Introduction to Molecular Electronics

Lecture 1: Basic concepts
“Plastic can indeed, under certain circumstances, be made to behave very like a metal - a discovery for which Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa are to receive the Nobel Prize in Chemistry 2000”.
Why Molecular Electronics?

- Low-cost devices (OLED, RF-ID, chemical sensors etc.)
- Beyond the Moor’s law: more devices per unit area and not only
- Self-assembly: new old way to assemble complicated devices
- Complex (designer) logical functions
- Interacting with living organisms: e.g. linking biological functions and electronic readout
Molecular electronics approach

Electronic devices based on molecules with specific conductance properties (e.g. OLEDs)
Characteristic dimensions are large compared with the size of a molecule
Huge ensemble of molecules is contacted by usually inorganic electrode. Molecules are not individually addressable
Molecular electronics approach

- Single molecular systems aim at individual contact to single molecules or small arrays of perfectly ordered molecules.
- HME: organic molecules are directly connected by inorganic electrodes (and eventually gates).
- MME: molecules are individually connected to each other forming a circuit. Electrodes are only used for data exchange and to supply energy.
Molecular building blocks

Linear elements

- **Conducting wires**: low resistance
- **Insulators**: high resistance, high breakdown voltage

Non-linear element

- **Rectifier** (diode): high forward/backward current ratio
- Switches: high on/off resistance ratio, reliable switching, low leakage in off position
- **Memory**: long storage time, low loss
- **Amplifier**: high gain

Auxiliary elements:

- **Anchoring groups**
Main quantum transport phenomena
Electron in a box

• Electron is characterized by its wavefunction

\[ \psi_k(r, t) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k} \cdot \mathbf{r} - iE(k)t / \hbar) \]

• Let’s consider a box:
  – Solve Schrodinger equation between the walls (V=0)
  – Impose boundary condition at the walls and find the coefficients

\[ \hat{H}\psi = E\psi \quad \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} \]

\[ \psi_k = A e^{ikx} + B e^{-ikx} \quad E_k = \frac{k^2 \hbar^2}{2m} \]

\[ \psi_k(0, L) = 0 \]

\[ \psi_n(x) = C \sin(n\pi x / L) \quad n = 1, 2, \ldots \]
Electron in a box

- Number of available states

\[
n = \int 2 \frac{d^3 \vec{k}}{(2\pi)^3} f(\vec{k})
\]

\[
E = \int 2 \frac{d^3 \vec{k}}{(2\pi)^3} E(\vec{k}) f(\vec{k})
\]

\[
\vec{J} = \int 2 \frac{d^3 \vec{k}}{(2\pi)^3} e\vec{\nu}(\vec{k}) f(\vec{k})
\]

\[
f_{eq}(\vec{k}) = f_F(E(\vec{k}) - \mu) = \frac{1}{1 + \exp[(E - \mu) / kT]}
\]
Electron in a box: example

• Electrons are sufficiently delocalized in conjugated molecules that they can be considered as an electron box

• Electronic absorption of $\beta$-carotene

1 $\beta$-Carotene
0.294nm

$\pi$ Bond
• Electronic absorption of $\beta$-carotene

22 electrons fill states up to $n=11$

$$\Delta E = E_{12} - E_{11} = \left( (n+1)^2 - n^2 \right) \frac{h^2}{8mL}$$
• Now we have confined states in two directions and a propagating state along X.
Quantum Mechanical Tunneling

- the wave nature of electrons allows penetration into a forbidden region of the barrier
- at low voltages ($V << \text{barrier height}$):
  \[ \sigma = A \exp(-Bd) \]
- at higher voltages the barrier tilt should be taken into account:
  \[ I = 2I_0 \left[ \frac{\pi CkT}{\sin(\pi CkT)} \right] \exp(-BV^2) \sinh\left(\frac{CV}{2}\right) \]
Molecules and contacts form two essential parts of a molecular device.

The contact of a molecule and bulk material is complicated, strongly influence device behaviour and only recently became a focus of intensive research.
Molecules and contacts

- Molecules can be contacted using:
  - **Covalent bonds** mechanically stable, short, allow overlap of molecular orbitals and delocalized states in the metal
    Examples: Au-thiol, Au-CN, Pt-amine etc.
  - **Van der Waals interaction** (e.g. Langmuir-Blodgett film deposited on a substrate): wave functions don’t overlap, electron transport goes via tunneling to and from the molecule.
Bond length effect

• If the distance is short enough that delocalized state of the molecule overlaps with the metallic electronic states, then the common delocalized state is formed and electron can be transmitted through the system.

• If the overlap is not achieved the wave function can be treated independently and the whole situation can be modeled as tunneling of an electron from electrode to a molecule.
Theory considerations: Contacts and MO overlap

- contribution of different MO to the current may very strongly depending on their spatial arrangement
- issue of contact is important: a “supermolecule” involving last few metal atoms should be in the calculations

HOMO: depleted at the contacts

LUMO: depleted in the middle

lower lying MO (~1eV) is important for current
Role of contacts

Role of Metal-Molecule Contacts

Rectification decreases as coupling increases at right interface.

• what type of behaviour we can expect for a complete system?
Ballistic conductor

Contacts of finite transparency

\[ \mu_1 \quad \mu_2 \]

• The model:
  – Electrons tunnel with some probability (contact transparency) into the channel
  – Transport is coherent
  – Contacts are ”reflectionless”

• The question:
  • What is the resistance of the channel? Where the heat is dissipated?
Ballistic conductor

• Electron in solids:
  – Solutions of Schroedinger equation are Bloch waves, and momentum is a quasimomentum now
    \[ \psi_{k,r}(r) = \exp(ikr)u_{k,p}(r) \]
  – we speak not about real electrons but rather quasielectrons: excitations above ground state of all electrons present
• Electrons moving from left to right have potential $\mu_1$, from right to left $\mu_2$. 

Ballistic conductor model
Waveguide with a constriction

- Only few states can pass through the constriction: "open channels"

\[ E_n = \frac{\pi^2 \hbar^2}{2m} \left[ \frac{n_y^2}{a^2(x)} + \frac{n_z^2}{b^2(x)} \right] \]
• The current:

\[ I = \frac{2e}{2\pi\hbar} N_{\text{open}} (\mu_L - \mu_R) = G_Q N_{\text{open}} V \]
Quantized conduction of a ballistic conductor

- The situation was first encountered in 2DEG system, e.g. B.J. van Wees et al, Phys Rev. Lett. 60, 848 (1988).
• Landauer-Buttiker theory: electron is transmitted through a state with a certain probability (transparency) $Tr(t,t')$
• Coherent conductance is expected to characterize most of short molecular wires.

• The conductance is given:

\[ g(E,V) = \frac{2e^2}{h} \sum_{i,j} t_{ij}(E,V) \]

- Quantum of conductance
- Probability to go from the transverse mode i in the left contact to the transverse mode j in the right contact
Atomic point contacts

- Conductance of a single atom
Variable range hopping

- for disordered materials the charge transfer goes by a process similar to diffusion as the mean free path is of the order of interatomic distance

- Mott equation

\[ \sigma = \sigma_0 \exp \left( - \left( \frac{T_0}{T} \right)^{1/4} \right) \]

1/3 for 2D and ½ for 1D
Shottky and Poole-Frenkel effects

- Barrier can be created at the interface due to charge redistribution (Shottky barrier)

\[ J \propto \exp \left( \frac{E \beta^{0.5}}{kT} \right) \]

Fowler-Nordheim tunneling

\[ J \propto E^2 \exp \left( \frac{-\gamma}{E} \right) \]

Poole-Frenkel effect
Charge quantization

- In solid state physics we consider quasi-electrons that are modeled as non-interactive particles.
- At nanoscale, charge brought by one electron becomes important.

**Energies involved:**

\[
E = \frac{Q}{2C} = \frac{N^2 e^2}{2C} = E_C N^2
\]

\[
\delta_s \approx \frac{E_F}{N_{at}}
\]

\[
\frac{\delta_s}{E_C} \approx \frac{E_F L}{e^2 N_{at}} \approx N_{at}^{-2/3}
\]

For 100nm particle:

- \(E_C \approx 100\text{mV}\)
- \(\delta_s \approx 10^{-8}\text{eV}\)
In SET design we have two transport electrodes and a gate.

Typical behaviour: current is blocked in regions coloured blue.
Design Challenges for Molecular Circuits

- Applicability of superposition principle is restricted as molecular parts can not be treated independently. Effect of molecular structure on density of states and geometry of MO should be considered.
- Coulomb blockade effects: conductance will depend on charge on subunits and the capacitance to the gate.
- Interference effects.
The challenges:

- how to attach molecules to the electrodes
- how to arrange them in the same direction