04: Electronic properties of nanostructures

January 25, 2010
Announcements

- PS1 due next W Feb/3
  - Some material is yet to be covered in lecture
- Mostafa’s office hours Th 4.30-6.30, 1363 GGB
Energy carriers

- **Electron** - subatomic particle carrying a negative charge
  → *interaction between electrons is the main cause of chemical bonding*

- **Photon** - quantum of electromagnetic field and the basic unit of light

- **Phonon** – a quantized mode of vibration in a lattice

- **Exciton** - a “quasiparticle”, a bound state consisting of an electron and a hole
  → *formalism for transporting energy without transporting net charge*
Size effects and confinement

- **Classical size effects**: When the carrier mean free path is comparable to the size of the system → the boundaries become important.

- **Quantum size effects**: When the carrier wavelength is comparable to the size of the system → the waves interfere in a coherent way, causing discretization of allowable energy levels.
  - The density of states is restricted
  - The band structure changes with size of the material
  - Due to aspect ratios, properties of a nanostructure can be highly anisotropic
  - The boundaries are also important in this regime
\[ \Psi = \text{wavefunction (complex function of position and time)} \]

\[ |\Psi|^2 = \text{probability density} \]
Size-dependent color of quantum dots

Frankel, Bawendi.
Absorption and emission

1. Stimulus

2. Emission

3. Hole

4. (1)

Idealized band model for a quantum dot, assuming strong confinement

\[ E_{nl} = E_g + \frac{2\hbar^2}{\mu} \frac{\chi_{nl}^2}{D^2} \]
\[ \mu^{-1} = m_e^{-1} + m_h^{-1} \]
As size increases (confinement decreases), absorption approaches bulk character.

![Absorption Spectra](image)

**Figure 1.** Absorption spectra of a size-series of large CdS nanocrystals ranging from $3.7 \pm 0.4$ nm to $5.2 \pm 0.4$ nm in diameter. The longest wavelength absorption feature occurs at a) $\lambda = 422$, b) 427, c) 432, d) 435, e) 439, f) 444, and g) 448 nm.

*Alivisatos.*
Examples: different semiconductor crystals

![Graph showing the relationship between Qdot diameter (nm) and Emission wavelength (nm) for various semiconductor crystals such as CdS, CdSe, CdTe, CdHgTe/ZnS, CdTe/CdSe, InP, InAs, and PbSe.](image)
Manufacturing: tuning optical properties by synthesis conditions

Fig. 4. Size series for samples prepared using four TOPSe concentrations: 1:1 Se/Cd, 2:1 Se/Cd, 5:1 Se/Cd, and 18:1 Se/Cd. For each TOPSe concentration, the average NC size was controlled by varying the temperature at a fixed flow rate. From bottom to top, the positions of the band-edge absorbance peaks in nm (and average NC radii in nm) are as follows: 510 (1.52), 535 (1.78), 545 (1.90), 551 (1.98), 555 (2.03), 561 (2.10), 569 (2.20), 575 (2.27), 579 (2.32), 585 (2.39), 592 (2.48), 586 (2.40), 597 (2.55), 606 (2.70).
Imaging with quantum dots

- Previous technology = fluorescent proteins
- New technology = semiconductor nanoparticles
  - Narrow emission peaks
  - Size-dependent emission
  - Long lifetime (resists photobleaching, i.e., photochemical degradation)
  - Diverse chemical linkages to surfaces

- Typical emission lifetimes (at $\sim 10^5$ photons/s)
  - Green fluorescent protein = 0.1-1 s
  - Organic dye = 1-10 s
  - CdSe/ZnS quantum dot = $10^5$ s

http://en.wikipedia.org/wiki/Photobleaching
Commerically-available quantum dots

We team with top companies to develop products based on our proprietary quantum dot technology. Our teaming formula can save time and money getting to market, accelerate market penetration, and drive product revenue.

Fast-tracking Quantum Dot Products to Market
Quantum Dots for Product Development

Life Sciences
Quantum dot products overcome many limits of existing fluorescent labels and probes.

Security & Markings
Better security and brand protection through quantum dots.

LEDs / Displays
New LED color application for applications with quantum technologies.

CdSe/ZnS Core-Shell Product Availability

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Add to cart:

490nm
50 mg
Add to Cart

http://www.evidenttech.com
Quantum dot LEDs

Light Emitting Diodes


evidot® LEDs provide new colors to solid state lighting, including tunable white LEDs with full spectrum control and high CRI capability.

http://www.evidenttech.com
Today’s agenda

- Dispersion relations and carrier statistics
- Development of band structure
- Examples:
  - Single electron transistors
  - Electrical properties of CNTs
Today’s readings

Nominal: (on ctools)

- Chen, Section 3.2
- Rogers, Pennathur, and Adams, excerpt on Nanoelectronics, from *Understanding Small Systems*
- Avouris, “Carbon-based electronics”

Extras: (on ctools)

- Sheldon et al., “Enhanced semiconductor nanocrystal conductance via solution grown contacts”
- Ho et al., “Scaling properties in transistors that use aligned arrays of single-walled carbon nanotubes”
More on crystals

- Many transport properties are determined by periodicity of the atomic lattice.
- Atomic arrangement determines allowable energy levels (recall from QM: wave modes) of energy carriers.
- In the literature, information is presented in reciprocal space.

![Diagram of real and reciprocal space with Brillouin zone and Wigner-Seitz unit cell]
Real space vs. reciprocal space lattices in 3D

Figure 3.8 Conventional and primitive unit cells in real and reciprocal unit cells of an fcc lattice (a) in real space, (b) in reciprocal space.
Dispersion relations

- **Dispersion relation:** the relationship between energy and momentum (frequency and wave-vector)

- Light in vacuum: \( \omega = ck \)

- In real materials, dispersion relations for electrons, phonons, photons, etc. are complicated: frequency a more complex function of wavelength

Electrons in a periodic system

The "free" electron

Schroedinger equation:
\[ -\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} - E \Psi = 0 \]

\[ \Psi(x) = A \exp(-ikx) + B \exp(ikx) \]

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

Parabolic dispersion

A periodic potential

U: Potential Energy

a+b
Conductors vs. insulators

Figure 3.7  Distribution of electrons (gray area) in (a) a covalent bonding crystal and (b) a metallic bonding crystal (after Ashcroft and Mermin, 1970).
Electrons in a periodic system

\[ -\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + (U - E) \Psi = 0 \]

\( U(x) = \begin{cases} 
0 & 0 < x \leq a \\
U_0 & -b < x \leq 0 
\end{cases} \)

**Bloch theorem:** \( \Psi[x + (a + b)] = \Psi(x) \exp[i k(a + b)] \)

Figure 3.11 One-dimensional periodic potential model: (a) sketch of atomic potential; (b) Kronig-Penney model.

Chen, chapter 3.
Dispersion relation -> energy gaps

- Wave effects leads to certain energies (frequencies) that are forbidden: band gaps

![Graph showing band gaps with normalized wavevector and energy plots](image-url)

Chen, chapter 3.
Some band diagrams of real materials

Plotted along directions of high symmetry

![Cu](image1)

![Si](image2)

![GaAs](image3)

Chen, chapter 3.
Carrier statistics

- **The occupation function, \( f(E) \):** Expected number of carriers with a given energy
- This is determined by statistical physics and carrier interactions, i.e. Pauli exclusion

- Bosons (Photons, phonons): 
  \[ f(E) = \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1} \]

- Fermions (Electrons, holes): 
  \[ f(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1} \]

- \( \mu \) is called the **chemical potential**. It's where occupancy is \( \frac{1}{2} \). At \( T = 0 \) K, \( \mu \) is called the **Fermi Energy** and is the highest filled energy state.
Carrier statistics

\[ f(E) = \frac{1}{\exp \left( \frac{E-\mu}{k_B T} \right) + 1} \]

The actual number of carriers in a state, per unit volume and energy:

\[ n(E) = f(E) \times \text{DOS} \]
Metal, semiconductor, insulator

A practical semiconductor has $\approx 3$ eV band gap

Fermi energy

![Diagram](image)

- **Conductor**: Occupied conduction band and valence band.
- **Semiconductor**: Conduction band overlaps valence band with a band gap.
- **Insulator**: Conduction band is separated from valence band by a band gap.

(a) $T = 0$ K
Fermi energy
Metal, semiconductor, insulator

Figure 3.16 Explanation of metals, insulators, and semiconductors based on the one-dimensional band structure.

(a) Electrons in metal partially fill a band. The top-most level ($E_f$) is called the Fermi level.

(b) Electrons fill to the top of the band. When the energy gap ($E_g$) is large, no electrons can be excited to the next higher energy band and the material is an electrical insulator.

(c) When the energy gap ($E_g$) is relatively small, some electrons can be thermally excited to the next higher energy band (called the conduction band), leaving the same number of empty states (holes) in the valence band. The material is an intrinsic semiconductor.

(d) Impurities (more commonly called dopants) may have an energy level close to that of the conduction band. Electrons can be excited from the impurities and fall into the conduction band, resulting in more electrons than holes. Such a semiconductor is called an n-type semiconductor and the dopants are called donors.

(e) When the impurity energy levels are close to the valence band, electrons are excited from the valence band into the impurity level, leaving more holes behind. Such semiconductors are called p-type and the impurities are called acceptors.

Still, the mean free path of an electron can be as long as thousands of angstroms, and the number of atoms in a cube on the order of one mean free path is enormous, $\sim 10^6$ to $\sim 10^8$ atoms. It is amazing that an electron can zigzag through these atoms without getting scattered. Because of this behavior, we often treat electrons as a gas and neglect the ions completely, except when considering their occasional scattering effect.

Although the above solution is valid only for one electron, the existence of multiple electrons does not affect the qualitative picture of the energy bands, as long as the Coulomb potential between electrons is small compared to the potentials between electrons and ions. With such a simple picture of the energy bands, we can begin to understand the difference between insulators, metals, and semiconductors.

In the first Brillouin zone, there are $N$ allowable wavevectors for a lattice chain with $N$ lattice points. Because each wavevector represents a wavefunction and each wavefunction can have a maximum of two electrons with different spins, each band can have a maximum of $2N$ electrons for a one-dimensional lattice.

At zero temperature, the filling rule for the electrons is that they always fill the lowest energy level first, as required by thermodynamics. For alkali metals and noble metals that have one valence (free) electron per primitive cell, the band is only half filled since there are only $N$ valence electrons in this case, as shown in figure 3.16(a). The topmost energy level that is filled with electrons at zero kelvin is called the Fermi level. The electron energy and momentum can be changed (almost) continuously within the same band because the separation between successive energy levels is small. Thus, these electrons can flow freely, making the materials good practical semiconductors.

A practical semiconductor has $\approx 3$ eV band gap.
Band formation from atoms

- Simple model for a solid: the one-dimensional solid, which consists of a single, infinitely long line of atoms, each one having one s orbital available for forming molecular orbitals (MOs).

When the chain is extended:

- The range of energies covered by the MOs is spread
- This range of energies is filled in with more and more orbitals
- The width of the range of energies of the MOs is finite, while the number of molecular orbitals is infinite: This is called a band.
Single electron transistor (SET)

**Figure 6.18** A single-electron transistor (SET). As opposed to the semiconductor channel in a field-effect transistor, the SET has an electrically isolated quantum dot located between the source and drain. (a) The SET in "off" mode. The corresponding potential energy diagram shows that it is not energetically favorable for electrons to tunnel from the source to the drain. This is made possible by first applying the proper gate voltage, $V_{G} = V_{Coulomb}$, so that the potential energy of the dot is made low enough to encourage an electron to tunnel through the Coulomb blockade barrier to the quantum dot. Once the electron tunnels through the Coulomb blockade on the other side, the potential energy rises. The electron then tunnels through the Coulomb blockade on the other side to reach the lower potential energy at the drain. With the dot empty, the potential lower again, the process repeats.

Rogers, Pennathur, Adams.
Single electron transistor

**FIGURE 6.19** The electrical behavior of an ideal SET as a function of gate voltage. The number of electrons on the quantum dot is zero until the Coulomb blockade is overcome at $V_{Coulomb}$, at which point electrons tunnel one at a time from the source to the drain via the quantum dot. Because the energy on the dot is quantized, only discrete gate voltages enable the tunneling of electrons and consequent increases in the number of electrons in the dot. The separation between these gate voltages is $e/2C$. This is the voltage necessary to increase the number of electrons on the dot by one. The current-versus-voltage chart at the bottom shows the corresponding spikes in the source-to-drain current through the transistor at discrete gate voltages. Between the spikes, the number of electrons on the dot remains fixed. Typical gate voltages for such a device are a few millivolts; typical source-to-drain currents are in the picoampere range.
CNT lattice and unit cell

“Closing” a CNT: forced periodicity

- Like the 0D quantum well, the geometric constraint of a seamless CNT forces periodicity on the wavefunction in the circumferential direction.

Figure 3.15 The von Karman boundary condition joins the two boundary points in (a) into a periodic loop in (b).
Boundary condition in reciprocal space

\[ k \cdot C = 2\pi p \]

\( p = \) integer
\( k = \) parallel to \( C \)

- A CNT is metallic if the “stripes” perpendicular to the circumferential direction intersect the K-points in reciprocal space
- This is geometrically satisfied by the \( n-m = 3p \) condition and means that the bands intersect to permit conduction, as in graphite
- Band gap is inversely proportional to diameter, so practically CNTs with >3 nm diameter exhibit metallic behavior at room temperature

Ducastelle, Saito.
K-point (reciprocal lattice point)

Allowed states

Metallic nanotube

Semiconducting nanotube
### Periodic Table of Carbon Nanotubes

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- $d_E (eV)$: energy gap
- $d_F (eV)$: Fermi energy
- $T (°C)$: transition temperature

### Parameters

- $a$: length of unit vector
- $a_1$, $a_2$: unit vectors
- $b_1$, $b_2$: reciprocal unit vectors
- $C_b$: circumference of tube
- $d_1$, $d_2$: diameter of tube
- $d_N$: highest common divisor of $(n+m)$

**Notes:**
- The semi-empirical bandgap $E_g$ is calculated according to H. Yonemasa and S. Muramatsu, Phys. Rev. B 52, 2723 (1995) for the semiconducting tubes (no curvature effects) and A. Klein et al., Phys. Rev. B 63, 073408 (2001) for the metallic and semimetallic tubes (includes curvature). All other values are evaluated from the expressions below.

### Expressions

- $a = \sqrt{a_1^2 + a_2^2} = 2.46 \text{ Å} (\text{graphite})$
- $b_1 = (\sqrt{3}/2, 1/2)$, $b_2 = (\sqrt{3}/2, -1/2)$
- $d_N = \text{gcd}(a_1, a_2)$
- $T = t_1 a_1 + t_2 a_2$ for $T$ the translational vector of the 1D unit cell
- $N = (a_1^2 + a_2^2 + a_3^2)/d_N$ for the number of atoms per 1D unit cell

**References:**
- Atomistix, www.atomi.com
Diffusive vs. ballistic transport

**Diffusive transport**

- $I_e << L$
- $R(L) = rL$

**Ballistic transport**

- $L < I_e$
- $R(L) = h/(Ne^2) = R_Q$

(P. Kim, @NT' 06)

(J. Chen, IBM)

SWNT resistance vs. length

SWNT array transistors

- Mixture of metallic and semiconducting SWNTs; contact effects.

Ho et al., Nano Letters (ASAP), 2010.
CNT interconnects (Fujitsu)

- ITRS 2005
- Solutions are NOT known
- CNTs on 300mm wafer

Y. Awano, Fujitsu / many publications
CNT interconnects (Fujitsu)

Y. Awano, Fujitsu / many publications