Excitons in Bulk Semiconductors
Seminar: Optical Properties of Semiconductors

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Contents

1 Introduction

The effects of an electric field on a semiconductor are described by examining the resulting polarisation. Polarisation describes the displacement of an electrically charged particle under such an external field and is expressed via the so called susceptibility

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

When a semiconductor is exposed to an electric field where the field frequency is equal to or larger than the bandgap energy of the semiconductor, an electron excitation from the valence band to the conduction band occurs so that an electron-hole-pair is created. This is a well known effect and relates to the bandstructure of semiconductors. The following work reveals that by taking the Coulomb interaction between the electron and the hole of a semiconductor into account one can create a new kind of quasi-particles, which will remind one of the hydrogen atom problem.

The desired results are achieved by describing the polarisation in quantum mechanical expressions and applying the equation of motion in the Heisenberg picture to find its time dependance. By applying the analogous solutions of the hydrogen atom problem to the newly found equation of motion one can determine the describing wavefunctions which describe the polarisation. This result enables us to finally derive the susceptibility and absorption to gain more insight into the physical interpretation.

2 The Interband Polarization

We start with the classical polarisation of a particle with the charge e, which is given by

$$P = L^3 n_0 e r. \tag{2}$$

To find a quantum mechanical expression we apply the expectation value of the polarisation in operator notation and introduce the second quantization with field operators $\hat{\psi}$. The polarisation is given by the expectation value of the dipole moment $e\mathbf{r}$

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

The expression above gives the average value of the polarisation. This is due to the equilibrium statistical operator ρ_0, which is explicitly included in the equivalent notation

$$\mathbf{P}(t) = \int \mathrm{d}^3 r \, \mathrm{tr} \left[\rho_0 \, \hat{\psi}^\dagger(\mathbf{r}, t) \, e\mathbf{r} \, \hat{\psi}(\mathbf{r}, t) \right], \tag{4}$$

where ρ_0 describes the state of the system before it is exposed into any light. By changing the basis we describe the electron field operators $\hat{\psi}$ by using Bloch functions

$$\hat{\psi}(\mathbf{r}, t) = \sum_{\lambda, \mathbf{k}} \hat{a}_{\lambda, \mathbf{k}}(t) \, \psi_\lambda(\mathbf{k}, \mathbf{r}). \tag{5}$$

λ describes the band, in which the corresponding particle is contained, while $\mathbf{k}$ describes the momentum state the particle represents. The annihilation operator $\hat{a}_{\lambda, \mathbf{k}}(t)$ therefore destroys a particle in band λ with momentum $\mathbf{k}$. Equation (3) therefore yields:

$$\mathbf{P}(t) = \sum_{\lambda, \lambda', \mathbf{k}, \mathbf{k}'} \int \mathrm{d}^3 r \, \langle \hat{a}^\dagger_{\lambda, \mathbf{k}}(t) \, \psi^*_\lambda(\mathbf{k}, \mathbf{r}) \, e\mathbf{r} \, \hat{a}_{\lambda', \mathbf{k}'}(t) \, \psi_{\lambda'}(\mathbf{k}', \mathbf{r}) \rangle \tag{6}$$

and also includes the creation operator $\hat{a}^\dagger_{\lambda,\mathbf{k}}(t)$. The wave functions can be excluded out of the mean value due to not being operators. Because the spacial dependancy is not present in the mean value the integral can be applied only to the dipole moment and the wave functions.

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

Introducing the *dipole approximation* where only identical $\mathbf{k}$-states in different bands $\lambda \neq \lambda'$ are coupled one can describe the integral as a product of a delta function and the dipole moment $\mathbf{d}_{\lambda\lambda'}$

$$\int \mathrm{d}^3r\; \psi^*_\lambda(\mathbf{k},\mathbf{r})\; e\mathbf{r}\; \psi_{\lambda'}(\mathbf{k}',\mathbf{r}) \simeq \delta_{\mathrm{k},\mathrm{k}'}\mathbf{d}_{\lambda\lambda'}. \tag{8}$$

This approximation is valid because the photon momentum of the light field is small in comparison to $\mathbf{k}$ and $\mathbf{k}'$. By applying this approximation the polarisation is simply expressed as

$$\mathbf{P}(t) = \sum_{\lambda,\lambda',\mathbf{k}} \langle a^\dagger_{\lambda,\mathbf{k}}(t)\, a_{\lambda',\mathbf{k}}(t) \rangle\, \mathbf{d}_{\lambda\lambda'} = \sum_{\lambda,\lambda',\mathbf{k}} P_{\lambda,\lambda',\mathbf{k}}(t)\, \mathbf{d}_{\lambda\lambda'}, \tag{9}$$

where $P_{\lambda,\lambda',\mathbf{k}}(t)$ is called the pair function. It is important to notice, that the polarisation $\mathbf{P}(t)$ is only implicitly time dependant, because the time dependant factors only show in the creation and annihilation operators. This will prove useful in calculating the equation of motion in the following sections.

With this result one can describe the dynamics of the system by applying the Heisenberg equation of motion. To do this, however, the Hamilton operator is needed. We describe the whole Hamiltonian by splitting it into three parts.

Kinetic Energy

The kinetic energy of the particles is simply given by

$$\mathcal{H}_{kin} = \sum_{\lambda,\mathbf{k}} E_{\lambda,k} a^\dagger_{\lambda,\mathbf{k}}\, a_{\lambda,\mathbf{k}}. \tag{10}$$

By introducing the *two band approximation* we can simplify the expression. We only consider λ to be the valence band v or the conduction band c.

$$\mathcal{H}_{kin} = \sum_{\mathbf{k}} \left(E_{c,k} a^\dagger_{c,\mathbf{k}}\, a_{c,\mathbf{k}} + E_{v,k} a^\dagger_{v,\mathbf{k}}\, a_{v,\mathbf{k}} \right) \tag{11}$$

As one can see the single particle energies include the corresponding effective masses and the bandgap energy between the two bands

$$E_{c,k} = \hbar\epsilon_{c,k} = E_g + \hbar^2 k^2/2m_c \tag{12}$$
$$E_{v,k} = \hbar\epsilon_{v,k} = \hbar^2 k^2/2m_v. \tag{13}$$

Electron-electric field interaction

The interaction between the electron and the electric field is given by

$$\mathcal{H}_I = \int \mathrm{d}^3r\; \hat{\psi}^\dagger(\mathbf{r})\; (-e\mathbf{r})\; \boldsymbol{\mathcal{E}}(\mathbf{r},t)\; \hat{\psi}(\mathbf{r}) \tag{14}$$

where the electric field can be split into a product of a time dependent and a spacial dependent part

$$\boldsymbol{\mathcal{E}}(\mathbf{r},t) = \boldsymbol{\mathcal{E}}(t)\, \frac{1}{2} \left(\exp\left(i\,\mathbf{q}\cdot\mathbf{r} \right) + \exp\left(-i\,\mathbf{q}\cdot\mathbf{r} \right) \right). \tag{15}$$

We again apply the dipole and two band approximations. The dipole approximation demands for the momentum of the electric field to be much smaller than the momentum of the particles, which are similar to each other

$$\mathbf{k} \approx \mathbf{k}' \gg \mathbf{q} \approx 0. \tag{16}$$

This approximation results in the vanishing of the integral over the spacial part of the electric field. One can also project the dipole moment $\mathbf{d}_{cv}$ (with the two band approximation already applied) into the direction of the electric field $\boldsymbol{\mathcal{E}}(t)$, so that one can drop the vector notation. By inserting the Bloch functions into equation 14 we get

$$\mathcal{H}_I \simeq -\sum_{\mathbf{k}} \mathcal{E}(t) \left(a^\dagger_{c,\mathbf{k}}\, a_{v,\mathbf{k}}\, d_{cv} + a^\dagger_{v,\mathbf{k}}\, a_{c,\mathbf{k}}\, d^*_{cv} \right) \tag{17}$$

Coulomb interaction

The Coulomb interaction is denoted by the exchange of momentum $\mathbf{q}$ between two particles $\mathbf{k}$ and $\mathbf{k}'$. The Hamilton operator therefore yields

$$\mathcal{H}_C = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0,\lambda,\lambda'} V_q\, a^\dagger_{\lambda,\mathbf{k}+\mathbf{q}}\, a^\dagger_{\lambda',\mathbf{k}'-\mathbf{q}}\, a_{\lambda',\mathbf{k}'}\, a_{\lambda,\mathbf{k}}. \tag{18}$$

In the above expressions it is assumed that the number of electrons in each band is conserved. This is because we do not consider relaxation from the conduction band due to Coulomb interaction; the interaction is also not sufficient to excite electrons from the valence band due to the large energetic differences between the Coulomb interaction and the bandgap energy.

The case for two bands is expressed as

$$\mathcal{H}_C = \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}\neq 0} V_q \tag{19}$$

$$\times \left(a^\dagger_{c,\mathbf{k}+\mathbf{q}}\, a^\dagger_{c,\mathbf{k}'-\mathbf{q}}\, a_{c,\mathbf{k}'}\, a_{c,\mathbf{k}} + a^\dagger_{v,\mathbf{k}+\mathbf{q}}\, a^\dagger_{v,\mathbf{k}'-\mathbf{q}}\, a_{v,\mathbf{k}'}\, a_{v,\mathbf{k}} + 2\, a^\dagger_{c,\mathbf{k}+\mathbf{q}}\, a^\dagger_{v,\mathbf{k}'-\mathbf{q}}\, a_{v,\mathbf{k}'}\, a_{c,\mathbf{k}} \right)$$

with the Coulomb potential

$$V_q = \frac{4\pi e^2}{\epsilon_0 L^3} \frac{1}{q^2}. \tag{20}$$

Equation of motion

By summing up the three different parts of the Hamilton operator, one can finally express the equation of motion for expectation values

$$i\hbar \left(\frac{\mathrm{d}\langle P_{vc,\mathbf{k}}(t)\rangle}{\mathrm{d}t} \right) = -\langle [\mathcal{H}, P_{vc,\mathbf{k}}(t)] \rangle + i\hbar \langle \underbrace{\left(\frac{\partial P_{vc,\mathbf{k}}(t)}{\partial t} \right)}_{= 0} \rangle \tag{21}$$

As previously mentioned the polarisation is not explicitly dependent on time, which results in the vanishing of the partial derivative. By inserting the polarisation and the full Hamilton operator, we achieve

$$i\hbar \left(\frac{\mathrm{d}\langle P_{vc,\mathbf{k}}(t)\rangle}{\mathrm{d}t} \right) = \hbar(\epsilon_{c,k} - \epsilon_{v,k})\, P_{vc,\mathbf{k}}(t) + [n_{c,\mathbf{k}}(t) - n_{v,\mathbf{k}}(t)]\, d_{cv}\mathcal{E}(t) + \sum_{\mathbf{k}',\mathbf{q}\neq 0} V_q$$

$$\times \Bigg(\langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}}\, a^\dagger_{v,\mathbf{k}-\mathbf{q}}\, a_{c,\mathbf{k}'}\, a_{c,\mathbf{k}} \rangle + \langle a^\dagger_{v,\mathbf{k}'+\mathbf{q}}\, a^\dagger_{v,\mathbf{k}-\mathbf{q}}\, a_{v,\mathbf{k}'}\, a_{c,\mathbf{k}} \rangle \tag{22}$$

$$+ \langle a^\dagger_{v,\mathbf{k}}\, a^\dagger_{c,\mathbf{k}'-\mathbf{q}}\, a_{c,\mathbf{k}'}\, a_{c,\mathbf{k}-\mathbf{q}} \rangle + \langle a^\dagger_{v,\mathbf{k}}\, a^\dagger_{v,\mathbf{k}'-\mathbf{q}}\, a_{v,\mathbf{k}'}\, a_{c,\mathbf{k}-\mathbf{q}} \rangle \Bigg)$$

with the particle number

$$n_{\lambda,\mathbf{k}} = \langle a^\dagger_{\lambda,\mathbf{k}} a_{\lambda,\mathbf{k}} \rangle. \tag{23}$$

As one can see, the equation consists of the parts, where the first one describes the kinetic energy, the second the electron-electric field interaction and the last one the Coulomb interaction. Our following task will be the simplfaction of the Coulomb term, to gain more insight into the formula. We approximate the 4-operator average values with products of two operator. This expansion would be exact if the wafefunction of the system were a Slater determinant.

$$\langle a^\dagger_i \, a^\dagger_j \, a_k \, a_l \rangle = \langle a^\dagger_i \, a_l \rangle \langle a^\dagger_j \, a_k \rangle - \langle a^\dagger_i \, a_k \rangle \langle a^\dagger_j \, a_l \rangle \tag{24}$$

to the match of creation and annihilation operators and postulate, that two particles in states $\mathbf{k}$ and $\mathbf{k}'$ must interact, therefore prohibiting the noninteraction via $q \neq 0$. With these assumptions the four-particle operator meanvalue can be described as the sum of the product of two two-particle operator meanvalues, where the delta function $\delta_{q,0}$ returns zero.

$$\begin{aligned}
\langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}} \, a^\dagger_{v,\mathbf{k}-\mathbf{q}} \, a_{c,\mathbf{k}'} \, a_{c,\mathbf{k}} \rangle \quad &\simeq \\
\langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}} \, a_{c,\mathbf{k}'} \rangle \langle a^\dagger_{v,\mathbf{k}-\mathbf{q}} \, a_{c,\mathbf{k}} \rangle \, \delta_{q,0} \quad &+ \quad \langle a^\dagger_{c,\mathbf{k}'+\mathbf{q}} \, a_{c,\mathbf{k}} \rangle \langle a^\dagger_{v,\mathbf{k}-\mathbf{q}} \, a_{c,\mathbf{k}'} \rangle \, \delta_{k-q,k'} \\
&= \quad P_{vc,\mathbf{k}'} \, n_{c,\mathbf{k}} \, \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'}.
\end{aligned} \tag{25}$$

By applying the same pattern to the remaining three parts of the sum one can find that

$$\begin{aligned}
\langle a^\dagger_{v,\mathbf{k}'+\mathbf{q}} \, a^\dagger_{v,\mathbf{k}-\mathbf{q}} \, a_{v,\mathbf{k}'} \, a_{c,\mathbf{k}} \rangle \quad &\simeq \quad P_{vc,\mathbf{k}} \, n_{v,\mathbf{k}'} \, \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'} \\
\langle a^\dagger_{v,\mathbf{k}} \, a^\dagger_{c,\mathbf{k}'-\mathbf{q}} \, a_{c,\mathbf{k}'} \, a_{c,\mathbf{k}-\mathbf{q}} \rangle \quad &\simeq \quad -P_{vc,\mathbf{k}} \, n_{c,\mathbf{k}-\mathbf{q}} \, \delta_{\mathbf{k},\mathbf{k}'} \\
\langle a^\dagger_{v,\mathbf{k}} \, a^\dagger_{v,\mathbf{k}'-\mathbf{q}} \, a_{v,\mathbf{k}'} \, a_{c,\mathbf{k}-\mathbf{q}} \rangle \quad &\simeq \quad -P_{vc,\mathbf{k}-\mathbf{q}} \, n_{v,\mathbf{k}} \, \delta_{\mathbf{k},\mathbf{k}'}.
\end{aligned} \tag{26}$$

We return to the expression for the Coulomb interaction and proceed in the simplification.

$$\begin{aligned}
\sum_{\mathbf{k}',\mathbf{q}\neq\mathbf{0}} V_q \big(& P_{vc,\mathbf{k}'} \, n_{c,\mathbf{k}} \, \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'} + P_{vc,\mathbf{k}} \, n_{v,\mathbf{k}'} \, \delta_{\mathbf{k}-\mathbf{q},\mathbf{k}'} - P_{vc,\mathbf{k}} \, n_{c,\mathbf{k}-\mathbf{q}} \, \delta_{\mathbf{k},\mathbf{k}'} - P_{vc,\mathbf{k}-\mathbf{q}} \, n_{v,\mathbf{k}} \, \delta_{\mathbf{k},\mathbf{k}'} \big) \\
= \sum_{\mathbf{q}\neq\mathbf{0}} V_q \big(& P_{vc,\mathbf{k}-\mathbf{q}} \, n_{c,\mathbf{k}} + P_{vc,\mathbf{k}} \, n_{v,\mathbf{k}-\mathbf{q}} - P_{vc,\mathbf{k}} \, n_{c,\mathbf{k}-\mathbf{q}} - P_{vc,\mathbf{k}-\mathbf{q}} \, n_{v,\mathbf{k}} \big) \\
= P_{vc,\mathbf{k}} & \sum_{\mathbf{q}\neq\mathbf{0}} V_q \left(n_{v,\mathbf{k}-\mathbf{q}} - n_{c,\mathbf{k}-\mathbf{q}} \right) + \sum_{\mathbf{q}\neq\mathbf{0}} P_{vc,\mathbf{k}-\mathbf{q}} V_q \left(n_{c,\mathbf{k}} - n_{v,\mathbf{k}} \right).
\end{aligned} \tag{27}$$

This expression can be but back into the equation of motion, giving the final solution

$$\hbar \left(i\frac{\mathrm{d}}{\mathrm{d}t} - (e_{c,k} - e_{v,k}) \right) P_{vc,\mathbf{k}}(t) = [n_{c,\mathbf{k}}(t) - n_{v,\mathbf{k}}(t)] \left(d_{cv}\mathcal{E}(t) + \sum_{\mathbf{q}\neq\mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} \, P_{vc,\mathbf{q}} \right). \tag{28}$$

One can finally see that the Coulomb interaction results in a mere shift of the energies with

$$e_{v,k} \quad = \quad \epsilon_{v,k} - \sum_{\mathbf{q}\neq\mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} \, n_{v,\mathbf{q}}/\hbar \tag{29}$$

$$e_{c,k} \quad = \quad \epsilon_{c,k} - \sum_{\mathbf{q}\neq\mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} \, n_{c,\mathbf{q}}/\hbar \tag{30}$$

and a shift of the electric field with the expression

$$\sum_{\mathbf{q}\neq\mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} \, P_{vc,\mathbf{q}}. \tag{31}$$

This solution will help us finding the polarisation wavefunctions.

As a quick reminder we compare our solution for the equation of motion with the corresponding result of noninteracting particles. The Coulomb potential yields $V_q = 0$ and we express the particle numbers in terms of Fermi distributions

$$n_{\lambda,\mathbf{k}}(t) \to f_{\lambda,k}, \tag{32}$$

which is a realistic assumption in the case of a quasi equilibrium. The equation of motion without Coulomb interaction is

$$\hbar \left[i\frac{\mathrm{d}}{\mathrm{d}t} - (\epsilon_{c,k} - \epsilon_{v,k}) \right] P^0_{vc,\mathbf{k}}(t) = [f_{c,k} - f_{v,k}]d_{cv}\mathcal{E}(t) \tag{33}$$

and is solved by Fourier transformation

$$P^0_{vc,\mathbf{k}}(\omega) = [f_{c,k} - f_{v,k}] \frac{d_{cv}}{\hbar(\omega - (\epsilon_{c,k} - \epsilon_{v,k}))} \mathcal{E}(\omega) \tag{34}$$

$$P(t) = \sum_{\mathbf{k}} P_{vc,\mathbf{k}}(t)d_{vc} + \text{c.c.} \tag{35}$$

$$\Rightarrow P^0(t) = \sum_{\mathbf{k}} \int \frac{\mathrm{d}\omega}{2\pi} |d_{cv}|^2 \frac{f_{c,k} - f_{v,k}}{\hbar(\omega - (\epsilon_{c,k} - \epsilon_{v,k}))} \mathcal{E}(\omega) \ e^{-i\omega t} + \text{c.c.} \tag{36}$$

3   Wannier Equation

The following process is dedicated to the solution of the full equation of motion of interacting particles. Because our system is a semiconductor we can assume that the crystal is initially unexcited, i.e.

$$f_{c,k} \equiv 0$$
$$f_{v,k} \equiv 1.$$

This simplification yields for the equation of motion

$$\left[\hbar\omega - E_g - \frac{\hbar^2 k^2}{2m_r} \right] P_{vc,\mathbf{k}}(\omega) = -\left(d_{cv}\mathcal{E}(\omega) + \sum_{\mathbf{q} \neq \mathbf{k}} V_{|\mathbf{k}-\mathbf{q}|} \ P_{vc,\mathbf{q}}(\omega) \right) \tag{37}$$

with the reduced mass including the effective masses of electrons and holes

$$\frac{1}{m_r} = \frac{1}{m_c} - \frac{1}{m_v}. \tag{38}$$

We now change from momentum space $\mathbf{k}$ into real space $\mathbf{r}$ with a Fourier transformation

$$f_{\mathbf{q}} = \frac{1}{L^3} \int \mathrm{d}^3r \ f(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}} \tag{39}$$

so that the equation of motion yields the following differential equation:

$$\left[\hbar\omega - E_g + \frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m_r} + V(r) \right] P_{vc,\mathbf{k}}(\mathbf{r},\omega) = -d_{cv}\mathcal{E}(\omega)\delta(\mathbf{r}) \ L^3. \tag{40}$$

To calculate the polarisation we solve the homogeneous part

$$-\left[\frac{\hbar^2\nabla_{\mathbf{r}}^2}{2m_r} + V(r) \right] \ \psi_\nu(\mathbf{r}) = E_\nu\psi_\nu(\mathbf{r}). \tag{41}$$

This so called Wannier equation is similar to hydrogen atom problem. The mere difference is given in the reduced mass, where the Wannier equation holds the effective masses of the electron and hole,

which are similar, in contrast to the proton and electron, which describe the hydrogen atom and where the mass of the electron dominates. The Wannier equation can be solved by splitting ψ_ν into radial and angular parts:

$$\psi_\nu = \psi_{n,l,m}(\mathbf{r}) = f_{n,l}(r)\, Y_{l,m}(\theta, \phi), \tag{42}$$

where $Y_{l,m}(\theta, \phi)$ is given by spherical harmonics and the calculation of $f_{n,l}(r)$ will reveal the exciton energy states E_n.

4 Excitons

The radial part of the hydrogen atom problem is given by the expression of the nabla operator in spherical coordinates

$$\left(\frac{1}{\rho^2} \frac{\partial}{\partial \rho} \rho^2 \frac{\partial}{\partial \rho} + \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right) f_{n,l}(\rho) = 0. \tag{43}$$

This expression introduces the scaled radius $\rho = r\alpha$ where $\alpha^2 = -(8m_r E_\nu)/\hbar^2$ and $E_\nu < 0$ for bound states. The factor $\lambda = 2/(a_0\alpha)$ includes $a_0 = (\hbar^2 \epsilon_0)/(e^2 m_r)$, which is the semiconductor Bohr radius. The angular part is already solved with the eigenvalues $l(l+1)$ of the angular momentum operator. The quantum number ν_{max} is finally given by $\nu_{max} + l + 1 = n$, so the energy states yield

$$E_n = -E_0 \frac{1}{n^2}, \quad n \in \mathbb{N} \tag{44}$$

with the energy unit

$$E_0 = \frac{e^4 m_r}{2\epsilon_0^2 \hbar^2}. \tag{45}$$

The energies $E_n < 0$ lie beneath the bandgap energy. The full wavefunction for bound states is

$$\psi_{n,l,m}(r, \theta, \phi) = -\sqrt{-\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, \rho^l e^{-\rho/2}\, L_{n+l}^{2l+1}(\rho)\, Y_{l,m}(\theta, \phi) \tag{46}$$

with the Laguerre polynomials L_{n+l}^{2l+1} and the scaled radius $\rho = 2r/(na_0)$. The case for larger energies $E_v \geq 0$ describes unbound (ionized) states, which results in an energy continuum of states. This continuum occurs in the conduction band and the wavefunction for the ionized states is

$$\psi_{k,l,m}(r, \theta, \phi) = \frac{(2ikr)^l}{(2l+1)!}\, e^{\pi|\lambda|/2}\, \sqrt{\frac{2\pi k^2}{R|\lambda|\ \sinh(\pi|\lambda|)}}\, \prod_{j=0}^{l}(j^2 + |\lambda|^2)$$
$$\times e^{-ikr} F(l+1+i|\lambda|; 2l+2; 2ikr)\, Y_{l,m}(\theta, \phi) \tag{47}$$

with the imaginary factor $\lambda = -i/(a_0 k)$ and the confluent hypergeometric functions $F(a, b, c) = F(l+1+i|\lambda|; 2l+2; 2ikr)$. The solution is given for the large radius $R \to \infty$. We have now expressed the wavefunction solutions for the Wannier equation which contains one part for bound and one for ionized states. These solutions of the homogeneous problem can provide the complete solution for the polarisation by finding the corresponding linear combination

$$P_{vc}(\mathbf{r}, \omega) = \sum_\nu b_\nu \psi_\nu(\mathbf{r}). \tag{48}$$

We acquire the coefficients b_ν by inserting this expression into the equation of motion, multiplying both sides with $\psi_\mu^*(\mathbf{r})$ and integrating over the space

$$\left[\hbar\omega - E_g + \frac{\hbar^2 \nabla_\mathbf{r}^2}{2m_r} + V(r) \right] P_{vc,\mathbf{k}}(\mathbf{r}, \omega) = -d_{cv}\mathcal{E}(\omega)\delta(\mathbf{r})\, L^3 \tag{49}$$

$$\sum_\nu b_\nu [\hbar\omega - E_g - E_\nu] \int \mathrm{d}^3 r\, \psi_\mu^*(\mathbf{r})\psi_\nu(\mathbf{r}) = -d_{cv}\mathcal{E}(\omega)\psi_\mu^*(\mathbf{r} = 0)\, L^3, \tag{50}$$

7

so that we get

$$b_\mu = -\frac{d_{cv}L^3\psi_\mu^*(\mathbf{r}=0)}{\hbar\omega - E_g - E_\mu}\mathcal{E}(\omega). \tag{51}$$

With this coefficient the pair function is given as

$$P_{vc}(\mathbf{r},\omega) = -\sum_\nu \mathcal{E}(\omega)\frac{d_{cv}L^3\psi_\mu^*(\mathbf{r}=0)}{\hbar\omega - E_g - E_\mu}\psi_\nu(\mathbf{r}). \tag{52}$$

With the Fourier transformation into momentum space we get

$$P_{vc}(\mathbf{r},\omega) = -\sum_\nu \mathcal{E}(\omega)\frac{d_{cv}\psi_\mu^*(\mathbf{r}=0)}{\hbar\omega - E_g - E_\mu}\int \mathrm{d}^3r\psi_\nu(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{53}$$

and return into our first expression for the polarisation as the sum of the pair functions

$$P(\omega) = \sum_\mathbf{k}(P_{cv,\mathbf{k}}(\omega)d_{vc} + P_{cv,\mathbf{k}}^*(-\omega)d_{vc}^*). \tag{54}$$

With the relation $\mathcal{E}^*(-\omega) = \mathcal{E}(\omega)$ for real electric fields and the relation

$$\int \mathrm{d}^3r\psi_\nu(\mathbf{r})\sum_\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}} = \int \mathrm{d}^3r\psi_\nu(\mathbf{r})2L^3\delta_{\mathbf{r},0} = 2L^3\psi_\nu(\mathbf{r}=0) \tag{55}$$

we achieve our final result for the optical polarisation

$$P(\omega) = -2L^3\sum_\nu |d_{cv}|^2|\psi_\nu(\mathbf{r}=0)|^2\mathcal{E}(\omega)\left[\frac{1}{\hbar\omega - E_g - E_\nu} - \frac{1}{\hbar\omega + E_g + E_\nu}\right]. \tag{56}$$

5   Optical Spectra

After we have found the full solution for the optical polarisation we can calculate the absorption spectrum. With the definition of the optical susceptibility

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

we can find

$$\chi(\omega) = -2|d_{cv}|^2\sum_\mu |\psi_\mu(\mathbf{r}=0)|^2\left[\frac{1}{\hbar\omega - E_g - E_\mu} - \frac{1}{\hbar\omega + E_g + E_\mu}\right]. \tag{57}$$

The wavefunction $|\psi_\mu(\mathbf{r}=0)|^2$ only gives a result for $l=0$ and $m=0$, as the higher order wavefunctions are not finite in the origin. By inserting the corresponding wavefunction one can express the optical susceptibility as

$$\chi(\omega) = -\frac{2|d_{cv}|^2}{\pi E_0 a_0^3}\left[\sum_n \frac{1}{n^3}\frac{E_0}{\hbar\omega - E_g - E_n} + \frac{1}{2}\int \mathrm{d}x\frac{xe^{\pi/x}}{\sinh(\pi/x)}\frac{E_0}{\hbar\omega - E_g - E_0 x^2}\right]. \tag{58}$$

The absorption coefficient can be found with the imaginary part of the susceptibility

$$\alpha(\omega) \simeq \frac{4\pi\omega}{n_b c}\chi''(\omega), \tag{59}$$

so that we conclusively have the so called Elliott formula for the optical absorption

$$\alpha(\omega) = a_0 \frac{\hbar\omega}{E_0} \left[\sum_{n=1}^{\infty} \frac{4\pi}{n^3} \delta(\Delta + 1/n^2) + \theta(\Delta) \frac{\pi e^{\pi/\sqrt{\Delta}}}{\sinh(\pi/\sqrt{\Delta})} \right] \tag{60}$$

with the energy detuning

$$\Delta = (\hbar\omega - E_g)/E_0. \tag{61}$$

The absorption spectrum is shown in figure 1. One can see that it consists of a part for bound states which live in the bandgap area. Here the absorption is expressed as delta functions in dependance of the energy and decreases in higher orders with the power of three. These energy peaks describe discrete energy levels which are an analogous result to the hydrogen atom. These bound states are the new solutions from our calculations and can be seen as quasi-particles called *excitons*. For higher energy, i.e. energies passing the bandgap energy the continuum from the conduction band can be observed. These continuous states are a basic result for a semiconductor and occur even without the consideration of Coulomb interaction. However, by including it into the calculations one can observe the effect of it to the free carries states, which translates into an enhancement of absorpion in the conduction band.
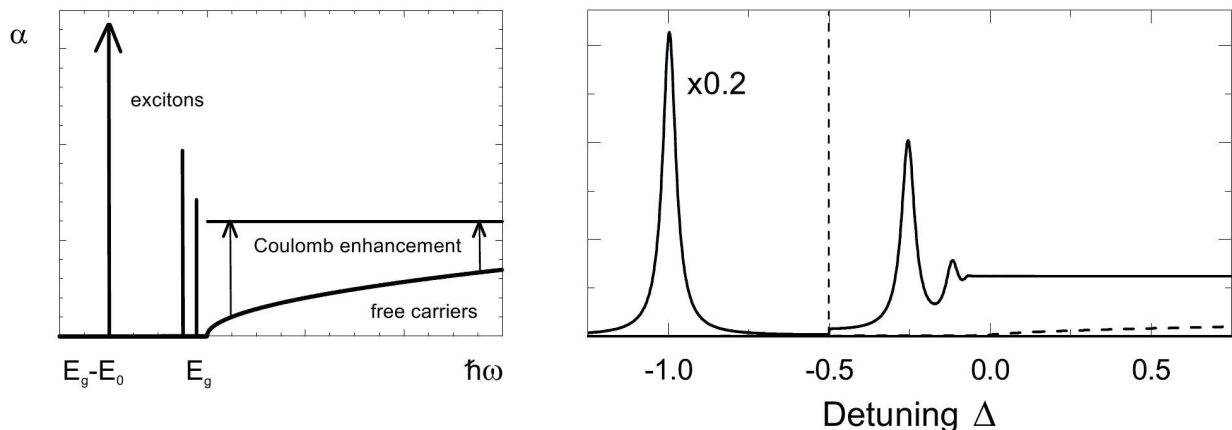

Figure 1: Band edge absorption (left: schematic, right:calculated). The peaks on the left sides are the bounds states and decrease in height with higher orders. The continuum is shown for noninteracting particles and particles with Coulomb interaction. One can see, that Coulomb interaction results in an enhancement of the absorption.

Summary

To describe the behaviour of a semiconductor in an electric field we have taken into account the kinetic energy of the electrons, the interaction of the electrons with the light field and most importantly the interaction between the excited electrons and holes in the conductionband and valenceband, respectively. These effects have been observed by calculating the polarisation of the electrons, where the solution is a joint expression between the energy continuum of the conduction band and newly found discrete energy states that lie in the energyband gap of the semiconductor. We were able to express the discrete states with the hydrogen atom wavefunctions by adjusting the masses in the new problem, where the proton-electron configuration is now replaced by a hole-electron system.
The calculated polarisation enabled us to express the susceptibility and the absorption of the semiconductor in an electric field, where the latter solution gave us an experimentally measurable parameter to confirm our theoretical results.

Sources

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