Introduction - Semiconductor quantum dots

Definition: a QD is a system which confines the motion of charge carriers *in all directions* and in a region of space which is small enough to render quantization effects apparent

Example: CdSe nanocrystals (or colloidal QDs) in solution - fluorescence image

Transmission electron microscopy (TEM) image





CdSe nanocrystal

Different size emit light at different energy (wavelength). Here sizes range from 2 to 6 nm.

 \rightarrow Same material, different sizes \rightarrow different color!

This doesn't happen at the macroscopic scale... just imagine breaking a piece of Silicon in tiny pieces...

Note: Photoluminescence

Fluorescence imaging and spectroscopy: simplest method to access energy levels of atoms, molecules, quantum dots...



Energy of emitted light related to energy levels of the system. Note that not all levels are necessarily associated to bright optical transitions \rightarrow only some levels contribute to the emission.



Quantum dots have discrete states as atoms \rightarrow "artificial atoms" They don't move around \rightarrow easier to study and integrate into optoelectronic devices

When can a region of space be considered a QD?

We must solve the Schrödinger equation for a QD potential and impose the condition that "quantization effects are apparent"

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Simplest approximation:

1.1 The infinite quantum box

infinitely deep barriers \rightarrow wavefunction $\psi = 0$ outside it Because of geometry we choose cartesian coordinates.

$$V(x, y, z) = \begin{cases} 0 & \text{inside box} \\ \infty & \text{outside box} \end{cases}$$



Potential can be decomposed as the sum of potentials which depend separately on x,y,z \rightarrow this allows separation of variables!

$$V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$$

$$V_a(a) = \begin{cases} 0 & 0 < a < L_a \\ \infty & \text{otherwise} \end{cases} \qquad \psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

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$$\sum_{a=x,y,z} -\frac{\hbar^2}{2m} \frac{\psi_a''(a)}{\psi_a(a)} + V(a) = E \quad \Rightarrow \quad -\frac{\hbar^2}{2m} \psi_a''(a) + V(a)\psi_a(a) = E_a \psi_a(a)$$
$$E = E_x + E_y + E_z$$

The problem is reduced to 1D. We can try solutions of the form:

$$\psi_a(a) = \begin{cases} A_a \sin k_a a & 0 < a < L_a \\ 0 & a \le 0 \text{ or } a \ge L_a \end{cases}$$

A and k can be obtained by:

- 1. Substituting into Schrödinger equation
- 2. Imposing that the wavefunction is continuous at the edges of the box
- 3. Imposing the normalization $\int_{0}^{L_{a}} da |\psi_{a}(a)|^{2} = 1 \rightarrow 0$

$$\rightarrow E_a = \frac{\hbar^2 k_a^2}{2m}$$

$$\rightarrow k_a = \frac{n_a \pi}{L_a}, \quad n_a = 1, 2...$$
$$\rightarrow A_a = \sqrt{\frac{2}{L_a}}$$

 $E = \frac{\pi^2 \hbar^2}{2m} \left| \left(\frac{n_x}{L_y} \right)^2 + \left(\frac{n_y}{L_y} \right)^2 + \left(\frac{n_z}{L_z} \right)^2 \right|$

Solution:

$$\psi(x, y, z) = 2\sqrt{\frac{2}{L_x L_y L_z}} \sin \frac{\pi n_x}{L_x} x \sin \frac{\pi n_y}{L_y} y \sin \frac{\pi n_z}{L_z} z, \quad n_x, n_y, n_z = 1, 2, \dots$$

1

Notes:

- Energy increases with the number of nodes in wavefunction
- Energy scales with the inverse of $m \rightarrow$ smaller mass makes quantization effects stronger
- The ground-state energy E_0 is dominated by the shortest side length \rightarrow it is enough to have one dimension "small enough" to see size effects… but this is not sufficient to have a QD
- The position of the first excited state E_1 relative to E_0 depends on the longest side

$$L_{z} < L_{y} < L_{x} \rightarrow E_{0} = \frac{\pi^{2}\hbar^{2}}{2m} \left[\frac{1}{L_{x}^{2}} + \frac{1}{L_{y}^{2}} + \frac{1}{L_{z}^{2}} \right], \quad E_{1} = \frac{\pi^{2}\hbar^{2}}{2m} \left[\frac{4}{L_{x}^{2}} + \frac{1}{L_{y}^{2}} + \frac{1}{L_{z}^{2}} \right]$$
$$\rightarrow \Delta E = E_{1} - E_{0} = 3\frac{\pi^{2}\hbar^{2}}{2mL_{x}^{2}}$$

When can a region of space be considered a QD?

We can ask that :

$$1)E_0 > 3K_BT \quad \& \quad 2)E_1 - E_0 > 3K_BT$$
$$\rightarrow L_x < \frac{\pi\hbar}{\sqrt{2mK_BT}}$$



- implies that the ground state energy is larger than the ",thermal energy". The system behaves differently from a ",bulk" box at the temperature T. But: a very flat box or a long wire could satisfy this condition as well.
- 2) implies that <u>all</u> dimensions are "small enough". If a particle is put in the ground state, it will stay there with high probability (the thermal energy is barely sufficient to promote it to the first excited state).

$$\begin{split} L_z < L_y < L_x \to E_0 &= \frac{\pi^2 \hbar^2}{2m} \left[\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2} \right], \quad E_1 = \frac{\pi^2 \hbar^2}{2m} \left[\frac{4}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2} \right] \\ \to E_1 - E_0 &= 3 \frac{\pi^2 \hbar^2}{2mL_x^2} \end{split}$$

 $\sqrt{2mK_BT}$

 $L_x < \lambda_{dB} \rightarrow L_x < \frac{\sqrt{2\pi\hbar}}{\sqrt{mK_BT}}$

When can a region of space be considered a QD?

We can ask that :

$$1)E_0 > 3K_BT \quad \& \quad 2)E_1 - E_0 > 3K_BT$$
$$\rightarrow L_x < \frac{\pi\hbar}{\sqrt{2 - W_BT}}$$

$$E_{1}$$

$$E_{0}$$

0

- implies that the ground state energy is larger than the "thermal energy". The system behaves differently from a "bulk" box at the temperature T. But: a very flat box or a long wire could satisfy this condition as well.
- 2) implies that <u>all</u> dimensions are "small enough". If a particle is put in the ground state, it will stay there with high probability (the thermal energy is barely sufficient to promote it to the first excited state).

→Whether a system can be considered a QD or not depends also on temperature! Another condition to define a QD is that the sizes are comparable or smaller than de Broglie wavelength λ_{dB} associated to the particle at a certain temperature *T*:

$$k = \frac{2\pi}{\lambda_{dB}} = \frac{\sqrt{2mE}}{\hbar} \to \lambda_{dB} = \sqrt{\frac{2}{mE}}\pi\hbar; \quad E \approx K_B T$$

Similar conclusion as above (a factor of 2 smaller)

When can a region of space be considered a QD?

Let's put numbers:

 $m = \alpha \ m_0, \quad m_0 \text{ free electron mass}$ $E_0 = \frac{\pi^2 \hbar^2}{2m} \left[\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2} \right] \approx \frac{376 \ meV}{\alpha} \left[\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2} \right] [nm^{-2}]$ $L_x < \frac{\pi \hbar}{\sqrt{2mK_BT}} \approx \frac{19 \ nm}{\sqrt{\alpha} \ K_BT[meV]} \approx \frac{3.8 \ nm}{\sqrt{\alpha}} \quad \text{At room temperature}$

If we would be able to confine an electron in vacuum, the box should be smaller than about 5 nm. In a semiconductor we can approximate electrons and holes as free carriers with an effective mass *m*, which is usually smaller than m_0 (α <1).

→ The QD must have sizes of some nanometer! Nanostructures are required to "see" quantum effects (at least at room temperature).

1.1.1 The colors of CdSe dots - exercise

Let us take now a small cube of CdSe. The energy bandgap of CdSe is $E_g=1.714$ eV. For electrons $\alpha_e=0.13$, for holes $\alpha_h=0.45$. What are the colors of "nanocubes" with 3, 6 and 10 nm side length?



Real quantum boxes are far from the idealized case of infinite depth For electrons in GaAs-AlGaAs systems, we usually $V_0 \sim 300 \text{ meV}$

We stay in 1D and we are interested in bound state only (E< V_0)

$$-\frac{\hbar^2}{2m}^2 \psi''(x) + V(x)\psi(x) = E\psi(x)$$

Region 1

$$\psi_1''(x) = -\frac{2mE}{\hbar^2}\psi_1(x) = -k^2\psi_1(x) \qquad k = \frac{\sqrt{2mE}}{\hbar}$$



$$E = \frac{\hbar^2 k^2}{2m}$$



Region 2 and 3

$$\psi''(x) = \frac{\sqrt{2m(V_0 - E)}}{\hbar^2} = \alpha^2 \psi(x) \qquad \qquad \psi_2(x) = Fe^{-\alpha x} + Ge^{\alpha x}$$
$$\varphi_3(x) = He^{-\alpha x} + Ie^{\alpha x}$$
$$\psi_3(x) = He^{-\alpha x} + Ie^{\alpha x}$$

We have to impose the boundary conditions ... but let's simplify the problem first

1) for $x \to \pm \infty$ the wavefunction should not explode $\to F = I = 0$

1) Since V(x) is simmetric, only simetric and anti-simmetric solutions can exist

1) For simmetry, we can just study the problem for x > 0

... in this way

$$\psi_1(x) = A \begin{cases} \sin \\ \cos \end{cases} (kx) \qquad \qquad \psi_3(x) = Ce^{-\alpha x}$$

If we now impose the boundary conditions

1. Continuity of the wavefunction

2.Continuity of the first derivative

3.By dividing the two

$$A\begin{cases} \sin\\\cos \end{cases} (\frac{kL}{2}) = Ce^{-\frac{\alpha L}{2}}$$

$$A \begin{cases} -\sin \\ \cos \end{cases} (\frac{kL}{2}) = -C\alpha e^{-\frac{\alpha L}{2}}$$

$$\begin{cases} \tan \\ -\cot \end{cases} (\frac{kL}{2}) = \sqrt{\frac{2mV_0}{\hbar^2 k^2}}$$

We finally have...





All the physical parameter of the well have been absorbed in one dimensionless parameter



A one dimensional quantum well has always at least one bound state

$$\frac{2}{\pi}\theta_0 = \frac{2}{\pi}\sqrt{\frac{mV_0L^2}{2\hbar^2}}$$

See Graphical solution...

Some useful remarks...

1) For a shallow quantum well
$$\theta \approx \sqrt{\frac{\theta_0}{\theta^2} - 1} \longrightarrow \varepsilon \approx V_0 - \frac{mL^2 V_0^2}{2\hbar^2}$$

BINDING ENERGY: $B = V_0 - \varepsilon \approx \frac{mL^2 V_0^2}{2\hbar^2}$

2) We should consider that the well and the barriers are made of different materials We would need to repeat the same calculations **but**

- In regions 1-2-3 we have to use the correct mass
- For the boundary condition we must use (we have to conserve the current)

$$\xrightarrow{\psi'(x)} \frac{\psi'(x)}{m_W} \bigg|_{x=L/2} = \frac{\psi'(x)}{m_b} \bigg|_{x=L/2}$$

$$\begin{cases} \tan \\ -\cot \end{cases} (\theta) = \sqrt{\frac{m_W}{m_b}} \sqrt{\frac{\theta_0}{\theta^2} - 1}$$

$$\theta_0 = \frac{m_w V_0 L^2}{2\hbar^2}$$

$$\theta = \frac{kL}{2}$$

....the first convincing evidence of quantum confinement (QW)



Conduction and valence band offset not known at that time...

The transmission spectrum reflects the density of states of the system

Peaks correspond to excitons... Later

Vertical transitions with $\Delta n=0$!!! Why??

R. Dingle et al. PRL 33 827 (1974)

Flat Quantum Dots



Cross-sectional TEM images of InGaAs QDs in GaAs. Depending on imaging conditions InAs appears darker or brighther than matrix.

From Wasilewski, J. Cr. Growth, 201, 1131 (1999)



\rightarrow Flat QDs

E. Müller (ETH Zürich), A. Rastelli, O.G. Schmidt (MPI Stuttgart)

Flat Quantum Dots

During the lecture we have studied the problem of a flat QD. Here, I summarize the important steps and the equations we have derived.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$
$$V(x, y, z) = \begin{cases} 0 & 0 < z < L_z(x, y) \\ \infty & \text{otherwise} \end{cases}$$



Basic approxiamtion (1) $h < < w_x, w_y$

In this conditions, the kinetic energy is dominated by the motion along z. In other words we can try to separate the vertical and lateral motion. (This is similar to the Born-Oppenheimer approximation for molecules): $\psi(x, y, z) = \psi_{xy}(x, y)\psi_z(z)$

 \rightarrow The vertical (along z) confinement acts as potential for the lateral (in x,y) motion

Flat quantum dots

$$V_{xy}(x, y) = \frac{\hbar^2 \pi^2}{2mL_z^2(x, y)}$$

For not too irregular shape we can expand V_{xy} around x,y=0 (higherst point of the dot).



h < < w

Х

h

W

 $L_{z}(x,y)$

This is a 2-dimensional harmonic oscillator potential plus an offset associated to z. The "angular frequencies" increase when:

- the curvature (sharpness) of the dot increases
- the height of the dot decreases
- the particle mass decreases

Flat quantum dots

Recalling the solution of the harmonic potential:

$$\begin{split} E(n_x, n_y) &= \frac{\hbar^2 \pi^2}{2mh^2} + \left(\frac{1}{2} + n_x\right) \hbar \omega_x + \left(\frac{1}{2} + n_y\right) \hbar \omega_y, \quad n_x, n_y = 0, 1, 2, \dots \\ \omega_a &= \frac{\hbar \pi}{mh} \sqrt{-\frac{1}{h} \frac{\partial^2 L_z}{\partial a^2}} \Big|_{x, y=0} \end{split}$$

Ground-state and first excited state energies ($w_y < w_x$)

$$E_0 = \frac{\hbar^2 \pi^2}{2mh^2} + \frac{\hbar}{2}(\omega_x + \omega_y)$$
$$E_1 = E_0 + \hbar \omega_x$$

Relative contribution of in-plane and vertical confinement to ground-state energy:

$$\frac{E_{x,y}}{E_z} = \frac{\sqrt{h}}{2} \left(\sqrt{-\frac{\partial^2 L_z}{\partial x^2}} \Big|_0 + \sqrt{-\frac{\partial^2 L_z}{\partial y^2}} \Big|_0 \right)$$

For flats QDs Eo is mainly determined by z

Flat quantum dots

To explicitly see the dependence on lateral sizes we can take a lens-shaped dot, $w_y < w_x$:

$$L_z(x, y) = h \left(1 - \frac{4x^2}{w_x^2} - \frac{4y^2}{w_y^2} \right) \qquad \omega_a = \frac{\hbar\pi}{mh} \sqrt{-\frac{1}{h} \frac{\partial^2 L_z}{\partial a^2}} \Big|_{x, y=0}$$

Angular frequencies and dependence on size:

$$\omega_x = \frac{2\sqrt{2}\hbar\pi}{mhw_x}$$

Contribution of lateral confinement to ground-state:

$$\frac{E_x}{E_z} = \frac{4\sqrt{2}}{\pi} \frac{h}{w_x}$$

1.2 Flat quantum dots

If we now assume that the dot is symmetric in x and y directions $\omega \equiv \omega_x = \omega_y$

$$\begin{split} V_{xy}(x,y) &\approx \frac{\hbar^2 \pi^2}{2mh^2} + \frac{1}{2} m \omega^2 \left(x^2 + y^2 \right) \\ \to E(n_x, n_y) &\approx \frac{\hbar^2 \pi^2}{2mh^2} + \left(1 + \underbrace{n_x + n_y}_{N} \right) \frac{\hbar^2 \pi}{mh} \sqrt{-\frac{1}{h} \frac{\partial^2 L}{\partial x^2}} \Big|_{x,y=0}, \quad n_x, n_y = 0, 1, 2, \dots \\ E(N) &= \frac{\hbar^2 \pi^2}{2mh^2} + \hbar \omega (1+N) = \frac{\hbar^2 \pi^2}{2mh^2} + \frac{2\sqrt{2}\hbar^2 \pi}{mhw} (1+N), \quad N = 0, 1, 2, \dots \end{split}$$

- For dots with small aspect ratio, the main contribution to the ground-state energy comes from the vertical confinement
- The spacing between excited states is constant and equal to $\hbar\omega$ which is inversely proportional on $hw \rightarrow$ the wider or taller the dot is, the closer the levels
- The degeneracy of excited states is N+1 and increases with energy

The level spacing is:
$$\Delta E \approx \frac{2\pi\sqrt{2}\hbar^2}{mhw} \approx \frac{677 \ meV}{\alpha hw[nm^2]}$$

Experimental examples (QDs)



FIG. 4. Evolution of the low temperature (4.2 K) emission spectrum as the excitation intensity is increased. The figure clearly reveals the absolute saturation of the emission of the three lowest states. The inset shows an example of multiple Gaussian fit to deconvolute the emission of each peak. The round dots are experimental points, the solid line is the resulting fit, and the dashed curves show the four Gaussians used to fit the spectrum.

- Photoluminescence (fluorescence) spectroscopy allows easy access to confined states
- Spectra of ensemble of InAs/GaAs QDs are «inhomogeneously» broadened
- Smaller dots show higher emission energy
- Smaller dots show larger level spacing
- Excited states become visible at high excitation power (level filling)
- When level separation is $\sim 2 k_B T$, first excited state is populated also at low excitation power
- At high excitation power, interaction between carriers produce slight red-shifts of emission

From S. Raymond, Phys. Rev. B 59, 7624 (1999)

Experimental examples (QDs)



Example of qualitative correlation between structural properties (from AFM) and optical properties. Smaller dots have both higher emission energy and larger level splitting



 $h \approx 8nm$ $\longrightarrow w \approx 60nm$

This is somewhat larger than the size seen in TEM. The most likely reason is the fact that we assumed infinitely deep barriers

Songmuang et al, J. Cryst. Growth 251, 166 (2003)

Experimental examples (reminder + some more detail)



FIG. 2. (Color online) Height histogram for buried In(Ga)As QDs after removal of the GaAs cap layer. The solid line represents the Gaussian fit. The inset shows a HAADF STEM image of a QD grown and capped with similar conditions. The dashed line is a line scan obtained from the AFM image shown in Fig. 1(e).

The larger dots in the previous slide emit at $1.3 \mu m$ wavelength and have level splitting of about 50 meV.

The size of the dots is shown on the left: $h \sim 7.6$ nm, w ~ 30 nm, aspect ratio $r = h/w \sim 0.25$

By using:
$$E_1 - E_0 \approx \frac{677 \text{ meV}}{\mu hw[nm^2]}$$

→ μ ~0.059, which is higher than what expected for InAs (0.021) and GaAs (0.056)

This discrepancy is in part due to the assumption of infinitely deep barriers

Data by F. Ding et al, Appl. Phys. Lett. 90, 173104 (2007)

Inhomogeneous broadening



Different QDs emits at different energies!!! "Avarage" information can be obtained



Exercise (solved during the lecture)

What are the maximum size fluctuations for flat dots to see well resolved excited states? Often dots in an ensemble have similar aspect ratio *r*. Assume it constant (0.25).

$$E(N) = \frac{\hbar^2 \pi^2}{2mh^2} + \hbar \omega (1+N) = \frac{\hbar^2 \pi^2}{2mh^2} + \frac{2\sqrt{2}\hbar^2 \pi}{mhw} (1+N), \quad N = 0,1,2,...$$

$$r = \frac{h}{w} \rightarrow E_N \approx E_g + \frac{\hbar^2 \pi^2}{2\mu m_0 h^2} \left[1 + \frac{4\sqrt{2}}{\pi} (1+N)r \right], \quad N = 0,1,2,...$$

Solution $r = 0.25 \rightarrow \frac{\delta h}{h} \le 15\%$

QD ensemble



FIG. 4. Evolution of the low temperature (4.2 K) emission spectrum as the excitation intensity is increased. The figure clearly reveals the absolute saturation of the emission of the three lowest states. The inset shows an example of multiple Gaussian fit to deconvolute the emission of each peak. The round dots are experimental points, the solid line is the resulting fit, and the dashed curves show the four Gaussians used to fit the spectrum. We have seen how a PL spectrum from ensemble of QDs looks like and we have seen how to derive some useful information on their structural properties.



Now, let's focus on single QDs...

To address single quantum dots with far field optics:

1) If dot density is high (such that interdot distance << laser beam size) → opaque apertures



AFM images 2×2 μm² of InAs/GaAs QDs

2) If dot density is less than $\sim 10^8 \text{ cm}^{-2}$ focusing down to diffraction limit is sufficient





Single dots addressed by random search (most commonly used method still nowadays!) Typical experimental apparatus for standard PL measurements



Let's have a look at the fundamental ingredients...

We need high spatial resolution to address the single QDs

Objective used for both excitation and PL collection





Diffraction limit: Numerical Aperture

 $d = \lambda / (2n\sin\theta)$ N.A.= $n\sin\theta$

Common objectives N.A. ~ 0.5

For λ = 800 nm, d = 800 nm

60x Plan Apochromat Objective

Typical PL spectrum of a single InAs QD at low excitation power and low temperature





Let's consider only the ground state (low excitation power, we populate only the s-shell)... we do not have just one peak as assumed before!!!!

Excitons in quantum dots

- no "free" electronhole- pairs exist due to the QD confinement. The fundamental excitation is the exciton itself and we refer to this transition for the binding energies.

- the Coulomb interaction is enhanced with respect to the bulk case due to the close proximity and compression of electron and hole wave functions. Calculation predicts binding energies of the order of 20 meV

- the Coulomb interaction competes with the confinement energy, which is a ~10 times larger



PRB 68, 073309 (2003)

FIG. 4. (Color online) Upper panel (a) Isosurfaces enclosing 75 and 40% of the state densities of the first three electron and the first hole states for an In_{0.6}Ga_{0.4}As dot. Lower panels: Isosurfaces of the state density differences $\rho_{\text{diff}} = \rho_e$ $-\rho_h$ for a pure InAs dot (b) and for an In_{0.6}Ga_{0.4}As dot (c). The electrons, compared to the holes, are more localized toward the top and base of the dots. All dots are lens shaped (b=25 nm, h= 3.5 nm).

The few particle characteristics are governed by the confinement potential... This leads to interesting consequences like the presence of "anti-binding" complexes, which in bulk would immediately dissociate into their components

Few particle states in a single QD



We are sensitive (in PL) only to transitions !!!!

We are sensitive (in PL) only to transitions

The energetic position of the lines depends on the specific structure of the QDs



As discussed, we need to consider **quantization and coulomb interactions**. If we focus only on the direct Coulomb term:

$$C_{ij} = \iint \frac{q_i q_j}{4\pi\varepsilon_r \varepsilon_0} \frac{|\Psi_i(r_1)|^2 |\Psi_j(r_2)|^2}{|r_1 - r_2|} dr_1 dr_2$$

Directo Couloumb term

$$E(X) = [\varepsilon(e) - \varepsilon(h)] + C_{eh}$$

$$E(XX) = [2\varepsilon(e) - 2\varepsilon(h)] + 4C_{eh} + C_{ee} + C_{hh}$$

$$E(X^-) = [2\varepsilon(e) - \varepsilon(h)] + 2C_{eh} + C_{ee}$$

$$E(X^+) = [\varepsilon(e) - 2\varepsilon(h)] + 2C_{eh} + C_{hh}$$

But we can access only transition energies...

$$\begin{split} &\hbar\omega_{X}(X \to 0) = E(X) \\ &\hbar\omega_{XX}(XX \to X) = E(XX) - E(X) \\ &\hbar\omega_{X^{-}}(X^{-} \to e) = E(X^{-}) - \varepsilon(e) \\ &\hbar\omega_{X^{+}}(X^{+} \to h) = E(X^{+}) - \varepsilon(h) \end{split}$$

If we now refer to the fundamental excitation, we can define binding energies as

$$\Delta_{bind}(XX) = \hbar \omega_X - \hbar \omega_{XX} = 2E(X) - E(XX) = -2C_{eh} - C_{ee} - C_{hh}$$

$$\Delta_{bind}(X^+) = -C_{eh} - C_{hh}$$
Please note
$$C_{ee}, C_{hh} > 0$$

$$\Delta_{bind}(X^-) = -C_{eh} - C_{ee}$$

$$C_{eh} < 0$$

The question of whether the binding energy is positive or negative is a question of the magnitude of the attractive and repulsive Coulomb interaction terms. In turn, this depends on the QD structural details.

For **InAs** QDs a general rule exists:
$$C_{ee} < |C_{eh}| < C_{hh}$$

Here holes are more localized than electrons and the center of mass of the two carriers are usually close.



However, experimental results reveal binding and anit-binding excitons... this cannot be explained taking into account direct Couloumb interactions only and more sophisticated models are needed. I fact

- We have disregarded, that the presence of additional charge carriers alters their wave functions, thus influencing the original Coulomb interaction terms.

-We have disregarded **correlation effects**. The ground state of the many-particle wave functions is then composed not only of the single-particle ground states but also has nonzero components in the single-particle excited states. (This includes the fact that electrons and holes rearrange to minimize Coulomb interaction + wave functions deforms in the presence of an additional charge carrier)

-We have disregarded the **exchange interaction**.

 $\langle \Psi_a^1 \Psi_b^2 | H_{coul} | \Psi_a^2 \Psi_b^1 \rangle$

ALL THESE TERMS DEPEND STRONGLY ON THE QD STRUCTURAL DETAILS Only considering all these effects the "anti-binding biexciton" can be explained