Intro: Non-equilibrium Green function theory

Nick Papior

SIESTA School

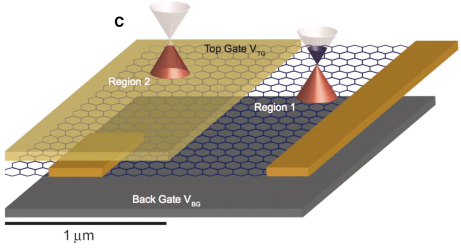
15 November 2024

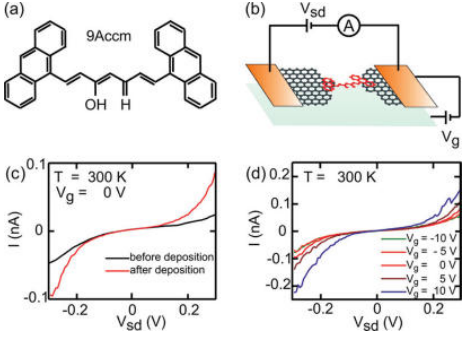
Outline

Motivation

Calculating transport properties of atomistic systems

Steady-state transport properties?



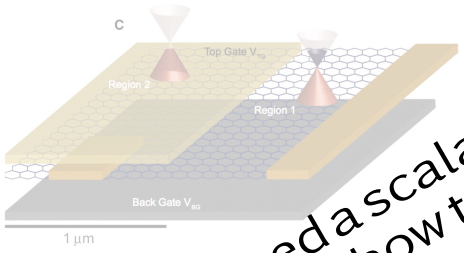


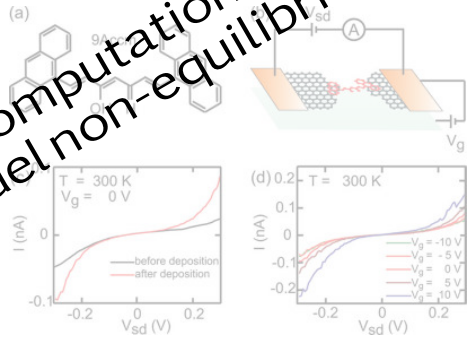
Williams *et.al.*: 10.1126/science.1144657

Prins *et.al.*: 10.1021/nl202065x

Calculating transport properties of atomistic systems

Steady-state transport properties?





We need a scalable computational model!
And . . . how to model non-equilibrium?

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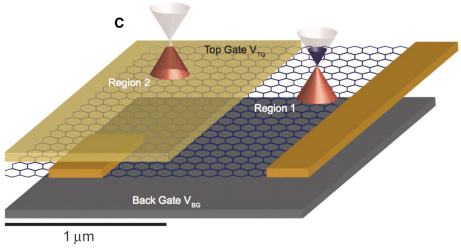
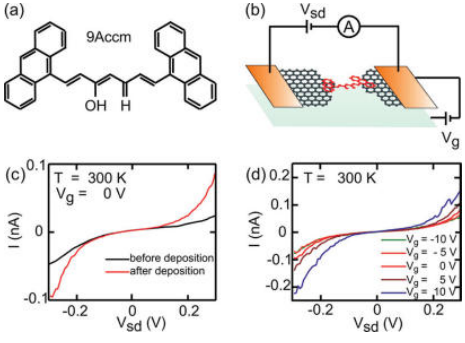
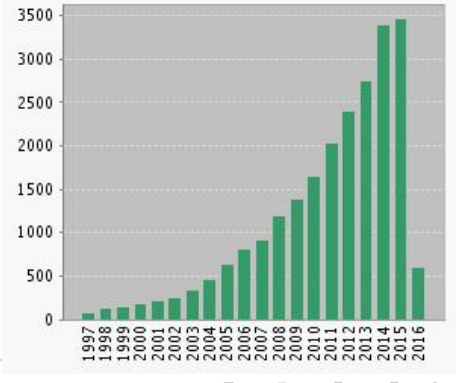




Simulation tool requirements

- Systems under non-equilibrium (applied bias)
- Large system calculations (incorporate full device)
- Multi-electrode devices

Non-Equilibrium Green function (NEGF)



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WebOfScience (NEGF)

Self-energy

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The concept

Self-energies – perturb the Hamiltonian

- A self-energy *renormalises* the Hamiltonian

$$\mathbf{H}' = \mathbf{H} + \Sigma$$

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- ! TBtrans allows custom (additional) self-energies, *even* when calculating transport from DFT Hamiltonians

Self-energy

Semi-infinity

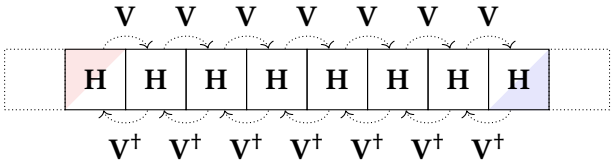
- Describes interaction of a system to a semi-infinite region
- Self-energy calculations *require* no more than nearest neighbour interactions between unit-cells

$$\Sigma_{\{1,1\}}(E) = \mathbf{V}^\dagger \left[E + i\eta - \mathbf{H} \right]^{-1} \mathbf{V}$$

$$\vdots$$

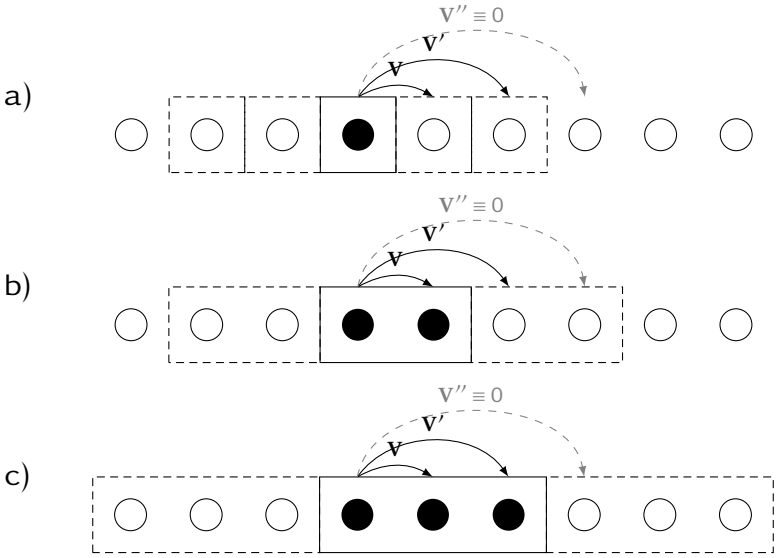
$$\Sigma_{\{i,1\}}(E) = \mathbf{V}^\dagger \left[E + i\eta - \mathbf{H} - \Sigma_{\{i-1,1\}}(E) \right]^{-1} \mathbf{V}$$

Continue until $\Sigma_{\{i,1\}} \approx \Sigma_{\{i+1,1\}}$



Self-energy

Semi-infinity – which unit-cells?



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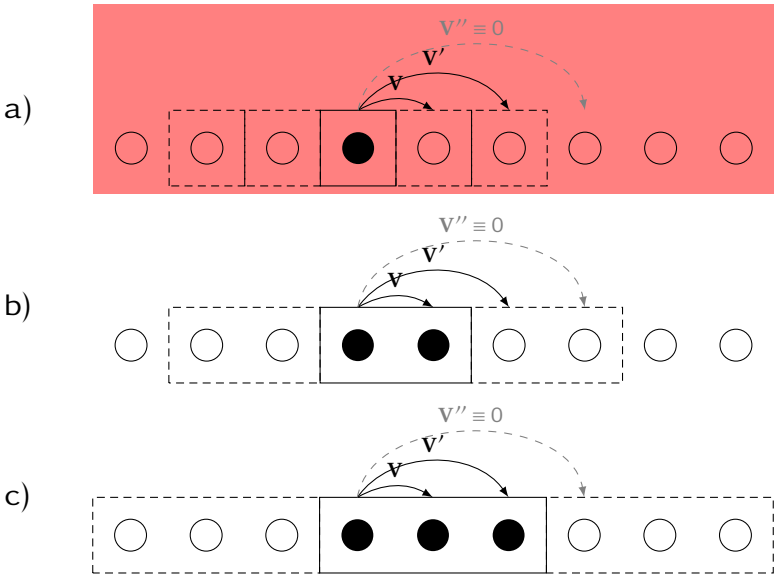

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Rules for using self-energies

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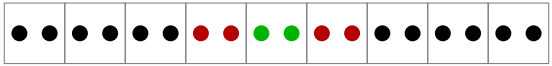

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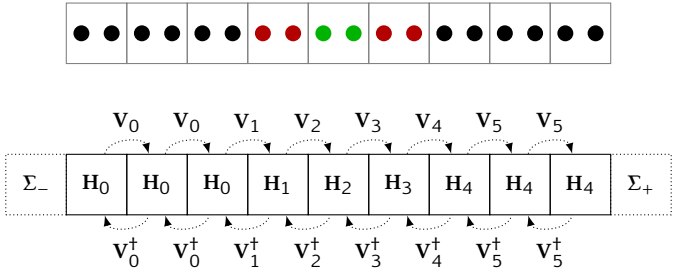

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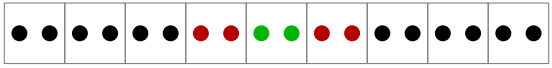

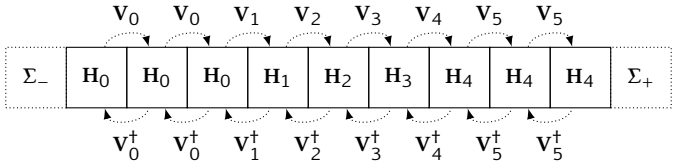

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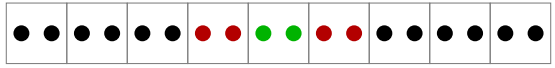

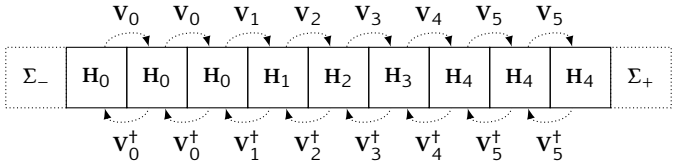

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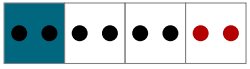

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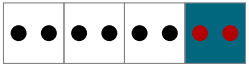

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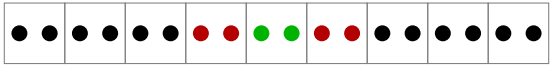

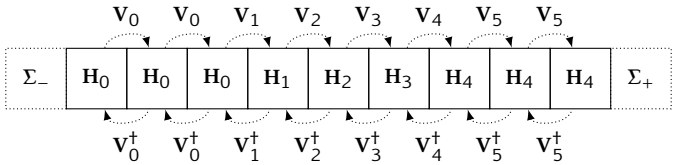

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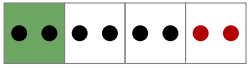

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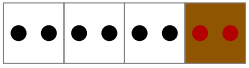

Green function theory

Green function

Introduction

- The single particle Green function may be written as:

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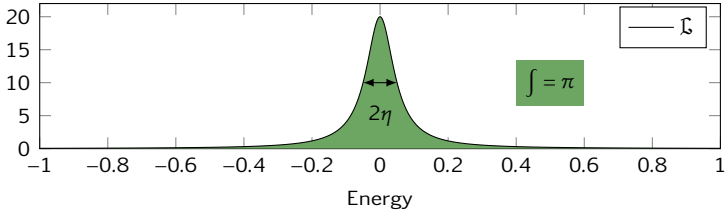

Numeric integration of Green function

$$\frac{-1}{\pi}\iint_{E'}^{E''} \mathrm{d}E\mathrm{d}\mathbf{k}\,\mathrm{Im}\mathbf{G}_{\mathbf{k}}(E) \approx \frac{-1}{\pi}\sum_{\mathbf{k}}\delta\mathbf{k}\sum_{j}^{(E''-E')/\delta E}\delta E\,\mathrm{Im}\mathbf{G}_{\mathbf{k}}(E'+j\delta E)$$

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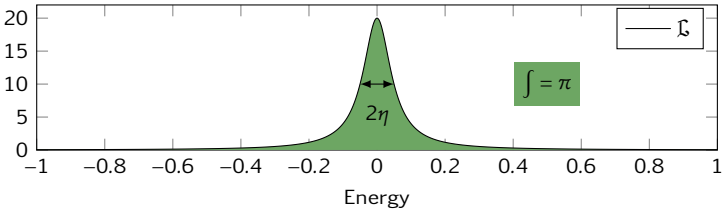

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  Good! The energy spacing is much smaller than FWHM.
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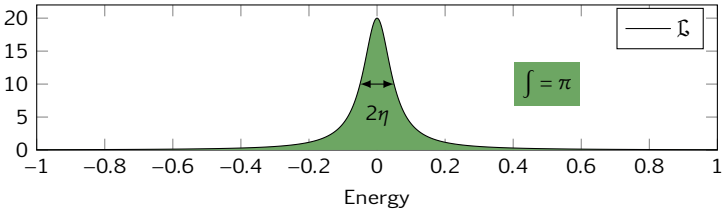
  Bad! The energy spacing is much larger than FWHM. Dependent on the initial E' you will find different DOS as some eigenstates may be passed.
- What if $\delta E \approx \eta$?
  Ok! The energy spacing is half-width at half-maximum. This will typically yield a fine integration.



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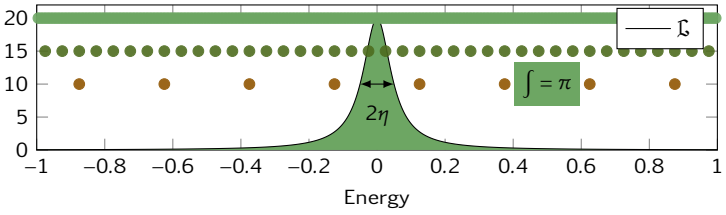

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- The Brillouin zone integration is just as important as the energy integration.
- Prior understanding of the electronic structure of the system is *important*!

Green function

Rules of integration – Brillouin Zone

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Difference between diagonalisation and Green function methods

Diagonalization	Green functions
1D-sampling	2D-sampling
k-points, all energy-eigenvalues	k and E-points are both required to be sampled

Advancing → NEGF

Single particle Green function

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Non-equilibrium Green function

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Additional terms:

- $\mathbf{S}$ is the *overlap matrix* which is needed for non-orthogonal basis sets.
- Σ is the *self-energy* which is describing semi-infinite directions (integrating out k in that direction)

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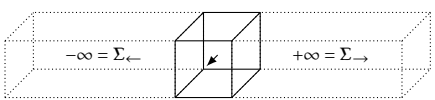

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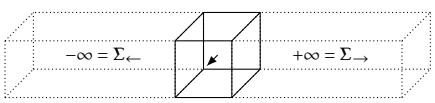

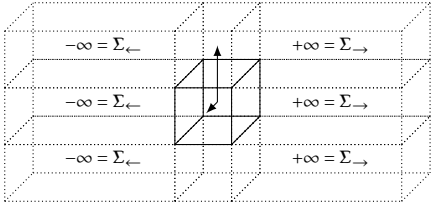

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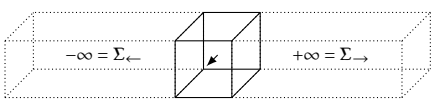
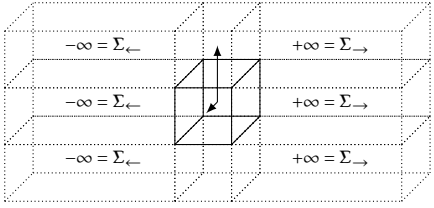
Additional terms:

- $\mathbf{S}$ is the *overlap matrix* which is needed for non-orthogonal basis sets.
- Σ is the *self-energy* which is describing semi-infinite directions (integrating out k in that direction)





- Self-energies have "large" imaginary components smearing the DOS for states coupled to the leads. The imaginary part (η) can thus often be neglected in the device region[a].

[a] Not for bound states.

Important

Understanding self-energies is like, really, really important.

Self-energy

Self-energies – perturb the Hamiltonian

- A self-energy *renormalises* the Hamiltonian

$$\mathbf{H}' = \mathbf{H} + \Sigma$$

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  - Absorbing potentials
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Self-energy

The concept

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- TranSiesta, self-energies are *only* semi-infinite leads
- ! TBtrans allows custom (additional) self-energies, *even* when calculating transport from DFT Hamiltonians

Self-energy

Semi-infinity

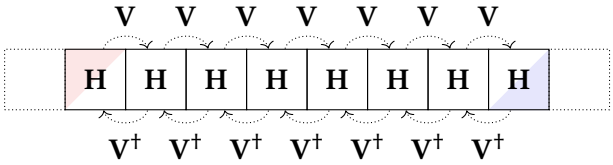
- Describes interaction of a system to a semi-infinite region
- Self-energy calculations *require* no more than nearest neighbour interactions between unit-cells

$$\Sigma_{\{1,1\}}(E) = \mathbf{V}^\dagger \left[E + i\eta - \mathbf{H} \right]^{-1} \mathbf{V}$$

$$\vdots$$

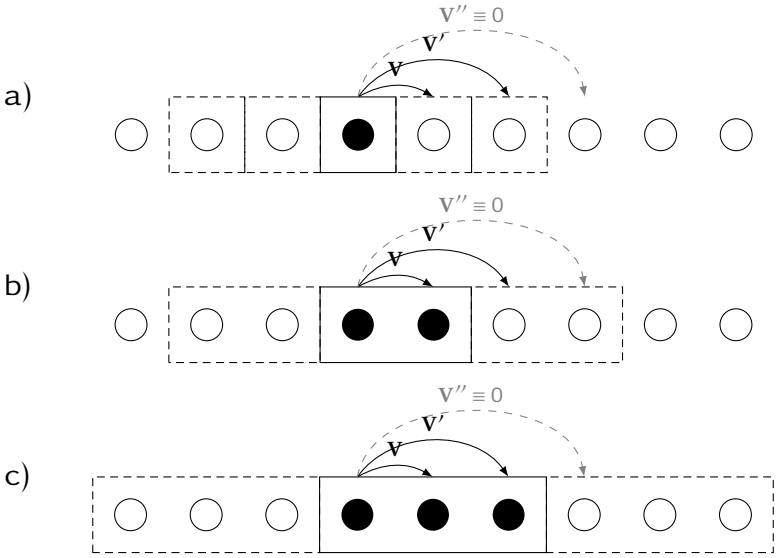
$$\Sigma_{\{i,1\}}(E) = \mathbf{V}^\dagger \left[E + i\eta - \mathbf{H} - \Sigma_{\{i-1,1\}}(E) \right]^{-1} \mathbf{V}$$

Continue until $\Sigma_{\{i,1\}} \approx \Sigma_{\{i+1,1\}}$



Self-energy

Semi-infinity – which unit-cells?



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Self-energy

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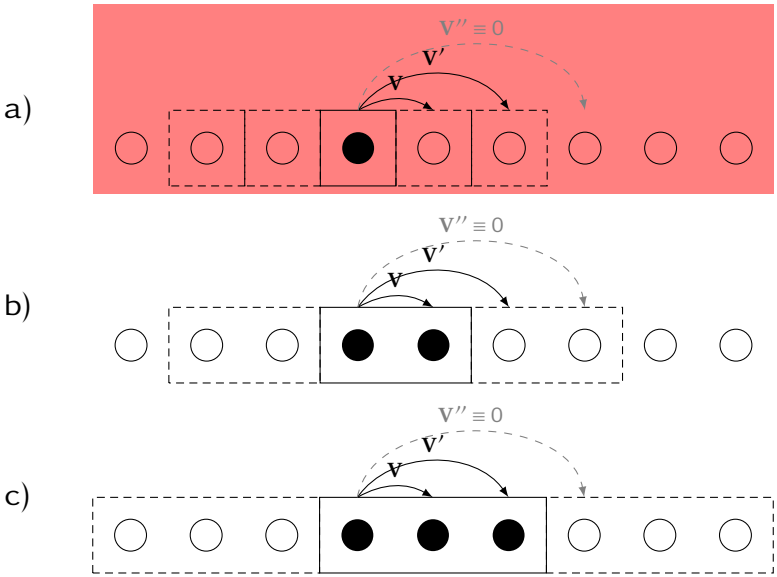

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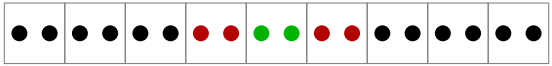
Rules for using self-energies

Coupling a *bulk* electrode to a device requires(!) coupling region to behave *bulk* as well.



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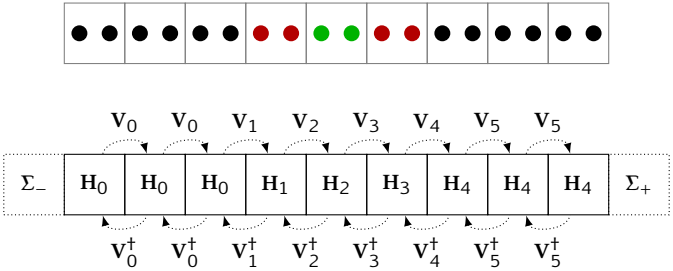

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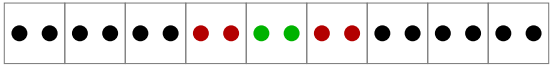

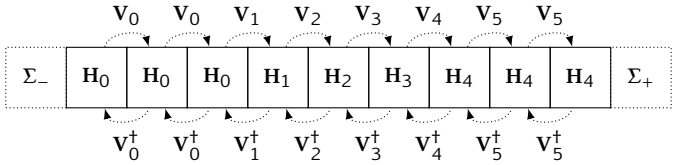

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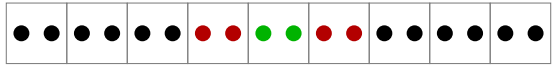

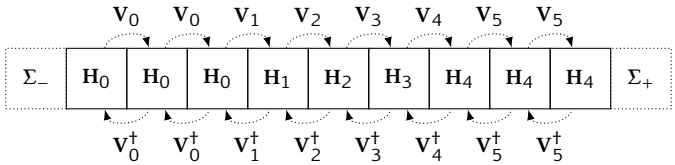

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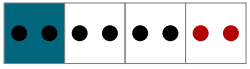

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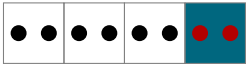

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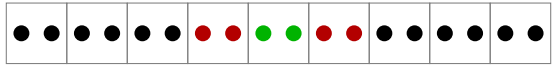

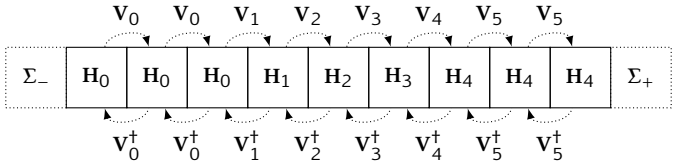

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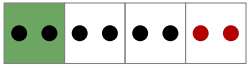

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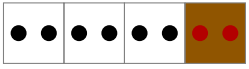

Non-equilibrium Green function

Non-equilibrium Green function

Variables

Important variables in Green function techniques

$\mathfrak{e}$	electrode index
$\mathbf{H_k}$	Hamiltonian
$\mathbf{S_k}$	Overlap, for orthogonal basis sets equals $\mathbf{I}$
$\boldsymbol{\rho}_\mathbf{k}$	Density matrix
$\boldsymbol{\Sigma}_\mathbf{k}(\epsilon)$	Self-energy (not necessarily an electrode!)
$\boldsymbol{\Gamma}_{\mathfrak{e},\mathbf{k}}(\epsilon)$	Scattering matrix from $\mathfrak{e}$
$\mathbf{G}_\mathbf{k}(\epsilon)$	Green function
$\mathcal{A}_{\mathfrak{e},\mathbf{k}}(\epsilon)$	Spectral function originating from $\mathfrak{e}$
$\mathcal{T}_{\mathfrak{e}\to\mathfrak{e}'}(\epsilon)$	Transmission function from $\mathfrak{e}$ to $\mathfrak{e}'$
$\mathcal{T}_\mathfrak{e}(\epsilon)$	Total transmission function out of $\mathfrak{e}$

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Basic equations for Green function techniques

$$\mathbf{G_k}(\epsilon) = \left[(\epsilon + i\eta)\mathbf{S_k} - \mathbf{H_k} - \sum_\mathfrak{e} \boldsymbol{\Sigma}_{\mathfrak{e},\mathbf{k}}(\epsilon - \mu_\mathfrak{e})\right]^{-1}$$

$$\boldsymbol{\Gamma}_{\mathfrak{e},\mathbf{k}}(\epsilon) = i\left(\boldsymbol{\Sigma}_{\mathfrak{e},\mathbf{k}}(\epsilon - \mu_\mathfrak{e}) - \boldsymbol{\Sigma}^\dagger_{\mathfrak{e},\mathbf{k}}(\epsilon - \mu_\mathfrak{e})\right)$$

$$\mathcal{A}_{\mathfrak{e},\mathbf{k}}(\epsilon) = \mathbf{G_k}(\epsilon)\boldsymbol{\Gamma}_{\mathfrak{e},\mathbf{k}}(\epsilon)\mathbf{G}^\dagger_\mathbf{k}(\epsilon)$$

- Density of states over all orbitals

$$\mathrm{DOS}(\epsilon) = \mathrm{Tr}[\boldsymbol{\rho}(\epsilon)\mathbf{S}]$$
$$\mathrm{DOS}(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}[\mathbf{G}(\epsilon)\mathbf{S}]$$
$$\mathrm{ADOS}(\epsilon) = \frac{1}{2\pi}\,\mathfrak{Re}\,\mathrm{Tr}[\mathcal{A}_{\mathfrak{c}}(\epsilon)\mathbf{S}]$$
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Go to Rules of integration

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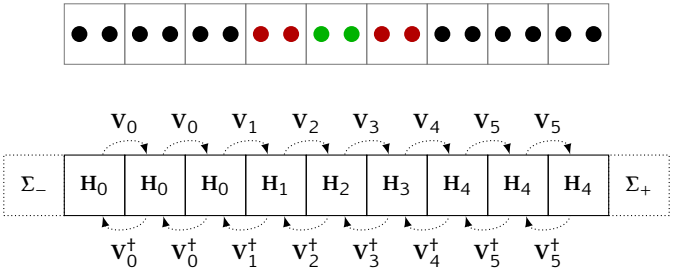
- The overlap matrix is extremely important when calculating the density of states!
- Σ broadens the DOS similarly to a large η value, for states coupling to the electrodes

Creating a benzene dithiol (BDT) geometry

Reiterate self-energy requirements

Rules for using self-energies

Coupling a *bulk* electrode to a device requires(!) coupling region to behave *bulk* as well.

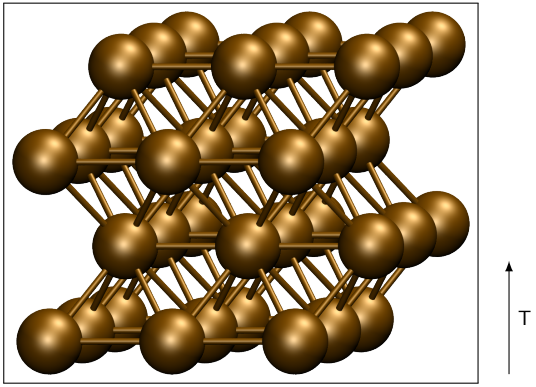


- Remember that $\Sigma_{-/+}$ is a correction to the Hamiltonian (i.e. $\mathbf{H}' = \mathbf{H} + \Sigma$)
- *Extremely* important in TranSiesta, electrostatics are long-range!

Benzene dithiol (BDT)

Electrode

- BDT attached to Gold electrodes
- We utilise 100 surface (AB-stacking)
- Converge k-point sampling in transverse direction



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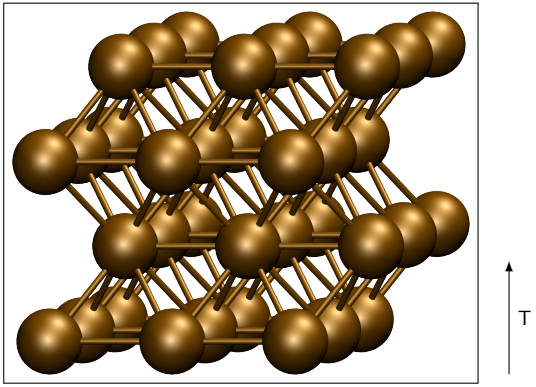

Is there anything special about this electrode?

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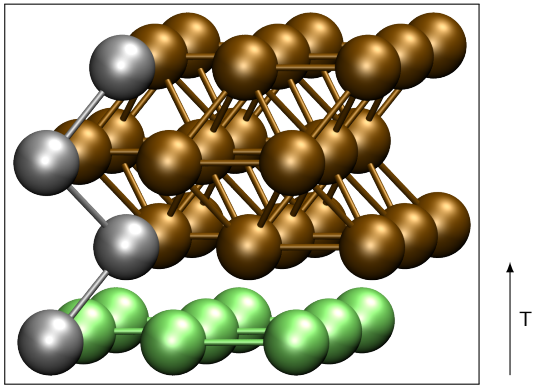

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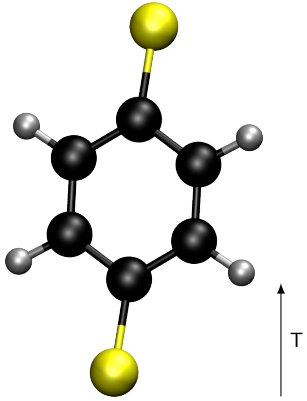
Benzene dithiol (BDT)

Define the molecule

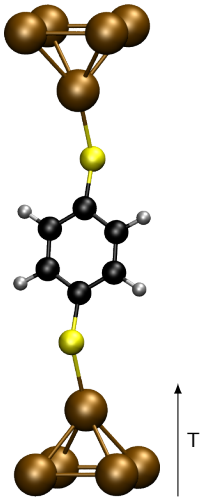


- Relax structure using SIESTA

Benzene dithiol (BDT)

Intermediate connect

Attach gold to the molecule

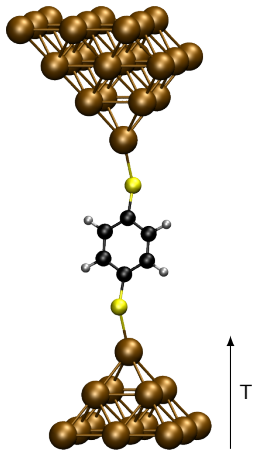


- Consider stacking of *pyramids*
  - A-BDT-A
  - A-BDT-B
  - B-BDT-B
- Relax structure *again*, constrain the *pyramids*

Benzene dithiol (BDT)

Intermediate electrode layers

Attach a couple of electrode layers

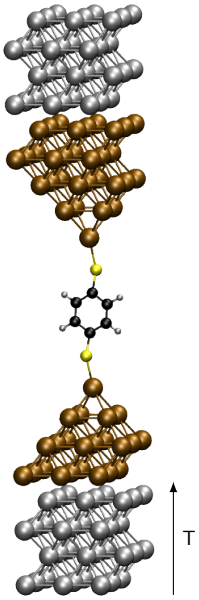


- *Follow* the stacking!
- Relax structure *again*, constrain the *electrode layers*

Benzene dithiol (BDT)

Attach electrode and more intermediate layers

Attach the electrodes on both sides (converge number of intermediate layers), use Bloch's theorem(!)



- *Follow* the stacking!
- Relax structure *again*, constrain the *electrode layers*
- Determining the extra number of layers:
  - Consider the molecule as a "defect"
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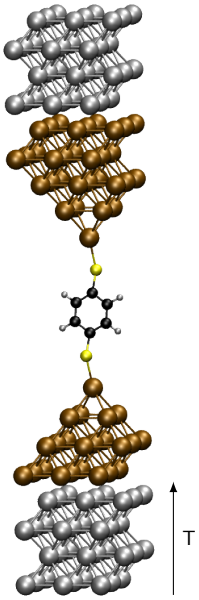

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  1. Bad screening → many extra electrode layers
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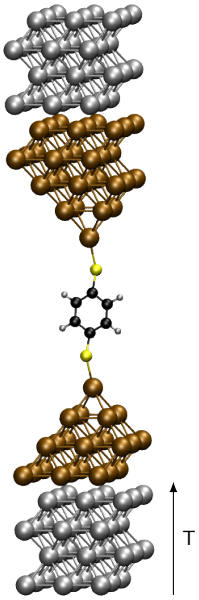

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DTU

Tutorial

- Tutorial focuses on *interpreting physical* things, such as potential drop, projected density of states
- More tutorials are available here:
  `https://github.com/zerothi/ts-tbt-sisl-tutorial`
- Doing this tutorial can be hard on Marenostrum (requires copying data back to your PC). Please use Google colab or your own computer.
- On the Discord channel in Day 5, you will find the link to the tutorial.