Tailoring the Fermi level of the leads in molecular electronic devices

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Outline

1 - Theoretical Method

2 - Preliminary calculations

- Energy levels
- Transport properties of BDT

3 - Molecules between alkali leads

- Alkali versus gold leads
- Length dependence

4 - Other systems

1 - Theoretical Method

SIESTA

- **Density functional theory**

$$\rho(r) \rightarrow \hat{V}_{\text{ext}}[\rho(r)] \rightarrow \hat{H}[\rho(r)] \rightarrow \Psi[\rho(r)]$$

- **Pseudopotentials**

$$\hat{V}_{\text{ion}}^{PP}(r)$$

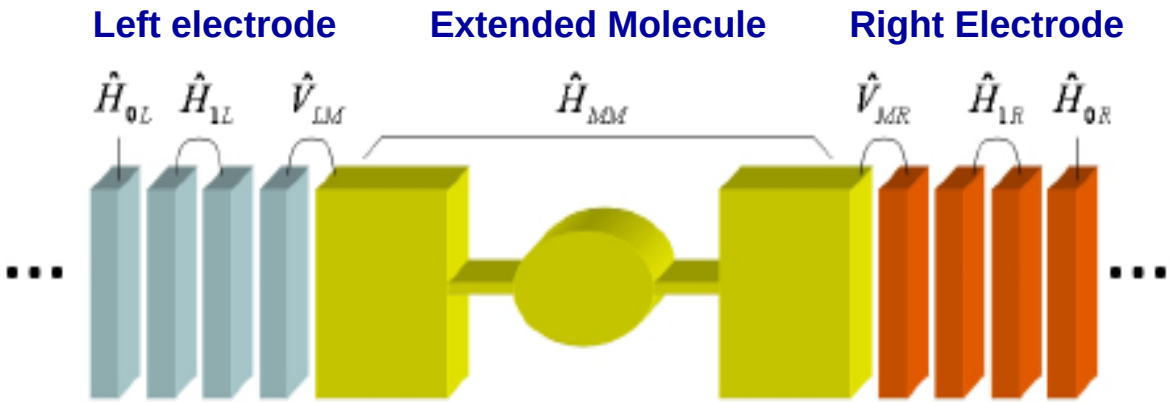
- **Linear combination of atomic orbitals**

$$\psi_n(r) = \sum_{\mu} c_{n\mu} \phi_{\mu}(r - d_{\mu})$$

Smeagol

Phys. Rev. B 73, 085414 (2006)
http://www.smeagol.tcd.ie

- Scattering problem



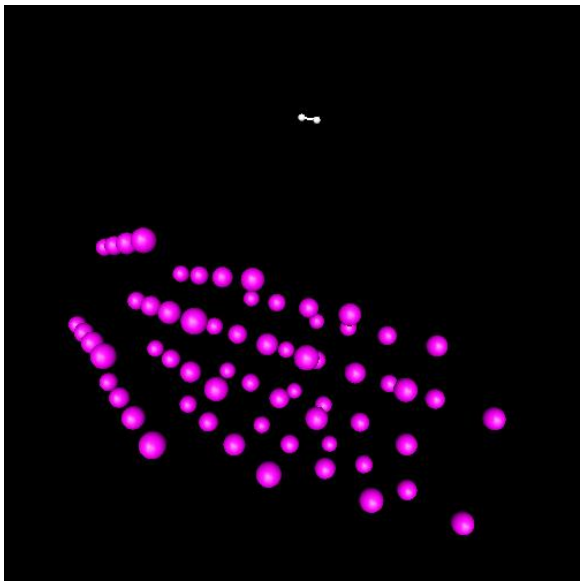
- Density matrix and transmission

$$\hat{\rho}_{MM}(r) = \frac{1}{2\pi i}\int \hat{G}^{<}_{MM}(r,E)\,\mathrm{d}E$$

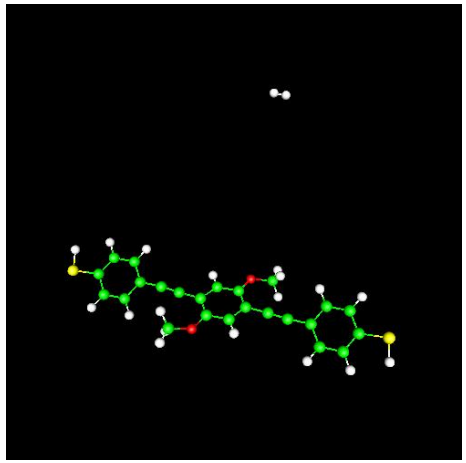
$$T(E) = \mathrm{tr}[\hat{\Gamma}_R \hat{G}^{\mathrm{R}}_{MM} \hat{\Gamma}_L \hat{G}^{\mathrm{A}}_{MM}](E)$$

2 - Preliminary calculations

Leads and molecules

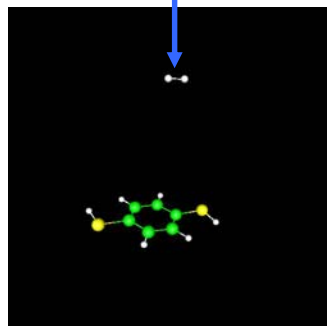


Metallic slab



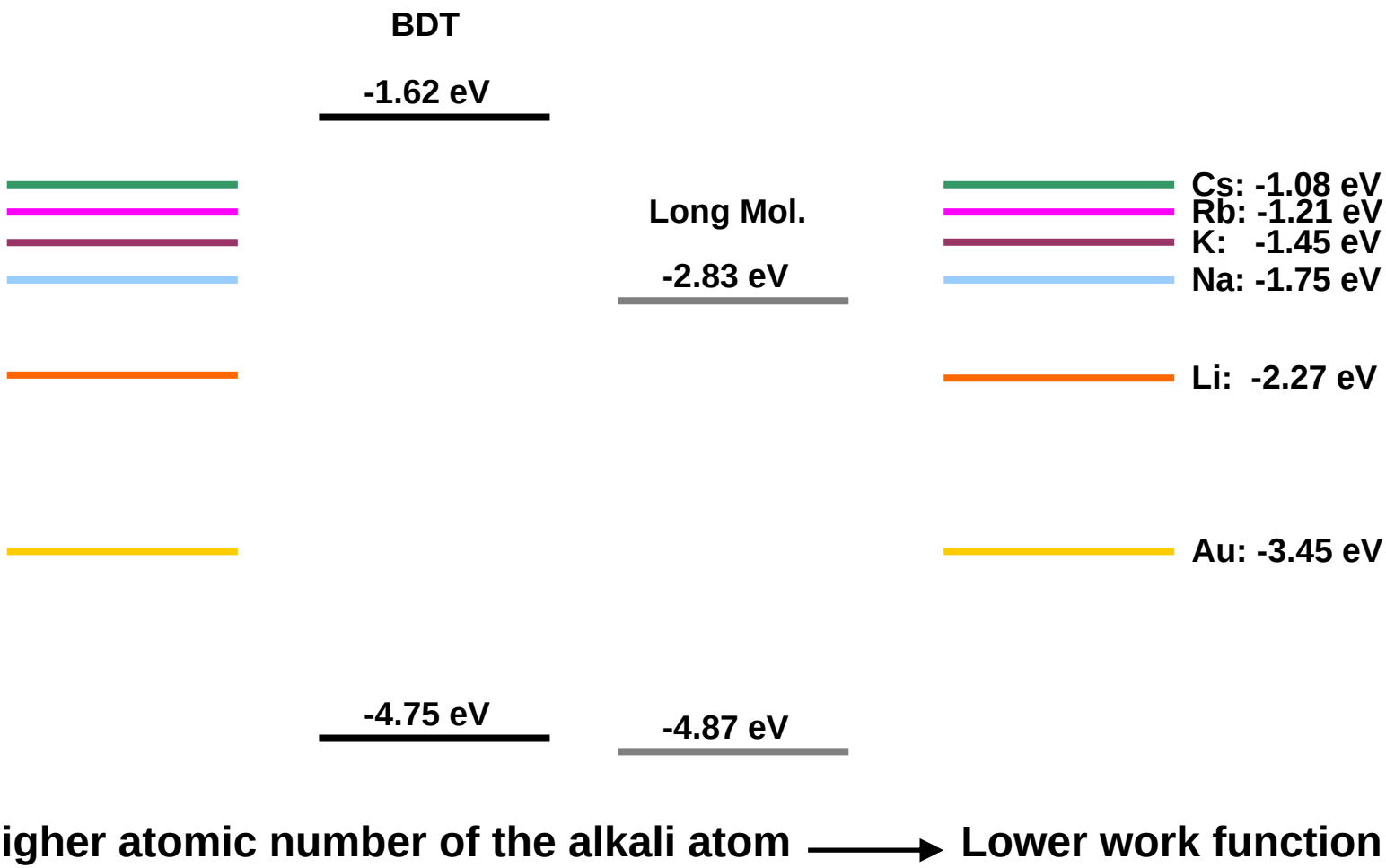
Long molecule

Hydrogen molecule used to determine a common energy origin



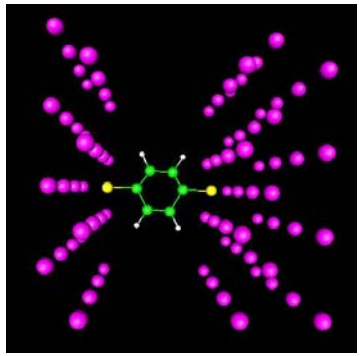
BDT

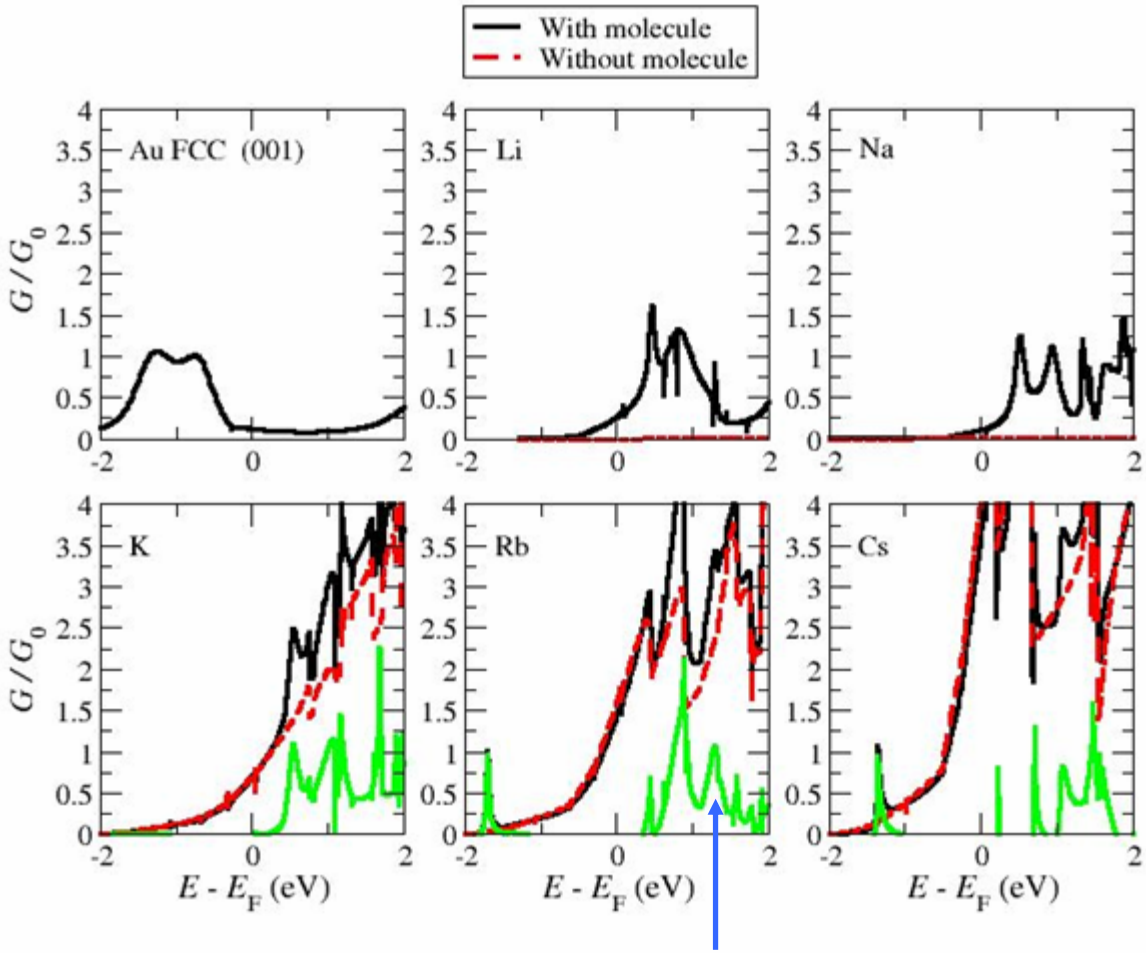
Energy levels



Higher atomic number of the alkali atom → Lower work function

Transport properties of BDT



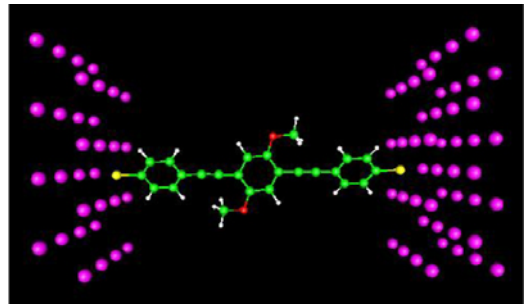


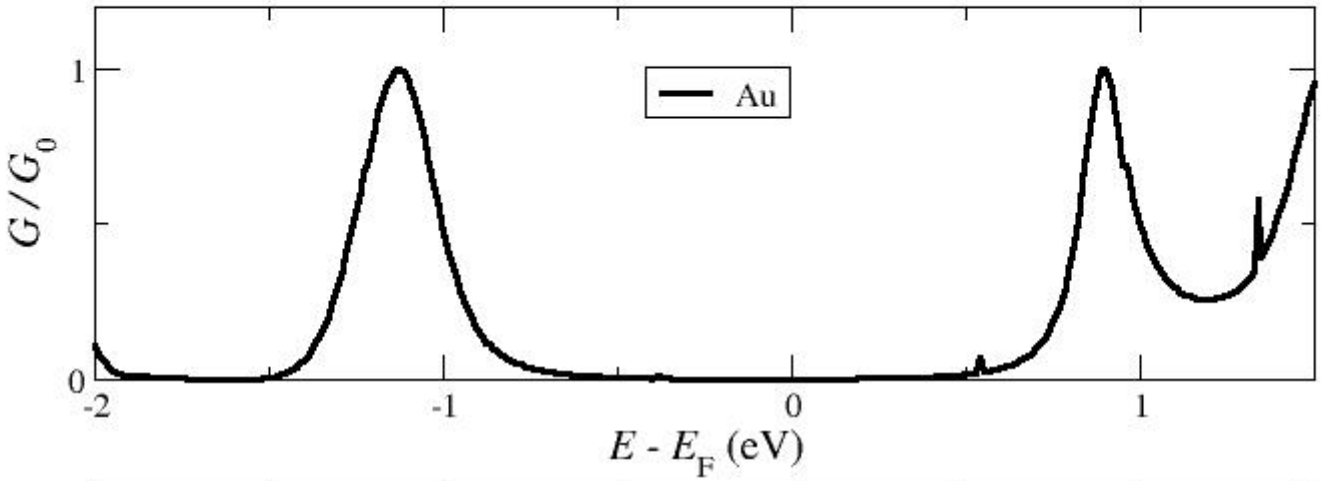
Conductance through the LUMO

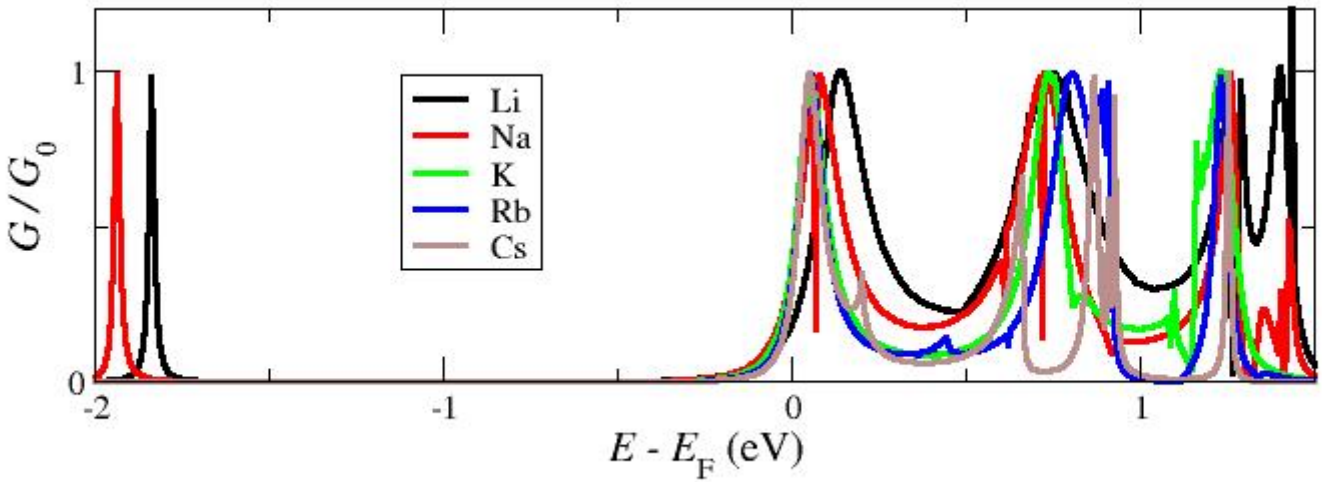
Difference between both cases

3 - Molecules between alkali leads

Transport properties of long molecules

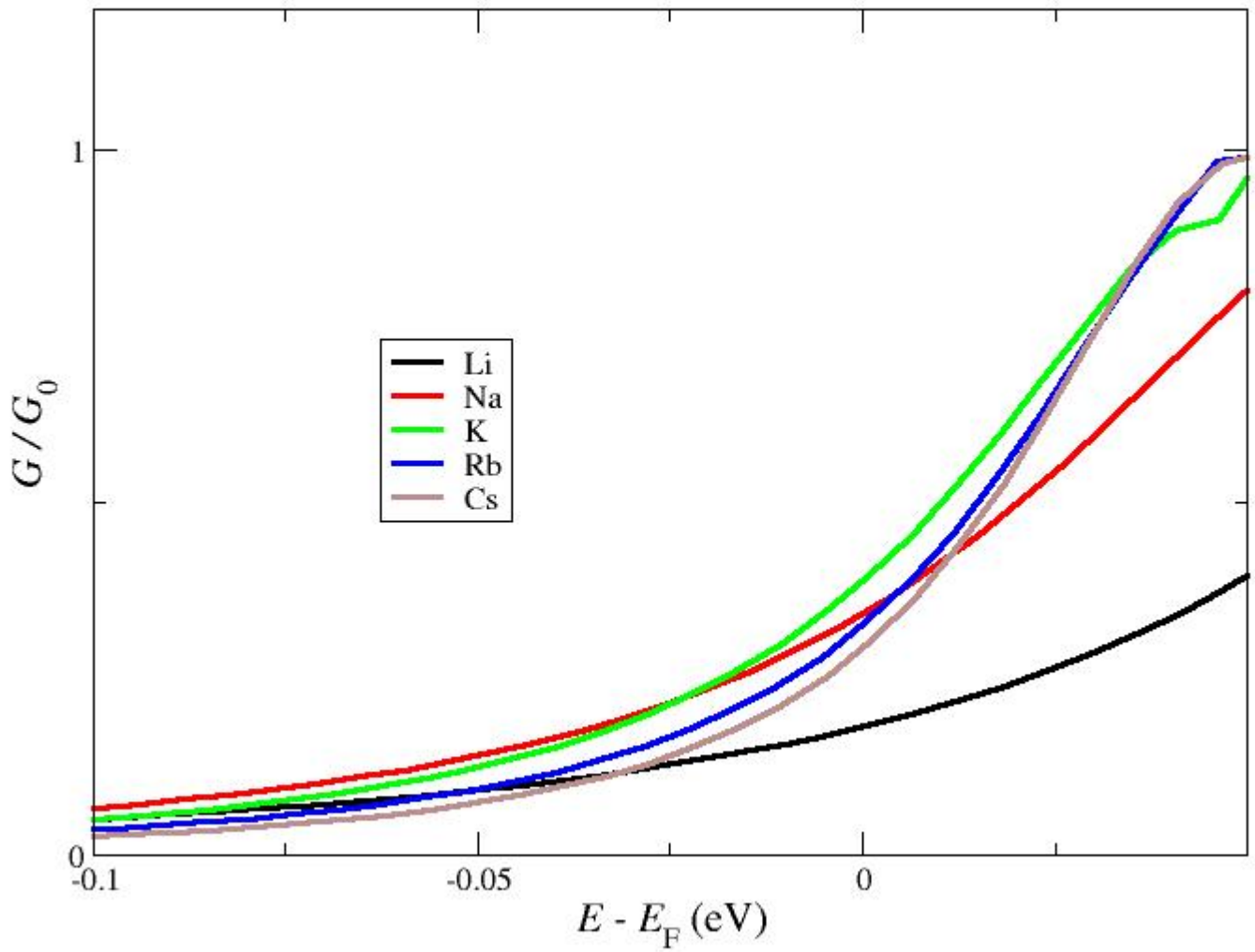




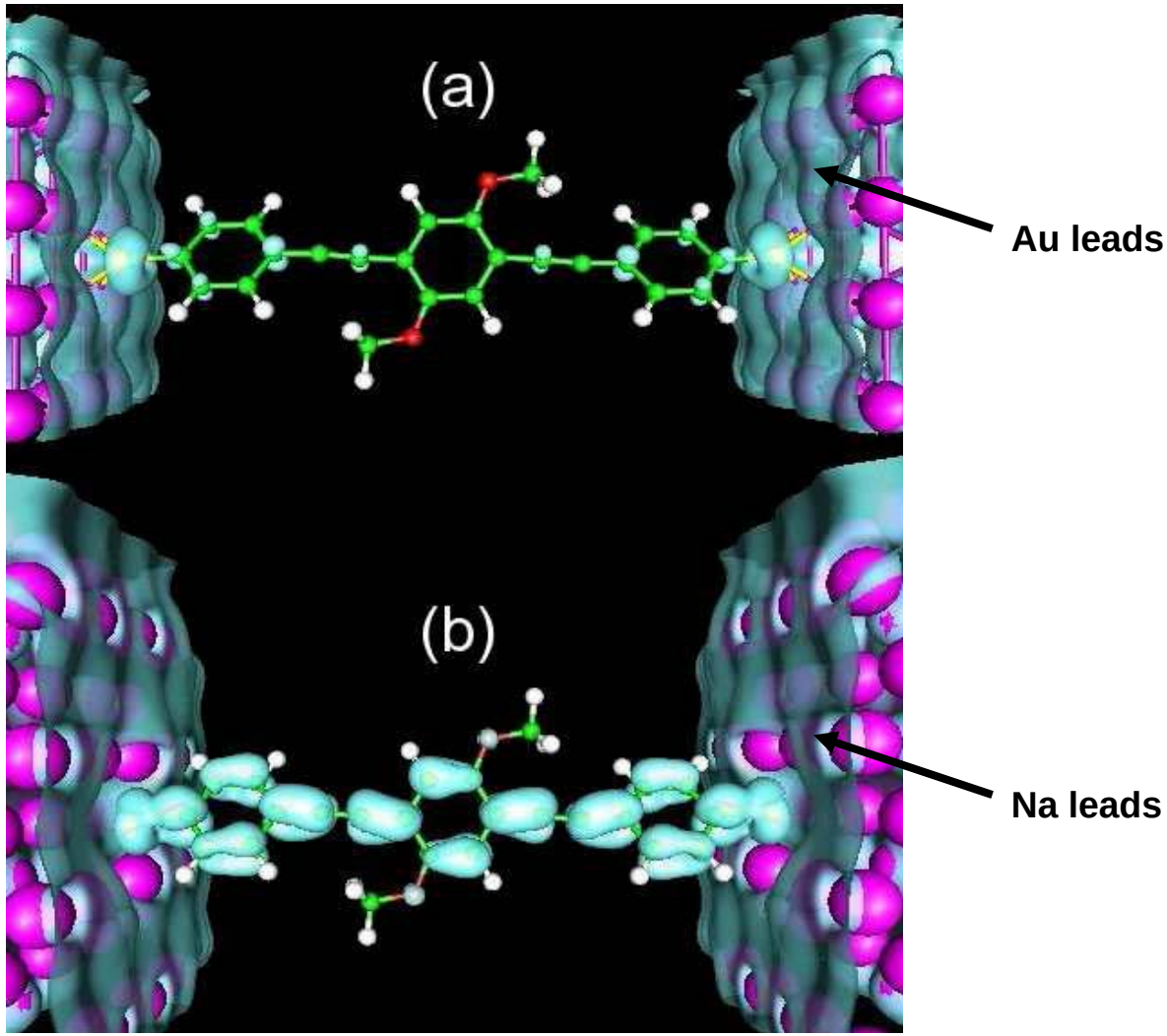


Conductance through the LUMO

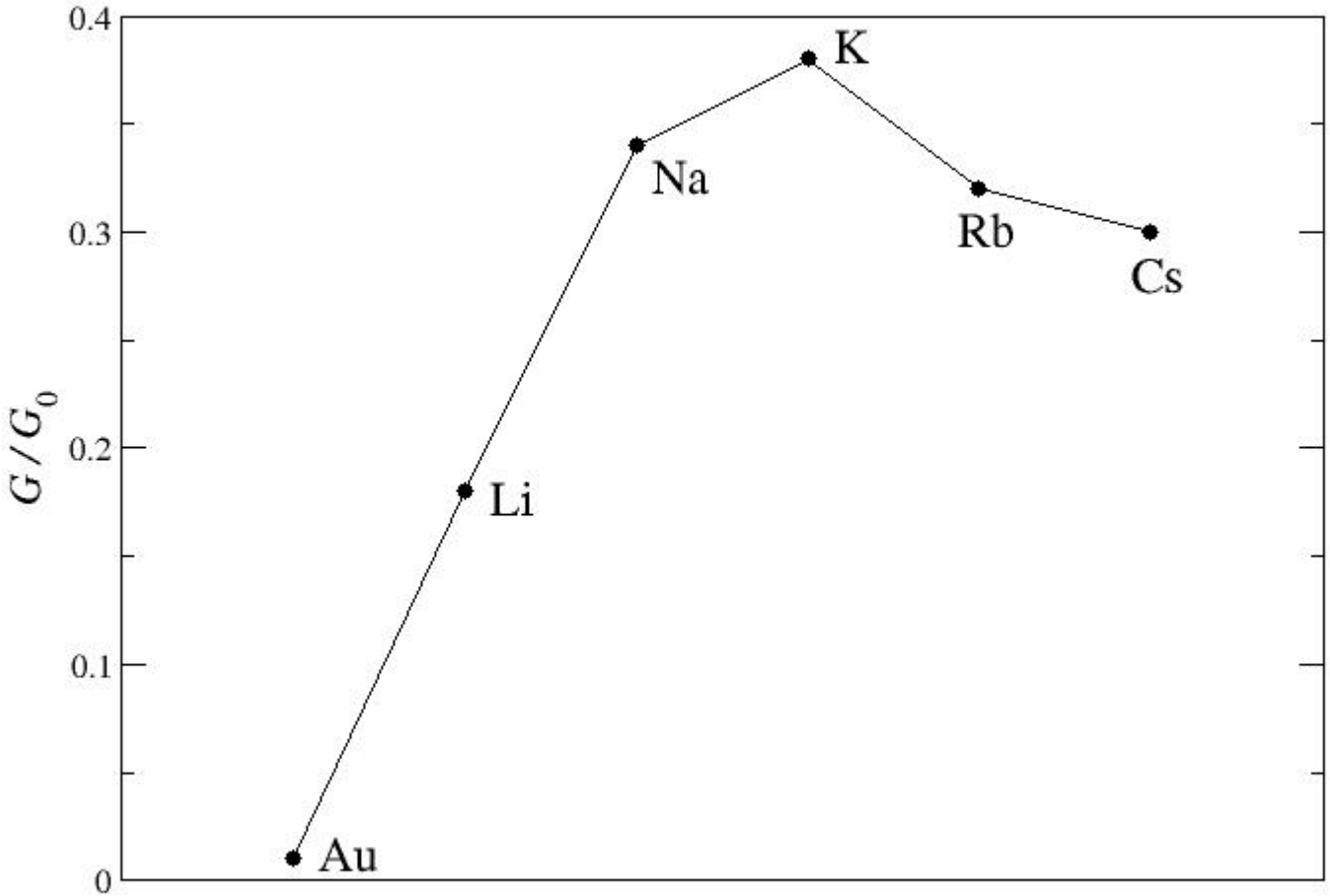
LUMO transport



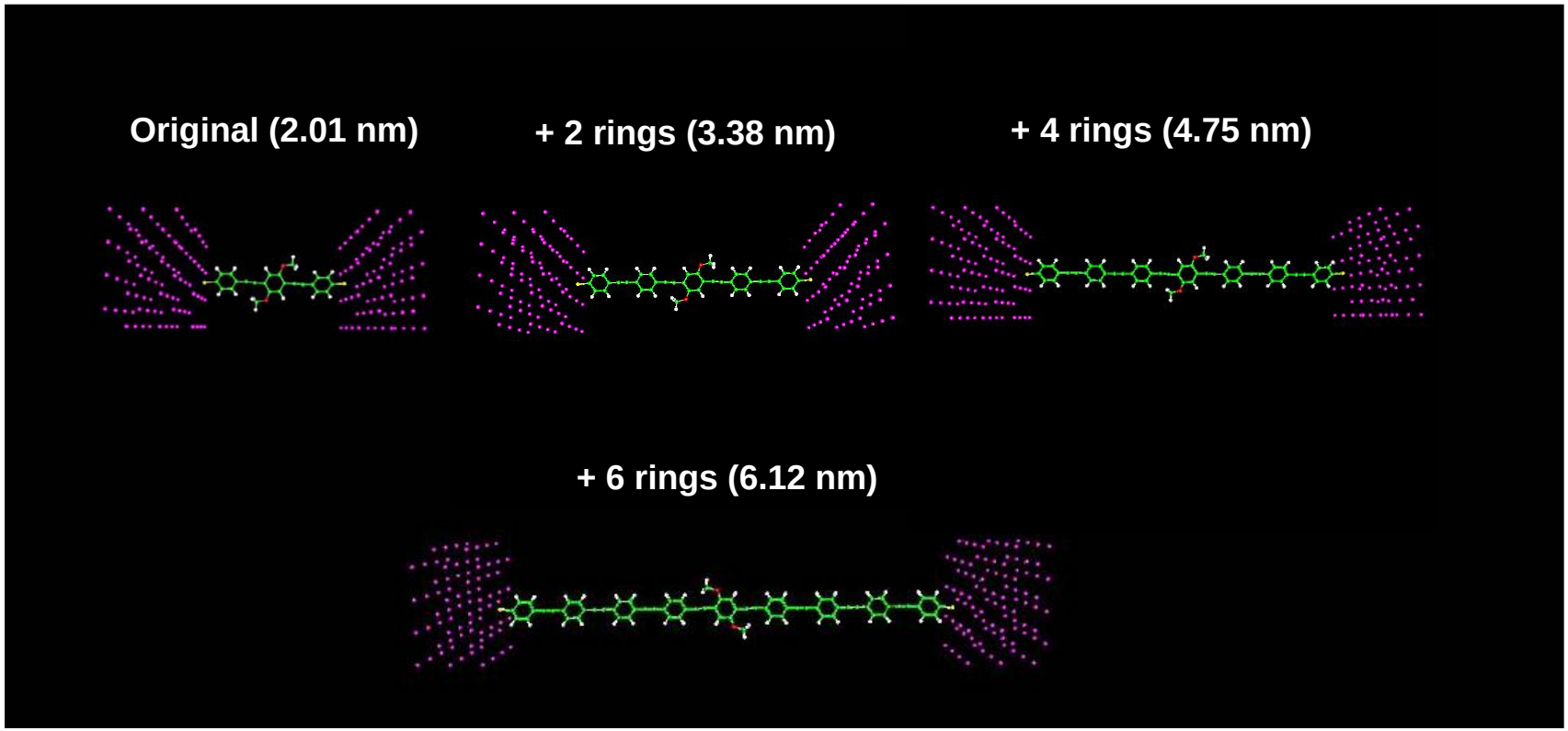
Spatial projection of the density of states



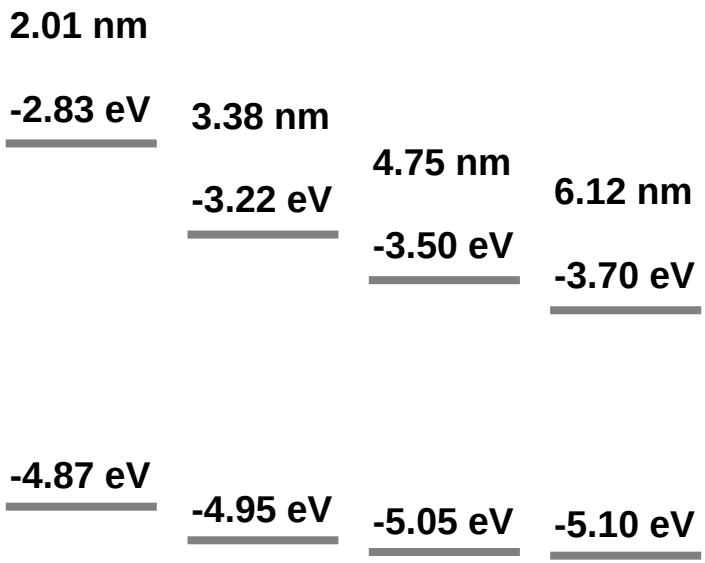
High conductance

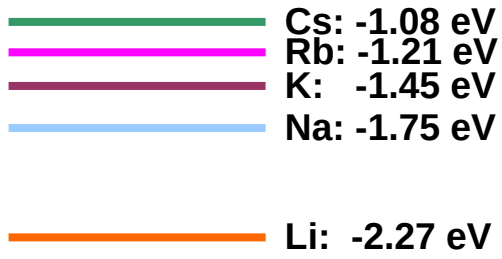


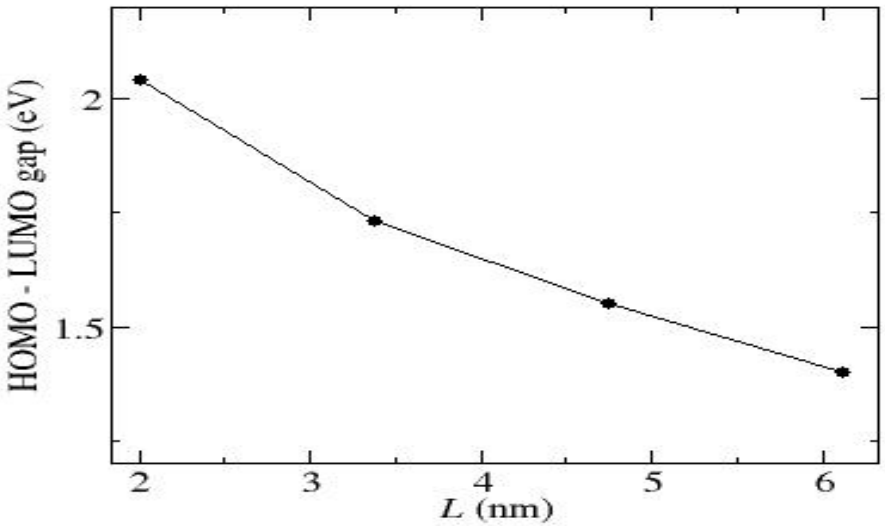
Length dependence



Molecular electronic properties

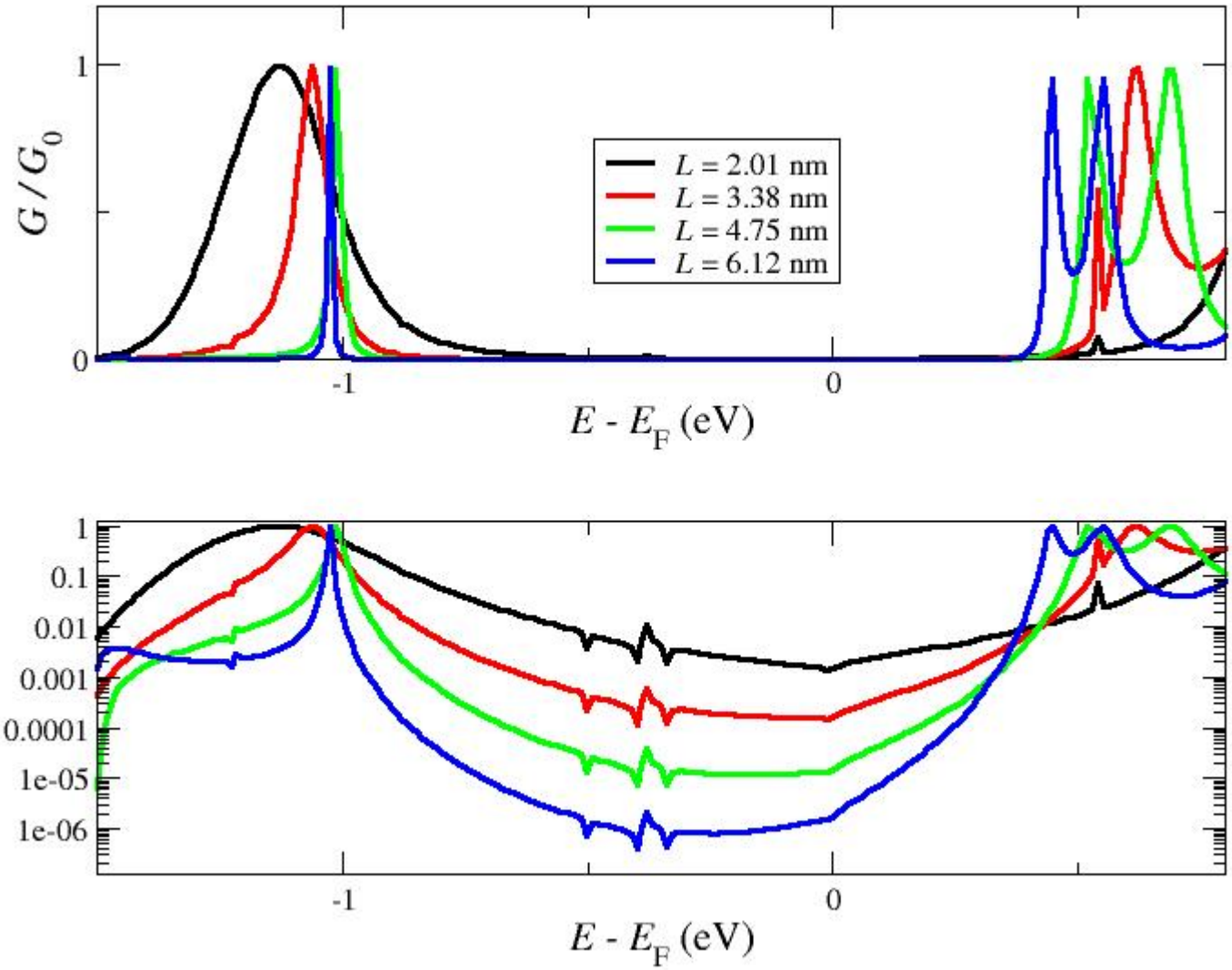




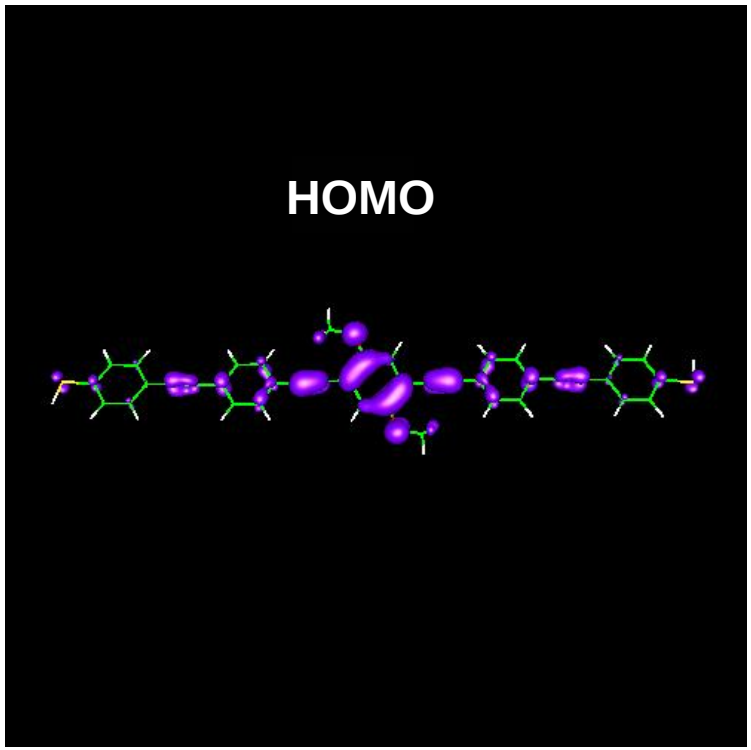


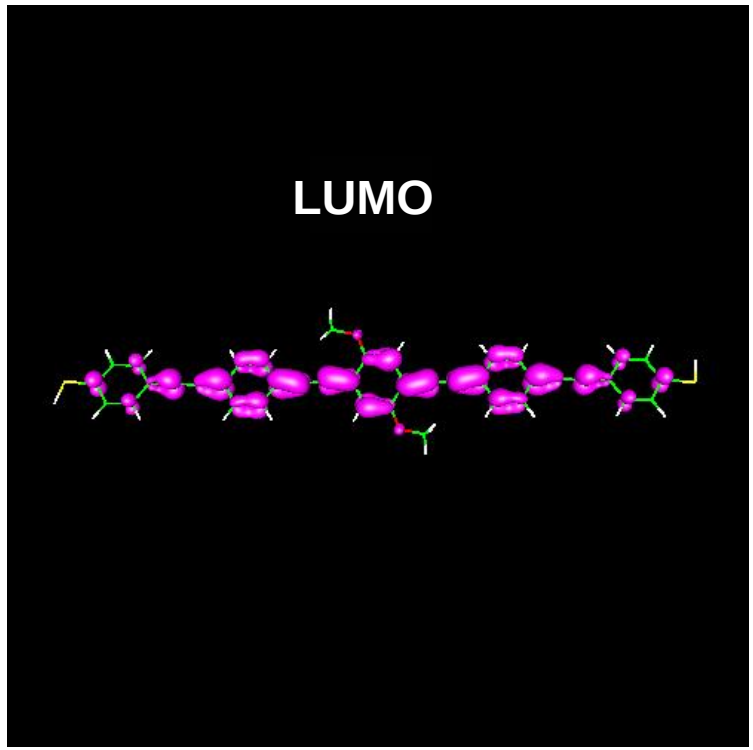
Reduction of the HOMO-LUMO gap

E_F in the HOMO-LUMO gap



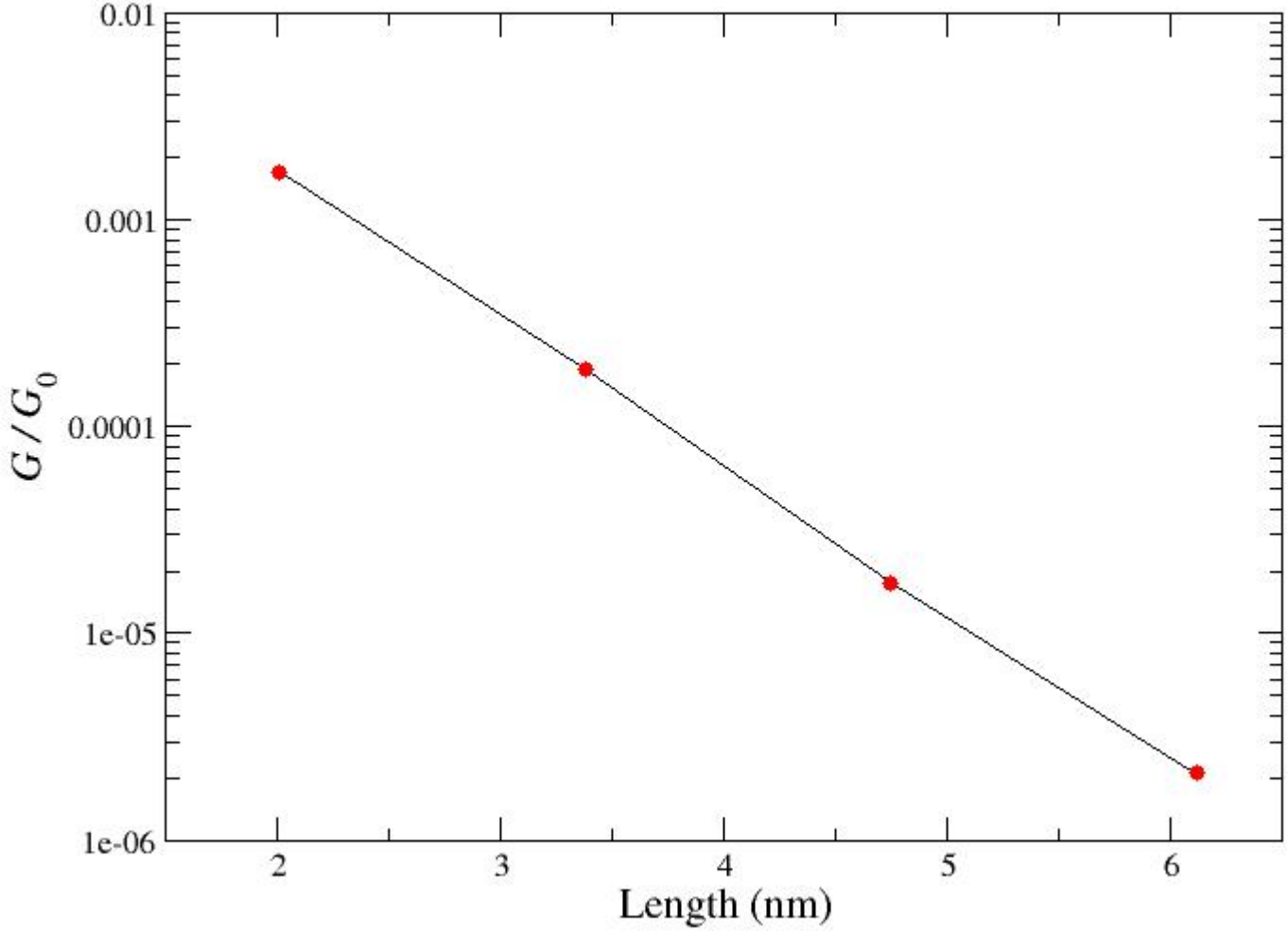
Spatial distribution of HOMO and LUMO



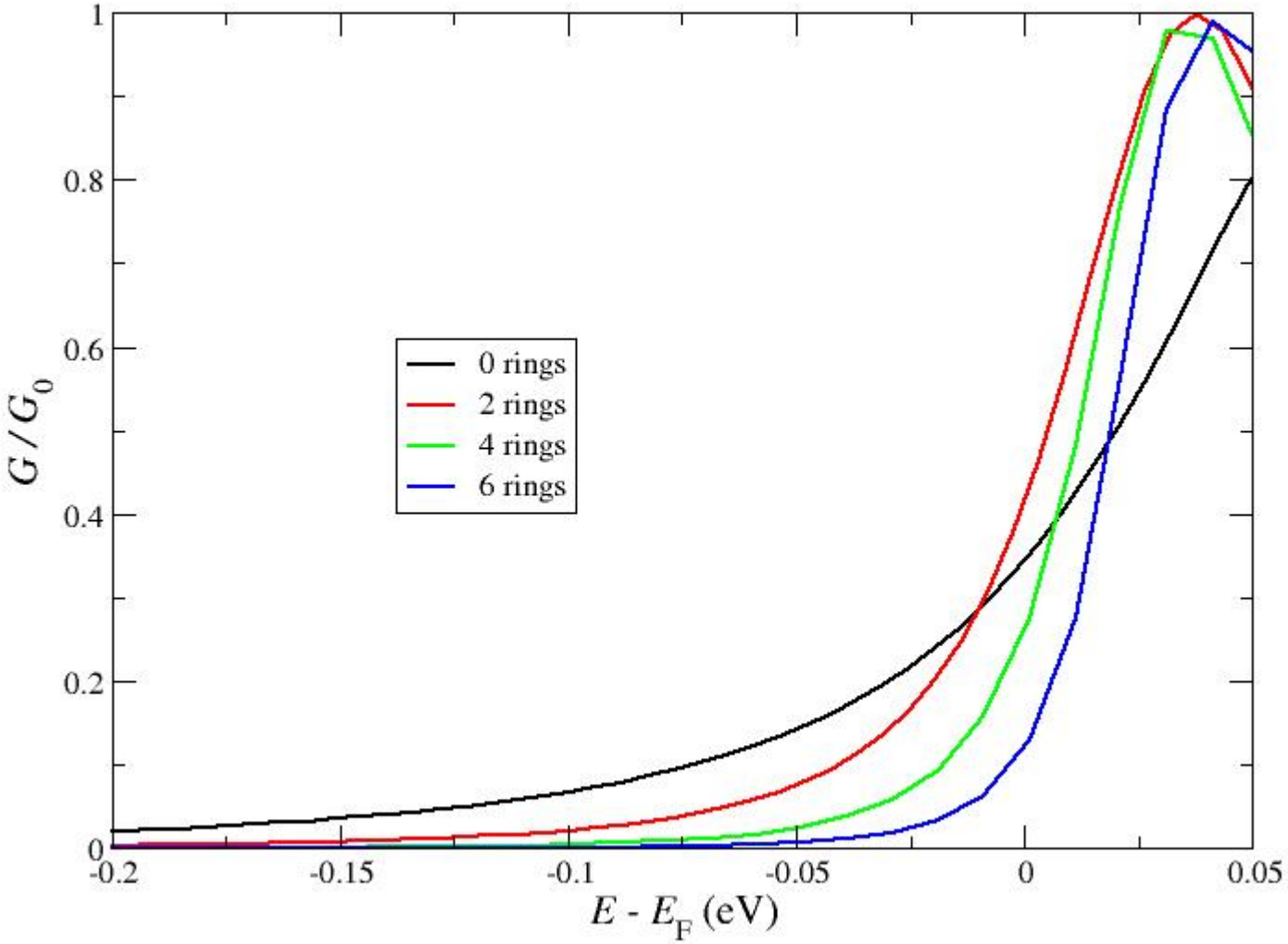


The LUMO is delocalized along the molecular backbone

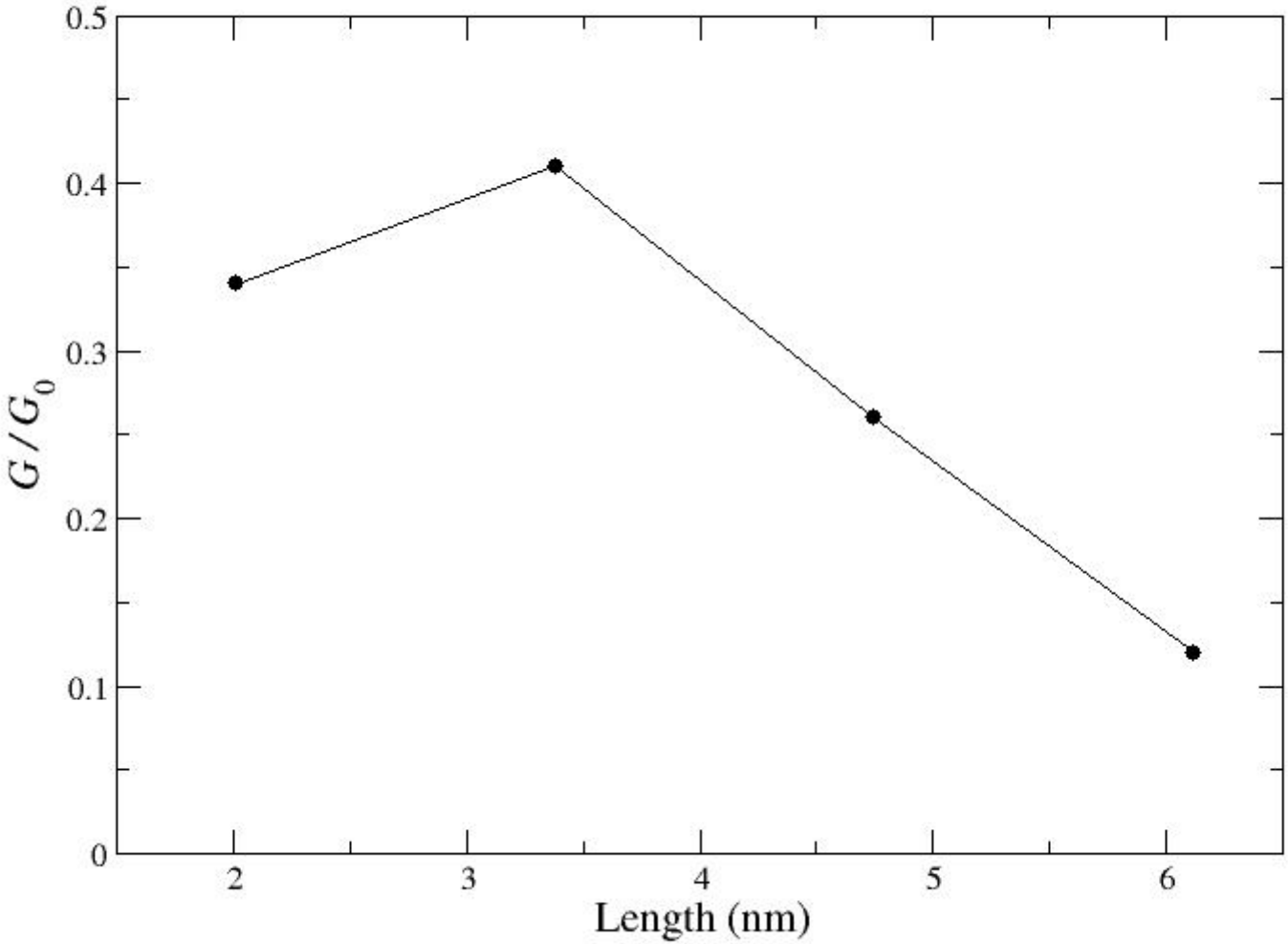
Exponential decay between gold leads



Pinning of E_F at the LUMO

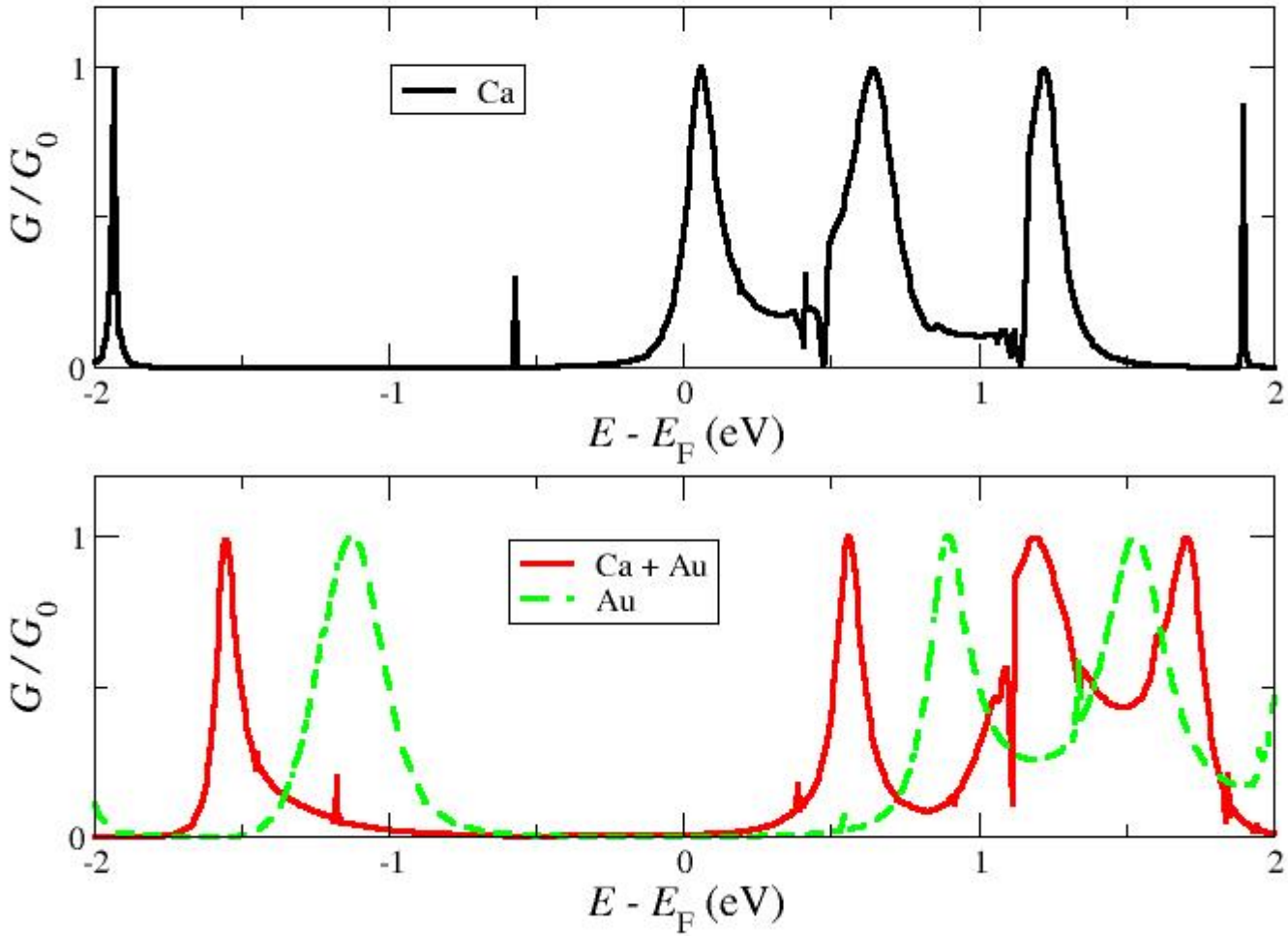


Non-exponential decay of the conductance



4 - Other systems

Exponential decay with a lower *b*



Conclusions

- Gold leads are not good candidates for molecular electronics devices

- It is possible to alter dramatically the alignment of Fermi level by changing the composition of the leads

- The pinning of the Fermi level at the LUMO modifies dramatically the transport properties

- New research is needed to find proper combinations of materials