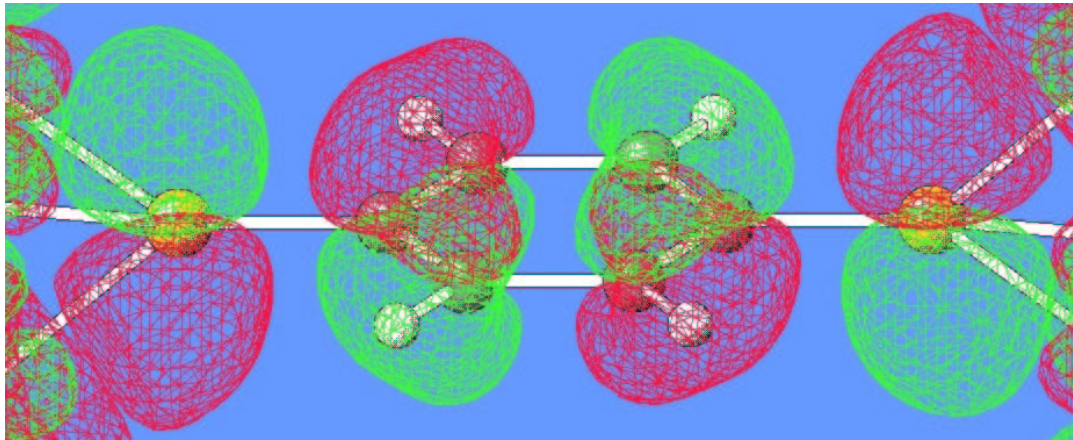
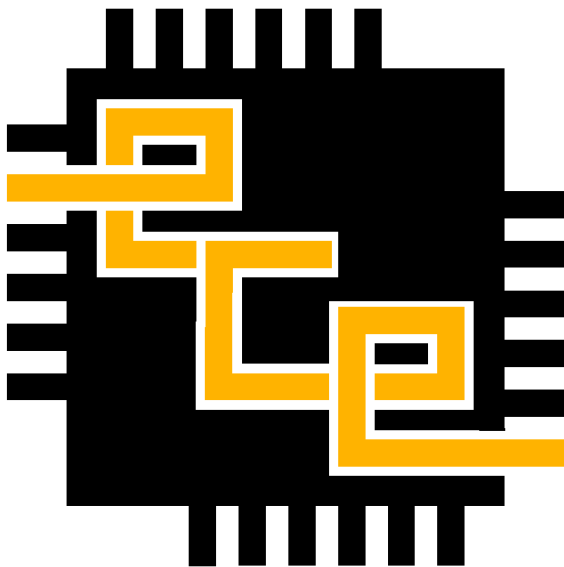


EXPLORING DEVICES AT THE NANO/MOLECULAR SCALE



Modeling the Device



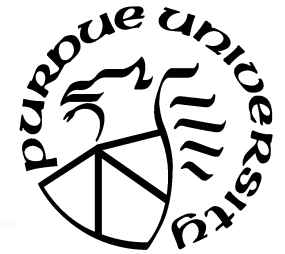
Magnus Paulsson

mpaulsso@purdue.edu

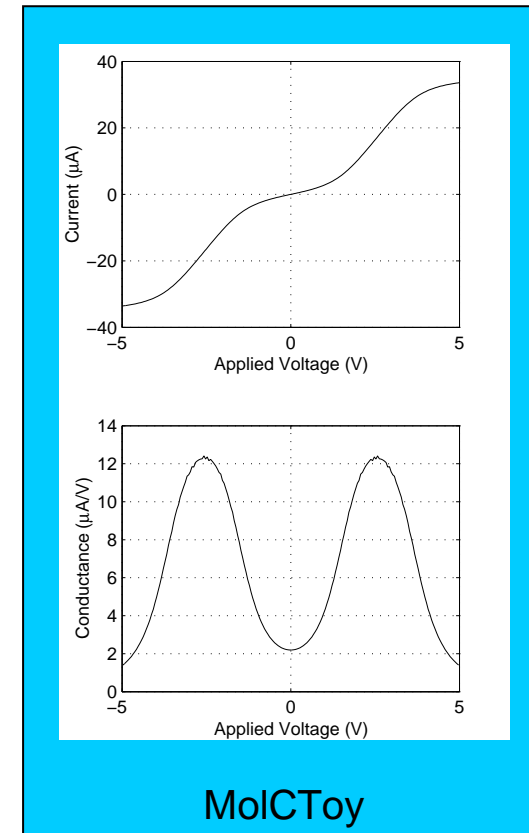
School of Electrical and
Computer Engineering
Purdue University



Overview



- Energy levels
 - Resonant tunneling through levels
 - Determines the conductance gap
- Contact / Broadening
 - Magnitude of the current
 - Fermi-Energy
- Charging effects
 - Shift in levels
 - Unrestricted solution? CB?



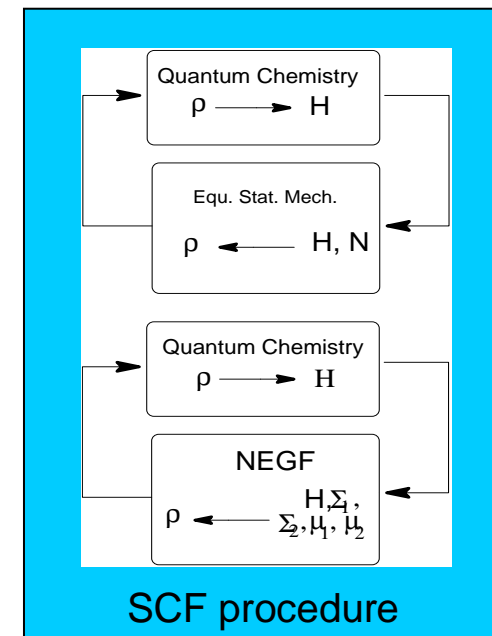
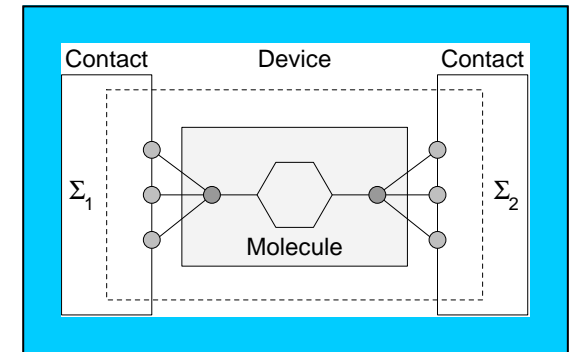
NEGF Method

- Divide system into:
 - Device (H)
 - Contacts (Σ , $\Gamma=i(\Sigma-\Sigma^+)$)

$$G_d = (E - H - \Sigma_1 - \Sigma_2)^{-1}$$

$$\rho = \int_{-\infty}^{\infty} f(E, \mu_1) G_d \Gamma_1 G_d^+ + f(E, \mu_2) G_d \Gamma_2 G_d^+ dE$$

$$I = \frac{e}{\pi \hbar} \int_{-\infty}^{\infty} [f(E, \mu_1) - f(E, \mu_2)] \text{Tr}[\Gamma_2 G_d \Gamma_1 G_d^+] dE$$

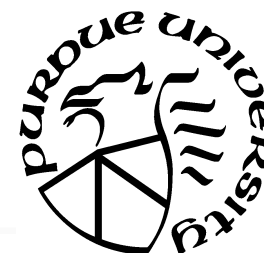


S. Datta, *Electronic transport in mesoscopic systems*. Cambridge University press

M. Paulsson *et al*, *Resistance of a Molecule*, Preprint available from mpaulsso@purdue.edu



Outline



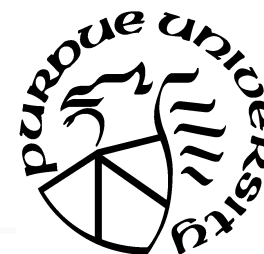
- Quantum Chemistry: Semi-Empirical
 - Hückel: One π -orbital / atom
 - Extended-Hückel: π - and σ -orbitals

Fast, simple, easy to interpret, accurate?

- Electrostatic potential
 - Electron-electron interactions
 - Do the contacts influence the potential?

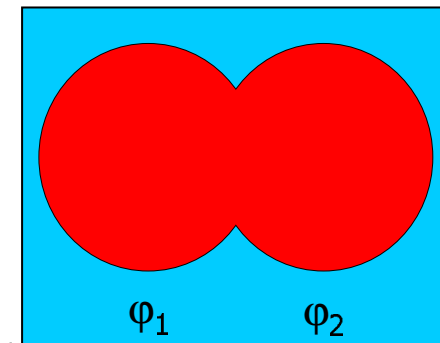
• Quantum Chemistry: Ab Initio

Quantum chemistry



Simple example: H₂ molecule

Choose a basis of one 1-s orbital / atom (φ_1, φ_2)



Solve the Schrödinger equation in this basis: $H\Psi = E\Psi$

$$\text{Hamiltonian: } H_{ij} = \langle \varphi_i | H | \varphi_j \rangle = \int \varphi_i^*(\vec{r}) H \varphi_j(\vec{r}) d^3\vec{r} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

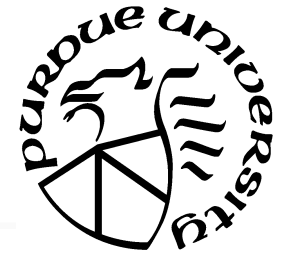
$$\text{Solutions: } E = \alpha \pm |\beta|$$

Bonding, anti-bonding

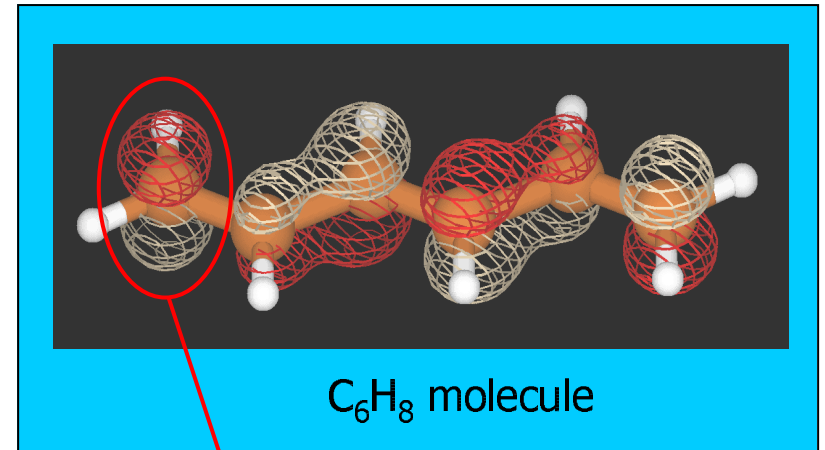
Semi-empirical: α, β fitted to experimental data

Ab-Initio: α, β calculated from first principles

Hückel (semi-empirical)



- Conjugated molecules
 - Flat, often carbon based molecules, e.g., graphite sheet, benzene
- Basis (nonorthogonal)
 - One π -orbital / atom (Slater type)
 - Overlap matrix S (calculated)
- Hamiltonian from the overlap
- Variations:
 - β chosen empirically
 - Su-Schiefer-Heeger Hamiltonian (orthogonal basis)



π -orbital

$$S_{ij} = \int \varphi_i^*(\vec{r}) \varphi_j(\vec{r}) d^3\vec{r}$$

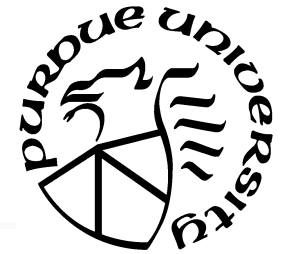
$$H_{ij} = \begin{cases} \alpha & i = j \\ k S_{ij} & i \neq j \end{cases}$$

$$H \Psi = E S \Psi$$

The HMO model and its application, E. Heilbronner, H. Bock, Wiley & Sons, 1976



Extended Hückel



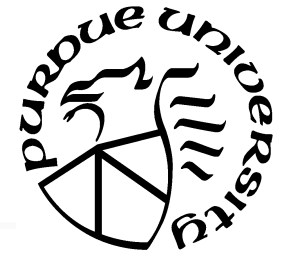
- Works with non-conjugated systems
- All valence electrons basis is used:
 - C : 2s and 2p orbitals
 - H : 1s
 - S : 3s and 3p
- Equations are the same as Hückel

$$S_{ij} = \int \varphi_i^*(\bar{r}) \varphi_j(\bar{r}) d^3\bar{r}$$

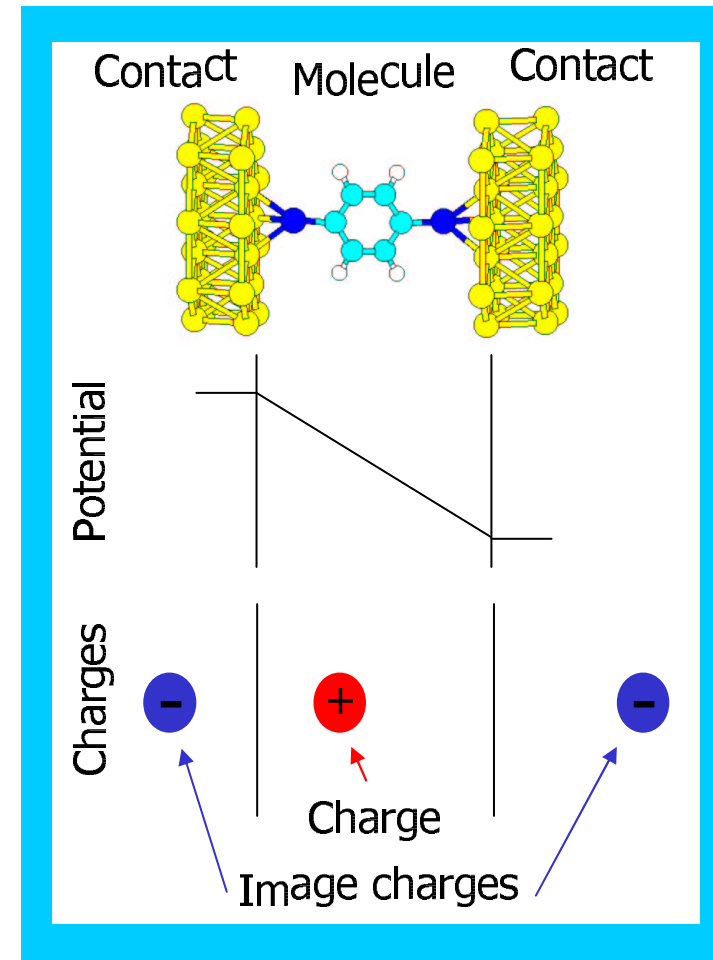
$$H_{ij} = \begin{cases} \alpha & i = j \\ k S_{ij} & i \neq j \end{cases}$$

$$H \Psi = E S \Psi$$

Electrostatic potential drop

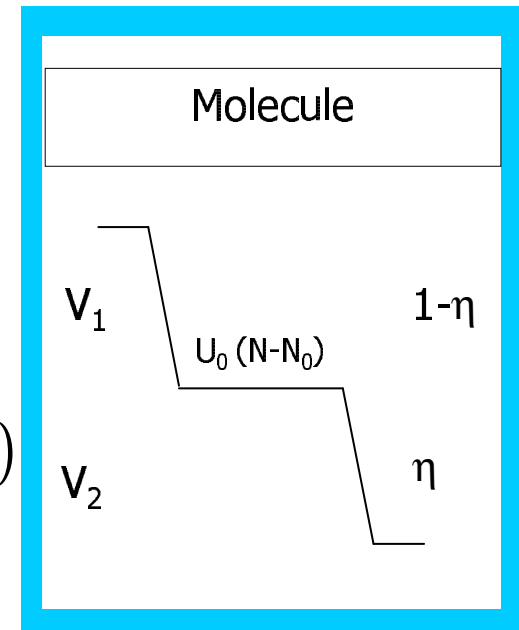


- Large voltage over small molecule
- Polarization?
- Need to include electron-electron interactions to describe fully
- Screening by the contacts



Simplest model

- Capacitor model
 - Assume that the all voltage drop occur at the contact-molecule junctions
- Potential $U = \eta eV_1 + (1-\eta)eV_2 + U_0(N - N_0)$
 - Voltage division factor: $0 < \eta < 1$
 - Charging energy: U_0
- Used by
 - MolCToy
 - Huckel 2.0

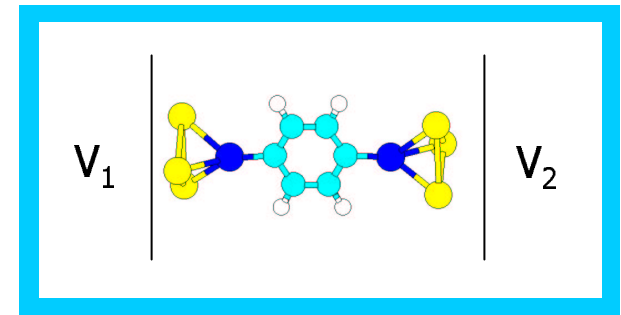


Spatially varying potential



- Solve Poisson equation
 - Geometry
 - Boundary conditions
- Easy for simple geometry
 - Plane capacitor
 - Homogenous solution
 - Particular solution
- Infinities
 - Pariser, Par, Pople (PPP)-model

$$-\nabla^2 U(\bar{r}) = \rho(\bar{r}) / \epsilon_0$$



$$U = U_{\text{homogen}} + U_{\text{part}}$$

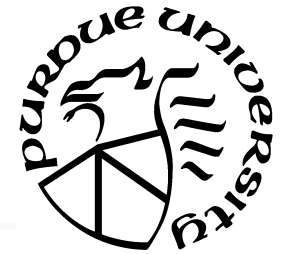
$$U_{\text{homogen}} = V_1 + \frac{x}{d} (V_2 - V_1)$$

$$U_{\text{part}}(\bar{R}) = \sum_{i \in \text{Charges}} \frac{q_i}{4\pi \epsilon_0 |\bar{R} - \bar{r}_i|} +$$

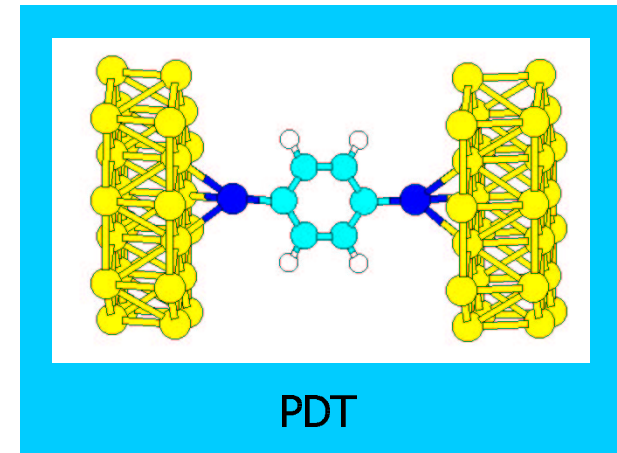
+ Image Charges

Semi-empirical SCF MO Theory of Molecules,
Murrell, Harget, Wiley & Sons 1972

Estimates of PDT charging energy



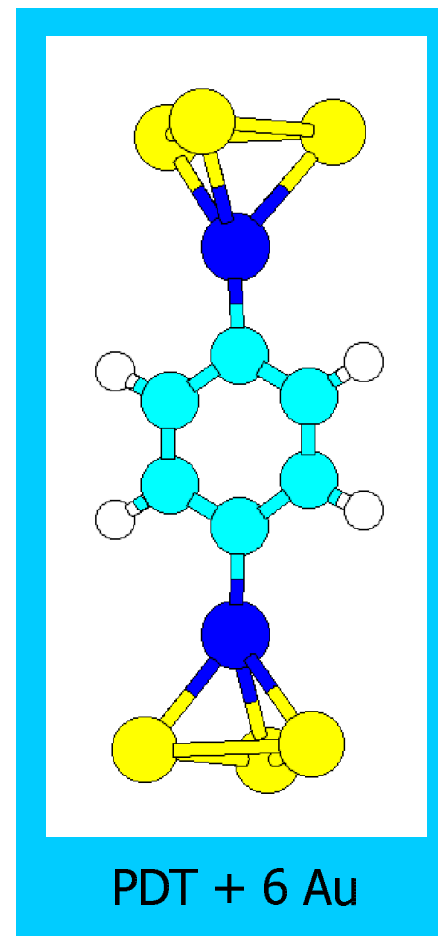
- Classical metallic sphere
(Radius: 10 Å)
 - $U_0 \approx 1.5$ eV
- Spatially varying potential
 - Hückel with PPP model for the potential
 - $U_0 \approx 3$ eV (without image charges)
 - $U_0 \approx 2$ eV



Ab Initio

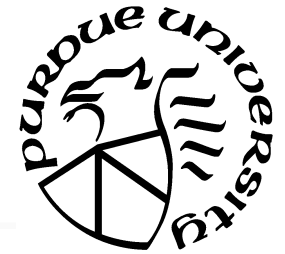


- Choose a basis
 - STO-3G, Au(?), S (9) C (5) H (1)
 - 6-31G*, Au(?), S(19), C(15), H (2)
 - Lanl2dz, Au (22), S (8), C(9), H(2), only valence electrons
- PDT molecule
 - STO-3G (54), 6-31G* (140), Lanl2dz (82)
- 6 gold atoms
 - Lanl2dz (132)
- In total 214 basis functions for Lanl2dz
- Calculate the integrals (α , β)





Hartree-Fock / DFT



- Hartree-Fock equation

$$F_{\mu\nu} = T_{\lambda\delta} + V_{\lambda\delta} + \sum_{\lambda,\delta} \rho_{\lambda\delta} \left(\langle \mu\nu | \sigma\lambda \rangle - \frac{1}{2} \langle \mu\lambda | \sigma\nu \rangle \right)$$

- Two-electron Integrals

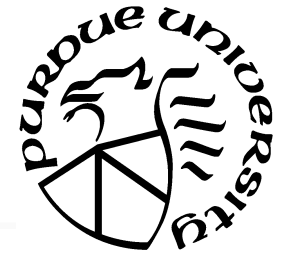
$$\langle \mu\nu | \sigma\lambda \rangle = \int dr_1 dr_2 \varphi_{\mu}^*(r_1) \varphi_{\nu}(r_1) \frac{1}{|r_1 - r_2|} \varphi_{\sigma}^*(r_2) \varphi_{\lambda}(r_2)$$

- $N^4 \approx 200^4 = 16 \cdot 10^6$ Integrals

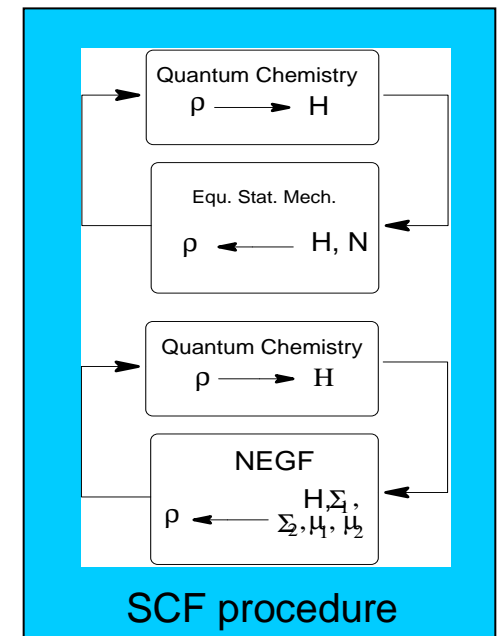
- Density functional theory (DFT)

- LDA, use effective potential formed from the local charge density

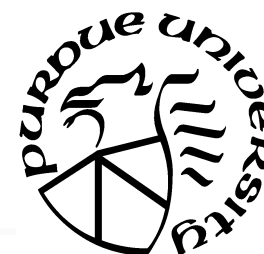
How?



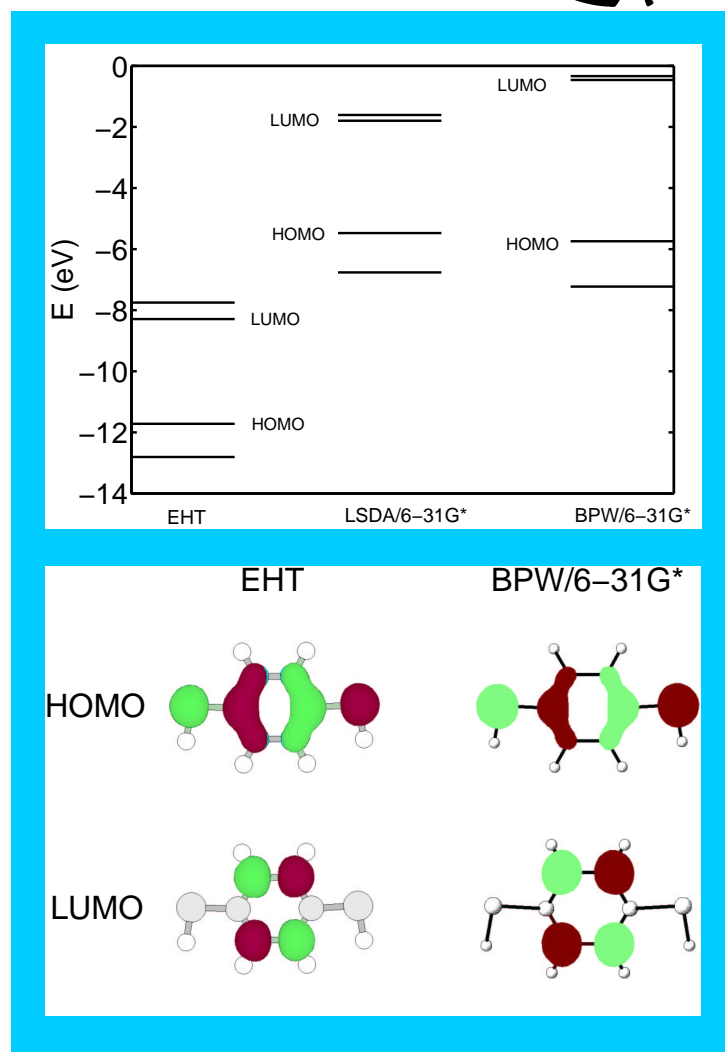
- Use existing quantum chemistry software
- Modify:
 - Calculation of the density matrix (ρ)
 - Include the external electric field
 - Add the effects of the screening by the contacts (image charges)
 - (or) Include enough contact atoms into the device
- Density matrix is in general complex



Levels and wavefunctions

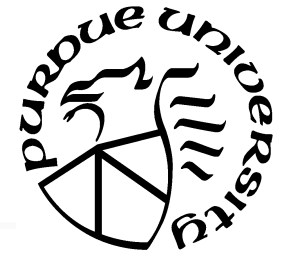


- Energy levels
 - Ab-Initio (HF, BPW, LDA)
 - Extended-Hückel
 - Differences
- Wavefunctions
 - Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied (LUMO)





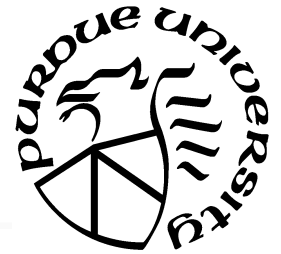
Summary



- Non Equilibrium Green's Functions
- Quantum Chemical description of the device
 - Semi-empirical methods
 - Fast, simple
 - Too many parameters
 - Ab-initio
 - Slow, complicated
 - Accurate
- Electrostatic potential
 - Applied potential
 - Potential from charges
 - Screening by the contacts



Summary



- Effects not included
 - Conformation changes?
 - Beyond mean-field theory?
- Why is this difficult?
 - Ab-Initio basis sets are large
 - Open system, i.e., infinite number of electrons
 - To get a finite system we describe the contacts with self-energies