TranSiesta an intro to non-equilibrium Green function

Nick Papior

SIESTA School

21 November 2025

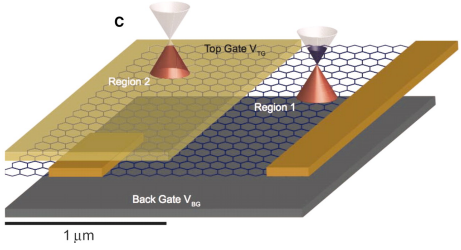
Outline

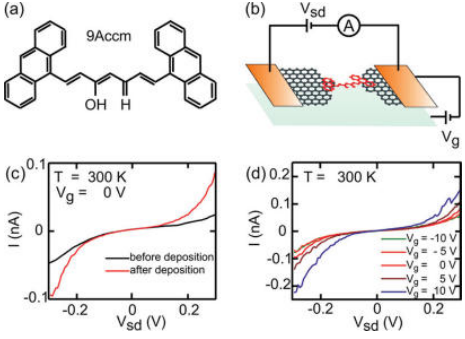
DTU

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

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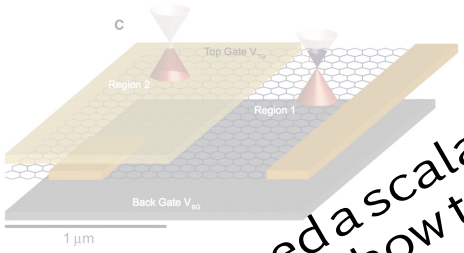

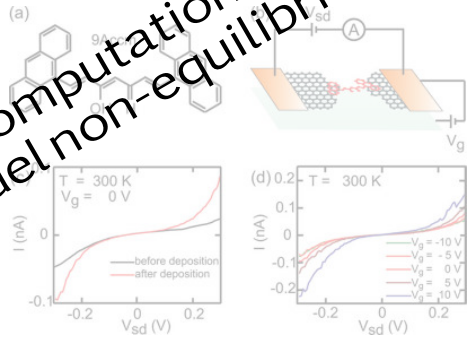

We need a scalable computational model!
And . . . how to model non-equilibrium?

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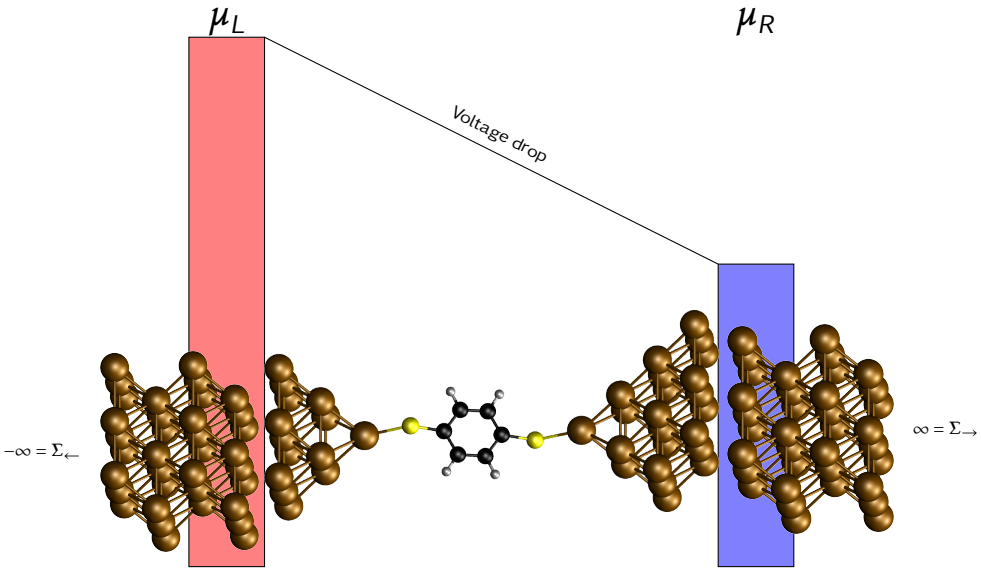
What do we want?

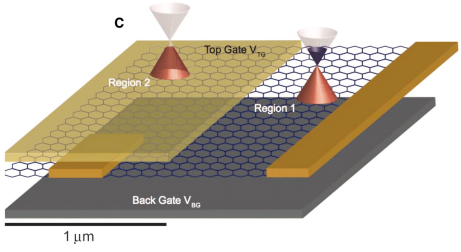
Applying a bias to a system

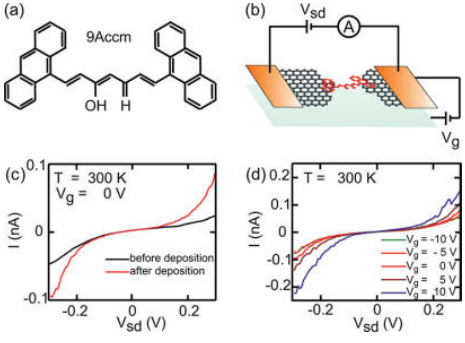


In a periodic simulation box!

Calculating transport properties of atomistic systems

Steady-state transport properties?

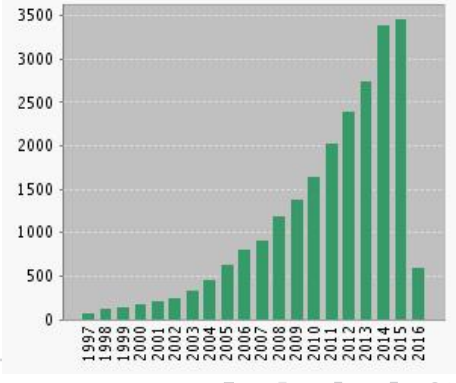




Simulation tool requirements

- 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)

Green function theory

Green function

Introduction

- The single particle Green function may be written as:

$$[(E + i\eta)\mathbf{I} - \mathbf{H_k}]\mathbf{G_k}(E) = \mathbf{I}$$

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$$\mathbf{G}_\mathbf{k}(E)=\sum_i \frac{|\psi_{i,\mathbf{k}}\rangle\langle\psi_{i,\mathbf{k}}|}{E+i\eta-\epsilon_{i,\mathbf{k}}}$$

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- Taking the imaginary part of the Green function yields

$$\mathrm{Im}\,\mathbf{G}_\mathbf{k}(E)=-\sum_i |\psi_{i,\mathbf{k}}|^2 \mathfrak{L}_{i,\mathbf{k}}(E)$$

$$\mathfrak{L}_{i,\mathbf{k}}(E)=\frac{\eta}{(E-\epsilon_{i,\mathbf{k}})^2+\eta^2}$$

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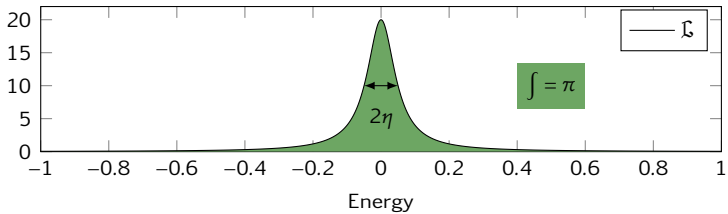

Numeric integration of Green function

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

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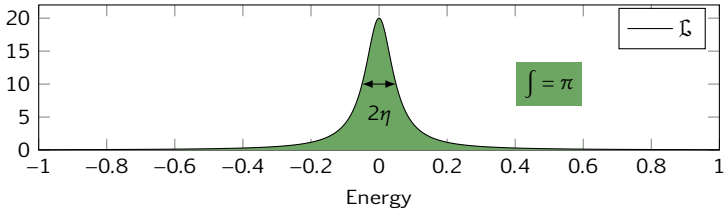
Are there any problems here?

- What if $\delta E \ll \eta$?
- What if $\delta E \gg \eta$?
- What if $\delta E \approx \eta$?



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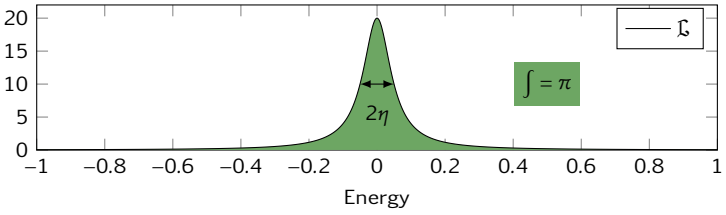
- What if $\delta E \ll \eta$?
  Good! The energy spacing is much smaller than FWHM.
- What if $\delta E \gg \eta$?
  Bad! The energy spacing is much larger than FWHM. Dependent on the initial E' you will find different DOS as some eigenstates may be passed.
- What if $\delta E \approx \eta$?
  Ok! The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



Return to DOS

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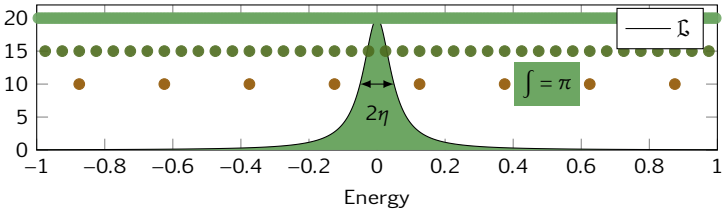

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- Prior understanding of the electronic structure of the system is *important*!

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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

$$[(E + i\eta)\mathbf{I} - \mathbf{H_k}]\mathbf{G_k}(E) = \mathbf{I}$$

Non-equilibrium Green function

$$[(E + i\eta)\mathbf{S} - \mathbf{H_k} - \sum_{\mathfrak{c}} \Sigma_{\mathfrak{c},\mathbf{k}}(E - \mu_{\mathfrak{c}})]\mathbf{G_k}(E) = \mathbf{I}$$

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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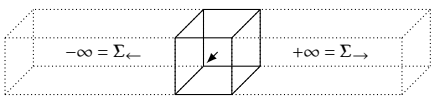

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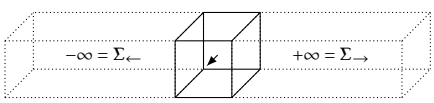

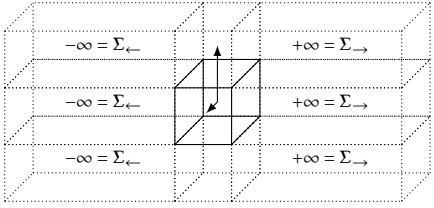

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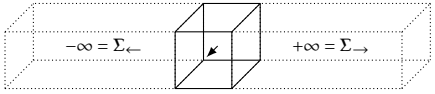

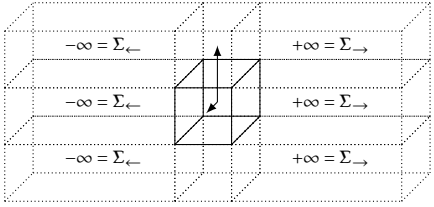

- Self-energies have "large" imaginary components smearing the DOS for states coupled to the leads. The imaginary part (η) can thus often be neglected in the device region[a].

[a] Not for bound states.

Self-energy

Self-energy

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

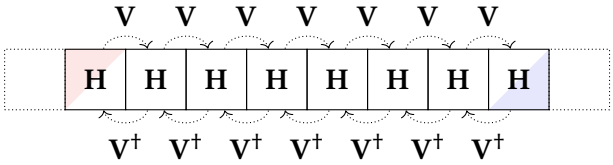
- Describes interaction of a system to a semi-infinite region
- Self-energy calculations *require* no more than nearest neighbor interactions between unit-cells

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

$$\vdots$$

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

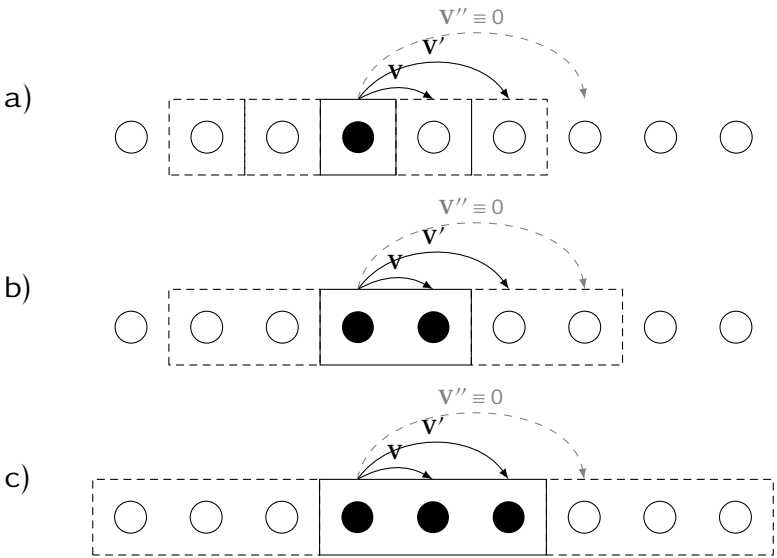
Continue until $\Sigma_{\{i,1\}} \approx \Sigma_{\{i+1,1\}}$



Self-energy

Semi-infinity – which unit-cells?

Self-energy calculations require no more than nearest neighbor interactions along the semi-infinite direction.



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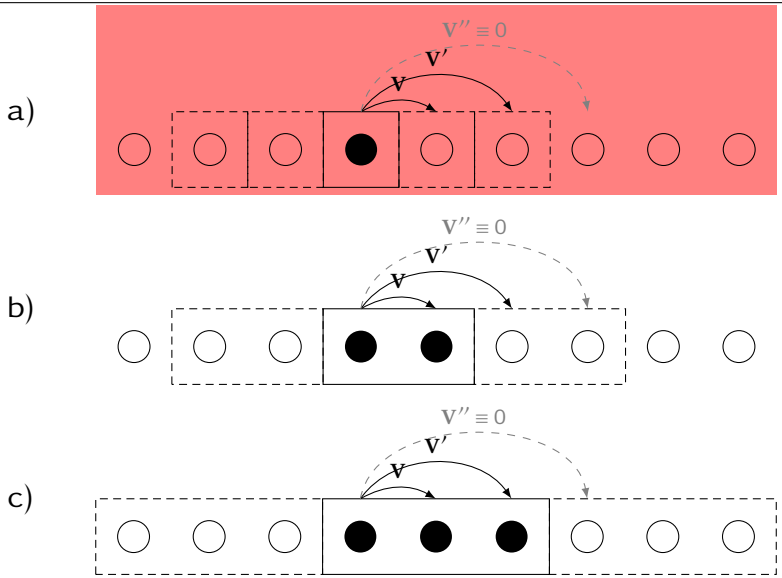

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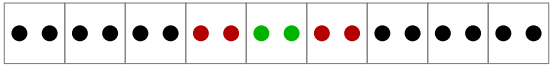
Rules for using self-energies

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



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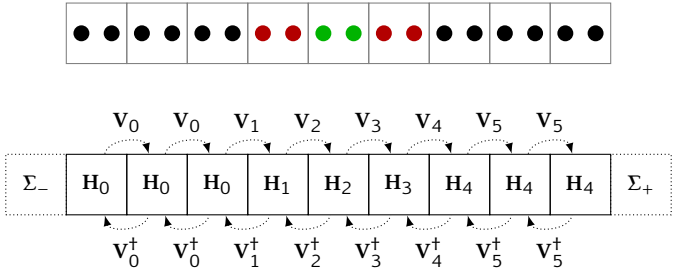

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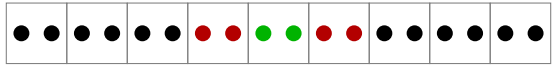

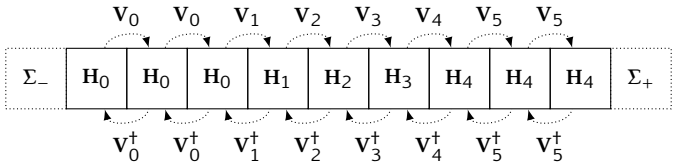

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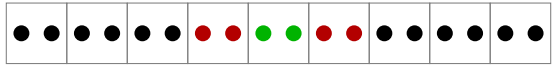

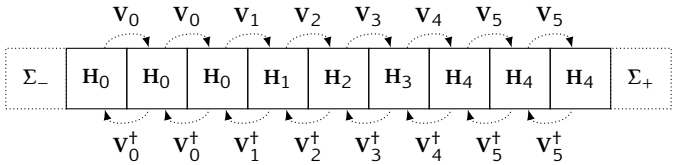

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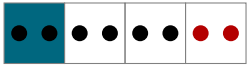
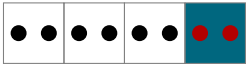


- Σ_- into 2nd $\mathbf{H}_0$?

- Σ_- into 3rd $\mathbf{H}_0$?

- Σ_- into $\mathbf{H}_1$?



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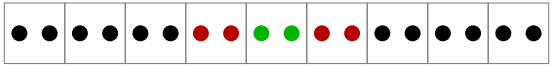
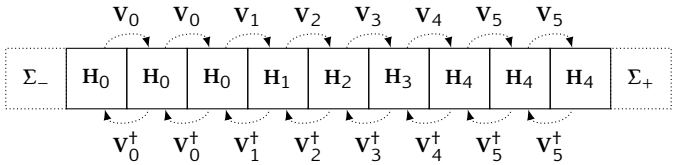
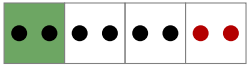




- Remember that $\Sigma_{-/+}$ is a correction to the Hamiltonian (i.e. $\mathbf{H}' = \mathbf{H} + \Sigma$)

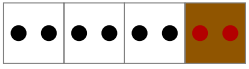
- Σ_- into 1st $\mathbf{H}_0$?



- Σ_- into 2nd $\mathbf{H}_0$?

- Σ_- into 3rd $\mathbf{H}_0$?

- Σ_- into $\mathbf{H}_1$?



Important

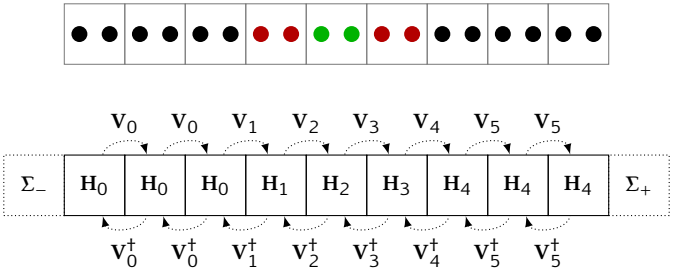
Understanding self-energies is like, really, really important.

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.

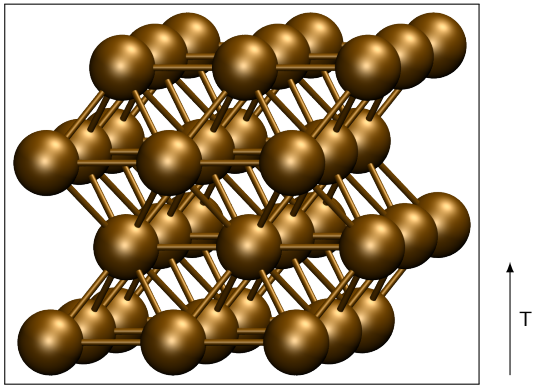


- Remember that $\Sigma_{-/+}$ is a correction to the Hamiltonian (i.e. $\mathbf{H}' = \mathbf{H} + \Sigma$)
- *Extremely* important in TranSiesta, electrostatics are long-range!

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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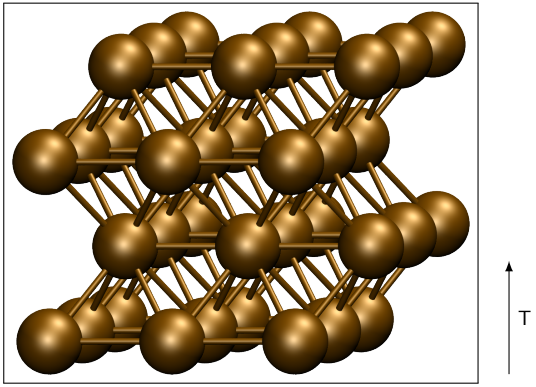

Is there anything special about this electrode?

Benzene dithiol (BDT)

Electrode

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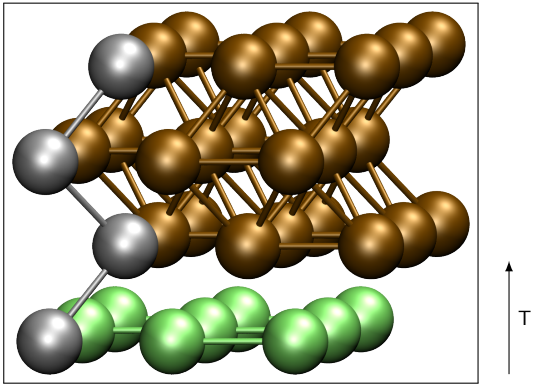
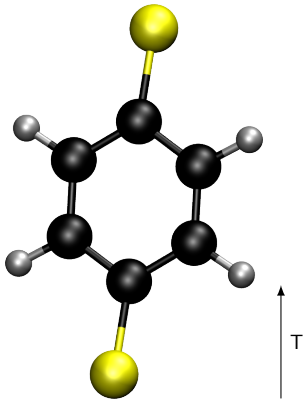


Is there anything special about this electrode?

Benzene dithiol (BDT)

Define the molecule

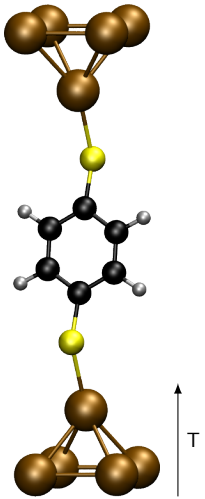


- Relax structure using SIESTA

Benzene dithiol (BDT)

Intermediate connect

Attach gold to the molecule

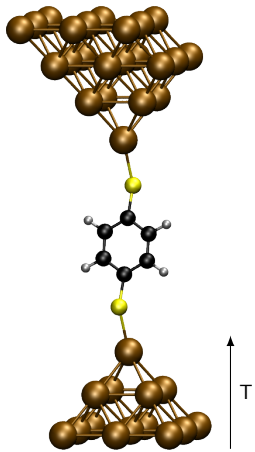


- Consider stacking of *pyramids*
  - A-BDT-A
  - A-BDT-B
  - B-BDT-B
- Relax structure *again*, constrain the *pyramids*

Benzene dithiol (BDT)

Intermediate electrode layers

Attach a couple of electrode layers

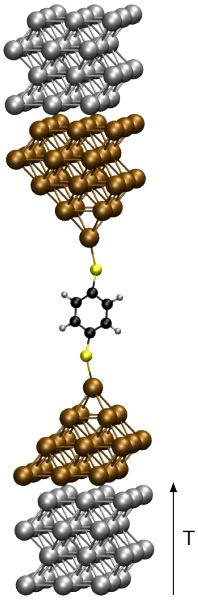


- *Follow* the stacking!
- Relax structure *again*, constrain the *electrode layers*

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"
  - The defect has a screening length in the central region (the extra electrode layers)
  - Ensure that the electrodes "behave as bulk" electrodes (away from defect)

Benzene dithiol (BDT)

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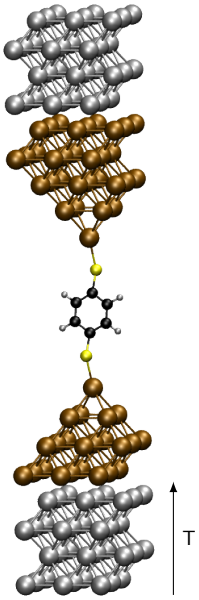

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  - The defect has a screening length in the central region (the extra electrode layers)
  - Ensure that the electrodes "behave as bulk" electrodes (away from defect)
- What does a metallic electrode require:
  1. Bad screening → many extra electrode layers
  2. Good screening → few extra electrode layers
- What does a semi-conducting electrode require:
  1. Bad screening → many extra electrode layers
  2. Good screening → few extra electrode layers

Benzene dithiol (BDT)

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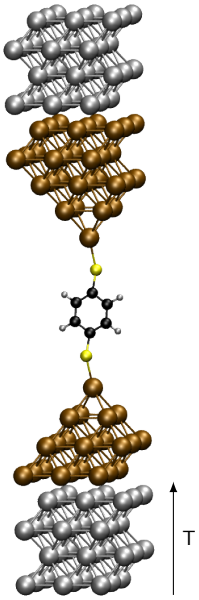

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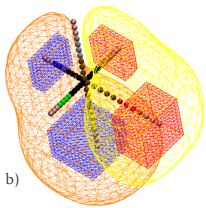
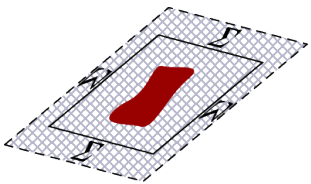
DTU

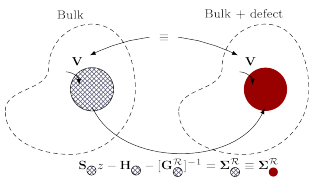
TranSiesta / TBtrans

- TranSiesta is a versatile and complex beast! There are *many* pitfalls, mainly because of the *self energy*.
  TranSiesta calculates the non-equilibrium *density* and *Hamiltonian* matrices.
- Start by converging parameters in plain Siesta calculations; then converge TranSiesta parameters, layers of electrodes (screening off the defect), energy points, etc.
- TBtrans (transmission function calculator) requires much finer $\mathbf{k}$ point sampling (recall slide 9 and 10)
  TBtrans uses a *Hamiltonian* matrix (e.g. a non-equilibrium) and can calculate (projected) density of states, transmissions, etc.
- One can do $N_\mathfrak{C} \geq 1$ electrodes!



- Completely removing periodic images possible:





Papior *et.al.*: 10.1103/PhysRevB.100.195417

Tutorials

There are additional tutorials covering NEGF using `sisl` on this web-page:
`https://github.com/zerothi/ts-tbt-sisl-tutorial`