Example: Molecular Transistor

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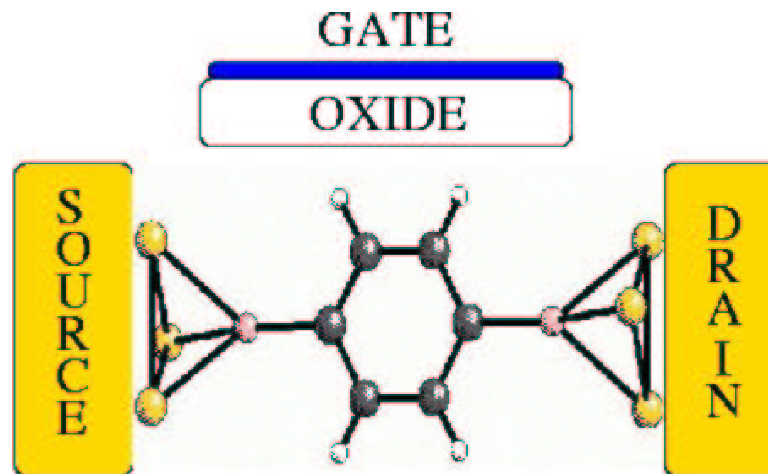
Purpose of this talk

- To illustrate the use of the NEGF formalism
- Example device: molecular transistor
- Molecule: Phenyl Dithiol ($C_6H_6S_2$)

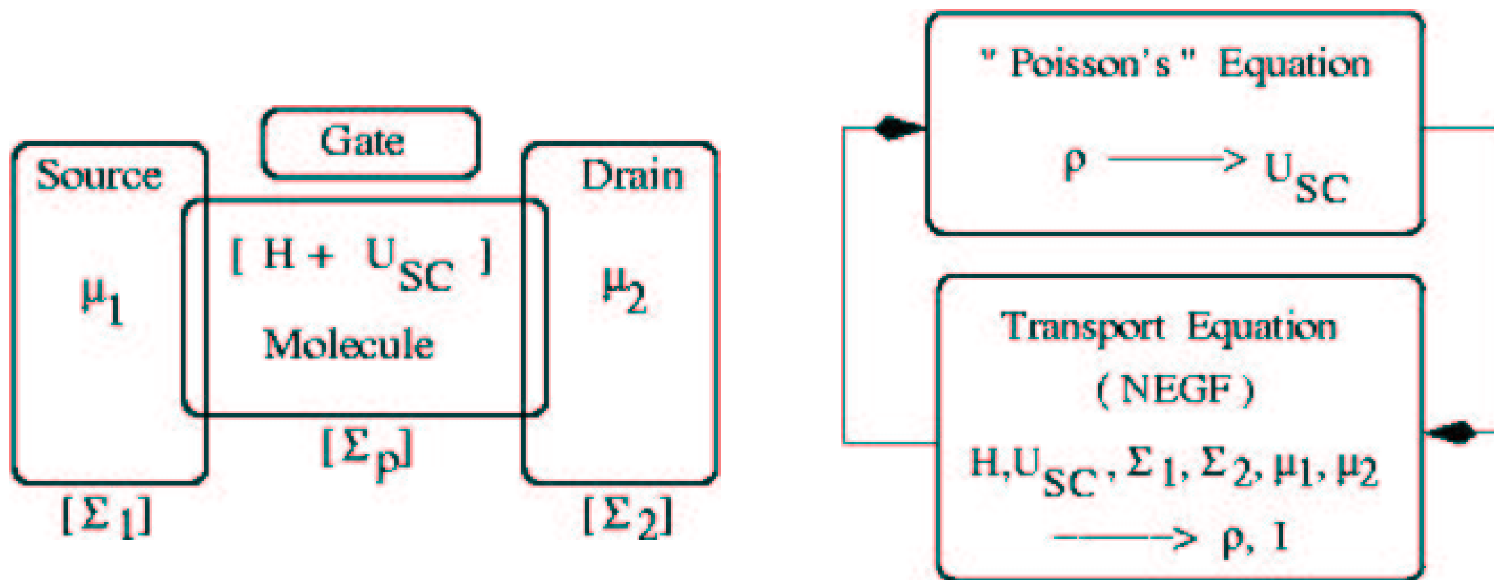


Outline

- Solution procedure
- Modeling the device
- Modeling the contacts
- Results
- Conclusion

Solution Procedure

Combine the NEGF formalism for quantum transport with an appropriate model (semi-empirical or ab initio) for electronic structure



Procedure…

1. Choose a basis
2. Set up Hamiltonian H and contact self-energy matrices $\Sigma_{1,2}$
3. Guess self-consistent potential U
4. Calculate density matrix ρ using NEGF
5. Solve “Poisson’s” eqn to get U from ρ
6. Repeat steps 4 and 5 till convergence
7. Use converged ρ to get electron density, current etc.

NEGF Formalism

$$G = (EI - F - \Sigma_1 - \Sigma_2)^{-1}$$

$$F = H + U$$

$$\rho = \frac{1}{2\pi} \int dE \, G(f_1 \Gamma_1 + f_2 \Gamma_2) G^+$$

$$f_{1,2}(E) = \left[1 + \exp\left(\frac{E - \mu_{1,2}}{k_B T} \right) \right]^{-1}$$

$$\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^+)$$

Outline

- Solution procedure
- Modeling the device
  - Hamiltonian, H
  - Self-consistent potential, U_{SC}
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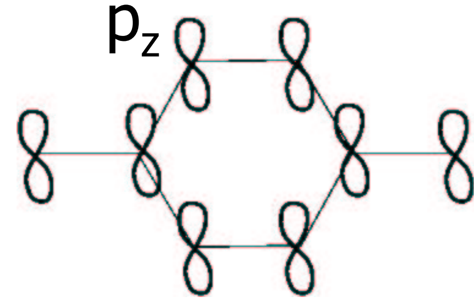
Hamiltonian (H)

- Basis: one p_z orbital on each atom
- Size of H: 8 x 8



Rigorous: $$H_{ij} = \langle p_z^i | \frac{-\hbar^2}{2m} \nabla^2 | p_z^j \rangle$$

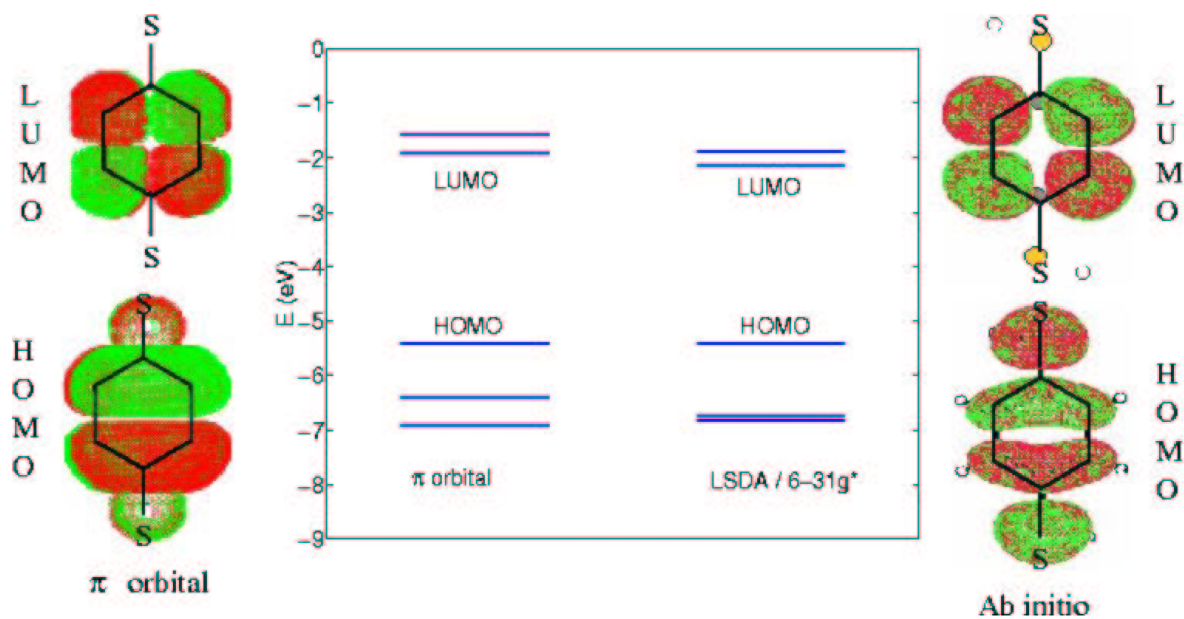
Simplify: $$H_{CC} = -2.5\ eV$$ (Carbon nanotubes)

$$H_{SC} = -1.5\ eV$$ (empirical)

(only nearest neighbors interact)

Hamiltonian (H)

- Test simple H: compare with ab initio H



Self-consistent potential (U_{SC})

Solve Poisson's equation:

$$\vec{\nabla} \, (\varepsilon \, \vec{\nabla} U) = -q^2 (n - n_0)$$

(U and n are functions of real space coordinates)

Two solution schemes:

1. Simple Capacitance Model
2. Numerical solution in real space

(May augment Poisson's (Hartree) potential with an appropriate exchange-correlation potential U_{XC})

Capacitance model

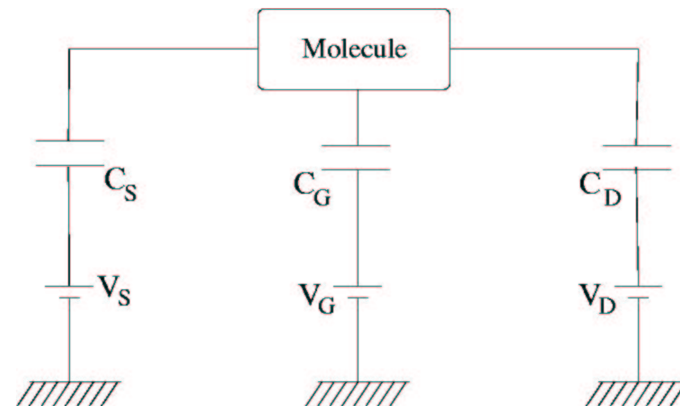
$$U = U_L + U_0(N - N_0)$$

$$U_L = \beta U_G + \frac{(1-\beta)}{2}(U_S + U_D)$$

$$\beta = \frac{C_G}{C_G + C_S + C_D}$$

$$U_0 \approx \frac{q}{C_G + C_S + C_D}$$

$$U_{SC}(i,i) = U, \quad (i = 1,..,8)$$



β is a measure of gate control -

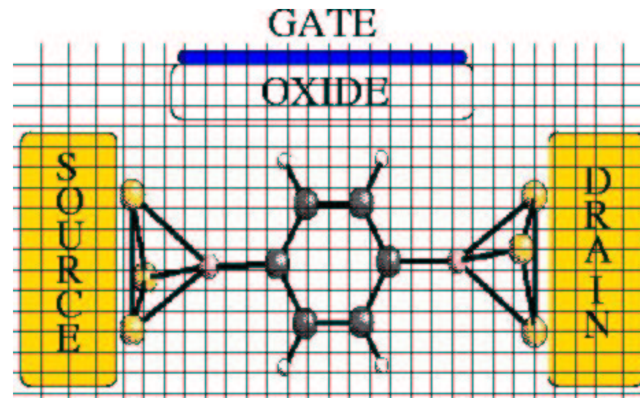
β = 0 : No gate

β = 1: Ideal gate

U_0 is the charging energy per electron

Numerical solution

- 2D rectangular grid in real space
- Vg, Vd give the boundary conditions
- K_{ox} = 3.9, K_{SAM} = 2



$$U_{SC}(i,i) = U(\vec{r}_i)$$

Outline

- Solution procedure
- Modeling the device
- Modeling the contacts
  - Self-energy
  - Where is the Fermi energy?
- Results
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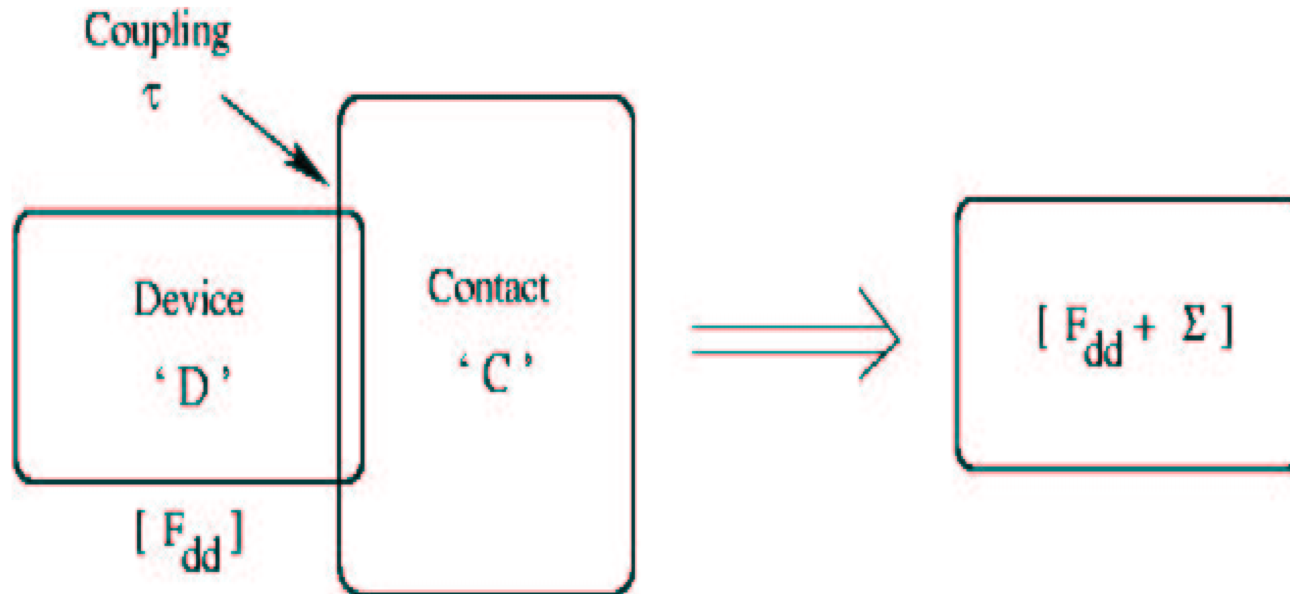
Self-energy by partitioning

$F = H + U_{SC}$

Σ is of the same size as F_{dd}



Partitioning…

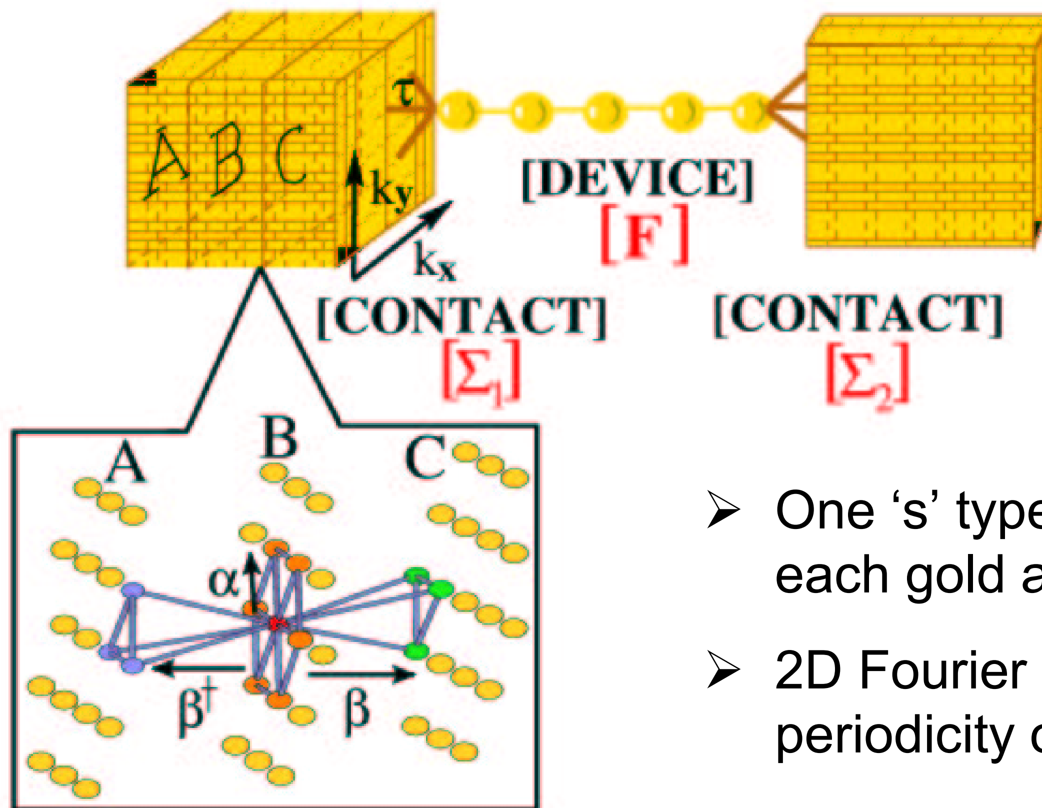
$$G = (EI - F + i0^{+})^{-1} = \begin{bmatrix} EI_{dd} - F_{dd} + i0^{+} & \tau \\ \tau^{+} & C \end{bmatrix}^{-1}$$

$$G_{dd} = [EI_{dd} - F_{dd} - \Sigma(E)]^{-1}$$

$$\Sigma(E) = \tau C^{-1} \tau^{+} = \tau g \tau^{+}$$

g : contact surface Green’s function

Self-energy

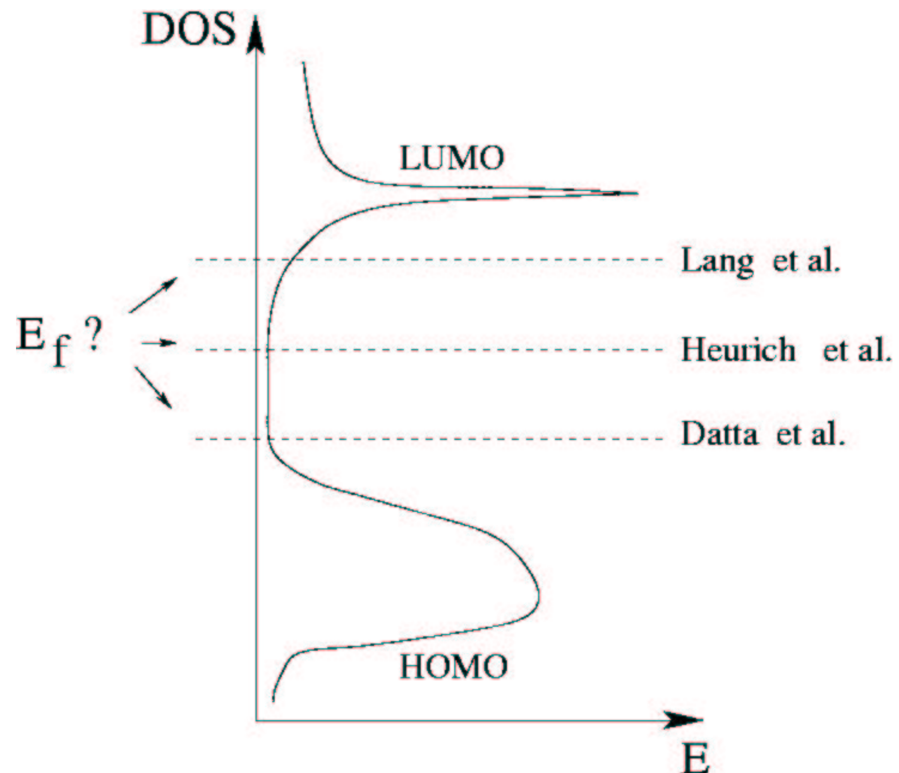


- One 's' type orbital basis on each gold atom
- 2D Fourier transform exploits periodicity of FCC gold
- Ef = -5.1 eV
- Surface DOS = 0.07 eV/atom

Where is the Fermi energy?

E_f is assumed closer to HOMO because:

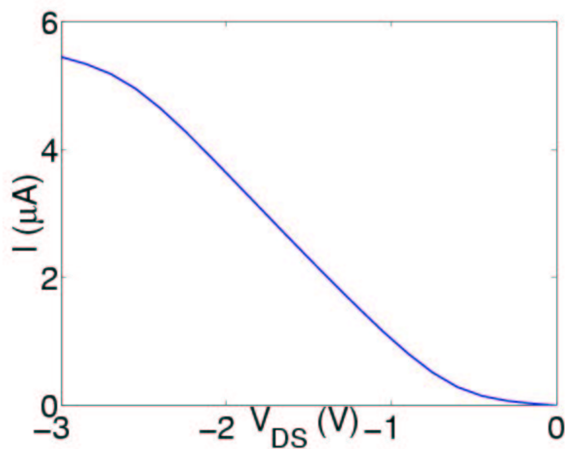
1. Ab initio calculation
2. Experimental evidence

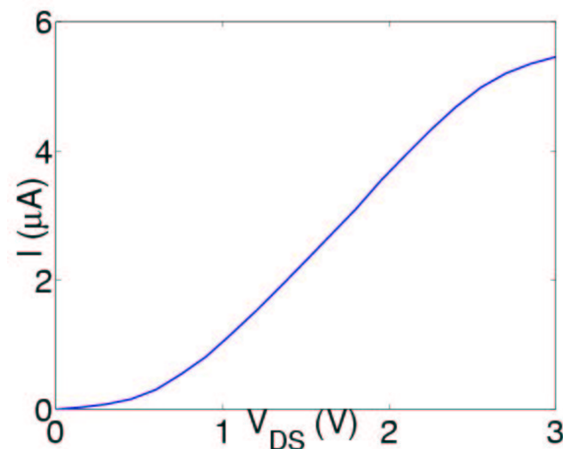


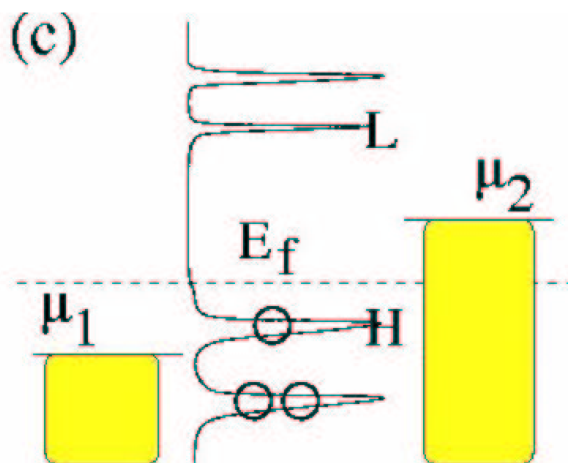
Outline

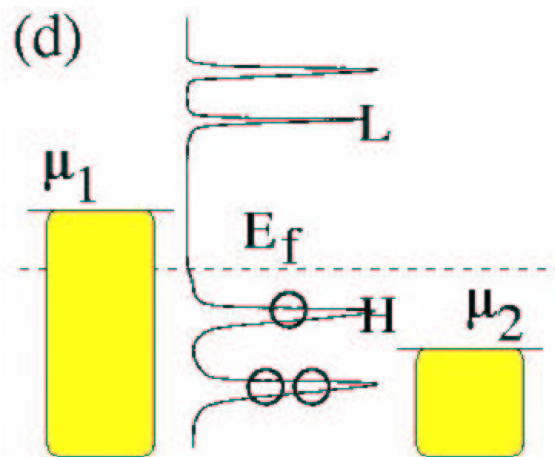
- ✓ Solution procedure
- ✓ Modeling the device
- ✓ Modeling the contacts
- Results
  - No gate (2 terminal)
  - Ideal gate (3 terminal)
  - Estimate of gate control
- Conclusion

No gate

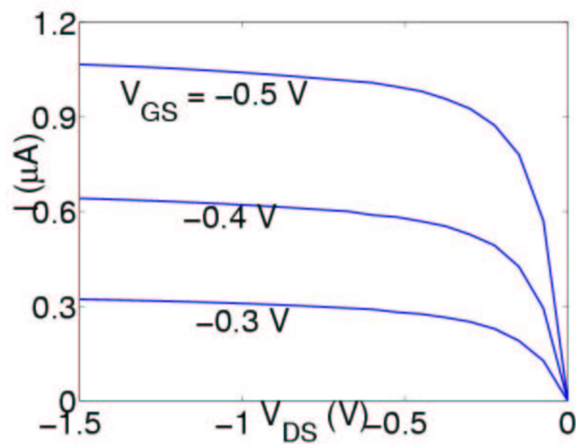


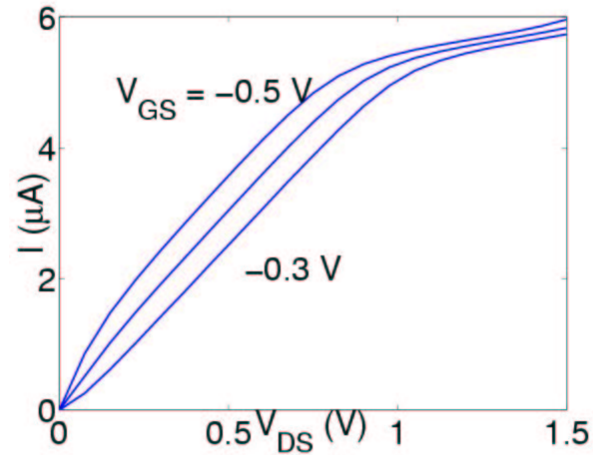


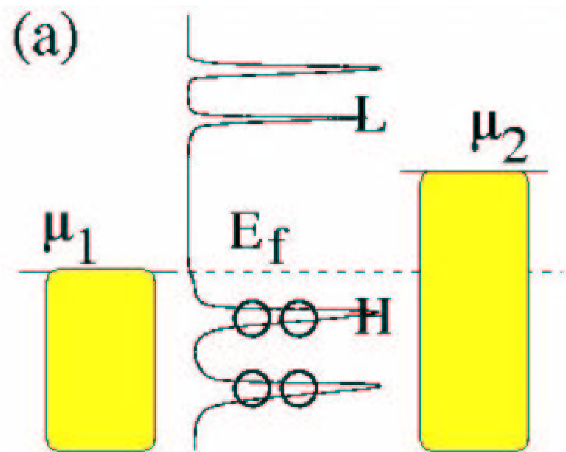


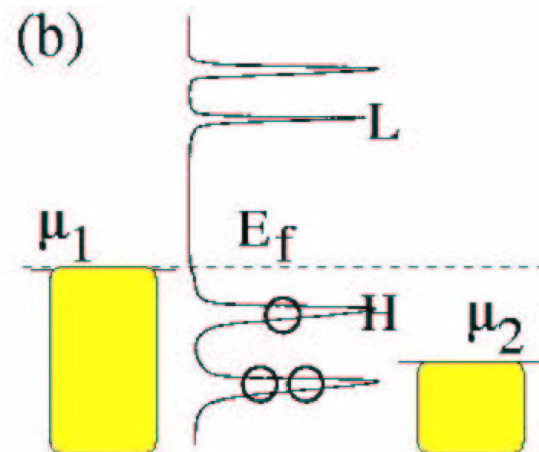


Ideal gate – on state



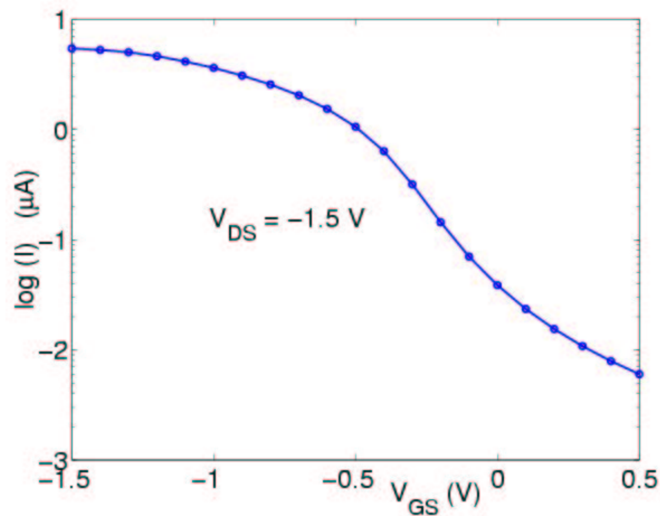




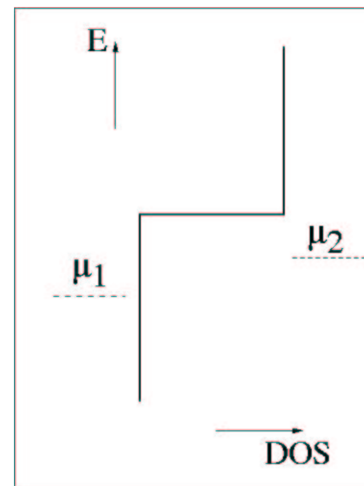


Ideal gate – off state

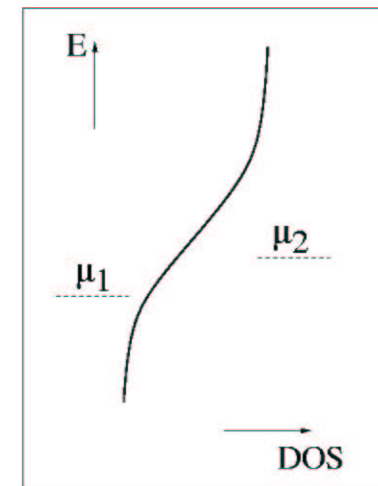
Temperature independent subthreshold slope of several hundred mV/decade !



Step DOS



Gradual DOS



$$S \propto \max\left(k_B T, \frac{1}{\frac{d(DOS)}{dE}} \right)$$

Estimate of gate control

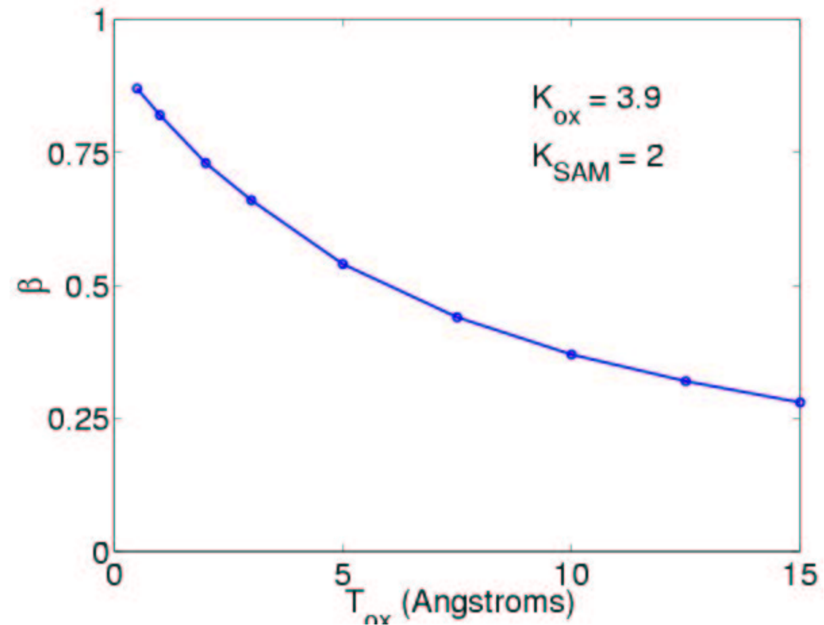
$\beta > 0.85$ needs $T_{ox} < 1$ Angstrom!

$$U_L = \beta U_G + \frac{(1-\beta)}{2}(U_S + U_D)$$

$$\beta = \frac{C_G}{C_G + C_S + C_D}$$

Also,

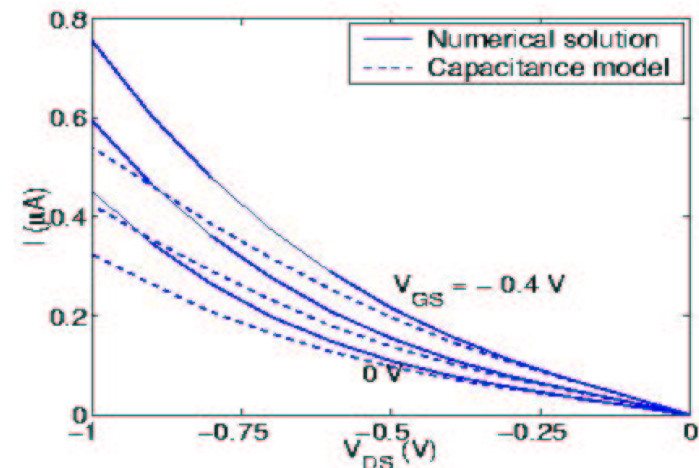
$$\beta = \frac{\partial U_L}{\partial U_G}$$



Comparison: two Poisson solns.

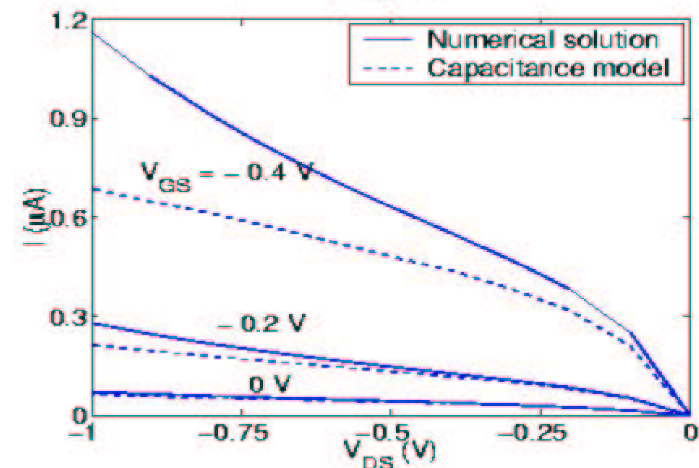
Realistic case : Tox = 1.5 nm

($\beta = 0.27$, $U_0 = 2$ eV)



"Absurd" case : Tox = 1 Angstrom

($\beta = 0.87$, $U_0 = 1$ eV)



Summary of Results

- No gate : Symmetric IV
- Good gate : Asymmetric IV
- Temperature independent subthreshold slope, several hundred mV/decade
- Molecular transistor is a poor switch for a rigid molecule
- Not considered conformational changes!

Conclusion

- NEGF formalism applied to a molecular transistor
- Rigid molecule is a poor switch
- Need other mechanism to understand experiments (e.g. Schon's SAMFET)
- Conformational changes?? (Hamiltonian changes due to applied field)