Nanoscience and nanotechnology as seen through quantum dots

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What is “nano”? 

Size scales

Categories
A preliminary look at the buzz

• What happens when the transistors are the size of electrons?

• What happens when the wires are molecules?

• How will computers work when they are no longer classical?

(Eigler)
Nano in the news: controversy

- Toxicity (asbestos revisited?)
- ‘Grey goo’? (self-assembly run amok) – Eric Drexler
- Playing God? – Ray Kurzweil, Bill Joy

- A reality check:
  courtesy of Rick Smalley (Rice) and George Whitesides (Harvard)
What is different about “nano”

Macroscopic device performing macroscopic tasks:
fire → steam engines → computers

Microscopic objects serving macroscopic tasks:
most of chemistry (“One word… plastics”)

A new paradigm:
microscopic functionality
NanoScience → NanoTechnology

- Computers
- Lasers
- Solar energy
- Medicine
- Materials
The path from science to technology

- MRI – a good thing!

- But where did it come from?
  - Quantum Mechanics (1920’s)
  - I.I. Rabi and atomic physics (Nobel 1944)

- NMR: fundamental and applied science (1950 – present)
- MRI: 1977
Nano and computers: Moore’s law

Minimum Feature Size

- Human hair, 100 μm
- Amoeba, 15 μm
- Red blood cell, 7 μm
- AIDS virus, 0.1 μm
- Buckyball, 0.001 μm

Integrated Circuit Complexity

(Intel)
Hitting the brick wall

dimensions and length scales

- Molecules <1nm
- IBM copper interconnect width 0.2μm
- The first transistor (1947)
- IBM PowerPC 750™ Microprocessor (1999)
  Die size: 5.14mm x 7.78mm
  6.35x10^6 transistors
- Semiconductor nanocrystal
  CdSe, diameter 6.5nm

*Courtesy of Andreas Kadavanich

(Scholes)
Hitting the brick wall

All the incremental progress will stop in a couple of decades!

(Intel)
Can we use nanoscience to make a ‘quantum leap’

• Analog circuits

• Digital circuits

• Quantum circuits???
  Incremental → Transformative?
Quantum computers?

• 101 - voltage or light (on/off/on)

\[ |\psi\rangle = a |000\rangle + b |001\rangle + c |010\rangle + d |011\rangle + e |100\rangle + f |101\rangle + g |110\rangle + h |111\rangle \]

• Lets turn on quantum mechanics..

• What does this \( |\psi\rangle \) mean?
Lasers: another good thing

- Telecommunications
- Surgery
- Medical imaging
- Machining
- Defense
- Fundamental Science
Lasers & Nano: smaller, cheaper, better

Making the Internet on the cheap – quantum wells

Making the Internet really cheap! quantum dots
Energy: Statement of the problem

- Increasing population + increasing energy needs/person = global energy problem

- Finding energy sources and ultimately finding clean energy sources

- Current consumption at 13 TW-year

- Projected need: 30 TW-year by 2050

- 600 TW of solar energy reaches earth at practical sites (10,000 TW total)

(data from Nozik, Crabtree & Lewis)
Solar cells: finding the Holy Grail

- The problem: global energy needs

- A solution: renewable energy (solar)

- The reality:
  - efficient & expensive
  - inefficient & cheap

(Crabtree & Lewis)
Nano and solar cells

• Harvesting, collecting, and storing energy

• Can we perform these operations cheaply and efficiently?

• Solutions:
  – Light harvesting
  – Quantum dots
  – Conducting polymers

(NREL)
A few other areas of NanoScience research

- **Materials** – learning from Nature

  (Comsol)

- **Medicine**
  - “monitoring, control, construction, repair, defense, and improvement of human biological systems, working from the molecular level, using engineered nanodevices and nanostructures.” (R. Freitas)
Our activities in nanoscience

- How do quantum dots actually work?
- Dynamics: lasers & photovoltaics
- Artificial atoms: cryptography & basic physics
- Optical gain: lasers and light sources

A box for electrons

(Zunger Nano Lett 2003)
A brief history of a quantum dot:

It’s routine to generate pulses < 1 nanosecond ($10^{-9}$ s). Researchers can generate pulses a few femtoseconds ($10^{-15}$ s) long.

10 fs light pulse
Computer clock cycle
Camera flash
1 minute
One month
Age of pyramids
Human existence
Age of universe
1 femtosecond

Such a pulse is to one minute as one minute is to the age of the universe.
One way of looking at things
with a fast camera

The "Galloping Horse"
Controversy
Palo Alto, CA  1872

Leland Stanford  Eadweard Muybridge

Time Resolution:
1/60th of a second

(Trebino’s notes)
Ultrafast Laser Spectroscopy: i.e. building a better camera
NanoTechnology and industry

- New materials
  - Imaging, paints, coatings, structures

- Simple applications
  - Drug delivery, lasers

- "Disruptive" applications
  - Quantum computing
  - Solar energy
Outlook

• Popular buzz has upside and downside

• There probably will be a Nanotech bubble – brace yourselves and invest wisely!

• After the bubble bursts, then the real fun will start!

• Consider the startup vs. the large company

• Get ready for some cool things in the coming decades!!!
A brief introduction to quantum dots

• What is a quantum dot
• How to make a quantum dot
• How to characterize it
• How to think of it physically
• Some key publications
What is a quantum dot

Figure 1. Density of states in metal (A) and semiconductor (B) nanocrystals. In each case the density of states is discrete at the band edges. The Fermi level is in the center of a band in a metal, and so $kT$ will exceed the level spacing even at low temperatures and small sizes. In contrast, in semiconductors, the Fermi level lies between two bands, so that the relevant level spacing remains large even at large sizes. The HOMO–LUMO gap increases in semiconductor nanocrystals of smaller size.

Figure 2. Idealized density of states for one band of a semiconductor structure of 3, 2, 1, and "0" dimensions. In the 3d case the energy levels are continuous, while in the "0d" or molecular limit the levels are discrete.

IIIv-IIIvII wurtzite CdSe nanocrystals.
What is a quantum dot
What is a quantum dot

![Diagram of bulk semiconductor and semiconductor nanocrystal](image)

**Figure 1**

A bulk semiconductor has continuous conduction and valence energy bands separated by a fixed energy gap, $E_g$, whereas a semiconductor nanocrystal (NC) is characterized by discrete atomic-like states and an NC size-dependent energy gap. In a simple model of a spherical quantum well with an infinite barrier, the NC energy gap, $E_g(\text{NC})$, relates to the bulk semiconductor energy gap, $E_g(\text{bulk})$, by the following expression: $E_g(\text{NC}) = E_g(\text{bulk}) + \frac{x^2}{8\pi^2 r^2}$, where $r$ is the NC radius, $m_r = (m_e^{-1} + m_h^{-1})^{-1}$, and $m_e$ and $m_h$ are the electron and hole effective masses, respectively. The NC energy structures are shown for the model case of a two-band semiconductor, which has a single parabolic conduction band and a single parabolic valence band.
What is a quantum dot

(a) In the case of CdSe nanocrystals (NCs), quantum confinement leads to mixing between different valence subbands, which produces a more complex structure of hole quantum states compared with those shown in Figure 1. Arrows indicate allowed indirect optical transitions. (b) A linear ground-state absorption spectrum of CdSe NCs with a mean radius of 4.1 nm. Arrows mark the positions of four well-resolved transitions that involve either the 1S or 1P electronic states.
What is a quantum dot?
What is a quantum dot

- How does one make a nanometer sized object?
- How do you make many (identical) nanometer sized objects?
- How do the optical and electrical properties of this nanoscale object change with size?
- How does its optical and electrical properties change with its “dimensionality”?
- How do charges behave in nanoscale objects?
- How does charge transport occur in these materials?
- Do these nanoscale materials possess new and previously undiscovered properties?
- Are they useful?
How to make a quantum dot

Reaction solution (1.9:1 Cd:Se): 166 μL Cd(CH$_3$)$_2$, 0.096 g Se$^v$ and 10 mL TBP are injected into 12 g TOPO

TBP = tributylphosphine
P[CH$_3$(CH$_2$)$_3$]$_3$

TOPO = trioctylphosphine oxide
O=P[CH$_3$(CH$_2$)$_7$]$_3$

360 °C crystal nucleation, 300 °C crystal growth

Isolation by methanol precipitation

Figure 5. Procedure for synthesizing high-quality, monodisperse CdSe nanocrystals by the pyrolysis of organometallic precursors. This open-atmosphere setup is designed to be used in a glove box. The reaction can be performed outside a glove box under argon.
How to make a quantum dot

Figure 2. Nanocrystal Quantum Dots (NQDs)
(a) An organometallic method is used for the fabrication of highly monodisperse CdSe NQDs. Nucleation and subsequent growth of NQDs occurs after a quick injection of metal and chalcogenide precursors into the hot, strongly coordinating solvent—a mixture of trietylphosphine (TOP) and trietylphosphine oxide (TOPO) in the case shown. After a fixed period, removing the heat source stops the reaction. As a result, NQDs of a particular size form. (b) The colloidal NQDs obtained by the method illustrated in (a) consist of an inorganic CdSe core capped with a layer of TOP/TOPO molecules. (c) Solutions of CdSe NQDs of different radii, under ultraviolet illumination, emit different colors because of the quantum size effect. A 2.4-nm-radius dot has an energy gap of about 2 eV and emits in the orange, whereas a dot of radius 0.9 nm has a gap of about 2.7 eV and emits a blue color.
How to characterize a quantum dot

1. Imaging – TEM, STM
2. Absorption, PL, PLE
3. TCSPC – lifetime
4. Dynamics – femtosecond spectroscopy
How to characterize a quantum dot

**Figure 2.** Room temperature optical absorption spectra of ~20–30 Å diameter CdS, CdSe, and CdTe crystallites.

**Figure 3.** Room temperature optical absorption spectra of CdSe crystallites dispersed in hexane and ranging in size from ~12 to 115

**Figure 5.** Typical room temperature band edge luminescence and absorption spectra for 35 Å diameter CdSe crystallites. No deep trap luminescence is detected.

**Figure 4.** HOMO LUMO transition energy of CdSe crystallites as a function of size (diamonds) compared with the prediction of the effective mass approximation (solid line).
How to characterize a quantum dot

FIG. 1. (a) Absorption (solid line) and photoluminescence (dashed line) spectra for ~28Å-radius quantum dots. In luminescence the sample was excited at 2.655 eV (467.0 nm). The downward arrow marks the emission position used in PLE. (b) PLE scan for ~28Å-radius dots.

FIG. 3. (a) Demonstration of the fitting procedure used to extract PLE peak positions. The PLE scan (solid line) is compared to the fit (dashed line) for a ~18Å-radius sample. The structure on the first absorption is clearly visible in this plot. (b) The individual Gaussian components (solid lines) and the cubic background (dashed line) which combine to form the fit. The first absorption peak is decomposed into two narrow features slightly to the red of a broader absorption peak. For comparison the peaks are labeled as in Fig. 4.

FIG. 4. Transition energies (relative to the first excited state) vs the energy of the first excited state. Peak positions are extracted from PLE data as described in the text and shown in Fig. 3. This plot shows all of our PLE data, including several PLE scans for each of our 24 samples. Strong (weak) transitions are denoted by circles (crosses). The solid (dashed) lines are visual guides for the strong (weak) transitions to clarify their size evolution.
How to think of a quantum dot

Chapter 3

Length scales

DeBroglie wavelength and exciton Bohr radius

Here we derive the relationship between the deBroglie wavelength and the exciton Bohr radius. The reason we do this is that often in the literature one sees a statement that a nanomaterial is in the “quantum confinement” regime because its size is smaller than the corresponding deBroglie wavelength of an electron or hole. At other times one sees the statement that a nanomaterial is quantum confined because its size is smaller than the corresponding exciton Bohr radius. We ask if these are the same statement.

In this section we show that the two are related and that, in fact, both statements essentially say the same thing.

Textbook Bohr radius

Here is the textbook equation for the Bohr radius of an electron

\[
\alpha_0 = \frac{4\pi\varepsilon_0 \hbar^2}{ma^2}
\]  

(3.1)

where \(\varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m (permittivity)}\), \(\hbar = 1.054 \times 10^{-34} \text{ J·s (Planck’s constant over } 2\pi)\), \(m_e = 9.11 \times 10^{-31} \text{ kg (mass of a free electron)}\) and \(q = 1.602 \times 10^{-19} \text{ C (charge)}\). If you plug all the numbers in and do the math you come up with the result

\[
\alpha_0 = 5.28 \times 10^{-11} \text{ meters}
\]

\[
= 0.528 \text{ Angstroms}
\]

(3.2)

This is the standard Bohr radius one sees all the time.

Derivation

Basically we need to equate the centripetal (center seeking) force of a carrier with the Coulomb attractive (inward) force.

\[
\frac{mv^2}{r} = \frac{q^2}{4\pi\varepsilon_0 r^2}
\]

(3.3)

Here we make use of the relation

\[
2\pi r = n\lambda
\]

(3.4)

where \(n\) is an integer. The deBroglie relation comes in by relating the wavelength \(\lambda = \frac{\hbar}{p}\) where \(\hbar\) is Planck’s constant and \(p\) is the momentum of the particle \((p = mv)\). Starting with the above equation we rearrange it to get

\[
\lambda = \frac{2\pi r}{n} = \frac{h}{p} = \frac{h}{mv}
\]

Solve for \(v\) to get (express \(v\) in terms of \(r\))

\[
v = \frac{n\hbar}{2\pi mv} = \frac{n\hbar}{mv}
\]

Replace this into the main equation (3.3)

\[
\frac{mv^2}{r} = \frac{q^2}{4\pi\varepsilon_0}
\]

Rearrange this to get

\[
r = \frac{4\pi\varepsilon_0 \hbar^2}{mv^2}
\]

If \(n = 1\) (the lowest orbit) this gives us the Bohr radius

\[
\alpha_0 = \frac{4\pi\varepsilon_0 \hbar^2}{mv^2}
\]

which is the standard textbook equation we showed earlier.
How to think of a quantum dot

At this point we note that if the electron or carrier is not in vacuum the equation should be modified to take into account the dielectric constant of the medium. (Instead of \( \varepsilon \) replace it with \( \varepsilon_0 \))

\[
a_b = \frac{4\pi \varepsilon_0 e^2 \hbar^2}{m^2}
\]

(3.5)

Furthermore, for the case of an exciton (electron hole pair) in a semiconductor just replace the mass of the electron with the effective mass of the exciton.

\[
\frac{1}{m_{eff}} = \frac{1}{m_e} + \frac{1}{m_h}
\]

(3.6)

where \( m_e \) and \( m_h \) are the effective masses of electron and hole in the material.

Note that equation 3.4 basically gives the relation between the deBroglie wavelength and the exciton Bohr radius. So, in effect, our initial statements about confinement dealing with either the exciton Bohr radius or deBroglie wavelength are essentially one and the same. The deBroglie wavelength or exciton Bohr radius are therefore natural length scales by which to compare the physical size of a nanomaterial. In general objects with dimensions smaller than these natural length scales will exhibit quantum confinement effects. This will be discussed in more detail in subsequent chapters.

Examples

Here are some values for some common systems where I've taken values of the dielectric constant, electron and hole effective masses from the literature. One can derive the exciton Bohr radius of these systems, using the values below, in a straightforward fashion. This list is not meant to be comprehensive and the interested reader should consult the Landolt-Börnstein tables for more complete values.

- **GaAs**
  - \( m_e = 0.067m_0 \)
  - \( m_h = 0.45m_0 \)
  - \( \varepsilon = 12.4 \)

- **InAs**
  - \( m_e = 0.02m_0 \)

- **InP**
  - \( m_e = 0.07m_0 \)
  - \( m_h = 0.45m_0 \)
  - \( \varepsilon = 14.5 \)

- **CIS**
  - \( m_e = 0.2m_0 \)
  - \( m_h = 0.7m_0 \)
  - \( \varepsilon = 8.6 \)

- **CdSe**
  - \( m_e = 0.15m_0 \)
  - \( m_h = 0.45m_0 \)
  - \( \varepsilon = 9.4 \)

**Worked example**

Case (GaAs)

\[
\frac{1}{m_{eff}} = \frac{1}{m_e} + \frac{1}{m_h} = \frac{1}{\frac{1}{0.067m_0} + \frac{1}{0.45m_0}}
\]

leading to the effective mass

\[
m_{eff} = 0.068m_0
\]

\[
a_b = \frac{4\pi \varepsilon_0 e^2 \hbar^2}{0.068m_0 \varepsilon_{GaAs}^2}
\]

\[
= \frac{4\pi \times 8.85 \times 10^{-12}}{(0.068)^2}\frac{12.4 \times 10^{-54} \times (1.602 \times 10^{-19})^2}{1.602 \times 10^{-19}}
\]

\[
= 11.3 \text{ nm}
\]

Exciton Bohr radius for GaAs.
How to think of a quantum dot

Case: \text{(CdSe)}

\[
\frac{1}{m_{\text{eff}}} = \frac{1}{m_e} + \frac{1}{m_h} = \frac{1}{0.013 m_0} + \frac{1}{0.45 m_0}
\]

leading to the effective mass

\[
m_{\text{eff}} = 0.1 m_0
\]

\[
e_h = \frac{4 \pi \hbar^2}{0.059 m_0 q^2} = 4 \pi (8.85 \times 10^{-12}) \left( \frac{2(0.41)(1.054 \times 10^{-34})^2}{(0.1)(0.11 \times 10^{-11})(1.662 \times 10^{-34})^2} \right) = 4.97 \text{ nm}
\]

Exciton Bohr radius for CdSe.

Exercises
1. What is the wavelength of a 1 eV photon?
2. What is the wavelength of a 2 eV photon?
3. What is the wavelength of a 3 eV photon?
4. What is your deBroglie wavelength (what's your weight in kg?) when moving at 10 m/s?
5. What is the deBroglie wavelength of a baseball (0.15 kg) moving at 50 m/s?
6. What is the deBroglie wavelength of C60 moving at 220 m/s? Read the corresponding article if you are interested. Amfit et al. Nature 401, 660 (1999).
7. Calculate the exciton Bohr radius for the following semiconductor. If needed use values for what is called the heavy hole. Consult a good resource such as Landolt-Börnstein. III-V compounds.
How to think of a quantum dot

Density of states

The idea here is that while the confinement of an axis gives rise to discrete energies (as we saw in the previous section on confinement), in cases such as the quantum well and quantum wire, there are additional states along the unconfined axes (degrees of freedom). Here it is not practical to try and calculate the energies of each state since they are actually continuous bands or energies. As a consequence one way to get an idea of what the energies look like is to perform the following density of states argument. So when put together with the confined energies from the last section, these density of states calculations provide a more thorough description of what the electronic structure of 3D, 2D, 1D and 0D materials look like.

3 Dimensions (bulk)

Consider the volume in “k” space

\[ V_k = \frac{4}{3} \pi k^3 \]

\[ (k^2 = k_x^2 + k_y^2 + k_z^2) \] where for a particle in this sphere

\[ k_x = \frac{2\pi}{L_x} \]

\[ k_y = \frac{2\pi}{L_y} \]

\[ k_z = \frac{2\pi}{L_z} \]

Note that the \( 2\pi \) arises from the constraints of a periodic boundary condition (Born-Von Karman conditions, named after Max Born and Theodore Von Karman) as opposed to the more general \( 2\pi/n \) where \( n = 0, 1, 2, \ldots \). The volume of a given mode is then \( k_x k_y k_z \). The number of modes \( N \) in the sphere are then

\[ N = \frac{V_k}{k_x k_y k_z} = \frac{4}{3} \pi k^3 \frac{L_x L_y L_z}{8\pi^3} \]

Say the particle is an electron and we consider the spin degeneracy (up and down), then we multiply \( N \) by 2.

\[ N' = 2N = 2\frac{4}{3} \pi k^3 L_x L_y L_z \]

\[ = \frac{k^3}{3\pi^2} L_x L_y L_z \] total number of states in sphere

Consider the density

\[ \rho = \frac{N'}{L_x L_y L_z} = \frac{k^3}{3\pi^2} \text{ number of states/unit volume} \]

Now consider the energy density defined as

\[ \rho' = \frac{dp}{dz} = \frac{d}{dz} \left( \frac{\hbar^2}{2m} \right)^{\frac{3}{2}} \frac{dz}{dz} = \frac{1}{3} \frac{dz}{dz} \]

(5.1)

where recall \( k = \sqrt{\frac{2mE}{\hbar^2}} \) (units of 1 over length) for a free electron or alternatively \( k^4 = \left( \frac{2mE}{\hbar^2} \right)^{\frac{3}{2}} \). The expression becomes

\[ \rho' = \frac{1}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{dz}{dz} \]

\[ \rho' = \frac{1}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{3}{2} \]

\[ \rho' = \frac{3}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \]

(5.2)

This is the “density of states” in 3 dimensions. Note the square root dependence on energy. Note also that the energies of the system are

\[ \epsilon = \frac{k^2\hbar^2}{2m} \]

(5.3)

where \( k = \sqrt{k_x^2 + k_y^2 + k_z^2} \) and \( k_{x,y,z} = \frac{2\pi n_x}{L_{x,y,z}} \).
How to think of a quantum dot

Exercises

1. Calculate the 3D density of states for free electrons with energy 0.1 eV. Express your answer in terms of eV and cm$^3$.

2. Assume the electron resides in a non-zero potential $V$. Express the 3D density of states in this situation. Hint: just alter the expression for $k$ below equation 5.3.

2 Dimensions (well)

Here we have 1 dimension that is quantized. Let’s assume its the $z$ direction. The total energy of this system is a sum of the energy along the quantized direction + the energy along the other 2 “free” directions. It is expressed as

$$\varepsilon_{\text{tot}} = \frac{\hbar^2 k_z^2}{2m} + \frac{\hbar^2}{2m} (k_x^2 + k_y^2)$$

where $k^2 = k_x^2 + k_y^2$ and $k_z = \frac{m}{\hbar} k_z$. Consider now an area in $k$ space

$$\delta k = \frac{2\pi}{L_z}$$

where for the particle

$$k_z = \frac{2\pi}{L_z}$$

CHAPTER 5. DENSITY OF STATES

$$k_y = \frac{2\pi}{L_y}$$

The area of a given mode is then $k_y \delta y$ with the total number of modes ($N$) in the area being

$$N = \frac{\pi k_y^2}{4\pi} L_x L_y = k_x^2 L_x L_y$$

Again if the particle is an electron and we consider spin, multiply by 2 to get

$$N' = 2N = \frac{k_x^2 L_x L_y}{2\pi}$$

total number of states in area

Consider now a density

$$\rho = \frac{N'}{L_x L_y} = \frac{k_x^2}{2\pi}$$

where recall that $k = \sqrt{2m\varepsilon}$. Replacing this above gives

$$\rho = \frac{m}{\hbar^2 \pi}$$

number of states per unit area.

Now consider the energy density

$$\rho' = \frac{d\rho}{d\varepsilon} = \frac{m}{\hbar^2 \pi}$$

This is the energy density of the subband for a given $k_z$ (or $\varepsilon_z$). For each successive $k_z$ there will be an additional $\frac{\hbar^2}{2m} k_z^2$ term and hence another subband. Therefore the density of states is written

$$\rho_{2D} = \frac{\hbar^2}{2m} \sum_k \Theta(\varepsilon - \varepsilon_k)$$

where $\Theta$ is the Heavyside function.

Exercises

1. Calculate the 2D density of states for free electrons with energy 0.1 eV. Consider only the lowest subband. Express your answer in eV and cm$^3$ units.
How to think of a quantum dot

1 Dimension (wire)

Consider now the situation where there are 2 dimensions confined and only 1 degree of freedom (say the z direction). The total energy of the system can be written as

\[ \varepsilon_{\text{tot}} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m} = \varepsilon_n + \varepsilon_m + \varepsilon_z \]  \hspace{1cm} (5.6)

where \( k_z = \frac{2n_p}{L_z} \). Furthermore along the confined directions, \( k_x = \frac{2n_x}{L_x} \) and \( k_y = \frac{2n_y}{L_y} \) and \( n_x, n_y \) are integers. Consider a length \( 2L \). The number of modes along this length is

\[ N = \frac{2k}{k_x} = \frac{2L}{(2\pi)} = \frac{kL_x}{\pi} \text{ number of states along the line} \]

Now if we consider an electron again, ensure to take into account the spin degeneracy

\[ N' = 2N = \frac{2kL_x}{\pi} \]

Now a density is

\[ \rho = \frac{N'}{L_x} = \frac{2k}{\pi} = \frac{2\sqrt{\frac{me}{\hbar^2}}}{\pi} \text{number of states per unit length} \]

Consider the energy density

\[ \rho' \propto \frac{d\rho}{d\varepsilon} = \frac{2}{\pi} \sqrt{\frac{2m}{\hbar^2}} \frac{d\varepsilon}{d\varepsilon} = \frac{2}{\pi} \sqrt{\frac{2m}{\hbar^2}} e^{-\frac{\varepsilon}{\varepsilon_0}} \]

\[ = \frac{1}{\pi} \sqrt{\frac{2m}{\hbar^2}} \frac{1}{\varepsilon_0} \]

(5.7)

This is the energy density for a given \( n, m \) value or \( (\varepsilon_n, \varepsilon_m) \) combination. The complete expression taking into account all \( n, m \) combinations is

\[ \rho'_{\text{tot}} \propto \frac{1}{\pi} \sqrt{\frac{2m}{\hbar^2}} \sum_{n,m} \frac{1}{\varepsilon_n - \varepsilon_m} \Theta (\varepsilon - \varepsilon_{nm}) \]  \hspace{1cm} (5.8)

where again, \( \Theta \) is the Heaviside function. Notice the inverse square root dependence of the density of states with energy.

![Figure 5.2: Density of states in a 2D material (quantum well)](image)

![Figure 5.3: Density of states in a 1D material (quantum wire)](image)

**Exercises**

1. Calculate the 1D density of states for free electrons with energy 0.1 eV above \( \varepsilon_{nm} \). Consider only the lowest subband. Express your result in units of eV and cm³. 
How to think of a quantum dot

0 Dimension (dot)

Here since all three dimensions are confined the density of states is basically a series of delta functions. The total energy of the system is

$$\varepsilon_{tot} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m} = \varepsilon_m + \varepsilon_n + \varepsilon_\sigma$$  \hspace{1cm} (5.9)

where $m, n, \sigma$ are integers and $k_x = \frac{nx}{L_x}, k_y = \frac{ny}{L_y}, k_z = \frac{nz}{L_z}$ The density of states is

$$\rho_{0D} = \delta(\varepsilon - \varepsilon_{m,n,\sigma})$$  \hspace{1cm} (5.10)

Figure 5.4: Density of states in a 0D material (quantum dot)

Exercises

1. Compare and contrast the density of states in the 0D case to the previous 3D, 2D and 1D cases.
How to think of a quantum dot

In the quantum world, the concept of a quantum dot is often introduced as a discrete energy level or sub-level of an atom or molecule. To think of a quantum dot, imagine a tiny, isolated atom or molecule that is confined to a very small volume, typically on the order of nanometers. This confinement can be achieved by various methods, such as nanoscale confinement, quantum confinement, or quantum well confinement.

The confinement of a quantum dot results in discrete energy levels, which can be described by the Hamiltonian. The Hamiltonian provides a mathematical framework for understanding the energy levels and wave functions of a quantum system. For a quantum dot, the Hamiltonian typically includes terms for the kinetic energy of the electron and the potential energy due to the confinement.

In this context, the wave function $\psi(r)$ describes the probability amplitude for finding the electron at a given position $r$. The energy levels of the quantum dot are related to the solutions of the Schrödinger equation, which is given by:

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

where $\hbar$ is the reduced Planck constant, $m$ is the mass of the electron, $V(r)$ is the potential energy, and $E$ is the energy level.

The eigenvalues of the Schrödinger equation give the allowed energy levels of the quantum dot. These energy levels are quantized due to the confinement, leading to discrete energy levels rather than a continuous spectrum.

Applications of Quantum Dots

Quantum dots have a wide range of applications, including semiconductor devices, sensors, and optoelectronic devices. Quantum dots are particularly useful in areas such as quantum computing, where they can be used as qubits, the fundamental unit of information in a quantum computer. They are also used in quantum cryptography, where the properties of quantum dots can be used to create secure communication channels.

In the field of biology, quantum dots are used as markers in biotechnology and medical imaging. Their unique optical properties allow for high-resolution imaging and tracking of biological processes with high sensitivity and specificity.

In summary, quantum dots are fascinating objects that combine the properties of quantum mechanics with the discrete nature of materials. They offer a rich field of study and have promising applications in various scientific and technological domains.
How to think of a quantum dot

Band Structure – Chemists View

\[ N = 2 \]

\[ N = 4 \]

\[ N = \infty \]
How to think of a quantum dot

Kronig-Penney Model

The solution to the Schrödinger equation for a periodic potential must be of the form (Bloch):

$$\psi_k(x) = u_k(x) \exp(ikx)$$

where $u_k(x) = u_k(x + a)$ has the period of the crystal lattice.

The solution to the Kronig-Penny model is

$$\psi_a(x) = Ae^{ikx} + Be^{-ikx}$$
$$\psi_b(x) = Ce^{i\alpha} + De^{-i\alpha}$$

$$E = \frac{\hbar^2 k^2}{2m}$$
$$E = U_0 - \frac{\hbar^2 \alpha^2}{2m}$$

The constant A, B, C, D are chosen so that the wave function and its derivatives are continuous. Using Bloch’s theorem we find:

$$\frac{P}{Ka} \sin(Ka) + \cos(Ka) = \cos(ka)$$

For simplicity we took the limit $b = 0, U_0 = \infty$ such that $P = Q^2 ba / 2$ is finite.
How to think of a quantum dot

Bands, Energy and Free Electrons

Plot of the solution of the Kronig-Penny model. The allowed values of the energy are given by those ranges of $Ka$ which the function lies between ±1. Other ranges are forbidden gaps in the energy spectrum.

If we plot the energy as a function of the wave number we observe regions of allowed states and regions of gaps.

- Metals
- Semiconductors
- Insulators
How to think of a quantum dot

Quantum Confinement

Effective Mass Approximation (in the context of nanocrystals this approximation was introduced by Efros and Efors (1982), and Brus (1983))

\[ H = -\frac{\hbar^2}{2m_e^*} \nabla^2 r_e + \frac{\hbar^2}{2m_h^*} \nabla^2 r_h - \frac{e^2}{\varepsilon |r_e - r_h|} \]

Zero’s order solution

\[ \Psi(r_e, r_h) = \phi(r_e)\phi(r_h) \]

In polar coordinates

\[ \phi(r_{e,h}) = \sqrt{\frac{2}{a^3}} \frac{j_{\ell_{e,h}}(\kappa_{n_{e,h},\ell_{e,h}} r_{e,h} / R)}{j_{\ell_{e,h}+1}(\kappa_{n_{e,h},\ell_{e,h}})} Y_{\ell_{e,h}n_{e,h}}(\theta_{e,h}, \phi_{e,h}) \]

where \( \kappa_{n,\ell} \) are the zeros of the spherical Bessel function
How to think of a quantum dot

Artificial Atoms

Atoms to bulk

Quantum dot

The nanocrystal states are labeled by the quantum number $n_e \ell_e n_h \ell_h$. For example, $1S_e 1S_h$ similar to the notation used for atoms.
How to think of a quantum dot

The First Exciton Energy

The first exciton

\[ E_{1S_e1S_h} = E_g + \frac{1}{2} \left( \frac{\hbar \pi}{R} \right)^2 \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R} \]

In reduced units

\[ \Delta E_{1S_e1S_h} = E_R \left( \frac{\pi a_B}{R} \right)^2 - \frac{1.8e^2}{\varepsilon R} \]

where \( E_R = \frac{\hbar^2}{2m_e a_B^2} \) and \( a_B = \frac{\varepsilon \hbar^2}{m_{eh} e^2} \)
How to think of a quantum dot

Confinement Regimes

Strong confinement
\[ a < a_B^e, a_B^h \]

Intermediate confinement
\[ a_B^h < a < a_B^e \]

Weak confinement
\[ a > a_B^e, a_B^h \]

<table>
<thead>
<tr>
<th>Material</th>
<th>( m_e )</th>
<th>( m_h )</th>
<th>( E_\text{g} ) (eV)</th>
<th>( a ) (nm)</th>
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<td>0.06</td>
<td>0.28</td>
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</table>
How to think of a quantum dot

Exciton Fine Structure

The band structure of semiconductors is often more complicated than the parabolic effective mass approximation. While in many cases the conduction band is well approximated by the effective mass model, the valence band is not. Spin-orbit coupling, crystal field splitting, and intraband coupling give rise to a much more complicated band structure.

Due to spin-orbit coupling the valence band is split into two bands, split-off band (J=1/2) and light and heavy hole bands (J=3/2 J_m=±1/2, J=3/2 J_m=±3/2). J is the sum of envelop and spin angular momentum.

In some cases due to crystal field the light hole and heavy hole are further split.
How to think of a quantum dot

K dot P Method

Due to the complexity of the real band structure more accurate quantum dot calculations require one to go beyond the simple effective mass approximation. One such approximation is based on the k dot p method. In this approximation the solution is expanded exactly around a particular point in k space. The single particle Schrödinger equation reads

\[
\left( \frac{p^2}{2m} + V(r) \right) \psi_k(r) = E_k \psi_k(r) \quad \Rightarrow \quad \left( \frac{(p+k)^2}{2m} + V(r) \right) u_k(r) = E_k u_k(r)
\]

We can partition the Hamiltonian into a k-independent term and a correction

\[
H_0 = \frac{p^2}{2m} + V(r) \quad \quad \quad H_1 = \frac{k \cdot p}{m}
\]

Using second order perturbation theory we find

\[
E_{nk} = E_{n0} + \frac{k^2}{2m} + \frac{1}{m^2} \sum_{m \neq n} \frac{|k \cdot p_{nm}|^2}{E_{n0} - E_{m0}} \quad \quad u_{nk}(r) = u_{n0}(r) + \frac{1}{m} \sum_{m \neq n} \frac{k \cdot p_{nm}}{E_{n0} - E_{m0}} u_{m0}(r)
\]
How to think of a quantum dot

Figure 4  The bulk band structure of a typical direct gap semiconductor with cubic or zinc blende lattice structure and band edge at the Γ-point of the Brillouin zone. The boxes show the region of applicability of the various models used for the calculation of electron and hole QSLs.
How to think of a quantum dot

in semiconductor nanocrystals [10,11]. It was puzzling why these systems typically exhibit emission lifetimes that are two to three orders of magnitude longer than the bulk crystal. The origin of this phenomenon is explained in Section III. Afterward, Section IV discusses recent work which moves beyond CdSe. In particular, InAs nanocrystals are described [12]. As a narrow-gap, III–V semiconductor, this system presents significant differences from CdSe. Studies of InAs have both confirmed and prompted further refinements in the theoretical model of nanocrystals [12]. Finally, Section IV concludes by briefly outlining some of the remaining issues in the electronic structure of nanocrystals.

Unfortunately, this chapter does not provide a comprehensive review of nanocrystal spectroscopy. Therefore, the reader is encouraged to look at the other chapters in this volume as well as the many excellent reviews and treatises that are now available on this topic [14–21].

II. THEORETICAL FRAMEWORK

A. Confinement Regimes

In Section I, we stated that the quantum size effect occurs when the size of the nanocrystal becomes comparable to or smaller than the natural length scale of the electron and hole. To be more precise, one can utilize the Bohr radius as a convenient length scale. In general, the Bohr radius of a particle is defined as

\[ a_B = \frac{n_e}{\hbar^2 a_0} \tag{1} \]

where \( n_e \) is the dielectric constant of the material, \( m^* \) is the mass of the particle, \( a_0 \) is the rest mass of the electron, and \( a_0 \) is the Bohr radius of the hydrogen atom [22]. (Note that throughout this chapter, the term particle refers to an atomic particle, such as an electron or hole, not the nanocrystal.) For the nanocrystal, it is convenient to consider three different Bohr radii: one for the electron (\( a_e \)), one for the hole (\( a_h \)), and one for the electron–hole pair or exciton (\( a_{eh} \)). The latter is a hydrogenic-like bound state that forms in bulk crystals due to the Coulombic attraction between an electron and a hole. Using Eq. (1), each of these Bohr radii can be easily calculated. In the case of the exciton, the reduced mass of the electron–hole pair is used for \( m^* \). With these values, three different limits can be considered [2].

1. First, when the nanocrystal radius, \( a_e \), is much smaller than \( a_e, a_h, a_{eh} \) (i.e., when \( a_e < a_e, a_h, a_{eh} \)), the electron and hole are each strongly confined by the nanocrystal boundary. This is referred to as the \textit{strong confinement} regime.

2. Second, when \( a_e \) is larger than both \( a_e \) and \( a_h \), but is smaller than \( a_{eh} \) (i.e., when \( a_e, a_h < a < a_{eh} \)), only the center-of-mass motion of the exciton is confined. This limit is called the \textit{weak confinement regime}.

3. Finally, when \( a_e, a_h, a_{eh} \) (e.g., when \( a_e < a_e, a_h, a_{eh} \)), one particle (e.g., the electron) is strongly confined and the other (e.g., the hole) is not. This is referred to as the \textit{intermediate confinement regime}.

Of course, the confinement regime which is accessed in an experiment depends on the nanocrystal material and size. For example, because the exciton Bohr radius in InAs is 38 nm and nanocrystals are typically much smaller than this size, InAs nanocrystals are in the strong confinement regime. In contrast, CuCl has an exciton Bohr radius of 0.7 nm. Accordingly, CuCl nanocrystals are in the weak confinement regime. CdSe nanocrystals can be in either the strong confinement or the intermediate confinement regime, depending on the size of the nanocrystal, because \( a_{eh} \) is 6 nm.

B. The Particle-in-a-Sphere Model

Although the description of the different confinement regimes is useful, it does not provide a quantitative description of the size-dependent electronic properties. To move toward such a description, one can begin with a very simple model: the particle-in-a-sphere model [2,6]. In general, this model considers an arbitrary particle of mass \( m_e \) inside a spherical potential well of radius \( a_e \).

\[ V(r) = \begin{cases} 0 & 0 < r < a_e \\ \infty & r > a_e \end{cases} \tag{2} \]

Following Flügge [23], the Schrödinger equation is solved yielding wave functions:

\[ \psi_n(r, \theta, \phi) = C_n \frac{\psi_n(\theta, \phi)}{r} \tag{3} \]

where \( C \) is a normalization constant, \( \psi_n \) is a spherical harmonic, \( \psi_n(\theta, \phi) \) is the \( n \)-order spherical Bessel function, and

\[ k_{n} = \frac{\alpha}{a} \tag{4} \]

with \( \alpha \) the nth zero of \( j_n \). The energy of the particle is given by

\[ E_{n} = \frac{\hbar^2 k_{n}^2}{2m_e} \tag{5} \]

Due to the symmetry of the problem, the eigenfunctions [Eq. (3)] are simple atomic-like orbitals which can be labeled by the quantum numbers \( n \) (1, 2,
How to think of a quantum dot
How to think of a quantum dot

So far, this treatment has completely ignored the Coulombic attraction between the electron and the hole, which is a higher-order contribution. Of course, the Coulombic attraction still exists in the nanocrystal. However, how it is included depends on the confinement regime. In the strong confinement regime, another approximation, the strong confinement approximation, is used to treat this term. According to Eq. (5), the confinement energy of each carrier scales as $1/a^2$. The Coulomb interaction scales as $1/a$. In sufficiently small crystallites, the quadratic confinement term dominates. Thus, in the strong confinement regime, the electron and hole can be treated independently and each is described as a particle in a sphere. The Coulomb term may then be added as a first-order energy correction. Thus, using Eqs. (3), (5), and (9), the electron-hole pair (e-hp) states in nanocrystals are written as

$$\Psi_{e-hp}(\vec{r}_e, \vec{r}_h) = \Psi_e(\vec{r}_e)\Psi_h(\vec{r}_h)$$

$$= u_e f_e(\vec{r}_e)u_h f_h(\vec{r}_h)$$

$$= e^{i\vec{k}_{\parallel} \cdot \vec{r}_e} u_e f_e(\vec{r}_e) u_h f_h(\vec{r}_h)$$

with the energies

$$E_{e-hp}(n_h l_h m_h l_m) = E_e + \frac{n^2 \epsilon^2}{2m_e^*} + \frac{n^2 \epsilon^2}{2m_h^*} - E_h$$

The states are labeled by the quantum numbers $n_h l_h m_h l_m$. For example, the lowest pair state is written as $1S_0 1S_0$. For pair states with the electron in the $1S_0$ level, the first-order Coulomb correction, $E_c$, is $1.8 \epsilon/3a_0$, where $\epsilon$ is the dielectric constant of the semiconductor [4]. Equations (11) and (12) are usually referred to as the particle-in-a-sphere solutions to the nanocrystal spectrum.

D. Optical Transition Probabilities

The probability to make an optical transition from the ground state, $|0\rangle$, to a particular electron-hole pair state is given by the dipole matrix element

$$P = |\langle 0 | \vec{d} | \vec{p} | 0 \rangle|^2$$

where $\vec{d}$ is the polarization vector of the light and $\vec{p}$ is the momentum operator. In the strong confinement regime, where the carriers are treated independently, Eq. (13) is commonly rewritten in terms of the single-particle states:

$$P = \left| \langle \Psi_e | \vec{d} \cdot \vec{p} | \Psi_h \rangle \right|^2$$

Because the envelope functions are slowly varying in terms of $\vec{r}$, the operator $\vec{p}$ acts only on the unit cell portion of the wave function. Equation (14) is simplified to

$$P = \left| \langle u_e | \vec{d} \cdot \vec{p} | u_h \rangle \right|^2$$

In the particle-in-a-sphere model, this yields

$$P = \left| \langle u_e | \vec{d} \cdot \vec{p} | u_h \rangle \right|^2 \delta_{n_h n_e} \delta_{l_h l_e} \delta_{m_h m_e}$$

due to the orthonormality of the envelope functions. Therefore, simple selection rules ($\Delta n = 0$ and $\Delta l = 0$) are obtained.
How to think of a quantum dot

Electronic Structure in Semiconductor Nanocrystals

A better description of the bulk bands must be incorporated into the theory. Although a variety of computational methods could be used, this route does not provide analytical expressions for the description of the bands. Thus, a more sophisticated effective mass approach, the \( k \cdot p \) method, is typically used [29]. In this case, bulk bands are expanded analytically around a particular point of \( k \)-space, typically \( k = 0 \). Around this point, the band energies and wave functions are then expressed in terms of the periodic functions \( u_{nk} \) and their energies \( E_{nk} \).

General expressions for \( u_{nk} \) and \( E_{nk} \) can be derived by considering the Bloch functions in Eq. (6). These functions are solutions of the Schrödinger equation for the single-particle Hamiltonian

\[
H_0 = \frac{\mathbf{p}^2}{2m} + V(x)
\]

where \( V(x) \) is the periodic potential of the crystal lattice. Using Eqs. (6) and (17), it is simple to show that the periodic functions \( u_{nk} \) satisfy the equation

\[
\left[ H_0 + \frac{1}{m_0} \left( k \cdot \mathbf{p} \right) \right] u_{nk} = \lambda_{nk} u_{nk}
\]

where

\[
\lambda_{nk} = E_{nk} - \frac{k^2}{2m_0}
\]

Because \( u_{nk} \) and \( E_{nk} \) are assumed known, Eq. (18) can be treated in perturbation theory around \( \lambda = 0 \) with

\[
H = \frac{k^2}{2m_0} + \frac{k^2}{2m_0} \sum_{nk} \left| \mathbf{p} \cdot \mathbf{p}_{nk} \right|^2
\]

Then, using nondegenerate perturbation theory to second order, one obtains the energies

\[
E_{nk} = E_{n0} + \frac{k^2}{2m_0} + \frac{1}{m_0} \sum_{nk'} \left| \mathbf{p} \cdot \mathbf{p}_{nk} \right|^2
\]

and functions

\[
u_{nk} = u_{nk} + \frac{1}{m_0} \sum_{nk'} \frac{\mathbf{p} \cdot \mathbf{p}_{nk'}}{E_{nk'} - E_{nk}}
\]

with

\[
\overline{\mathbf{p}}_{nk} = \langle u_{nk} | \mathbf{p} | u_{nk} \rangle
\]
How to think of a quantum dot

**Figure 8** A simplistic model for describing the optical transitions between the conduction and valence bands. Each valence band contributes a ladder of parabolic states. The optical transitions then occur between the states arising from the conduction band. This model shows that the states due to mixing of the different hole ladders, as a result of the Coulomb interaction and other interactions, are coupled.

**Figure 9** Summary of quantum numbers and important interactions in semiconductor nanocrystals. The total electron–hole pair angular momentum (N) has contributions due to both the electron (F_e) and hole (F_h). Each carrier's angular momentum (F) may then be further broken down into a unit-cell component (J) due to the atomic basis (l) and spin (s) of the particle and an envelope function component (L) due to the particle-in-a-sphere orbital.
How to think of a quantum dot

Figure 13 Energy level diagram describing the exciton fine structure. In the spherical model, the band-edge exciton (1S\(_{3/2}\)1S\(_{0}\)) is eightfold degenerate. This degeneracy is split by the nonspherical shape of the dots, their hexagonal (wurtzite) lattice, and the exchange interaction.
How to think of a quantum dot
Some key results: synthesis


Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites

C. B. Murray, D. J. Norris, and M. G. Bawendi*

*Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

*Received March 22, 1993*

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Synthesis and Characterization of Strongly Luminescing ZnS-Capped CdSe Nanocrystals

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*Received: August 10, 1995; In Final Form: October 16, 1995*

We describe the synthesis of ZnS-capped CdSe semiconductor nanocrystals using organometallic reagents by a two-step single-flask method. X-ray photoelectron spectroscopy, transmission electron microscopy and optical absorption are consistent with nanocrystals containing a core of nearly monodisperse CdSe of 27–30 Å diameter with a ZnS capping 6 ± 5 Å thick. The ZnS capping with a higher bandgap than CdSe protrudes the core crystallite removing the surface traps. The nanocrystals exhibit strong and stable band-edge luminescence with a 50% quantum yield at room temperature.
Some key results:

characterization

Observation of the “Dark Exciton” in CdSe Quantum Dots
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Beam Theory Section, Naval Research Laboratory, Washington, D.C. 20375
(Received 30 May 1995)

We use external magnetic fields to identify the band edge emitting state in CdSe quantum dots. The field dependence of emission decays and LO phonon spectra show the importance of exciton spin dynamics in the recombination mechanism. To interpret our results we calculate the band edge exciton structure, including the effects of the electron-hole exchange interaction and a nonspherical shape. The exchange term, negligible in the bulk, is strongly enhanced by quantum confinement and allows the observation of an optically passive “dark” excitonic state.

PACS numbers: 73.20.De, 63.20.Ka, 71.70.Ej, 71.70.Gm

Size dependence of exciton fine structure in CdSe quantum dots
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(Received 18 July 1995)

We use photoluminescence excitation and fluorescence line narrowing spectroscopies to study size structure observed in the band-edge absorption spectra of CdSe quantum dots. We study samples ranging from ~15 to ~50 Å in radius to probe the size dependence of this structure. We compare our results with mean theories, which predict band-edge exciton splittings in CdSe dots due to their internal crystal structure, nonspherical shape, and the exchange interaction between the electron and hole. We find reasonable agreement between our data and theory, supporting the observation of exciton fine structure.

Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots
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(Received 2 March 1995)

We use photoluminescence excitation to study the electronic spectrum of CdSe quantum dots ranging from ~12 to ~53 Å in radius. We follow the size evolution of ten quantum dot absorption features. Comparison of the spectra with theoretical predictions allows us to confidently assign six of these transitions. We discuss the most likely assignments for the remaining four. We find that the n1S1,1S2, and n2S1,1S2 transitions dominate the spectra, accounting for half of the observed features. Our size-dependent data exhibit two strong avoided crossings, demonstrating the importance of valence-band structure in the description of the excited states.

[80163-1829/96/0/7220-7]
Some key results: single dot

Quantum-Confined Stark Effect in Single Cd Nanocrystallite Quantum Dots
S. A. Empedocles and M. G. Bawendi*

The quantum-confined Stark effect in single cadmium selenide (CdSe) nanocrystal quantum dots was studied. The electric field dependence of the single-dot spectra is characterized by a highly polarizable excited state (~10°C cubic anisotropy, compared to a typical molecular value of order 10 to 100 cubic anisotropies), with independent local electric fields that change over time. These local fields result in anisotropic spectral diffusion and contribute to ensemble inhomogeneous broadening. Shifts of the lowest excited state more than two orders of magnitude larger than the linewidth were observed, suggesting the potential use of these dots in electro modulation devices.

Photoluminescence Spectroscopy of Single CdSe Nanocrystallite Quantum Dots
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(Received 18 July 1996)

We collect and spectrally resolve photoluminescence from single CdSe nanocrystallite quantum dots. The elimination of spectral inhomogeneities reveals resolution limited spectral linewidths (~120 µeV at 10 K) more than 50 times narrower than expected from ensemble measurements. Light-driven spectral diffusion is observed as a form of power broadening. These studies confirm the atomic-like nature of the emitting state in CdSe nanocrystals. [S0003-0499(96)01286-X]

PACS numbers: 73.20.Dx, 61.46.+w, 78.55.Et

Non-blinking semiconductor nanocrystals
Xiaoyong Wang1, Xiaofan Ren1, Keith Kahn1, Megan A. Hahn1, Manju Rajeswaran1, Sara Maccagnano-Zacher1, John Silcox1, George E. Craig2, Alexander L. Efros3 & Todd D. Krauss1,4

Fluorescence intermittency in single cadmium selenide nanocrystals
M. Nirmal1, B. O. Dabbousi1, M. G. Bawendi1, J. J. Macklin1, J. K. Troutman1, T. D. Norris2, & L. E. Brus3

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Nanocrystallite nanocrystals offer the opportunity to study the evolution of bulk materials properties as the size of a system increases from the molecular scale. In addition, their strong size-dependent optical properties make them promising candidates as tunable light absorbers and emitters in optoelectronic devices such as light-emitting diodes and quantum-dot lasers, and as optical probes of biological systems. Here we show that light emission from single fluorescing nanocrystals of cadmium selenide under continuous excitation turns on and off intermittently with a characteristic timescale of about 0.5 seconds. This intermittency is not apparent from ensemble measurements on many nanocrystals. This dependence on excitation intensity and the change in on/off times when a precipitating, high-komplex-shell of zinc sulphide encapsulates the nanocrystal suggests that the abrupt turning off of luminescence is caused by photoinduced hindrance of the nanocrystal. Thus spectrophotometric measurement on single nanocrystals can reveal hitherto unknown aspects of their photophysics.
Some key results: electrical

\textbf{n-Type Conducting CdSe Nanocrystal Solids}

Dong Yu, Congjun Wang, Philippe Guyot-Sionnest

A bottleneck limiting the widespread application of semiconductor nanocrystal solids is their poor conductivity. We report that the conductivity of thin films of \textit{n}-type CdSe nanocrystals increases by many orders of magnitude as the occupation of the first two electronic shells, 1S and 1P\textsubscript{\textit{d}}, increases, either by potassium or electrochemical doping. Around half-filling of the 1S shell, a peak in the conductivity is observed, indicating shell-to-shell transport. Introducing conjugated ligands between nanocrystals increases the conductivities of these states to \(\text{\texttimes}10^{-2}\) siemens per centimeter.

\textbf{Electroluminescence from single monolayers of nanocrystals in molecular organic devices}

Seth Eastwood, Ming-Ming Wang, Kees Meijer, & Vladimir Bulovic

The integration of organic and inorganic materials at the nanometer scale into hybrid optoelectronic structures enables active devices that combine the diversity of organic materials with the high-performance electronic and optical properties of inorganic nanocrystals. The optimization of such hybrid devices ultimately depends upon the precise positioning of the functionally distinct materials. Previous studies have already emphasized that this is a challenge, owing to the lack of well-developed nanometer-scale fabrication techniques. Here we demonstrate a hybrid light-emitting diode (LED) that combines the ease of processability of organic materials with the broad-band, efficient luminescence of colloidal quantum dots (QDs). To isolate the luminescence processes from charge conduction, we fabricate a quantum-dot LED (QD-LED) that contains only a single monolayer of QDs, sandwiched between two organic thin films. This is achieved by a method that uses material phase segregation between the QD aliphatic capping groups and the semiconducting organic materials. In our devices, where QDs function exclusively as luminophors, we observe a 25-fold improvement in luminescence efficiency (1.6 \(\text{A}\text{W}^{-1}\) at 2.040 \(\text{cd}\text{m}^{-2}\)) over the best previous QD-LED results. The reproducibility and precision of our
Some key results: dynamics

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**Femtosecond 1P- to 1S Electron Relaxation in Strongly Confined Semiconductor Nano**

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(Received 21 October 1997)

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**Coherent Acoustic Phonons in a Semiconductor Quantum Dot**

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(Received 10 July 1997)

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**Direct Observation of Electron-to-Hole Energy Transfer in CdSe Quantum Dots**

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**Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots**

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**Slow Electron Cooling in Colloidal Quantum Dots**

Arnaud Pandey and Philippe Guyot-Sionnest*
Some key results: solar
Research in the Kambhampati group
State-Resolved Exciton Dynamics in Quantum Dots

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1. Overview of quantum dots
2. State-resolved quantum dynamics
3. Optical gain
4. The artificial periodic table
5. Spherical quantum well superlattices
What do we imply by ‘nano’?

**Size scales?**
- 100 nm colloid?
- Benzene ⇔ Anthracene?
- Size tunable properties

**Semantics?**
- ‘k’ space vs. ‘x’ space?
- Electron transfer vs. conductance?
- Solid state physics vs. physical chemistry?

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**Excitons in nanoscale systems**

Nanoscale systems are forecast to be a means of integrating desirable attributes of molecular and bulk regimes into easily processed materials. Notable examples include plastic light-emitting devices and organic solar cells, the operation of which hinge on the formation of electronic excited states, excitons, in complex nanostructured materials. The spectroscopy of nanoscale materials reveals details of their collective excited states, characterized by atoms or molecules working together to capture and redistribute excitation. What is special about excitons in nanometre-sized materials? Here we present a cross-disciplinary review of the essential characteristics of excitons in nanoscience. Topics covered include confinement effects, localization versus delocalization, exciton binding energy, exchange interactions and exciton fine structure, exciton–vibration coupling and dynamics of excitons. Important examples are presented in a commentary that overviews the present understanding of excitons in quantum dots, conjugated polymers, carbon nanotubes and photosynthetic light-harvesting antenna complexes.

Scholes Nature Mater. 2006→
Nano Electronics

• What happens when the transistors are the size of electrons?

• What happens when the wires are molecules?

• How will computers work when they are no longer classical?

  • Current IN + Light OUT lasers, LEDs, telecomm, quantum cryptography

  • Light IN + Current OUT solar energy conversion!
Semiconductor quantum dots:
the cartoon picture

- Size must be on the order of the exciton Bohr radius
  \( a_0 = \frac{4\pi\varepsilon_0\varepsilon\hbar^2}{mq^2} \)
  (1 - 10 nm; \(10^2 - 10^5\) atoms)

- Size tunable properties – a new degree of freedom

Central Issues:
physical understanding → materials & applications

- Electronic structure: 1985 – 2000 (?)
- Carrier relaxation dynamics: 1990 - present
- Carrier recombination dynamics: 1995 - present
- Exciton-phonon coupling: 1985 - present
- Optical gain: 1995 – present
- Multi-excitons: 1995 – present
- Single particle blinking: 1996 - present
- Carrier multiplication: 2005 - present

Current projects
1D_e

1P_e

1S_e

1S_{3/2}
1P_{3/2}
2S_{3/2}
3S_{1/2}

Electronic structure:

- Particle confinement
- Enhanced Coulomb & Exchange interactions
- Degeneracy breaking: spin-orbit, crystal field splittings
- Effective mass vs. atomistic theory?

\[ F = (l + s) + L \]
Quantum dots have a resolvable eigenstate spectrum like atoms or molecules.

Consequently there should be state-specific dynamics which may be measurable.

These state-specific processes may include relaxation dynamics, many-body interactions, optical gain, etc.

Or... what really happens inside a quantum dot?
1. Overview of quantum dots
2. State-resolved quantum dynamics
3. Optical gain
4. The artificial periodic table
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A brief history of a quantum dot: beyond phenomenology

10 – 100 fs: 
  electronic coherences

100 fs – 1000 fs: 
  electronic population relaxation
  spin flips

0.1 – 5 ps: 
  vibrational coherences

10 – 100 ps: 
  surface trapping
  Multi-exciton recombination

1-100 ns: 
  emission

1 μs – 1 ms: 
  blinking
The Solution:
Exciton selective spectroscopy (PRB 2006)

- **Time + Frequency domain:**
  statistical vs. systematic uncertainties

  ![Energy vs. Intensity Graph](image)

  - Energy (eV) vs. Intensity (a.u.)
  - Energy $E = 2.12$ eV
  - $R = 2.01$ nm

- **Pump/probe experiment:** 40 fs pulses → Good (statistical)
- **Tunable pump:** exciton selectivity → Better (systematic)
- **Two experiments performed simultaneously** → Still Better (variance)

- **Result:** *state-to-state dynamics* with 10 fs precision

![Experimental Setup Image]
Exciton relaxation dynamics
(a portion of the history)

• How to climb down the ladder?
• Is there a bottleneck?

\[ \Delta E \sim 10\hbar \omega_{LO} \]

\[ \Delta E \sim 4\hbar \omega_{LO} \]

\text{(Efros & Nozik, Nano Lett 2006)}
So what’s the mechanism of exciton relaxation?
(PRL 2007, PRB 2007)

Excitonic trajectories

\[
\begin{align*}
|1P_e - 1P_{3/2}\rangle & \xrightarrow{k_1} |1P_e - 1S_{3/2}\rangle \\
|1P_e - 1S_{3/2}\rangle & \xrightarrow{k_2^{\text{Auger}}} |1S_e - 3S_{1/2}\rangle \\
|1S_e - 3S_{1/2}\rangle & \xrightarrow{k_3^{\text{NA}}} |1S_e - 1S_{3/2}\rangle
\end{align*}
\]

Upshot:
A unified picture of all pathways by which hot excitons relax in quantum dots
Outline

1. Overview of quantum dots
2. State-resolved quantum dynamics
3. **Optical gain**
4. The artificial periodic table
5. Spherical quantum well superlattices
Optical gain in quantum dots

- Threshold
- Temperature stability, Room temperature operation
- Wavelength range
- Single photon sources
- Integration, packaging, processibility

(Krauss Nature 2007)
Semantics

• **Stimulated Emission** – measured in a pump/probe experiment

• **Amplified Spontaneous Emission** – measured in a PL experiment

• The pump pulse bleaches the absorption spectrum
Prior work focused on the material

First observation of gain in colloidal quantum dots (2000). (only observed for thin films)

\[ \Delta \text{OD} + \text{OD} < 0 \]

(Klimov Science 2000)

Gain observed in qdot solutions only for large sizes and only for large \( N \) (2004)

(Ivanov JPCB 2004)

Gain threshold at single exciton achieved for novel Type II material (2007)

\[ \Delta \text{OD}/\text{OD} > 1 \]

(Klimov Nature 2007)
State resolved studies of optical gain
(PRL 2009, JCP 2009)

Absorption + linear absorption = nonlinear absorption

\[ \Delta \text{OD}(|i\rangle, N, \lambda, \tau) + \text{OD}(\lambda) < 0 \]

Result

Initial quantum state controls development of optical gain
Recovering universal gain in dots

Result

The ‘worst’ materials can yield the best performance ever.
Gain Tailoring
(PRL 2009, JCP 2009)

Result
Stimulated emission bandwidth can be tailored!
A completely new effect not seen in traditional systems (quantum wells and molecules)
Shells can control gain lifetime

**Question**
What physical processes and material conditions control the duration of optical gain?

(Krauss 2006)
Outline

1. Overview of quantum dots
2. State-resolved quantum dynamics
3. Optical gain
4. The artificial periodic table
5. Spherical quantum well superlattices
• Biexcitons are bound states in quantum dots

• Shifting of transitions due to many body interactions

• Prior work was not able to probe specific biexcitonic states

• So what??
  • Optical gain
  • multiple-exciton generation (solar)
  • photon entanglement

(Woggon 2003)
Is there a biexciton spectrum?

(Zunger Nano Lett 2003)
How to observe biexcitons
(PRB 2006, JCP 2008, PRB 2009)

With Pump On, $E_{xx}$ shifts the absorption spectrum of sample to lower energy.

Leads to induced absorption in Pump/Probe experiment.

**Absorption =**
- Pump Off
- Pump On (Shifted by $E_{xx}$)

**Pump Probe Signal =**
- Pump On – Pump Off
Or... The artificial He atom

\[ |XX_1\rangle \equiv |1\rangle |1\rangle \]

\[ |XX_2\rangle \equiv |2\rangle |1\rangle \]

\[ |XX_3\rangle \equiv |3\rangle |1\rangle \]

\[ |XX_4\rangle \equiv |4\rangle |1\rangle \]
Electronic structure of XX
(PRB 2009)

Experiment:
Stokes shift

Theory:
Real electronic structure
(a many-body interactions)

So what?
Completely determines NLO
Calculations explain observed trend:
(Zunger & Franceschetti)
The artificial periodic table

The Biexciton (XX) has a unique eigenstate spectrum in analogy to He vs. H

Can we observe other artificial atoms?

Band edge pump can only create biexcitons, while $1P_e$ pump can higher order multiexcitons

Ground state for excitonic complexes of $N = 2 – 6$

He, Li, Be, B, C
A “space-time” picture of nanoscience
(forgive me Mssr. Feynman)

•Q: Hey, I thought “nano” was all about space?

•A: Nope. You gotta get from point A to point B!

•Context: relating the “good states” to the “bad states”
Exciton-phonon coupling

- Effect of quantum confinement on exciton-phonon coupling?
  - LO (Frohlich) and LA (deformation potential)
  - Increasing or decreasing with size?

- Why do we care?
  - Homogeneous linewidth
  - Relaxation dynamics
  - Benchmark of electronic structure
Controversy

- Theory predicts all forms of size dependence
- Experiments disagree with each other
- Disagreement spans three orders of magnitude!

(Shank/Alivisatos) (Wise/Krauss) (Cerullo/Banin)

(Bawendi) (Alivisatos)
• What is the strength of exciton-phonon coupling?

• Unanimous disagreement about nearly every aspect of exciton-phonon coupling!

• Key result: First simultaneous observation of coherent optical and acoustic phonons
Intrinsic vs. Extrinsic couplings
(the space-time thing..)

- **Intrinsic** couplings for each state (femto)

- **Extrinsic** coupling for trapped state (CW – Raman, PL)

- Time dependent coupling
Exploring new mechanisms for coherent phonon generation

- Impulse mechanisms
  - Direct optical (molecules and qdots)
- Lattice heating (metal nanoparticles, bulk)
- Piezoelectric screening (q-wells)
Evidence for impulsive piezo effects

• Several possible mechanisms for coherent phonon generation

• Amplitude directly related to surface passivation

• Surface passivation argues against all previously known impulses

• Surfaces trap charges on the sub-ps (impulsive) timescale

• Details of trapping kinetics and TA spectra in JCP 2008, PRB 2009
Quantizing extrinsic piezoelectricity

• Excitation yields a distribution of multiexcitons of occupancy $<N>$

• Surface trapping competes with intraband relaxation

• Fraction of surface trapped charges (holes) yields impulsive perturbation via piezo

• Piezo is quantized ($<N>$ is quantized)

• Piezo is extrinsic!
Take home message (so far)

• Exciton selectivity yields **state-resolved** exciton dynamics

• Excitons in quantum dots relax via **multiple pathways**

• State-resolved **exciton-phonon couplings** and **decoherence pathways**

• State-resolved optical pumping yields **universal gain**

• Excited states of multi-excitons: towards an **artificial periodic table**

• Coupled nanostructures: **charge transport**
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Publications

1. “State-to-state exciton dynamics in semiconductor quantum dots”  
2. “Light harvesting and carrier transport in core/barrier/shell semiconductor nanocrystals”  
3. “Breaking the phonon bottleneck for holes in semiconductor quantum dots”  
4. “Unified picture of electron and hole relaxation pathways in semiconductor quantum dots”  
5. “State-resolved exciton-phonon couplings in CdSe semiconductor quantum dots”  
6. “Size dependent, state-resolved studies of exciton-phonon couplings in strongly confined semiconductor quantum dots”  
7. “State-resolved processes in semiconductor quantum dots: biexciton interactions and surface trapping dynamics”  
8. “Single dot spectroscopy of two-color quantum dot/quantum shell nanostructures”  
9. “Gain tailoring in semiconductor quantum dots via state-resolved optical pumping”  
10. “Experimental tests of effective mass vs. atomistic pictures of quantum dot electronic structure”  
11. “Direct observation of the structure of band-edge biexcitons in quantum dots”  