Quantum Dots Energy Levels

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Introduction

- Quantum dots are zero-dimensional semiconducting nano-structures.
- Sizes are of the order of $O((1-10nm)^3)$.
- They exhibit unique optical and electronic properties due to quantum effects.
- Known as "artificial atoms" because their properties can be controlled and changed.

Properties and Applications

- Restricted motion of electrons or holes in 3D leads to Quantum confinement.
- Applications include:
  - Diode lasers
  - Single-electron transistors
  - Sensors
  - Display technologies

Production Methods

- **Epitaxial growth (Stranski–Krastanow mode):**
  - Molecular-Beam Epitaxy (MBE) used.
  - Formation of thin films and small nano-islands.
- **Electrical Gating:**
  - Doped semiconductor layer grown on undoped semiconductor.
  - Formation of quantum dots by applying negative voltage.
  - Nano electrodes (or gates) on top of the structure by electron-beam lithography.
- **Electron Beam Lithography:**
  - Semiconductor scanned with electron beam.
  - Quantum dots isolated using reactive ion etching.

Molecular-Beam Epitaxy (MBE)

- **Process Overview:**
  - substrate is positioned in a vacuum chamber, where several effusion cells with the desired substance and heating coils.
  - Heating coils in effusion cells emit molecular beams towards substrate forming thin films and small nano-islands on the substrates.
  - By controlling the temperature one can control the rate of deposition on the substrate, and thus manipulate the sizes and shpes of QDs.
  - three primary modes: Volmer–Weber, Frank–van der Merwe, Stranski–Krastanov
- **Stranski–Krastanov Mode (Asaro–Tiller–Grinfeld instability):**
  - Initially forms 2D nano-surfaces up to a certain thickness.
  - Transition to 3D isolated islands after a critical height.
- **Quantum Dots Formation:**
  - Buffer undoped layers of GaAs deposited first.
  - Followed by deposition of QDs material (InAs).
  - Capping with undoped semiconductor at tuned temperatures.

MBE

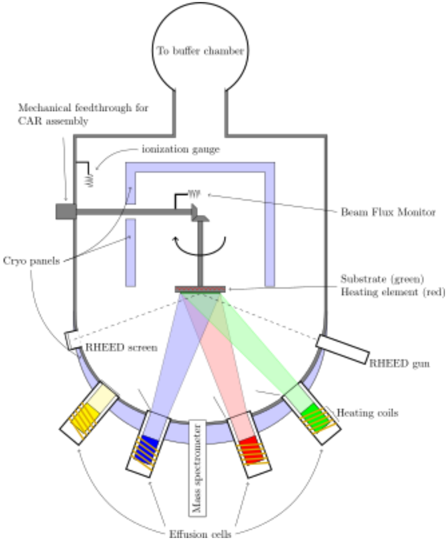


Figure: MBE apparatus
By Vegar Ottesen - Own work https//:commons.wikimedia.org/w/index.php?curid=16957521

Electron Beam Lithography

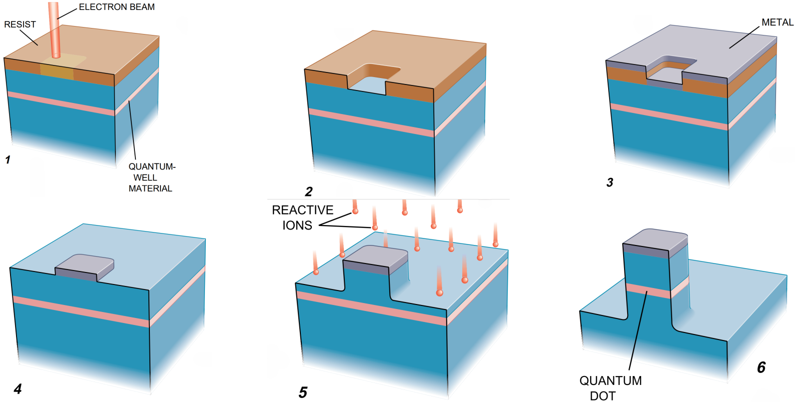
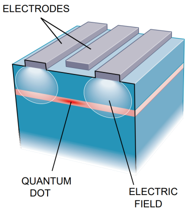


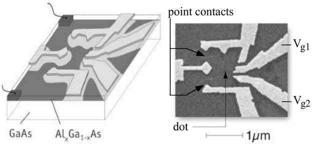
Figure: Building in Zero Dimensions from Quantum Dots by Mark A. Reed

Electric Gating

- Uses MBE (in Frank–van der Merwe mode) to grow the doped semiconducting layer (e.g. AlGaAs) over an undoped substrate (e.g. GaAs).
- Uses EBL to grow nano-electrodes on the substrate.
- By controlling the applied voltage to the nano-electrode, potential barriers form, and the electrons are confined.
- Easier control over size and shape.
- SET.



(a)



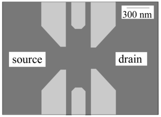
(b)

Figure: (a) from Quantum Dots by Mark A. Reed. (b) SET from Statistics and Parametric Correlations of Coulomb Blockade Peak Fluctuations in Quantum Dots by J. A. Folk(1996)

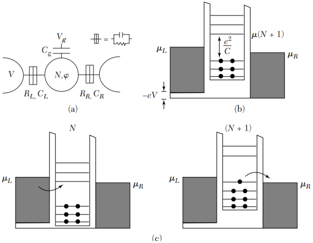
Electric Gating

Single Electron Transistor

- Under certain tunneling conditions, electrons from adjacent 2D electron reservoirs can tunnel through the quantum dot.
- tunneling is blocked by the Coulomb blockade.
- if the energy of the dot decrease and a potential difference is introduced between both reservoirs (call them drain and source) such that $\mu_d < E_{N+1} < \mu_s$ then current will flow from the source to the drain.



(a)



(b)

Figure: (a) SET from Statistics and Parametric Correlations of Coulomb Blockade Peak Fluctuations in Quantum Dots by J. A. Folk(1996). (b) Coulomb Blockade (Kittel)

Energy Calculation

Simple QW model

- Quantum dots are usually modeled as 3D quantum wells.
- Spherical Finite and infinite wells have shown high accuracy for measuring the transition energies of spherical quantum dots with errors smaller than 3% in the energy value.

$$E_{n,l} = \frac{\hbar^2 \beta^2 n, l^2}{2 m_{\text{eff}} R^2}$$

- this model shows that Energy levels confinement goes down as $\Delta E \propto 1/R^2$

Energy Calculation

Simple QW model

- Quantum dots are not restricted to spherical shapes. Based on the growth process different more complicated shapes are possible.
- Here I will tackle a case of InAs Quantum dot. Where the Stranki-Krastanov results in a conic shape of the dot.
- The dot is assumed to have a perfect conic shape with a small elevation angle of $\pi/15$.
- The transition energies were solved for holes and electrons. by numerically solving the Schrodinger Equation.
- The parameters were obtained from J.Y. Marzin paper.

Numerical Solution

- Discretization of space, and vectorization of the $2D$ $(N \times M)$ grid to NM-dimensional vector.

$(M-1)N$	.	.	.	.	$(M-1)N + i$	.	.	.	$MN-1$
.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.
jN	.	.	.	.	$jN+i$	.	.	.	$(j+1)N$
.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.
N	$N+1$	$N+2$	.	.	$N+i$	.	.	.	$2N-1$
0	1	2	.	.	i	.	.	.	$N-1$

0	1	...	N	$N+1$	...	$jN+i$	...	...	$MN-1$

Numerical Solution

- Due to Azimuthal symmetry we can write the Hamiltonian as:

$$\mathcal{H}(r,z) = -\frac{\hbar^2}{2}\left(\frac{1}{m}\frac{\partial^2}{\partial z^2} + \frac{1}{m}\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\right) - \frac{n^2}{mr^2} + \mathrm{V}(r,z) \quad (1)$$

- redefine $r = r/R$ and $z = z/Z$ so that r, z are dimensionless where R, Z are big enough to be considered infinite (in this scenario, I chose $Z = R = 40nm$)
- Under these transformations, the Hamiltonian can be written in a matrix form as:

$$\begin{aligned} H_k^i = &\frac{-\hbar^2}{2mR^2}\left(\frac{\delta_k^{i-1} - 2\delta_k^i + \delta_k^{i+1}}{\Delta r^2} + \frac{\delta_k^{i-1} - \delta_k^{i+1}}{2r_i\Delta r} - \frac{n^2}{r_i^2}\delta_k^i\right) \\ &+ \frac{-\hbar^2}{2mZ^2}\left(\frac{\delta_k^{i-N} - 2\delta_k^i + \delta_k^{i+N}}{\Delta z^2}\right) + V^i\delta_k^i \end{aligned} \quad (2)$$

Numerical Solution

- The discretization length I took was $N = M = 128$, $NM = 16384$.
- The aforementioned Hamiltonian is a sparse matrix, therefore I used **scipy.sparse** python library to solve for its eigenvalues.
- Boundary Conditions:
  - $\psi(r \to \infty, z, \phi) = \psi(r, z \to \pm\infty, 0) = 0$
  - $\frac{\partial}{\partial r}\psi(r, z, \phi)\Big|_{r\to 0} = 0$
  - The first condition is satisfied be default with the definition of the matrix
  - The second condition is achieved by defining modifying the derivative matrices as follows:

$$\partial_r^2[0,0]_{(r=0)} = -1 \tag{3}$$

$$\partial_r[0,1] = 0 \tag{4}$$

Result

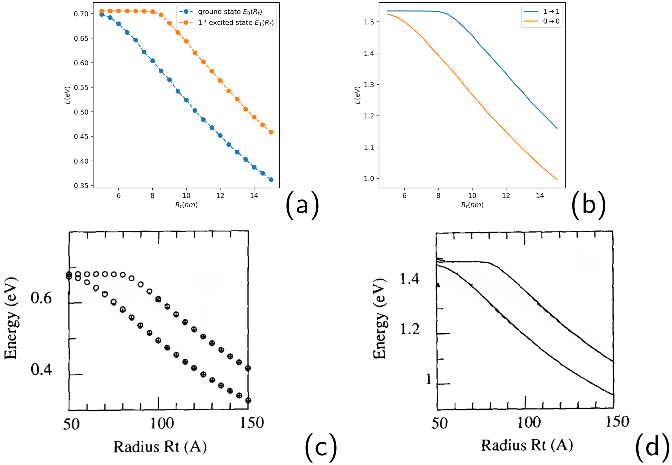


Figure: Results for solving for the state energies and transition energies in InAs/GaAs QD. The paper's results are included for comparison, the paper reported that the average transition energy of InAs/GaAs QD at $R = 13.5nm$ is $1.07eV$ while it was found using my code to be 1.0677 eV

Energy Dependence in Effective Mass

- Correction by introducing energy dependence in effective mass term.
- Iterative non-linear scheme used for solving.
- Effective mass recalculated with updated energy values until convergence.

$$\frac{1}{m(E)} \propto \left(\frac{2}{E + E_g - V} + \frac{1}{E + E_g + \Delta - V} \right)$$

$$H(E) = -\frac{P^2}{2m(E)} + V(r,z)$$

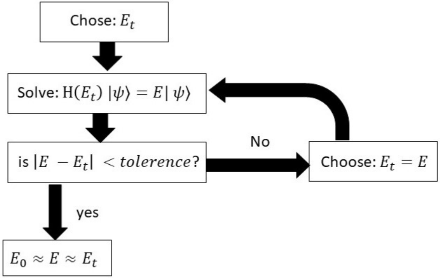


Figure: Iterative scheme for solving non-linear eigenvalue problems

Density Functional Theory (DFT)

limitations of Simple models

- As the size of the dot gets smaller surface area to volume ratio increase.
- As a result, surface defects (legends, additional atoms, or missing atoms) will have high impact on the energy levels.
- smooth surfaces approximation are no longer be valid. And Incorporating such changes will require finer discretizations.
- More suffocated methods and approximations can provide a better understanding of the behaviour and solution. One of these methods is the DFT.
- Useful for studying the Coulomb blockade related effects, such as the peak spacing in the conductance through the dot

Kohn-Sham Hamiltonian and Energy Functional

Energy Functional

$$\hat{H}^\sigma = -\frac{1}{2}\nabla^2 + V^\sigma_{\text{ext}}(\mathbf{r}) + V^\sigma_{\text{H}}(\mathbf{r}) + V^\sigma_{\text{XC}}(\mathbf{r})$$

- **Spin**: $\sigma \in \{\alpha, \beta\}$
- **Exchange-Correlation Potential**: V_{XC} - purely quantum term from fermions' anti-symmetric behavior.
- **Hartree Potential**: $E \int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r}$

$$E[n^\alpha(\mathbf{r}), n^\beta(\mathbf{r})] = T[n^\alpha(\mathbf{r}), n^\beta(\mathbf{r})] + \int_{\mathbf{r}} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) \, d\mathbf{r} + \int_{\mathbf{r}} \int_{\mathbf{r}'} \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' + E_{\text{XC}}[n^\alpha(\mathbf{r}), n^\beta(\mathbf{r})]$$

- **Density of Spin Orbitals**: $n^\sigma(\mathbf{r}) = \sum_i^{N^\alpha} |\psi_i^\sigma(\mathbf{r})|^2$

Kinetic Energy and Iterative Scheme

Exchange-Correlation Energy Approximations

$$T[n^\alpha(\mathbf{r}), n^\beta(\mathbf{r})] = -\frac{1}{2}\sum_{i,\sigma}\langle\psi_i^\sigma|\nabla^2|\psi_i^\sigma\rangle$$

- **Single Electron States**: $\{\psi_i^\sigma(\mathbf{r})\}$

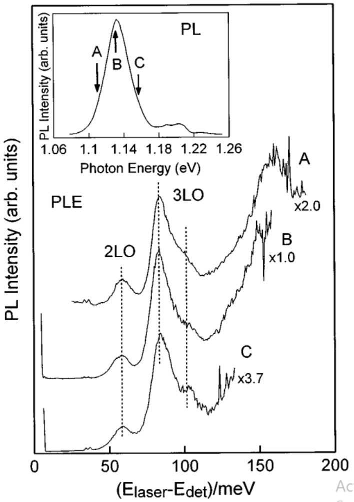
$$\hat{H}^\sigma|\psi_i^\sigma(\mathbf{r})\rangle = \epsilon_i^\sigma|\psi_i^\sigma(\mathbf{r})\rangle$$

- **Iterative Scheme**:
  - Assume trial functions $\{\psi_i^\sigma(\mathbf{r})\}$
  - Find $\{n^\alpha(\mathbf{r}), n^\beta(\mathbf{r})\}$
  - Calculate $E[n^\alpha(\mathbf{r}), n^\beta(\mathbf{r})]$
  - Check for convergence based on energy values
  - Solve for $\{\psi_i'^\sigma(\mathbf{r})\}$

Drawbacks: No exact method to calculate E_{XC}, therefore Spin-polarized uniform electron gas is used to approximate E_{XC} (local-spin-density approximation (**LSDA**)).

Experimental Results: PL and PLE

- Electromagnetic radiation emission from any form of matter after the absorption of photons. In PL the absorbed photon is applied and the emitted photons are observed, in case of PLE the opposite is being done.
- Sensitive to phonon emissions, as excited electron may not relax directly to ground state, with relaxation efficiency that depends on energy.
- excited-state energies cannot be determined directly from the spectra.



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CV Analysis of Quantum Dots

- CV test can analyze the energy gap of Quantum dots.
- Hole energy at the top of the valence band and electron energy at the edge of the conduction band are proportional to respective cathodic and anodic peaks in the CVs.
- The voltage difference directly correlates to the dot's band gap.
- As the Q-dot size decreases, the cathodic and anodic peaks shift to higher energies, increasing the gap energy.

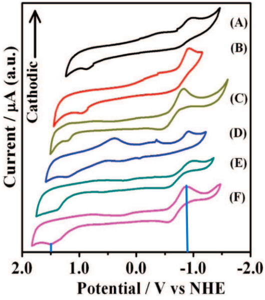


Figure: CV Spectrum for Different QD Sizes

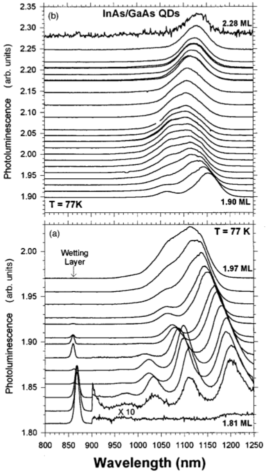
Energy tuning

Growth Temperature

- The shell structure can be tuned by adjusting the substrate temperature during the formation of the QDs.
- Larger QDs with smaller band gap energies are obtained at higher growth temperatures.
- The intermixing between QDs is reduced when the growth temperature is lowered, increasing the uniformity of the QDs.

Energy tuning
QD Density

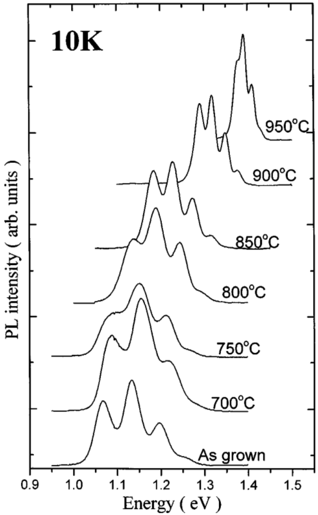
- To obtain uniform QDs with well-defined energy levels, the QD density must be kept low.
- Stranski-Krastanow growth mode for InAs/GaAs occurs at about 1.6 ML (And higher).
- For denser coverages, wave function states from neighboring dots starts to overlap.



Energy tuning

Thermal Annealing

- Tuning of the QD interband transition energy can be achieved using rapid thermal annealing (RTA).
- RTA has the effects of blue-shift, narrowing PL line-width, and decreasing intersublevel spacing energies as the annealing temperature increases.
- TEM images show that the QD size does not change significantly with RTA.
- Changes in energy levels are attributed to the increase of Ga concentration in QDs due to the inter-diffusion of In–Ga atoms at the interface between the QD and the GaAs barrier.



Graphene Quantum Dots

- As expected, the energy gap decreases as the size of the GQD increases, however, with some types of GQDs, the proportionality is $\Delta E \propto 1/L$ which is different from the conventional case, and marks the possibility to produce bigger quantum dots where confinement is still possible.
- Whether GCDs have been experimentally made is still a matter of dispute, some papers claim that they have successfully made GCDs at laboratories, others argue that are these are rather fluorescent organic dots