Carbon nanotubes in a nutshell

What is a carbon nanotube?
Start by considering graphite.

$sp^2$ bonded carbon.
Each atom connected to 3 neighbors w/ 120 degree bond angles.
Hybridized $\pi$ bonding across whole sheet.

Graphite band structure

Conduction band and valence band meet at 6 equivalent points in the Brillouin zone.
Result: graphite is a semimetal.
Cut the graphite sheet and reattach.

Label tubes by ordered pairs \((n,m)\) that describe reattachment.

Band structure depends crucially on reattachment.

Result: tubes are metallic if \(n-m\) is divisible by 3.

Otherwise tubes are semiconducting.

**Resulting band structure**

- Periodic BC around tube circumference change bands from graphite.
- 1d subbands, each with a van Hove singularity.
- Band gap in semiconducting tubes \(\sim 1/d\).
Types of tubes

- Tubes may be “armchair”, “zigzag”, or chiral.
- Large number of possible tube diameters.
- Can also have multiwalled nanotubes:

![Image of SWNT, MWNT, and open MWNT](image) 5 nm

History

- Discovered 1991 by Iijima et al. in Japan - byproduct of carbon arc furnace synthesis of C\(_{60}\).
- Yield of tubes, particularly SWNT, much enhanced when tiny amount of transition metal (Ni, Fe, Co) added to furnace - 1992.
- Field emission from nanotubes ~ 1995.
- HiPCO, CVD methods ~ 1998
How are nanotubes made?

- Carbon arc discharge

![Diagram of carbon arc discharge process]

Laser ablation

![Diagram of laser ablation process]

image from Ecole Polytechnique in Lausanne

image from Yakobson/Smalley Am. Sci. article
HiPCO

- Flow high pressure carbon monoxide past catalyst particles at high temperatures.
- Industrially scaleable!
- Can now produce largely single-walled nanotubes in kilogram quantities.
- Pilot reactor is down the hall!

CVD - chemical vapor deposition

![Image](image from Ecole Polytechnique in Lausanne)

Advantage: can pattern catalyst particles on substrate.
Patterned growth

Electric field during growth aligns growing tubes.

Directed growth
Growth mechanism:

- Still poorly understood.
- Role of catalyst shape and kinetics at surface of catalyst are active objects of study.
- Why does growth terminate?
- Is it possible to somehow extend preexisting tubes?
- Is it possible to control the chirality of the tubes via the catalyst or processing conditions?

Mechanical properties

Bulk solids deform and fail due to motion of dislocations (imperfections) and sliding of grain boundaries.

Perfect nanotubes lack these mechanisms - should be very strong!

Can infer elastic modulus from clamped vibration amplitude due to thermal agitation.

\[ \sigma = Y \frac{\delta \ell}{\ell} \]  
(equivalent to \( f = kx \))

Result: Young’s modulus = 1.2 TPa

For comparison, steel \( Y = 0.19 \) TPa

Nanotubes as AFM tips

Can now attach individual SWNT to cantilevers for use as AFM tips. Extremely tiny radius of curvature allows ~ 1 nm lateral resolution - the best there is.

Tubes are extremely robust. Buckle reversibly rather than failing catastrophically.

How do nanotubes break?

Nucleation of defects - pentagon/heptagon pairs. These pairs migrate and leave behind a band of smaller-diameter tube. Enhanced stress causes more defect nucleation.
Electrical properties

Metallic tubes are impressive conductors.

- Calculations say 2 conducting channels in a metallic tube. Expected conductance = $4 e^2/h$.
- Conductance appears to be ballistic over micron scales, even at room temperature(!), though some issues still unresolved.
- Ballistic = no dissipation in the tube itself = very high current densities are possible.

Nanotube single electron transistors

First attempts (1997) at electrical transport measurements in nanotube transistors showed Coulomb blockade physics.

High resistance contacts + bending issues at contacts.
Nanotube FETs

With low resistance contacts, FETs made from semiconducting tubes can be quite high quality. Carriers in early tubeFETs seemed to be holes.

Ambipolar FETs

- Most nanotube FETs are $p$-type, apparently because oxygen adsorption at Au contacts pins the Fermi level near the valence band.

- With great care + TiC contacts, it's possible to get ambipolar behavior - electrons or holes, depending on sign of gate voltage.
Ballistic FETs

Very recently, nanotube FETs with palladium contacts have been shown to exhibit ballistic transport.

Ballistic behavior inferred from conductance at low $T$ and interference effects.

Still a bit mysterious:

- Why no barrier for Pd ($\Phi \sim 5.1$ eV), but definitely a barrier for Au ($\Phi \sim 5.1$ eV) and Pt ($\Phi \sim 5.7$ eV)?
- What limits the conductance at higher temperatures?


Single-molecule inverters

By carefully controlling doping, single SWNT molecules have been used to construct logic devices like this inverter.

Two transistors of opposite polarity, all in one molecule.
Nanotubes for field emission

- Emission of electrons from metals is enhanced at large electric fields.
- Electric fields near a tip with radius of curvature $r$ go like $1/r$ for a given voltage.
- Nanotubes are incredibly sharp tips ($r < \sim 1$ nm), so they can emit efficiently at low voltages (a few V).

Samsung, SWNT protruding from a metal cathode.

Field emission displays

Emitted electrons can hit phosphor-coated transparent ground plane (ITO).

FEDs tend to be very bright and very fast compared to LCDs.

Field emission displays are the most realistic short-term electronic application of nanotubes.
Complications for applications of nanotubes in technology:

- Separating tubes from each other.
- Effects of impurities, + adsorption.
- Distinguishing tube types.
- Functionalization.
- Solvation for study / applications.

Nanotube ropes

Nanotubes like to stick together to form “ropes” because of the van der Waals interaction between the tube sidewalls.

That interaction energy scales linearly with tube length, and can be on the order of ~ eV per micron (!).

A major research problem is, what is the efficient way to get individual tubes?

Common separation method: sonication.
Nanotubes for gas storage

Nanotubes have very high specific surface areas.
Hydrogen has a substantial chemisorption energy onto nanotubes - greater than room temperature!
Controversial results show that 1 g of SWNT material could adsorb up to ~ 0.1 g of hydrogen. Effective packing density is vastly higher than storing hydrogen as a high pressure gas.
Possible applications for hydrogen-powered cars, fuel cells, etc.
Adsorption detectable through electrical properties: sensors

Separating chiralities

Known fabrication methods all produce a variety of tube chiralities.
Separating tubes by type is extremely difficult.
One very recent development for assessing distribution of tube types: spectroscopy of individual, encapsulated tubes.

Fix excitation on absorption peak, and look for emission peaks.
Van Hove singularities in d.o.s.

Separating chiralities


Separating chiralities

Chirality-specific chemistry

Now that we can identify the types of tubes present, it would be great to be able to chemically manipulate particular types:

Selective chemistry can now be performed that reversibly alters the properties of just metallic tubes!


Functionalization

Upside to chemical stability: do-able to separate tubes from other things like amorphous carbon.

Downside: functionalizing tubes for strong bonding to other materials is very challenging chemistry.

One materials example: tube / epoxy composites tend to fail under stress because epoxy does not transfer mechanical load to the tubes effectively.
Conclusions

- Carbon nanotubes are remarkable materials.
- Molecular structure directly related to impressive electrical, mechanical, physical, and chemical properties.
- Most promising short-term technological uses: field emission displays, light / strong materials, hydrogen storage.
- Outstanding challenges: bulk fabrication, selecting tube types, mastering chemistry of these and related compounds, “the wiring problem”.
- Potentially revolutionary, especially considering the material was unknown 15 years ago.
The story so far:

- Arrangement of atoms + their chemical properties give rise to bands of allowed energies for single-particle states in solids.
- Filling up single-particle states tells us about conducting properties of material.
- Doping can shift Fermi level (chemical potential) around.
- Junctions between materials result in charge transfer and band bending - local variations in conducting properties, carrier densities, etc.

Today: quantum confinement

Definition:

Quantum confinement effects are deviations in the electronic properties (energy levels, wavefunctions) from those in a bulk system due to potential variations (including local variations in band structure and interfaces).

Examples:

1d: Bound state levels in quantum wells
- subband spacings in 2deg
2d: Wavefunctions + levels in 2deg quantum dots
3d: excitons in semiconductor nanocrystals
    (quantum dots)
Assumptions:

- Bloch waves are a reasonable guess for trial wavefunctions.
- $x$, $y$, $z$ components may be separated nicely.
- Interface potential doesn’t mix valence and conduction bands.
- Start w/ varying band structure in the $z$ direction:

Finite square well - qualitative

What do we expect to happen to energy spectrum?

- Energies in FSW lower than ISW - wavefunction can spread out more.
- Bound single-particle levels should get close together near top of well, rather than spreading out.
Finite square well for electrons

\[ \Psi = \sum_{A,B} \exp(i k \cdot r) u_{\chi_{A,B}}(r) \chi_n(z) \]

wavevector in x-y plane

Envelope function

Within approximations, envelope function obeys:

\[ \left( -\frac{\hbar^2}{2m(z)} \frac{\partial^2}{\partial z^2} + E_n(z) \right) \chi_n(z) = E_n(z) \chi_n(z) \]

\[ \chi_n(z) \left( \frac{1}{m(z)} \frac{\partial \chi_n}{\partial z} \right) \text{ must be continuous.} \]

Finite square well solution

\[ V = V_0 \]

\[ V = 0 \]

where

\[ E_n = \frac{\hbar^2 k_n^2}{2m_A} - V_0 = -\frac{\hbar^2 K_n^2}{2m_B} \] for \(-V_0 < \varepsilon < 0\)
Finite square well boundary conditions

Applying continuity conditions gives:

\[
\left( \frac{k}{m^A} \right) \tan \left( \frac{kL}{2} \right) = \frac{K}{m^B},
\]

\[
\left( \frac{k}{m^A} \right) \cot \left( \frac{kL}{2} \right) = -\frac{K}{m^B}
\]

If the effective masses aren’t very different, this becomes

\[
\cos \left( \frac{kL}{2} \right) = \frac{k}{k_0}, \quad \text{for} \quad \tan \left( \frac{kL}{2} \right) > 0,
\]

\[
\sin \left( \frac{kL}{2} \right) = \frac{k}{k_0}, \quad \text{for} \quad \tan \left( \frac{kL}{2} \right) < 0
\]

where \( k_0 = \frac{2m^*V_0}{\hbar^2} \)

Graphical solution

![Graphical solution](image)

Fig. 7. Graphical solution for Eqs. (7) and (8). Solutions are located at the intersections of the straight line with slope \( k_0^1 \) with curves \( y = \cos \left( \frac{kL}{2} \right) \) (with \( \tan \left( \frac{kL}{2} \right) > 0 \); --- even wave functions) or \( y = \tan \left( \frac{kL}{2} \right) \) (with \( \tan \left( \frac{kL}{2} \right) < 0 \); --- odd solutions).

Number of bound states = \[1 + \text{Int} \left( \frac{2m^A V_0 L^2}{\pi^2 \hbar^2} \right)^{1/2} \]
Holes in bulk - qualitative

Holes in GaAs are more complicated than electrons because of valence band degeneracy at $|k| = 0$.

Usual treatment:

- Spin is no longer a good quantum number (!).
- Total angular momentum $\mathbf{J}$ still is, as is $J_z$.
- Four-fold degeneracy at $k = 0$ modeled as $J = \frac{3}{2}$.

Physically, holes exchange angular momentum with the lattice, through spin-orbit coupling.

Holes in bulk - qualitative

Luttinger Hamiltonian:

$$H = \frac{\hbar^2}{2m_0} \left[ (\gamma_1 + \frac{5}{2}\gamma_2)k^2 - 2\gamma_2(k_+^2J_z^2 + k_-^2J_z^2 + k_+^2J_z^2) - 4\gamma_3\{k_+ \cdot k_+, \{J_+ \cdot J_z + \cdots\}\} \right]$$

The $\gamma$s are the Luttinger parameters.

If $z$ is the [100] direction,

$$E = \frac{\hbar^2k_z^2}{2m_0} (\gamma_1 - 2\gamma_2) \quad J_z = \pm \frac{3}{2}$$

$$E = \frac{\hbar^2k_z^2}{2m_0} (\gamma_1 + 2\gamma_2) \quad J_z = \pm \frac{1}{2}$$

The angular momentum coupling is related to the heavy and light hole effective masses.
Holes confined in wells

To meet boundary conditions at the well interfaces, must consider linear combinations (mixing!) of $J_z = 3/2$ and $J_z = 1/2$ states.

Results:

- Effective masses of holes in quantum wells can be very different from those in bulk!
- Angular momentum properties of holes in wells can also be very different from bulk.

Triangular wells - infinite

Triangular potential wells are quite common in real devices.

Examples: Si MOSFETs; single-interface GaAs/Al$_{0.3}$Ga$_{0.7}$As heterojunctions.

Idealization:
Bound states

\[
\begin{pmatrix}
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + eFz
\end{pmatrix} \chi_n(z) = \varepsilon_n(z) \chi_n(z)
\]

**electric field**

**Boundary conditions:**
- \( \chi_n(0) = 0 \)
- \( \chi_n(z \to \infty) = 0 \)

**Solution:**
- \( \chi_n(z) = A_i \left( \sqrt[3]{\frac{2m}{\hbar^2 e^2 F^2}} \right)^{1/3} \left( eFz - \varepsilon_n \right) \)

**Airy function**

Eigenvalues set by requiring argument to correspond to a zero of Airy function when \( z = 0 \):

\[
\varepsilon_n = \left( \frac{e^2 F^2 \hbar^2}{2m} \right)^{1/3} \quad a_n = \left( \frac{\hbar^2}{2m} \right)^{1/3} \left( \frac{3\pi eF}{2} \left( n + \frac{3}{4} \right) \right)^{2/3}
\]

\( n = 0, 1, \ldots \)

---

**Real triangular wells: modulation doping**

\( \text{Al}_{0.3}\text{Ga}_{0.7}\text{As} \quad \text{GaAs} \)

- Invented by Horst Stormer and colleagues, 1977.
- Result: 2d electron gas at interface, with donor ions “far away” in AlGaAs barrier.
- Some penetration of wavefunctions into barrier material.
Real triangular wells: modulation doping

Assume $n_{2d}$ electrons per unit area are transferred across boundary.
To first order, electric field in well is constant:

$$F = \frac{n_{2d}e}{\varepsilon_0 e} \quad \text{from Gauss’ law.}$$

Infinite trian. well: $E_1(n_{2d}) \approx \left( \frac{\hbar^2}{2m_e} \right)^{1/3} \left( \frac{9\pi e^2 n_{2d}}{8\varepsilon_0 e} \right)^{2/3}$

Potential well + energy of bound states depend on number of electrons transferred. Must solve self-consistently.

Use 2d d.o.s. to find Fermi level on GaAs side:

$$E = E_1 + \frac{n_{2d}}{V_{2d}} = E_1 + \frac{\pi\hbar^2}{m_e} n_{2d}$$

Real triangular wells: modulation doping

That must = the Fermi energy on the AlGaAs side.

Assume depletion width $W$.
Voltage built up across interface:

$$V = -\int_0^W Fdz = \int_0^W eN_d z dz = \frac{eN_d W^2}{2\epsilon_i \varepsilon_0}$$

If $N_d = 3$ density of donors, $n_{2d} = N_d W$.

So, given the conduction band offset $\Delta E_c$, and the donor binding energy $\epsilon_d$, we find:

$$\Delta E_c - \frac{en_{2d}^2}{2\epsilon_i \varepsilon N_D} - \epsilon_d = E_1(n_{2d}) + \frac{\pi\hbar^2}{m_e} n_{2d}$$

Implicit equation for $n_{2d}, \ldots$
Modulation doping complications

- Donor levels in $\text{Al}_{x}\text{Ga}_{1-x}\text{As}$ depend on $x$ - are typically ~ 10 meV for $x \sim 0.2-0.3$.
- Not all Si donors are electrically active.
- Better device properties at low $T$ after exposure to light.

Excitons

- *Bound* electron-hole pairs. Worry about direct gap case.
- Common excitations in semiconductors, especially produced optically.
- Can decay optically also: luminescence
- Because of hole constituent, can be very strongly affected by local changes in band structure.
- Natural basis are exciton states:

$$\Phi(K, r) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp(iK \cdot \mathbf{R}) \phi(\mathbf{R}, \mathbf{R} + r)$$

- exciton wavevector
- relative coordinate
- exciton wavefunction
- hole coordinate
Excitons in bulk

Define reduced mass: \[ \mu = \frac{m_e m_h}{m_e + m_h} \]

Total mass: \[ M = m_e + m_h \]

Exciton energy: \[ E_{nk} = E_g + \frac{\hbar^2 K^2}{2M} - \frac{1}{n^2} \text{Ry}_* \]

Binding energy: \[ \text{Ry}_* = \frac{1}{(4\pi\epsilon_0\epsilon)^2} \frac{\mu e^4}{2\hbar^2} = \text{Ry} \times \frac{\mu}{\epsilon^2 m_0} \]

Bohr radius: \[ a_{\mu} = \frac{4\pi\epsilon_0\epsilon\hbar^2}{\mu e^2} \]

Confined excitons

Plugging in numbers for GaAs, we again find that the effective Bohr radius \( \sim 10 \text{ nm} \).

What happens in a quantum well 5 nm thick?

In the limit that \( d << a_{\mu} \), one gets the 2d hydrogenic result:

\[ E_{2d-\text{bind}} (n) = \text{Ry}_* \frac{1}{\left( n - \frac{1}{2} \right)^2} \]

In this as on previous slide, \( n \) is exciton principle quantum number.

Excitons can have usual values of \( l, m \).
Confined excitons

Assuming GaAs, square quantum well.

Note exciton binding energies increase as well size shrinks.

This 1d confinement result is true for more constrained systems, too.

Optical properties of confined systems

Confinement’s effects on excitonic levels apparent in optical properties of nanoscale semiconductor systems.

CdSe nanocrystal

Vials of various nanoscale CdSe crystals in solution, fluorescing after optical excitation.

Images from Quantum Dot Corp.
To summarize:

- Can solve for \( z \) envelope function for Bloch electrons in quantum wells - looks much like usual Schr. Eqn.
- Finite number of bound states for finite square wells.
- Holes act differently than electrons - spin-orbit complications, effective masses that can vary under confinement.
- Modulation doping can produce triangular quantum wells: two-dimensional electron gas.
- Excitons, bound e-h pairs, can show profound confinement effects, detectable through optical properties.

Next time:

- From coupled quantum wells to superlattices.
- Intro to quantum dots
The story so far:

- Can use semiconductor structures to confine “free” carriers (electrons and holes).
- Can get away with writing Schroedinger-like equation for Bloch envelope function to understand, e.g., $z$-confinement and $z$-subband energies in quantum wells.
- Excitons, bound e-h pairs, can show profound confinement effects, detectable through optical properties.
- Again, energy scales are set by boundary conditions on (envelope) wavefunctions at interfaces.

Double wells

No reason one cannot have double-well structures:

```
E_c
B A B A B

E_v
```

- With MBE growth, can control well thicknesses and spacings at atomic scale.
- Can place wells close enough to allow controlled overlap of bound state wavefunctions.
Coupled wells

Consider just electrons in conduction band:

Effective Schroedinger:

\[
\left( \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + V_1(z) + V_2(z) \right) \psi(z) = \varepsilon \psi(z)
\]

Assume wavefunction is l.c. of isolated well states:

\[
\psi(z) = a_1 \psi_1(z) + a_2 \psi_2(z)
\]

Coupled wells

where the well states satisfy

\[
\left( \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + V_1(z) \right) \psi_1(z) = E_1 \psi_1(z)
\]

\[
\left( \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + V_2(z) \right) \psi_2(z) = E_2 \psi_2(z)
\]

Assumes identical isolated wells.

Overlap matrix element =

\[
V_{12} = \langle \psi_1(z) | H | \psi_2(z) \rangle = \langle \psi_1(z) | \psi_2(z) | \psi_2(z) \rangle = \langle \psi_2(z) | \psi_1(z) | \psi_1(z) \rangle
\]

Define \( V_0 = \langle \psi_1(z) | \psi_2(z) | \psi_2(z) \rangle = \langle \psi_2(z) | \psi_1(z) | \psi_1(z) \rangle \)

Resulting Schr. Eqn.:

\[
\begin{pmatrix}
E_1 + V_0 - \varepsilon \\
V_{12}^* \\
V_{12}
\end{pmatrix}
\begin{bmatrix}
a_1 \\
a_2
\end{bmatrix}
= \begin{bmatrix}
0 \\
0
\end{bmatrix}
\]
Resulting states:

Energy eigenvalues are $\varepsilon = E_1 + V_0 + |V_{12}|$

No big surprise: bonding and antibonding states in $z$, while still “free” in $x$ and $y$.

One could just as easily imagine making a real-life Kronig-Penney system of wells.

Such a system is called a superlattice:

Resulting bands of well states are called “minibands”.

Precise control of miniband structure is possible.

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Superlattices

Start with a regular superlattice of identical wells.

Same “tight-binding” / molecular orbital theory approach works well here.

$S$ equivalent to alpha,

$T$ equivalent to beta,

$q$ runs from $1/Nd$ to $(N-1)/Nd$.

Result is a miniband.
Minibands and “Band Gap Engineering”

Density of states for simple superlattice in tight-binding approx.: 

\[ \nu(\varepsilon) = N \frac{m_2}{\pi \hbar^2} \arccos \left( \frac{\varepsilon - E_i - S_i^*}{2T_i} \right) \]

By playing with superlattice, can tune miniband structure.

Quantum cascade lasers

Why would you want to tune miniband structure?
Engineering of optical properties!
0d structures: quantum dots

• What happens when we confine electrons in the x and y plane as well as the z direction?
  
  When confinement is \( \sim \) Fermi wavelength of carriers, will see discrete single-particle states.

• How do we make such structures?
  
  Physical or electrostatic confinement, often starting from a 2deg confined in a quantum well or single interface.

• Why are they interesting?
  
  Controlled environment for studying fundamental many-body physics.
  Possible utility for future technologies (quantum computers? Charge sensors?)

Examples of quantum dots

- CdSe nanocrystal
- Physically confined GaAs 2deg
- Electrostatically confined GaAs 2deg
- CdSe nanocrystal

Image from Kouwenhoven/Marcus
Quantum dots - artificial atoms

Just as $z$-confinement from band structure leads to effective Schrödinger Eqn. for Bloch envelope function in $z$-direction, lateral confinement does same in transverse directions.

Assume some form for confining potential and solve: result are discrete bound single-particle states and energy spectrum – orbitals.

For confinement with high symmetry, get easy-to-understand spectrum – classical periodic orbits, easily identifiable quantum numbers.

For nonsymmetric b.c., get complicated spectrum – classical chaotic motion.

How are these bound states filled? Aufbau process, with exceptions, just as in real periodic table.

Example: circular dot from 2deg

Common model: 2d harmonic oscillator, natural frequency $\omega$.

Quantum numbers:

- $n =$ principle quantum number
- $l =$ orbital angular momentum in plane
- $s =$ spin $= 1/2$
- $s_z =$ $z$-component of spin

Energy spectrum: $E_{n,l} = (2n+|l|+1)\hbar \omega$

Include magnetic field:

$$E_{n,l} = (2n+|l|+1)\hbar \left(\omega^2 + \frac{1}{4} \omega_c^2\right)^{1/2} - \frac{1}{2} \hbar \omega_c$$

where $\omega_c \equiv \frac{eB}{m*}$ cyclotron frequency
What do wavefunctions and spectrum look like?

- Magnetic field splits states by $l$ value.
- Magnetic field ‘shrinks’ wavefunctions.

Images from Kouwenhoven

How are they probed?

- Optical spectroscopy
- Microwave spectroscopy
- Transport spectroscopy.

Transport spectroscopy relies on moving charges onto and off dot.

We’ll learn more about the details next week. For now, consider the following cartoon:

- Charge can only flow well from source to drain if there is a dot level energetically degenerate with $\mu$ of source and drain.
- Can shift dot levels ($\mu$) by capacitive coupling with gate electrode.
Classical Coulomb Blockade

Spacing between dot states not just spacing between single-particle dot levels!

Coulomb interactions: some charging energy cost to put an additional charge on the dot.

How much? Suppose total dot capacitance = $C$. Charging energy is then $e^2/C$.

No quantum mechanics here – true for metal particles, too. Need barriers, but not insurmountable ones....

Classical Coulomb Blockade

So, total addition energy to drop another charge onto the dot at fixed conditions = $\Delta E + e^2/C$.

Without this much energy available, no current may flow: Coulomb Blockade.

Write total capacitance as: $C = C_s + C_d + C_g$

Dot energy: $U(N) = \frac{1}{2C} \left(e(N - N_0) + C_g V_g \right)^2 + \sum E_{nl}(B)

For a fixed $V_g$ there is a value of $N$ that is closest to the minimum energy.

Assume $V_{sd}$ is small.

If $V_g$ is varied, there is some value for which $U(N)$ and $U(N+1)$ are equal – charge on dot can change.
Classical Coulomb blockade

Result:

(ignoring $E_{nl}$)

Conductance is peaked as a function of gate voltage.

Width of peaks is proportional to $T$.

Classical charging energy $E_c = e^2/C$.

To see Coulomb blockade, need $k_BT << E_c$.

Charging energies

What are some reasonable values for $E_c$?

Suppose source/drain capacitances are small. For a metal nanoparticle (disk) 100 nm in diameter, separated by a 2 nm SiO$_2$ layer ($\varepsilon = 3.9$) from a gate electrode.

$C = 136$ aF. $\Rightarrow E_c = 1.89 \times 10^{-22}$ J $\sim$ 14 K.

Challenging to get $E_c$ values high enough to see Coulomb charging effects at room temperature.
Constant interaction model

Precise interaction effects are more complicated than just a classical charging energy. Consider circular dot.

One simple approximation: if electrons are being added to bound states with the same $n$, the energy differences between subsequent states are uniform for $B=0$.

So, look at peak spacings in gate voltage. Whenever there’s a change in the spacing at zero $B$, we’re seeing a transition from one closed shell to the beginnings of a new shell.

Result: “magic numbers”, just as in atomic shells.

Magic numbers and shell structure
Variations of peak energies with magnetic field

Remember, for nice, round quantum dot,

\[ E_{n,l} = (2n+|l|+1)\hbar\left(\omega^2 + \frac{1}{4}\omega_l^2\right)^{1/2} - \frac{1}{2}\hbar\omega_l. \]

- Orbital angular momentum couples to external magnetic fields.
- Can watch magnetic field dependence of Coulomb blockade peaks as a function of \( V_g \), and confirm which peaks correspond to which states!

Filling the states – what do we expect:

- Two electrons per orbital state \( \rightarrow \) pairs of peaks should correlate.
- Expect to see crossings as \( l \) states trade places energetically.
Does this simple picture work?

Hund’s rule

- Constant interaction picture misses funny business at low fields.
- Hund’s rule shows up here, just as in “real” atoms.
- *Exchange* energy – electronic correlations beyond the simple constant interaction picture.
What about non-symmetric and chaotic dots?

- Can’t analytically solve for energies and wavefunctions.
- Dependence of state energies on magnetic field and dot shape can be extremely complicated.
- General theory is possible to describe statistics of peak spacings, peak heights, field dependences, etc.

Summary:

- By tuning composition, can engineer bound state energies precisely.
- Through superlattices, can create impressive optical devices.
- Confinement in all 3d directions leads to discrete “0d” states – quantum dots.
- Coulomb blockade allows transport spectroscopy of states.
- Simple dots are laboratories for “atomic” physics.
- Complicated dots can actually be understood statistically.
Next time:

- Classical + semiclassical transport.