Tools for Quantum transport: the gDFTB code

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gDFTB family codes

1st Gen. (2001-2003) — **Equilibrium:** DFTB; Green's Func. + DFTB

2nd Gen. (2002-2004) — **Non Equilibrium:** gDFTB (SCC + Open BC); NEGF+phonons (non SCC)

3rd Gen. (2003-2005) — GW DFTB; gDFTB+phonons

4th Gen. (2005-2006) — NEGF + GW; Spin Transport

The DFT approach

Atomistic simulations with an approximate DFT method:

$$\hat{H}[n(\vec{r})]\psi_k(\vec{r}) = E_k\psi_k(\vec{r})$$

$$E = \sum_k n_k \left\langle \psi_k \left| T_0 + \tfrac{1}{2}\int \frac{n(\vec{r}\,')}{|r-r'|}dr' \right| \psi_k \right\rangle + E_{xc}\left[n(\vec{r})\right] + E^{rep}$$

2nd order expansion of LDA functional $n(\vec{r}) = n_0(\vec{r}) + \delta n(\vec{r})$

$$E = \sum_k n_k \left\langle \psi_k \left| H_0[n_0] \right| \psi_k \right\rangle +$$

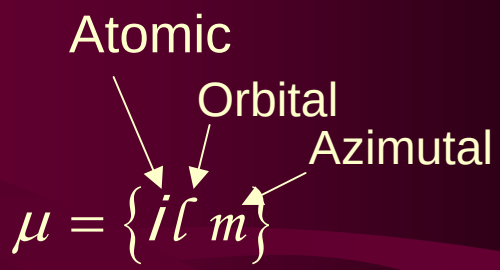
$$+\iint \delta n(r)\left[\frac{1}{|r-r'|} + \frac{\delta v_{xc}(r)}{\delta n(r')}\right]\delta n(r')drdr' + E^{rep}$$

LCAO expansion

[Porezag *et al.*, PRB 51, 12947 (1995)]

LCAO expansion

$$\psi_k = \sum_\mu c_{k\mu}\phi_\mu$$



Secular equation (Kohn-Sham)

$$\sum_k c_{k\nu}\left[H_{\mu\nu} - E_k S_{\mu\nu}\right] = 0$$

Second order correction

$$H_{\mu\nu} = H^0_{\mu\nu} + H^{Scc}_{\mu\nu}$$

$$H^0_{\mu\nu} = \begin{cases} \varepsilon_\mu^{free-atom} & \mu = \nu \\ \left\langle \phi_\mu \middle| H(\rho^0_\mu + \rho^0_\nu) \middle| \phi_\nu \right\rangle & \mu \neq \nu \end{cases}$$

Main approximations

- Use of a minimal (but optimized) basis set
- Neglect of three center integrals
- Neglect of crystal field

II order terms

$$n_{i\ell}(r) = \frac{1}{2\ell+1}\sum_{m=-\ell}^{\ell}\left|\phi_{i\ell m}(r)\right|^2 \qquad \bar{\mu} = \{i\ell\}$$

Mulliken type approximation

$$\phi_\mu(r)\phi_\nu(r) \approx \frac{1}{2}S_{\mu\nu}\left[n_{\bar{\mu}}(r) + n_{\bar{\nu}}(r)\right] \qquad \rho(r) = \sum_{\bar{\mu}} q_{\bar{\mu}} n_{\bar{\mu}}(r)$$

Mulliken charge projection on each atomic shell:

$$q_{\bar{\mu}} = \sum_{m\in\mu}\sum_{\nu}\mathrm{Re}\left\{\rho_{\mu\nu}S_{\mu\nu}\right\} \qquad \Delta q_{\bar{\mu}} = q_{\bar{\mu}} - q^0_{\bar{\mu}}$$

The gamma approx.

$$\gamma_{\bar{\mu}\bar{\sigma}} = \iint \left[\frac{1}{|r - r'|} + \frac{\delta V_{xc}(r)}{\delta \rho(r')} \right] \delta n(r) \delta n(r') dr dr' \approx \sum_{\bar{\mu},\bar{\sigma}} \gamma_{\bar{\mu}\bar{\sigma}} \Delta q_{\bar{\mu}} \Delta q_{\bar{\sigma}}$$

$$H_{\mu\nu}^{Scc} = \frac{1}{2} S_{\mu\nu} \sum \left(\gamma_{\bar{\mu}\bar{\sigma}} + \gamma_{\bar{\nu}\bar{\sigma}} \right) \Delta q_{\bar{\sigma}}$$

Interaction between two orbitals on atoms i and j including XC

$$\gamma_{\bar{\mu}\bar{\sigma}} = \iint n_{\bar{\mu}}(r) \left[\frac{1}{|r - r'|} + \cancel{\frac{\delta V_{xc}(r)}{\delta \rho(r')}} \right] n_{\bar{\sigma}}(r') dr dr'$$

At large distances is ~1/R

At short distances (onsite)
Depends on a Hubbard term

$$\gamma_{\bar{\mu}\bar{\sigma}} = U_{\bar{\mu}}^{H} \delta_{\bar{\mu}\bar{\sigma}}$$

Interpolation method

$$\gamma_{\bar{\mu}\bar{\nu}} = \frac{1}{R_{ij} + \frac{1}{2}\left(U^H_{\bar{\mu}} + U^H_{\bar{\nu}}\right)}$$

Mataga-Nishimoto

Elstner-Porezag approximation scheme

[Elstner *et al.*, PRB 58, 7260 (1998)]

Impose a fixed functional form

$$\gamma_{\bar{\mu}\bar{\nu}} = \iint n_{\bar{\mu}}(r)\frac{1}{|r - r'|}n_{\bar{\nu}}(r')drdr' = \frac{1}{R_{ij}} - S\left(\tau_{\bar{\mu}}, \tau_{\bar{\nu}}, R_{ij}\right)$$

With a radial atomic charge density like

$$n_\alpha(r) = \frac{\tau_\alpha^3}{8\pi}\exp\left[-\tau_\alpha\left|r - R_i\right|\right] \qquad \tau_\alpha = \frac{16}{5}U^H_\alpha$$

Analogy to γ-functional

$$\upsilon_{\bar{\mu}\bar{\nu}} = \iint n_{\bar{\mu}}(r)\frac{1}{|r-r'|}n_{\bar{\nu}}(r')drdr'$$ Pure Hartree

Hartree+local XC $$\gamma_{\bar{\mu}\bar{\sigma}} = \iint n_{\bar{\mu}}(r)\left[\frac{1}{|r-r'|}+\frac{\delta v_{xc}(r)}{\delta\rho(r')}\right]n_{\bar{\sigma}}(r')drdr'$$

Computation of [υ] is done exploiting the γ result
But the on-site parameters should not contain XC, just the Hartree term

$$\upsilon_{\bar{\mu}\bar{\sigma}} = U^{ee}_{\bar{\mu}}\delta_{\bar{\mu}\bar{\sigma}}$$

U^H and U^{ee}

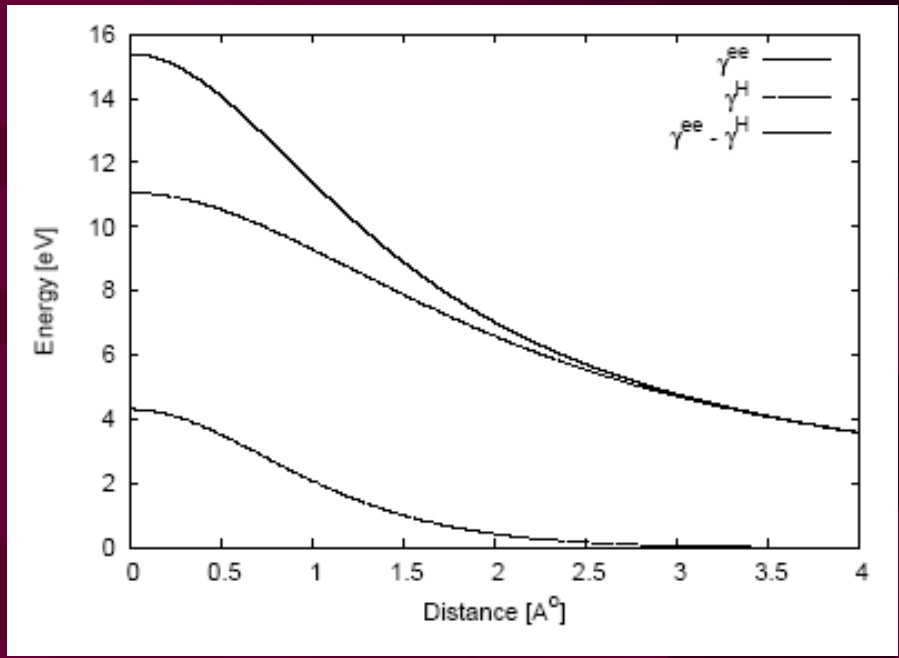
Element	Parameter	r_0 $[a.u.]$	Value [eV]
Hydrogen			
	U_0^H	∞	11.06
	U_0^{ee}	∞	15.39
	U_0^{ee}	3.0	21.36
Carbon			
	U_0^H	∞	10.81
	U_1^H	∞	10.81
	U_0^{ee}	∞	15.66
	U_1^{ee}	∞	14.15
	U_0^{ee}	2.7	17.98
	U_1^{ee}	2.7	18.72
	$(\phi_{00}\phi_{1m'}\|\phi_{00}\phi_{1m'})$	∞	3.01
	$(\phi_{1m}\phi_{1m'}\|\phi_{1m}\phi_{1m'})$	∞	0.75

Hubbard and e-e repulsion integrals for H and C and different compression radii

The XC of DFTB

$$v^{xc}[n] = \sum_k \langle \psi_k | v^{xc}[n_0] | \psi_k \rangle + \iint \delta n(r) \frac{\delta v_i^{xc}(r)}{\delta n(r')} \delta n(r') dr dr'$$

$$= \sum_{\bar{\mu},\bar{\nu}} q_{\bar{\mu}}^{ii} \left[\frac{\delta v^{xc}}{\delta n} \right]_{\bar{\mu}\bar{\nu}} \Delta q_{\bar{\nu}}$$

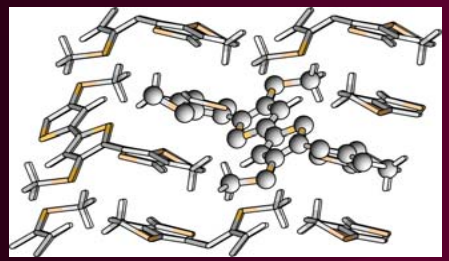


$$\left[\frac{\delta v^{xc}}{\delta n} \right]_{\bar{\mu}\bar{\nu}} = \gamma(R, U_{\bar{\mu}}^H, U_{\bar{\nu}}^H) - \gamma(R, U_{\bar{\mu}}^{ee}, U_{\bar{\nu}}^{ee})$$

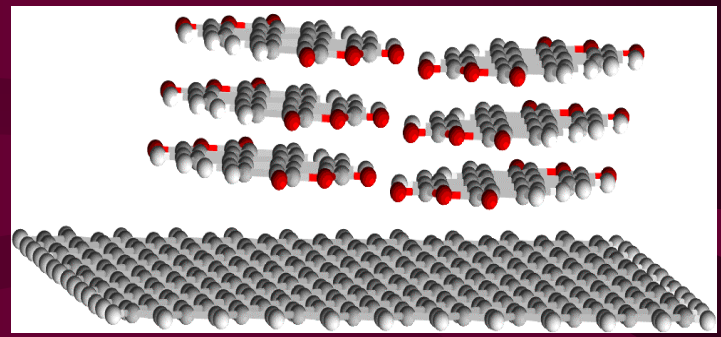
Applications of DFTB

[Paderborn, Heidelberg, Harward, Rome]

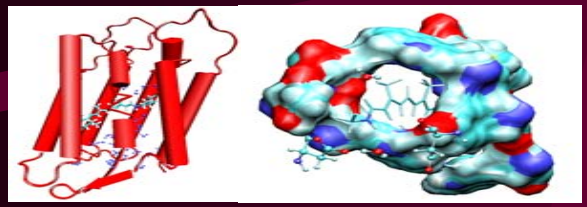
J. Phys.: Condens. Matter 14 (2002) 3015–3047



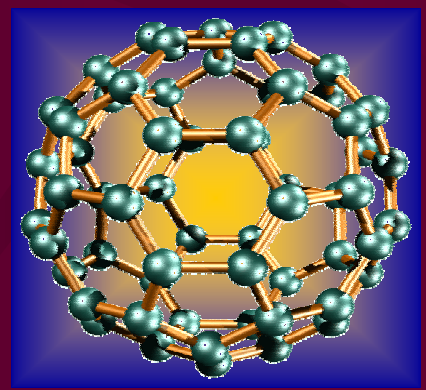
Triclinic tiophene



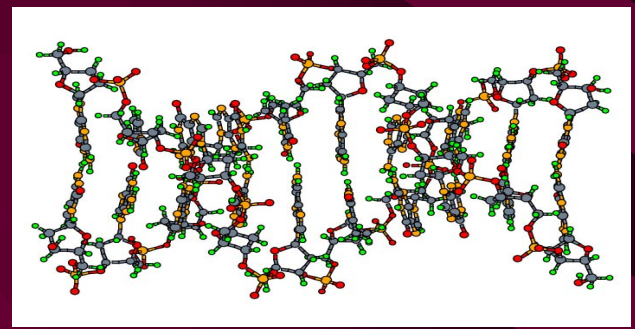
PTCDA on metal



Bacteriorhodopsin



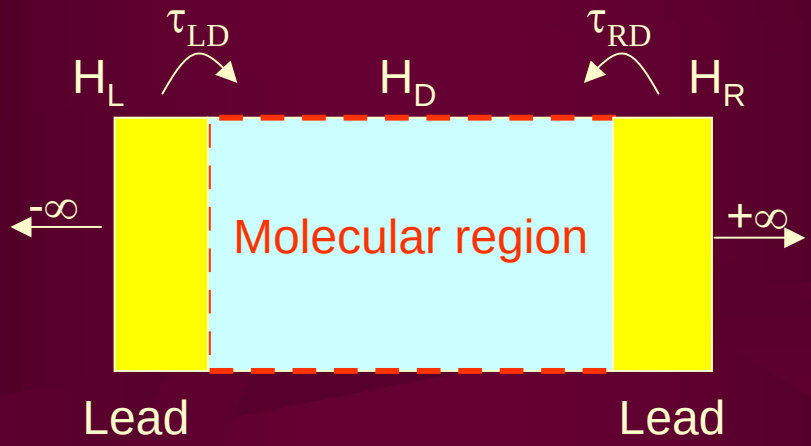
C_{60} Ultrafast-spectr.



DNA-dodecamer

Transport extensions

Green's Function Approach



Retarded (r) and advanced (a) Green functions are defined as follow

$$\left[(E \pm i\eta)\mathbf{I} - \mathbf{H}\right]\mathbf{G}^{r,a} = \mathbf{I}$$

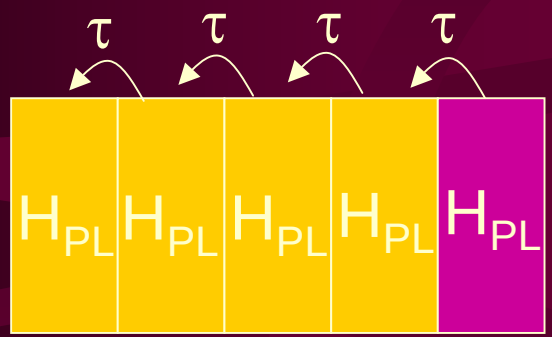
Let us write H and G in a block form

$$\mathbf{H} = \begin{bmatrix} H_L & \tau_{LD} & 0 \\ \tau_{DR} & H_D & \tau_{DR} \\ 0 & \tau_{RD} & H_R \end{bmatrix} \qquad \mathbf{G} = \begin{bmatrix} G_L & G_{LD} & G_{LR} \\ G_{DL} & G_D & G_{DR} \\ G_{RL} & G_{RD} & G_R \end{bmatrix}$$

Transmission coefficient

With these definitions and considering that $\left[(E \pm i\eta)\mathbf{I} - \mathbf{H}_{L,R}\right] g_{L,R} = \mathbf{I}$

defines the Green function $g_{L,R}$ of the semi-infinite lead
(which can be easily calculated)



$$\mathbf{H} = \begin{bmatrix} H_L & \tau & & & \\ \tau^\dagger & H_L & \tau & & \\ & \tau^\dagger & H_L & \tau & \\ & & \tau^\dagger & H_L & \tau \\ & & & \tau^\dagger & \ddots \end{bmatrix}$$

$$G_D = \left(E - H_D - \Sigma_L - \Sigma_R\right)^{-1}$$

$$\Sigma_L = \tau_{DL} g_L \tau_{LD}$$

$$\Sigma_R = \tau_{DR} g_R \tau_{RD}$$

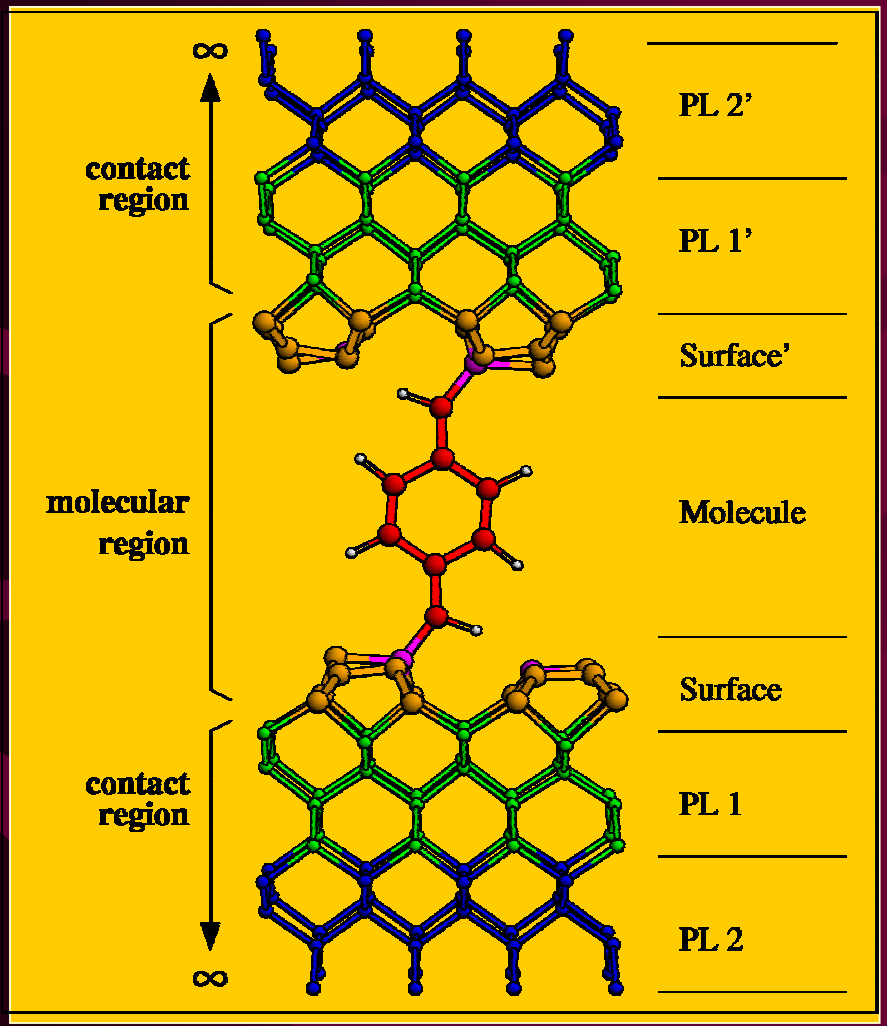
Self-energy

$$\Gamma_{L,R} = i\left[\Sigma^r_{L,R} - \Sigma^a_{L,R}\right]$$

$$T = tr\left(\Gamma_L G^r_D \Gamma_R G^a_D\right)$$

Transmission coefficient

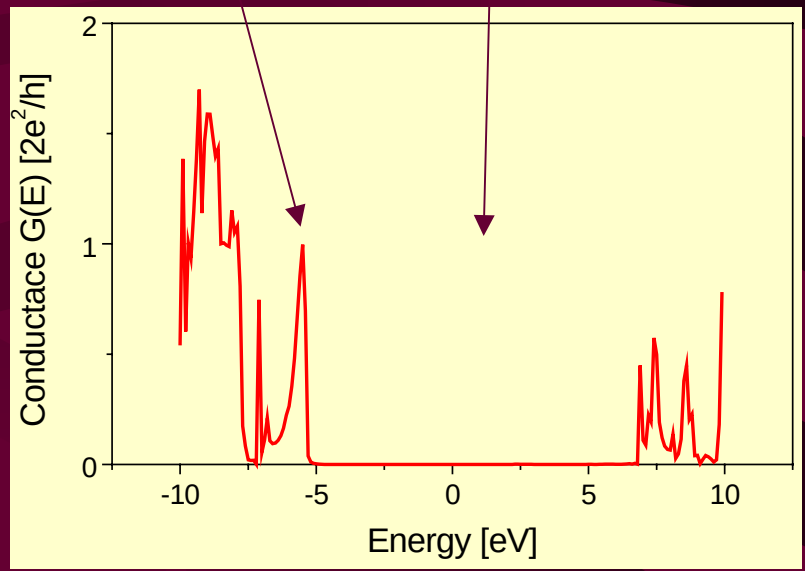
Illustrative example



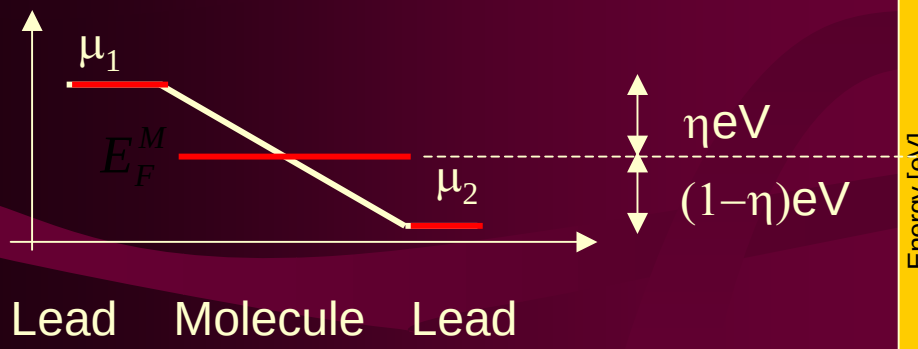
Transmission in diamond

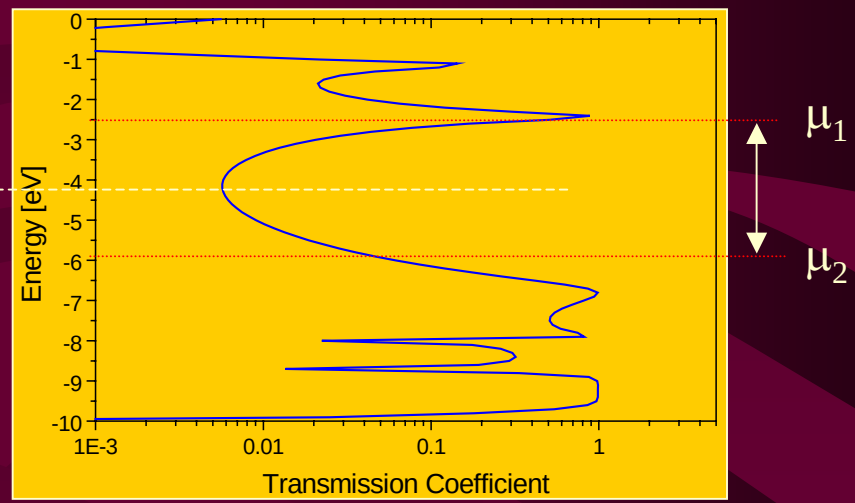
HOMO

Energy Gap



Simple approximation





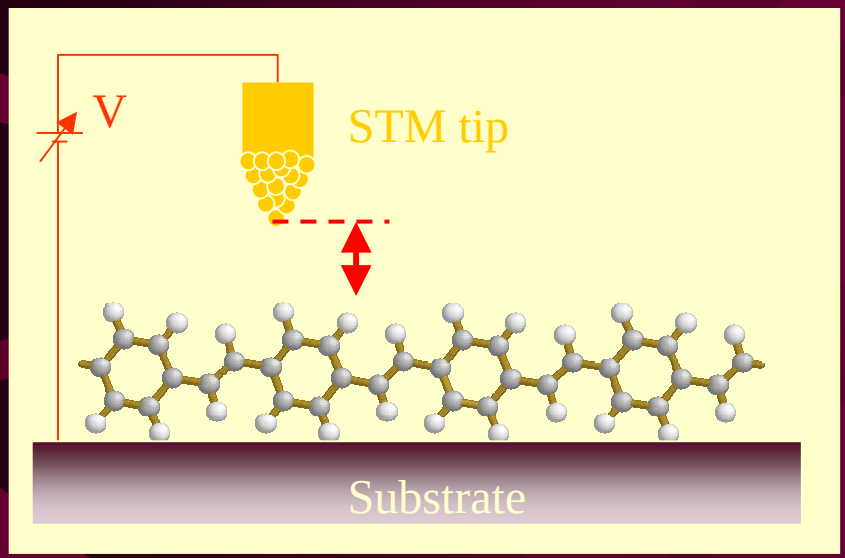
$$I(V,0K) = \frac{2e}{h} \int_{\mu_2(V)}^{\mu_1(V)} dE \; T(E)$$

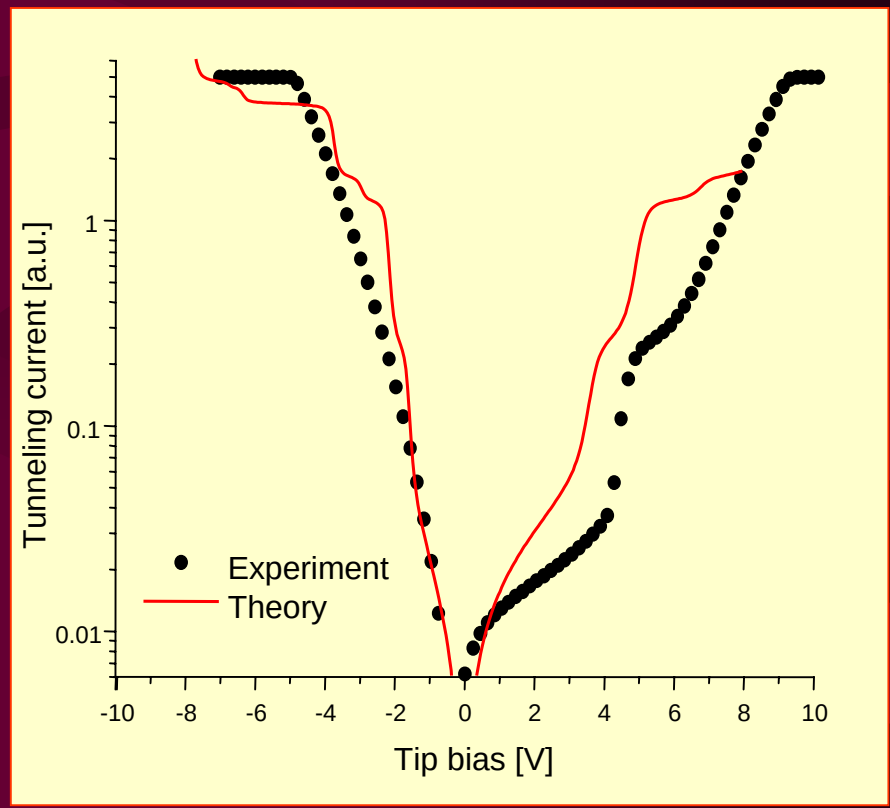
The transmission coefficient does not depend on V

Many simple calculations can be done alredy in this way

STM current in PPV

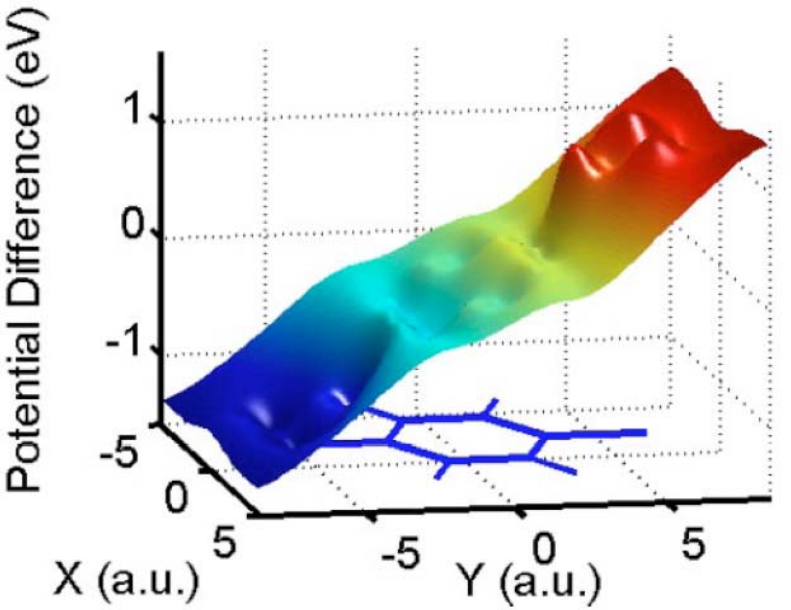
$$J(V) = \int_{-\infty}^{+\infty} dE\ T(E)\left[f\left(E-\mu_{tip}\right) - f\left(E-\mu_{sub}\right)\right]$$

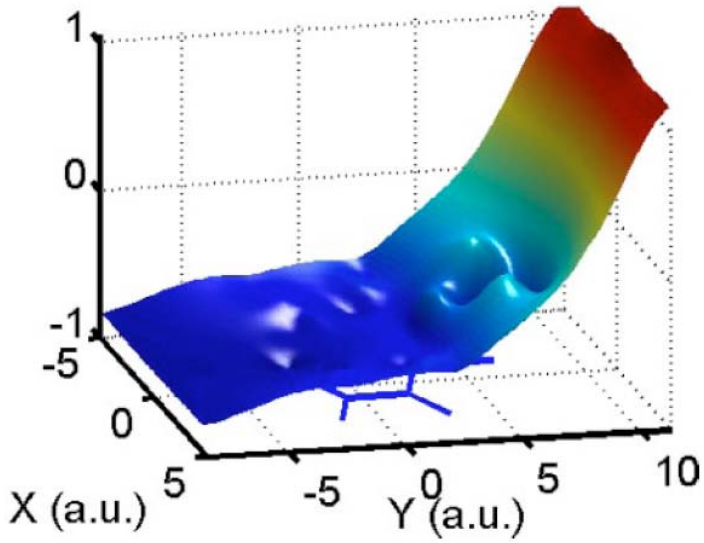


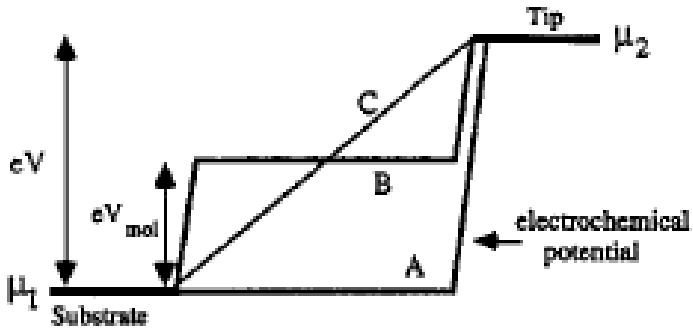


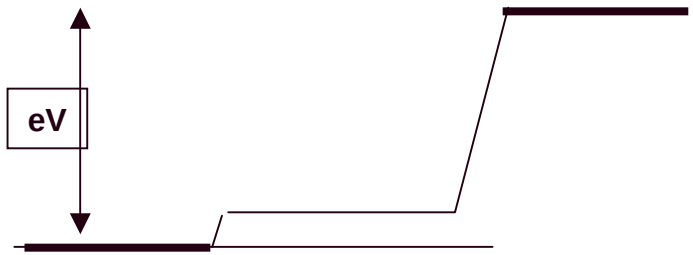
Rinaldi et al. PRB 63 076311 (2001)

Self-consistent potential







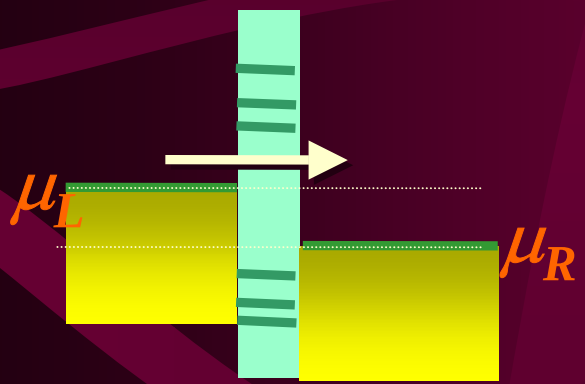


Non equilibrium density

The electrostatic potential can be included back into H

In order to compute V(r) we need the local $\rho(r)$

In the absence of scattering
We can build the n.e. density matrix



$$iG^{<}_{\mu\nu} = \rho^{L}_{\mu\nu} f_L(E) + \rho^{R}_{\mu\nu} f_R(E)$$

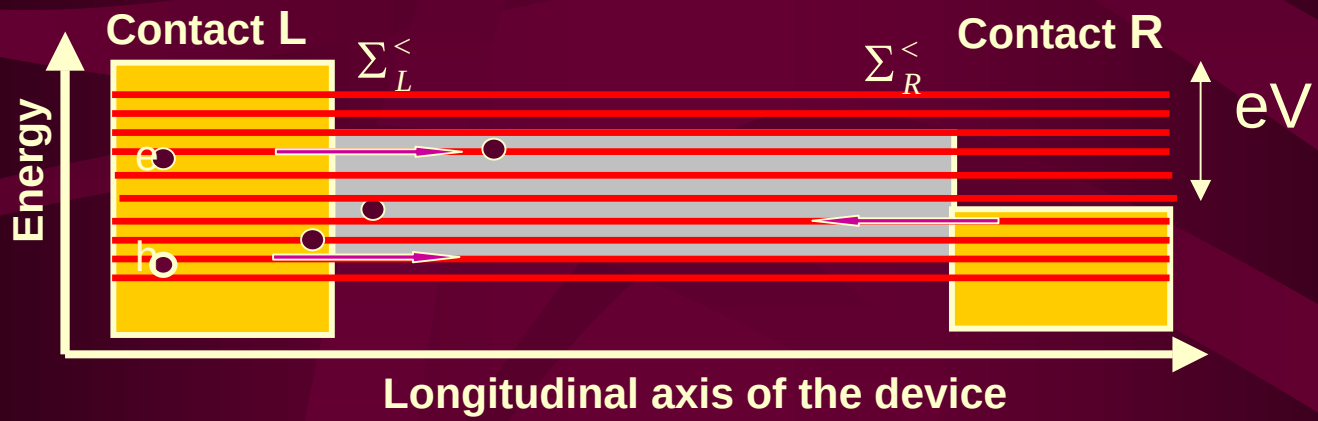
$$\rho_{\mu\nu} = \frac{1}{2\pi i}\int dE \; G^{<}_{\mu\nu}(E)$$ Density Matrix

Non-Equilibrium GF

Central result is the Kinetik equation:

$$G^{<}(E) = G^{r}(E)\Sigma^{<}(E)G^{a}(E)$$

$$G^{r}(E) = G_0^{r} + G_0^{r}\Sigma^{r}G^{r}$$



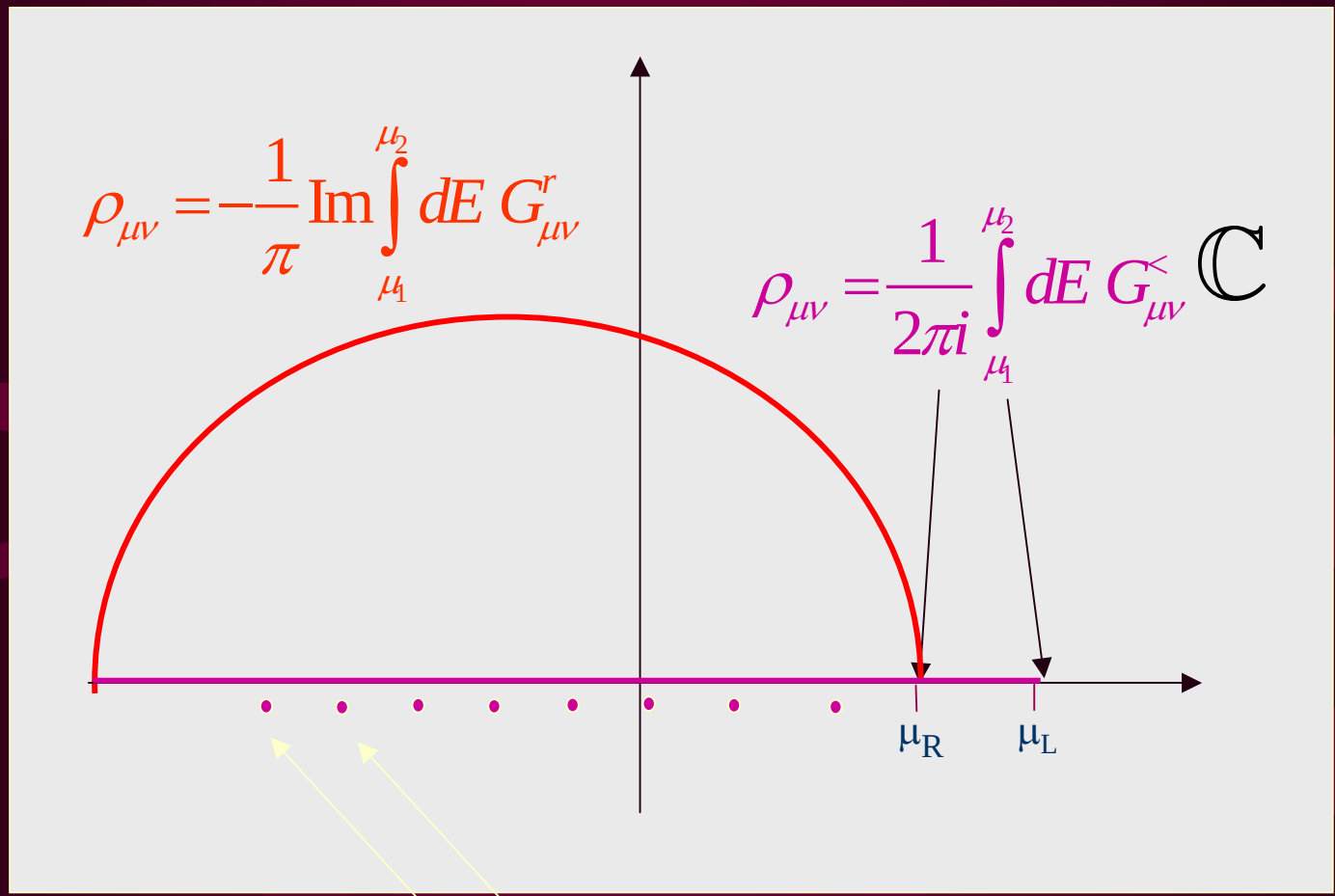
○ ⟷ $G^{>}$ **hole density**

$\Sigma^{<}$ **electron inscattering**

↑ ⟷ $G^{<}$ **electron density**

$\Sigma^{>}$ **hole inscattering**

Complex integration



Mulliken charges

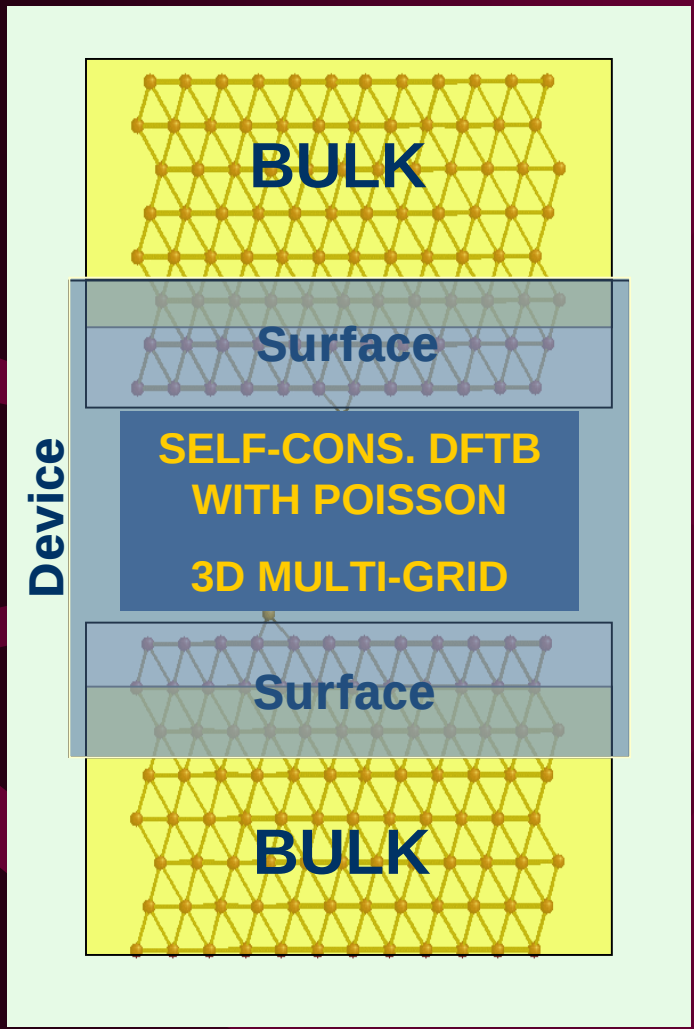
Mulliken charge is a projection of the LCAO wavefunctions on the atomic orbitals to get the total atomic charge

As in standard **equilibrium DFTB** we compute the Mulliken charges in order to build the II order functional

Now we use the non-equilibrium density matrix:

$$\Delta q_\mu = -e\left(\sum_\nu \rho_{\mu\nu} S_{\mu\nu} - q_\mu^0\right)$$

Poisson Equation



The Poisson's equation is solved with a 3D Multi-grid algorithm.

$$\delta n(r) = \sum_{\mu} \Delta q_{\mu} n_{\mu}(r)$$

Discretize in real space

This allows to solve complex boundary conditions (bias, gate)

$$\nabla^2 V = -4\pi\delta n$$

projection back in AO

Now we need to project the solution into the local basis set

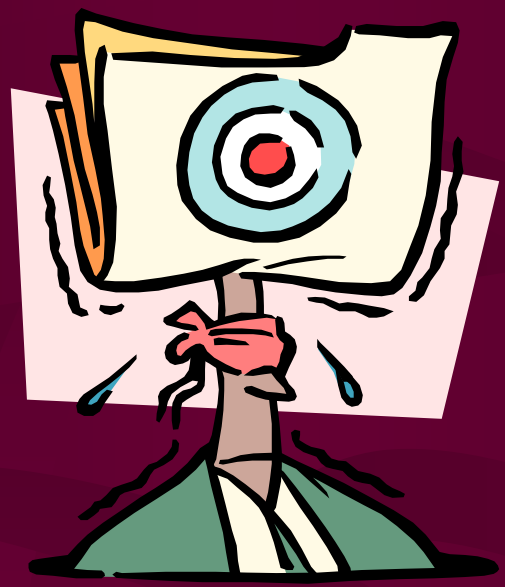
$$V_\mu = \iiint d^3 r V(r) n_\mu(r)$$

This can be viewed as an approximation of the rigorous matrix elements of V(r).

This is consistent with standard DFTB

$$H_{\mu\nu} = H^0_{\mu\nu} + \frac{1}{2} S_{\mu\nu}(V_\mu + V_\nu)$$

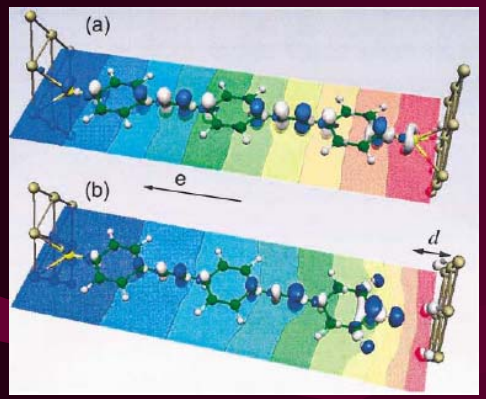
And now ?

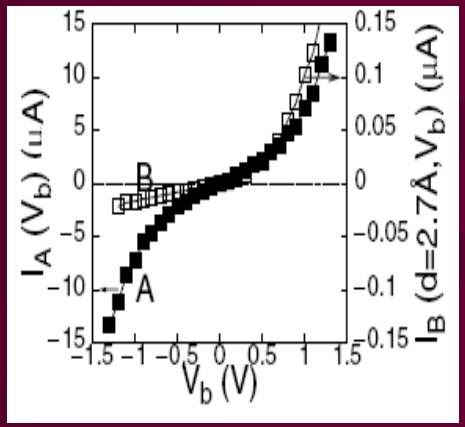


… Loop over and hope it converges …

Implementations of NEGF

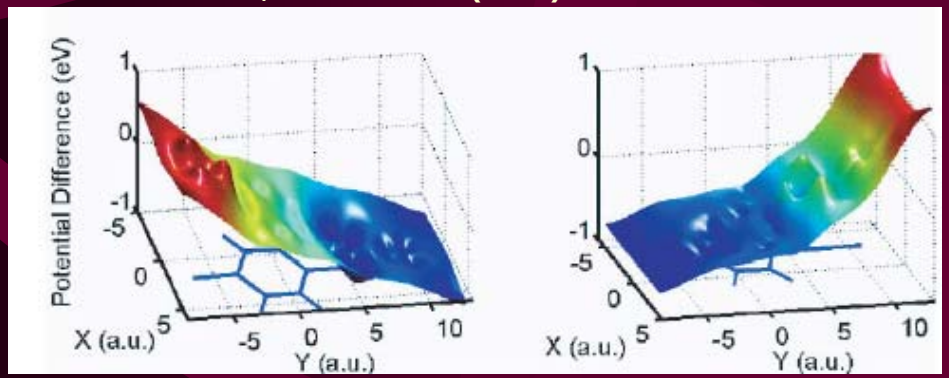
J. Taylor, M. Brandbyge, K. Stokbro, PRL 89 138301 (2002)





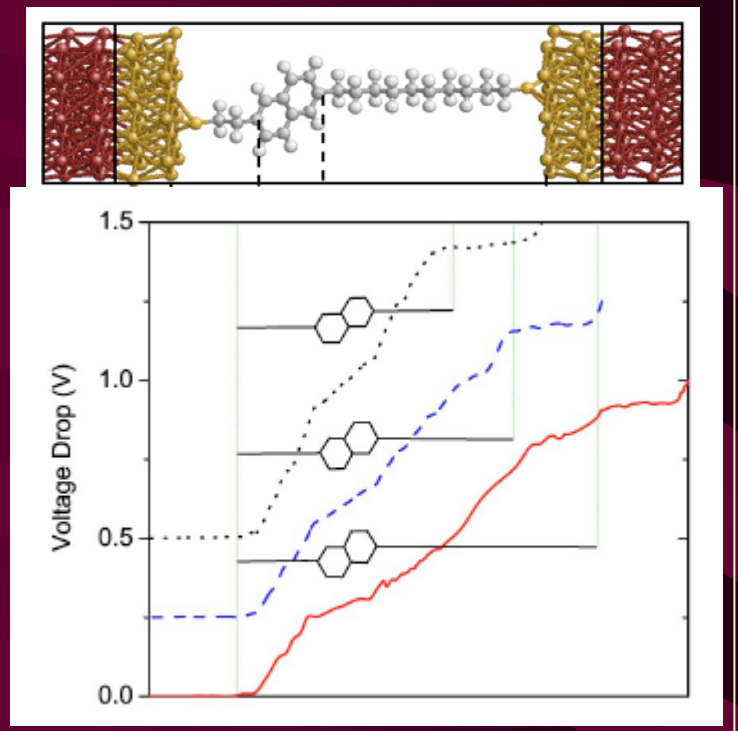
Implementation of NEGF on SIESTA

Xue and Ratner, PRB 115406 (2003)



Implementation of NEGF on DFT+GAUSSIAN

Larade and Bratkowski, PRB 68, 235305 (2003)



Ab-initio DFT with LCAO

Non-Equilibrium + scattering

Central result is the Kinetik equation:

$$G^{<}(E) = G^{r}(E)\Sigma^{<}(E)G^{a}(E)$$

$$G^{r}(E) = G_0^{r} + G_0^{r}\Sigma^{r}G^{r}$$

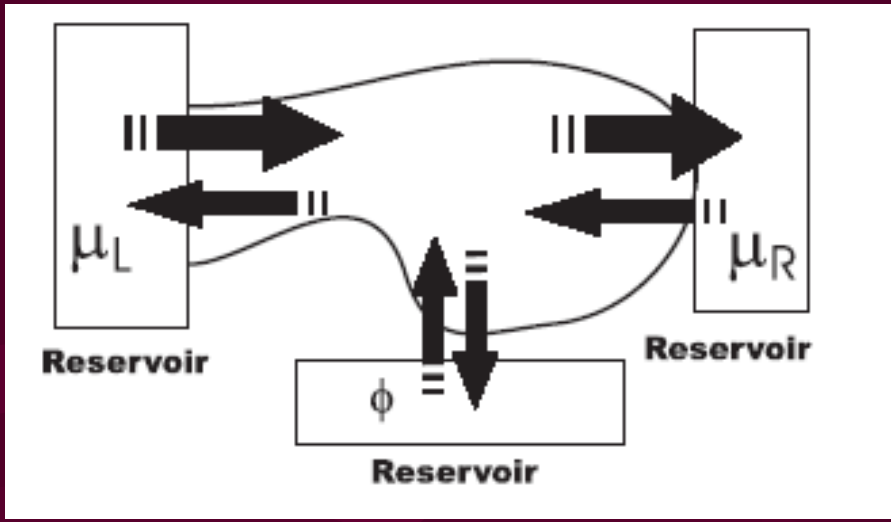
Self-cons. loop

$$\Sigma^{<}(E) = \Sigma_L{}^{<}(E) + \Sigma_R{}^{<}(E) + \Sigma^{<}_{scatt}(E)$$

$$\Sigma^{<}_{L,R}(E) = 2if_{L,R}(E)\,\mathrm{Im}\{\Sigma^{r}_{L,R}(E)\}$$

$$\Sigma^{<}_{el-ph}(E) = D \otimes G^{<}$$

contact currents



Density of empty states

Density of occupied states

Rate of electrons in

Rate of electrons out

$$I_\alpha = \frac{2e}{h}\int \mathrm{d}E\,\mathrm{Tr}\left[\Sigma_\alpha^<(E)G^>(E) - \Sigma_\alpha^>(E)G^<(E)\right],$$

$$I_\phi = \frac{2e}{h}\int \mathrm{d}E\,\mathrm{Tr}\left[\Sigma_\phi^<(E)G^>(E) - \Sigma_\phi^>(E)G^<(E)\right].$$

Should be 0 for current conservation

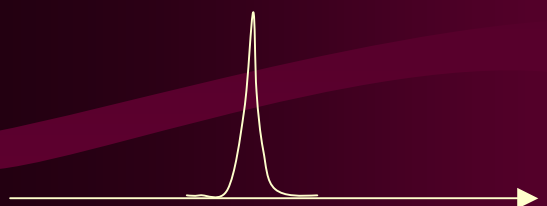
Coherent and incoh. Currents

$$i_{\alpha,\mathrm{coh}} = \frac{e}{h}\sum_{\beta}\int \mathrm{d}E\,\mathrm{Tr}\left[\Sigma_{\alpha}^{<}G^{\mathrm{r}}\Gamma_{\beta}G^{\mathrm{a}} - \Gamma_{\alpha}G^{\mathrm{r}}\Sigma_{\beta}^{<}G^{\mathrm{a}}\right],$$

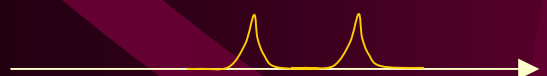
$$i_{\alpha,\mathrm{incoh}} = \frac{e}{h}\int \mathrm{d}E\,\mathrm{Tr}\left[\Sigma_{\alpha}^{<}G^{\mathrm{r}}\Sigma_{\phi}^{>}G^{\mathrm{a}} - \Sigma_{\alpha}^{>}G^{\mathrm{r}}\Sigma_{\phi}^{<}G^{\mathrm{a}}\right].$$

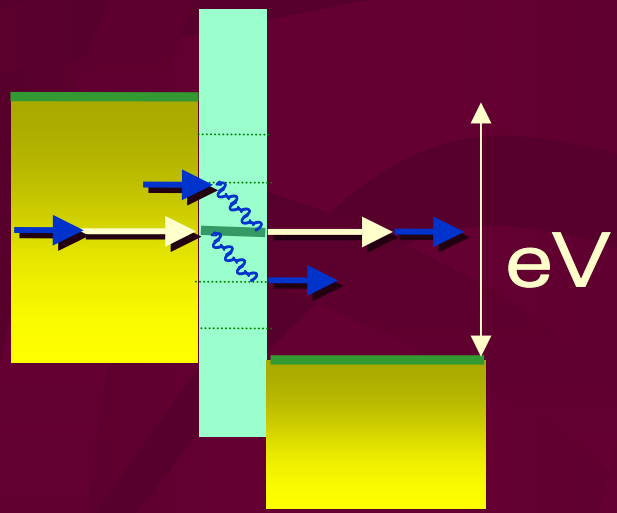
Contact L

coherent



incoherent

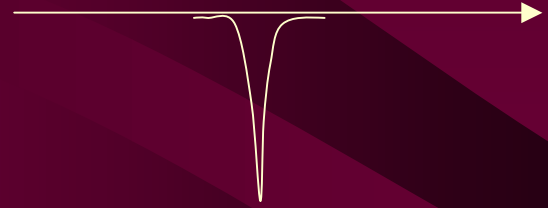




Virtual contact

Contact R

coherent



incoherent

Self-cositent Born approx.

Coherent decreases

Two, three phonon processes