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<https://www.uni-regensburg.de/physik/evers/teaching/comp-nano-bose-2021/index.html>

Computational Nanoscience: Exercise Sheet No. 10

Exercise 10.1: Transport calculation for a new molecule

In this exercise, you will create your own geometry of an electrode-S-CH₂-CH₂-CH₂-S-electrode junction and subsequently, perform a transport calculation for it.

- (a) Relax the geometry Au-S-CH₂-CH₂-CH₂-S-Au. Use the control file

```
phy318:/loctmp/comp_nanoscience/06_sheet_10/1_relax/control.in
```

that contains reliable numerical parameters for a geometry optimization.

- (b) You find the electrode that we use in this exercise in

```
/loctmp/comp_nanoscience/06_sheet_10/3_transport_large_electrode  
/fcc111.cluster.natoms37.x1.aims
```

Add the electrodes with avogadro as discussed in the youtube video 15.9. After creating the xyz file that should look similar as Fig. 15.10 in the lecture notes (we use an electrode with more atoms here, our junction should have 85 atoms), execute the xyz2aims.x script (see Exercise 7.1)

```
xyz2aims.x junction.xyz > geometry.in
```

to obtain the geometry for the FHI-aims KS-DFT calculation. Quickly check geometry.in with a text editor (e.g. vim). Execute a PBE calculation as in Exercise 9.1 (c). This calculation may take four hours using four cores.

- (c) Get the atom numbers to define the self-energy layer in the electrodes with avogadro as discussed in the youtube video 15.9. Perform a transport calculation with aitranss as in Exercise 9.1 (e) and report a plot of $\mathcal{T}(E)$. Do you also observe a distinct peak close to the Fermi level? One could further investigate this peak by plotting the corresponding molecular orbitals, as for example in Fig. 7 in *J. Am. Chem. Soc.* **130**, 318-326 (2008) (what is beyond the scope of this exercise).

Exercise 10.2: Questions on DFT-based electron transport

Please comment whether following statements are true or false and give a reason for your decision.

- (a) We impose that conducting electrons do not tunnel from the left lead to the right lead. As a consequence, when performing a transport calculation based on a KS-DFT calculation, the conducting electrons temporarily occupy molecular orbitals in the extended molecule during transport.
- (b) In the situation of (a), the conduction electrons only occupy molecular orbitals in the extended molecule that are unoccupied in the DFT calculation. Occupied orbitals in DFT (occupied with a spin-up and spin-down electron) do not participate in transport.

- (c) Transport calculations based on the extended-molecule approach are exact when using a KS-DFT calculation with the exact exchange-correlation functional and when including a sufficient number of electrode layers in the extended molecule.

Please answer the following questions:

- (d) How is the Fermi level determined in a transport calculation based on DFT? Why is the Fermi level important in a transport calculation?
- (e) Organic molecules can have a large HOMO-LUMO gap of up to 10 eV. The Fermi level can vary between ϵ_{HOMO} and ϵ_{LUMO} , so their variation can be 10 eV for the molecule with 10 eV HOMO-LUMO gap. Considering this situation, how is possible to determine a reasonable Fermi level for a junction with a small organic molecule sandwiched between gold electrodes? In which way are many electrode atoms necessary in order to perform a reasonable transport calculation?

Exercise 10.3: Analytical model calculation

Consider the two-level model from Sec. 15.6 of the lecture notes. Here, we test the approximation of absorbing boundary conditions (ABC) that is

$$\Sigma_L^{\text{ABC}}(E) = \Sigma_R^{\text{ABC}}(E) = \begin{pmatrix} -i\eta & 0 \\ 0 & -i\eta \end{pmatrix} \quad (1)$$

if we couple both levels of the central system to the left and the right lead.

- (a) Show that the total transmission with the ABC self-energy model is given by

$$\mathcal{T}^{\text{ABC}}(E) = \frac{1}{(E - \epsilon_0)^2/(4\eta^2) + 1} + \frac{1}{(E - \epsilon_1)^2/(4\eta^2) + 1}. \quad (2)$$

- (b) Discuss similarities and differences to the results for $\mathcal{T}(E)$ in the lecture notes (Eq. (15.50) ff).
- (c) Quantum interference terms (as e.g. $T_{01}(E)$ in the lecture notes) are absent in $\mathcal{T}(E)$ for the two-level model with ABC in Eq. (2). ABC model self-energies are used in DFT-based transport calculations. How is it possible that quantum interference effects are included in DFT-based transport calculations?