First principles simulations of the mechanical and electrical properties of metallic nanocontacts submitted to tensile forces

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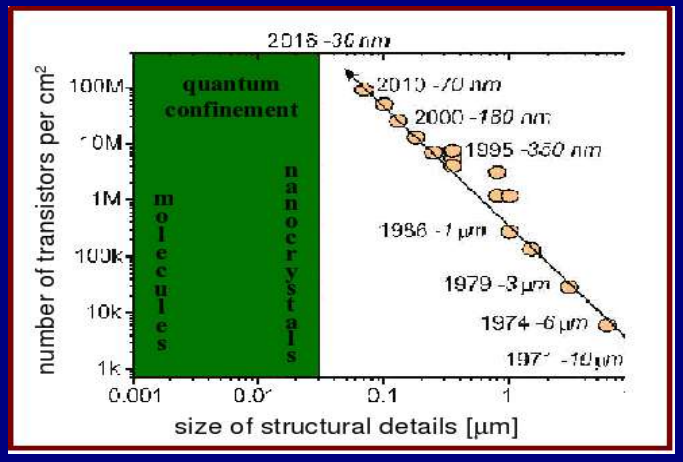
Outline

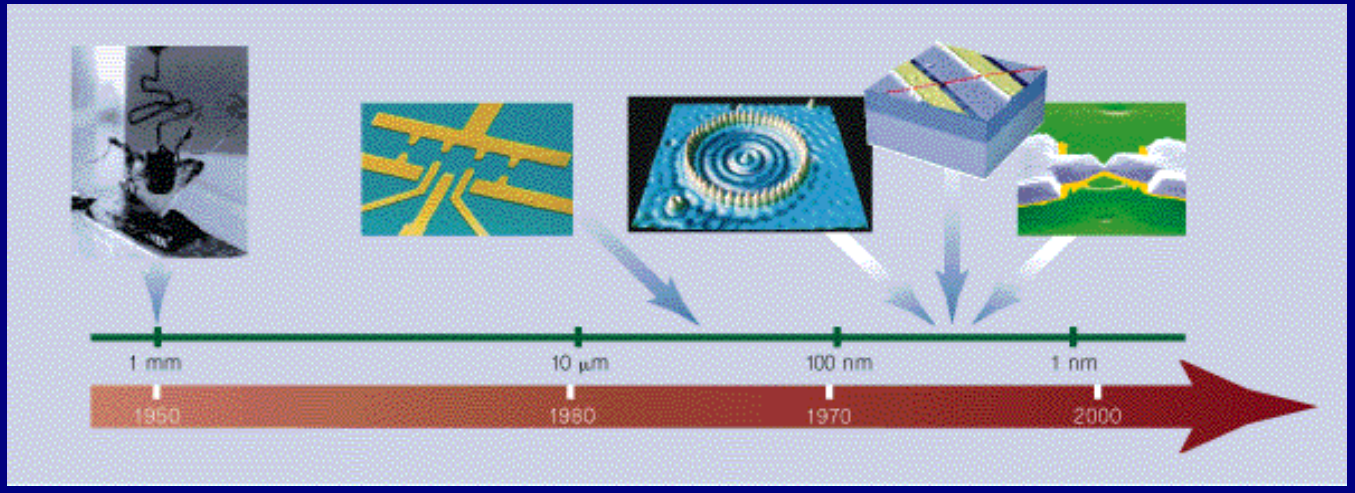
- Introduction
- Experiments: Conductance quantization, Force vs conductance relation, eigenchannels & histograms.
- First-principles simulations of the whole stretching process up to the nanocontact breaking: structure and conductance
- Simple (sp) metals: Al nanocontacts
  - Thin Al (111) nanocontacts: evolution & final “dimer” configuration.
  - Role of the defects (impurities, vacancies).
  - Thick Al nanocontacts with (111) and (100) orientations.
- Au nanocontacts : Chain formation
- Au chains + impurity: fractional quantum conductance
- Conclusions

Introduction I

- Ongoing miniaturization of electronic devices (CPU – 90nm)



- Progress of experimental methods (Scanning Probes etc.)



Introduction II

Atomic scale is different.....

New effects

- Breakdown of Ohm's Law
- Conductance quantization
- Spintronics
- Quant. Wells ; Quant. Dots
- Nanofriction

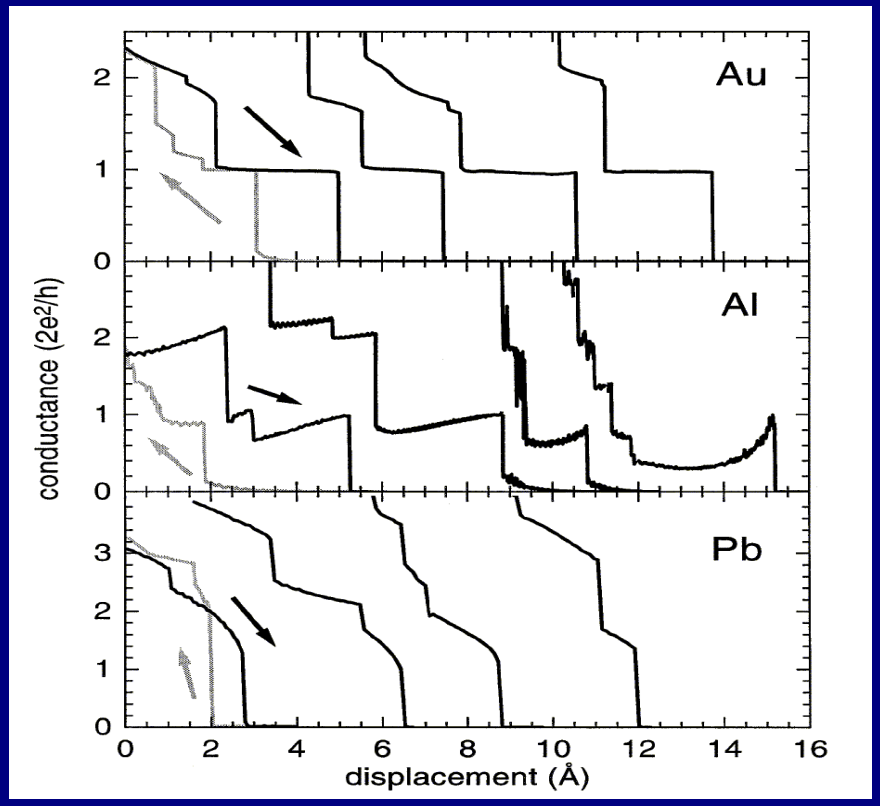
New material properties

- Different conduction properties on different scale (Au vs. Pb)
- Larger yield stress of metallic nanowires
- Superlubricity

New electronic devices

Experimental part 1

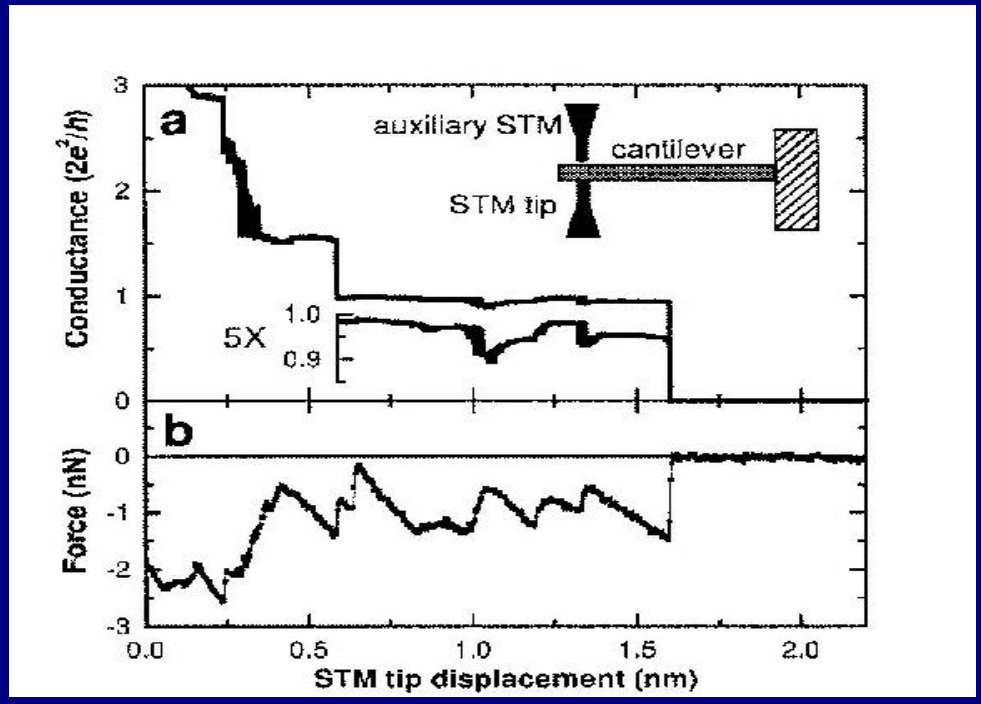
Conductance quantization



J.C. Cuevas et al. PRL **81**, 2990 (1998)

- Stepwise character of conductance
- Characteristic values and shapes of conductance steps

Forces vs. conductance

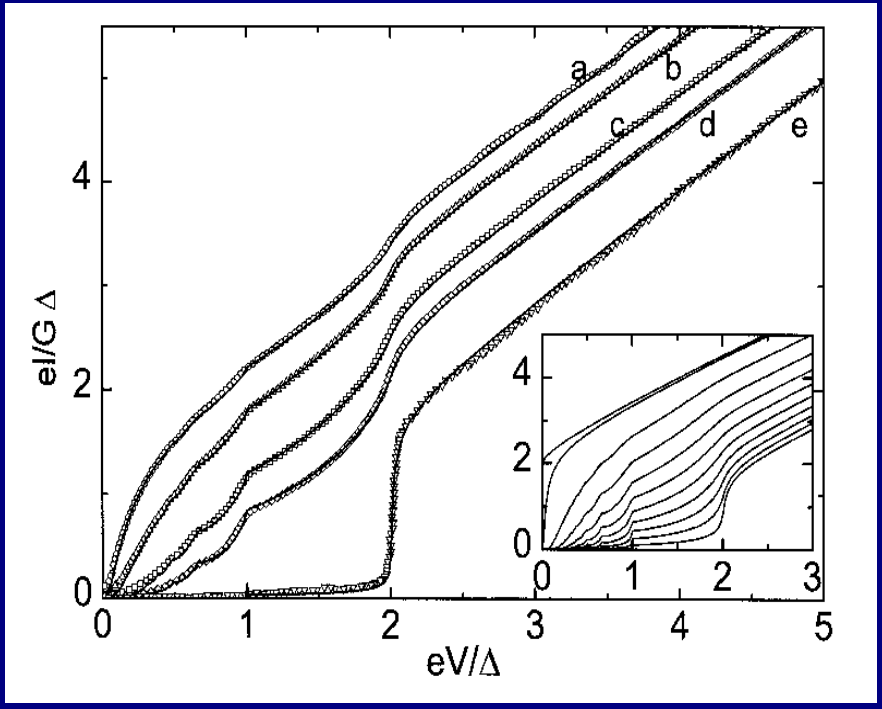


G.Rubio-Bollinger et al. PRL **87**, 26101 (2001)

- Relation between tensile forces and conductance
- Relation between geometry of nanocontacts and conductance
- Mechanical properties of nanowires

Experimental part 2

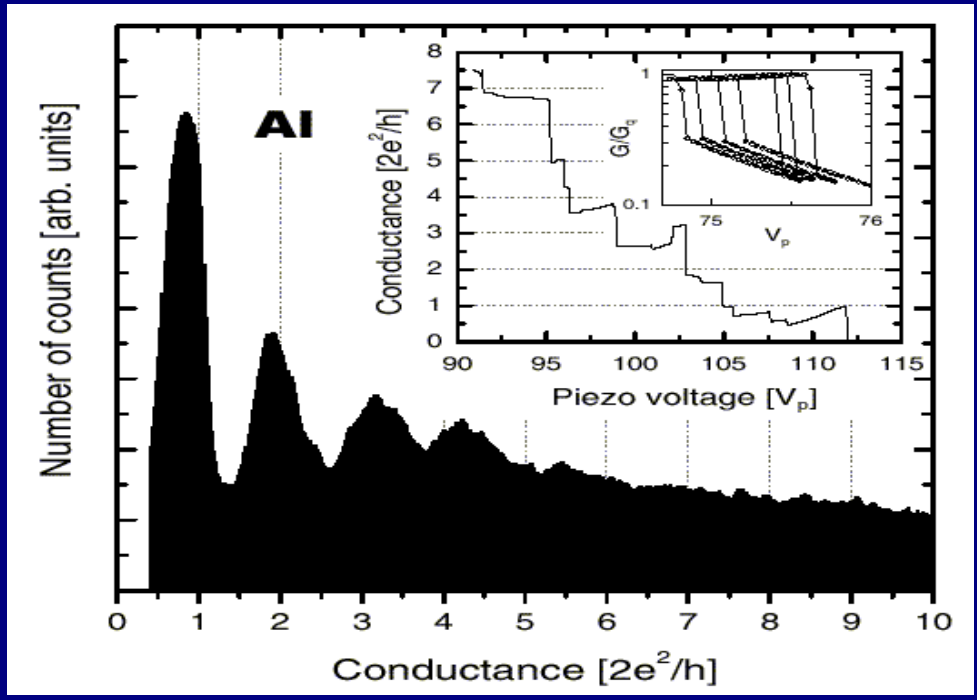
Channels



E. Scheer et al. Nature **394**, 154 (1998)

- Analysis of contributing channels and transmission probabilities of electrons
- Chemical valence determines the electrical resistance of an atom

Conductance histogram

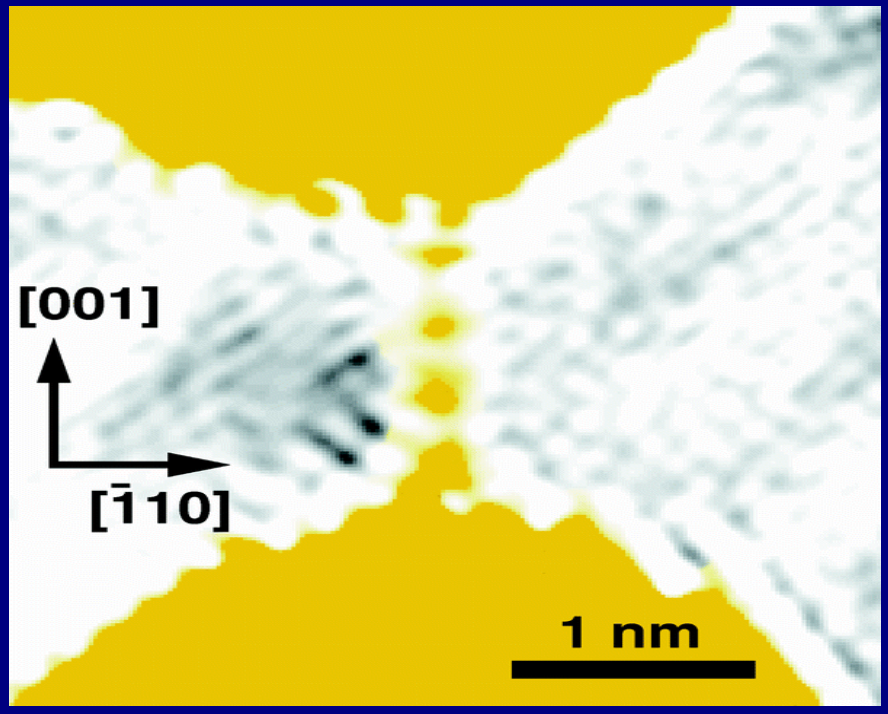


A. I. Yanson PhD Thesis, Univ. Leiden (2001)

- Reflects effects of conductance quantization and atomic rearrangements
- Favorable atomic configurations cause peaks in histogram

Experimental part 3

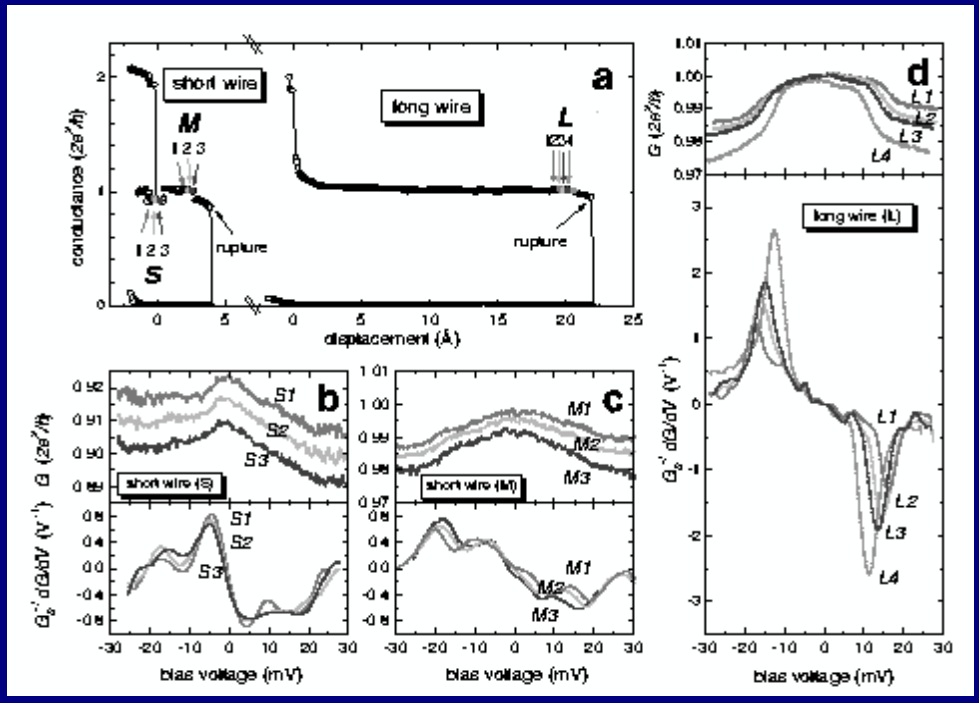
TEM



H. Onishi et al. Nature **395**, 780 (1998)

- Direct visualization of atomic nanoconacts
- Au monoatomic chains

Inelastic transport



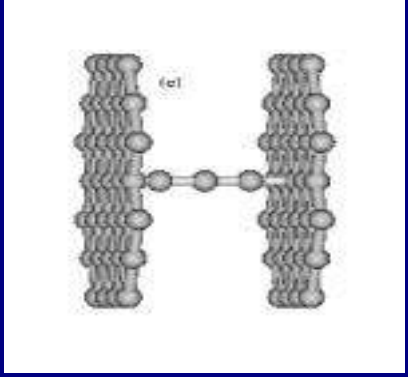
N. Agrait et al. PRL **88**, 216803 (2001)

- Voltage dependency of the current - inelastic scattering of electrons
- Dissipation sensitive to the strain
- e-ph interaction of one-dimensional system

Theoretical calculations

- **State of the art**
  - **Accuracy / scale (ab initio vs. classical potentials)**
  - **Most of ab initio calculations use implicit ideal structures**
  - **Non-equilibrium process (bias voltage etc.)**
  - **Evolution of the system along the elongation …??**

    A. Nakamura et al PRL **82**, 1538 (1999)
  - **Influence of defects, impurities, temperature etc.**

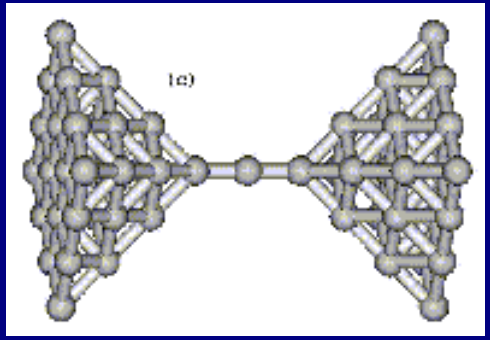


N.D. Lang PRB **52**, 5335 (1995)

C.C. Wan et al PRB **71**, 419 (1997)

J.C. Cuevas et al PRL **80**, 1066 (1998)

J.J.Palacios et al PRB **66**, 035322 (2002)



Our computational approach

First-principles simulations of the whole stretching process up to the nanowire breaking: structure and conductance

- **Motivation**
  - **Simulation of the whole stretching process of metallic nanocontacts**
  - **Determination of the atomic structure of nanocontacts (experimentally unreachable)**
  - **Explanation of distinct phenomena and material properties**
  - **Relation between mechanical and electrical properties**
  - **Effect of defects and impurities on the material properties**

Computational scheme

- **Part I: Structure optimization**
  - Ab-initio DFT-LDA total energy calculations
  - Combination of fast / accurate methods
  - Local orbital-DFT (Fireball) and PW-DFT (Castep)

P. Jelinek et al cond-mat/0409509 (accepted PRB)

M.Payne et al Rev. Mod. Phys. **64**, 1045 (1992)

- **Part II: Calculation of electrical properties**
  - Keldish-Green's function formalism (beyond pert. theory)
  - TB-Hamiltonian from Fireball code
  - T= 0 K; no bias voltage (equilibrium conditions)

P. Jelinek et al. Surf. Sci. **566-568**, 13 (2004)

WELCOME TO FIREBALL

ab initio tight-binding molecular dynamics

http://www.physics.byu.edu/research/lewis/fireball/index.htm

- Fireball as exploratory ab initio tool with favourable *fast/accuracy* balance
  - real space DFT Molecular dynamics method
  - local 'Fireball' pseudoatomic orbitals (*s,p,d* DN basis set)
  - Harris-Foulkes functional (ρ_{in}) (*J.Harris* PRB **31**, 1770 (1985))
  - 3-center approximation; integrals in tables (fast interpolation)
  - norm conserving KB pseudopotencial
  - parallel, linear-scaling implementation
  - Multi-center average density approximation for XC matrix
  - TDDFT
  - spin-polarization
  - Kohn-Sham scheme + grid method

} **in progress**

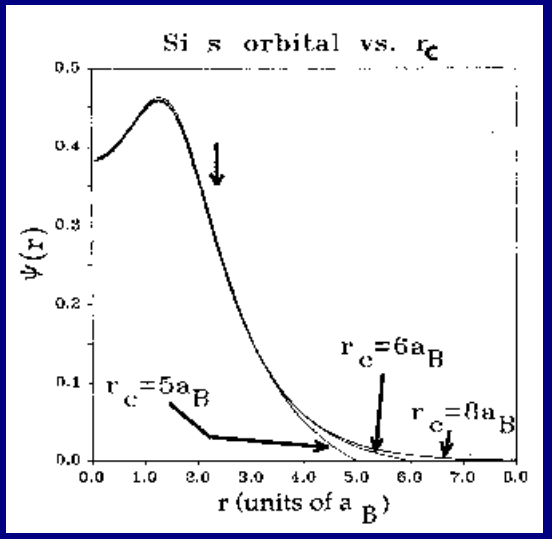
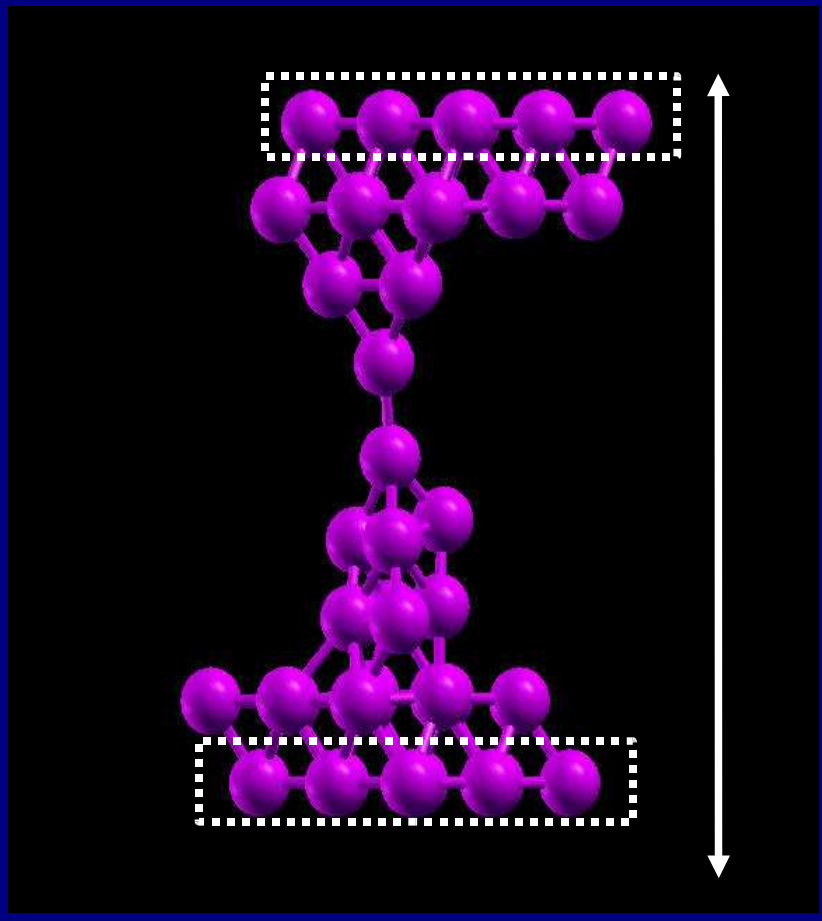


Fig. *'Fireball'* orbital

O. F. Sankey and D.J. Niklewski PRB **64**, 1045 (1989)
A. Demkov et al. PRB **52**, 1618 (1995)
J.P. Lewis et al. PRB **64**, 195103 (2001)
S.D. Shellman et al. J.Comp.Phys. **188**, 1 (2003)
P. Jelinek et al. cond-mat/0409509 (accepted PRB)

Total energy calculation

- Nanocontact: a neck sandwiched between two leads (slabs)
- Initial structure derived from ideal bulk geometry (48-145 atoms)
- PBC applied in all x,y,z-axis
- Stretching process controlled via PBC in z-axis
- Marked internal layers of slab are fixed (white box)
- For each distance atomic positions relaxed using CG
- Effect of the temperature NOT included
- Different surface orientations; impurities
- Tensile forces ~ total energy derivative with respect to the displacement
- SCF TB Hamiltonian of optimized structure to transport code

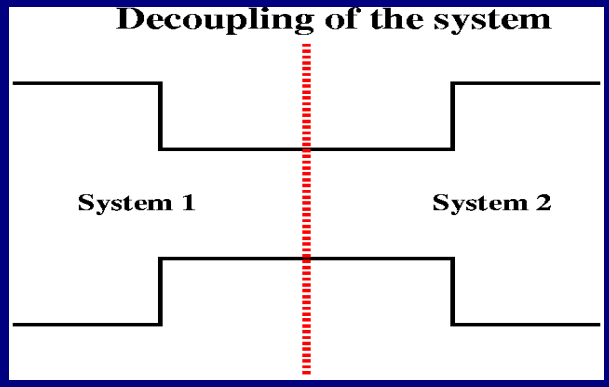


Transport calculation: formalism

conductance across the interface:

$$G = \frac{dI}{dV} = \frac{4\pi e^2}{\hbar} \mathrm{Tr}[\hat{T}_{12}\hat{\rho}_{22}(E_F)\hat{D}^r_{22}(E_F)\hat{T}_{21}\hat{\rho}_{11}(E_F)\hat{D}^a_{11}(E_F)]$$

decoupling:



multiple scattering terms:

$$\hat{D}^r_{22} = [\hat{1} - \hat{T}_{21}\hat{g}^r_{11}(\omega)\hat{T}_{12}\hat{g}^r_{22}(\omega)]^{-1};$$

$$\hat{D}^a_{11} = [\hat{1} - \hat{T}_{12}\hat{g}^a_{22}(\omega)\hat{T}_{21}\hat{g}^a_{11}(\omega)]^{-1};$$

transfer matrix:

$$\hat{t}^+ = 2\pi\hat{\rho}^{1/2}_{22}\hat{T}^{eff}_{21}\hat{\rho}^{1/2}_{11}, \quad \hat{T}^{eff}_{21} = \hat{D}^r_{22}\hat{T}_{21};$$

$$\hat{t} = 2\pi\hat{\rho}^{1/2}_{11}\hat{T}^{eff}_{12}\hat{\rho}^{1/2}_{22}, \quad \hat{T}^{eff}_{12} = \hat{D}^r_{11}\hat{T}_{12};$$

Landauer formalism:

$$G = \frac{2e^2}{h}\mathrm{Tr}[\hat{t}(E_F)\hat{t}^+(E_F)];$$

eigenchannels:

$$G = \frac{2e^2}{h}\sum_{i=1}^{N}\tau_i(E_F), \quad 0 < \tau_i < 1;$$

$$\mathrm{Tr}(\hat{t}\hat{t}^+) = \mathrm{Tr}(\hat{t}'^+\hat{t}'), \quad t_{mn} = (t'_{nm})^*;$$

...the formalism is equivalent to other approaches

for details see *F.J. Garcia-Vidal et al. Prog. Surf. Sci.* **74**, 177 (2003)

Transport calculation: scheme

Fireball: non-orthogonal TB $\hat{H}^x(r)$, $\hat{S}(r)$

↓

k-space: $\hat{H}^x(r)$, $\hat{S}(r) \rightarrow \hat{H}^x(k)$, $\hat{S}(k)$

↓

orthogonalization: $\hat{H}(k) = \hat{S}(k)^{-½}\, H^x(k)\, \hat{S}(k)^{-½}$

↓

partition: $\hat{H}_1(k) + \hat{H}_2(k) + \check{T}_{12}(k)$

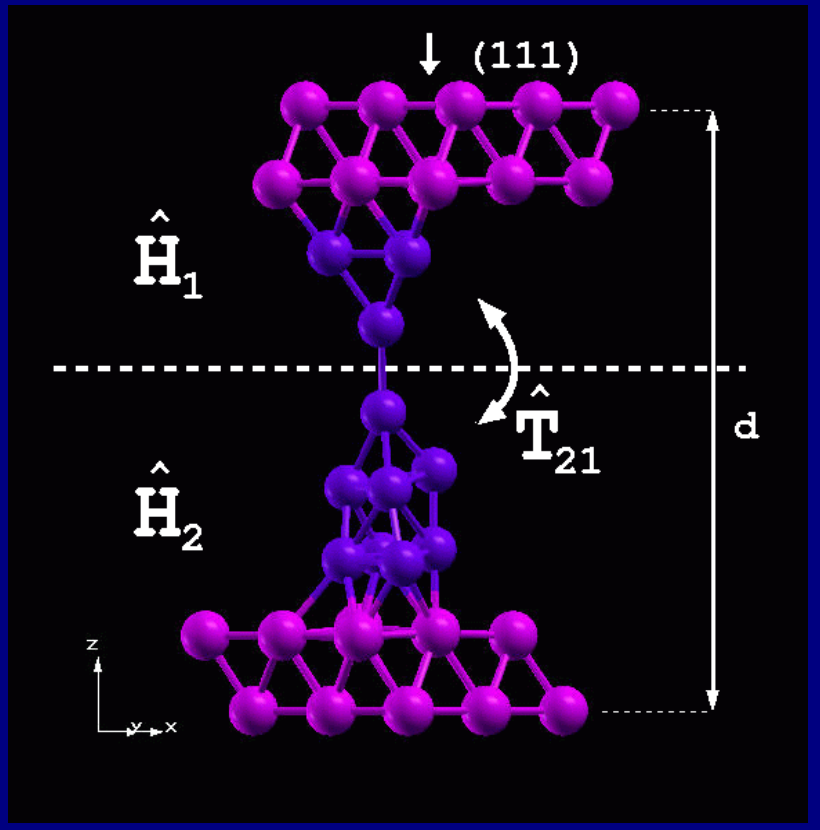
↓

r-space: $\hat{H}_i(r)$, $\check{T}_{12}(r)$

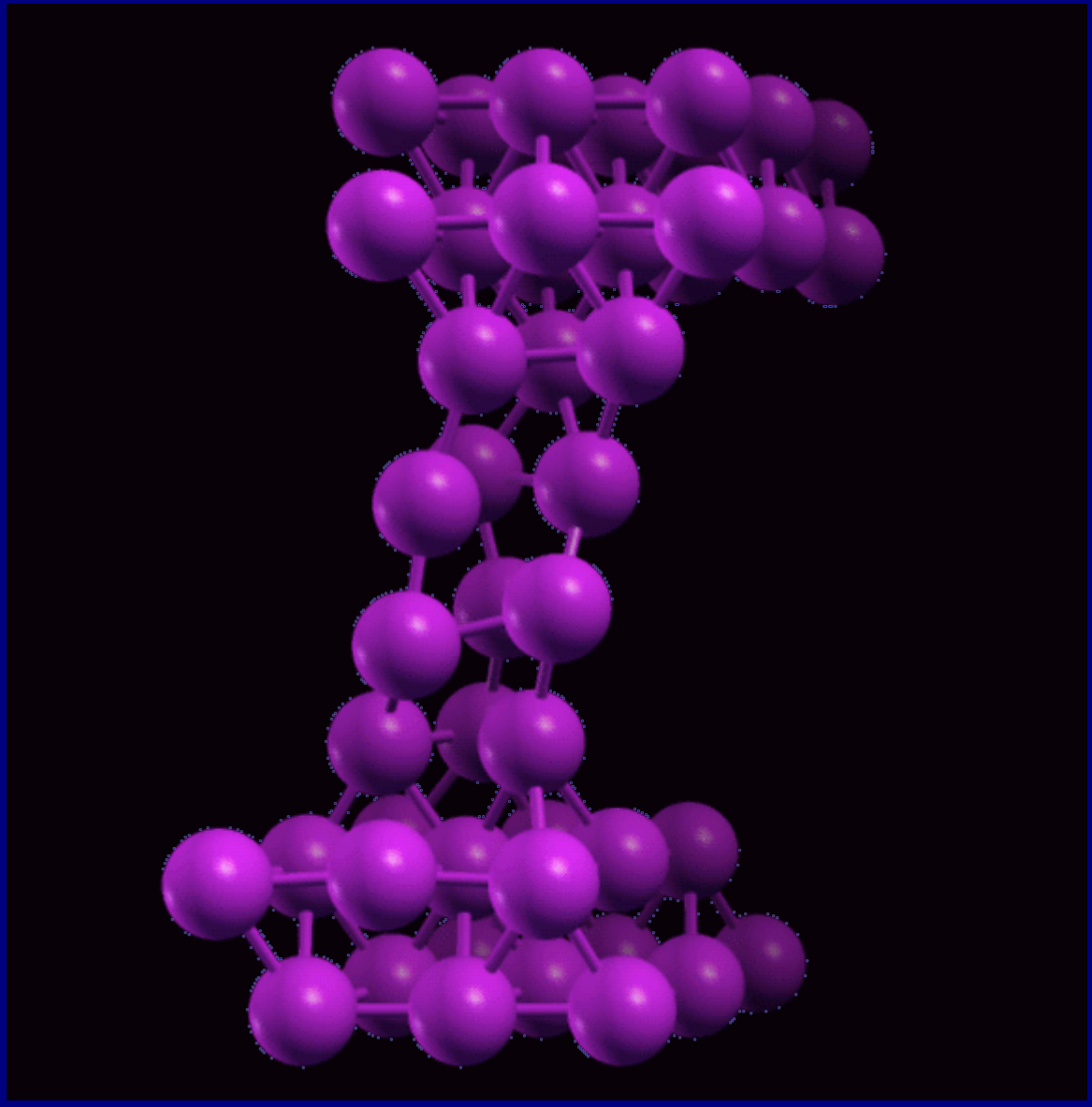
↓

$$g_{ii}^{r,a} = [\omega - \hat{H}_{ii} \pm i\eta\,]^{-1}$$

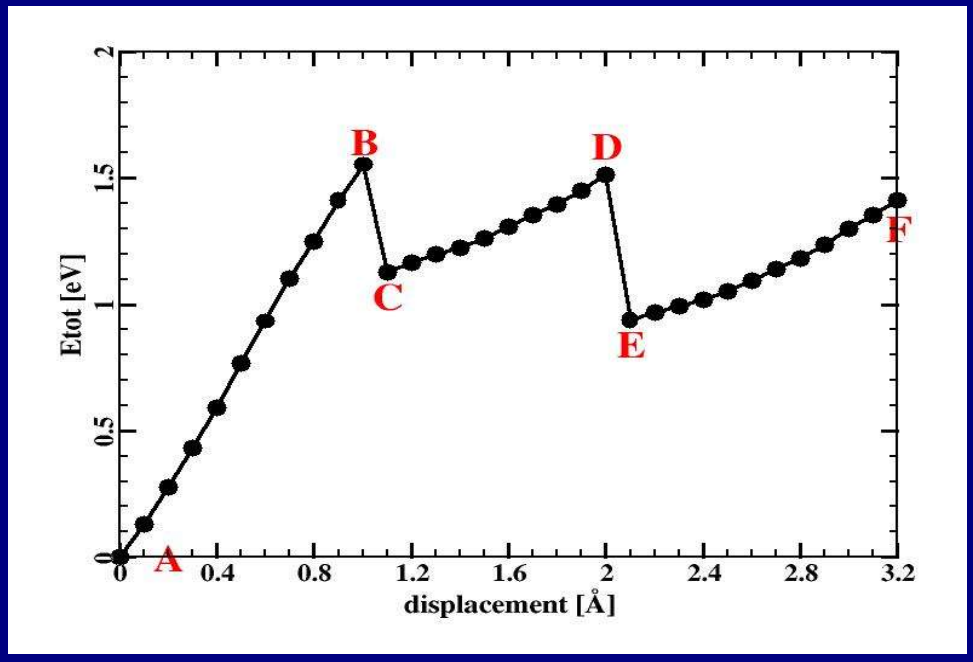
$$G = \frac{2e^2}{h}\mathrm{Tr}[\hat{t}(E_F)\hat{t}^{+}(E_F)]$$

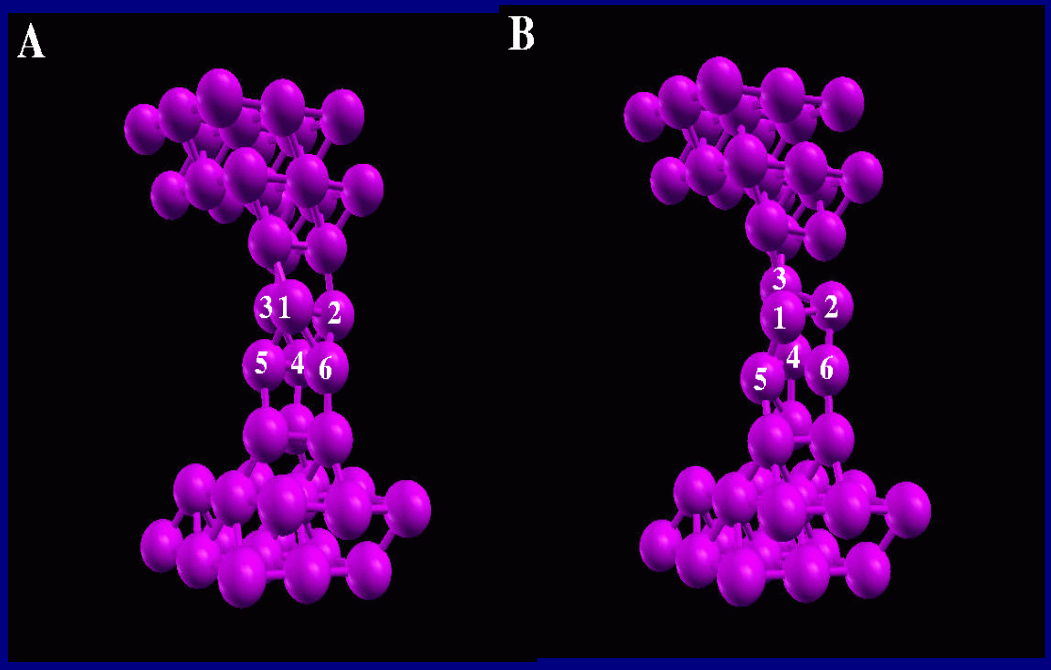


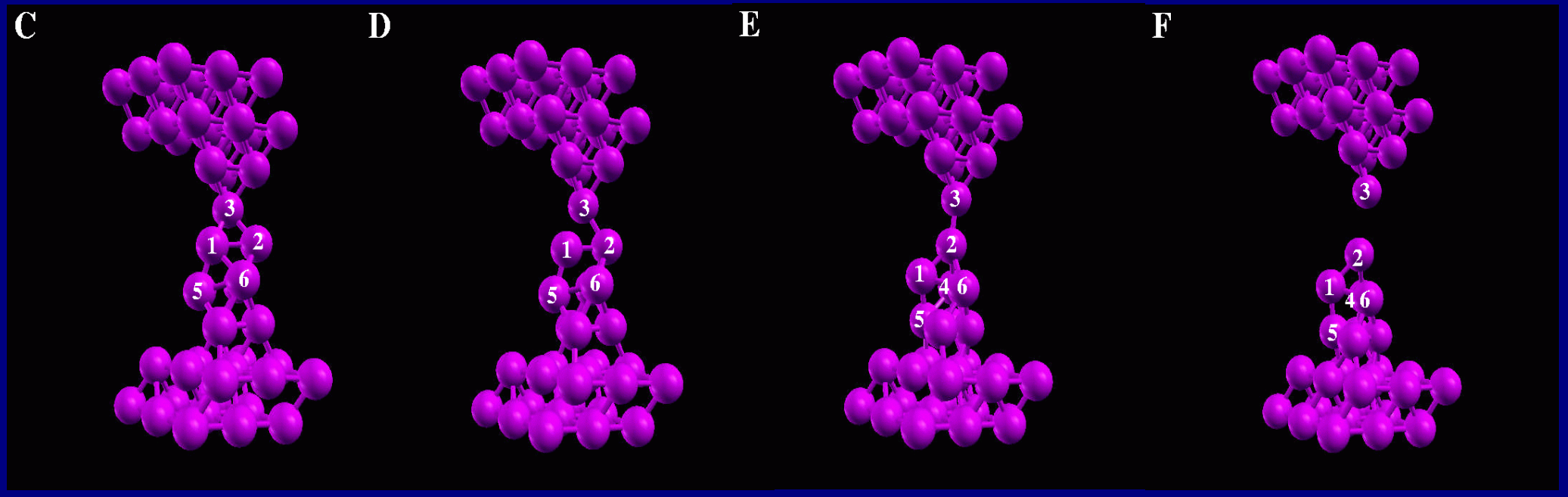
Al nanocontacts



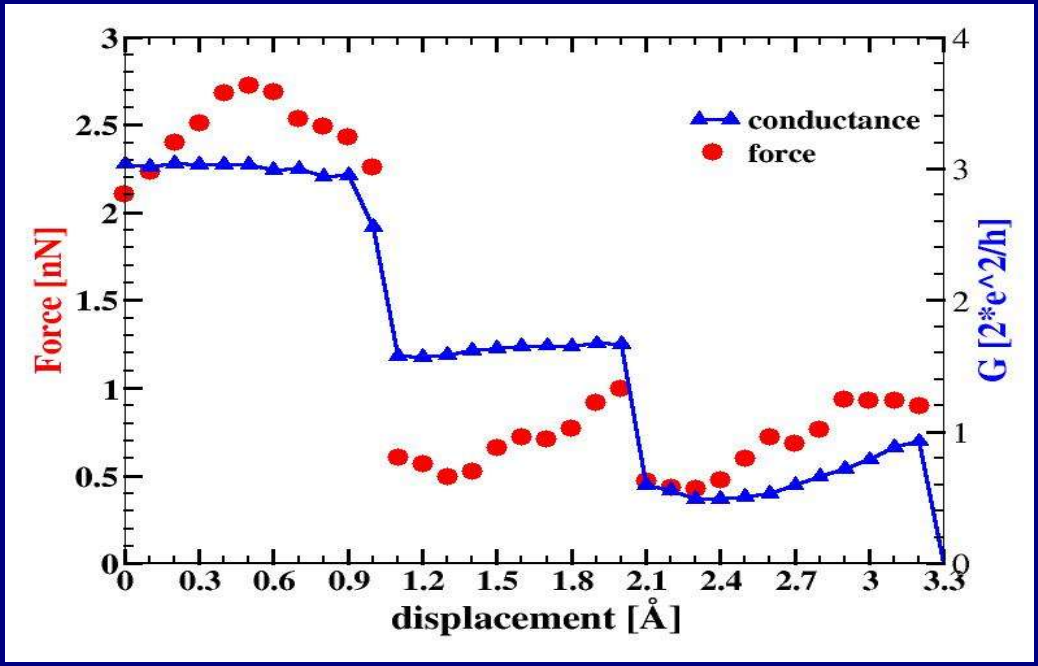
3x3-4l: structure



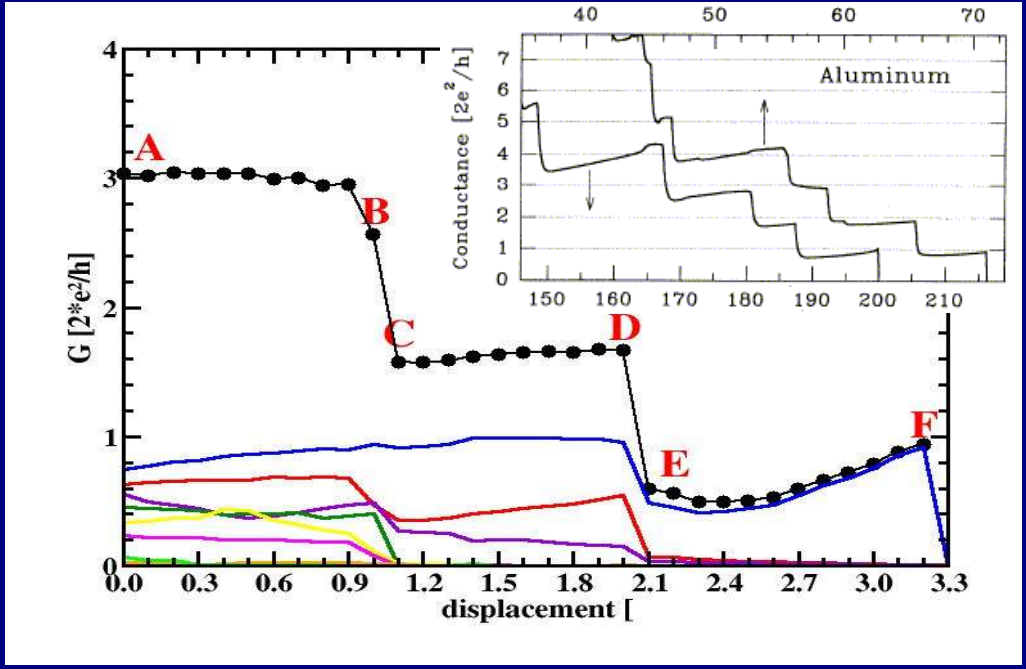




3x3-4l: conductance



- Direct relation between tensile forces, conductance and structure
- Abrupt changes related to reconstruction of the neck
- Forces ~ 0.5 ÷2.7 nN



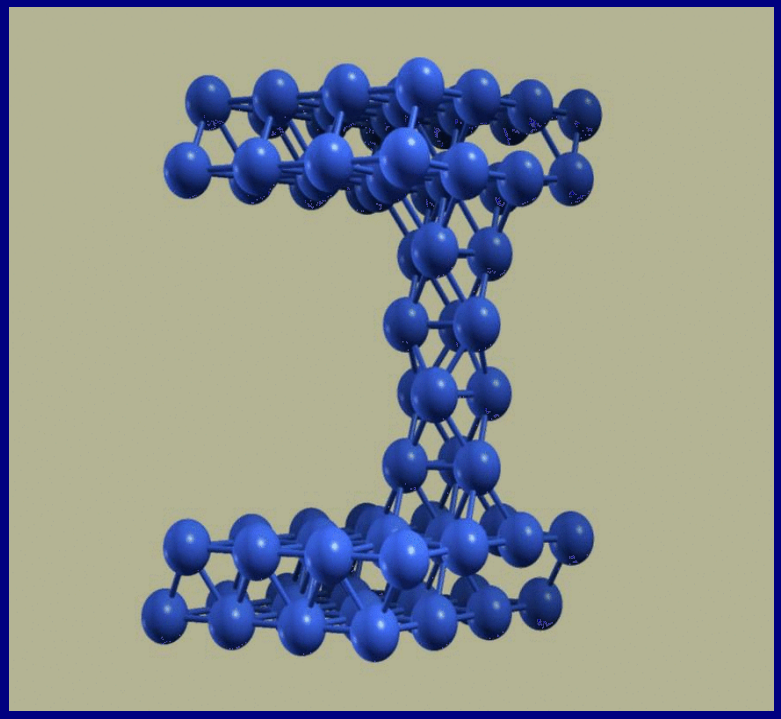
- Number of open channels depends on the geometry and changing with distance
- Ascending shape of last step
- G on steps near 3,2,1 value

P.Jelinek et al. PRB **68**, 085403 (2003)

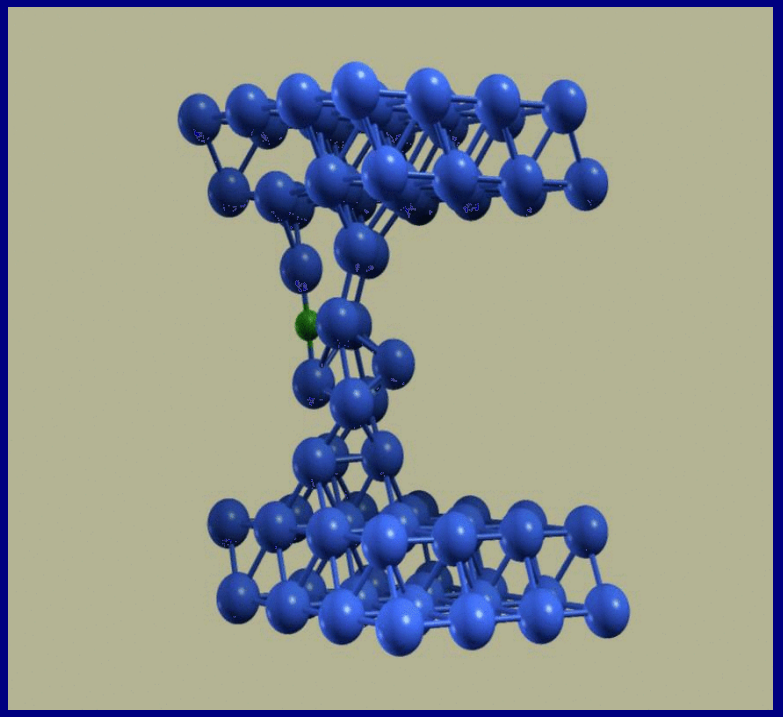
Are these results reliable?

- Different initial conditions: different length (5I & 8I) and periodicity (4x4).
- Role of defects: Vacancies & Impurities (Si, C, H & O)
- Thicker wires with different orientations: Al(111)-(5x5-5I) & Al(100)-(5x5-4I)

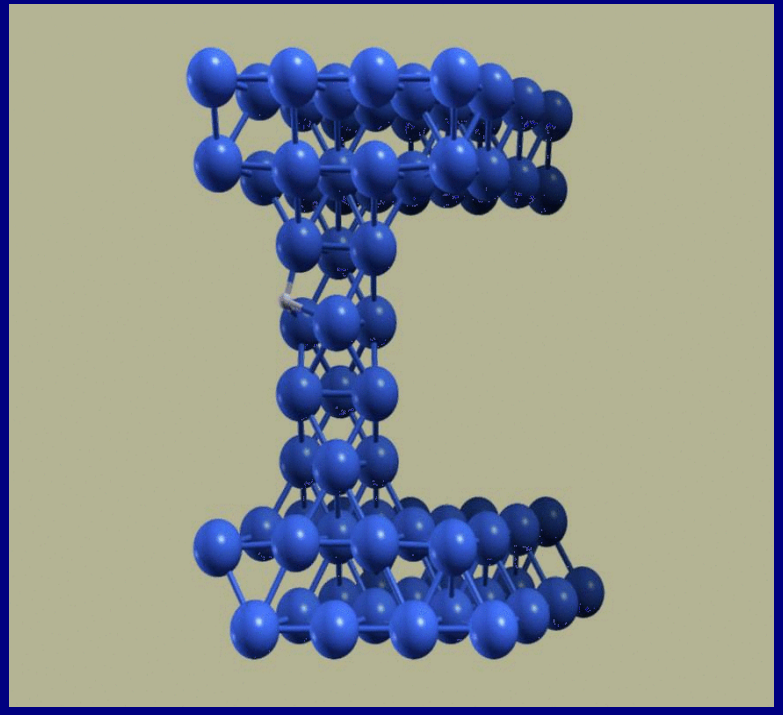
Al-4x4



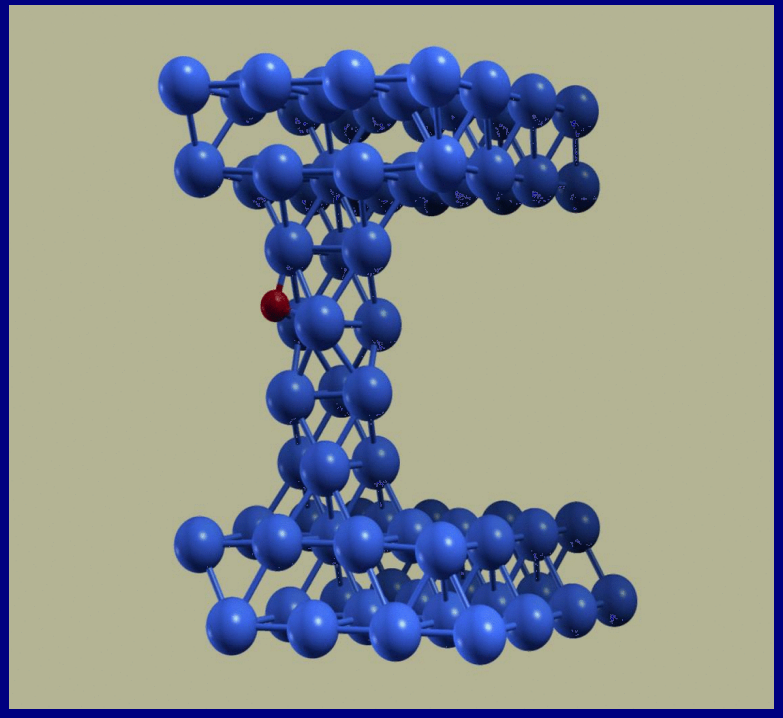
C



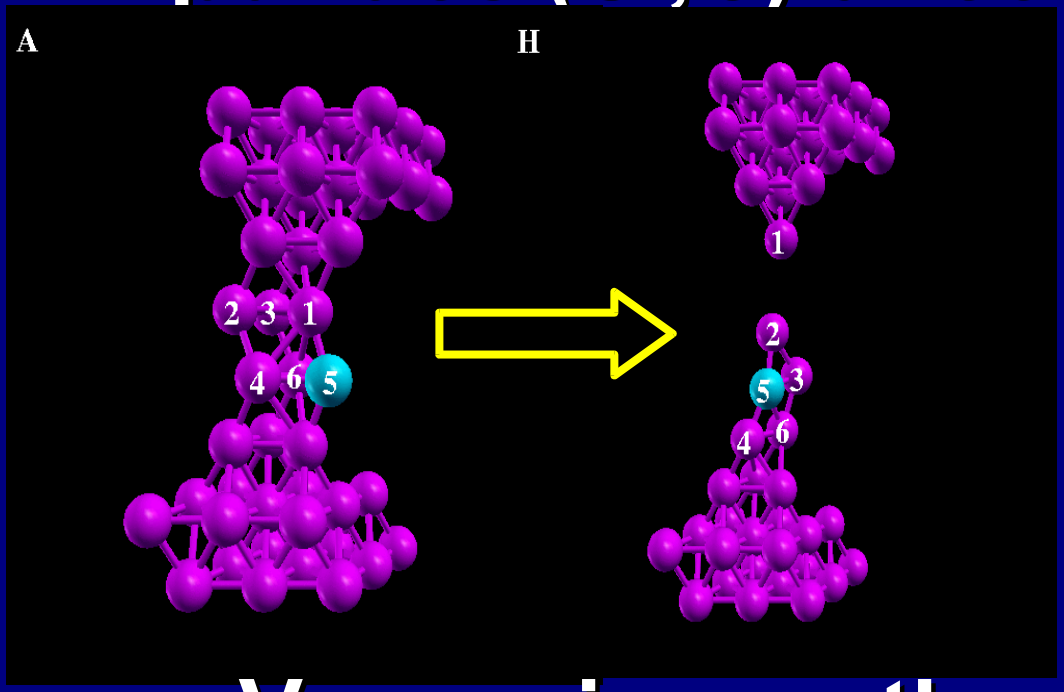
H

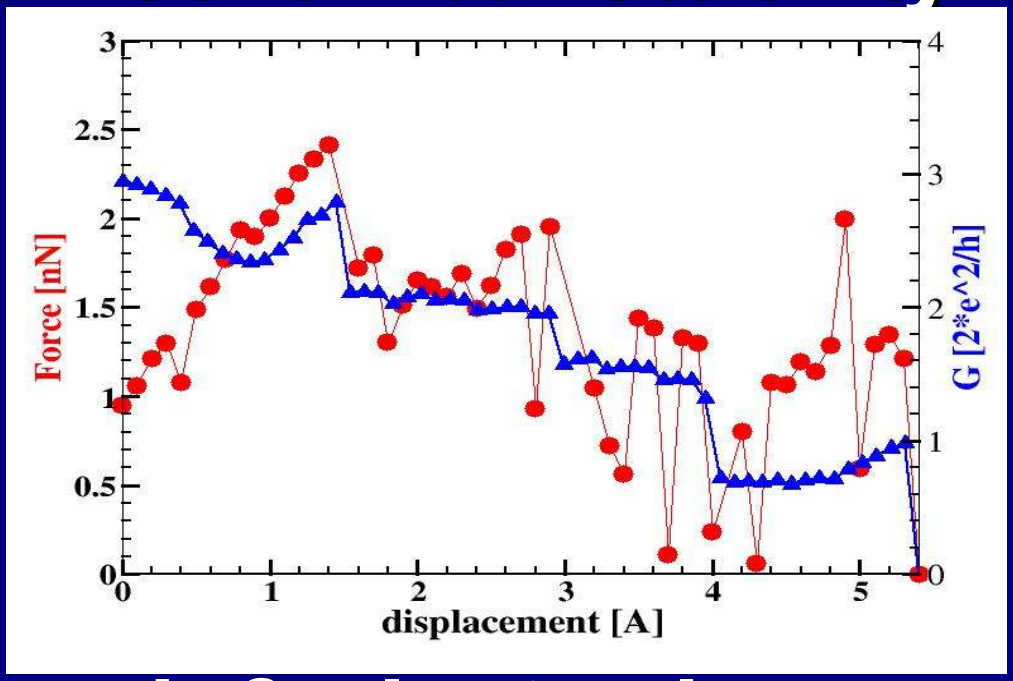


O

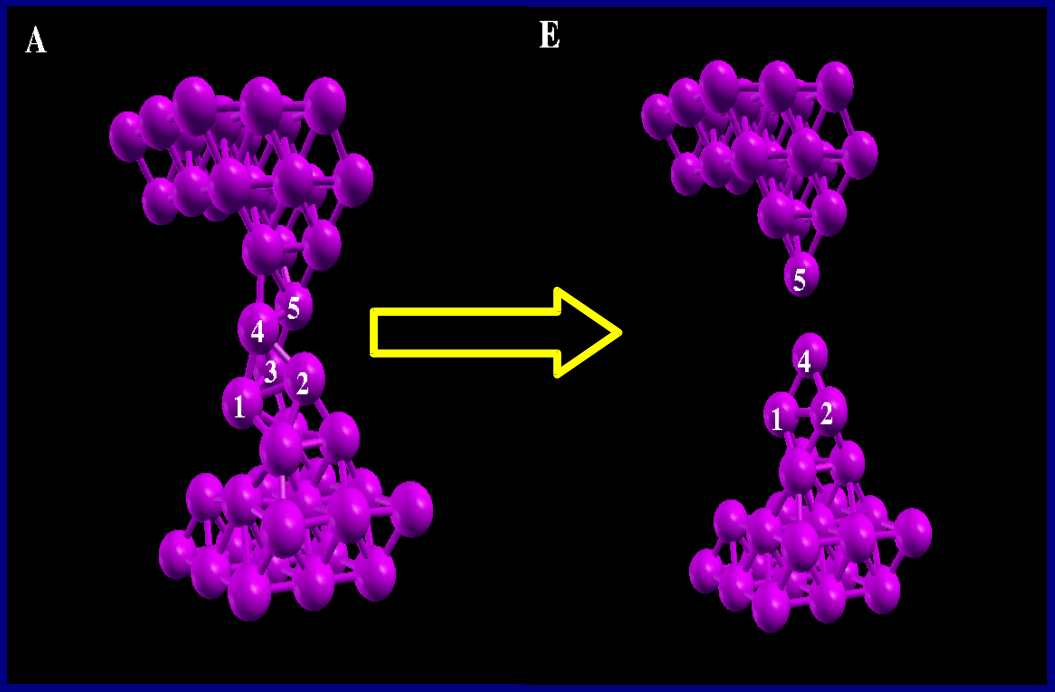


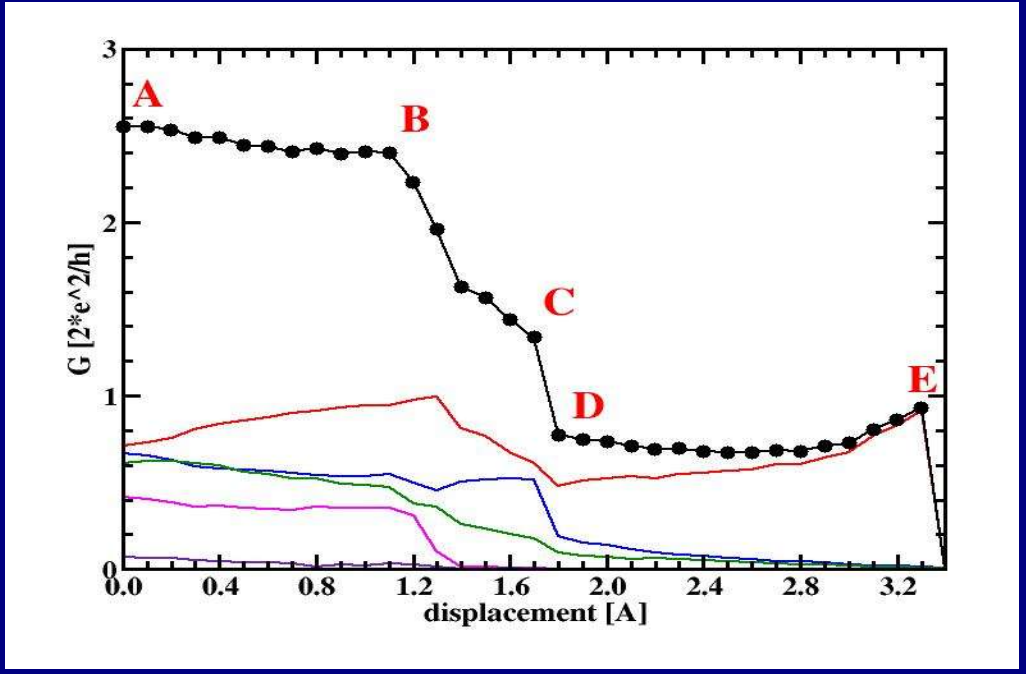
Impurities (Si,C) affect Mechanical Stability



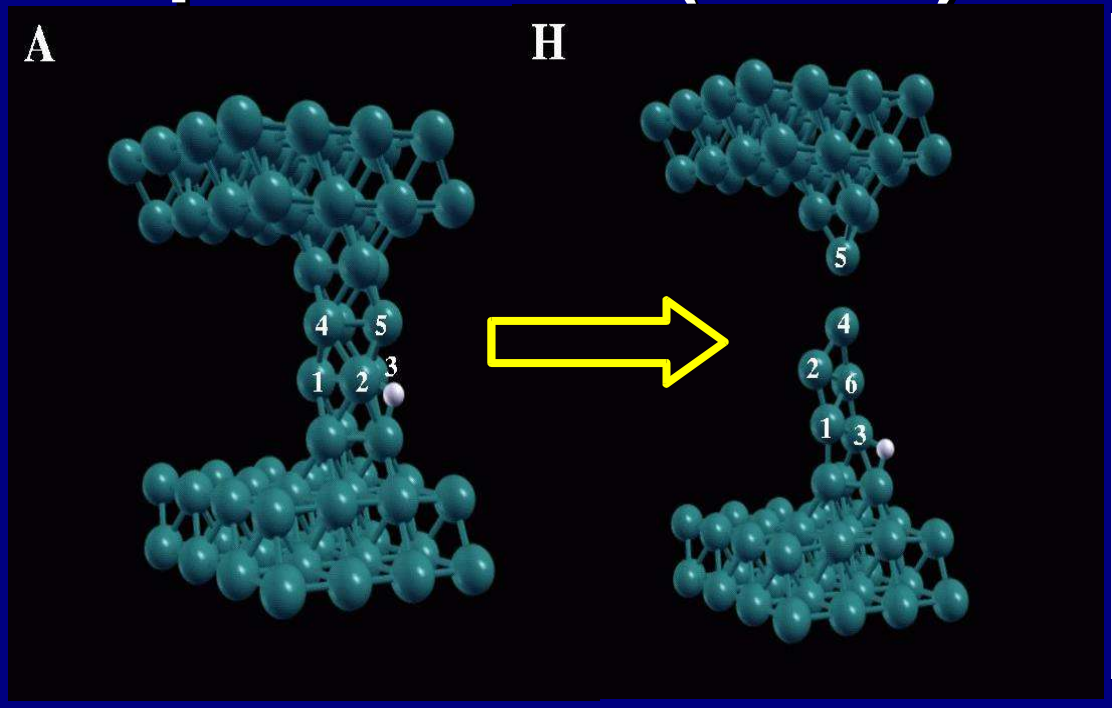


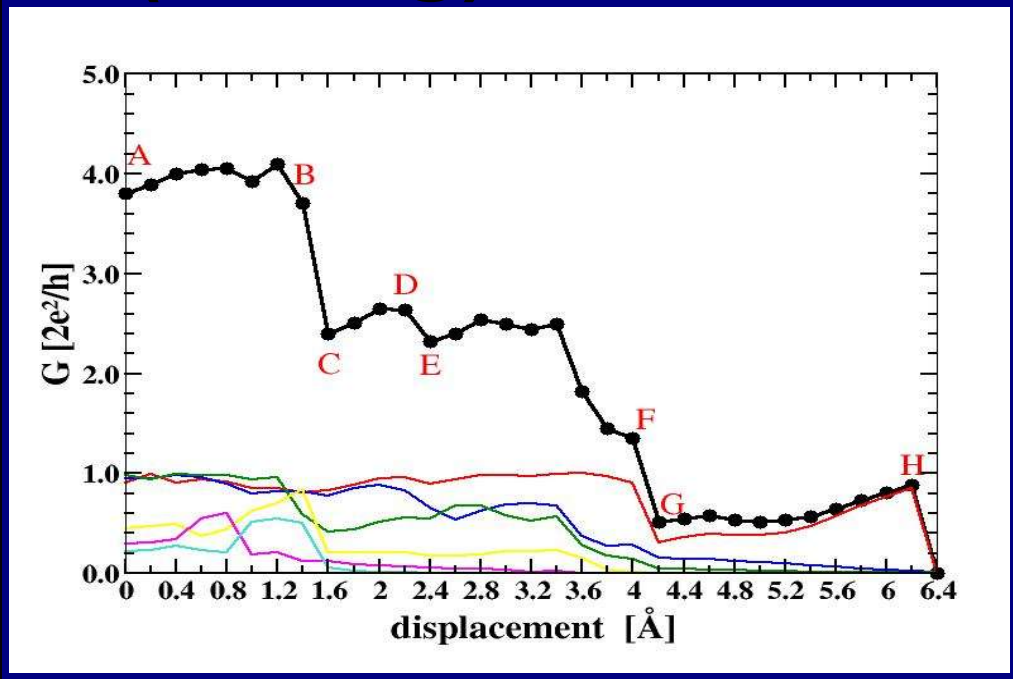
Vacancies on the neck & electrodes

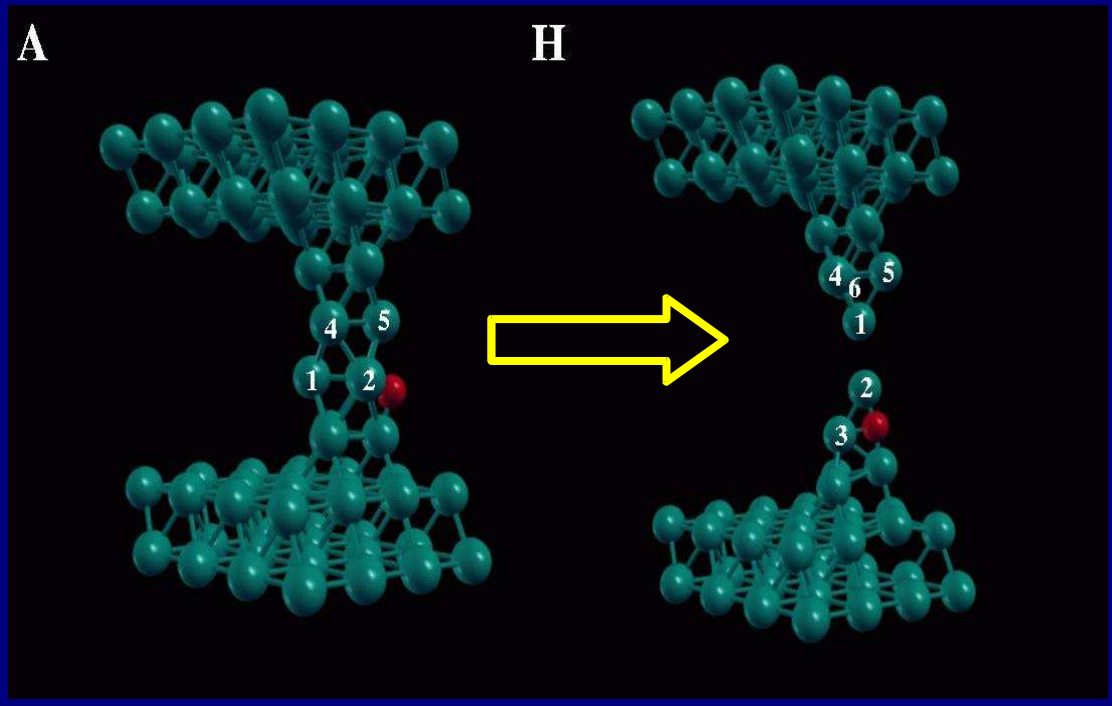


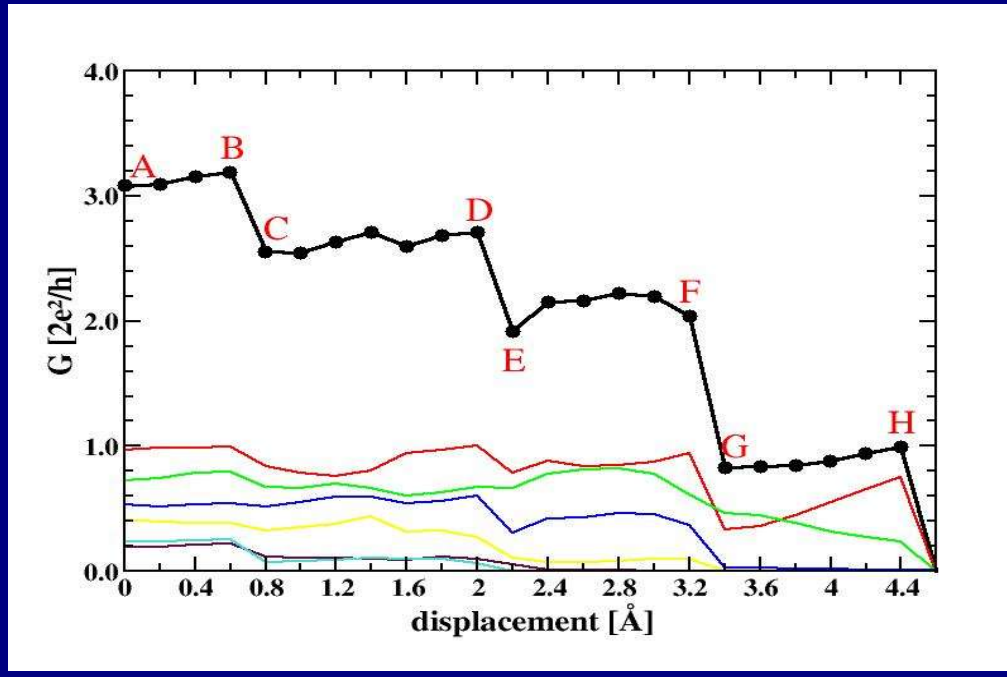


Impurities: H (weak) vs O (strong) influence

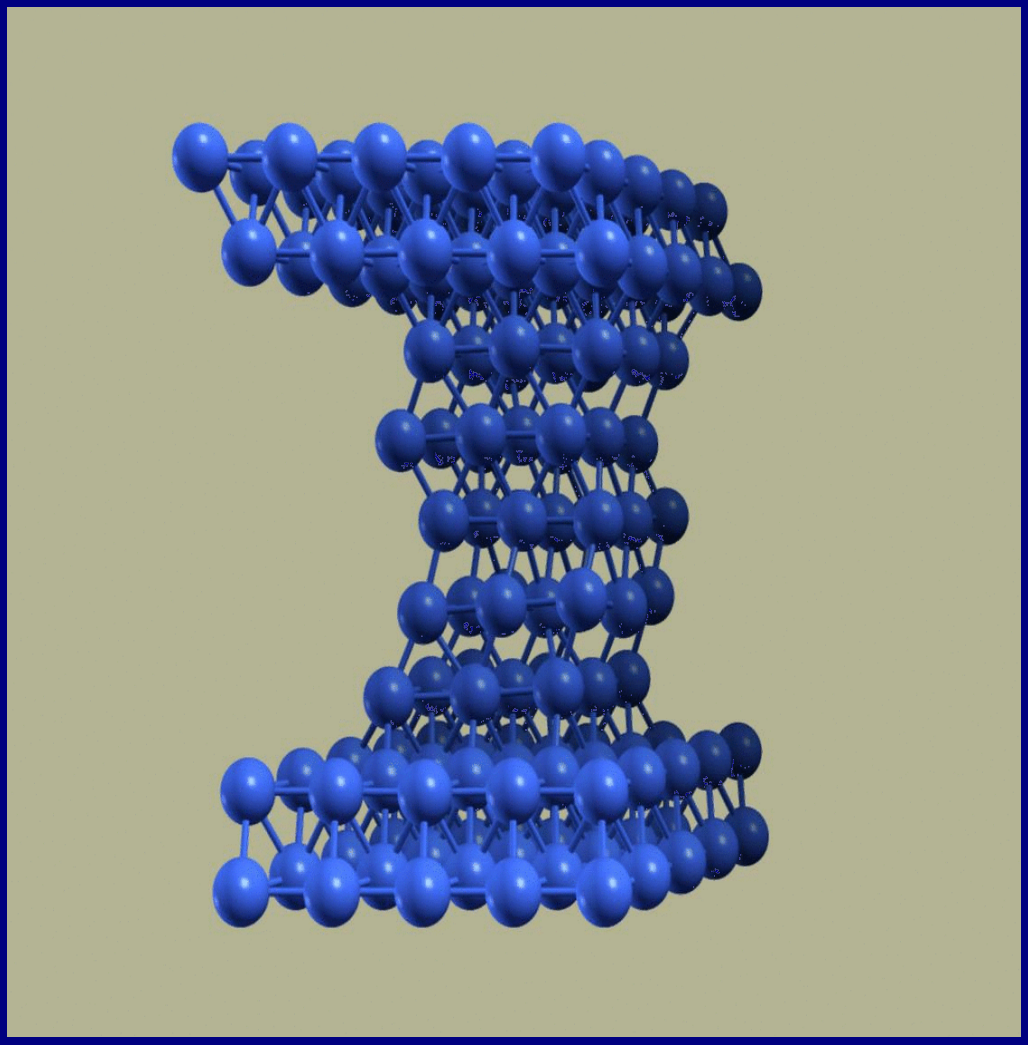




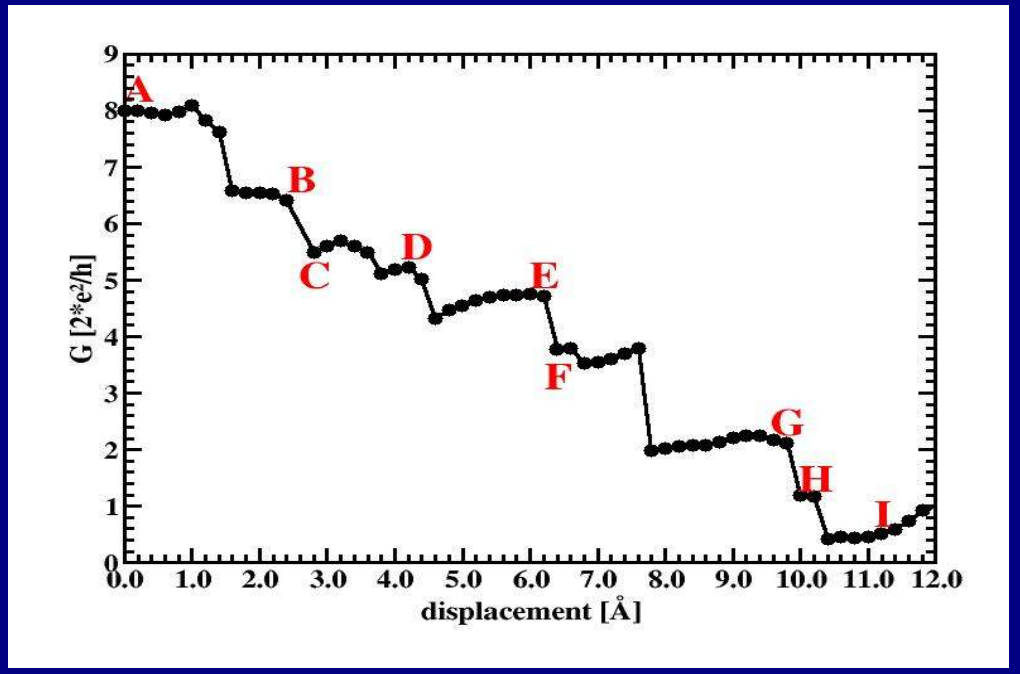




Al(111)(5x5-5l) nanowire: struc. & conductance

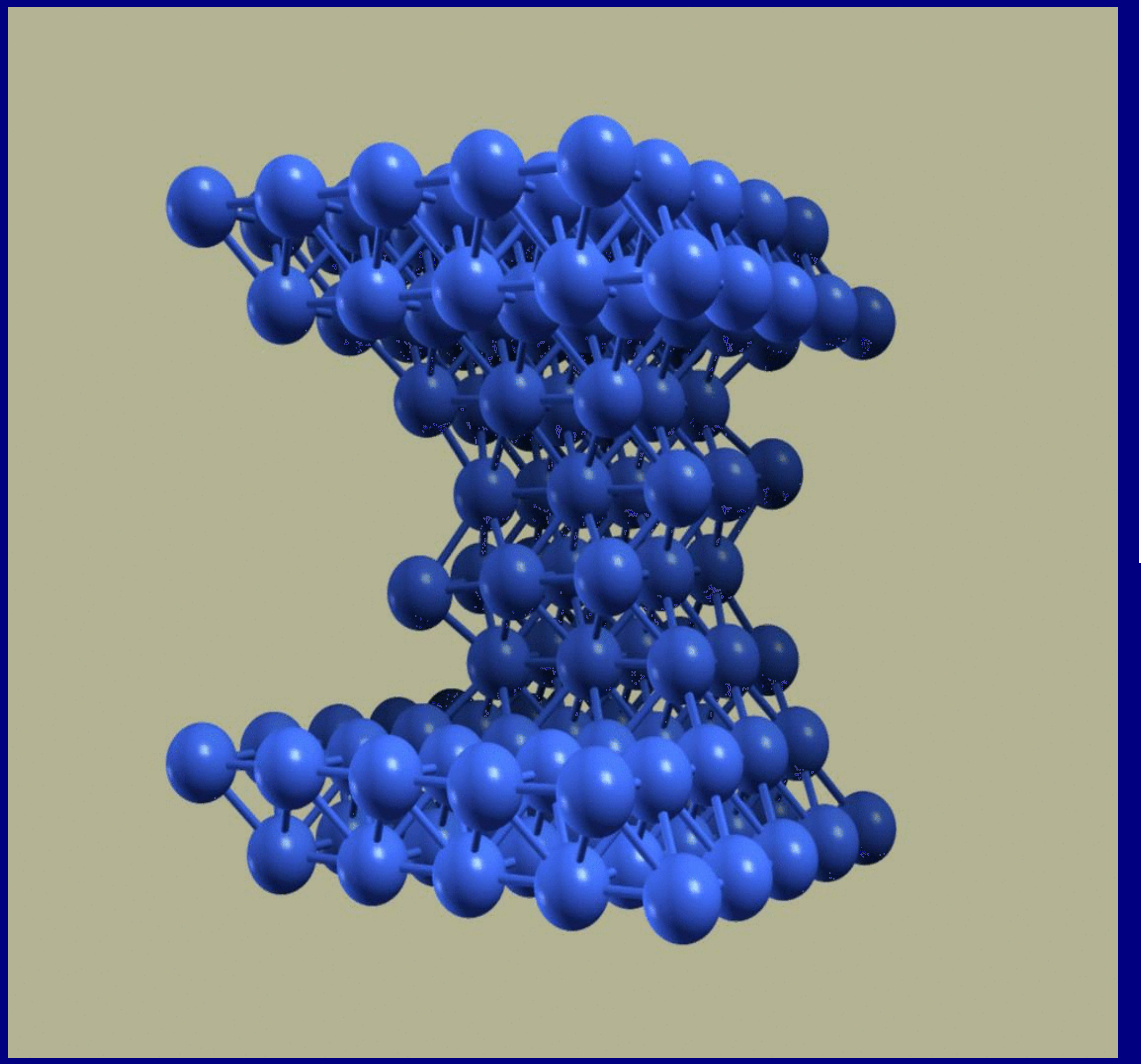


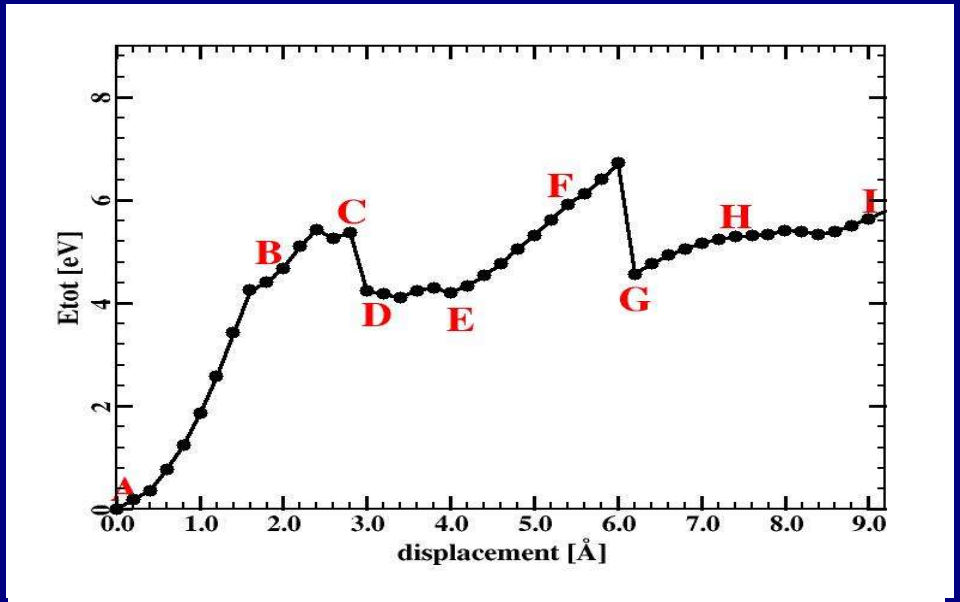
Large scale first principles simulation including 145 atoms

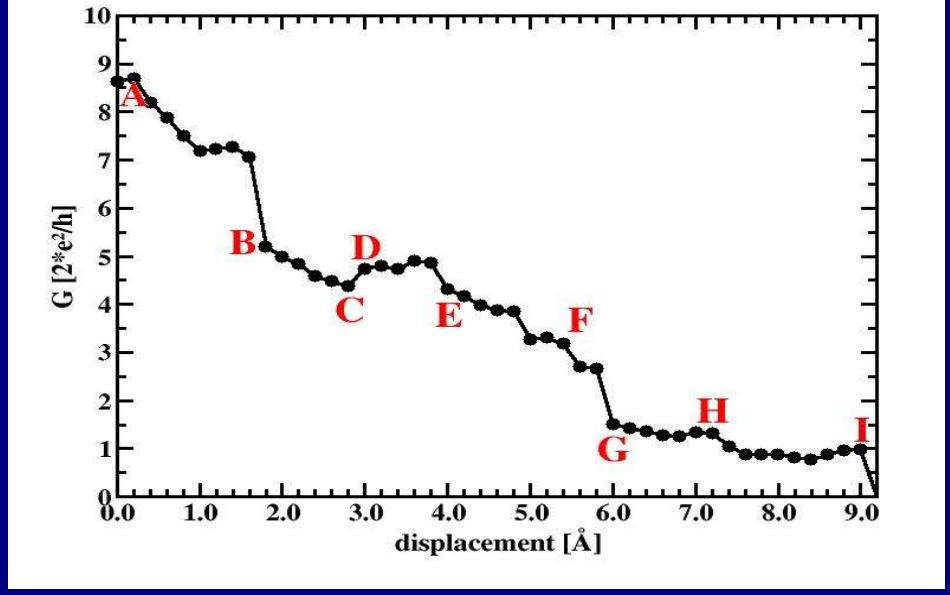


- Ascending form of the plateaus
- Final breaking:'dimer' structure
- Last plateau: G ~ 1 ($2e^2/h$) (3 channels: 1 dominant & 2 minor)

Al(100)(5x5-4l) nanowire: struc. & conductance

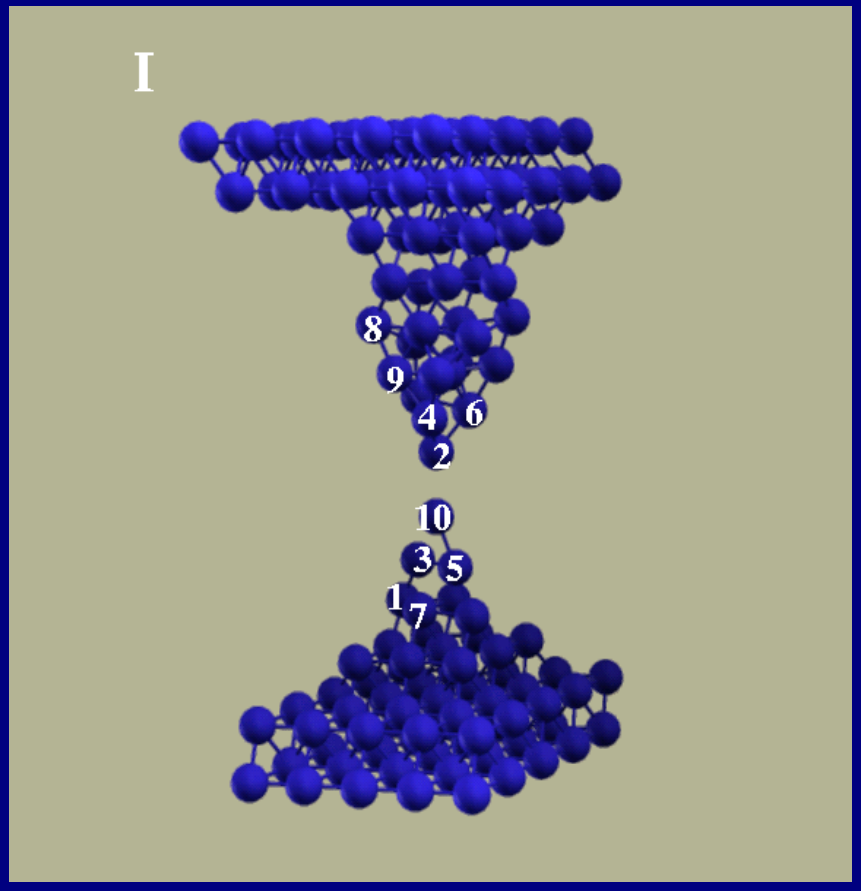






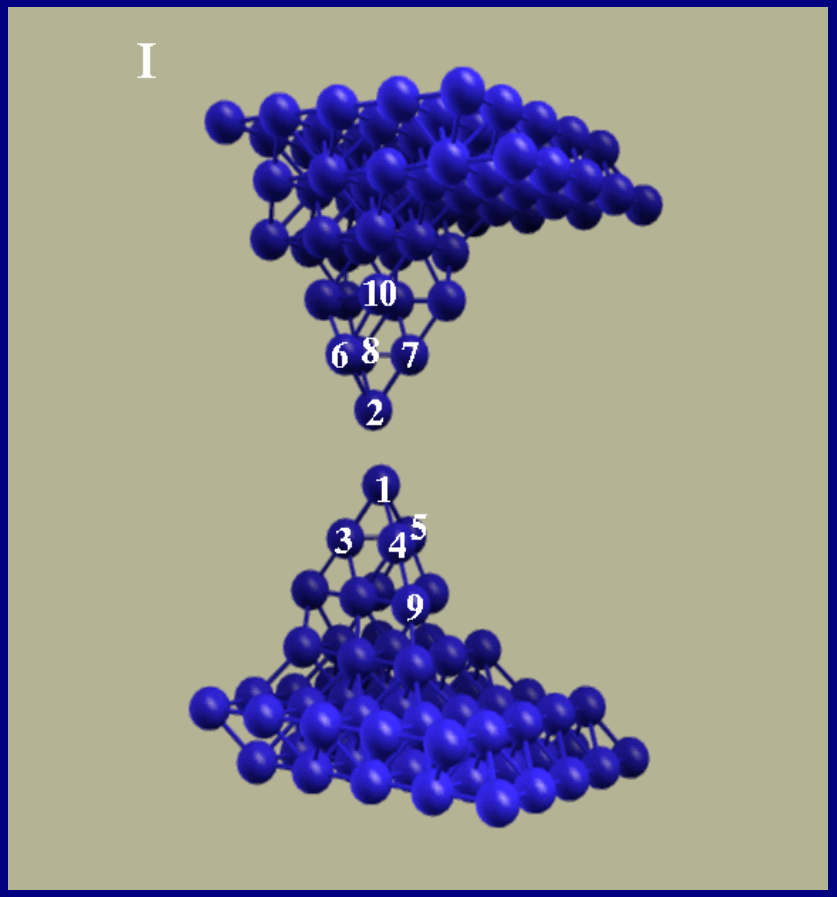
Surface orientation: Comparison

Al – surface (111)



- max. forces ~ 4.9nN (~0.55 nN/atm)
- breaking forces ~ 1.02 nN

Al – surface (100)



- max. forces ~ 6.1nN (~0.7 nN/atm)
- breaking forces ~ 1.03 nN

Nanowire final configuration: reordering to form a more compact (111) structure !!!

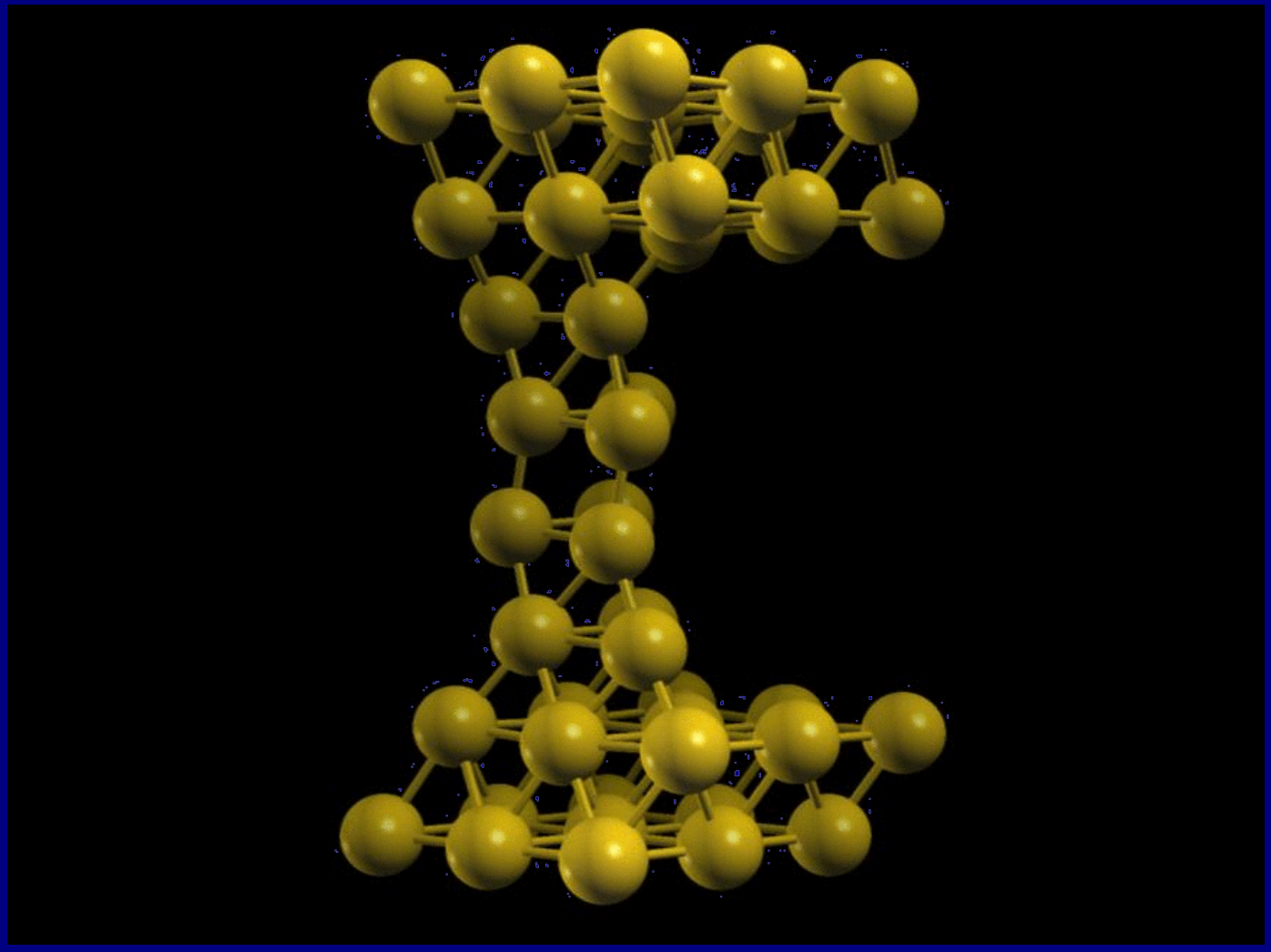
Brief summary for different Al nanowires

- ✓ Final breaking 'dimer-like' structure with conductance ~ 1 ($2e^2/h$)
- ✓ Characteristic ascending shape of plateaus
- ✓ Initial number of open channels depends on the structure
- ✓ Conductance values for plateaus mostly near ~ 3,2,1 ($2e^2/h$) in agreement with the conductance histograms
- ✓ Impurities and vacancies affect atomic rearrangement, modify the breaking distance and lower breaking value of G
- ✓ Surface orientation: reoredering to (111) compact structure
- ✓ Large breaking tensile forces with universal value ~1 nN

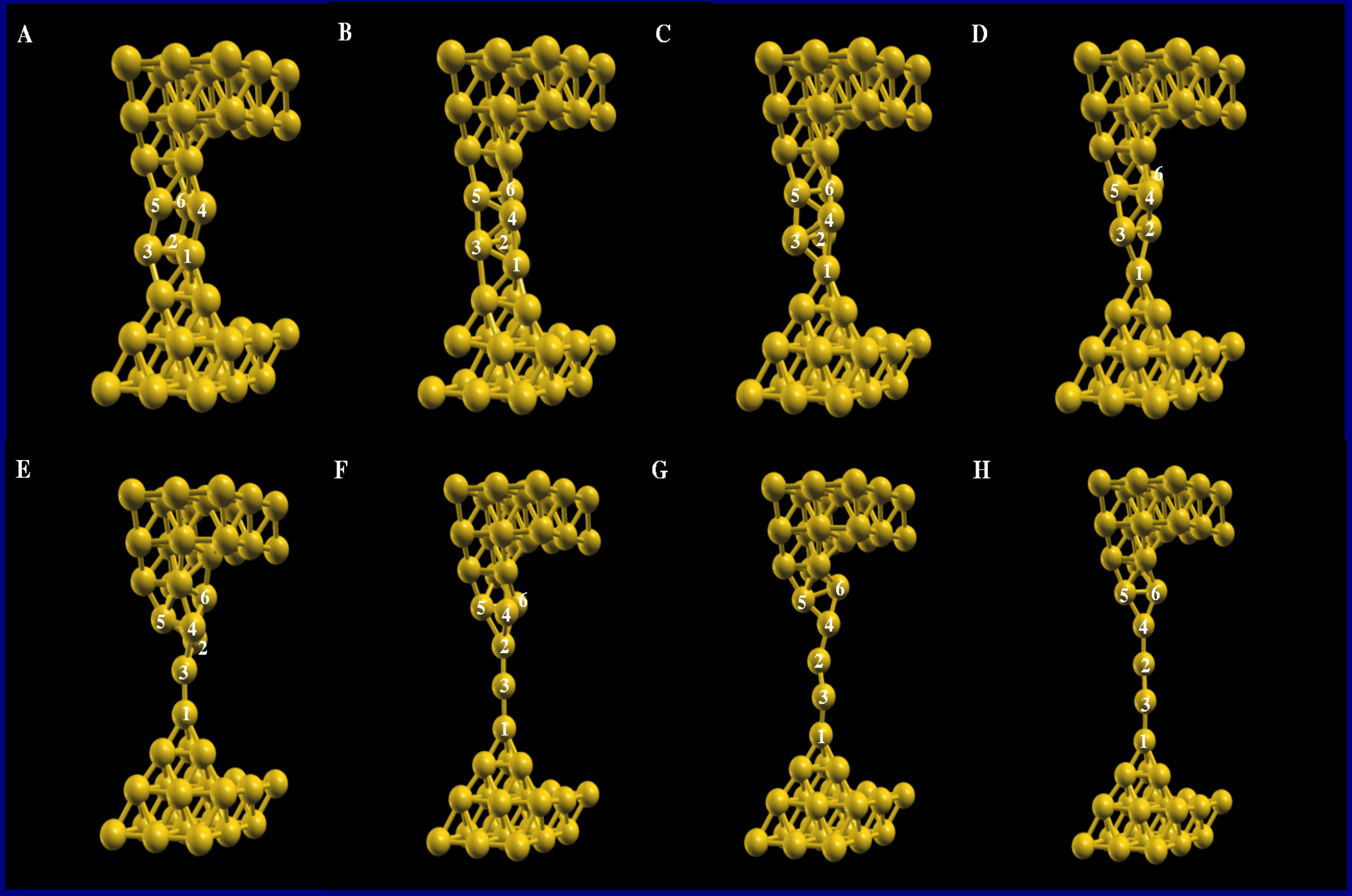
- ✗ Origin of the ascending form of the conductance plateaus ??

P. Jelínek et al. PRB ***68****, 085403 (2003)*
P. Jelínek et al. Surf. Sci. **566-568**, 13 (2004)
P. Jelínek et al. Nanotechnology (2005) (accepted)

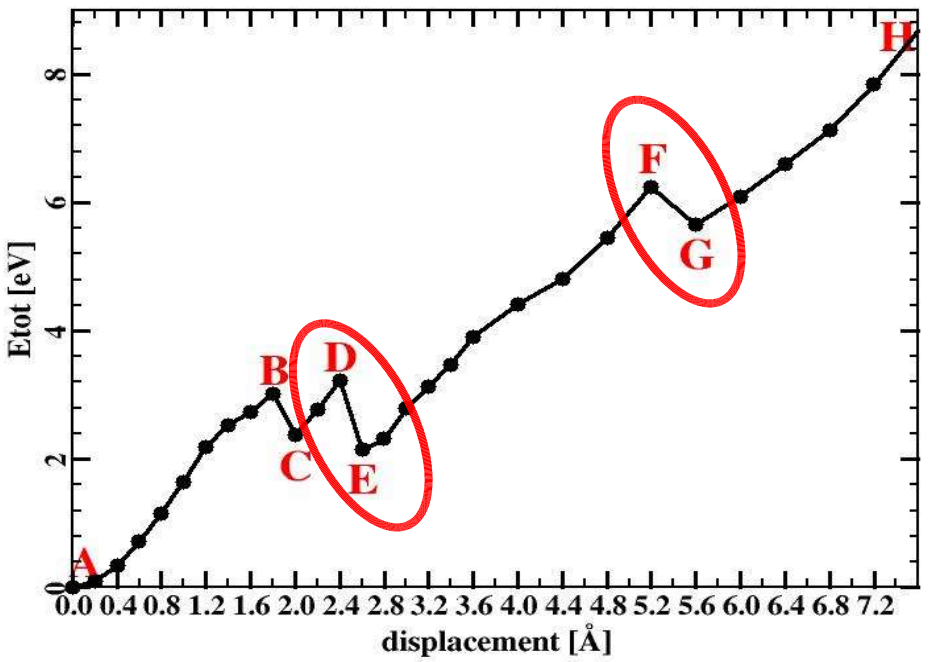
Au nanocontact (3x3-4l): Structural evolution during the stretching process

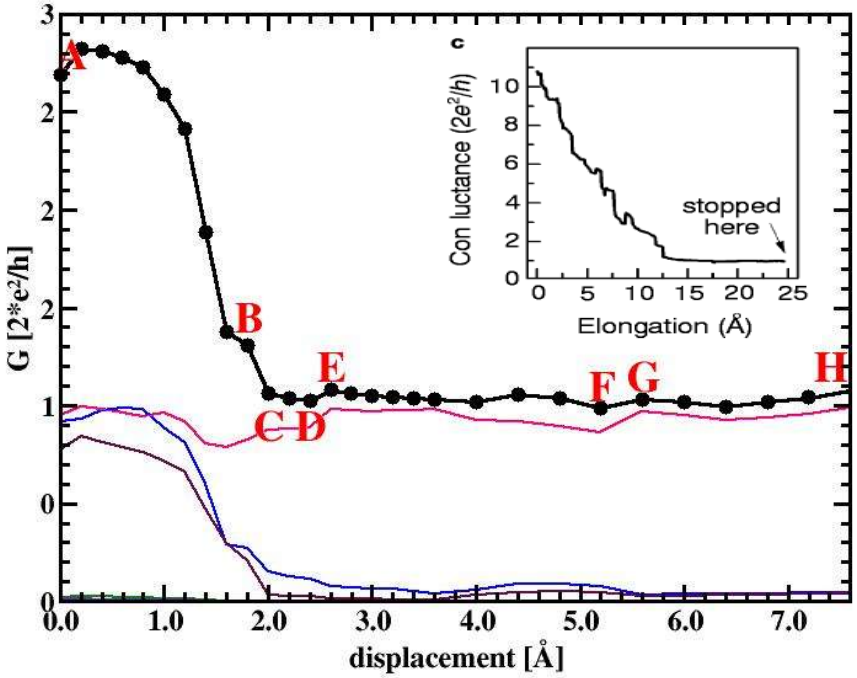


Au (111)-nanowire: chain formation



Au (111)-nanowire: Conductance



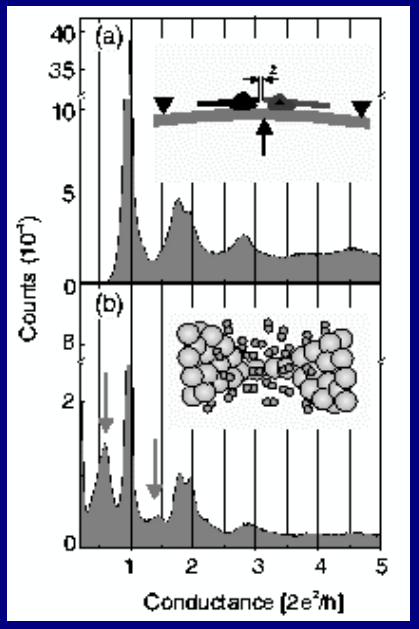


- Characteristic monoatomic chains (up to 4 atoms in chain)
- Final breaking distance ~ 8.0 Å
- Distance Au-Au ~ 2.6 Å

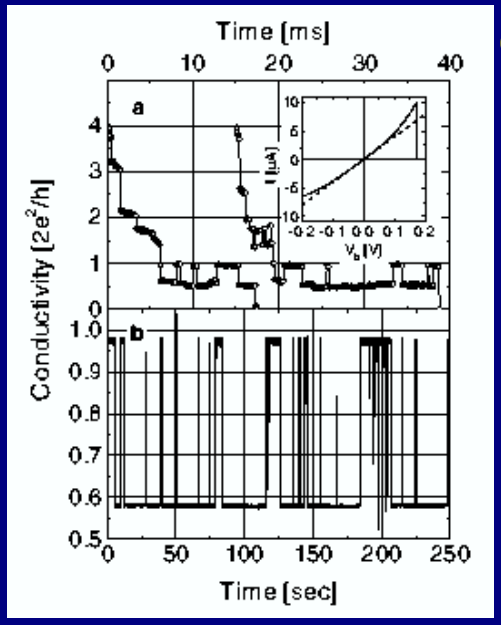
- Zig-zag vs. straight structure
- Long plateau (monoatomic chain formation): G ~ 1 ($2e^2/h$)
- Mostly 1 channel on last plateau
- Conductance oscillation along the process of elongation of the monoatomic chain (odd & even number of atoms)

Au-wire + H: fractional quantum conductance

Sz. Csonka et al. PRL **90**, 116803 (2003)

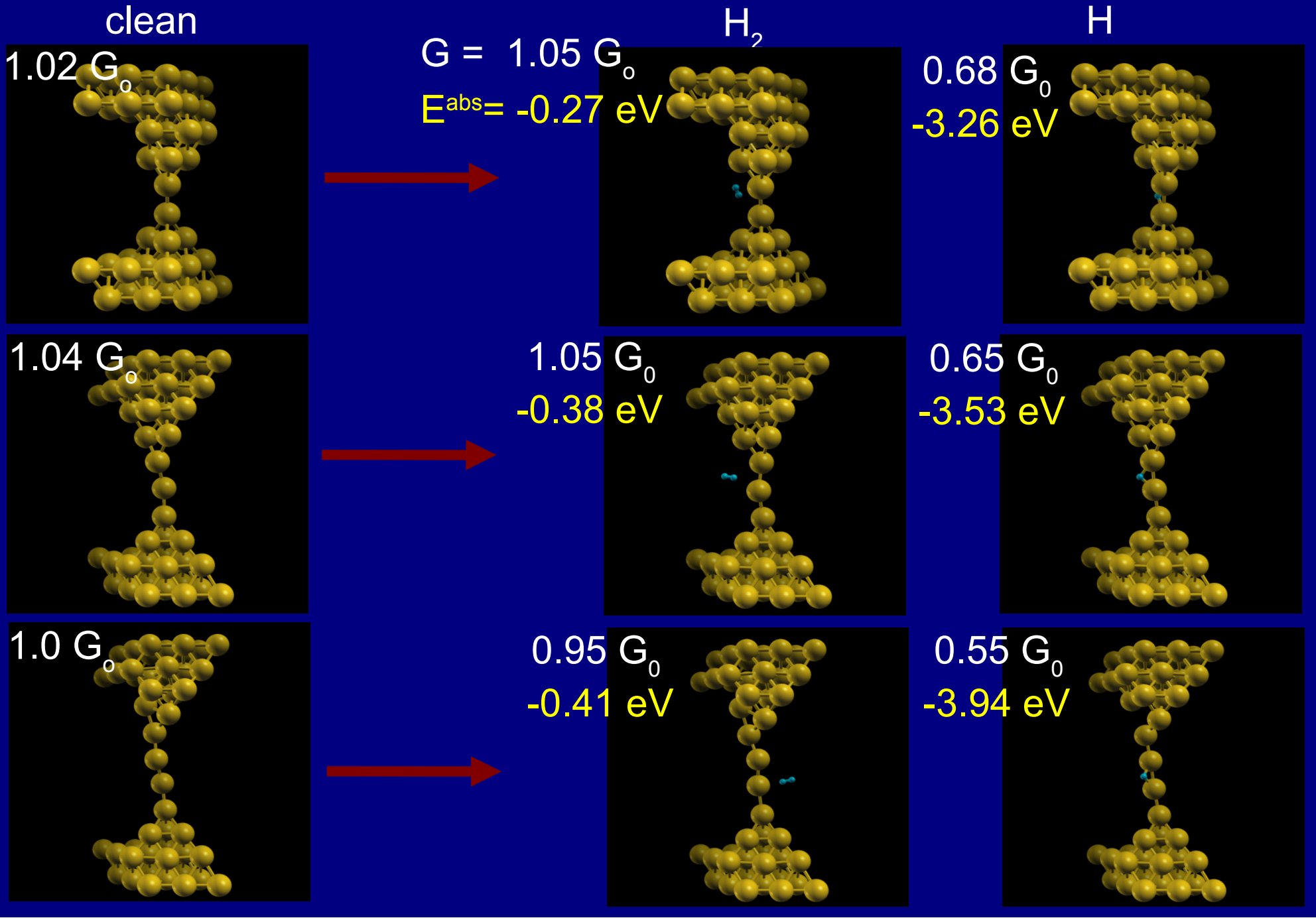


- experiment: MCBJ presence of H_2 molecules in atmosphere T = 20K, V^{bias}= 20 meV
- histogram shows an additional peak ~0.6 G_0 → new unknown structure
- reversible fractional quantum conductance 1 ↔ ~0.6 G_0 (75% of records), time scale ~ seconds
- Ag, Cu do not show the fractional peaks
- Conclusion: the presence of H_2 molecules leads to dimerization of the Au monoatomic chains



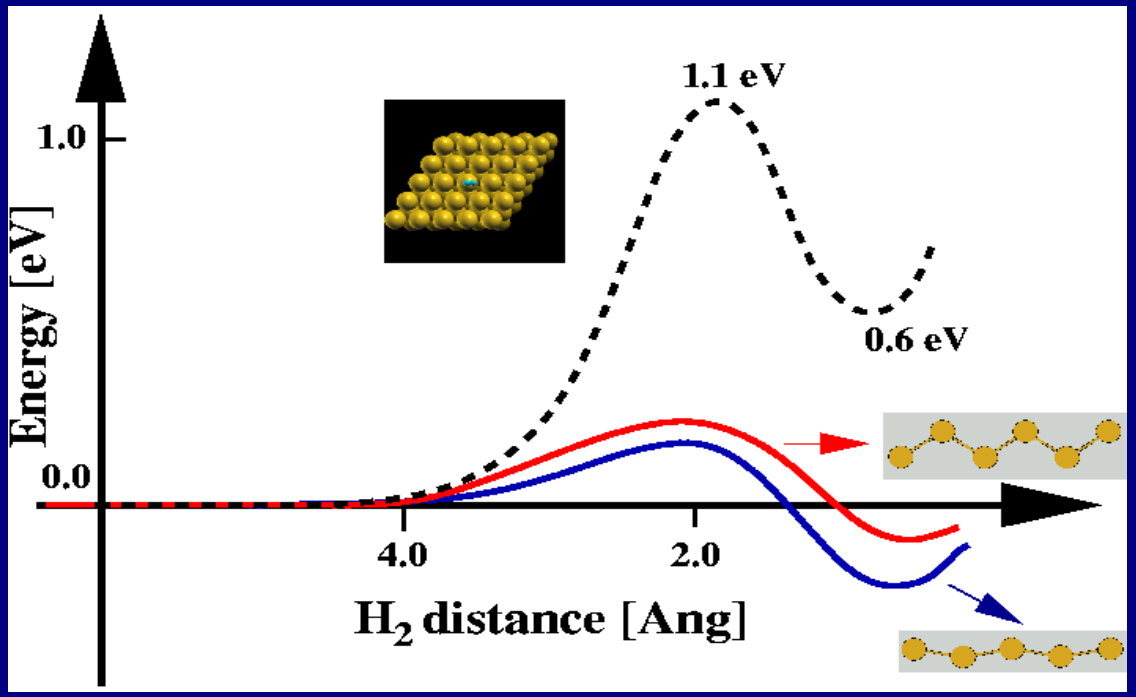
- Does H_2 molecules react with monoatomic Au chains?
- Can the presence of H_2 molecules change the conductance of Au nanocontact?
- Can H_2 molecules dissociate on the Au-chain?
- Does depend the reactivity on the stress in the chain?

Au-nanocontact + H_2 (H): simulations



Au-wire+H_2: dissociation ?

- Surface Au (111)+H_2: PW-GGA calculation → no direct dissociation, E^b = 1.1 eV (*B. Hammer and J.K. Norskov Nature* ***376,*** *238 (1994)*)
- Au nanocontacts: local orbital (LO) Fireball DFT-LDA → no direct dissociation, H_2 molecule slightly bonded vertically to the chain
- PW-LDA/GGA study of a simplified case: ideal monoatomic Au wire



Ideal Au chain + H_2:

PW-LDA: direct dissociation

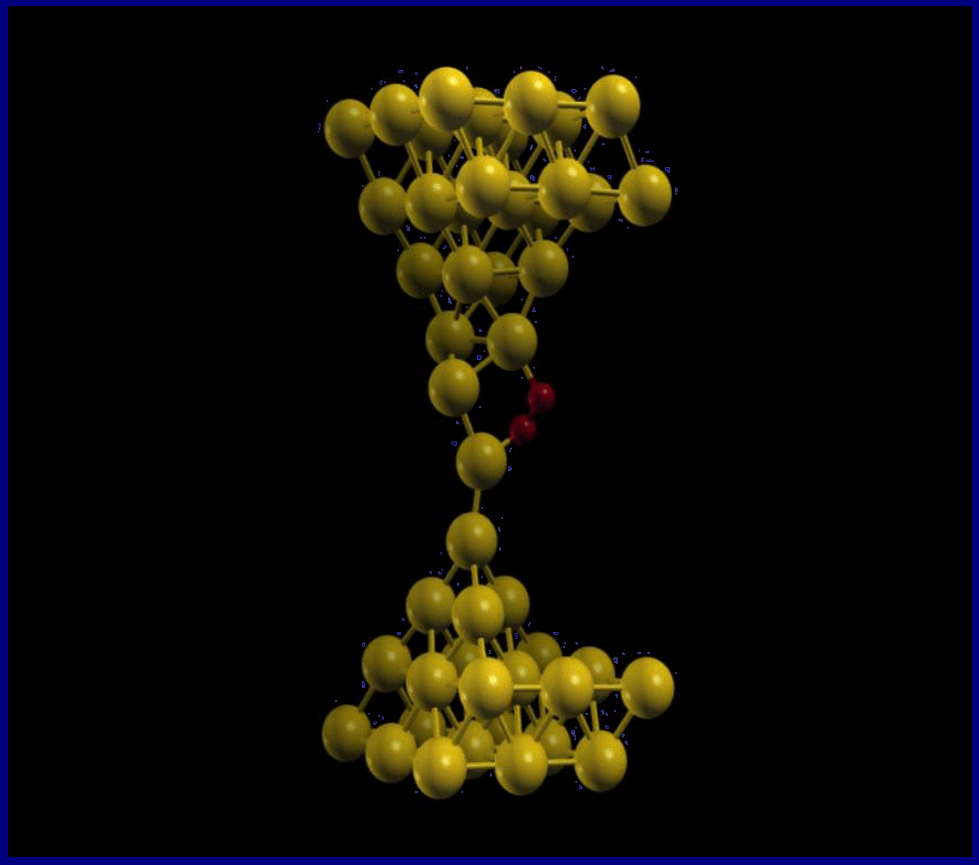
PW-GGA: E^b ~ 0.1-0.4 eV

Preliminary conclusion: dissociation barrier ~0.1-0.4 eV depending on the orientation of H_2 molecule, but still in progress...

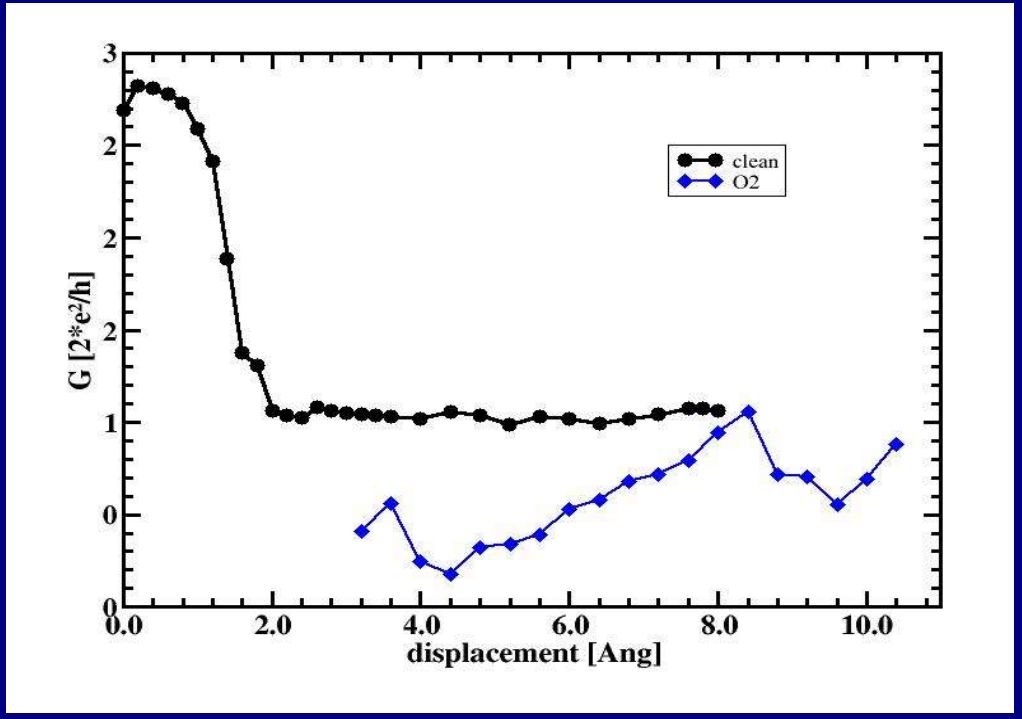
Au-wire+H_2: summary

- The simulations show the stronger reactivity of the atomic Au chains than surfaces or bulk (order of eV in the case of atomic H).
- The reactivity increases with the tension in the chain.
- H_2 molecules weakly bonded with Au chains, the conductance similar to clean Au chains near ~1.0 G_0.
- H atoms reacts strongly with Au chains changing the conductance to ~0.6 G_0 in very good agreement to the experiment.
- The dissociation of H_2 molecule is still open question (in progess), energetic barrier ~0.3 eV.

Au-wire + O_2



Conductance vs. displacement



Conclusions

- Complex first principles calculation of the whole stretching process for different metallic nanocontacts.
- Close relation between structure, electrical & mechanical properties.
- Very good agreement with experimental results (increase of the Al conductance in the last plateau reproduced for the 1st time).
- Al: "*dimer*" structure before final breaking (independent of defects, impurities, or initial nanocontact orientation).
  - Conductance before breaking ~ 1.00 ($2e^2/h$) with 1 dominant and 2 minority channels.
  - Breaking tensile forces ~ 1 nN (~ 0.7 nN per bond in bulk).
- Transition metals: monoatomic chain formation in Au. (G ~ $2e^2/h$, 1 channel; conductance fluctuations).
- Au-wire+H_2:The presence of H atoms strongly affects the conductance (G ~ 0.6 e^2/h); the dissociation of H_2 still open question.