_{K_{\text{ex}}}) = \frac{2\pi}{\hbar} \left( \frac{eA}{m_0} \right)^2 \delta_{K_{\text{ex}}} \left| \sum_k A(k) \mathbf{a} \cdot \mathbf{p}_{cv}(k) \right|^2 \delta(E_{\text{ex}} - E_0 - \hbar\omega) \]

X expansion coefficients
ground-state energy

Again assume that \( \mathbf{p}_{cv} \) is independent of \( k \):

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

Recall Fourier transform relation:

\[ F_{nlm}(r) = \sum_k A_{nlm}(k) e^{i k \cdot r} \]

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

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

Ref: Singh
Thus the absorption rate is given by

$$W(\psi_0 \rightarrow \psi_{K_{ex}}) = \frac{2\pi}{\hbar} \left( \frac{eA_0}{m_0} \right)^2 \delta_{K_{ex}} |\alpha \cdot p_{if}(0)|^2 \frac{\delta\left( E_{ex}^n - E_0 - \hbar\omega \right)}{\pi \alpha_{ex}^3 n^3}$$

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

$$N_{cv}(\hbar\omega) \rightarrow \frac{\delta\left( E_{ex}^n - E_0 - \hbar\omega \right)}{\pi \alpha_{ex}^3 n^3}$$

Include a Gaussian broadening:

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

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

$$\alpha(\hbar\omega) = \frac{\pi e^2 \hbar}{2n_0 \varepsilon_0 cm_0 (\hbar\omega)} \frac{2 |p_{cv}|^2}{m_0} \alpha_P \left( \frac{1}{\sqrt{1.44\pi}} \frac{1}{\sigma} \frac{1}{\pi \alpha_{ex}^3} \exp \left( -\frac{(\hbar\omega - E_{ex})^2}{1.44 \sigma^2} \right) \right)$$

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:

\[
D_{ex}(E) = 2n^3 \frac{\partial n}{\partial E} \frac{\delta(K_{ex})}{\delta(E_{ex})} = \frac{n^3}{R_{ex}}
\]

So, extend the transition rate expression by including a final density of excitonic states

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

\[
= \frac{2\pi}{\hbar} \left( \frac{eA_0}{m_0} \right)^2 |\mathbf{a} \cdot \mathbf{p}_{if}(0)|^2 \frac{1}{\pi a_{ex}^3} \frac{1}{R_{ex}}
\]

Ref: Singh
Near the band edge the absorption coef. becomes

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

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