Series - Electronic and optical semiconductor devices

Series 13 Excitonic effects in direct band gap semiconductors

Excitonic effects close to the Brillouin zone center (Γ point)

1 - Equation (1.5) can be compared to that of the hydrogen atom. As a first approximation, the exciton corresponds to a hydrogen-like system where the proton is replaced by a hole (this is made possible here since we neglect exchange and correlation terms). A noticeable difference of the excitonic system with the hydrogen atom relies in the fact that the two particles interacting via the Coulomb interaction have a mass which is relatively close to each other whereas $m_{proton} \sim 1836\, m_e$. In this latter case, the reduced mass μ of the system is very close to m_e since $\mu = \frac{m_e m_p}{m_e + m_p} \sim m_e \left(1 - \frac{m_e}{m_p}\right)$. It means that the center of mass of this system is nearly superimposed on the proton and that the relative particle can be identified to a very good approximation with the electron, which justifies the use of the Born-Oppenheimer approximation.

2 - $\vec{R} = \frac{m_e \vec{R_e} + m_h \vec{R_h}}{M}$ and $\vec{r} = \vec{R_e} - \vec{R_h}$

the introduction of these new coordinates is such that

$$\nabla^2_{\vec{R_e}} = \frac{\partial^2}{\partial \vec{R_e}^2} = \frac{\partial}{\partial \vec{R_e}} \frac{\partial}{\partial \vec{R_e}}$$

and $\frac{\partial}{\partial \vec{R_e}} = \frac{\partial}{\partial \vec{R}} \frac{\partial \vec{R}}{\partial \vec{R_e}} + \frac{\partial}{\partial \vec{r}} \frac{\partial \vec{r}}{\partial \vec{R_e}}$

i.e. $\frac{\partial}{\partial \vec{R_e}} = \frac{m_e}{M} \frac{\partial}{\partial \vec{R}} + \frac{\partial}{\partial \vec{r}}$ so that $\nabla^2_{\vec{R_e}} = \frac{m_e}{M} \frac{\partial}{\partial \vec{R_e}} \frac{\partial}{\partial \vec{R}} + \frac{\partial}{\partial \vec{R_e}} \frac{\partial}{\partial \vec{r}}$

As a result $\nabla^2_{\vec{R_e}} = \left(\frac{m_e}{M}\right)^2 \frac{\partial^2}{\partial \vec{R}^2} + \frac{m_e}{M} \frac{\partial}{\partial \vec{r}} \frac{\partial}{\partial \vec{R}} + \frac{m_e}{M} \frac{\partial}{\partial \vec{R}} \frac{\partial}{\partial \vec{r}} + \frac{\partial^2}{\partial \vec{r}^2}$

which leads to $\nabla^2_{\vec{R}_e} = \left(\frac{m_e}{M}\right)^2 \frac{\partial^2}{\partial \vec{R}^2} + \frac{\partial^2}{\partial \vec{r}^2} + 2\frac{m_e}{M}\frac{\partial}{\partial \vec{R}}\frac{\partial}{\partial \vec{r}}$

Similarly, we get $\nabla^2_{\vec{R}_h} = \left(\frac{m_h}{M}\right)^2 \frac{\partial^2}{\partial \vec{R}^2} + \frac{\partial^2}{\partial \vec{r}^2} - 2\frac{m_h}{M}\frac{\partial}{\partial \vec{R}}\frac{\partial}{\partial \vec{r}}$

In turn, equation (1.5) can be rewritten as:

$$\left[-\frac{\hbar^2}{2M^2} m_e \frac{\partial^2}{\partial \vec{R}^2} - \frac{\hbar^2}{2M^2} m_h \frac{\partial^2}{\partial \vec{R}^2} - \frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial \vec{r}^2} - \frac{\hbar^2}{2m_h}\frac{\partial^2}{\partial \vec{r}^2} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right]\Phi(\vec{R},\vec{r}) = E\,\Phi(\vec{R},\vec{r})$$

So that $\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \vec{R}^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \vec{r}^2} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right]\Phi(\vec{R},\vec{r}) = E\,\Phi(\vec{R},\vec{r})$

The variables $\vec{R}$ and $\vec{r}$ being decoupled, the exciton envelope wavefunction $\Phi(\vec{R},\vec{r})$ can be written as the product of two functions such that:

$\Phi(\vec{R},\vec{r}) = \psi_K(\vec{R})\,\phi_{nlm}(\vec{r})$ and the two resultant equations are:

$$\boxed{\begin{aligned} &-\frac{\hbar^2}{2M}\nabla^2_{\vec{R}}\,\psi_K(\vec{R}) = E_R\,\psi_K(\vec{R}) \\ &\left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{r}} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right)\phi_{nlm}(\vec{r}) = E_r\,\phi_{nlm}(\vec{r}) \end{aligned}}$$

3. The first equation describes the motion of a free particle which means that the solution is that of a plane wave. Therefore we get:

$$\boxed{\psi_K(\vec{R}) = N^{-1/2}\exp(i\vec{K}.\vec{R}) \quad \text{and } E_R = \frac{\hbar^2 K^2}{2M}}$$

E_K corresponds to the kinetic energy of the center of mass.

4. $E_r(n) = E_r(\infty) - \frac{R^*}{n^2}$

$E_r(\infty)$ is the minimum energy of the continuum of states, i.e. the band gap energy E_g. Excitonic states therefore corresponds to bound states lying below the gap.

5. From equations (1.8) and (1.9) and knowing that we deal with a

solid state system characterized by a relative dielectric constant ε_r and excitonic quasiparticles with a reduced mass μ, we obtain:

$$\boxed{\begin{aligned} R^* &= \frac{\mu e^4}{2\hbar^2 (4\pi\varepsilon_0\varepsilon_r)^2} = \frac{\mu}{m_0 \varepsilon_r^2} E_{H_I} \\ \text{and } a_B &= \frac{\hbar^2 4\pi\varepsilon_0\varepsilon_r}{\mu e^2} = \frac{m_0 \varepsilon_r}{\mu} a_0 \end{aligned}}$$

where $E_{H_I} \sim 13.6$ eV is the ionization energy of the hydrogen atom and a_0 corresponds to its Bohr radius

6- $$\boxed{\begin{aligned} \Phi_{nlm}(\vec{R}, \vec{r}) &= \frac{1}{\sqrt{N}} \exp(i\vec{K}\cdot\vec{R})\, R_{nl}(r)\, Y_{lm}(\theta, \phi) \\ E_{nlm} &= E_R + E_r = E_g + \frac{\hbar^2 K^2}{2M} - \frac{R^*}{n^2} \end{aligned}}$$

7- See the figure which illustrates the case of GaAs.

8-

	R^*_{th} (meV)
GaAs	5.1
InP	6.0
CdTe	15.9
ZnTe	12.0
ZnSe	30.5
ZnS	80.8

It is thus seen that for "small" band gap semiconductors (here essentially III-V compounds) a satisfactory agreement between experiment and theory is obtained. For II-VI semiconductors which are characterized by a strong ionic behavior, the hydrogen-like model fails in reproducing experimental results.

9- From the expression of E_{nlm}, it is seen that the energy separation between levels $n=1$ and $n=2$ for the exciton is such that:

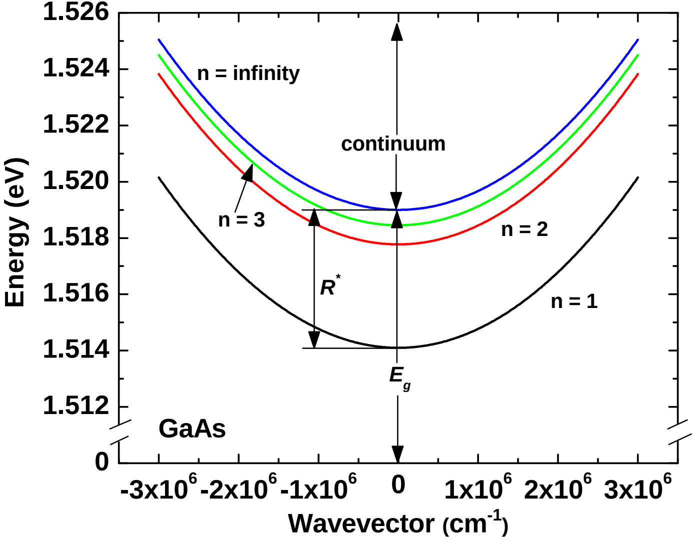
$E_2 - E_1 = -\frac{R^*}{4} + R^* = \frac{3}{4} R^*$. Graphically, we then derive that:

$R^*_{X_A} \sim 24.2$ meV
$R^*_{X_B} \sim 24.2$ meV
$R^*_{X_C} \sim 27.5$ meV

$\rightarrow$ Value in good agreement with the 23.5 meV deduced from question 5 knowing that $m_e^* \sim 0.22\, m_0$, $m_h^* \sim 1.1\, m_0$ and $\varepsilon_r \sim 10.3$ ($X_A \equiv$ heavy hole case)

Nota bene: For information, we have added a figure illustrating various states in semiconductors in a one-electron band picture and in a two-particle picture.

Extra information on the determination of the joint density of states can be found in "Diode Lasers and Photonic Integrated Circuits" by L. Coldren & S. Corzine, J. Wiley & Sons, New York, 1995.


1.526
1.524
1.522
1.520
1.518
1.516
1.514
1.512
0
Energy (eV)
n = infinity
continuum
n = 3
n = 2
n = 1
R*
E_g
GaAs
-3x10^6
-2x10^6
-1x10^6
0
1x10^6
2x10^6
3x10^6
Wavevector (cm^-1)

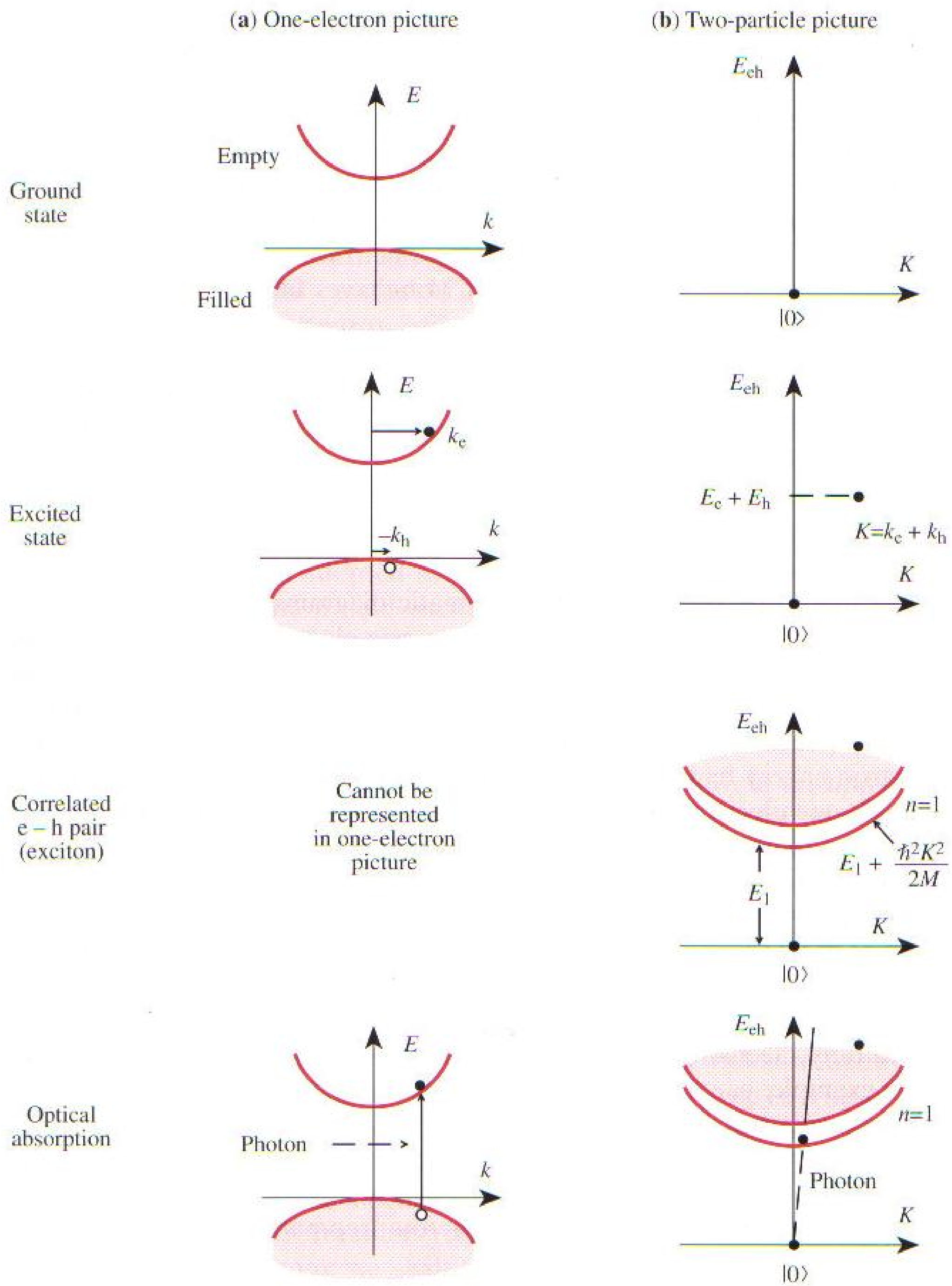


Fig. 6.20. Comparison between the energy levels of the ground state and excited states of a semiconductor in a one-electron band picture (**a**) and in a two-particle picture (**b**). Also, schematic diagrams showing processes in which a photon is absorbed while producing an electron-hole pair