Exercise 12.1: Exciton binding energy

1) The inclusion of Aluminum in GaAs increases the bandgap. In a GaAs/$Al_{0.3}Ga_{0.7}As$ quantum-well (QW), which semiconductor is used for the barriers and for the well?

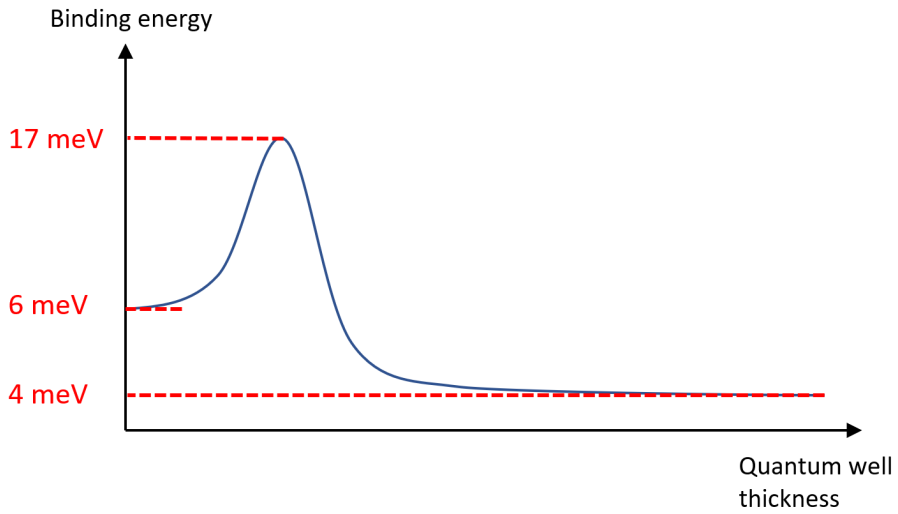
2) The binding energy of the excitons in bulk GaAs and $Al_{0.3}Ga_{0.7}As$ are 4 meV and 6 meV, respectively. When the exciton's confinement is maximal, its binding energy is 17 meV. Discuss qualitatively how you would expect the exciton binding energy in such a QW to vary with the QW thickness.

3) How does the exciton binding energy in quantum wells compare to the one in quantum dots?

Exercise 12.1 solution.

1) The bandgap is higher for AlGaAs than for GaAs. Thus, we are considering a AlGaAs/GaAs/AlGaAs quantum well (QW).

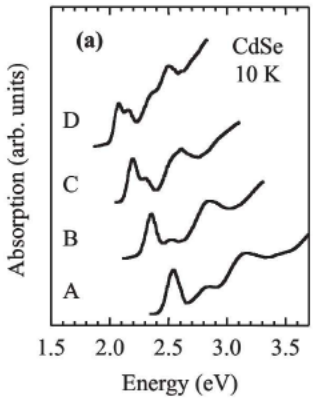
2) Bulk GaAs corresponds to a QW thickness $d = \infty$, resulting in an exciton binding energy of 4 meV. Decreasing d from ∞, the binding energy increases and reaches a maximum of 17meV when the d is of the order of the exciton's size. Further decreasing d results in the exciton's delocalization in the barriers, thus the exciton's binding energy decreases, towards the barrier's bulk binding energy. When $d = 0$ the binding energy reaches 6 meV (bulk AlGaAs).



3) The confinement in a quantum dot (QD) is 3D instead of 1D in a QW. The average separation between electron and holes is reduced, resulting in enhanced coulombic interactions and thus higher binding energy.
As a consequence, the excitonic peak in the spectrum at RT is usually much more pronounced in QDs than in QWs.

Exercise 12.2: Absorption in quantum dots

1) From the absorption spectra, sort the following CdSe quantum dots A, B, C and D by increasing size.



2) Estimate the exciton binding energy for sample A, knowing the diameter d = 3.03 nm, the reduced mass μ = 0.1 m_0 (m_0 = 9.11 x 10^{-31} kg) and the bandgap of bulk CdSe (1.85 eV at 10K).

Exercise 12.2 solution.

1) In the Figure, one notes that the absorption energy is experiencing a red-shift (decrease in energy) from sample A to D. This means that the confinement effect decreases, ie. the quantum dot's size is increasing.

   Be careful with the units: x-axis in eV.

   Note: the reduced mass is also affected by confinement in fact. Indeed band structure is slightly different

2) In the lecture we saw that the energy of the first excitonic peak is given by

$$\hbar\omega = E_g + E_{nl} - E_{ex}$$

Where E_g is the bulk bandgap energy, E_{nl} is the confinement energy and E_{ex} is the exciton binding energy. Thus,

$$E_{ex} = E_g + E_{nl} - \hbar\omega.$$

- From the measured absorption of sample A (see graph), we estimate that $\hbar\omega = 2.55\ eV$.
- We know that for CdSe at 10K, $E_g = 1.85\ eV$.
- Finally,

$$E_{nl} = \frac{2\hbar^2}{\mu}\frac{\pi^2}{R_0^2}$$

Where μ is the reduced mass and $R_0 = 1.515\ nm$ is the nanoparticle radius.
We find that $E_{nl} = 10.49 \cdot 10^{-19} J = 6.55$ eV.

Thus, altogether we find that $E_{ex} = 1.85 + 6.55 - 2.55 = 5.85\ eV$.
This value is extremely large.

Exercise 12.3: Luminescence linewidth in QD

How does the PL linewidth of a single QD compare to the one of the ensembles (consider an undoped sample)? What is the main factor ultimately defining the linewidth and which factors contribute to a larger linewidth? What is the effect of a metallic dopant such as copper on the PL linewidth?

Exercise 12.3 solution.

For an ensemble of QDs, a typical PL linewidth is 100-150meV, measured with PL spectroscopy. For single QD it is in the order of 50meV, measured with single particle PL spectroscopy. Linewidth as small as a few μeV have already been observed.
For single QDs, the factor that ultimately defines the linewidth is the radiative lifetime: The accessible excitonic energies are almost discrete, but according to the uncertainty principle $\Delta\tau\Delta\mathrm{E} > \hbar$, they still have a certain uncertainty ΔE (the linewidth) related to their radiative lifetime.

The factors that can contribute to a larger linewidth are:

- Thermal broadening, if the thermal energy exceeds ΔE. This is equivalent to doppler broadening. It is due to the doppler shift caused by the motion, relative to the observer, of the atoms which emit light.

- The inhomogeneous size distribution or aggregation of QDs (statistical broadening), if the PL is measured on an ensemble of QDs.
- Doping: inhomogeneous broadening (different energies related to different spatial location of the impurity atoms. In particular surface versus core) and broadening of the vibronic states due to distortion at the dopant atom.