Excitons in Bulk Semiconductors

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Content

Introduction & Approach

- Polarization $\mathcal{P}$ describes the interaction of an electron with an electric field $\mathcal{E}$ in a semiconductor

$$\mathcal{P}(\omega) = \frac{P(\omega)}{L^3} = \chi(\omega)\mathcal{E}(\omega) \tag{1}$$

- Excitation of an electron from valence band to conduction band creates an electron-hole-pair
- Coulomb-Interaction occurs between electron and hole

Introduction & Approach

Hamilton Operator includes

- kinetic energy of electrons (holes) $\mathcal{H}_{kin}$
- interaction between electrons (holes) and electric field $\mathcal{H}_I$
- electon-hole-interaction (Coulomb interaction) $\mathcal{H}_C$

$$\mathcal{H} = \mathcal{H}_{kin} + \mathcal{H}_I + \mathcal{H}_C \tag{2}$$

Dynamics of the system is described via Heisenberg equation of motion

$$\frac{\mathrm{d}\langle \hat{P} \rangle}{\mathrm{d}t} = \frac{i}{\hbar}\langle [\mathcal{H}, \hat{P}] \rangle + \langle \frac{\partial \hat{P}}{\partial t} \rangle, \quad P = \langle \hat{P} \rangle = \mathrm{tr}[\rho \hat{P}] \tag{3}$$

The Interband Polarization

Classical polarization:

$$P = L^3 n_0 e r \tag{4}$$

Quantummechanical polarization is defined as expectation value of the electric dipole $e\mathbf{r}$:

$$\mathbf{P}(t) = \int \mathrm{d}^3 r \; \langle \hat{\psi}^\dagger(\mathbf{r}, t) \; e\mathbf{r} \; \hat{\psi}(\mathbf{r}, t) \rangle \tag{5}$$

Change electron field operators $\hat{\psi}$ into different basis by using Bloch functions:

$$\hat{\psi}(\mathbf{r}, t) = \sum_{\lambda, \mathbf{k}} \hat{a}_{\lambda, \mathbf{k}}(t) \; \psi_\lambda(\mathbf{k}, \mathbf{r}) \tag{6}$$

Equation (5) yields:

$$\mathbf{P}(t) = \sum_{\lambda, \lambda', \mathbf{k}, \mathbf{k}'} \int \mathrm{d}^3 r \; \langle \hat{a}^\dagger_{\lambda, \mathbf{k}}(t) \; \psi^*_\lambda(\mathbf{k}, \mathbf{r}) \; e\mathbf{r} \; \hat{a}_{\lambda', \mathbf{k}'}(t) \; \psi_{\lambda'}(\mathbf{k}', \mathbf{r}) \rangle \tag{7}$$

The Interband Polarization

$$\mathbf{P}(t) = \sum_{\lambda,\lambda',\mathbf{k},\mathbf{k}'} \langle \hat{a}^{\dagger}_{\lambda,\mathbf{k}}(t)\ \hat{a}_{\lambda',\mathbf{k}'}(t)\rangle \int \mathrm{d}^3 r\ \psi^*_{\lambda}(\mathbf{k},\mathbf{r})\ e\mathbf{r}\ \psi_{\lambda'}(\mathbf{k}',\mathbf{r}) \quad (8)$$

Dipole approximation: only identical **k**-states in different bands $\lambda \neq \lambda$ are coupled.

$$\int \mathrm{d}^3 r\ \psi^*_{\lambda}(\mathbf{k},\mathbf{r})\ e\mathbf{r}\ \psi_{\lambda'}(\mathbf{k}',\mathbf{r}) \simeq \delta_{\mathrm{k},\mathrm{k}'}\mathbf{d}_{\lambda\lambda'}. \quad (9)$$

Concluding in:

$$\mathbf{P}(t) = \sum_{\lambda,\lambda',\mathbf{k}} \langle a^{\dagger}_{\lambda,\mathbf{k}}(t)\ a_{\lambda',\mathbf{k}}(t)\rangle\ \mathbf{d}_{\lambda\lambda'} = \sum_{\lambda,\lambda',\mathbf{k}} P_{\lambda,\lambda',\mathbf{k}}(t)\ \mathbf{d}_{\lambda\lambda'} \quad (10)$$

Hamilton Operator: $\mathcal{H} = \mathcal{H}_{kin} + \mathcal{H}_I + \mathcal{H}_C$

Kinetic energy Hamiltonian:

$$\mathcal{H}_{kin} = \sum_{\lambda,\mathbf{k}} E_{\lambda,k} a^{\dagger}_{\lambda,\mathbf{k}} \; a_{\lambda,\mathbf{k}} \tag{11}$$

Two band approximation: $\lambda =$ valence band v,
$\lambda' =$ conduction band c.

$$\mathcal{H}_{kin} = \sum_{\mathbf{k}} \left(E_{c,k} a^{\dagger}_{c,\mathbf{k}} \; a_{c,\mathbf{k}} + E_{v,k} a^{\dagger}_{v,\mathbf{k}} \; a_{v,\mathbf{k}} \right) \tag{12}$$

with single particle energies including effective mass:

$$\begin{aligned} E_{c,k} &= \hbar\epsilon_{c,k} = E_g + \hbar^2 k^2 / 2m_c \\ E_{v,k} &= \hbar\epsilon_{v,k} = \hbar^2 k^2 / 2m_v \end{aligned}$$

Hamilton Operator: $\mathcal{H} = \mathcal{H}_{kin} + \mathcal{H}_I + \mathcal{H}_C$

Electron-electric field interaction:

$$\mathcal{H}_I = \int \mathrm{d}^3 r \; \hat{\psi}^\dagger(\mathbf{r}) \; (-e\mathbf{r}) \; \mathcal{E}(\mathbf{r}, t) \; \hat{\psi}(\mathbf{r}) \tag{13}$$

with electric field

$$\mathcal{E}(\mathbf{r}, t) = \mathcal{E}(t) \; \frac{1}{2} \left(\exp\left(i \; \mathbf{q} \cdot \mathbf{r}\right) + \exp\left(-i \; \mathbf{q} \cdot \mathbf{r}\right) \right). \tag{14}$$

Dipole Approximation: $\mathbf{k} \approx \mathbf{k}' \gg \mathbf{q} \approx 0$.
Two band approximation
Inserting Bloch functions in equation 13:

$$\mathcal{H}_I \simeq -\sum_{\mathbf{k}} \mathcal{E}(t) \; \left(a^\dagger_{c,\mathbf{k}} \; a_{v,\mathbf{k}} \; d_{cv} + a^\dagger_{v,\mathbf{k}} \; a_{c,\mathbf{k}} \; d^*_{cv} \right) \tag{15}$$

Hamilton Operator: $\mathcal{H} = \mathcal{H}_{kin} + \mathcal{H}_I + \mathcal{H}_C$

Electron-hole Coulomb interaction:

$$\mathcal{H}_C = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0,\lambda,\lambda'} V_q \; a^\dagger_{\lambda,\mathbf{k}+\mathbf{q}} \; a^\dagger_{\lambda',\mathbf{k}'-\mathbf{q}} \; a_{\lambda',\mathbf{k}'} \; a_{\lambda,\mathbf{k}} \tag{16}$$

Note: Number of electrons in each band is conserved.
Two band approximation:

$$\begin{aligned} \mathcal{H}_C = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0} V_q \Big(& \; a^\dagger_{c,\mathbf{k}+\mathbf{q}} \; a^\dagger_{c,\mathbf{k}'-\mathbf{q}} \; a_{c,\mathbf{k}'} \; a_{c,\mathbf{k}} \\ + & \; a^\dagger_{v,\mathbf{k}+\mathbf{q}} \; a^\dagger_{v,\mathbf{k}'-\mathbf{q}} \; a_{v,\mathbf{k}'} \; a_{v,\mathbf{k}} \\ +2 & \; a^\dagger_{c,\mathbf{k}+\mathbf{q}} \; a^\dagger_{v,\mathbf{k}'-\mathbf{q}} \; a_{v,\mathbf{k}'} \; a_{c,\mathbf{k}} \Big) \end{aligned} \tag{17}$$

with the Coulomb potential

$$V_q = \frac{4\pi e^2}{\epsilon_0 L^3} \frac{1}{q^2}.$$

Heisenberg Equation of Motion

$$i\hbar\left(\frac{\mathrm{d}\langle P_{vc,\mathbf{k}}(t)\rangle}{\mathrm{d}t}\right) = -\langle[\mathcal{H}, P_{vc,\mathbf{k}}(t)]\rangle + i\hbar\langle\left(\frac{\partial P_{vc,\mathbf{k}}(t)}{\partial t} = 0\right)\rangle$$

$$\begin{aligned} &= \hbar(\epsilon_{c,k} - \epsilon_{v,k})\ P_{vc,\mathbf{k}}(t) + [n_{c,\mathbf{k}}(t) - n_{v,\mathbf{k}}(t)]\ d_{cv}\mathcal{E}(t) \\ &+ \sum\nolimits_{\mathbf{k}',\mathbf{q}\neq 0} V_q \\ &\times\Big(\langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}}\ a^\dagger_{v,\mathbf{k}-\mathbf{q}}\ a_{c,\mathbf{k}'}\ a_{c,\mathbf{k}}\rangle + \langle a^\dagger_{v,\mathbf{k}'+\mathbf{q}}\ a^\dagger_{v,\mathbf{k}-\mathbf{q}}\ a_{v,\mathbf{k}'}\ a_{c,\mathbf{k}}\rangle \\ &+\langle a^\dagger_{v,\mathbf{k}}\ a^\dagger_{c,\mathbf{k}'-\mathbf{q}}\ a_{c,\mathbf{k}'}\ a_{c,\mathbf{k}-\mathbf{q}}\rangle + \langle a^\dagger_{v,\mathbf{k}}\ a^\dagger_{v,\mathbf{k}'-\mathbf{q}}\ a_{v,\mathbf{k}'}\ a_{c,\mathbf{k}-\mathbf{q}}\rangle\Big) \end{aligned} \tag{18}$$

with particle number

$$n_{\lambda,\mathbf{k}} = \langle a^\dagger_{\lambda,\mathbf{k}} a_{\lambda,\mathbf{k}}\rangle \tag{19}$$

Approximations

Wick's theorem:

$$\langle a_i^\dagger\ a_j^\dagger\ a_k\ a_l\rangle = \langle a_i^\dagger\ a_l\rangle\langle a_j^\dagger\ a_k\rangle - \langle a_i^\dagger\ a_k\rangle\langle a_j^\dagger\ a_l\rangle$$

Particle number

$$n_i = \langle a_i^\dagger\ a_i\rangle$$

Pair function

$$P_{ij} = \langle a_i^\dagger\ a_j\rangle$$

Approximations

Noninteraction is not allowed: $q \neq 0$

$$\begin{array}{rcl} \langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}}\ a^\dagger_{v,\mathbf{k}-\mathbf{q}}\ a_{c,\mathbf{k}'}\ a_{c,\mathbf{k}}\rangle & \simeq & \\ \langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}}\ a_{c,\mathbf{k}'}\rangle\langle a^\dagger_{v,\mathbf{k}-\mathbf{q}}\ a_{c,\mathbf{k}}\rangle\ \delta_{q,0} & + & \langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}}\ a_{c,\mathbf{k}}\rangle\langle a^\dagger_{v,\mathbf{k}-\mathbf{q}}\ a_{c,\mathbf{k}'}\rangle\ \delta_{k-q,k'} \\ & = & P_{vc,\mathbf{k}'}\ n_{c,\mathbf{k}}\ \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'} \end{array}$$

Accordingly:

$$\begin{array}{rcl} \langle a^\dagger_{v,\mathbf{k}'+\mathbf{q}}\ a^\dagger_{v,\mathbf{k}-\mathbf{q}}\ a_{v,\mathbf{k}'}\ a_{c,\mathbf{k}}\rangle & \simeq & P_{vc,\mathbf{k}}\ n_{v,\mathbf{k}'}\ \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'} \\ \langle a^\dagger_{v,\mathbf{k}}\ a^\dagger_{c,\mathbf{k}'-\mathbf{q}}\ a_{c,\mathbf{k}'}\ a_{c,\mathbf{k}-\mathbf{q}}\rangle & \simeq & -P_{vc,\mathbf{k}}\ n_{c,\mathbf{k}-\mathbf{q}}\ \delta_{\mathbf{k},\mathbf{k}'} \\ \langle a^\dagger_{v,\mathbf{k}}\ a^\dagger_{v,\mathbf{k}'-\mathbf{q}}\ a_{v,\mathbf{k}'}\ a_{c,\mathbf{k}-\mathbf{q}}\rangle & \simeq & -P_{vc,\mathbf{k}-\mathbf{q}}\ n_{v,\mathbf{k}}\ \delta_{\mathbf{k},\mathbf{k}'} \end{array}$$

Approximation

Coulomb part of the equation of motion simplified:

$$\sum_{\mathbf{k}',\mathbf{q}\neq\mathbf{0}} V_q\big(P_{vc,\mathbf{k}'}\; n_{c,\mathbf{k}}\; \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'} + P_{vc,\mathbf{k}}\; n_{v,\mathbf{k}'}\; \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'}$$

$$-P_{vc,\mathbf{k}}\; n_{c,\mathbf{k}-\mathbf{q}}\; \delta_{\mathbf{k},\mathbf{k}'} - P_{vc,\mathbf{k}-\mathbf{q}}\; n_{v,\mathbf{k}}\; \delta_{\mathbf{k},\mathbf{k}'}\big)$$

$$= \sum_{\mathbf{q}\neq\mathbf{0}} V_q\big(P_{vc,\mathbf{k}-\mathbf{q}}\; n_{c,\mathbf{k}} + P_{vc,\mathbf{k}}\; n_{v,\mathbf{k}-\mathbf{q}}$$

$$-P_{vc,\mathbf{k}}\; n_{c,\mathbf{k}-\mathbf{q}} - P_{vc,\mathbf{k}-\mathbf{q}}\; n_{v,\mathbf{k}}\big)$$

$$= P_{vc,\mathbf{k}} \sum_{\mathbf{q}\neq\mathbf{0}} V_q\left(n_{v,\mathbf{k}-\mathbf{q}} - n_{c,\mathbf{k}-\mathbf{q}}\right) + \sum_{\mathbf{q}\neq\mathbf{0}} P_{vc,\mathbf{k}-\mathbf{q}} V_q\left(n_{c,\mathbf{k}} - n_{v,\mathbf{k}}\right)$$

(Simplified) Heisenberg Equation of Motion

equation of motion for interband pair polarization

$$\hbar\left(i\frac{\mathrm{d}}{\mathrm{d}t}-(e_{c,k}-e_{v,k})\right)\ P_{vc,\mathbf{k}}(t) =$$
$$+[n_{c,\mathbf{k}}(t)-n_{v,\mathbf{k}}(t)]\left(d_{cv}\mathcal{E}(t)+\sum_{\mathbf{q}\neq\mathbf{k}}V_{|\mathbf{k}-\mathbf{q}|}\ P_{vc,\mathbf{q}}\right) \qquad (20)$$

with energy shift

$$e_{v,k} = \epsilon_{v,k}-\sum_{\mathbf{q}\neq\mathbf{k}}V_{|\mathbf{k}-\mathbf{q}|}\ n_{v,\mathbf{q}}/\hbar$$
$$e_{c,k} = \epsilon_{c,k}-\sum_{\mathbf{q}\neq\mathbf{k}}V_{|\mathbf{k}-\mathbf{q}|}\ n_{c,\mathbf{q}}/\hbar$$

Comparison: Non-Interacting Particles

Interband Polarisation without Coulomb interaction ($V_q = 0$)

$$n_{\lambda,\mathbf{k}}(t) \rightarrow f_{\lambda,k}$$

for a quasi-equilibrium.

$$\hbar \left[i \frac{\mathrm{d}}{\mathrm{d}t} - (\epsilon_{c,k} - \epsilon_{v,k}) \right] \; P^0_{vc,\mathbf{k}}(t) = [f_{c,k} - f_{v,k}] d_{cv} \mathcal{E}(t)$$

Solved by Fourier transformation:

$$\begin{aligned} P^0_{vc,\mathbf{k}}(\omega) &= [f_{c,k} - f_{v,k}] \; \frac{d_{cv}}{\hbar(\omega - (\epsilon_{c,k} - \epsilon_{v,k}))} \; \mathcal{E}(\omega) \\ P(t) &= \sum_{\mathbf{k}} P_{vc,\mathbf{k}}(t) d_{vc} + \mathrm{c.c.} \\ P^0(t) &= \sum_{\mathbf{k}} \int \frac{\mathrm{d}\omega}{2\pi} \; |d_{cv}|^2 \; \frac{f_{c,k} - f_{v,k}}{\hbar(\omega - (\epsilon_{c,k} - \epsilon_{v,k}))} \; \mathcal{E}(\omega) \; e^{-i\omega t} + \mathrm{c.c.} \end{aligned}$$

Wannier Equation

Assume an unexcited crystal, i.e.:

$$
\begin{aligned}
f_{c,k} &\equiv 0 \\
f_{v,k} &\equiv 1
\end{aligned}
$$

Equation of motion:

$$
\left[\hbar\omega - E_g - \frac{\hbar^2 k^2}{2m_r}\right] \; P_{vc,\mathbf{k}}(\omega) = -\left(d_{cv}\mathcal{E}(\omega) + \sum_{\mathbf{q}\neq\mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} \; P_{vc,\mathbf{q}}(\omega)\right) \qquad (21)
$$

with reduced mass including effective masses:

$$
\frac{1}{m_r} = \frac{1}{m_c} - \frac{1}{m_v}.
$$

Wannier Equation

Change from momentum space **k** into real space **r** with Fourier transformation

$$f_{\mathbf{q}} = \frac{1}{L^3} \int \mathrm{d}^3 r \; f(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}}$$

yields

$$\left[\hbar\omega - E_g + \frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m_r} + V(r)\right] \; P_{vc,\mathbf{k}}(\mathbf{r},\omega) = -d_{cv}\mathcal{E}(\omega)\delta(\mathbf{r}) \; L^3. \quad (22)$$

Homogeneous part of the equation is called

Wannier equation

$$-\left[\frac{\hbar^2 \nabla_{\mathbf{r}}^2}{2m_r} + V(r)\right] \; \psi_\nu(\mathbf{r}) = E_\nu \psi_\nu(\mathbf{r}) \quad (23)$$

Wannier equation

- Wannier equation is identical to Hydrogen Atom problem
- Solved accordingly by splitting ψ_ν into radial and angular parts:

$$\psi_\nu = \psi_{n,l,m}(\mathbf{r}) = f_{n,l}(r)\ Y_{l,m}(\theta,\phi) \tag{24}$$

- $Y_{l,m}(\theta,\phi)$ is given by spherical harmonics
- Calculation of $f_{n,l}(r)$ reveals exciton energy states E_n

Excitons

Radial part is given by

$$\left(\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\rho^2\ \frac{\partial}{\partial\rho}+\frac{\lambda}{\rho}-\frac{1}{4}-\frac{l(l+1)}{\rho^2}\right)f_{n,l}(\rho)=0 \qquad (25)$$

with

- Scaled radius $\rho = r\alpha$ where $\alpha^2 = -(8m_r E_\nu)/\hbar^2$ and $E_\nu < 0$
- $\lambda = 2/(a_0\alpha)$ where $a_0 = (\hbar^2\epsilon_0)/(e^2 m_r)$ semiconductor Bohr radius
- Eigenvalues of angular momentum operator $l(l+1)$
- Quantumnumber ν_{max} is given by $\nu_{max} + l + 1 = n$

Excitons

exciton bound state energies

$$E_n = -E_0 \frac{1}{n^2} \quad n \in \mathbb{N} \tag{26}$$

with the energy unit

$$E_0 = \frac{e^4 m_r}{2\epsilon_0^2 \hbar^2} \tag{27}$$

$\nu_{\max}$	n	l	$f_{n,l}(\rho) = C\rho^l e^{-\rho/2} \sum_\nu \beta_\nu \rho^\nu$	E_n
0	1	0	$f_{1,0}(r) = a_0^{-3/2} 2e^{-r/a_0}$	$E_1 = -E_0$
1	2	0	$f_{2,0}(r) = (2a_0)^{-3/2}(2 - r/a_0)e^{-r/a_0}$	$E_2 = -E_0/4$
0	2	1	$f_{2,1}(r) = (2a_0)^{-3/2}(r/(\sqrt{3}a_0))e^{-r/a_0}$	$E_2 = -E_0/4$

normalized radial wavefunctions

Excitons

exciton wavefunction for bound states

$$\psi_{n,l,m}(r,\theta,\phi) = -\sqrt{-\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \times \rho^l e^{-\rho/2} L_{n+l}^{2l+1}(\rho) \; Y_{l,m}(\theta,\phi) \qquad (28)$$

with

- Laguerre polynomials L_{n+l}^{2l+1}
- scaled radius $\rho = 2r/(na_0)$

Ionization Continuum

- Bound states have been found for negative energies $E_\nu < 0$
- Exciton binding energy is less than bandgap energy $E_n < E_{gap}$
- $E_v \geq 0$ describes unbound (ionized) states
- Continuum occurs in conduction band

Excitons

exciton wavefunction for ionized states

$$\psi_{k,l,m}(r,\theta,\phi) = \quad \frac{(2ikr)^l}{(2l+1)!}\ e^{\pi|\lambda|/2}\ \sqrt{\frac{2\pi k^2}{R|\lambda|\ \sinh(\pi|\lambda|)}\ \prod_{j=0}^{l}(j^2+|\lambda|^2)}$$

$$\times \qquad e^{-ikr} F(l+1+i|\lambda|; 2l+2; 2ikr)\ Y_{l,m}(\theta,\phi)$$

with

- $\lambda = -i/(a_0 k)$
- confluent hypergeometric function
  $F(a,b,c) = F(l+1+i|\lambda|; 2l+2; 2ikr)$
- $R \to \infty$

Optical Spectra

Solutions from the Wannier equation can provide complete solution for the polarisation

$$P_{vc}(\mathbf{r},\omega) = \sum_{\nu} b_\nu \psi_\nu(\mathbf{r}). \tag{29}$$

In equation of motion:

$$\begin{aligned} \left[\hbar\omega - E_g + \frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m_r} + V(r)\right] P_{vc,\mathbf{k}}(\mathbf{r},\omega) &= -d_{cv}\mathcal{E}(\omega)\delta(\mathbf{r})\ L^3 \\ \sum_{\nu} b_\nu[\hbar\omega - E_g - E_\nu] \int \mathrm{d}^3 r \psi_\mu^*(\mathbf{r})\psi_\nu(\mathbf{r}) &= -d_{cv}\mathcal{E}(\omega)\psi_\mu^*(\mathbf{r}=0)\ L^3 \end{aligned}$$

so that

$$b_\mu = -\frac{d_{cv} L^3 \psi_\mu^*(\mathbf{r}=0)}{\hbar\omega - E_g - E_\mu}\mathcal{E}(\omega). \tag{30}$$

Optical Spectra

$$P_{vc}(\mathbf{r},\omega) = -\sum_{\nu} \mathcal{E}(\omega) \frac{d_{cv} L^3 \psi^*_{\mu}(\mathbf{r}=0)}{\hbar\omega - E_g - E_{\mu}} \psi_{\nu}(\mathbf{r}) \tag{31}$$

with Fourier transformation into momentum space yields

$$P_{vc}(\mathbf{r},\omega) = -\sum_{\nu} \mathcal{E}(\omega) \frac{d_{cv} \psi^*_{\mu}(\mathbf{r}=0)}{\hbar\omega - E_g - E_{\mu}} \int \mathrm{d}^3 r \psi_{\nu}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{32}$$

Fourier transformation of general Optical Polarization is expressed as:

$$P(\omega) = \sum_{\mathbf{k}} (P_{cv,\mathbf{k}}(\omega) d_{vc} + P^*_{cv,\mathbf{k}}(-\omega) d^*_{vc}) \tag{33}$$

.

Optical Spectra

with $\mathcal{E}^*(-\omega) = \mathcal{E}(\omega)$ and

$$\int \mathrm{d}^3 r \psi_\nu(\mathbf{r}) \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} = \int \mathrm{d}^3 r \psi_\nu(\mathbf{r}) 2L^3 \delta_{\mathbf{r},0} = 2L^3 \psi_\nu(\mathbf{r}=0) \quad (34)$$

the Optical Polarization in frequency space resutlts in

$$\begin{aligned} P(\omega) &= -2L^3 \sum_\nu |d_{cv}|^2 |\psi_\nu(\mathbf{r}=0)|^2 \mathcal{E}(\omega) \\ &\times \left[\frac{1}{\hbar\omega - E_g - E_\nu} - \frac{1}{\hbar\omega + E_g + E_\nu} \right] \end{aligned} \quad (35)$$

Susceptibility

electron-hole-pair susceptibility

$$\chi(\omega) = -2|d_{cv}|^2 \sum_{\mu} |\psi_\mu(\mathbf{r}=0)|^2 \times \left[\frac{1}{\hbar\omega - E_g - E_\mu} - \frac{1}{\hbar\omega + E_g + E_\mu}\right] \quad (36)$$

with

$$\chi(\omega) = \frac{P(\omega)}{L^3 \mathcal{E}(\omega)}$$

Optical Spectra

Susceptibility for $l = 0$ and $m = 0$ gives

$$\begin{aligned} \chi(\omega) &= -\frac{2|d_{cv}|^2}{\pi E_0 a_0^3}\left[\sum_n \frac{1}{n^3}\frac{E_0}{\hbar\omega - E_g - E_n}\right. \\ &+ \left.\frac{1}{2}\int \mathrm{d}x\, \frac{x e^{\pi/x}}{\sinh(\pi/x)}\frac{E_0}{\hbar\omega - E_g - E_0 x^2}\right] \end{aligned} \tag{37}$$

So that with

$$\alpha(\omega) \simeq \frac{4\pi\omega}{n_b c}\chi''(\omega) \tag{38}$$

Absorption Coefficient

Elliott formula

$$\alpha(\omega) = a_0 \frac{\hbar\omega}{E_0} \left[\sum_{n=1}^{\infty} \frac{4\pi}{n^3} \delta(\Delta + 1/n^2) + \theta(\Delta) \frac{\pi e^{\pi/\sqrt{\Delta}}}{\sinh(\pi/\sqrt{\Delta})} \right] \quad (39)$$

with

$$\Delta = (\hbar\omega - E_g)/E_0 \quad (40)$$

Optical Spectra

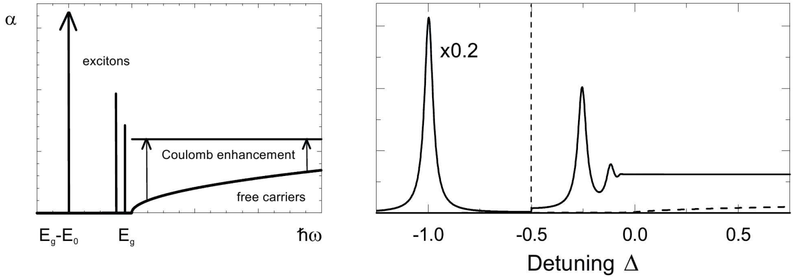

Figure: Band edge absorption (left: schematic, right:calculated)

Results

- Coulomb interaction reveals quasi particles: Excitons
- Polarization wavefunctions derivable with hydrogen atom solutions
- Wafefunctions include bound states in bandgap and continuum in conduction band
- Calculation of electron-hole pair susceptibility and absorption coefficient possible

Sources

- Haug, Hartmut ; Koch, Stephan W.: *Quantum Theory of the Optical and Electronic Properties of Semiconductors*. 3rd Edition. Singapore : World Scientific, 1998