Evolution of Molecular Binding in the MCBJ Junctions

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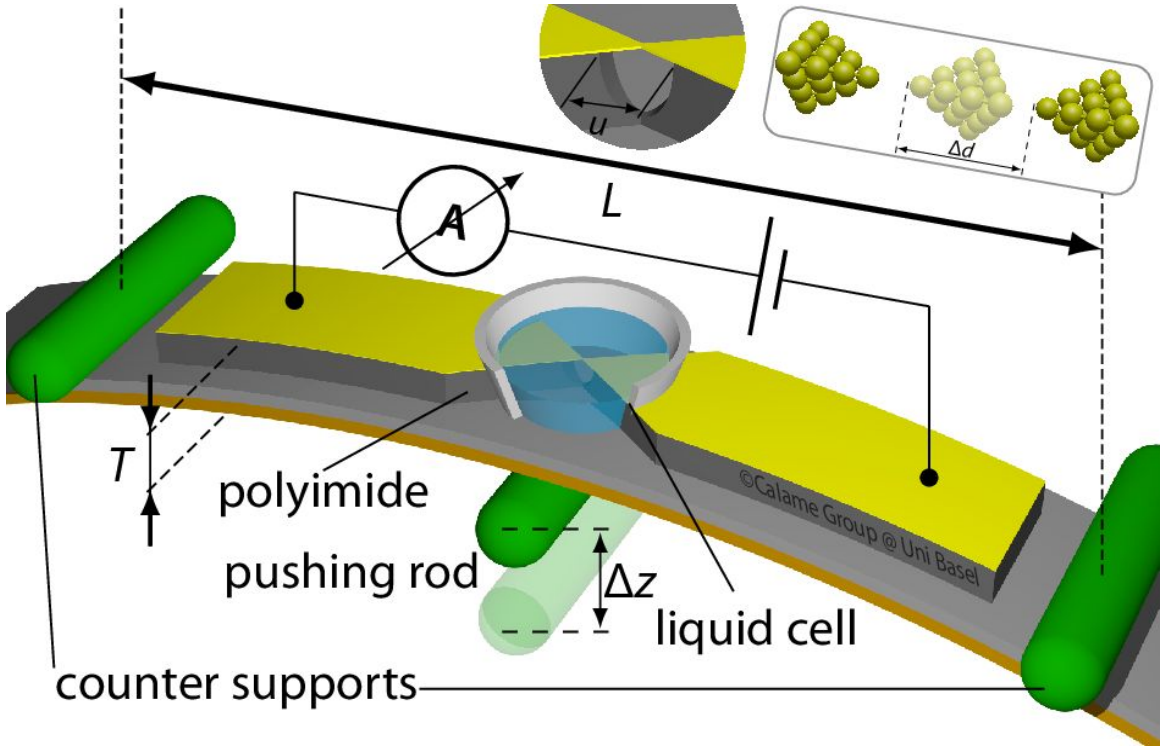
Introduction

Mechanically controlled Break-Junctions

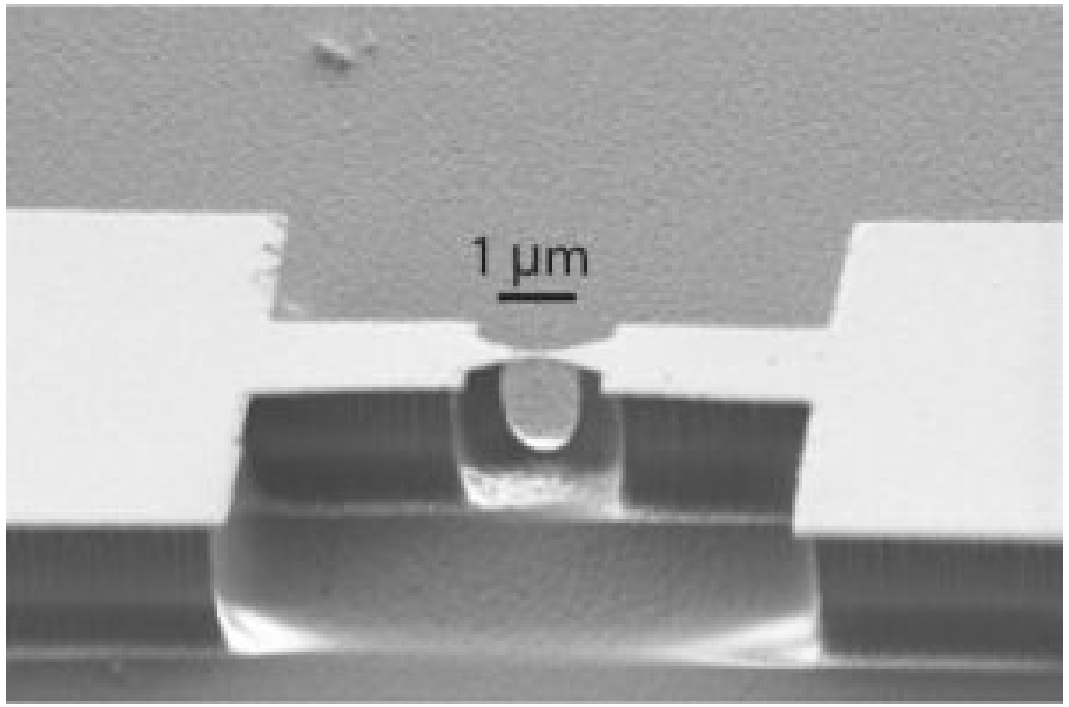
DRESDEN concept

Mechanically controlled Break-Junctions

schematic MCBJ



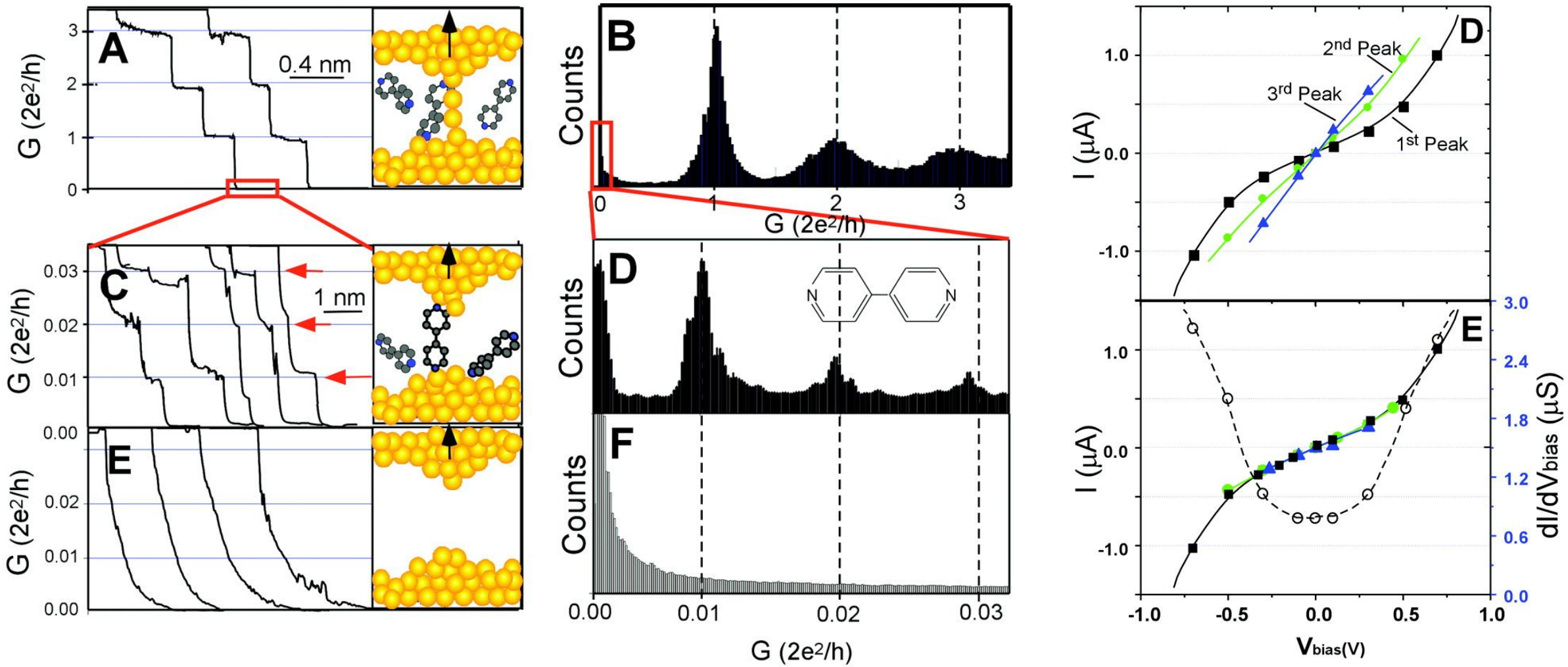
SEM Image



- Au-Au nanoconstriction fabricated using lithographic techniques
- Main principle: Controllably break a metallic wire to form atomistically shaped electrodes
- Probe molecules trapped btw. the sub-nanometer gap
- Attenuation factor?

Source: Phd-thesis, Anton Vladyka, Uni Basel, 2017

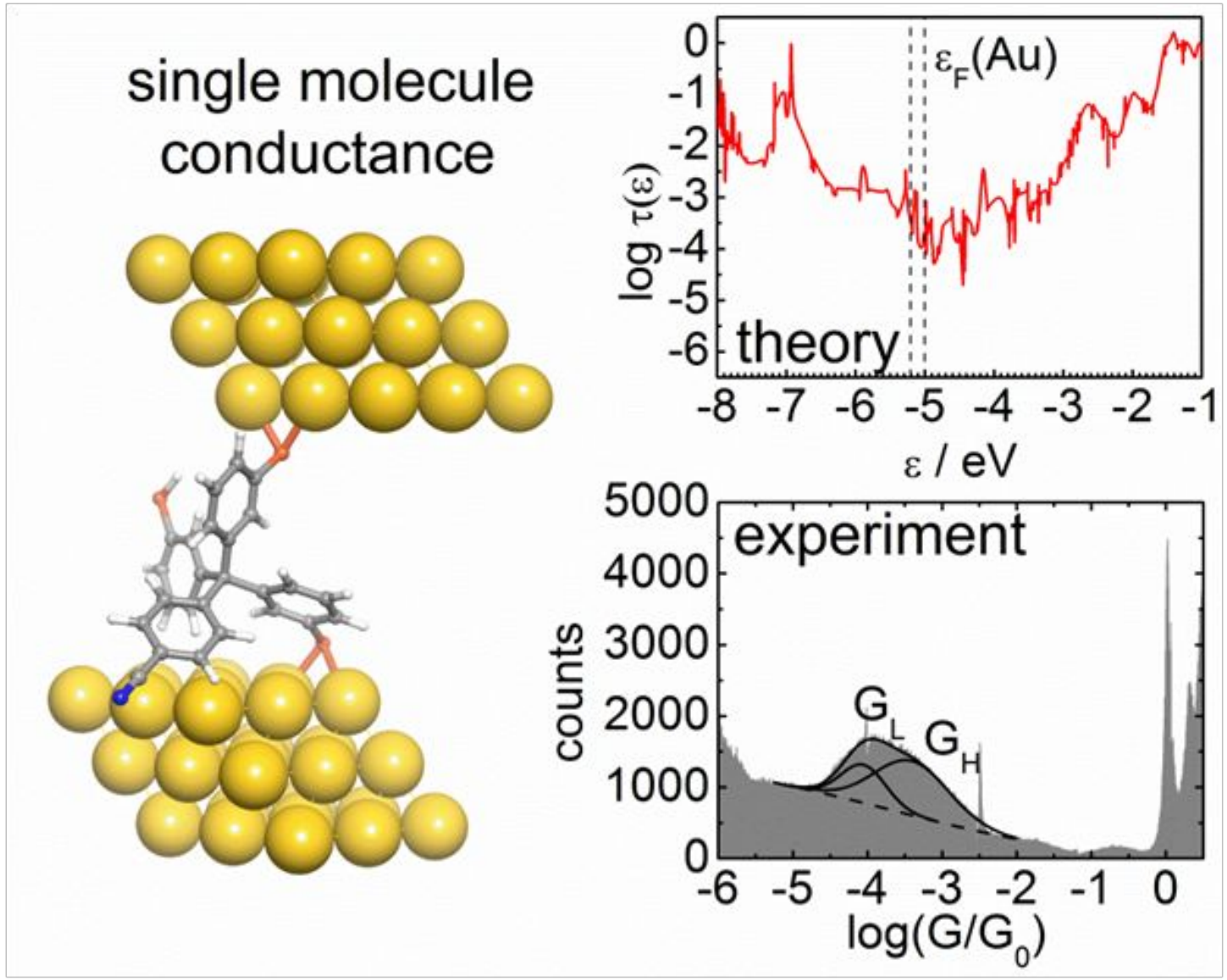
Electrical signature of single molecules



- Metallic bridges ‣ flat conductance plateaus | molecules ‣ reclining conductance plateaus
- Metallic bridges ‣ linear IV | molecules ‣ S-shaped IV ‣ *Fit single level model* [ε | Γ]
- Typically multiple measurements are performed (statistical significance)

Source: Bingqian Xu et. al., Science 301, 5637, 1221-1223 (2003)

Electrical signature of single molecules using NEGF + static configurations



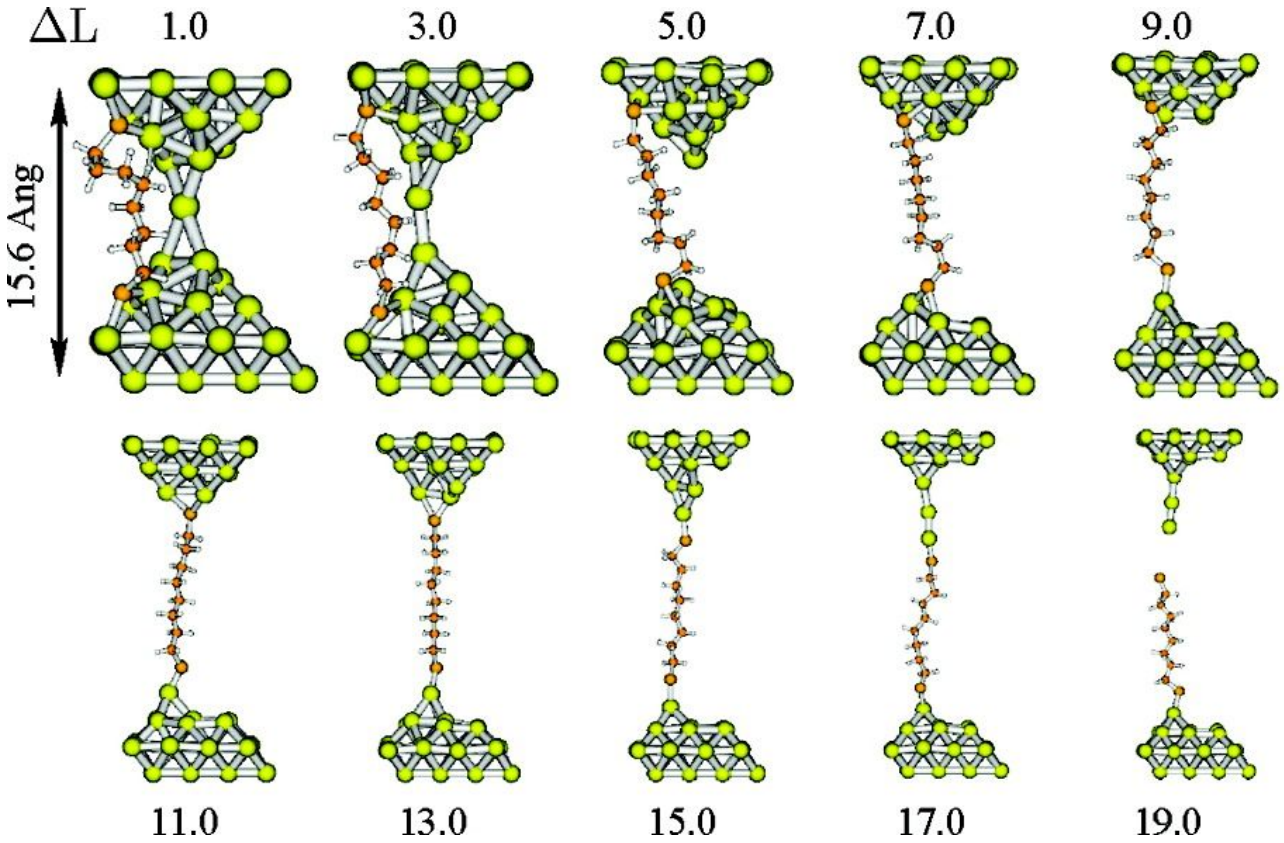
- Representative | energetically most favorable configuration
- Transmisson using NEGF to evaluate HOMO/LUMO mediated transport
- NEGF calculations computationally expensive ◀ Measurements are performed numerous times

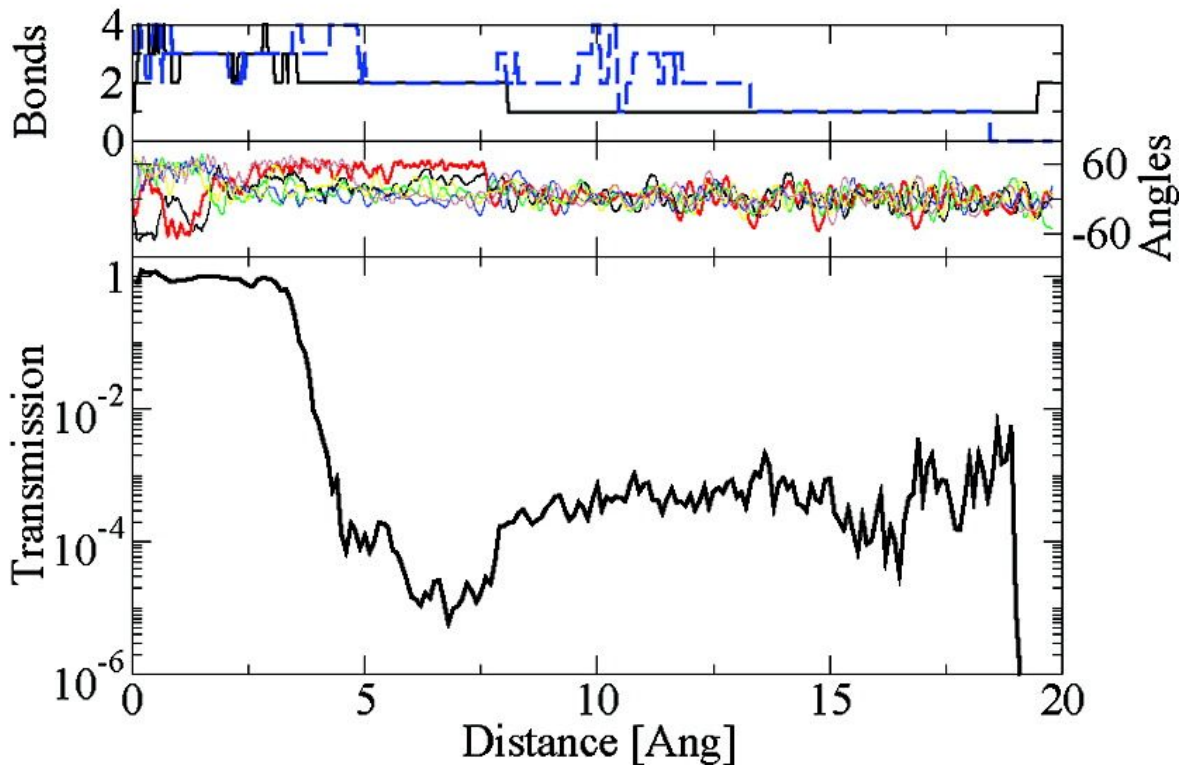
- strongly reduced coverage of the configurational space

- Steady state assumption
  - Tip shape do not change considerably
  - several measurement filter out statistically insignificant configurations

Source: Sebechlebská, T., et al., Electrochimica Acta 258, 1191-1200 (2017).

Electrical signature of single molecules using NEGF + MD Simulations





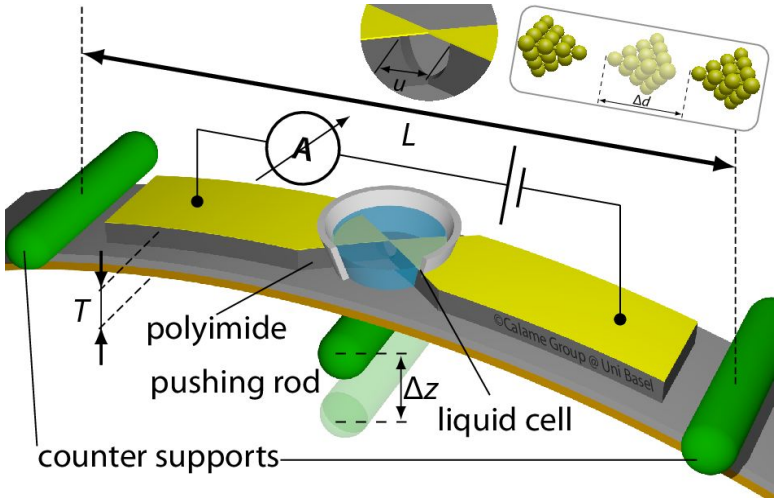
- Representative configuration for each tip-tip separation
- Energetically most favorable configuration | Snapshots from limited tragectories using MD-Simulations

- Are molecules in steady state during the IV-measurement?
- Adequate coverage of the configurational space?

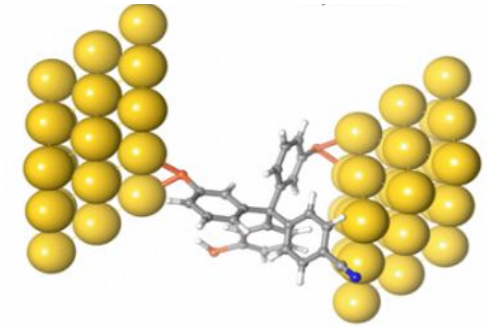
Source: Magnus Paulsson et. al. ,Nano Lett. 9, 1, 117-121 (2009)

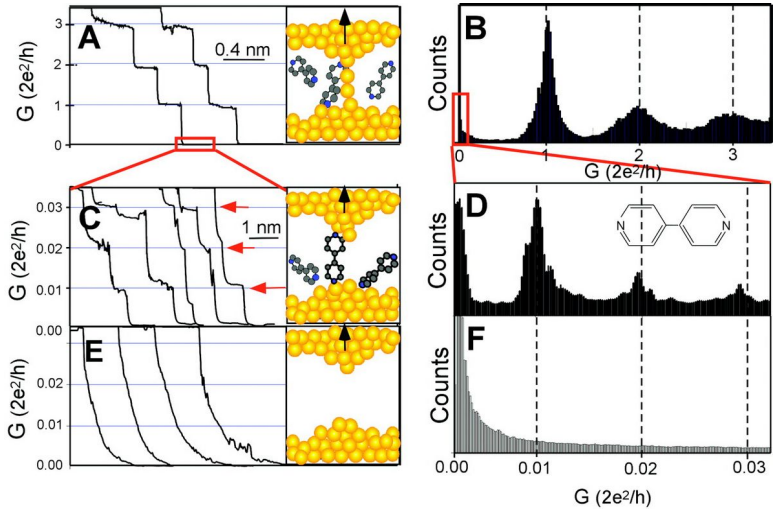
Interpretation MCBJ experiments using NEGF

- Attenuation factor in experiments
- Real tip-tip separation cannont be determined precisely
  [substrate bending non-uniform | different tip shapes | tip deformation]
- Statistical measurements



- NEGF calculations computationally expensive
- Strongly reduced configurational space
- Steady state assumption





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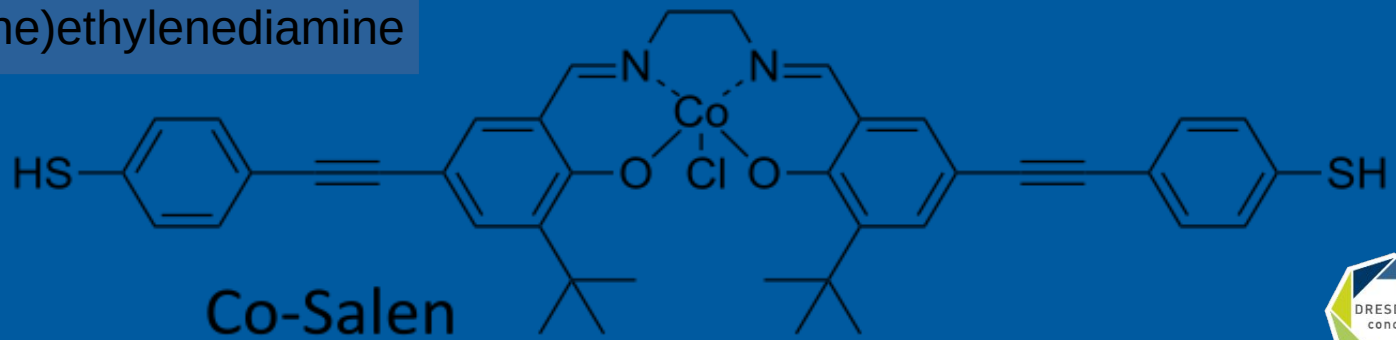
„Time“ evolution of Molecular binding in MCBJs

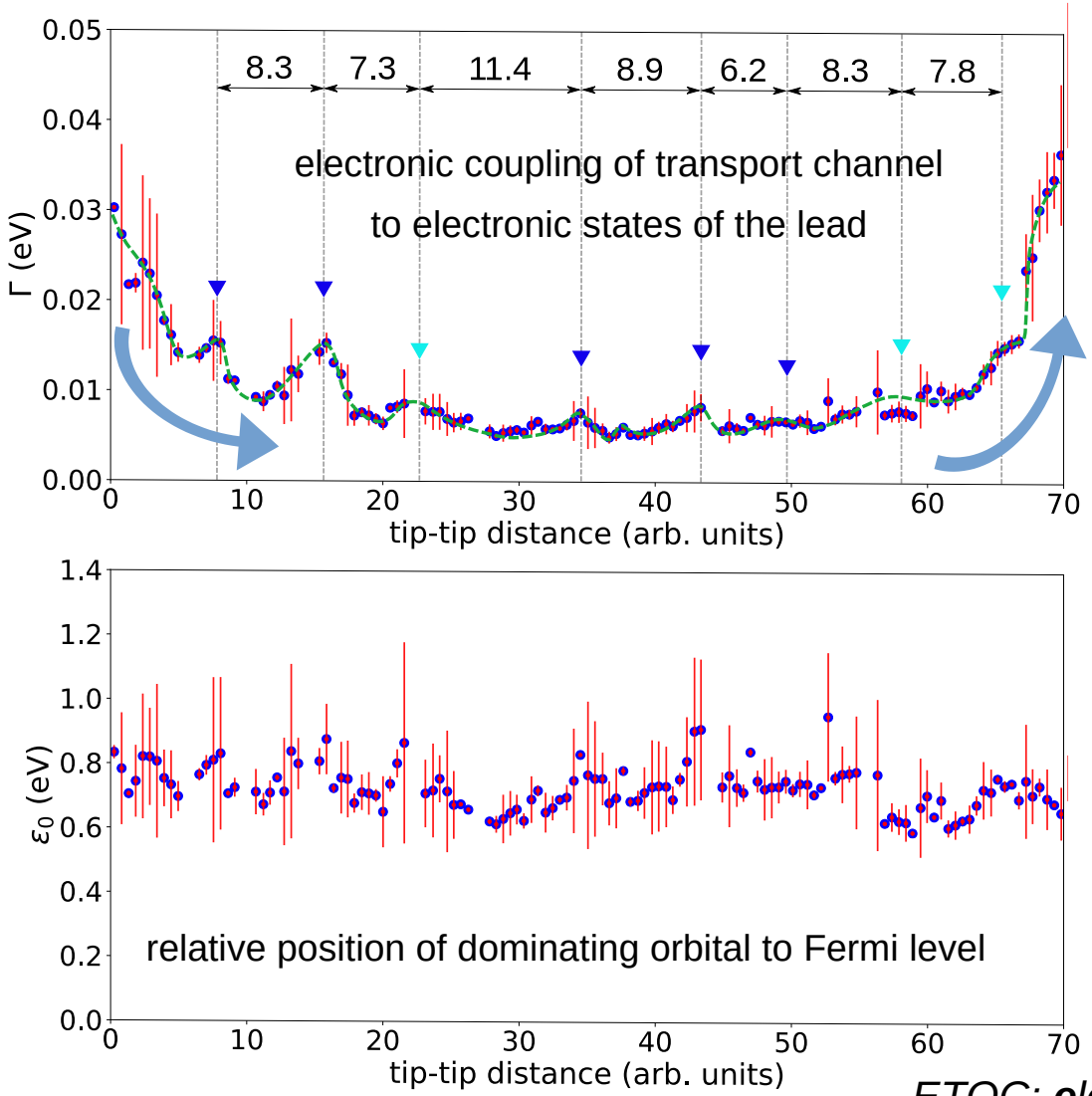
Recent experimental results on SALEN

N,N’-Bis(5-ethynylbenzenthiolsalicylidene)ethylenediamine



Co-Salen

Opening curve measurement MCBJ



Difference to previous MCBJ experiments

- Focus on single measurements | not statistics
- Follow „time“ evolution of ETCQs at the time scale of measurements

„Time“ Evolution of ETCQs

- Γ „bathtub“-curve with recurrent peak-features
- ε_0 oscillates in the range [0.6eV , 1.0eV]

  - steady state not neccesarily presumable
  - need to include geometrical distortions of the molecule and docking dynamics on gold facets
  - „perform“ statistics using DFT+NEGF

*ETQC: **e**lectronic **t**ransport **c**haracteristic **q**uantities*

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Scheme to follow
„Time“ evolution ETCQs using DFTB+NEGF

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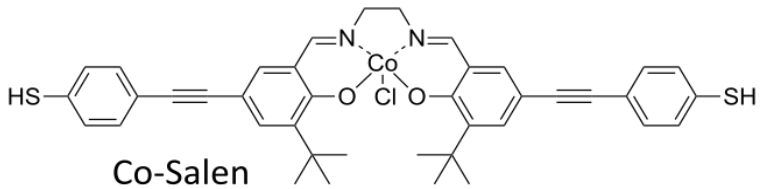
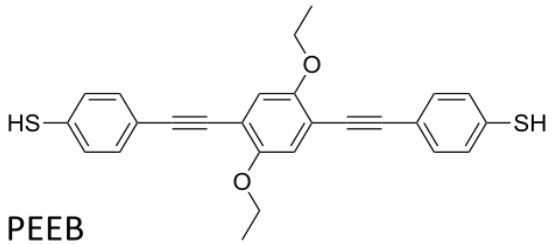
„Time“ Evolution of ETCQs ▸ „perform“ statistics using DFT+NEGF



Co-Salen



PEEB

- reduce computational effort ‣ PEEB instead of SALEN
- both bear thiol-anchoring-groups ‣ similar binding to Au
- „Time“-evolution of Γ expected to be similar
- Slakos for Co-Salen unavailable

- local-coordination of gold facets [fcc] ‣ numerous docking posibilities
- PEEB flexible ‣ include geometric deformation [bending | streching]

- can PEEB slide on Au-Facet? ‣ ensemble of configuration

suitable characterization of the configuration ensemble

▸ Transport setup | Docking Grid

▸ Parse facet docking energy landscape

▸ include geometric deformations

▸ „Random Walk“ more suitable instead of „normal boltzmann“ distribution

▸ incorporates surface dynamics

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Transport Setup | Docking Grid | Facet Energy Landscape

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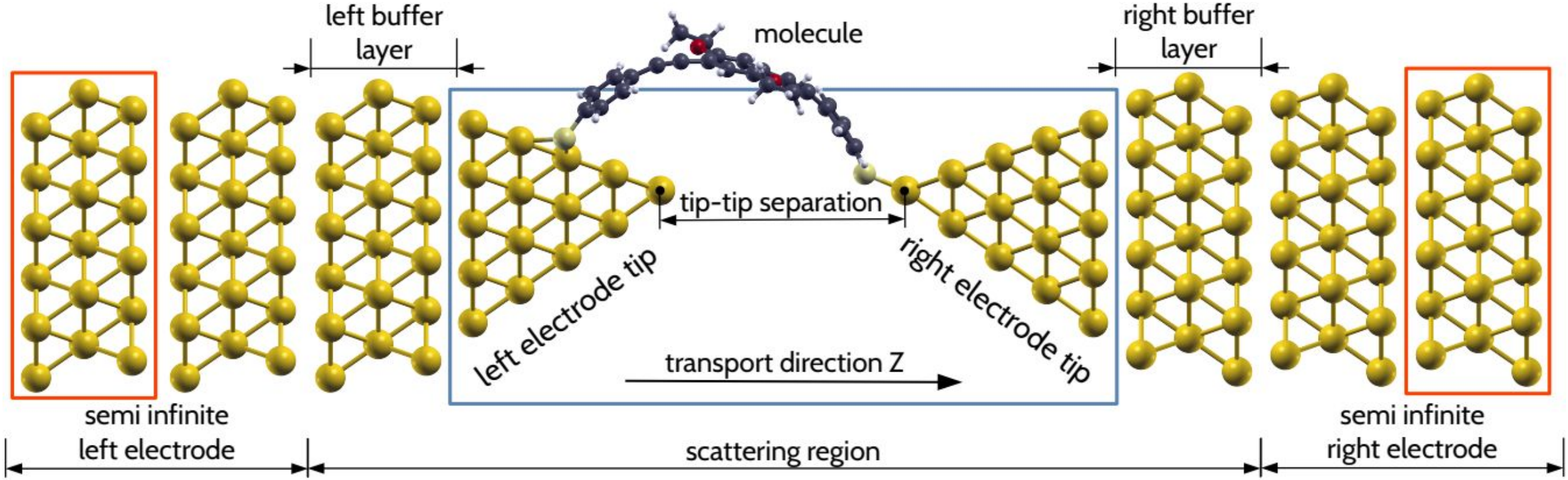
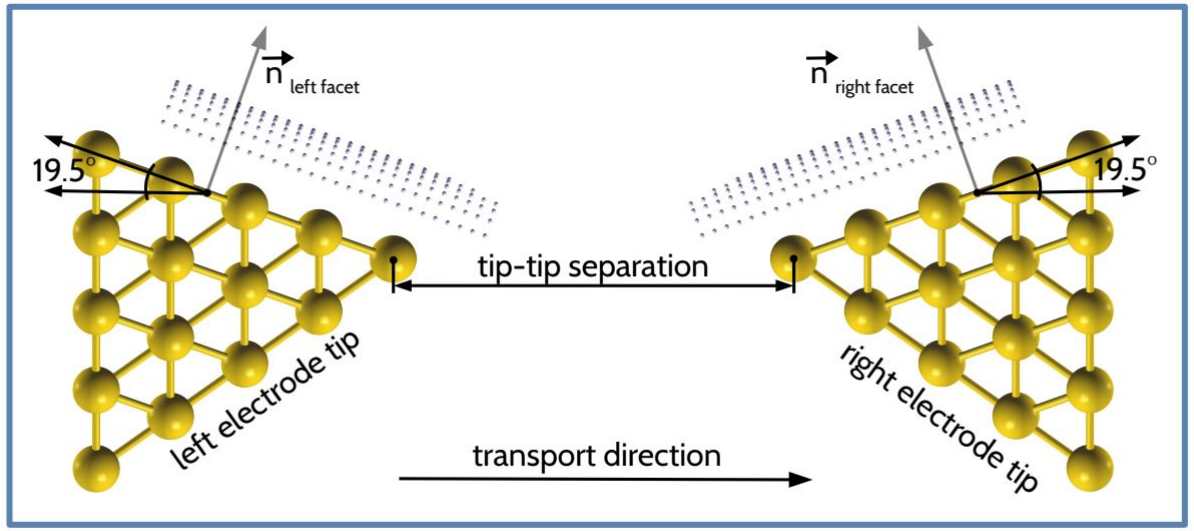
Transport Setup | evaluating zero-bias Transmission

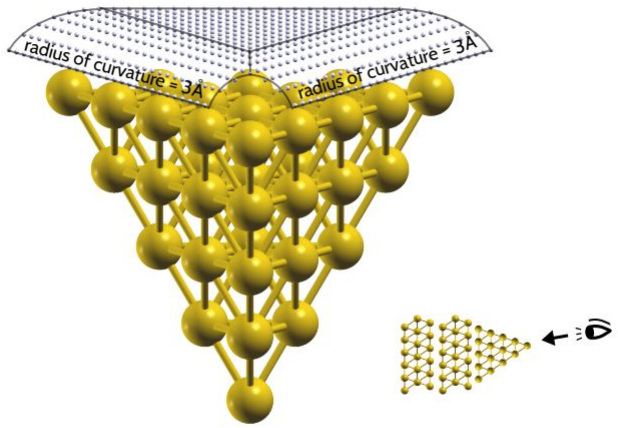


- electrode tips – equilateral triangular pyramids (baselength 5x Au-Au)
- buffer/semi-infinite layers (3 Au Layer 6x6)
- local-coordination-environment ▸ face-centered-cubic
- tip-tip separation [11.54Å, 27.24Å]

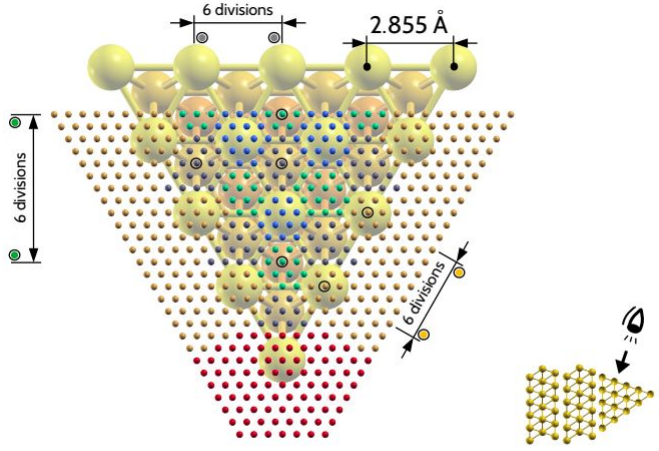
Docking grid



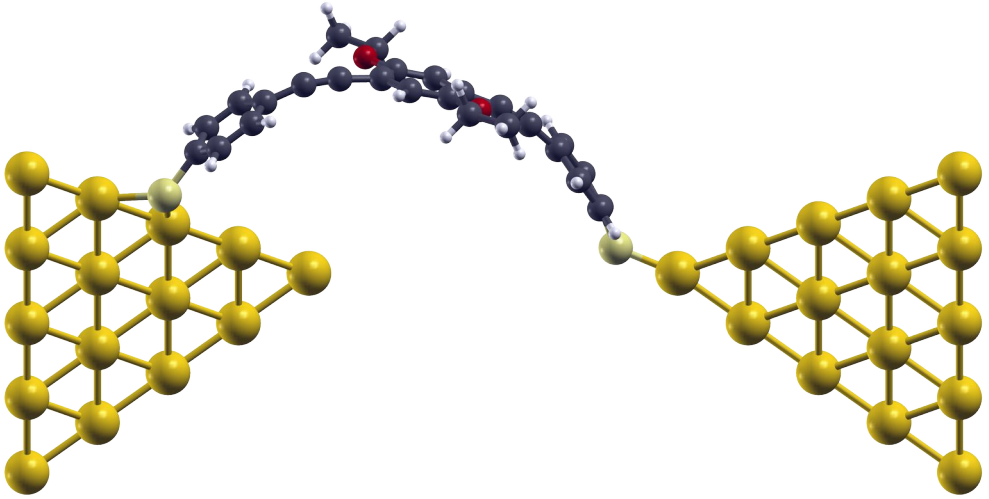
(a) docking grids on left-/right facets



(b) curvature of docking grid about the facet edges



(c) grid division of docking positions on the facet edges



- Is the molecule with thiol anchoring groups at equlibrium for all tip-tip separations?
- Can the anchoring S-atoms slide freely on the gold facets?
- How much can the molecule be bend or streched? Alteration of electronic states?

- Grid spacing accomodates midpoints between high symmetry sites
- Additional grid points chosen protruding over the facet-edges

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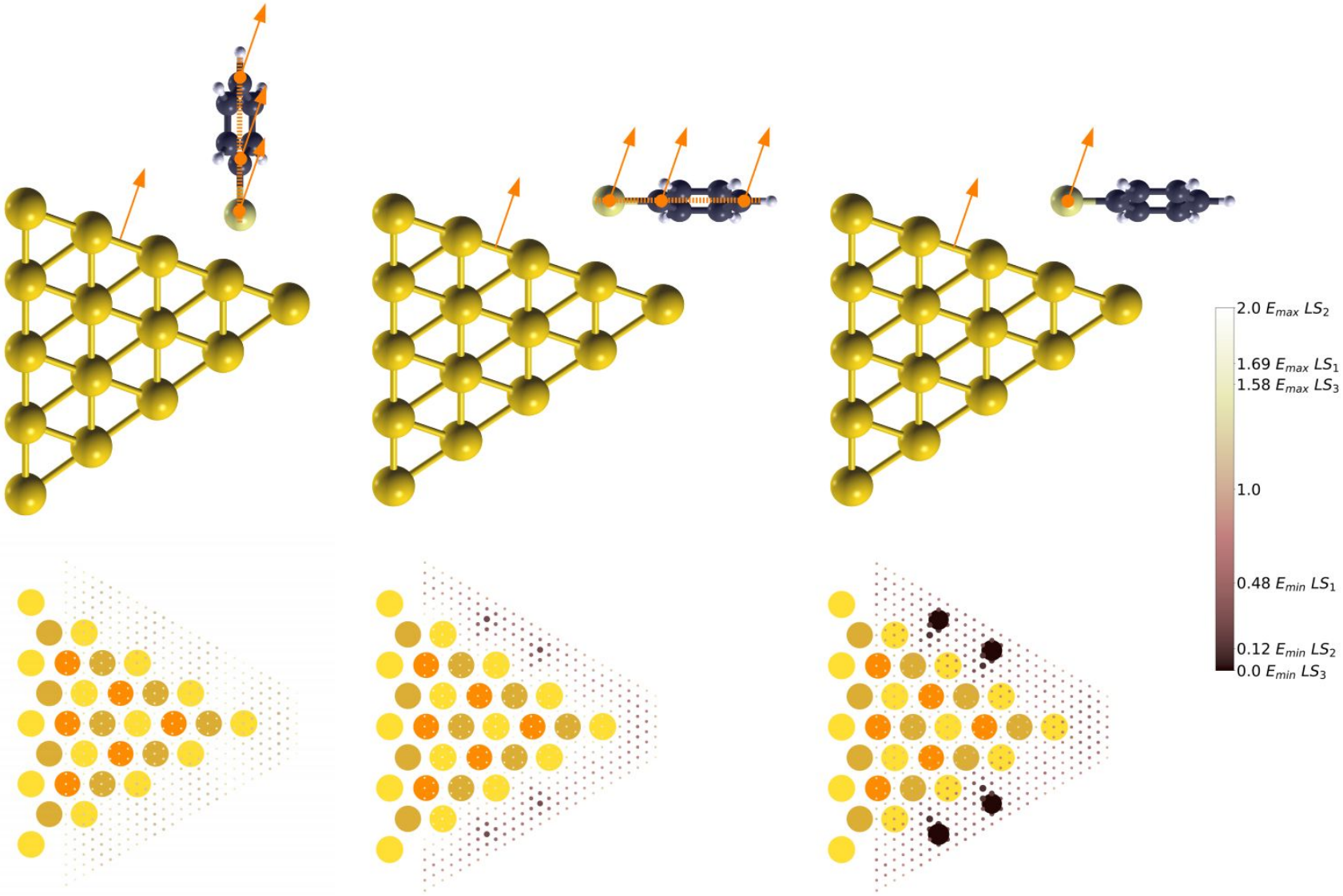
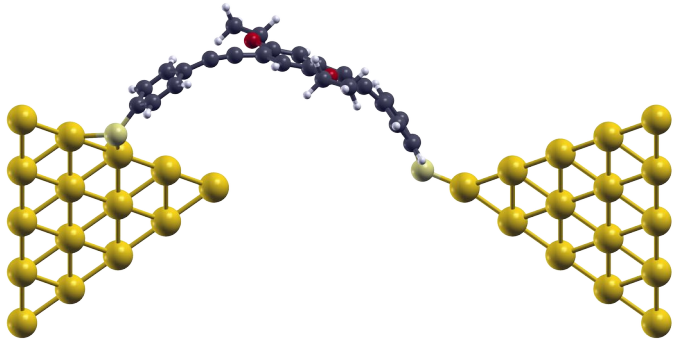
Facet Energy Landscape

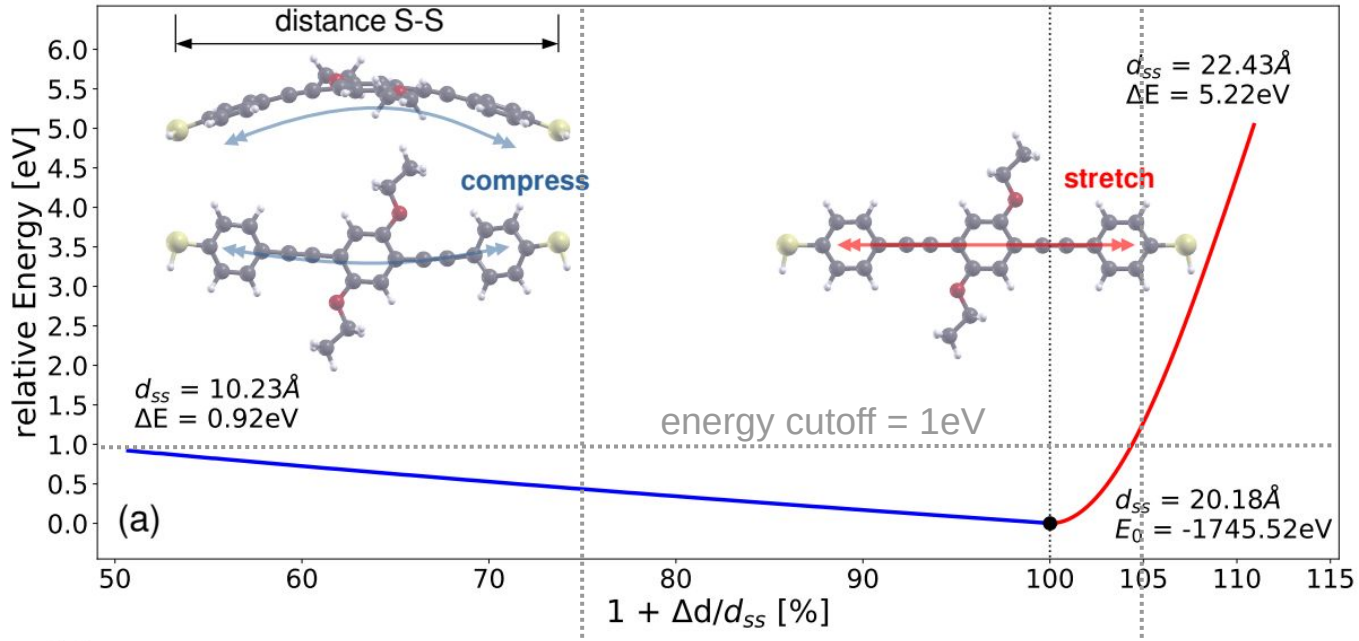


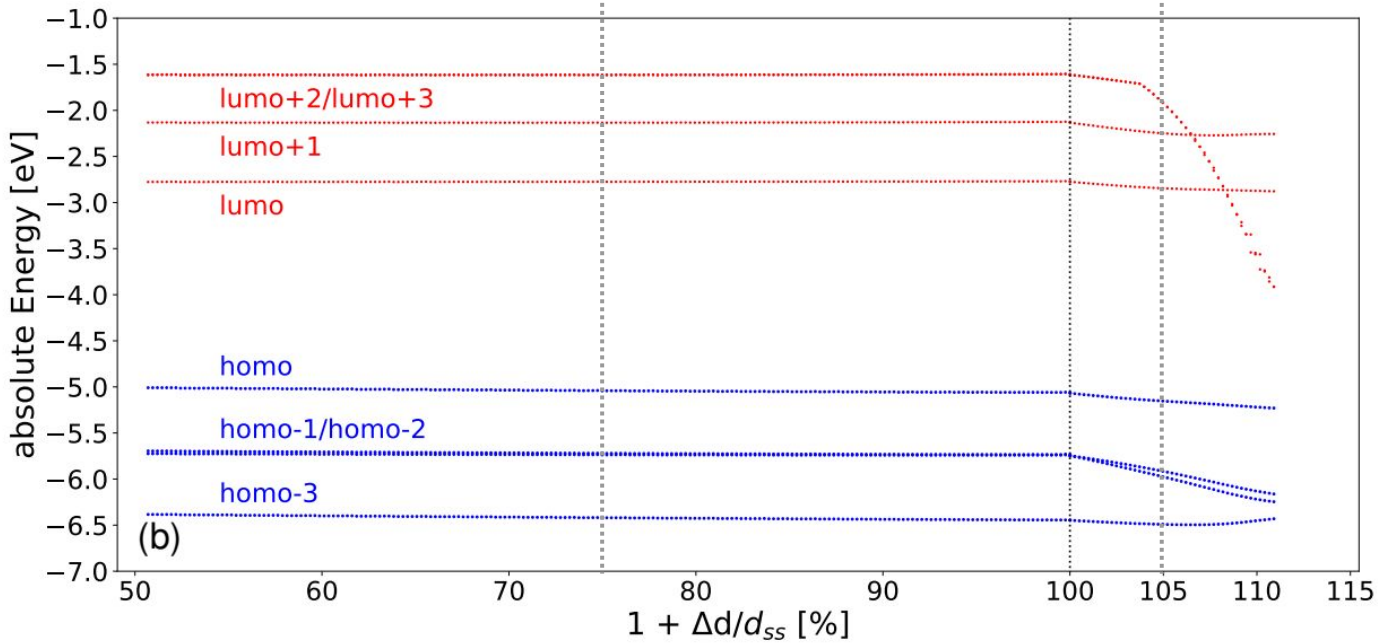


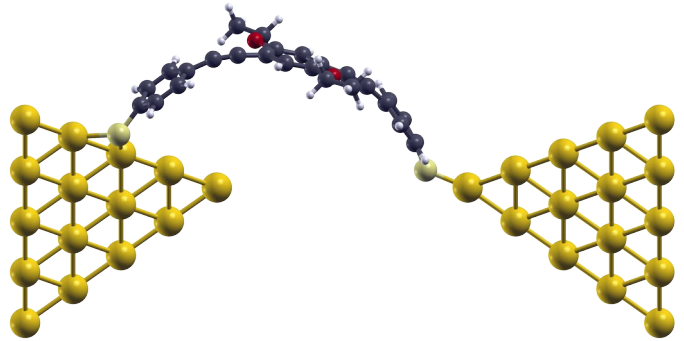
- Thiophenyl
  – vertical, horizontal orientation
  – unrestricted
- Anchoring S-Atom moves along the facet normal

- Energy landscape
  – recurrent features and energy minimum at edges
  – tip region energectically unfavorable

Geometric Deformation



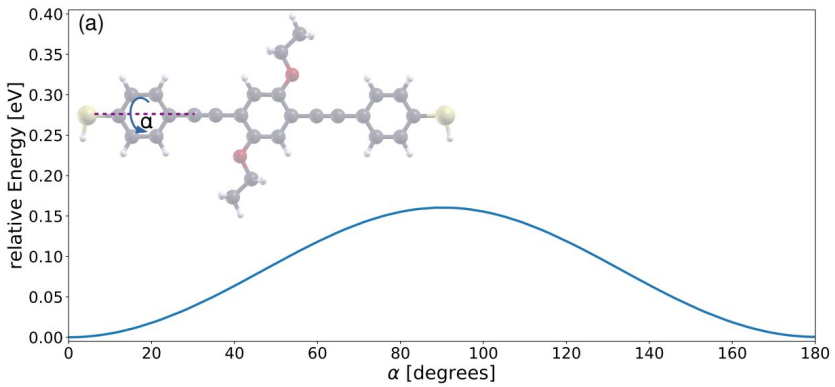


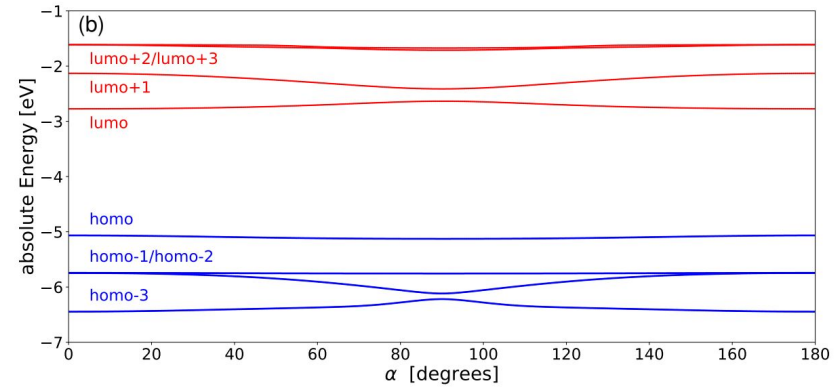


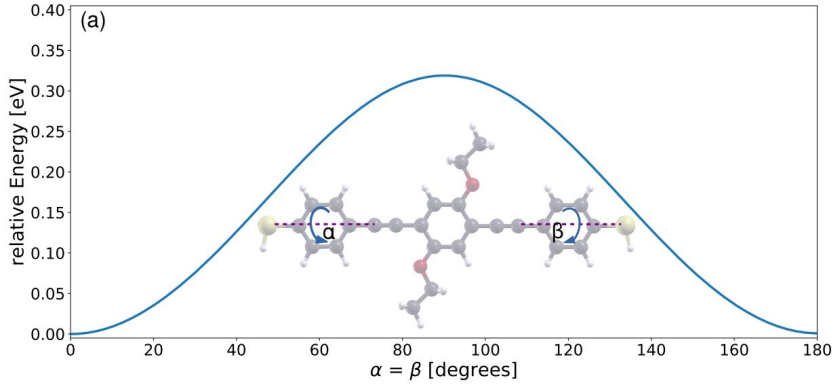
- Stretching follows Hooke‘s Law (parabola)
- Compression linear ▸ in-plane and out-of-plane buldging
- Initial energy cutoff 1eV
- Distortions included [0.75, 1.05] * d_{ss}

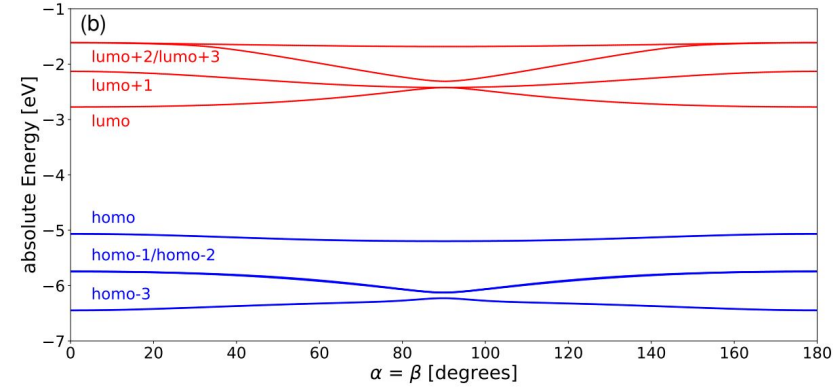
- Energy crossover of unoccupied levels [1.05, 1.10] * d_{ss}
- Splitting on HOMO-1/-2 neglible

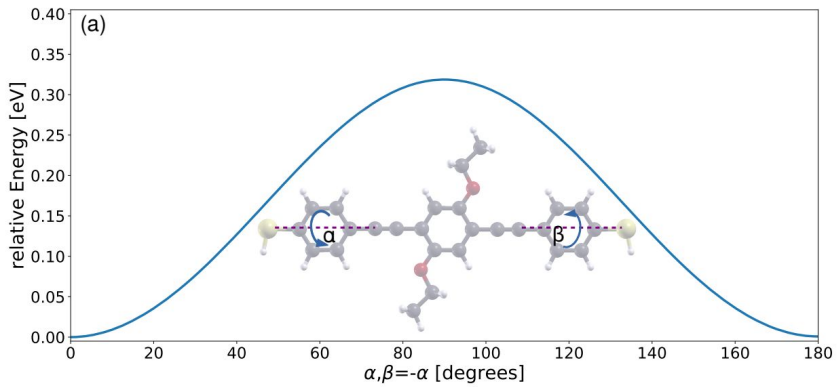
Inducing torsion – perturbation of electronic states

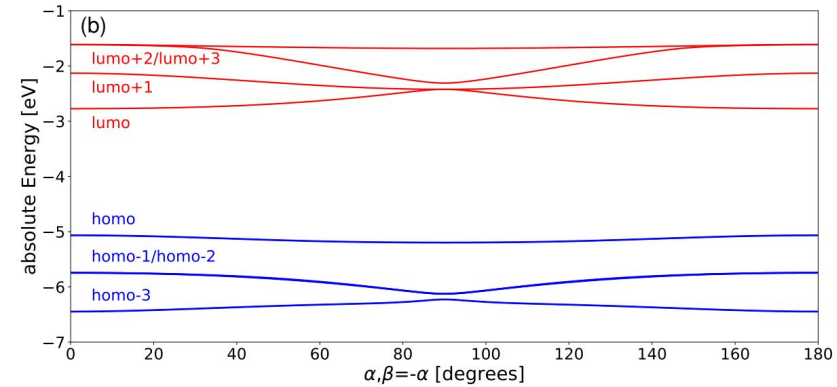












- In all three cases, crossover of unoccupied/occupied level occurs at torsonal distortion [60°, 120°]
-
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Random Walk | Surface Dynamics

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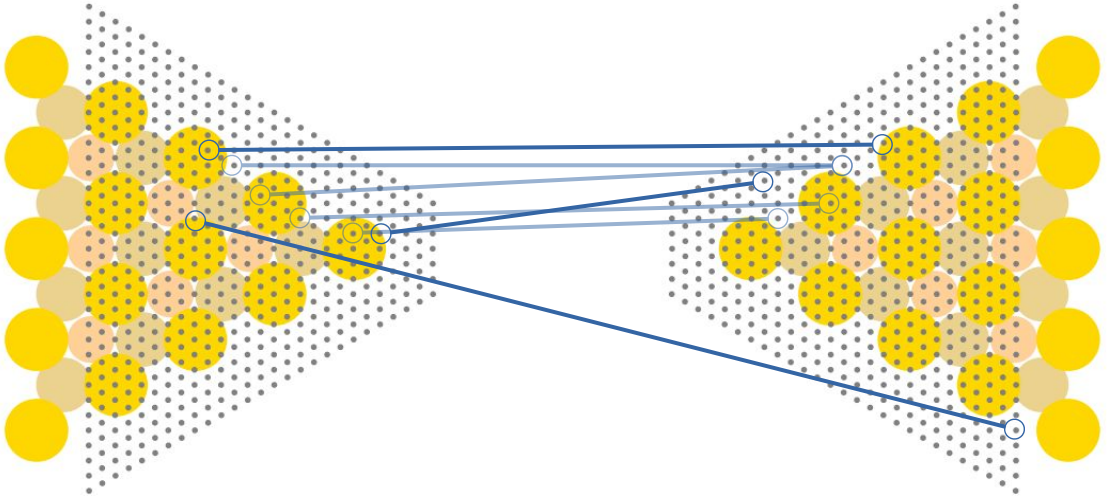
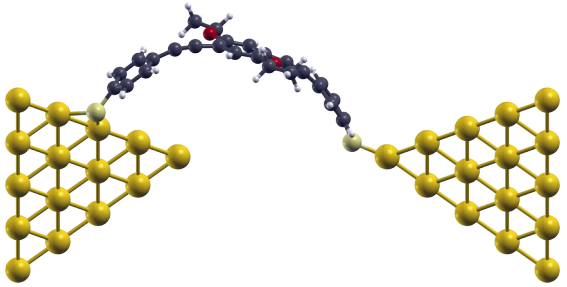
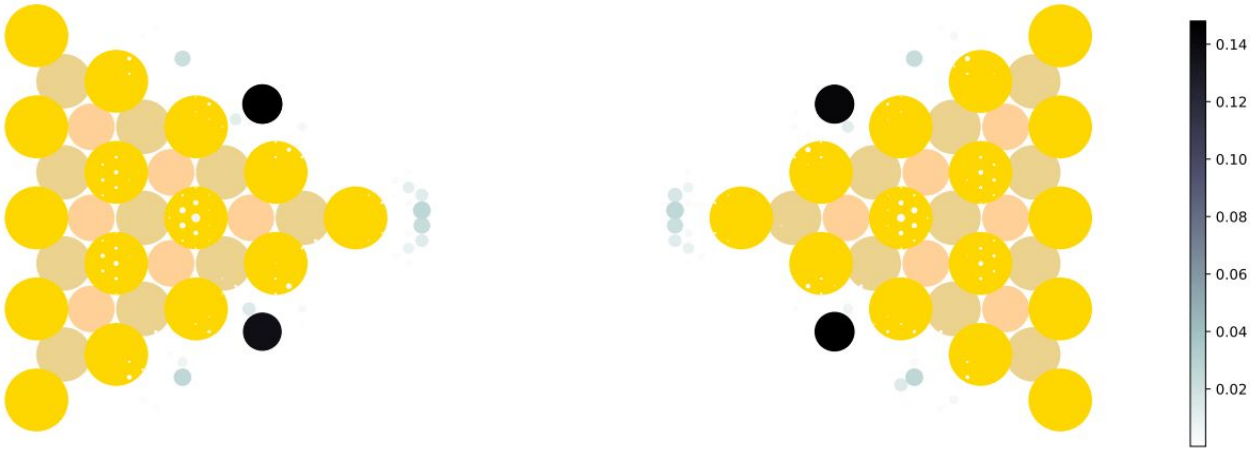
Random Walk | Surface Dynamics

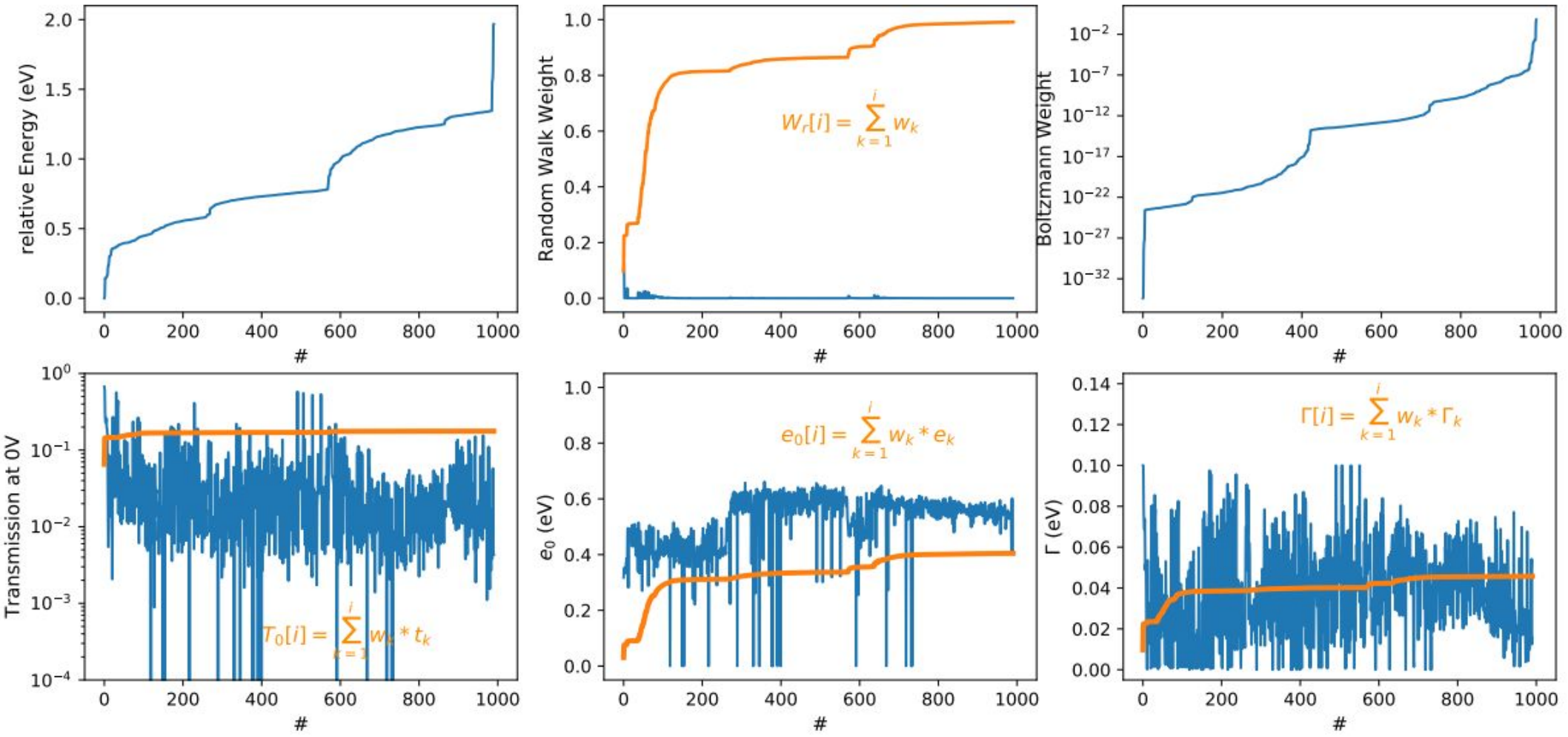




- Driving Force for surface dynamics
- Randow walk – transitions to nearest neighbours allowed



Random Walk | Surface Dynamics



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„Time“ evolution ETCQs using DFTB+NEGF

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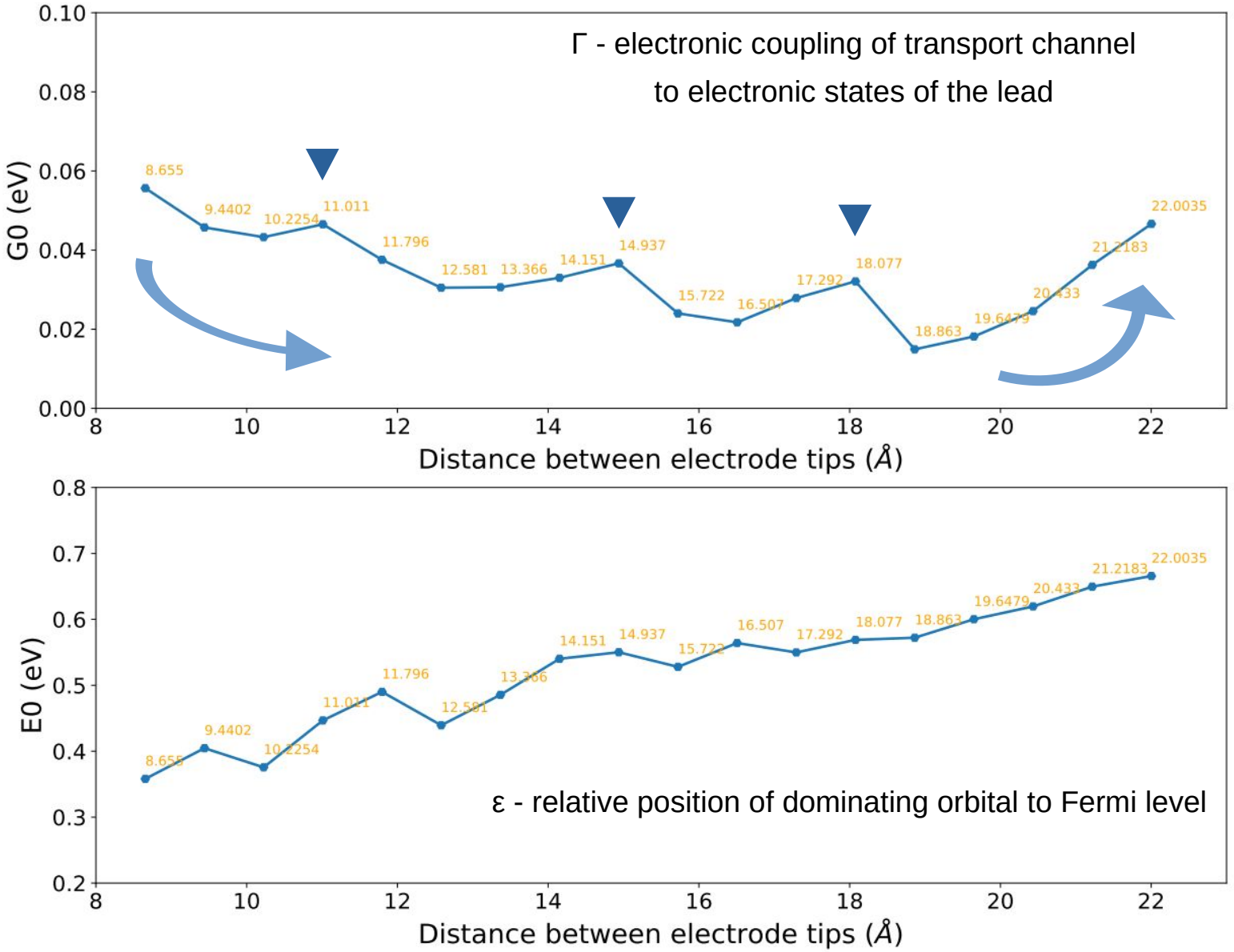
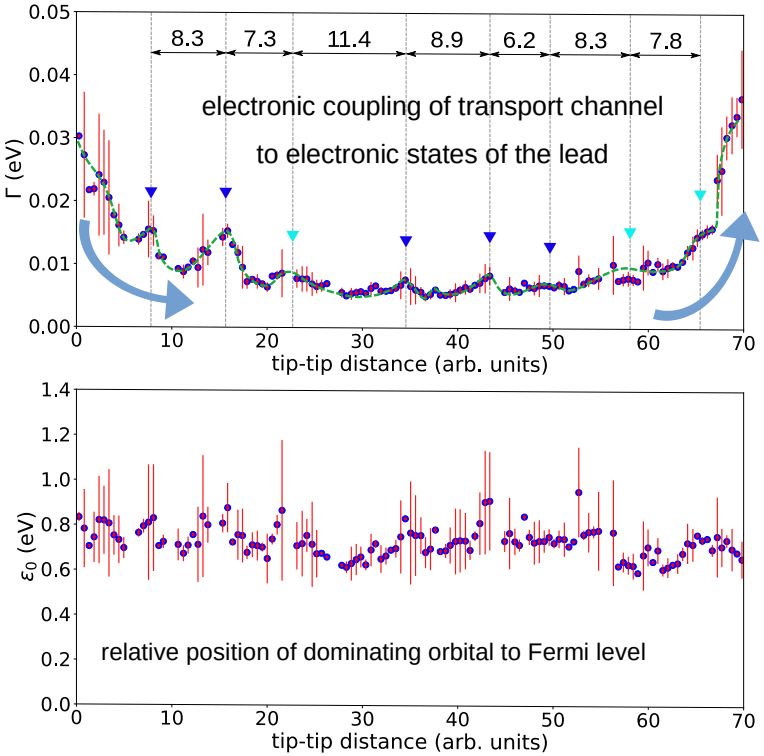
„Time“ Evolution of ETCQs





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Characterizing configuration Ensemble

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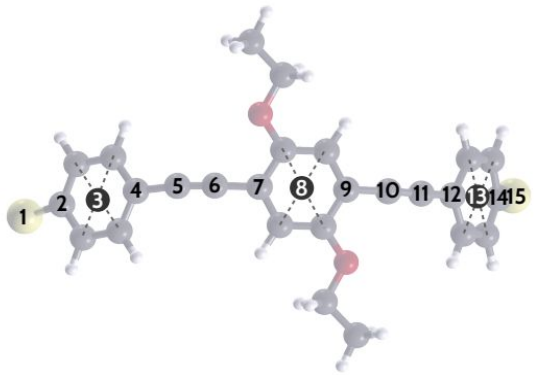
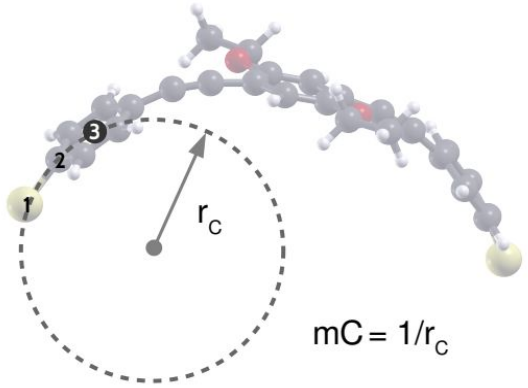
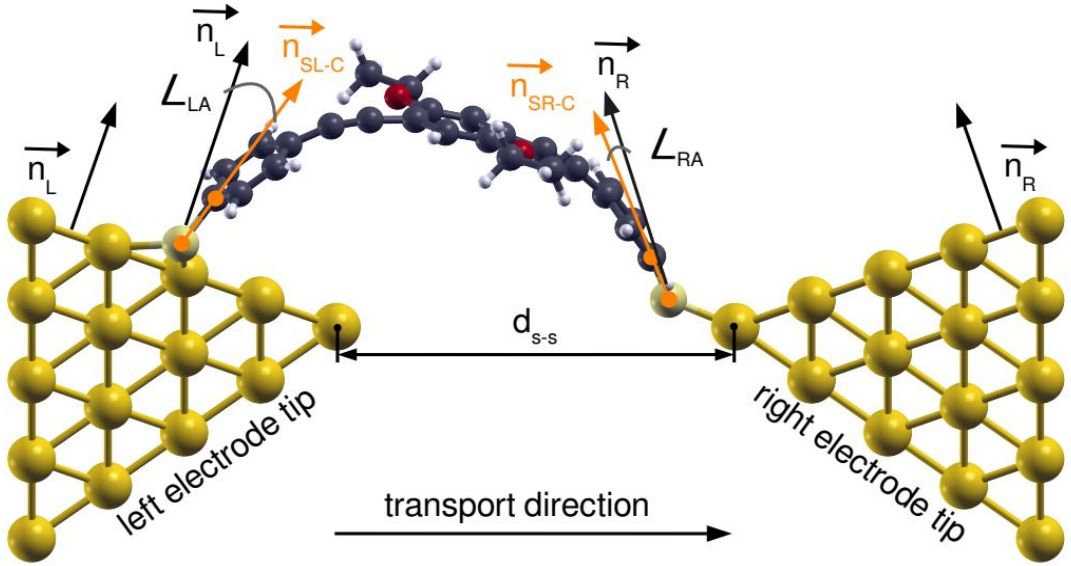
Characterizing configuration ensemble

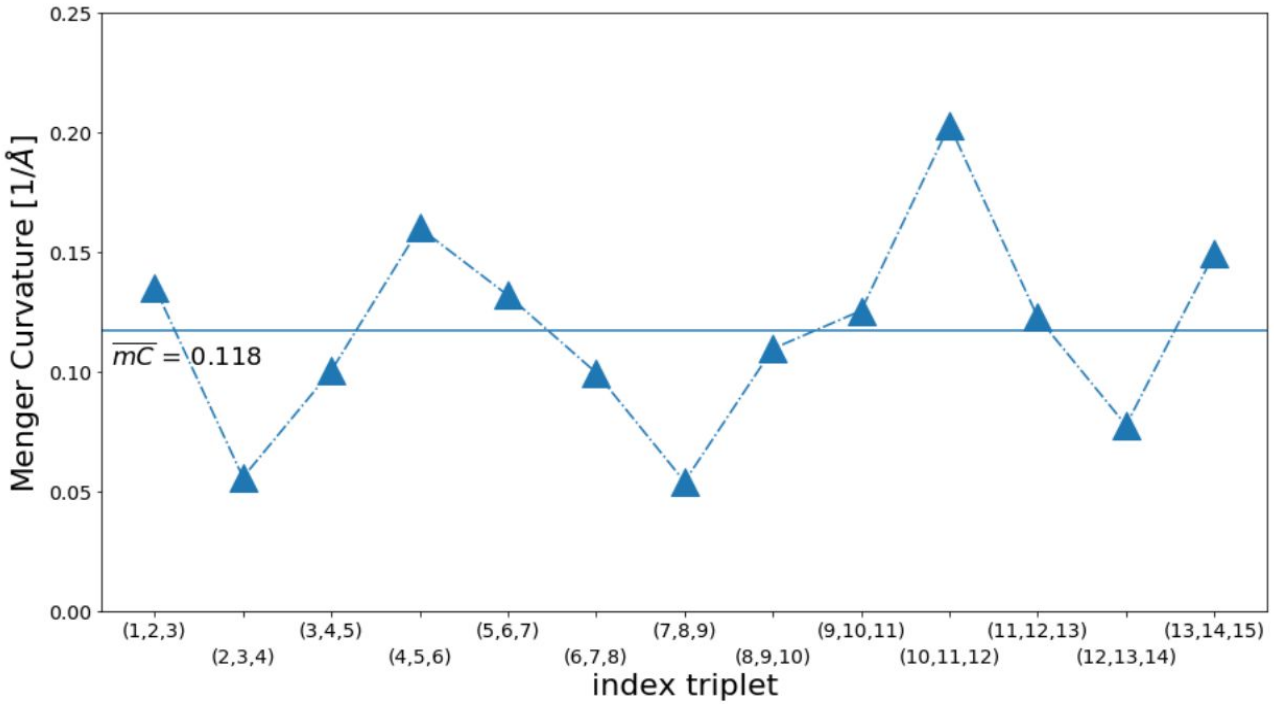


(a) enumeration of atoms and ring centers of the molecular backbone



(b) radius of curvature of a triplet





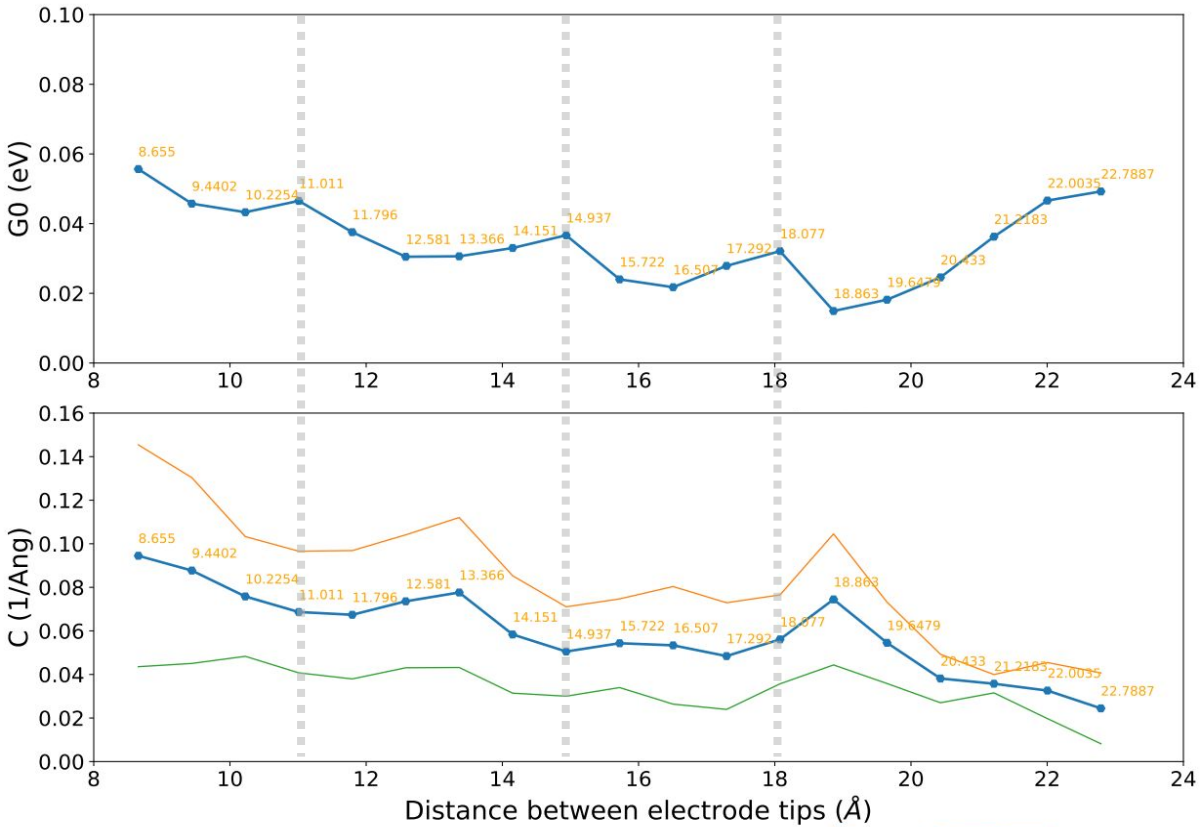
(c) Menger Curvature

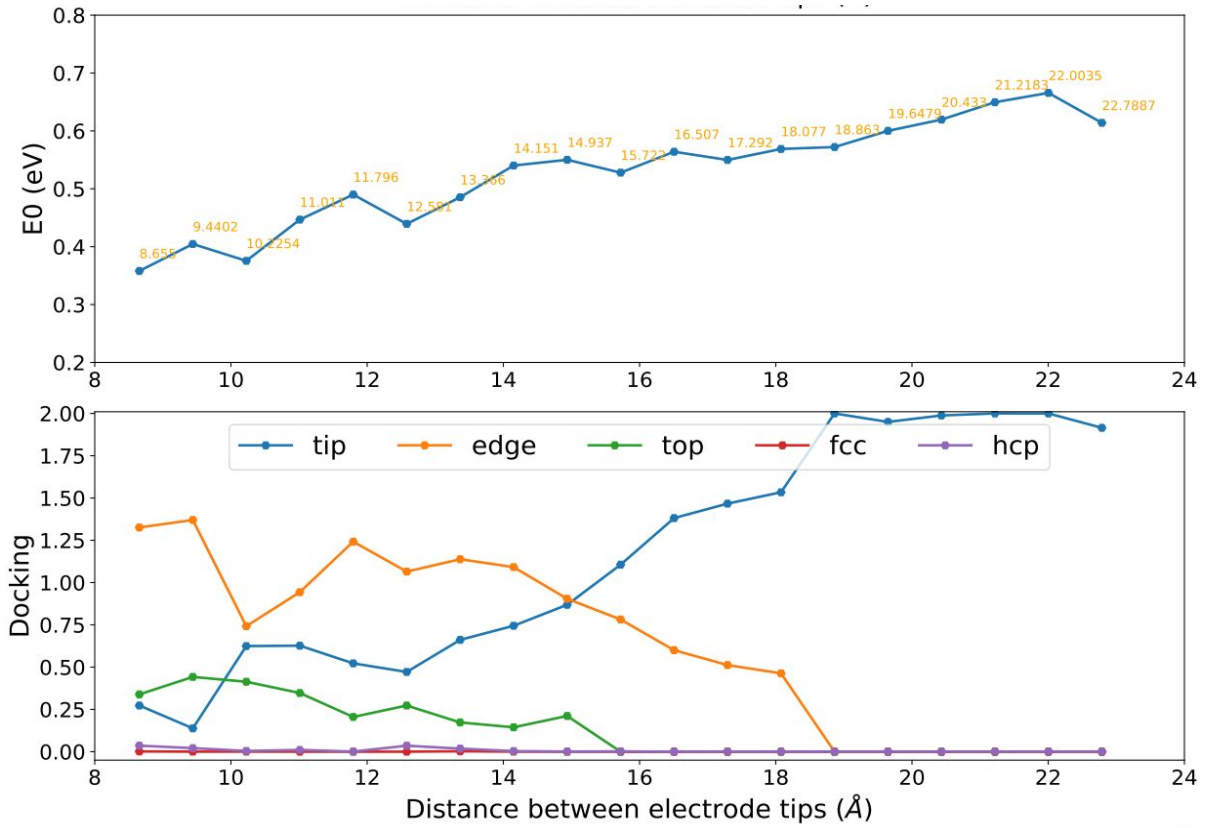
- Tip-tip separation
- Average Menger Curvature of succesive triplets along the molecular backbone
- Local-coordination of docking position

- S-S separation
- Angle btw. Facet normals and S-C bond vector
- Torsion angle

Source: J. Leger, Annals of Mathematics. 149 (3): 831–869 (1999)

Characterizing configuration ensemble





- Recurrent feature in „time“ evolution of Γ linked to overall curvature of PEEB molecular backbone
- Binding predominantly on edges for shorter tip separations ▸ Coupling to multiple facet states
- At larger distances, binding to tip states ▸ Au-S-C bonding angle optimal
- Evolution of ε ▸ reduction of image charge ▸ reduction of renormalization

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Conclusion and Outlook

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- JO

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Vielen Dank für Ihre Aufmerksamkeit

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