Lecture on

Semiconductors / 半導体

(Physics of semiconductors)

2021.5.12 Lecture 05

10:25 – 11:55

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Review of lecture in the last week

Doping and carrier distribution

Temperature dependence of carrier concentration

Exciton

Chapter 4 Optical properties (bulk)

Quantization of electromagnetic field

Number state, coherent state

Optical response of two-level system

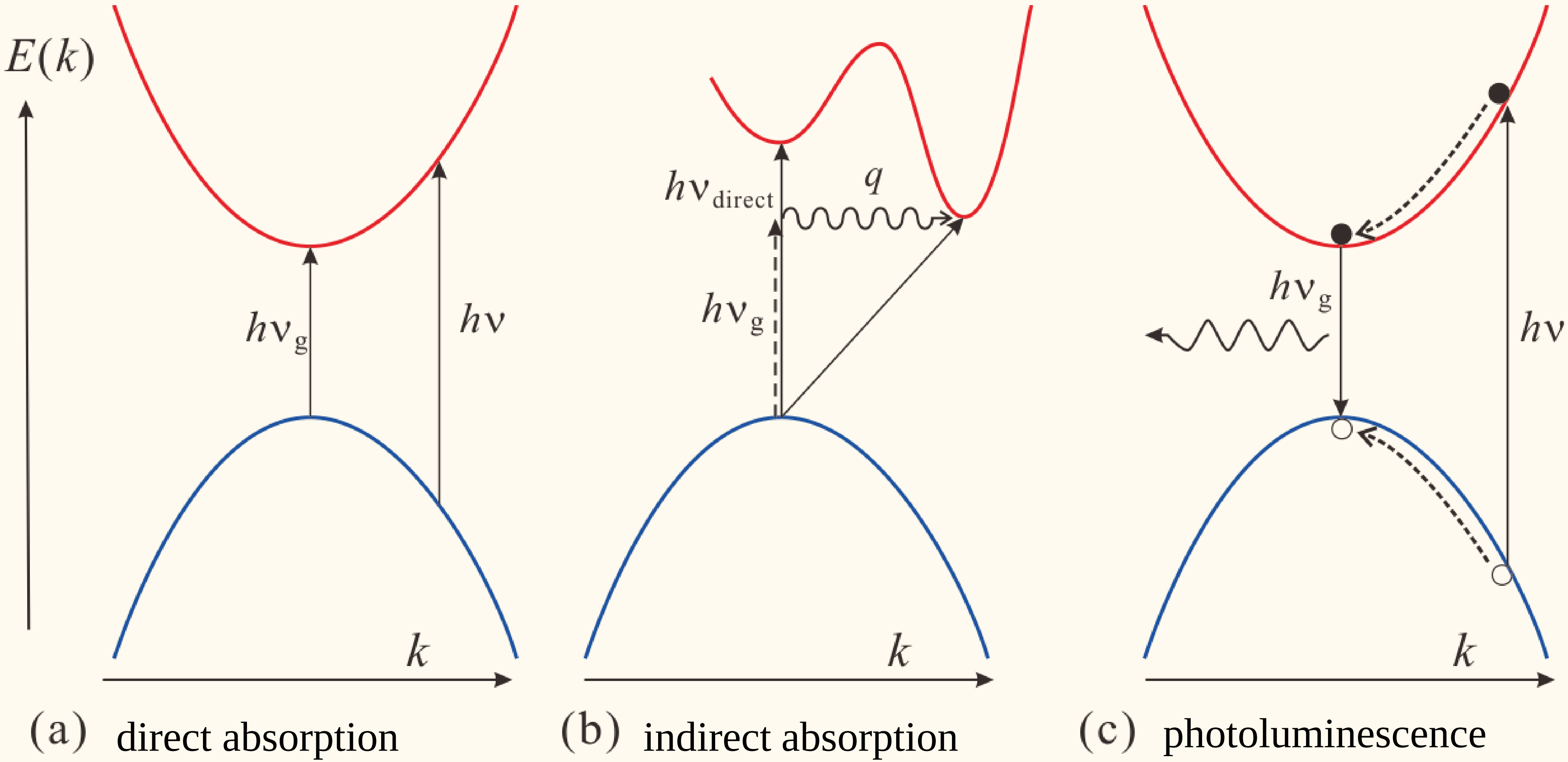
Optical absorption with inter-band transition

Contents today

- Optical absorption with inter-band transition
- Photon emission from inter-band transition
- Optical absorption with exciton formation
- Photon emission from exciton recombination
- Concept of exciton-polariton

Light absorption and luminescence in semiconductors

Application to extended states



(a) direct absorption (b) indirect absorption (c) photoluminescence

Photon momentum $\hbar k_p$ can be ignored in most cases.

Optical absorption with transition from valence to conduction

Plane wave vector potential $\boldsymbol{A} = A_0 \boldsymbol{e} \cos(\boldsymbol{k}_p \cdot \boldsymbol{r} - \omega t)$ $\quad \boldsymbol{k}_\mathrm{p} = (0, 0, k_\mathrm{p}),\ \boldsymbol{e} = (1, 0, 0)$

$$\boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t}, \quad \boldsymbol{H} = \frac{\mathrm{rot} \boldsymbol{A}}{\mu}$$

Poyinting vector $\boldsymbol{I} = \langle \boldsymbol{E} \times \boldsymbol{H} \rangle = \dfrac{\epsilon_0 c \bar{n} \omega^2 A_0^2}{2} \boldsymbol{e}_z$ $\quad \bar{n} = c/c' = \sqrt{\epsilon_1 \mu_1}$

$I(z) = I_0 \exp(-\alpha z)$ Definition of absorption coefficient α

W: number of photons absorbed per unit time

$$\alpha = \frac{\hbar \omega W}{I} = \frac{2\hbar \omega W}{\epsilon_0 c \bar{n} \omega^2 A_0^2}$$

perturbation

$$\mathscr{H}' = \frac{e A_0}{m_0} \boldsymbol{e} \cdot \boldsymbol{p}$$

Conduction electron $|c\boldsymbol{k}\rangle$, valence hole $|v\boldsymbol{k}'\rangle$ Transition probability is

$$W_\mathrm{vc} = \frac{2\pi e A_0^2}{\hbar m_0} |\langle c\boldsymbol{k}|\boldsymbol{e}\cdot\boldsymbol{p}|v\boldsymbol{k}'\rangle|^2 \delta(E_c(\boldsymbol{k}) - E_v(\boldsymbol{k}') - \hbar\omega)$$

$$= \frac{\pi e^2 A_0^2}{2\hbar m_0^2} |M|^2 \delta(E_c(\boldsymbol{k}) - E_v(\boldsymbol{k}') - \hbar\omega)$$

Optical absorption with transition from valence to conduction (2)

Bloch electrons

$$|c\boldsymbol{k}\rangle = u_{c\boldsymbol{k}}e^{i\boldsymbol{k}\boldsymbol{r}}, \quad |v\boldsymbol{k}\rangle = u_{v\boldsymbol{k}}e^{i\boldsymbol{k}\boldsymbol{r}}$$

$$\begin{aligned} M &= \int_V \frac{d^3r}{V} e^{i(\boldsymbol{k}_p+\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}} u^*_{c\boldsymbol{k}}(\boldsymbol{r})\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{k}')u_{v\boldsymbol{k}'}(\boldsymbol{r}) \\ &= \frac{\sum_l e^{i(\boldsymbol{k}_p+\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{R}_l}}{V}\int_\Omega d^3r u^*_{c\boldsymbol{k}}(\boldsymbol{r})\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{k}')u_{v\boldsymbol{k}'}(\boldsymbol{r}) \\ &= \frac{N}{V}\delta_{\boldsymbol{k}_p+\boldsymbol{k}'-\boldsymbol{k},\boldsymbol{K}}\int_\Omega d^3r u^*_{c\boldsymbol{k}}(\boldsymbol{r})\boldsymbol{e}\cdot(\boldsymbol{p}+\hbar\boldsymbol{k}')u_{v\boldsymbol{k}'}(\boldsymbol{r}) \end{aligned}$$

$$M = \int_\Omega \frac{d^3r}{\Omega} u^*_{c\boldsymbol{k}}(\boldsymbol{r})\boldsymbol{e}\cdot\boldsymbol{p}u_{v\boldsymbol{k}}(\boldsymbol{r})$$

Absorption coefficient
for direct absorption

$$\alpha_{\mathrm{da}} = \frac{\pi e^2}{\bar{n}\epsilon_0\omega c m_0^2}|M|^2 \underline{\sum_{\boldsymbol{k}}\delta(E_c(\boldsymbol{k})-E_v(\boldsymbol{k})-\hbar\omega)}$$

joint density of states $\equiv J_{cv}(\hbar\omega)$

$$E_{cv}(\boldsymbol{k}) \equiv E_c(\boldsymbol{k}) - E_v(\boldsymbol{k})$$

Γ point $\quad E_{cv}(\vec{0}) = E_{\mathrm{g}}(\Gamma)$

$$J_{cv}(\hbar\omega) = \sum_{\boldsymbol{k}}\delta(E_{cv}(\boldsymbol{k})-\hbar\omega) = 2\int\frac{d^3k}{(2\pi)^3}\delta(E_{cv}(\boldsymbol{k})-\hbar\omega)$$

Optical absorption with transition from valence to conduction (3)

$$d^3k = dS dk_\perp = dS \frac{dk_\perp}{dE_{cv}} dE_{cv} = dS |\boldsymbol{\nabla}_{\boldsymbol{k}} E_{cv}|^{-1} dE_{cv}$$

$$\therefore J_{cv}(\hbar\omega) = \frac{2}{(2\pi)^3} \int \frac{dS}{|\boldsymbol{\nabla}_{\boldsymbol{k}} E_{cv}(\boldsymbol{k})|_{E_{cv}=\hbar\omega}}$$

Minimum at $\boldsymbol{k}_0$

$$E_{cv}(\boldsymbol{k}_0) = E_{\mathrm{g}}, \quad \boldsymbol{\nabla}_{\boldsymbol{k}} E_{cv} = \mathbf{0}$$

$$E_{cv}(\boldsymbol{k}) = E_{\mathrm{g}} + \sum_i \frac{\hbar^2}{2\xi_i}(k_i - k_{i0})^2, \quad \xi_i > 0 (i = 1, 2, 3) \text{ for simplicity.}$$

Change of variables

$(\hbar/(2\xi_i)^{1/2})(k_i - k_{i0}) = s_i$

$$E_{cv} = E_{\mathrm{g}} + \sum_i s_i^2 \equiv E_{\mathrm{g}} + s^2, \;\; d^3k = \frac{\sqrt{8\xi_1\xi_2\xi_3}}{\hbar^3} ds_1 ds_2 ds_3$$

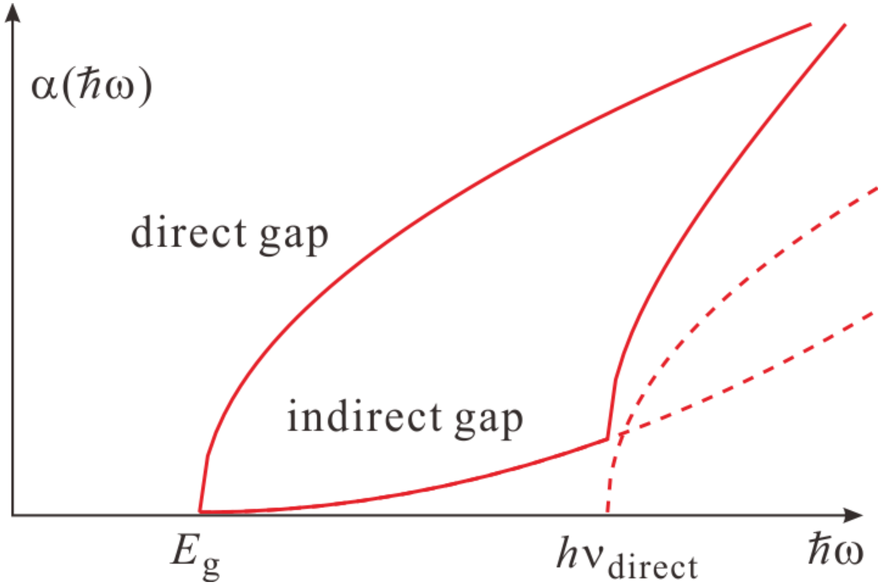
$|\boldsymbol{\nabla}_{\boldsymbol{s}} E_{cv}| = 2s$

$$J_{cv} = \frac{2}{(2\pi)^3} \frac{\sqrt{8\xi_1\xi_2\xi_3}}{\hbar^3} \int \frac{dS}{2s} = \frac{1}{2\pi^2} \frac{\sqrt{8\xi_1\xi_2\xi_3}}{\hbar^3} \sqrt{\hbar\omega - E_{\mathrm{g}}}$$

$$\frac{1}{m_r} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

$$= \frac{\sqrt{2}}{\pi^2} \frac{m_r^{3/2}}{\hbar^3} \sqrt{\hbar\omega - E_{\mathrm{g}}}$$

Optical absorption with transition from valence to conduction (4)

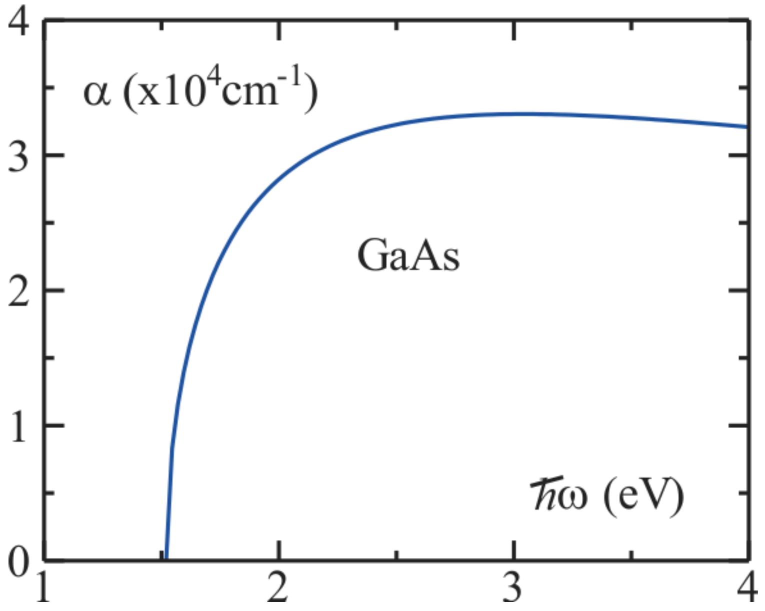


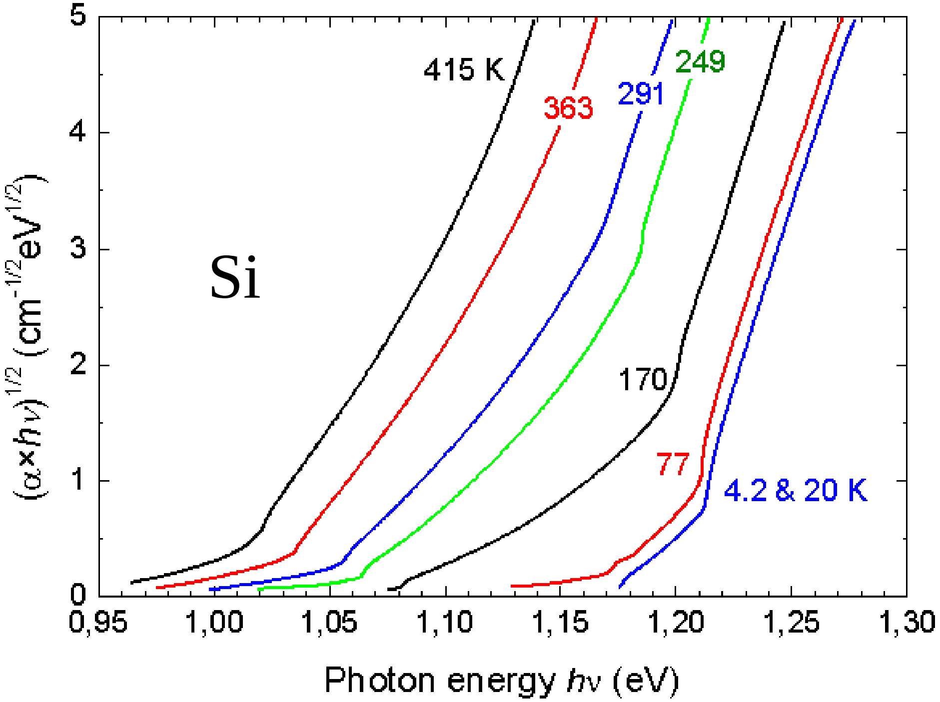
Absorption coefficient $\alpha(\hbar\omega) = \dfrac{e^2(2m_r)^{3/2}|M|^2}{2\pi\epsilon_0 m_0^2 \bar{n}\omega c\hbar^3}\sqrt{\hbar\omega - E_g}$

Oscillator strength $f_{vc} = \dfrac{2|M|^2}{m_0\hbar\omega}$

Indirect gap semiconductors $\alpha_{id}(\hbar\omega) \propto (\hbar\omega - E_g)^2$

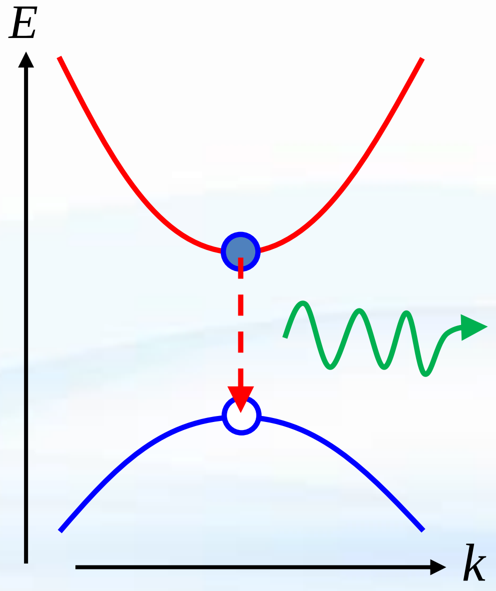
Example GaAs





Luminescence by inter-band transition

Electron-hole recombination:
- Radiative recombination
- Non-radiative recombination



Classification of luminescence with excitations

- Photoluminescence
- Electroluminescence
- Thermoluminescence
- Cathode luminescence
- Sonoluminescence
- Triboluminescence
- Chemiluminescence

Pseudo-Fermi level

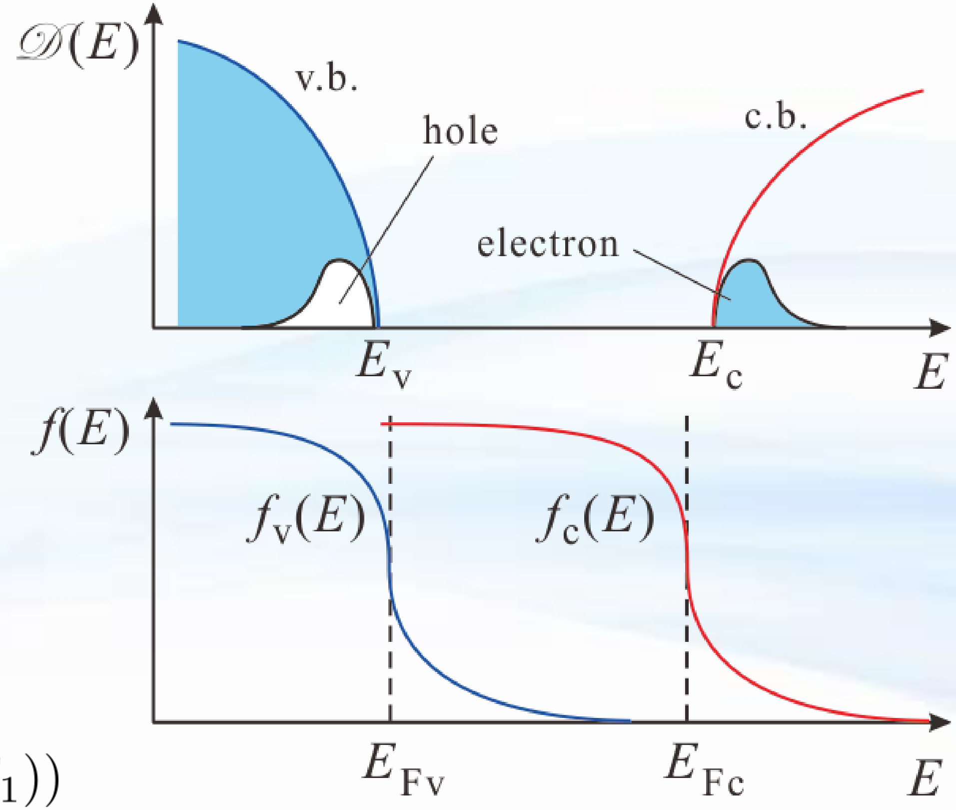
Planck distribution
$$P(E) = \frac{8\pi\bar{n}^3 E^3}{h^3 c^3} \frac{1}{\exp(E/k_B T) - 1}$$

Semiconductor under irradiation

Introduction of pseudo-Fermi levels: $E_{Fc}, \quad E_{Fv}$

Electron distribution function in conduction band
$$f_c(E) = \left[\exp\left(\frac{E - E_{Fc}}{k_B T}\right) + 1\right]^{-1},$$

Electron distribution function in valence band
$$f_v(E) = \left[\exp\left(\frac{E - E_{Fv}}{k_B T}\right) + 1\right]^{-1}.$$



optical absorption
$$R(1 \to 2) = B_{12} f_v (1 - f_c) P(\hbar\omega)$$

spontaneous emission
$$R(sp, 2 \to 1) = A_{21} f_c(E_2)(1 - f_v(E_1))$$

stimulated emission
$$R(st, 2 \to 1) = B_{21} f_c(E_2)(1 - f_v(E_1)) P(\hbar\omega)$$

balance equation
$$R(1 \to 2) = R(sp, 2 \to 1) + R(st, 2 \to 1)$$

Einstein relation
$$A_{21} = \frac{8\pi\bar{n}^3 E_{21}^3}{h^3 c^3} B_{21}, \quad B_{12} = B_{21}$$

Relation with phenomenological approach

So far: Optical response of two-level system → Extended states → Inter-band absorption

Other effects : refractive index

? ↕

Macroscopic phenomenological approach

Starting point:

Maxwell equation

$$\mathrm{div}\boldsymbol{D} = \rho, \quad \mathrm{div}\boldsymbol{B} = 0,$$
$$\mathrm{rot}\boldsymbol{E} = \frac{\partial \boldsymbol{B}}{\partial t}, \quad \mathrm{rot}\boldsymbol{H} = \boldsymbol{j} + \frac{\partial \boldsymbol{D}}{\partial t},$$
$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{P}, \quad \boldsymbol{B} = \mu_0 \boldsymbol{H} + \boldsymbol{M}$$

Non-magnetic dielectric $\boldsymbol{M} = \vec{0} \qquad \boldsymbol{j} = \vec{0}$

Wave equation
$$\Delta \boldsymbol{E} - \epsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \boldsymbol{P}}{\partial t^2}$$

Effect of polarization $\boldsymbol{P} = \sum_i \boldsymbol{p}_i$

Relation with phenomenological approach (2)

Linear response approximation $\boldsymbol{P} = \epsilon_0 \boldsymbol{\chi} \boldsymbol{E}$ $\boldsymbol{\chi}:$ susceptibility

Relative dielectric function ε_r $\boldsymbol{D} = \epsilon_0 \boldsymbol{\epsilon}_{\mathrm{r}} \boldsymbol{E}, \quad \boldsymbol{\epsilon}_{\mathrm{r}} = 1 + \boldsymbol{\chi}$

Below we consider isotropic crystal: response function tensor → scalar

The effect of polarization is normalized into the term of time-derivative

$$\Delta \boldsymbol{E} - \epsilon_0 \mu_0 \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = \epsilon_0 \mu_0 (\epsilon_{\mathrm{r}} - 1) \frac{\partial^2 \boldsymbol{E}}{\partial t^2} \quad \rightarrow \quad \Delta \boldsymbol{E} - \frac{\epsilon_{\mathrm{r}}}{c^2} \frac{\partial^2 \boldsymbol{E}}{\partial t^2} = 0$$

Polariton equation $c^2 \boldsymbol{k}^2 = \omega^2 \epsilon_{\mathrm{r}}(\omega, \boldsymbol{k})$

Absorption: imaginary part of response function: complex dielectric function, or

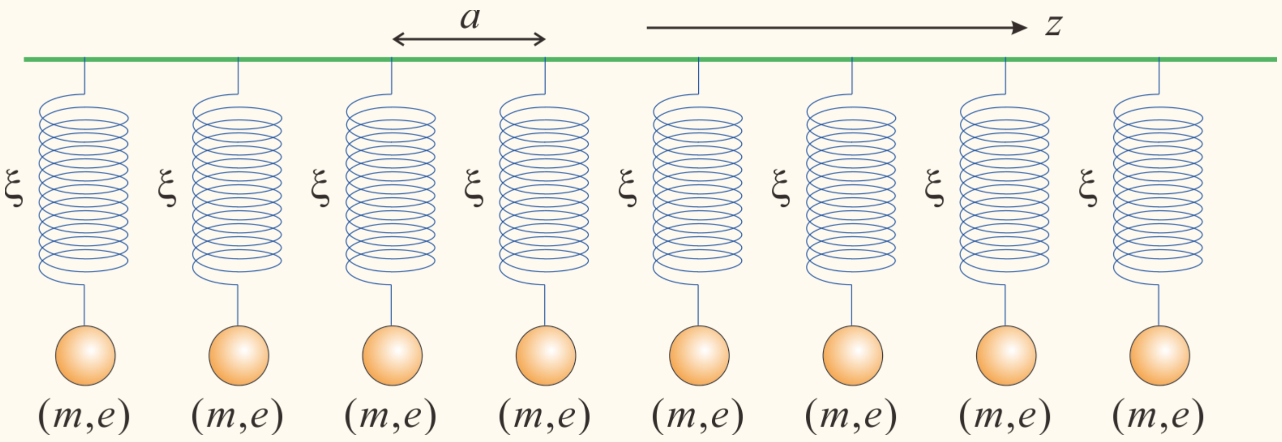
complex refractive index $\tilde{n}(\omega, \boldsymbol{k}) = n(\omega, \boldsymbol{k}) + i\kappa(\omega, \boldsymbol{k})$

absorption coefficient $\alpha = \dfrac{2\omega}{c} \kappa(\omega, \boldsymbol{k})$

Phenomenological approach: Lorentz model

Electromagnetic field in Materials:
set harmonic oscillators (m, e, ξ)

$$m\frac{d^2x}{dt^2} + \underbrace{\Gamma m\frac{dx}{dt}}_{\text{energy dissipation}} + \xi x = eE_0\exp(-i\omega t)$$



oscillator concentration N

eigenfrequency $\omega_\mathrm{h} = \sqrt{\dfrac{\xi}{m}}$

long term stable solution $x(t) = x_\mathrm{p}\exp(-i\omega t)$

$$P = N(ex_\mathrm{p}(\omega)) = \underbrace{\frac{Ne^2}{m}\frac{1}{\omega_\mathrm{h}^2 - \omega^2 - i\omega\Gamma}}_{\chi\ \text{susceptibility}}E_0$$

relative dielectric function

$$\epsilon_\mathrm{r}(\omega) = 1 + \frac{Ne^2}{\epsilon_0 m}\frac{1}{\omega_\mathrm{h}^2 - \omega^2 - i\omega\Gamma}$$

Multimode:
ration of mode j
→ f_j

$$\epsilon_\mathrm{r}(\omega) = 1 + \frac{Ne^2}{\epsilon_0 m}\sum_j \frac{f_j}{\omega_\mathrm{h}^2 - \omega^2 - i\omega\Gamma_j}$$

f_j: oscillator strength

Optical absorption by excitons

Exciton wavefunction (effective mass approximation)

$$\Phi_{n\boldsymbol{K}}(\boldsymbol{r},\boldsymbol{R}) = \frac{1}{\sqrt{V}}\exp(i\boldsymbol{K}\cdot\boldsymbol{R})\underbrace{\phi_n(\boldsymbol{r})}_{\text{exciton local wavefunction}}$$

- $\boldsymbol{r}$: electron-hole relative coordinate
- $\boldsymbol{R}$: center of mass coordinate

Fourier transform

$$\begin{aligned}
F_{n\boldsymbol{K}}(\boldsymbol{k}_\mathrm{e},\boldsymbol{k}_\mathrm{h}) &= \frac{1}{V}\int d^3\boldsymbol{r}_\mathrm{e} d^3\boldsymbol{r}_\mathrm{h} e^{-i\boldsymbol{k}_\mathrm{e}\cdot\boldsymbol{r}_\mathrm{e}} e^{-i\boldsymbol{k}_\mathrm{h}\cdot\boldsymbol{r}_\mathrm{h}}\Phi_{n\boldsymbol{K}}(\boldsymbol{r},\boldsymbol{R}) \\
&= \frac{1}{\sqrt{V}}\int d^3\boldsymbol{r} d^3\boldsymbol{R}\underline{e^{-i\boldsymbol{R}\cdot(\boldsymbol{k}_\mathrm{e}+\boldsymbol{k}_\mathrm{h}-\boldsymbol{K})}}\phi_n(\boldsymbol{r})e^{-i\boldsymbol{k}^*\cdot\boldsymbol{r}} \\
&= \frac{1}{\sqrt{V}}\int d^3\boldsymbol{r} e^{-i\boldsymbol{k}^*\cdot\boldsymbol{r}}\phi_n(\boldsymbol{r})\underline{\delta_{\boldsymbol{K},\boldsymbol{k}_\mathrm{e}+\boldsymbol{k}_\mathrm{h}}}, \qquad \boldsymbol{k}^* \equiv \frac{m_\mathrm{h}\boldsymbol{k}_\mathrm{e} - m_\mathrm{e}\boldsymbol{k}_\mathrm{h}}{m_\mathrm{e}+m_\mathrm{h}}.
\end{aligned}$$

exciton total wavelength $\boldsymbol{K} = \boldsymbol{k}_\mathrm{e} + \boldsymbol{k}_\mathrm{h}$

ground state $\Phi_0 = \phi_{\mathrm{c}\boldsymbol{k}_\mathrm{e}}\phi_{\mathrm{v}\boldsymbol{k}_\mathrm{e}} \xrightarrow{\text{excitation}} \Phi_{n\boldsymbol{K}}(\boldsymbol{r},\boldsymbol{R})$

Transition probability

$$\begin{aligned}
w_\mathrm{if} &= \frac{2\pi}{\hbar}\frac{e^2}{m^2}|A_0|^2\frac{1}{V}\sum_{\lambda}|\langle\Phi_{\lambda\boldsymbol{K}}|\exp(i\boldsymbol{k}_\mathrm{p}\cdot\boldsymbol{r})\boldsymbol{e}\cdot\boldsymbol{p}|\Phi_0\rangle|^2\delta(E_\mathrm{g}+E_\lambda-\hbar\omega) \\
&= \frac{2\pi}{\hbar}\frac{e^2}{m^2}|A_0|^2\frac{1}{V}\sum_{\boldsymbol{k}_\mathrm{e}\lambda}|F_{\lambda\boldsymbol{K}}(\boldsymbol{k}_\mathrm{e},-\boldsymbol{k}_\mathrm{e})\langle\phi_{\mathrm{c}\boldsymbol{k}_\mathrm{e}}|\boldsymbol{e}\cdot\boldsymbol{p}|\phi_{\mathrm{v}\boldsymbol{k}_\mathrm{e}}\rangle|^2\delta(E_\mathrm{g}+E_\lambda-\hbar\omega).
\end{aligned}$$

Optical absorption by excitons (2)

Because $\boldsymbol{k}_\mathrm{e} = -\boldsymbol{k}_\mathrm{h}$ $\quad F_{n\boldsymbol{K}}(\boldsymbol{k}_\mathrm{e}, -\boldsymbol{k}_\mathrm{h}) = \frac{1}{V}\int d^3\boldsymbol{r}_\mathrm{e} d^3\boldsymbol{r}_\mathrm{h} \exp[-i\boldsymbol{k}_\mathrm{e}\cdot(\boldsymbol{r}_\mathrm{e}-\boldsymbol{r}_\mathrm{h})]\Phi_{\lambda\boldsymbol{K}}(\boldsymbol{r}_\mathrm{e},\boldsymbol{r}_\mathrm{h})$

Because the sum will be taken over $\boldsymbol{k}_\mathrm{e}$ $\quad \boldsymbol{r}_\mathrm{e} = \boldsymbol{r}_\mathrm{h}$

$F_{n\boldsymbol{K}}$ is large only for $\boldsymbol{k}_\mathrm{e} \approx \vec{0}$ while $\langle \phi_{\mathrm{c}\boldsymbol{k}_\mathrm{e}} | \boldsymbol{e}\cdot\boldsymbol{p} | \phi_{\mathrm{v}\boldsymbol{k}_\mathrm{e}} \rangle$ is almost constant

which is $M = \int_\Omega \frac{d^3 r}{\Omega} u^*_{c\boldsymbol{k}}(\boldsymbol{r})\boldsymbol{e}\cdot\boldsymbol{p}u_{v\boldsymbol{k}}(\boldsymbol{r})$

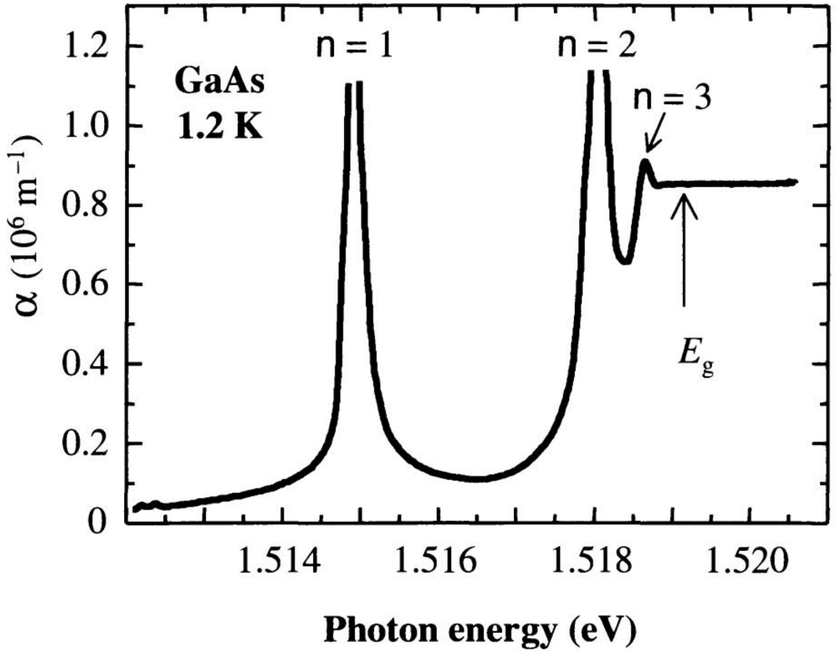
Fermi's golden rule: $w_\mathrm{if} = \frac{2\pi}{\hbar}\frac{e^2}{m^2}|A_0|^2 \sum_\lambda |M|^2 |\phi_\lambda(0)|^2 \delta(E_\mathrm{g} + E_\lambda - \hbar\omega)$

For $\phi(0)$ not to be 0, ϕ must be an *s*-state $\quad |\phi_n(0)|^2 = \frac{1}{\pi a_\mathrm{ex}^3 n^3}, \quad E_n = -\frac{E_\mathrm{ex}}{n^2}$

Imaginary part of the complex relative dielectric function $\quad \epsilon_{\mathrm{r}2}(\omega) = \frac{\pi e^2}{\epsilon_0 m^2 \omega^2}|M|^2 \frac{1}{\pi a_\mathrm{ex}^3}\sum_n \frac{1}{n^3}\delta\left(E_\mathrm{g} - \frac{E_\mathrm{ex}}{n^2} - \hbar\omega\right)$

(spin degree of freedom: factor of 2)

Optical absorption by excitons (3)



Exciton absorption peaks in GaAs.
Fehrenbach *et al.*, J. Luminescence **30**, 154 (1985).

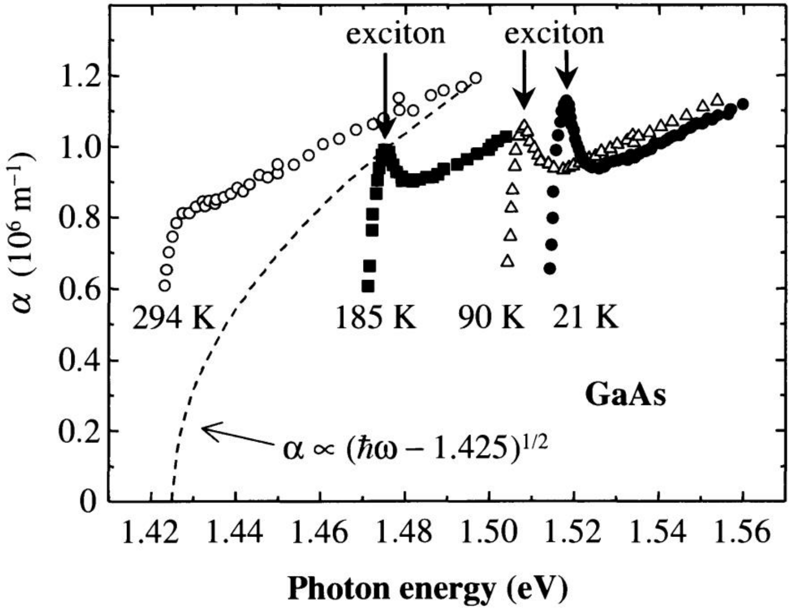
in simplest form
$$\epsilon_{\mathrm{r}2} = C\delta\left(E_{\mathrm{g}} - \frac{E_{\mathrm{ex}}}{n^2} - \hbar\omega\right)$$

identity
$$\lim_{\Gamma\to+0}\frac{1}{x_0 - x - i\Gamma} = \mathcal{P}\frac{1}{x_0 - x} + i\pi\delta(x_0 - x)$$

comparison gives
$$\epsilon_{\mathrm{r}2} = \mathrm{Im}\left\{\frac{C/\pi}{E_{\mathrm{g}} - \dfrac{E_{\mathrm{ex}}}{n^2} - (\hbar\omega + i\delta)}\right\}$$

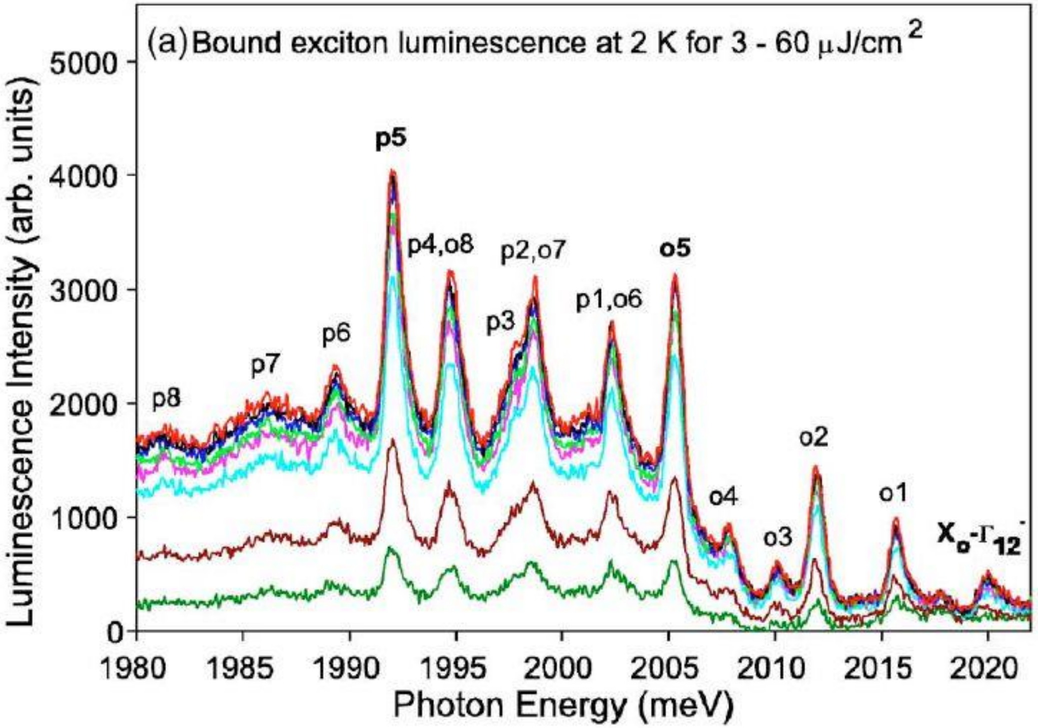
Kramers-Kronig relation
$$\chi_1(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\chi_2(\omega')}{\omega' - \omega}d\omega'$$

$$\epsilon_{\mathrm{r}} = \frac{C/\pi}{E_{\mathrm{g}} - \dfrac{E_{\mathrm{ex}}}{n^2} - (\hbar\omega + i\Gamma)}$$



Sturge, Phys. Rev. **127**, 768 (1962)

Photoemission by exitons



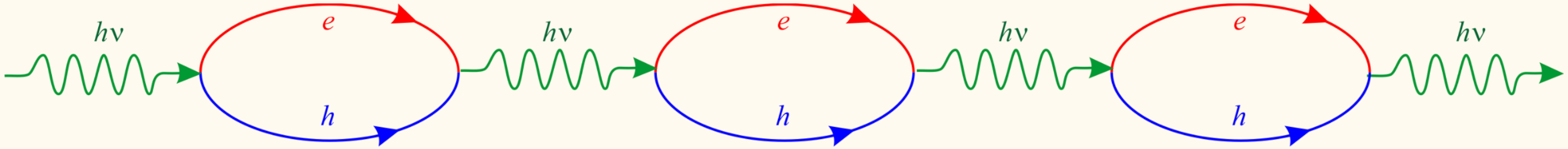
Jang *et al.*, Phys. Rev. B **74**, 235204 (2006)

Photoemission: reversal process

Bound exciton emission peaks in Cu_2O

Exciton-polariton

Concept of exciton-polariton



Chain of photon-exciton

1 cycle $\sim$ few fs

coherent propagation in solids

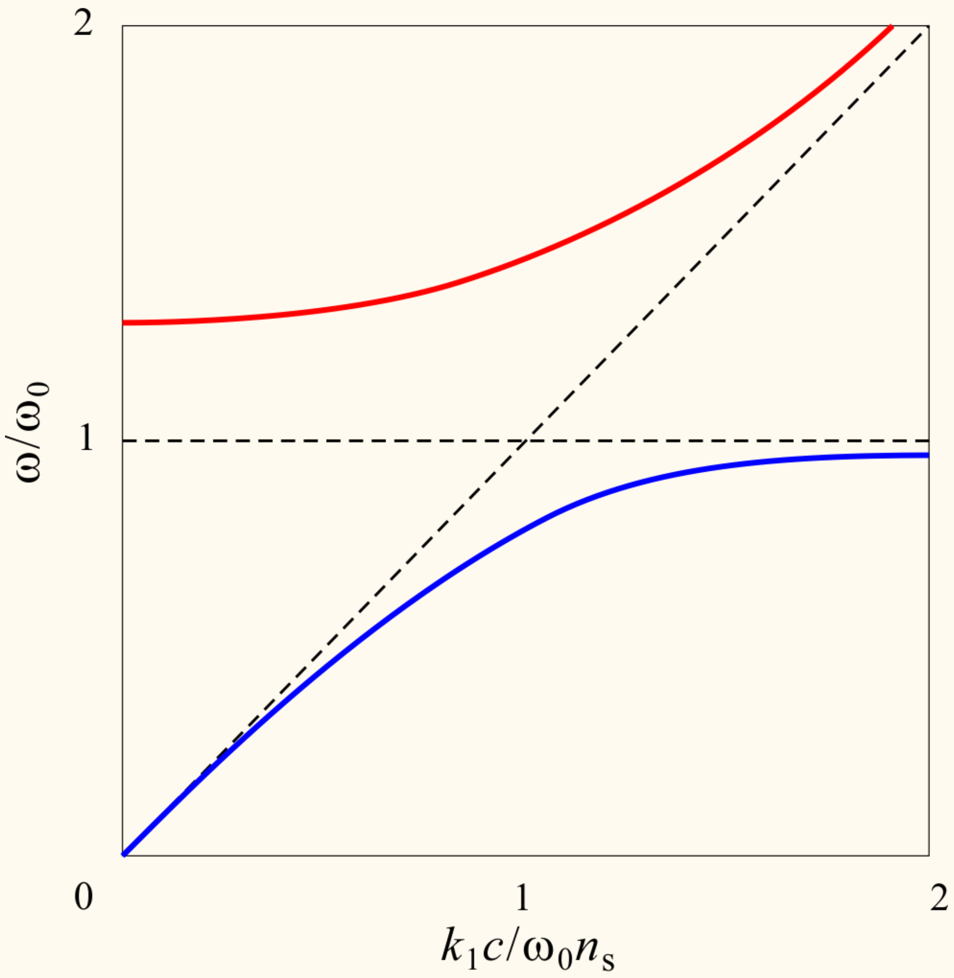
$\epsilon_{\rm s}$: contributions other than from excitons $$\epsilon_{\rm r}(\omega) = \epsilon_{\rm s}\left(1 + \frac{\Delta_{\rm ex}}{\omega_0 - \omega - i\gamma}\right)$$

transverse wave: $\left.\begin{array}{l} \boldsymbol{k}\cdot\boldsymbol{E} = 0 \\ \omega_{\rm t} = \omega_0 \end{array}\right\}$ polariton equation $c^2\boldsymbol{k}^2 = \omega_0^2\epsilon_{\rm r}(\omega_0, \boldsymbol{k})$

Longitudinal wave: $\omega_{\rm l} = \omega_0 + \Delta_{\rm ex} = \omega_{\rm t} + \Delta_{\rm ex}$

$\Delta_{\rm ex}$: longitudinal-transverse splitting

Exciton-polariton (2)



$$k = k_1 + ik_2$$

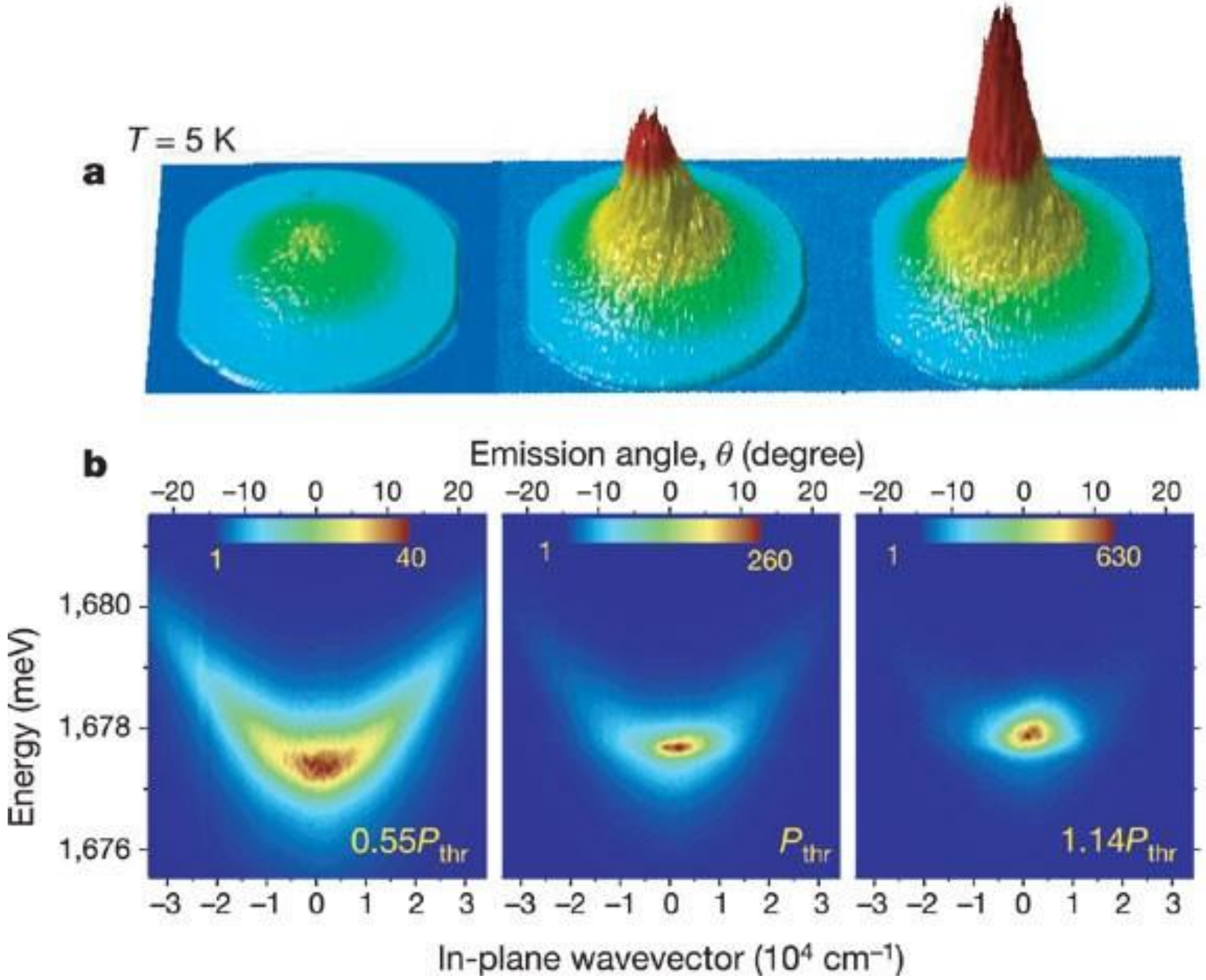
$$\begin{cases} \dfrac{\omega^2\epsilon_{\mathrm{s}}}{c^2}\left(1+\dfrac{\Delta_{\mathrm{ex}}}{\omega_0-\omega}\right)=k_1^2-k_2^2, \\ \pi\delta(\omega-\omega_0)\dfrac{\omega_0^2\epsilon_{\mathrm{s}}}{c^2}=2k_1k_2 \end{cases}$$

Resonance

Dispersion relation

$$\omega\sqrt{\frac{\omega-\omega_{-}\Delta_{\mathrm{ex}}}{\omega-\omega_0}}=\frac{ek_1}{\sqrt{\epsilon_{\mathrm{s}}}}$$

Bose-Einstein condensation of exciton-polaritons



J. Kasprzak *et al*., Nature **443**, 409 (2006).