Electron-vibration interaction and inelastic transport in nano-contacts from DFT

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Acknowledgements:

- Inelastic transport (phonon interaction):

Thomas Frederiksen (Ph.D. stud., MIC, DTU, Denmark)

Magnus Paulsson (Post doc., MIC, DTU, Denmark)

N. Lorente (IRSAMC, Université P. Sabatier, Toulouse)

A.-P. Jauho (MIC, DTU, Denmark)

- Elastic transport (*TranSIESTA*):

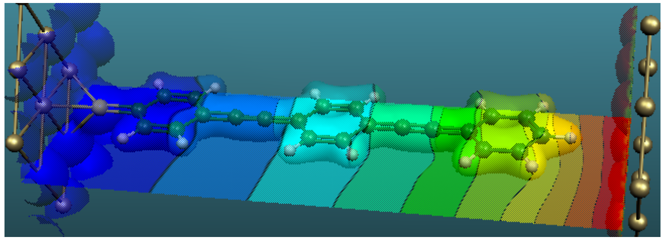
J.-L. Mozos, P. Ordejon (ICMAB, UAB, Barcelona, Spain)

K. Stokbro, J. Taylor (Atomistix.com, Copenhagen, Denmark)

Outline

- Motivation – why inelastic transport ?
- Method – how to do it
  - Elastic transport (TranSIESTA = DFT+NEGF)
  - Inelastic effects in conductance (NEGF)
  - **L**owest **O**rder **E**xpansion of SCBA expressions
- Applications – how does it work
  Comparison with experiments:
  - Atomic gold wire systems
  - IETS of hydrocarbon molecules
- Summary/Conclusions

Motivation – why inelastic



- Molecular-scale electronics:
  - Inelastic effects: Dissipation – stability
  - Inelastic effects: Maybe usefull operations e.g. switching

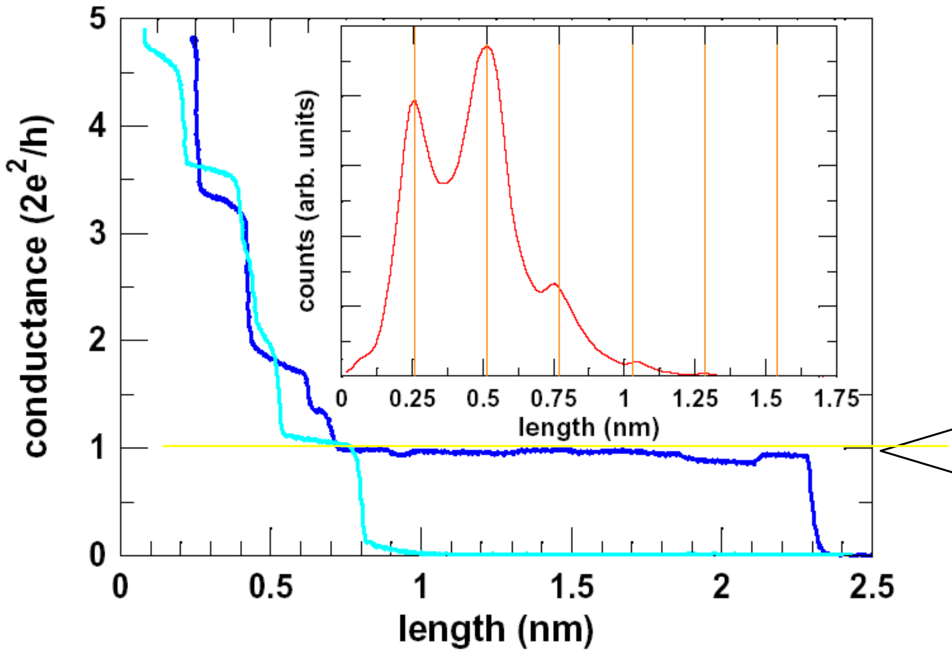
- Current-Voltage (*IV*) spectroscopy
  - Structure is not known – only conductance – information from inelastic signals

<u>We want to model/predict</u>

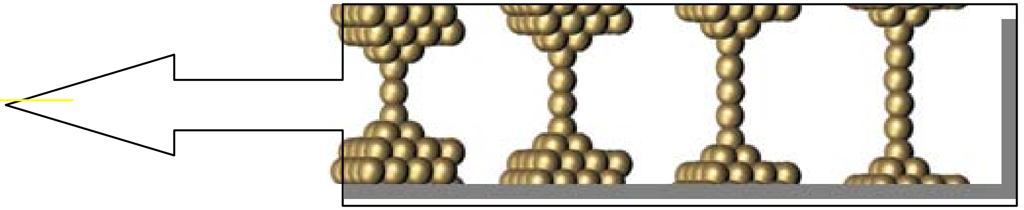
Atomic gold chains

We’ve got to crawl before we can walk!

atomic gold chains - a benchmark atomic scale conductor



Chain formation



A. Yanson *et al*., Nature 395, 783 (1998)
C. Untiedt *et al*. Phys. Rev. B **66**, 085418 (2002)

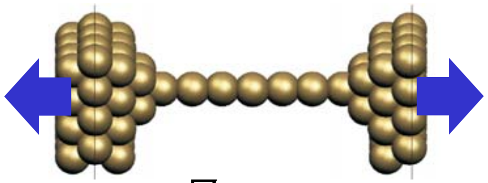
Inelastic phonon signal

VOLUME 88, NUMBER 21 PHYSICAL REVIEW LETTERS 27 MAY 2002

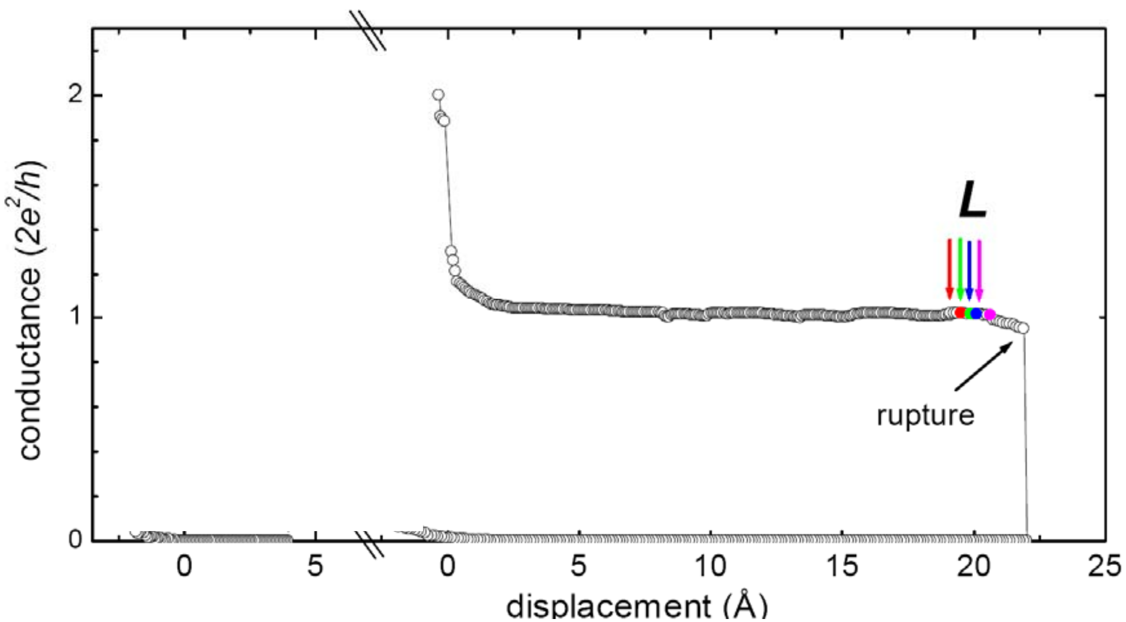
Onset of Energy Dissipation in Ballistic Atomic Wires

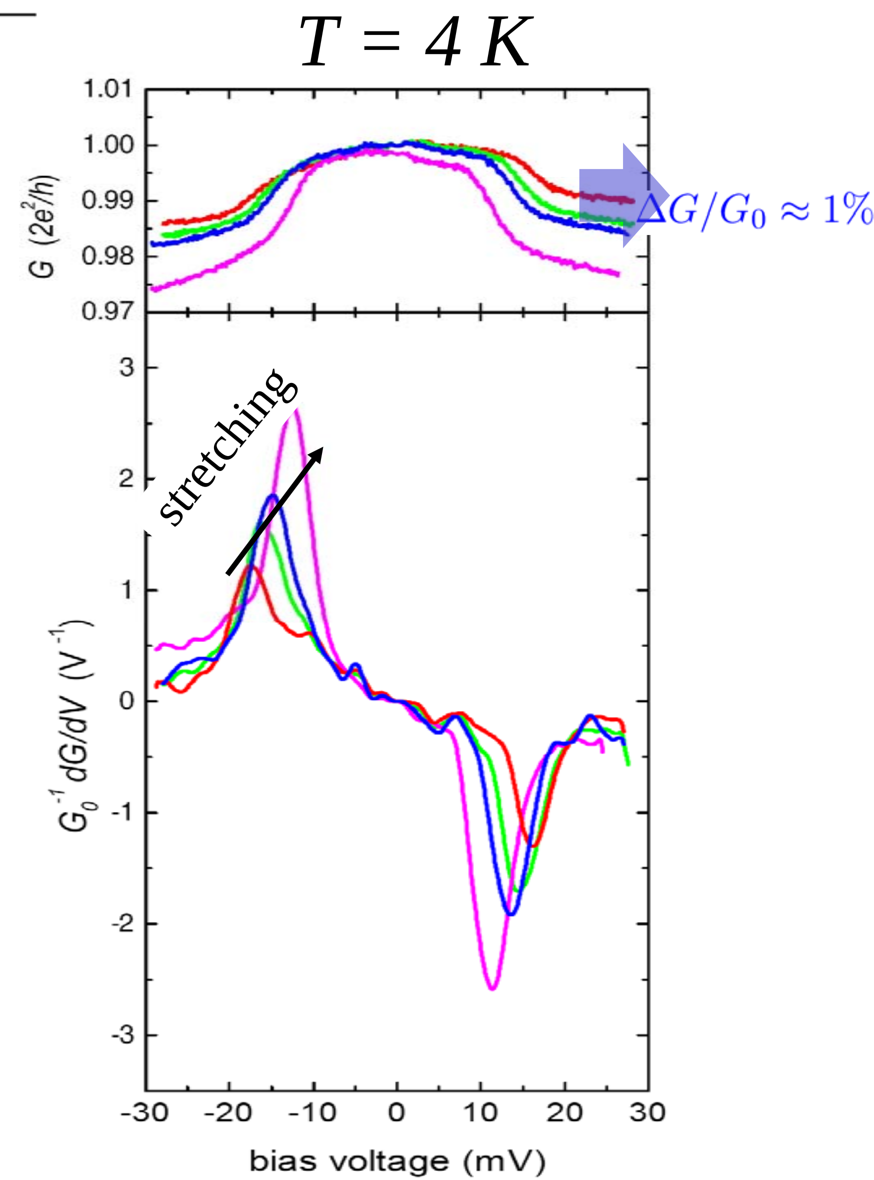
Nicolás Agraït,* Carlos Untiedt,† Gabino Rubio-Bollinger, and Sebastián Vieira

Pulling a gold single-atomic wire

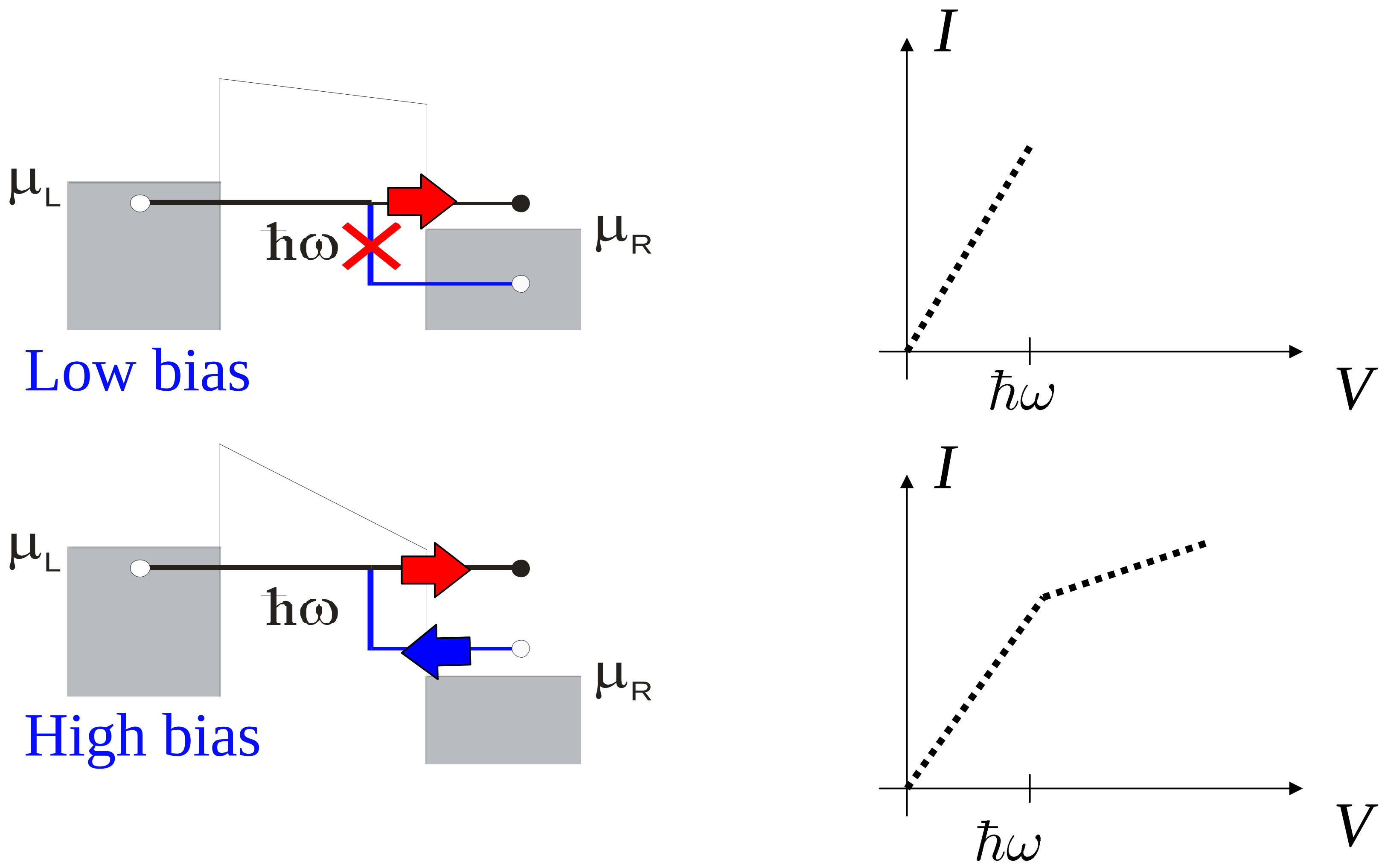


~ 7 atoms

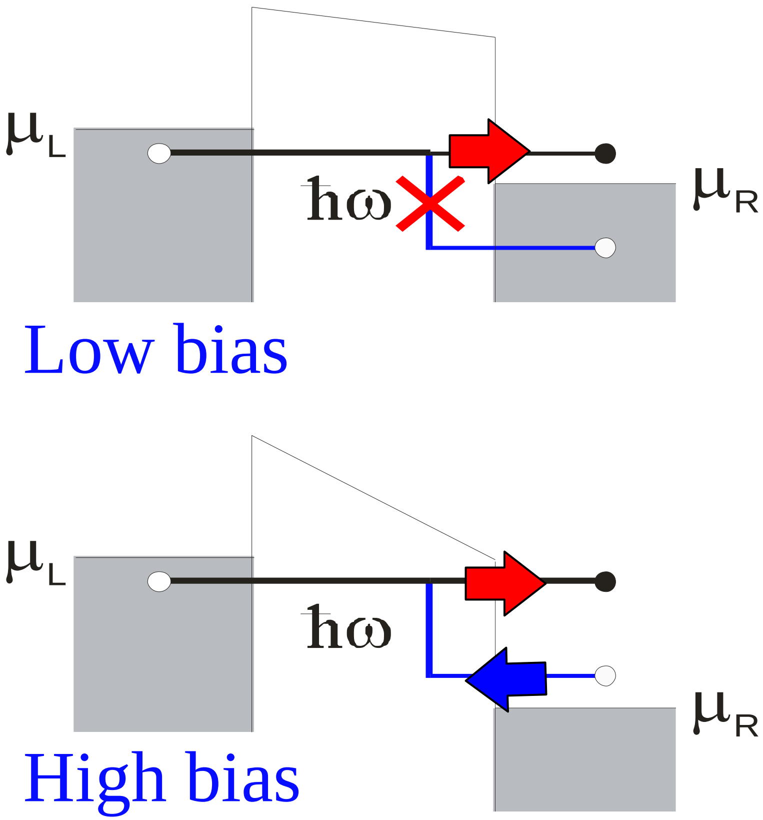


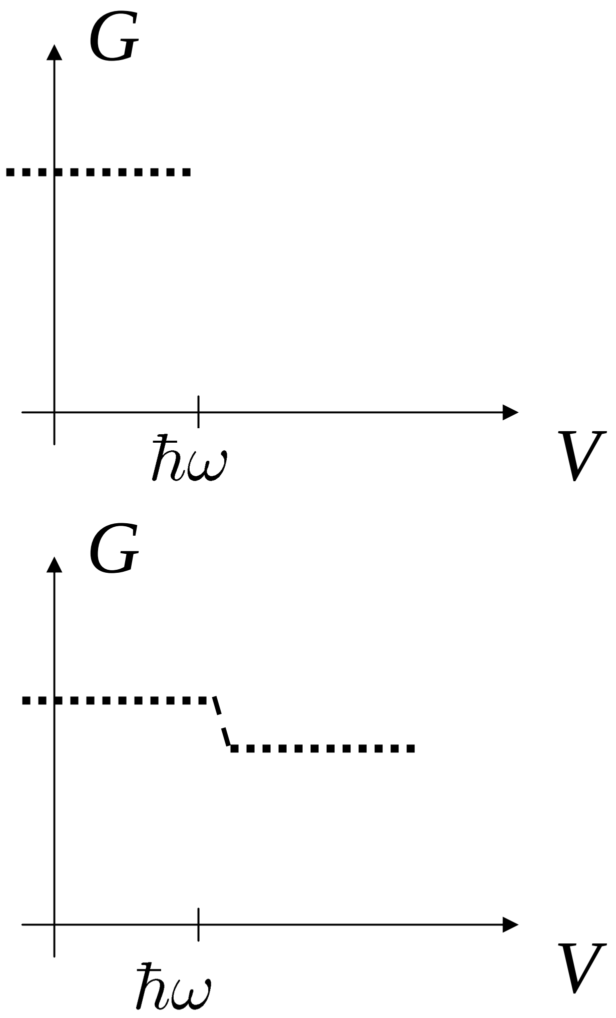


Phonon-interaction: Signal



Phonon-interaction





Inelastic phonon signal

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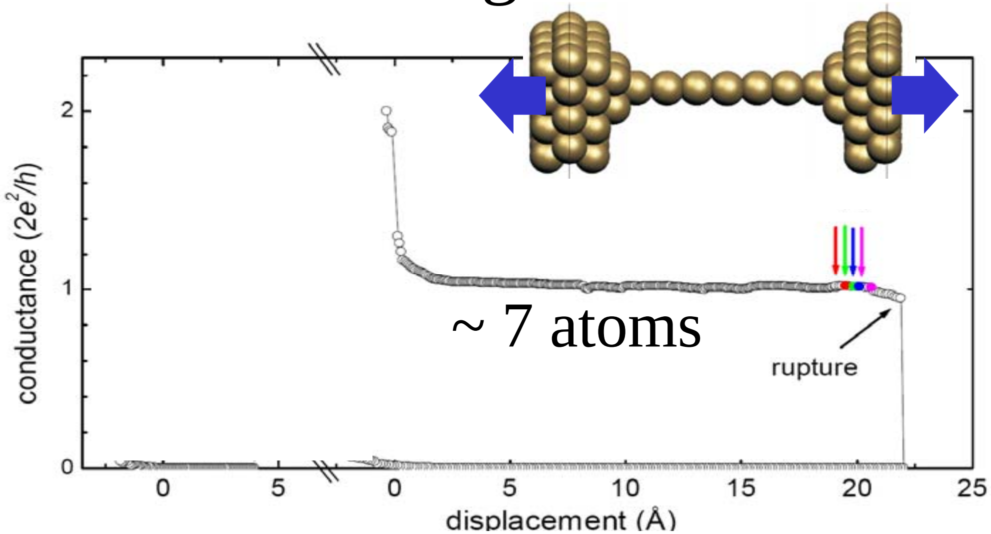
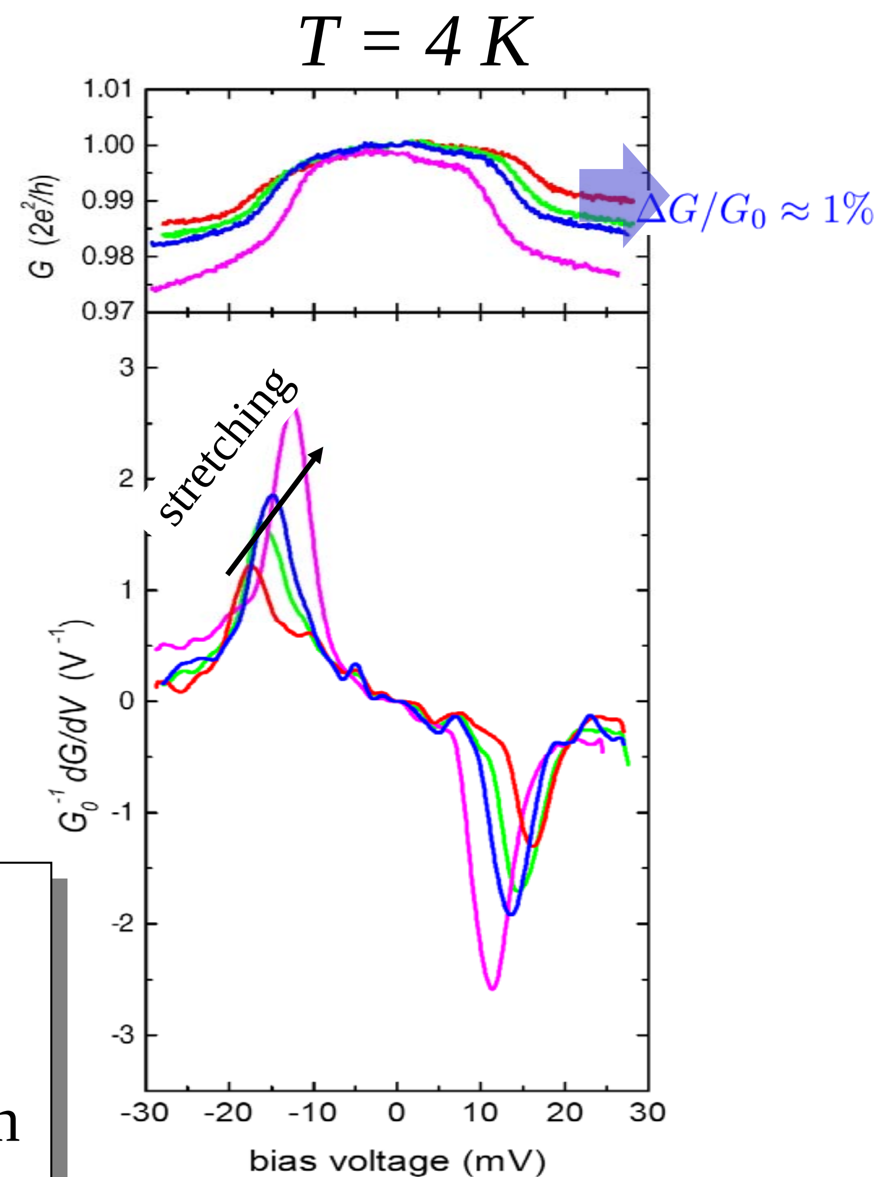
Gold single-atom wire





Experiment:

- Mode selective (only one main peak seen)
- Conductance drop (1-1.5%) increase with stretch
- Streching 1Å gives 7 meV frequency shift

Outline

- Motivation – why inelastic transport ?
- Method – how to do it
  - Elastic transport (TranSIESTA)
  - Inelastic effects in conductance (NEGF)
  - **L**owest **O**rder **E**xpansion of SCBA expressions
- Applications – how does it work

  Comparison with experiments:
  - Atomic gold wire systems
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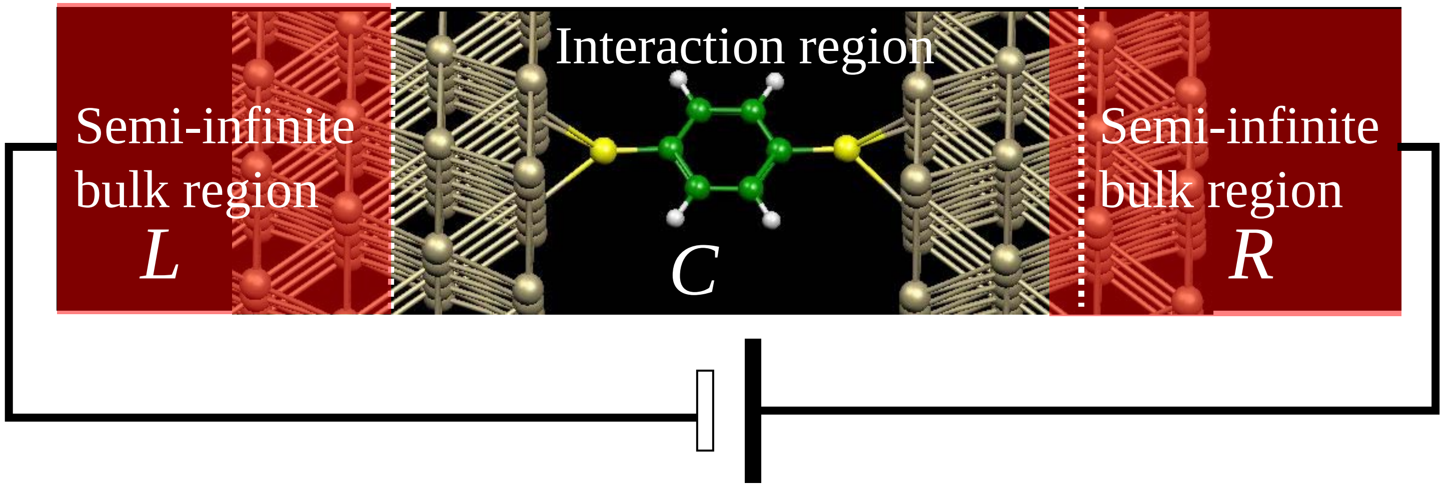
Modelling atomic-scale conductors

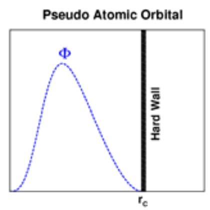


Density Functional Theory

– SIESTA code [J. M. Soler *et al*. J. Phys. C **14**, 2745 (2002)]

– Pseudopotentials

– Pseudo-AO basis set with *finite* range

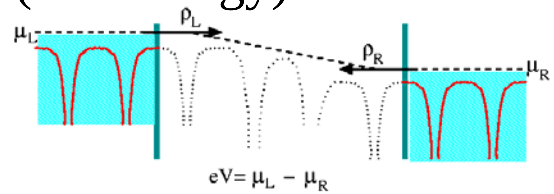


+

Non-equilibrium Green's functions (NEGF)

= Coupling to semi-infinite bulk treated *exact* (self-energy)

= Electron density at finite applied voltage

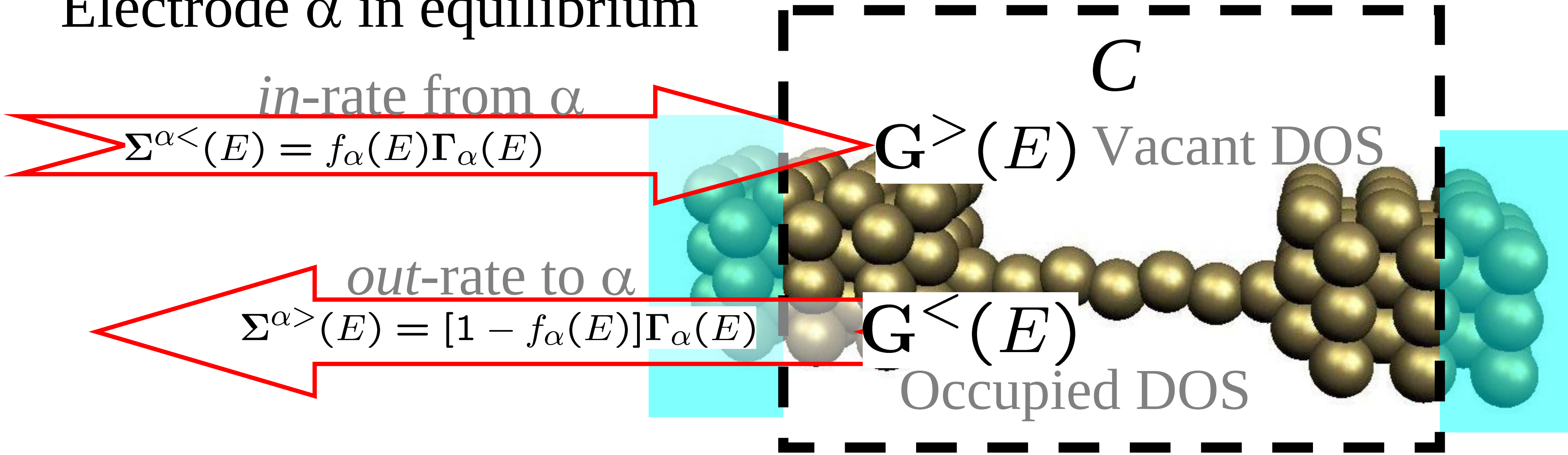


= transport calculations *incl.* many-body interactions in central region

TranSIESTA: Brandbyge *et al*., MRS proc. 636, (2001); PRB 65, 165401 (2002)

Non-equlibrium Greens functions

Electrode α in equilibrium



- Density $\mathbf{D} = \int dE\, \mathbf{G}^{<}(E)$
- Current from α: $J^{\alpha} = \int dE\, \mathrm{Tr}[\boldsymbol{\Sigma}^{\alpha,<}(E)\mathbf{G}^{>}(E) - \boldsymbol{\Sigma}^{\alpha,>}(E)\mathbf{G}^{<}(E)]$
- Power from α: $P^{\alpha} = \int dE\, E\, \mathrm{Tr}[\boldsymbol{\Sigma}^{\alpha,<}(E)\mathbf{G}^{>}(E) - \boldsymbol{\Sigma}^{\alpha,>}(E)\mathbf{G}^{<}(E)]$

Y. Meir, N. S. Wingreen, PRL **68**, 2512 (1992)

NEGF: Interactions

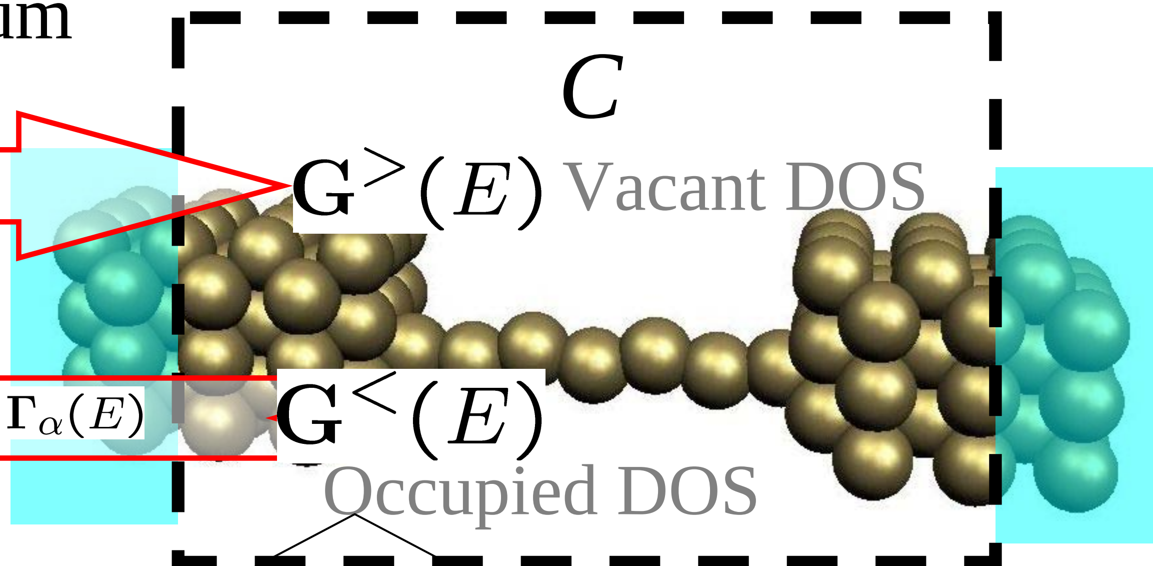
Electrode α in equilibrium

in-rate from α

$$\Sigma^{\alpha<}(E) = f_\alpha(E)\Gamma_\alpha(E)$$

out-rate to α

$$\Sigma^{\alpha>}(E) = [1 - f_\alpha(E)]\Gamma_\alpha(E)$$

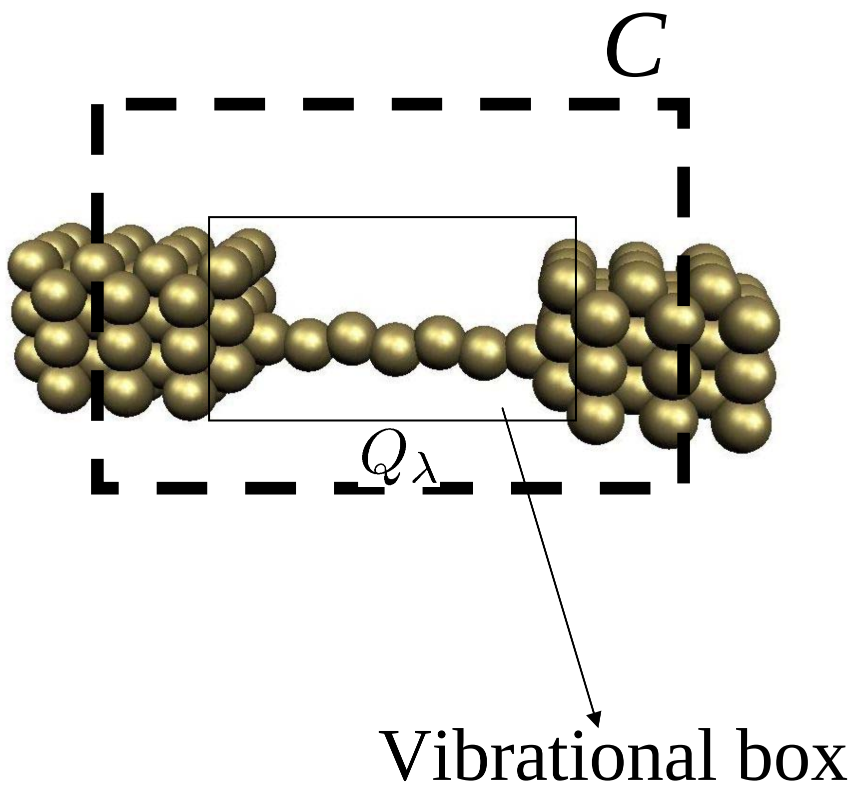


in-rate due to local vibration (Ω) in C:

$$\Sigma^{<}_{\rm ph}(E) = \mathbf{M}_{\rm ph}\left[\underbrace{(N+1)\mathbf{G}^{<}(E+\hbar\omega)}_{\text{emission}} + \underbrace{N\mathbf{G}^{<}(E-\hbar\omega)}_{\text{absorbtion}}\right]\mathbf{M}_{\rm ph}$$

•Self-consistent Born Approximation

Phonon interaction

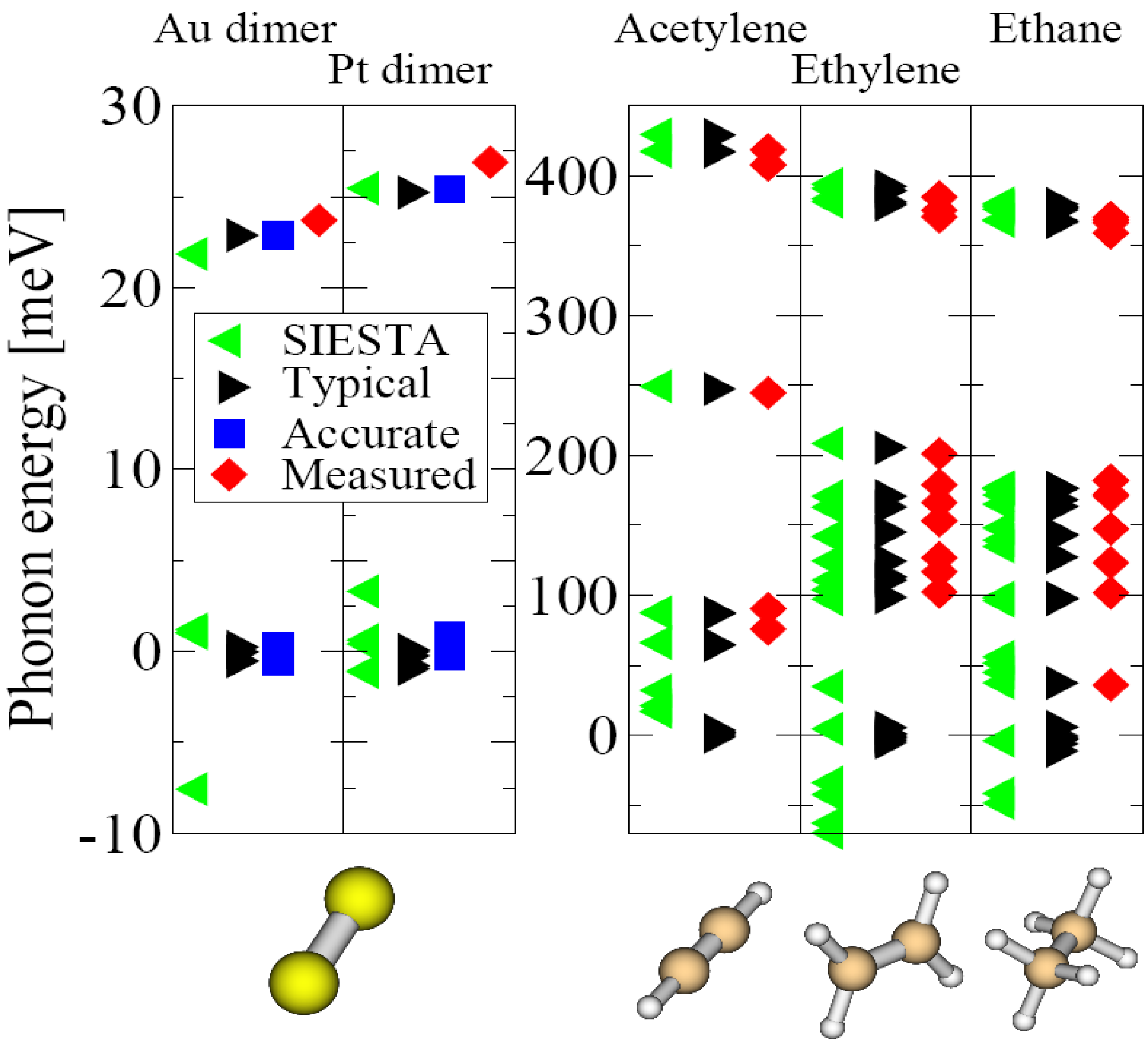


- Harmonic approximation
- Phonon modes from DFT
- Free motion of the modes (undamped)

$$\mathbf{H}_{\mathrm{e-ph}} \approx \sum_{\lambda} \left(\frac{\partial \mathbf{H}_{\mathrm{DFT}}}{\partial Q_\lambda} \right) \hat{Q}_\lambda = \sum_{\lambda=1}^{3N} \mathbf{M}_\lambda (b_\lambda^\dagger + b_\lambda)$$

Vibrational properties from DFT

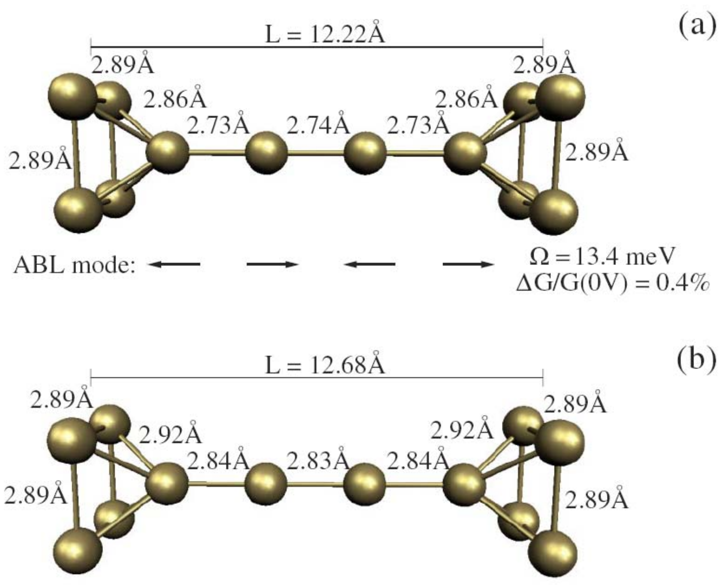
- Harmonic approximation
- Finite differences
- **Correcting dynamical matrix for the egg-box effect**
- Vibrational frequencies
  - test systems show an accuracy ~ 5 %
- Electron-phonon couplings using finite differences

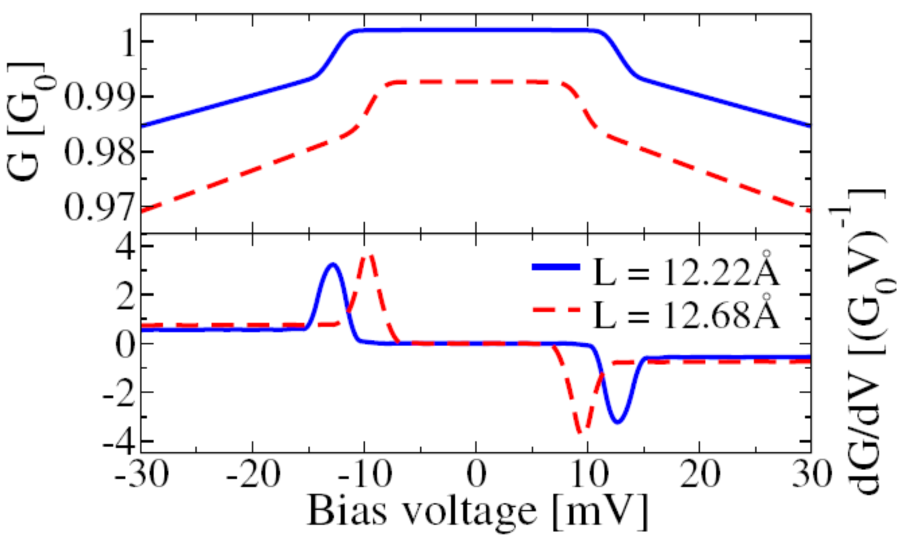


DFT-NEGF-SCBA calculation

Frederiksen *et al.*, Phys. Rev. Lett. 93, 256601 (2004):

Calculations using Self-consistent Born Approximation





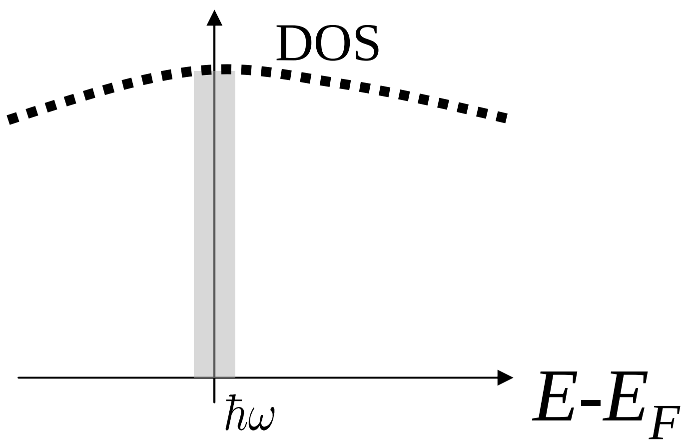
SCBA is time-consuming:

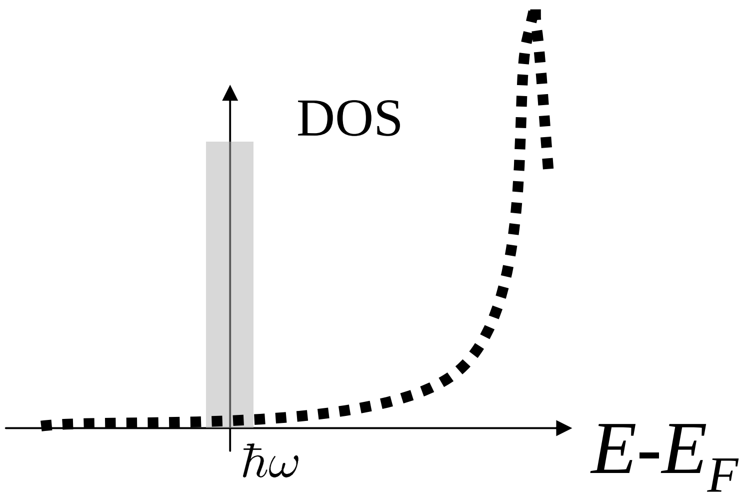
We want to investigate *many* and *larger* structures

Lowest Order Expansion of SCBA

Paulsson, Frederiksen, Brandbyge, PRB **72,** 201101R (2005)

Vibrational energies are ”small”: Slow variation in electronic structure



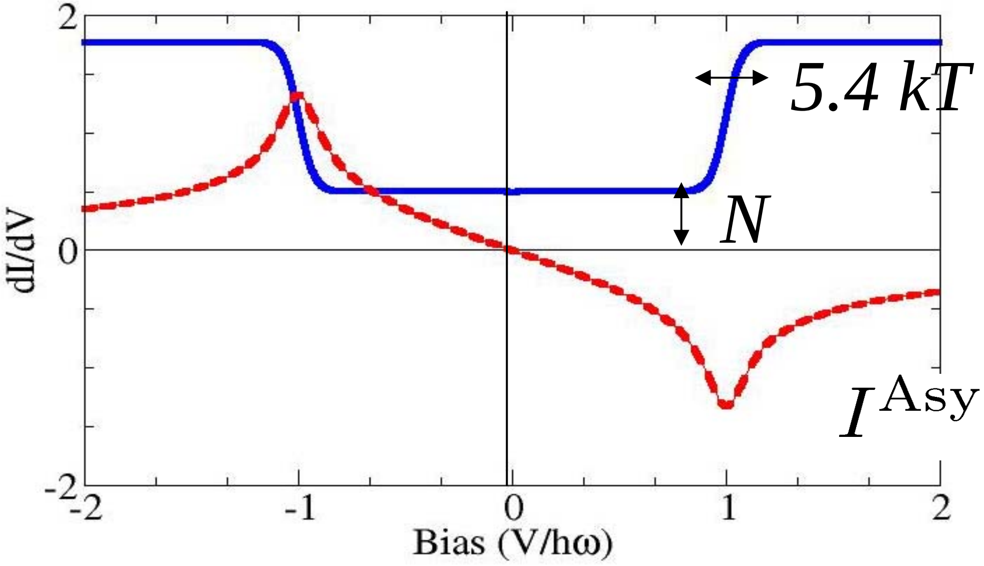


- Evaluate all quantities at E_F, *e.g.* $\mathbf{G}(E) \approx \mathbf{G}(E_F)$
- Weak e-ph coupling - Lowest order expansion: $\delta I^{\alpha} \approx \sum_{\lambda} M_{\lambda}^{2} \ldots$
  - Avoid SCBA: FAST calculations even for LARGE systems

Lowest order expansion of SCBA

$$I^{\text{LOE}} = I^{(0)} + \sum_{\lambda} \left(I_{\lambda}^{\text{Sym}} + I_{\lambda}^{\text{Asym}} \right)$$

$$I^{\text{Sym}} = \mathcal{I}_{\text{Sym}}(eV, \hbar\omega, kT, N) \times C_{\text{Sym}}$$



Universal functions

$$I^{\text{Asym}} = \mathcal{I}_{\text{Asym}}(eV, \hbar\omega, kT) \times C_{\text{Asym}}$$

- Electronic structure constants (at E_F) *e.g.*

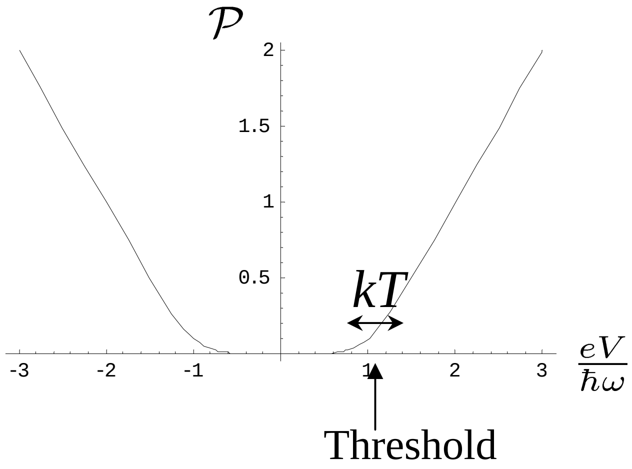
$$C_{\text{Asym}} = \text{Tr}\left[G^{\dagger}\Gamma_1 G \left(\Gamma_2 G^{\dagger} M_{\lambda} G \left\{ \Gamma_2 - \Gamma_1 \right\} G^{\dagger} M_{\lambda} + \text{h.c.} \right) \right]$$

Paulsson, Frederiksen, Brandbyge, PRB **72,** 201101R (2005)

Power into phonon system

$$P^{\rm LOE} = \hbar\omega\gamma_{\rm eh}\left(n_B(\hbar\omega) - N\right) + \mathcal{P}(eV,\hbar\omega,kT) \times {\rm Tr}\left[M_\lambda G \Gamma_1 G^\dagger M_\lambda G \Gamma_2 G^\dagger\right]$$

e-h damping   Non-equilibrium term



$$\mathcal{P}(V,\omega,kT) = \frac{(\hbar\omega)^2}{\pi\hbar}\frac{\left(\cosh\left(\frac{eV}{kT}\right)-1\right)\coth\left(\frac{\hbar\omega}{2kT}\right) - \frac{eV}{\hbar\omega}\sinh\left(\frac{eV}{kT}\right)}{\left(\cosh\left(\frac{\hbar\omega}{kT}\right)-\cosh\left(\frac{eV}{kT}\right)\right)}$$

Steady state:

$$P^{\rm LOE} = 0 \Rightarrow \hbar\omega\,\gamma_{\rm eh}\left(n_B(\hbar\omega) - N\right) + \mathcal{P}(eV,\hbar\omega,kT) \times C_{\rm Pow} = 0$$

Non-eq. no. phonons

Power into phonon system

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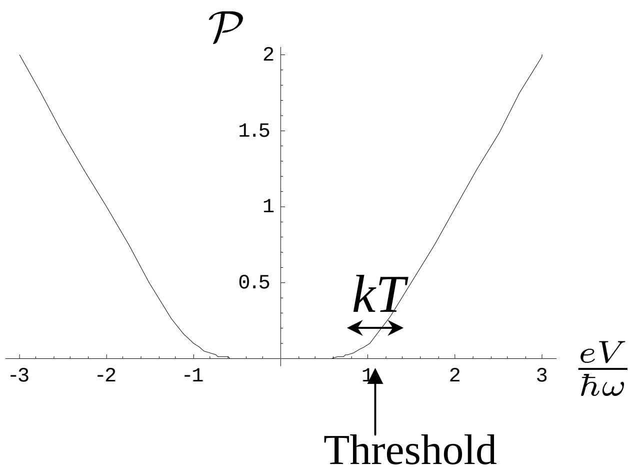
e-h damping Non-equilibrium term



$$\mathcal{P}(V,\omega,kT) = \frac{(\hbar\omega)^2}{\pi\hbar}\frac{\left(\cosh\left(\frac{eV}{kT}\right)-1\right)\coth\left(\frac{\hbar\omega}{2kT}\right) - \frac{eV}{\hbar\omega}\sinh\left(\frac{eV}{kT}\right)}{\left(\cosh\left(\frac{\hbar\omega}{kT}\right)-\cosh\left(\frac{eV}{kT}\right)\right)}$$

Steady state:

"External damping"

$$P^{\rm LOE} = 0 \Rightarrow \hbar\omega(\gamma_{\rm eh} + \gamma_d)\left(n_B(\hbar\omega) - N\right) + \mathcal{P}(eV,\hbar\omega,kT) \times C_{\rm Pow} = 0$$

Non-eq. no. phonons

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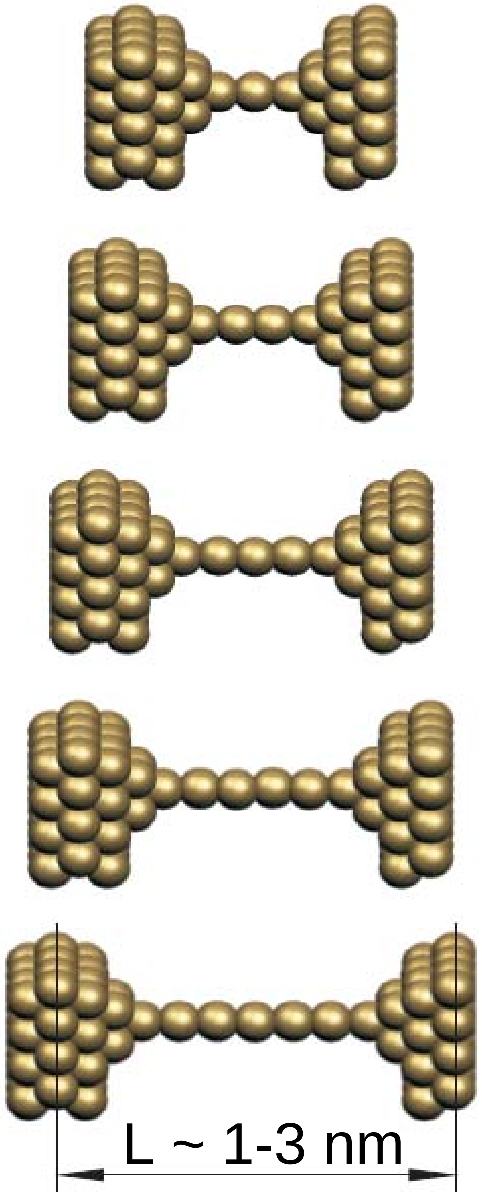
- Applications – how does it work
  Comparison with experiments:
  – Atomic gold wire systems
  – IETS of hydrocarbon molecules

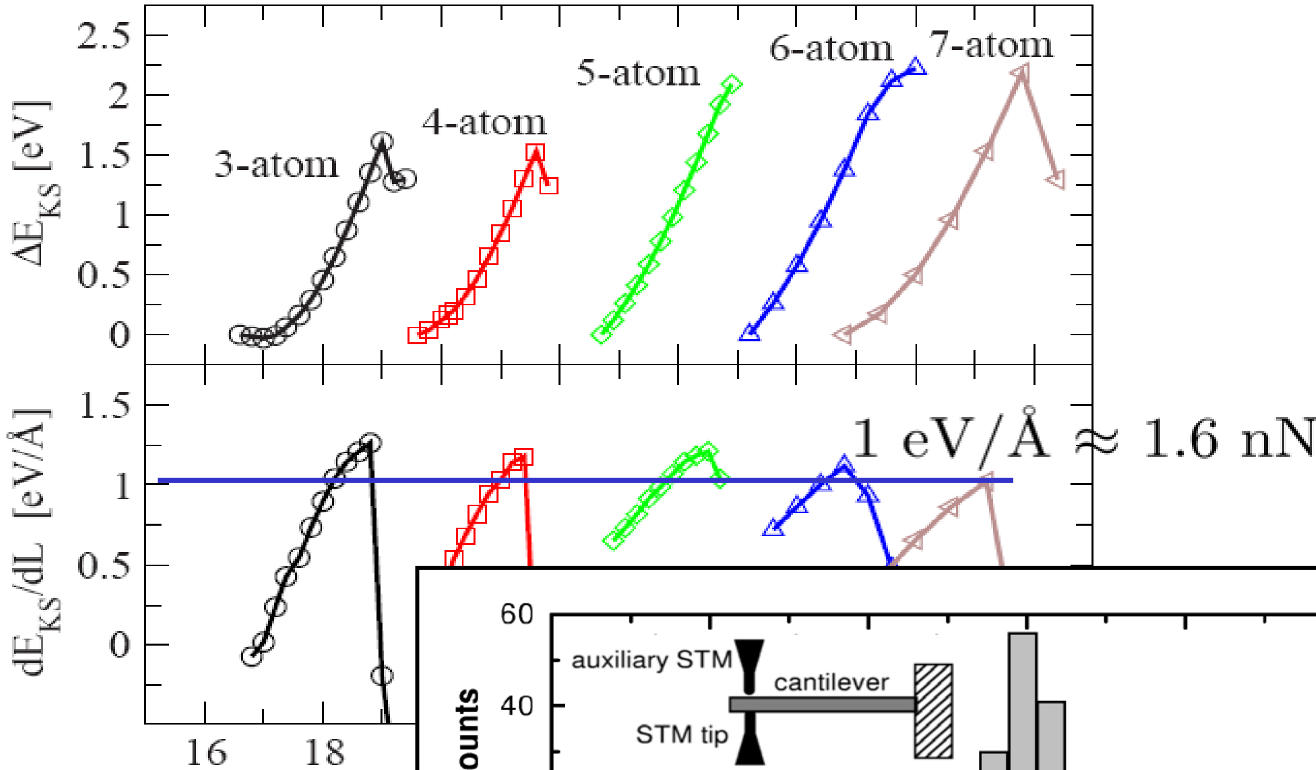
From T. Frederiksen *et al., submitted to PRB*

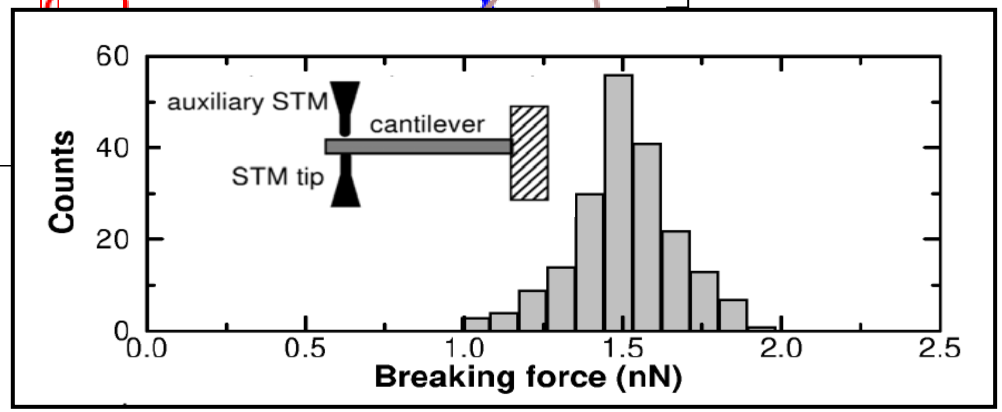
- Summary/Conclusions

Gold chains with DFT+NEGF+LOE



Frederiksen et al., cond-mat/06115602

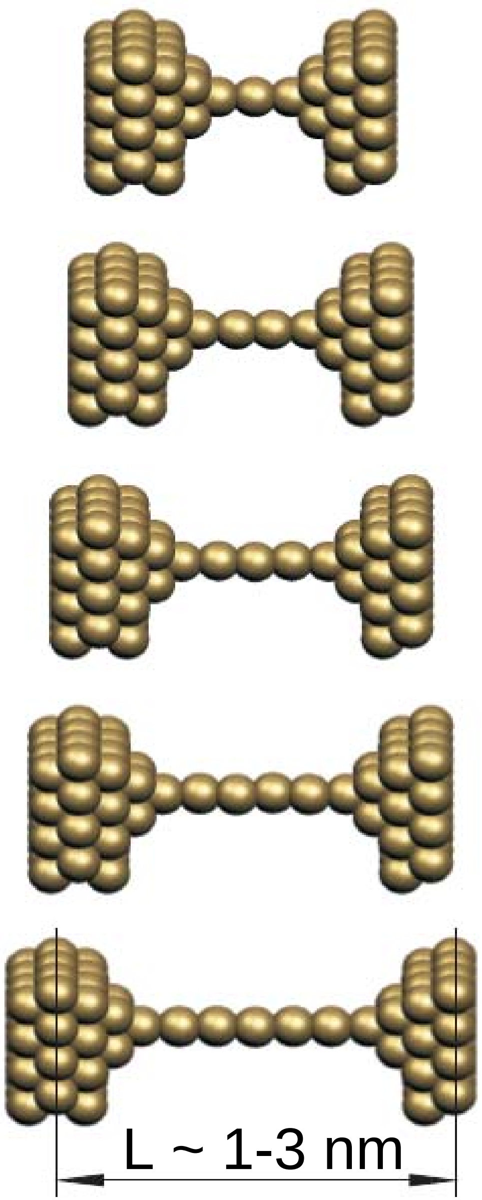


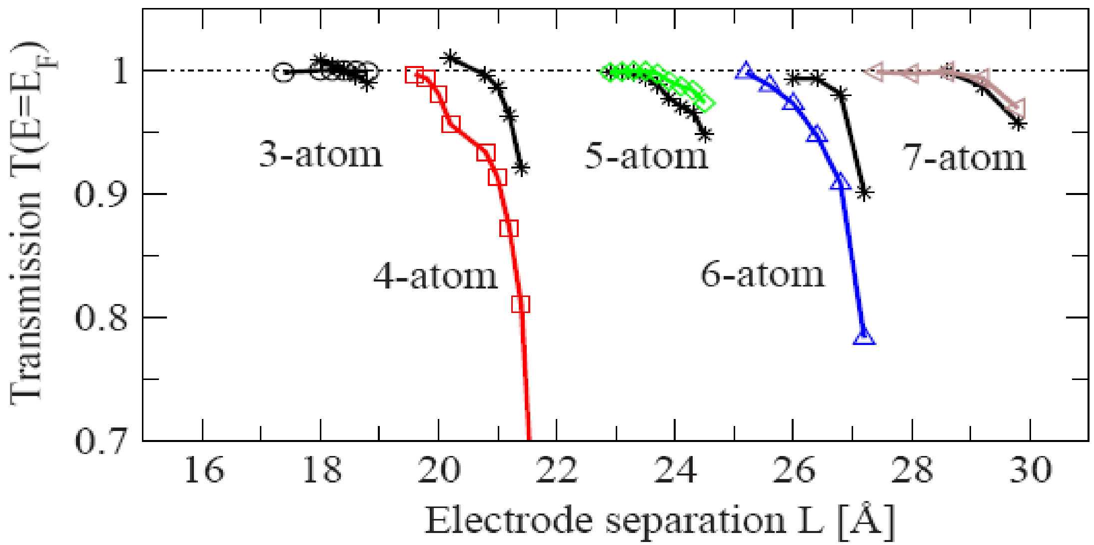


G. Rubio-Bollinger *et al.*, PRL **87**, 026101 (2001)

Elastic transport

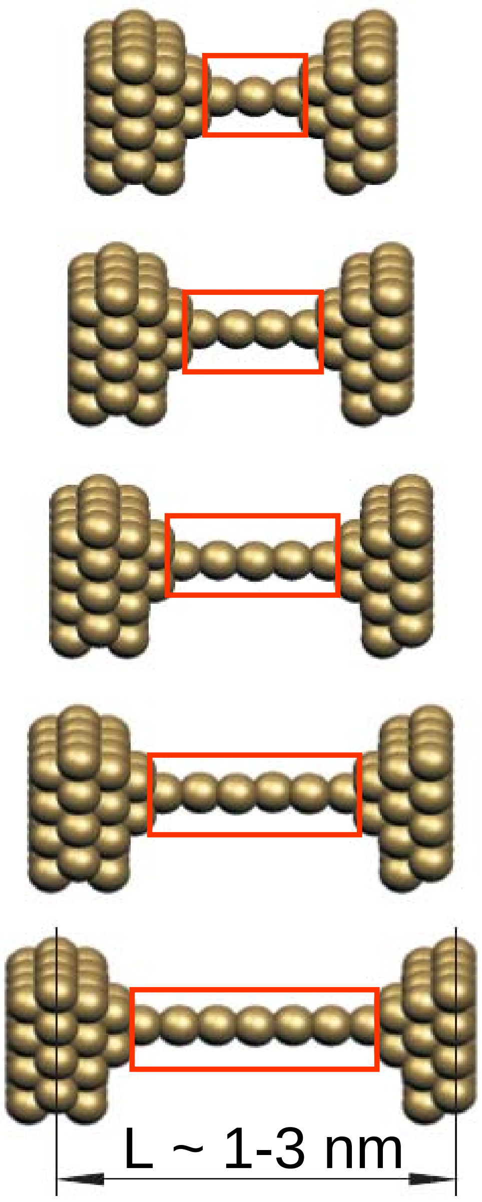
Frederiksen et al., cond-mat/06115602

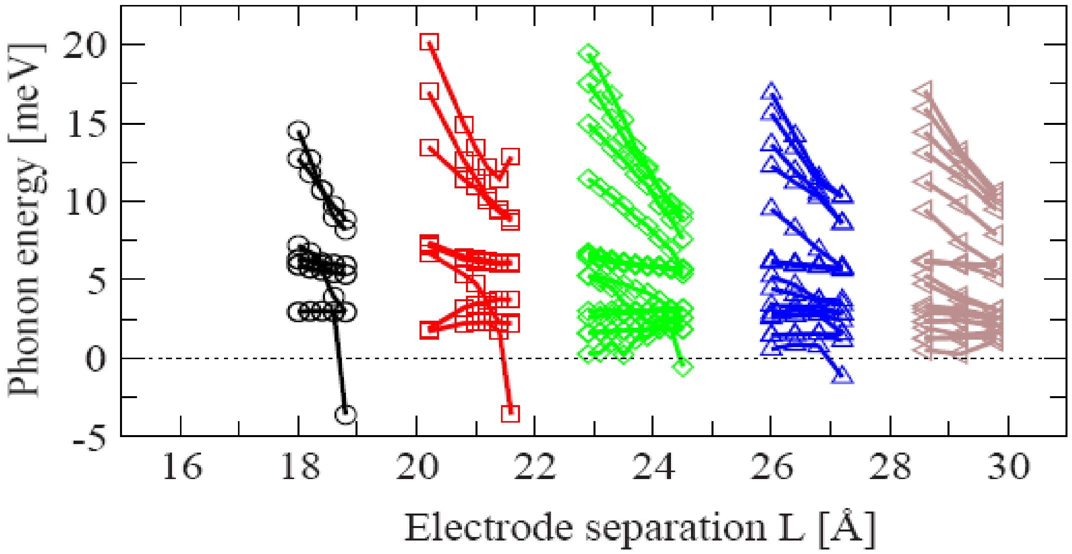




Phonon frequencies from DFT

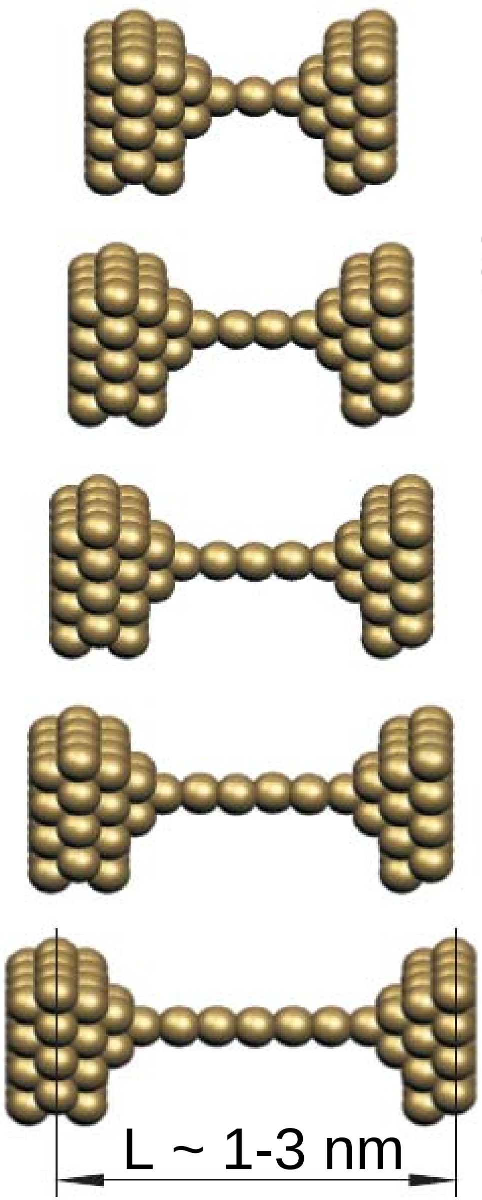
Frederiksen et al., cond-mat/06115602

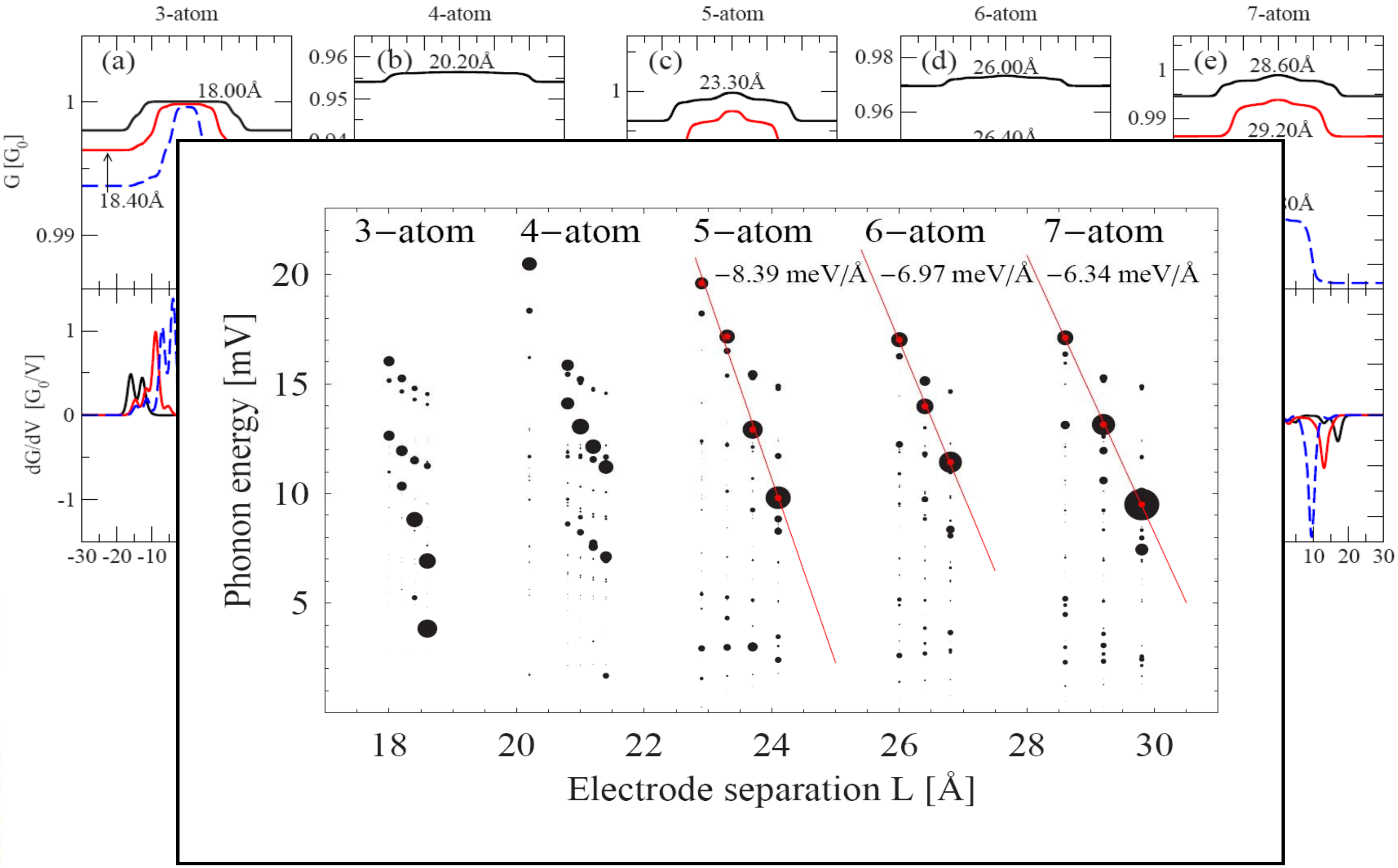




Inelastic transport

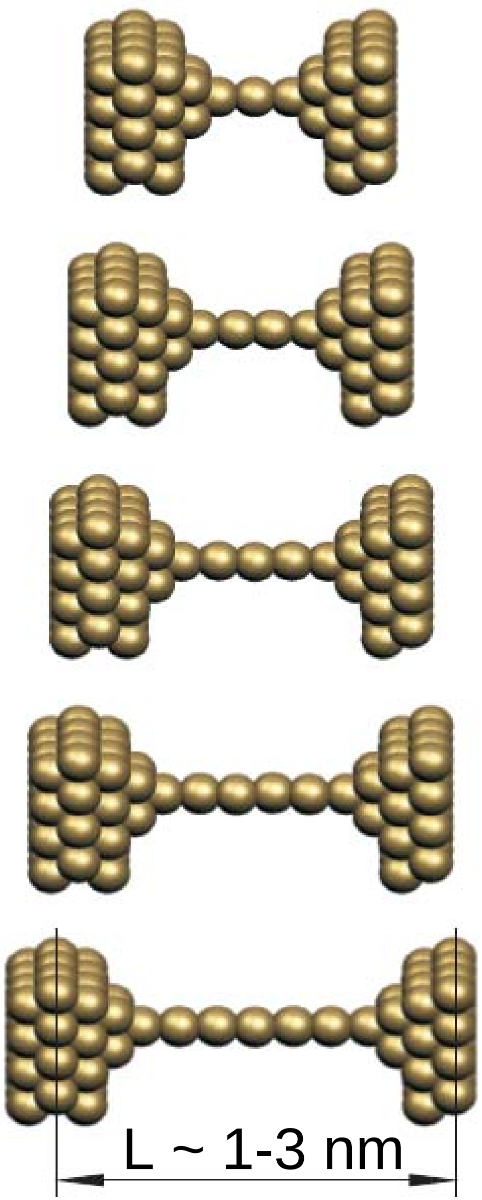
Frederiksen et al., cond-mat/06115602

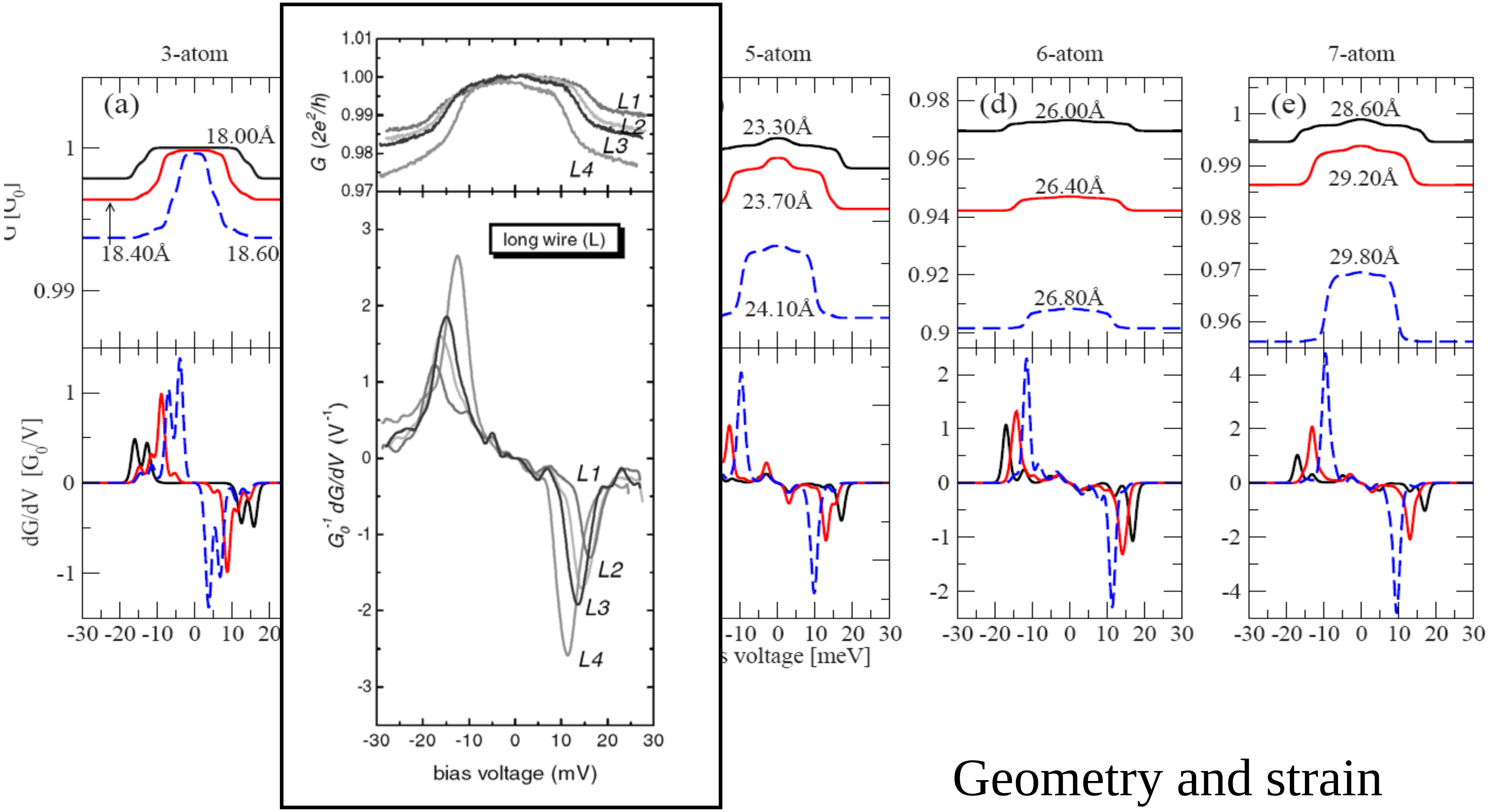




Inelastic transport

Frederiksen et al., cond-mat/06115602



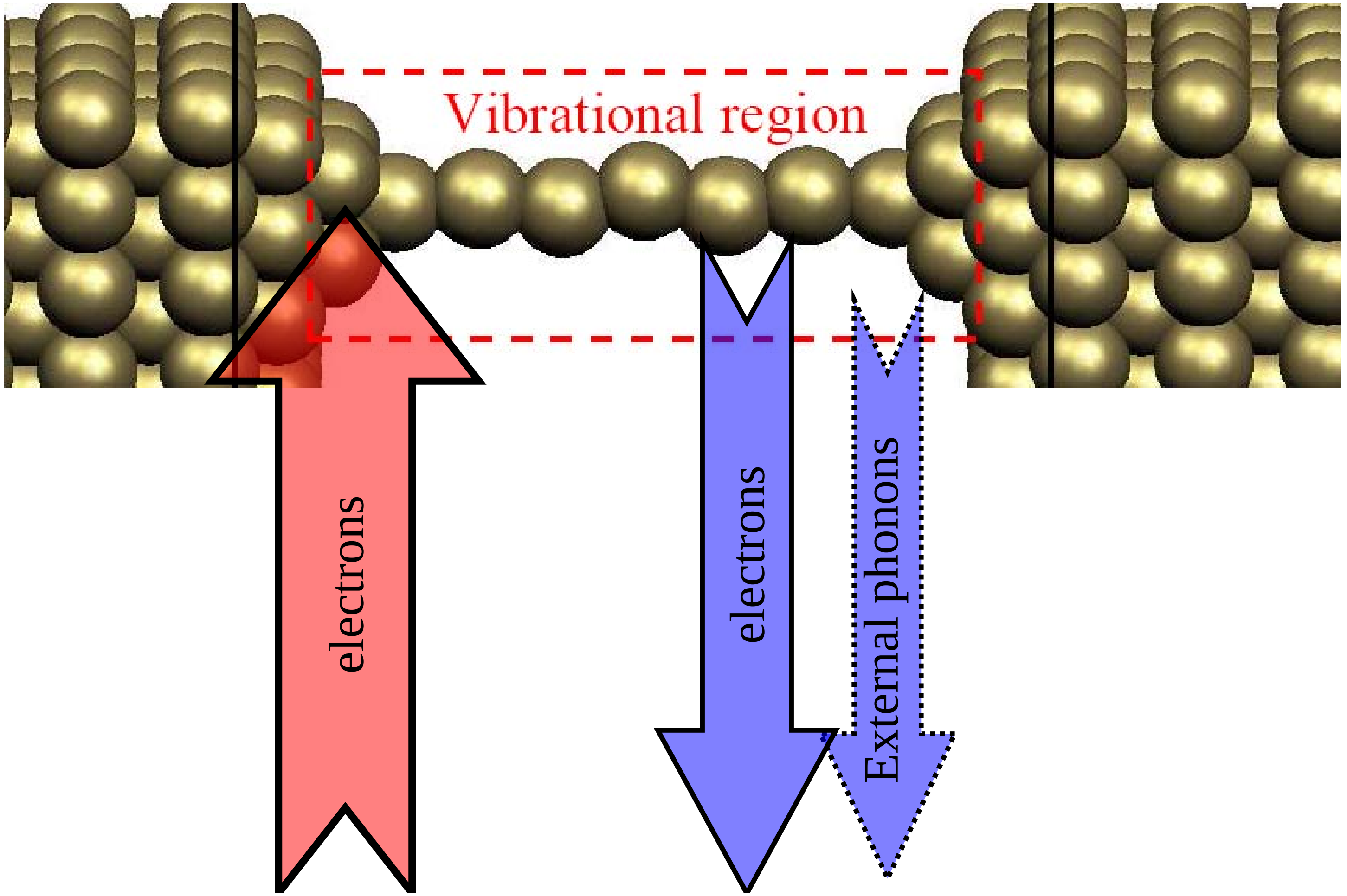


Geometry and strain dependence OK

but flat plateaux!

N. Agraït *et al.*, PRL **88**, 216803 (2002)
N. Agraït *et al.*, Chem. Phys. **281**, 231 (2002)

Steady state: Power balance



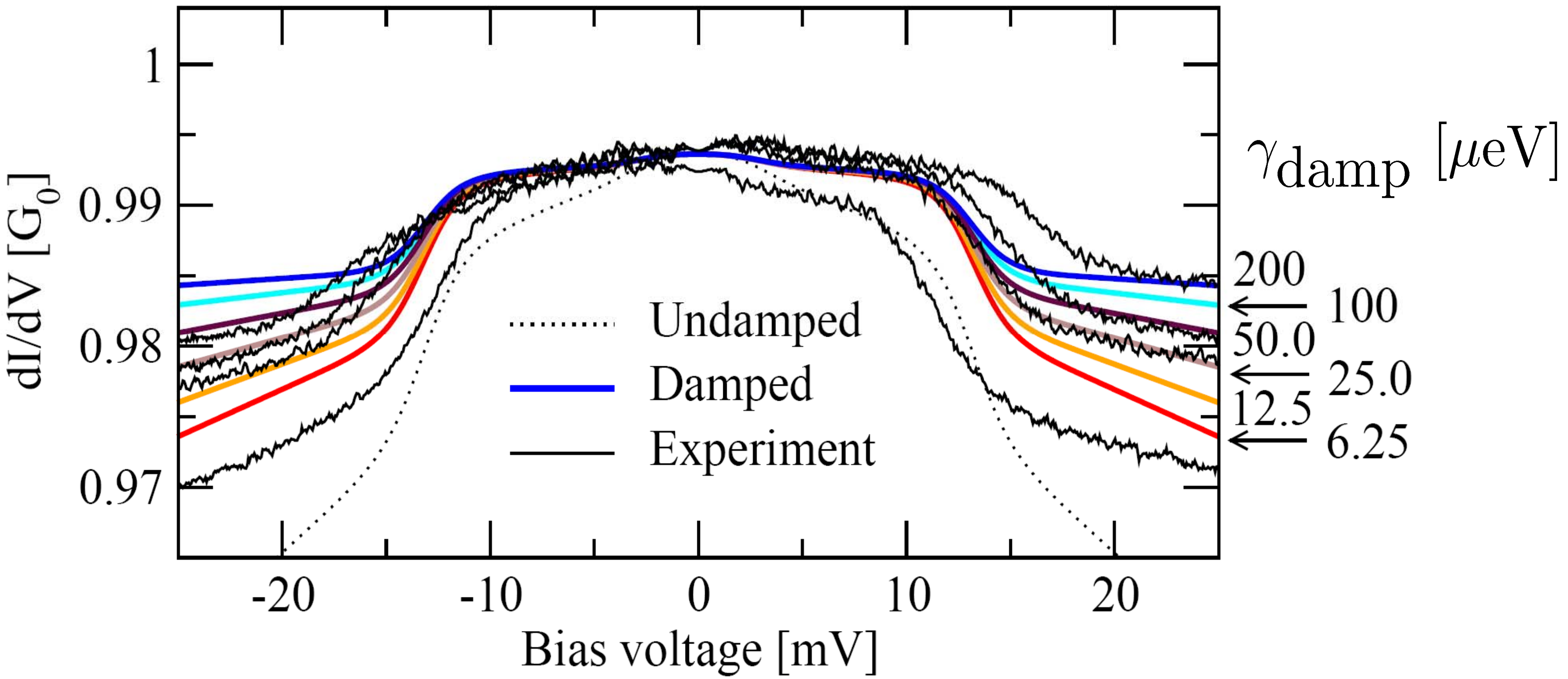
$$P^{\mathrm{LOE}} = 0 \Rightarrow \mathcal{P}(eV, \hbar\omega, kT) \times C_{\mathrm{Pow}} + \hbar\omega(\gamma_{\mathrm{eh}} + \gamma_{\mathrm{damp}})\,(n_B(\hbar\omega) - N) = 0$$

T. Frederiksen *et al.*, PRL 93, 256601 (2004)

Paulsson, Frederiksen, Brandbyge, PRB 201101R (2005)

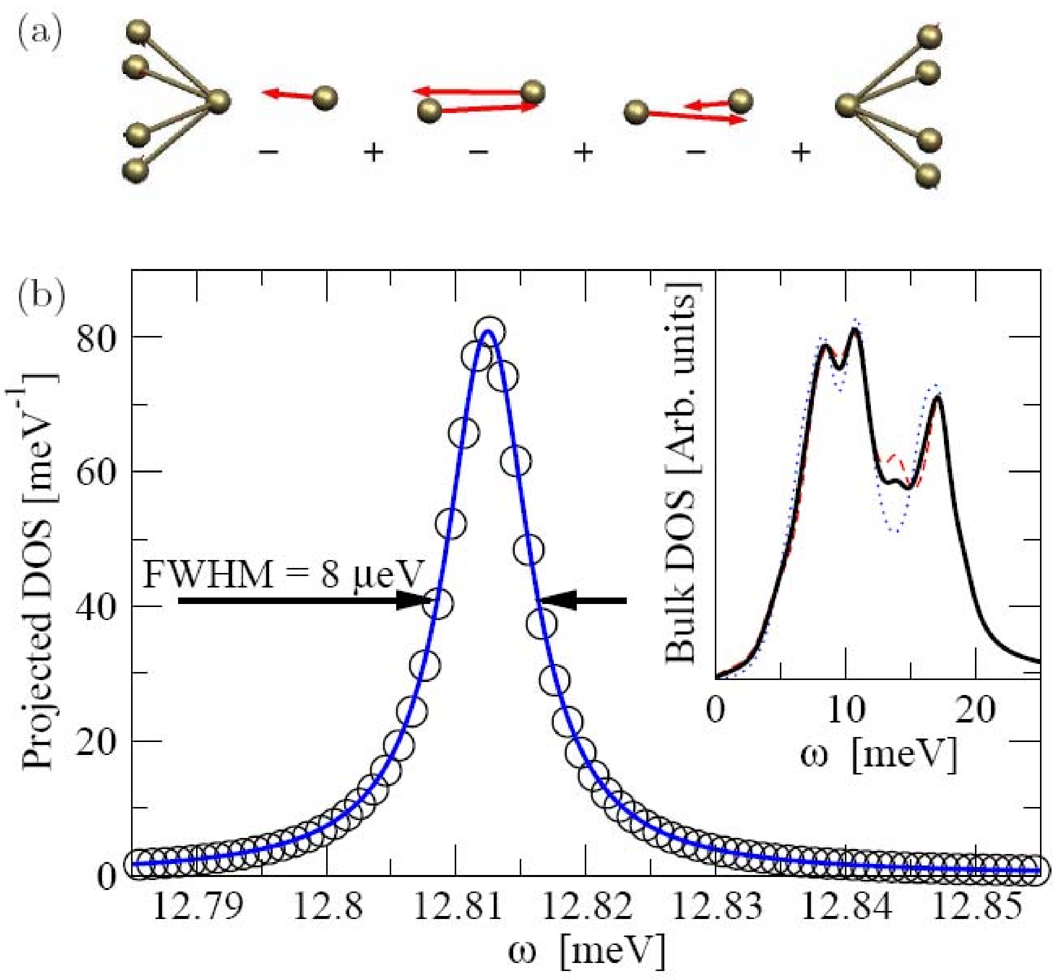
Comparison with experiments

Frederiksen et al., cond-mat/06115602



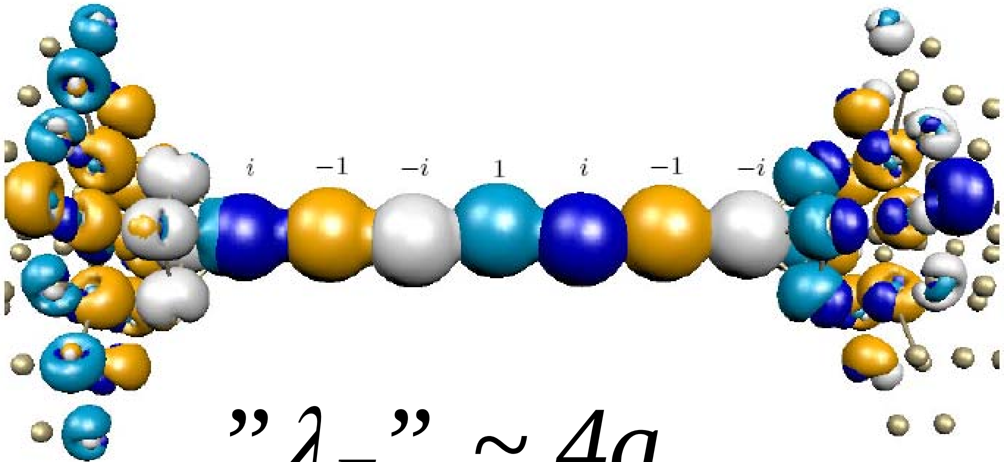
Calculating the external damping

7-atom chain, L=29.2Å

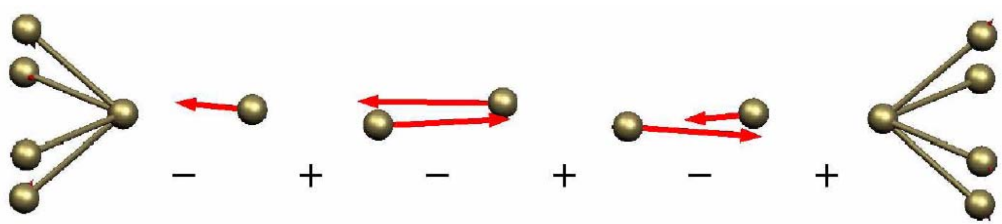


Mode selectivity: Gold chain

The "conducting" scattering state (Eigenchannel with *T* ~ *1*):

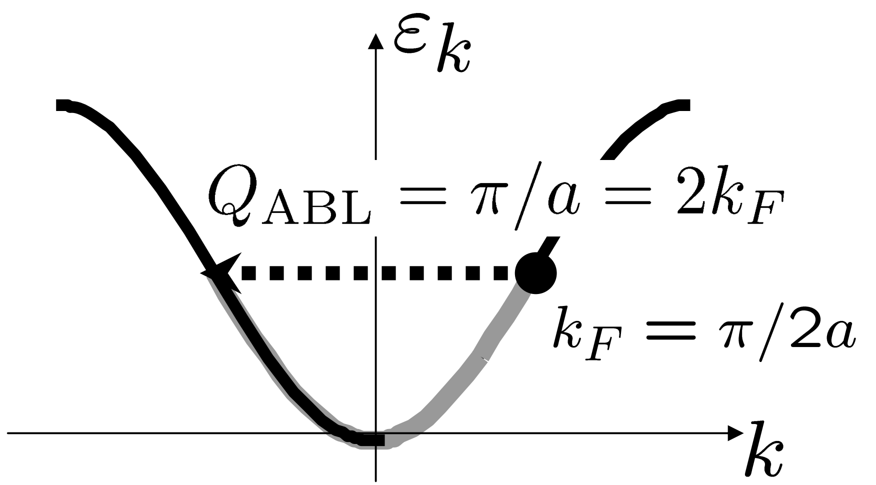


$$"\lambda_F" \sim 4a$$



Alternating **B**ond **L**ength mode

Infinite 1D half-filled chain



Electron transport and phonons in atomic wires

Nicolás Agraït*, Carlos Untiedt[1], Gabino Rubio-Bollinger, Sebastián Vieira

Chemical Physics 281 (2002) 231–234

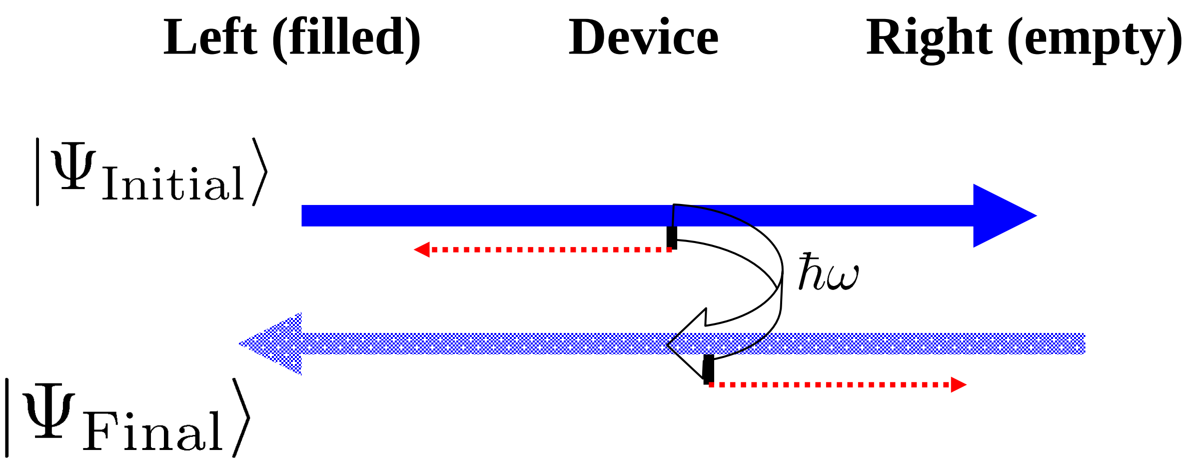
Frederiksen *et al.*, Phys. Rev. Lett. 93, 256601 (2004).

Propensity rules

Many vibrational modes – only **few** signals in the *I*-*V* :

Simple picture from single-particle scattering states at high bias:

- **<u>High</u>** transmission (T=1):



- "Fermi golden-rule" argument:

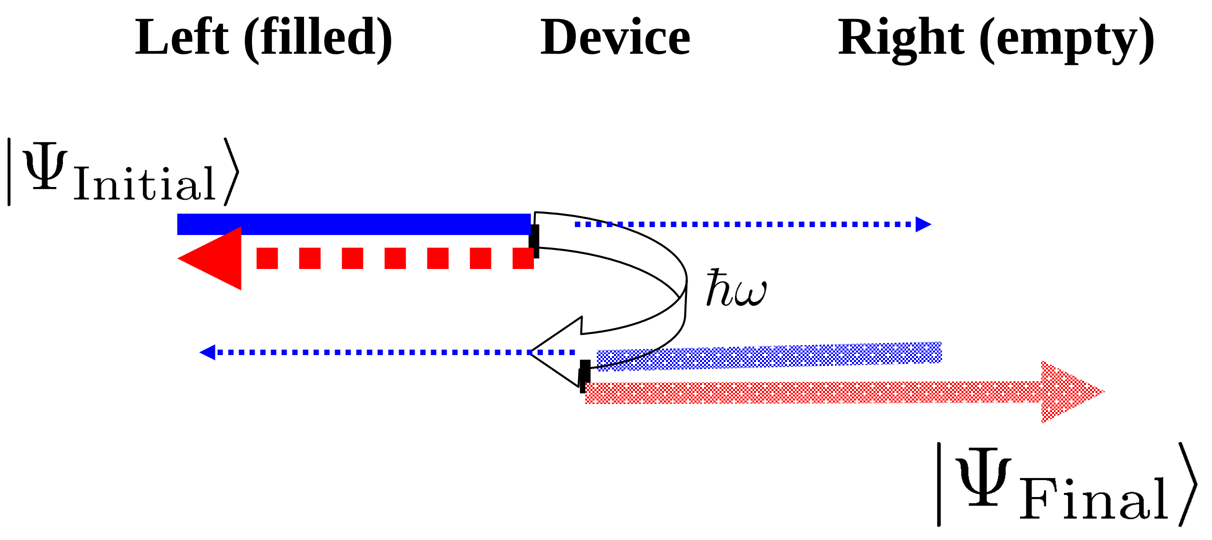
$$\Delta G(\lambda) \propto -|\langle \Psi_{\mathrm{Final}} | M_\lambda | \Psi_{\mathrm{Initial}} \rangle|^2 < 0$$

Propensity rules

Many vibrational modes – only **few** signals in the *I*-*V* :

Simple picture from single-particle scattering states at high bias:

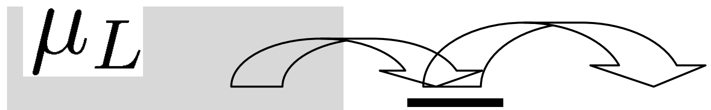
- **<u>Low</u>** transmission (T ~ 0):



•"Fermi golden-rule" argument

$$\Delta G(\lambda) \propto +|\langle\Psi_{\text{Final}}|M_\lambda|\Psi_{\text{Initial}}\rangle|^2 > 0$$

Single-site model



We may encounter more complicated scenarios (several partly transmitting channels): Difficult to interpret!

M. Paulsson, T. Frederiksen, M. Brandbyge, J. Physics: Conf. Series 35, 247-254 (2006).

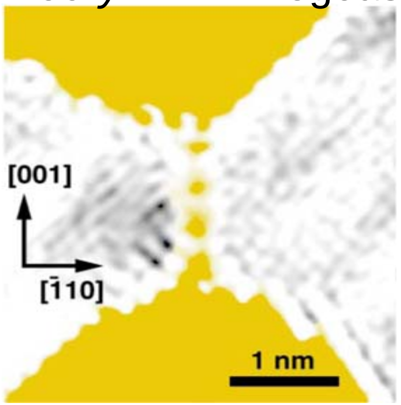
Impurities in gold wire systems

Large Au-Au bond distance:

Exp: H. Ohnishi *et al.*, Nature (1998)

Theory: F. D. Novaes *et al.*, PRL (2003)

Theory: F. D. Legoas *et al.*, PRL (2002), PRL (2004)

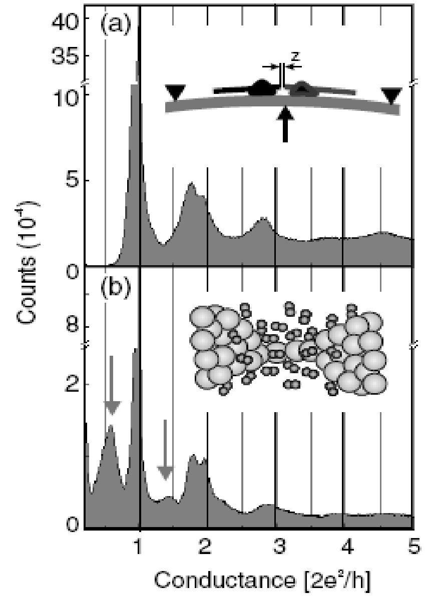


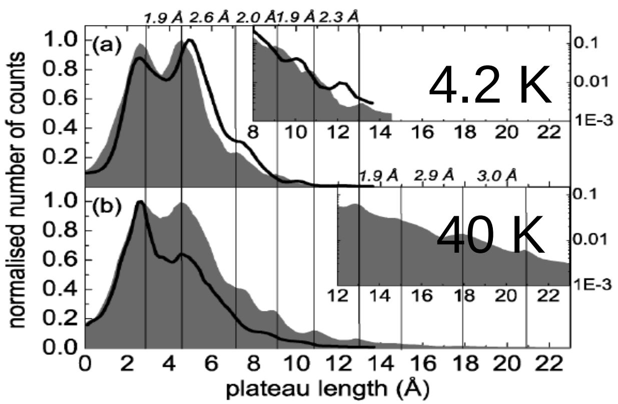
Au+Hydrogen:

Exp: Sz. Csonka *et al.*, PRL (2003), PRB (2006)

Theory: R. N. Barnett *et al.*, Nano Lett. (2004)

Theory: P. Jelínek *et al.*, PRL (2006)



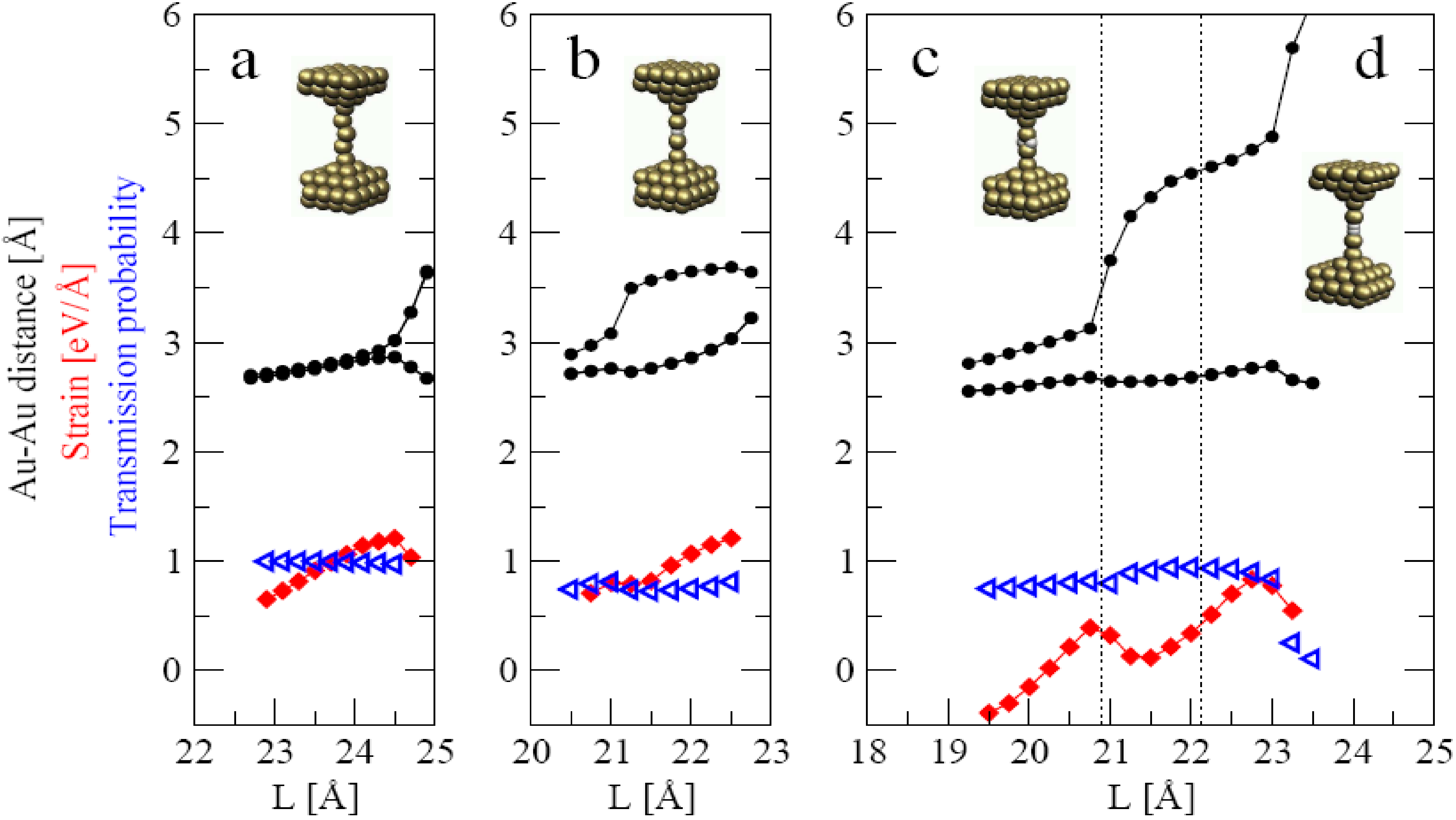


Au+Oxygen:

Exp: W. H. A. Thijssen *et al.*, PRL (2006)

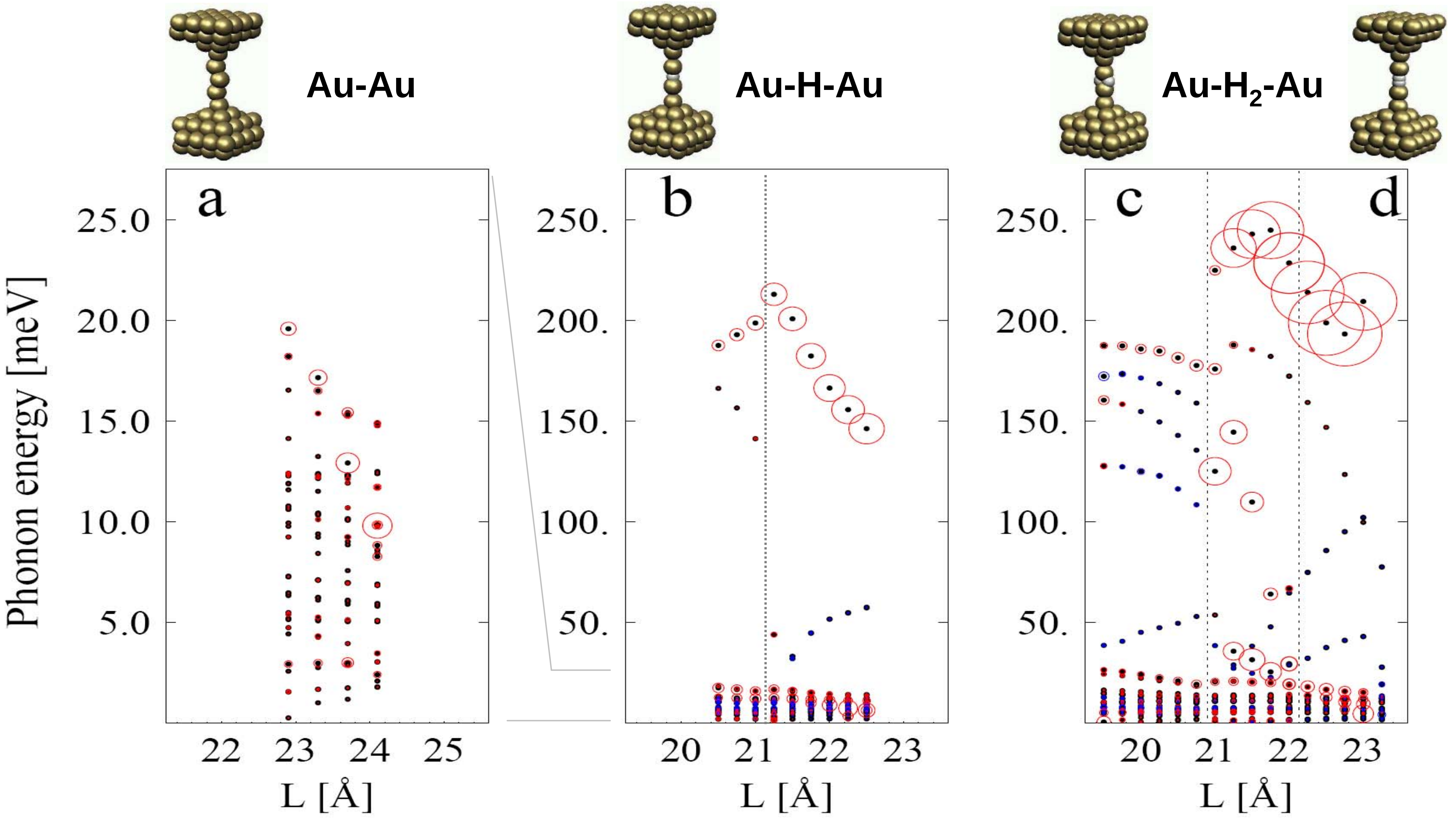
Theory: F. D. Novaes *et al.*, PRL (2006)

Hydrogen in Au wires



Frederiksen, Paulsson, Brandbyge, cond-mat/0608510

Inelastic signals



Frederiksen, Paulsson, Brandbyge, cond-mat/0608510

Outline

- Motivation – why inelastic transport ?

- Method – how to do it
  - Elastic transport (TranSIESTA)
  - Inelastic effects in conductance (NEGF)
  - **L**owest **O**rder **E**xpansion of SCBA expressions

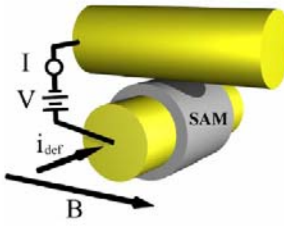
- Applications – how does it work

  Comparison with experiments:
  - Atomic gold wire systems
  - IETS of hydrocarbon molecules

Paulsson, Frederiksen, Brandbyge, Nano Lett. **6**, 258, 2006

- Summary/Conclusions

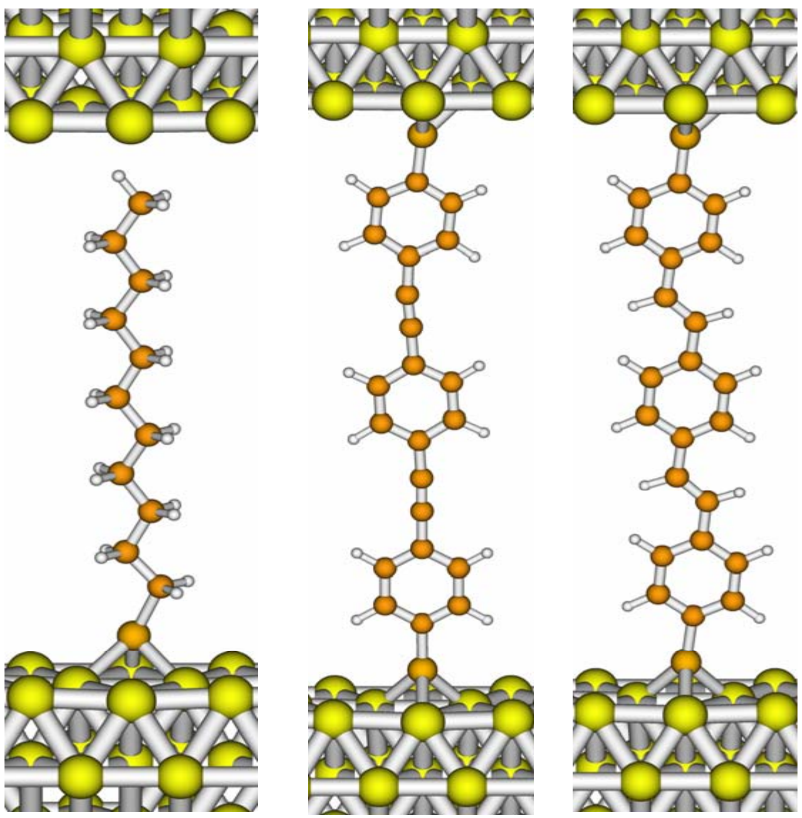
Transport in Molecules: IETS



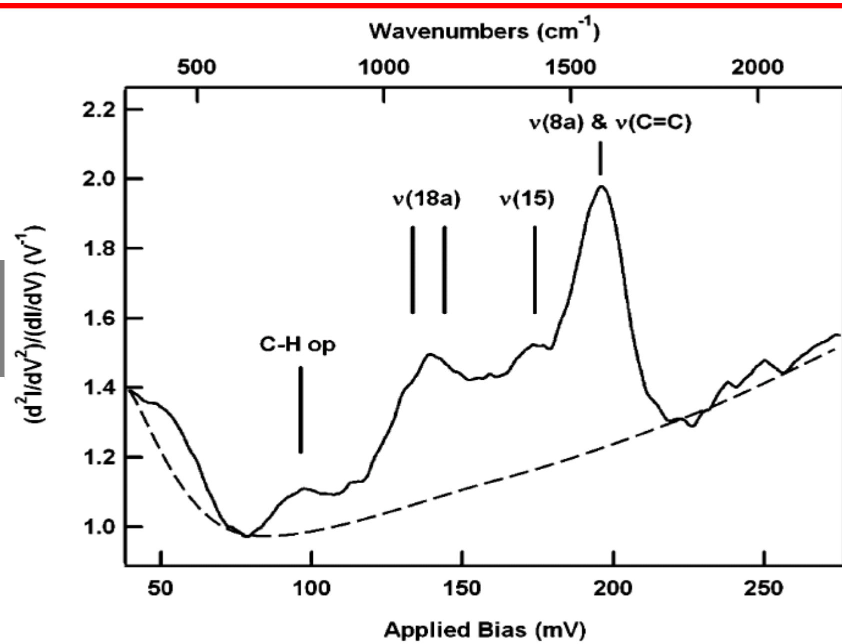
Inelastic electron tunneling spectra (IETS)

Measured for three different molecules by Kushmerick *et al.*

C_{11} OPE OPV



$$\frac{d^2 I}{dV^2} / \frac{dI}{dV}$$

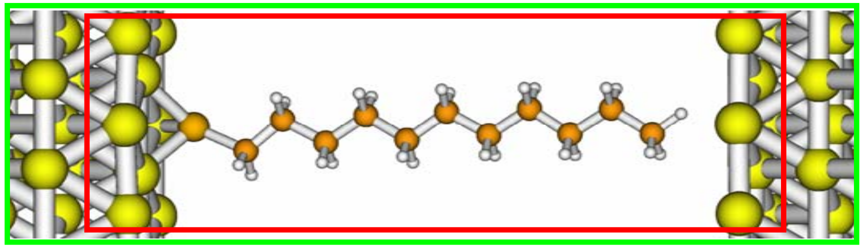


Exp. Measurments on the OPV molecule by Kushmerick et al. Nano Letters **4**, 639, 2004

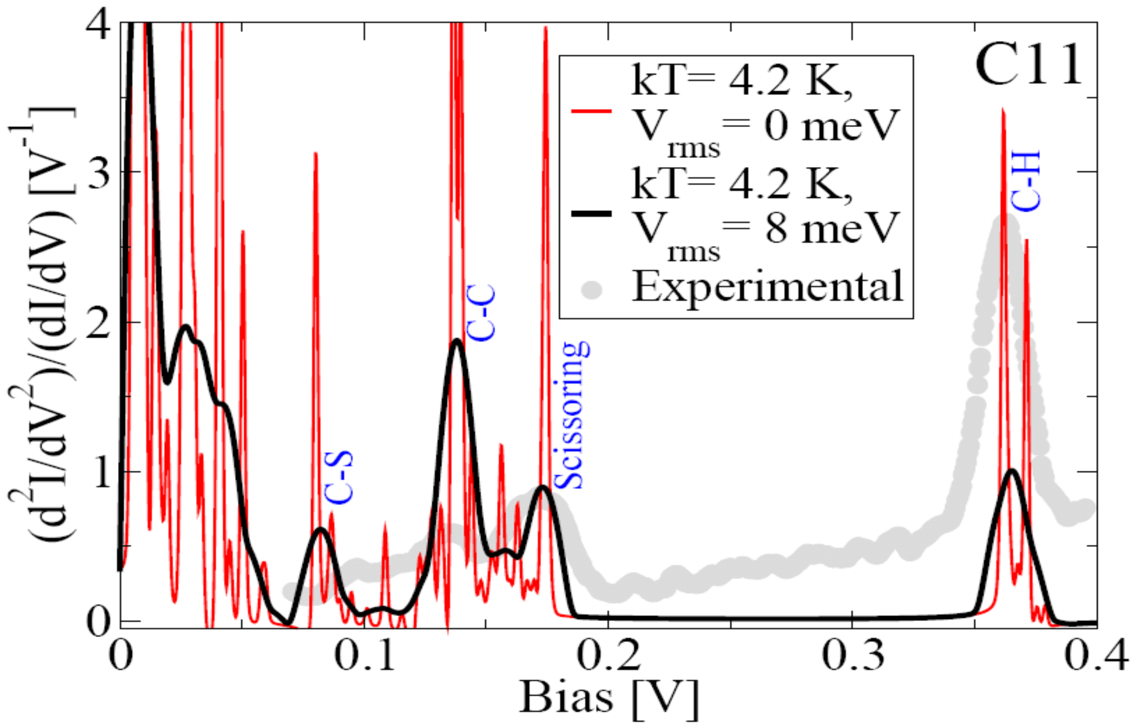
Paulsson, Frederiksen, Brandbyge, Nano Lett. **6**, 258, 2006

C_{11}: Width of IETS signal

- Width determined by
  - Temperature FWHM ≈ 5.4 *kT*
  - Lock-in technique FWHM ≈ $1.7V_{RMS}$
  - Phonon lifetime, not included



- No significant asymmetry!



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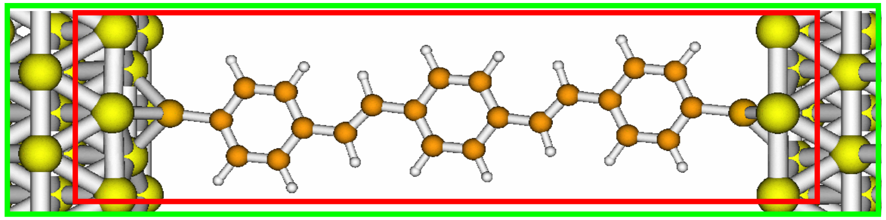
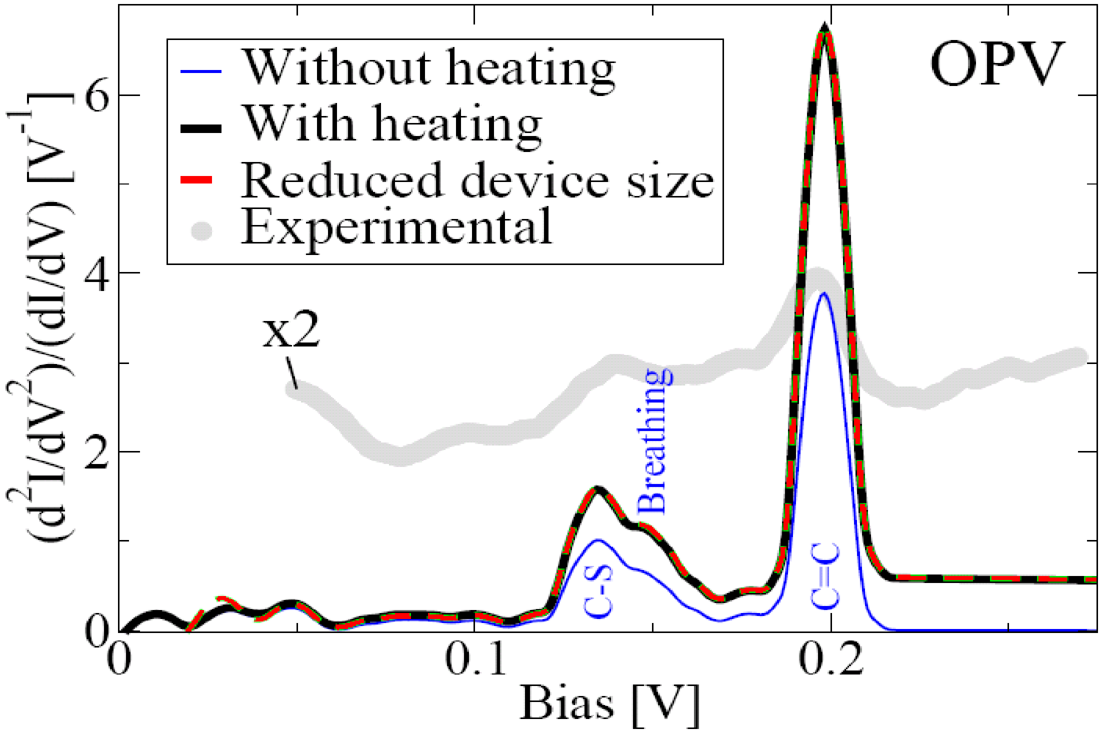
OPV: Heating of phonon system

- Phonon emission
  - Heating important
  - Increase peak height
  - Slope in conductance
  - Damping mechanism
  - Limit on heating

$$N \leq (eV/\hbar\omega - 1)$$



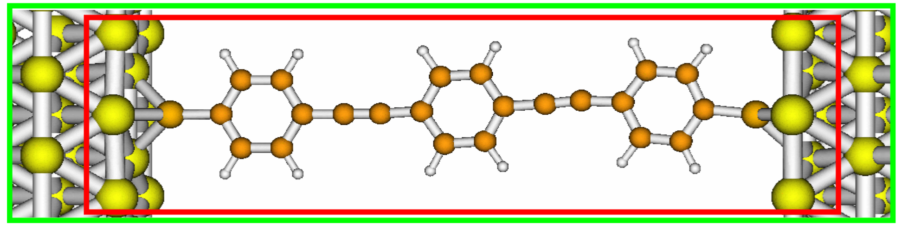


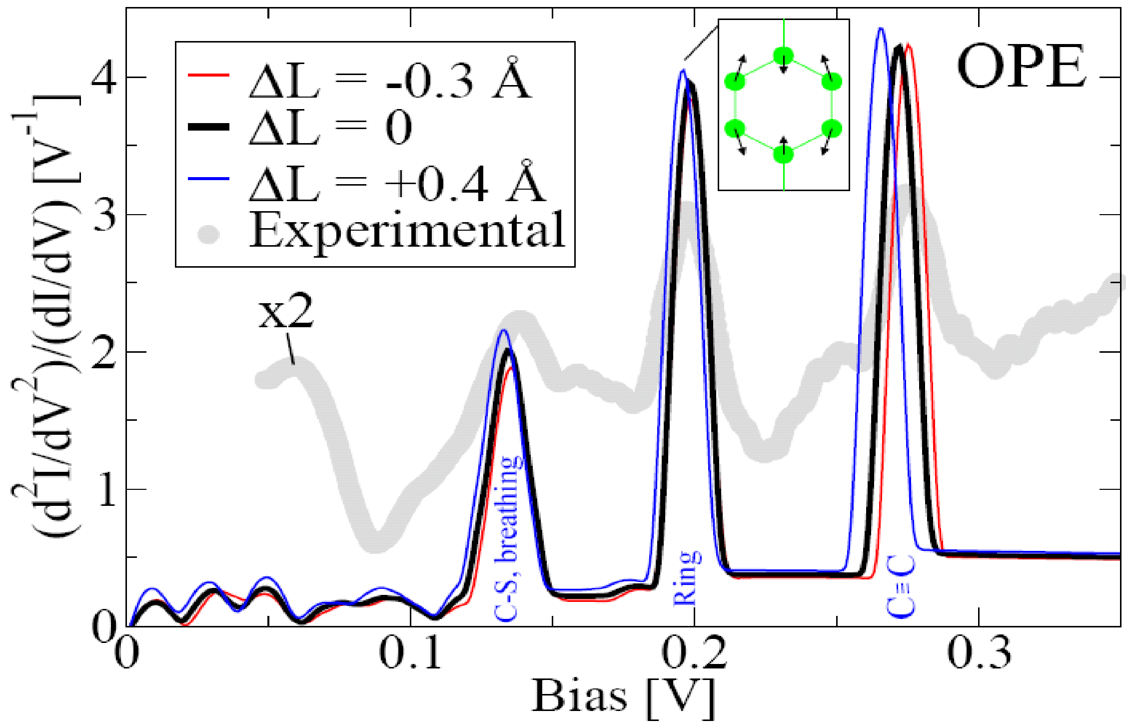
Paulsson, Frederiksen, Brandbyge, Nano Lett. **6**, 258, 2006

OPE: Similarities to OPV

- Effect of stretching
  - Small
- Similarities to OPV
  - C-S, ring breathing
  - C=C, Ring mode
  - C≡C
- Propensity rules:

The DFT states involved in transport has the right symmetry!





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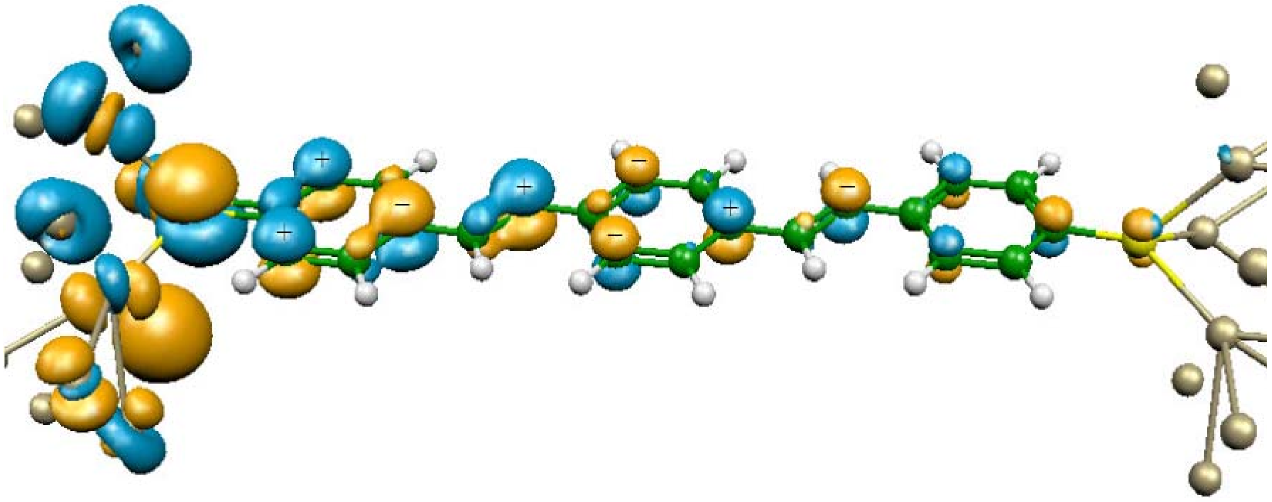
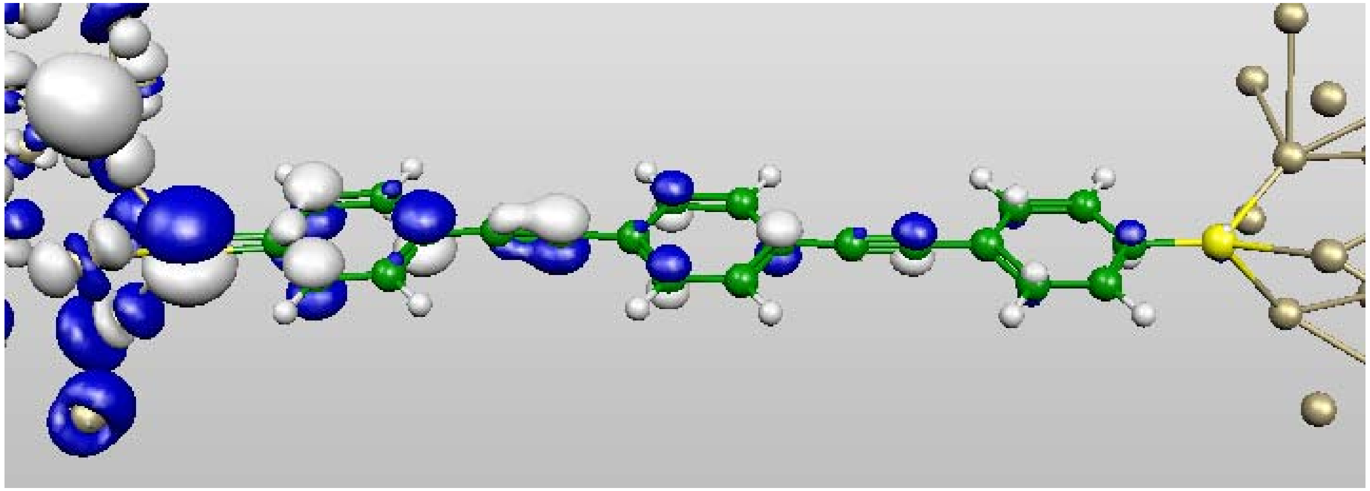
Scattering states

OPV

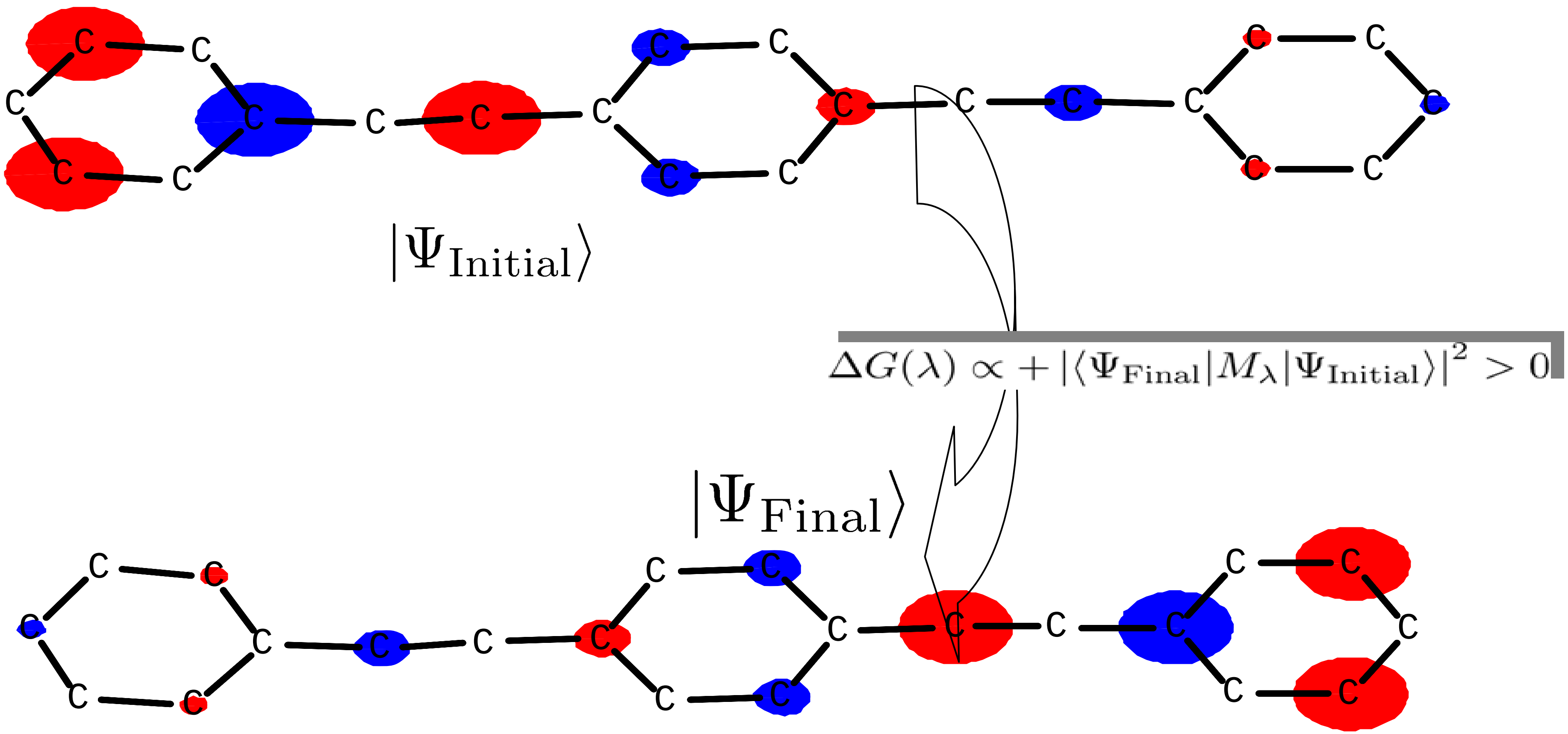


OPE



Similar to gold!

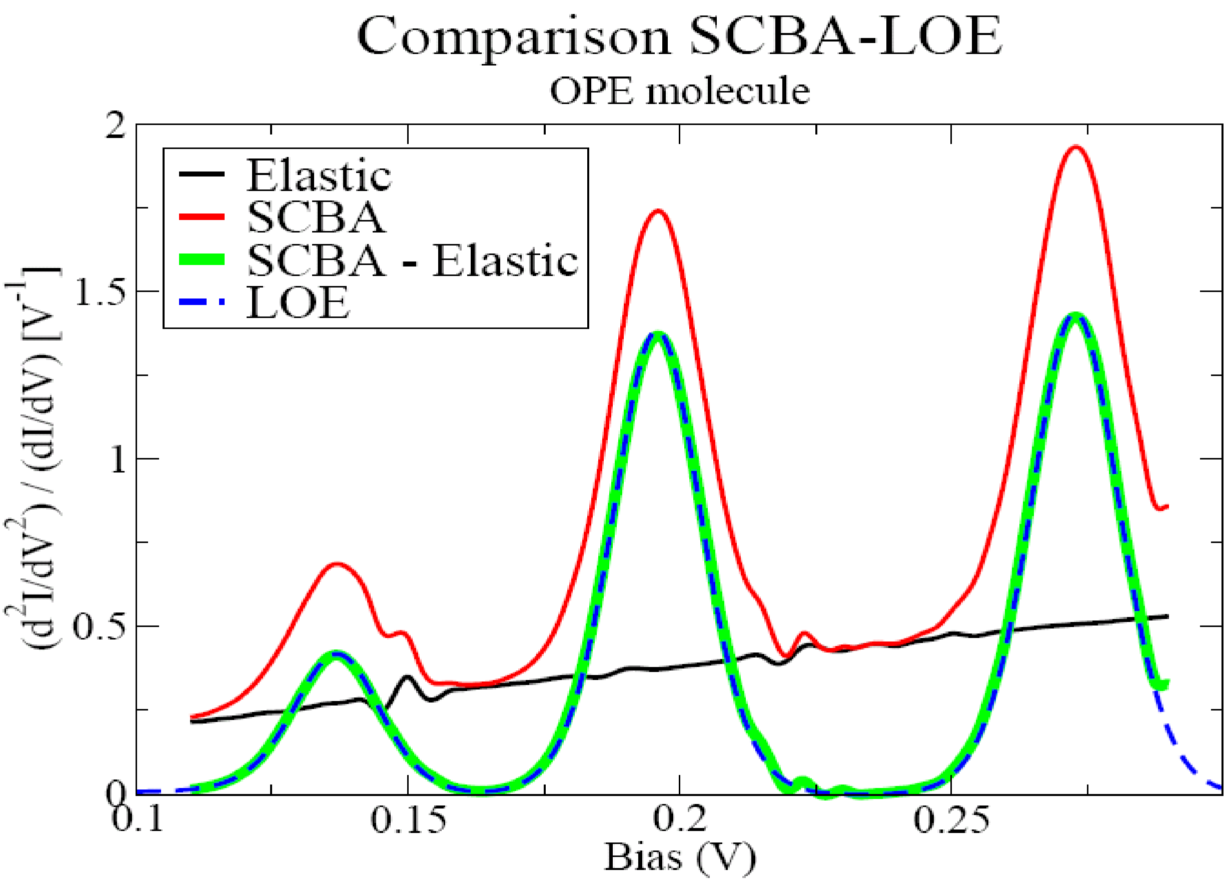
As in the Au wires: ”λ_F” ~ $4a$



Contributing modes λ have ABL character

SCBA – LOE comparison

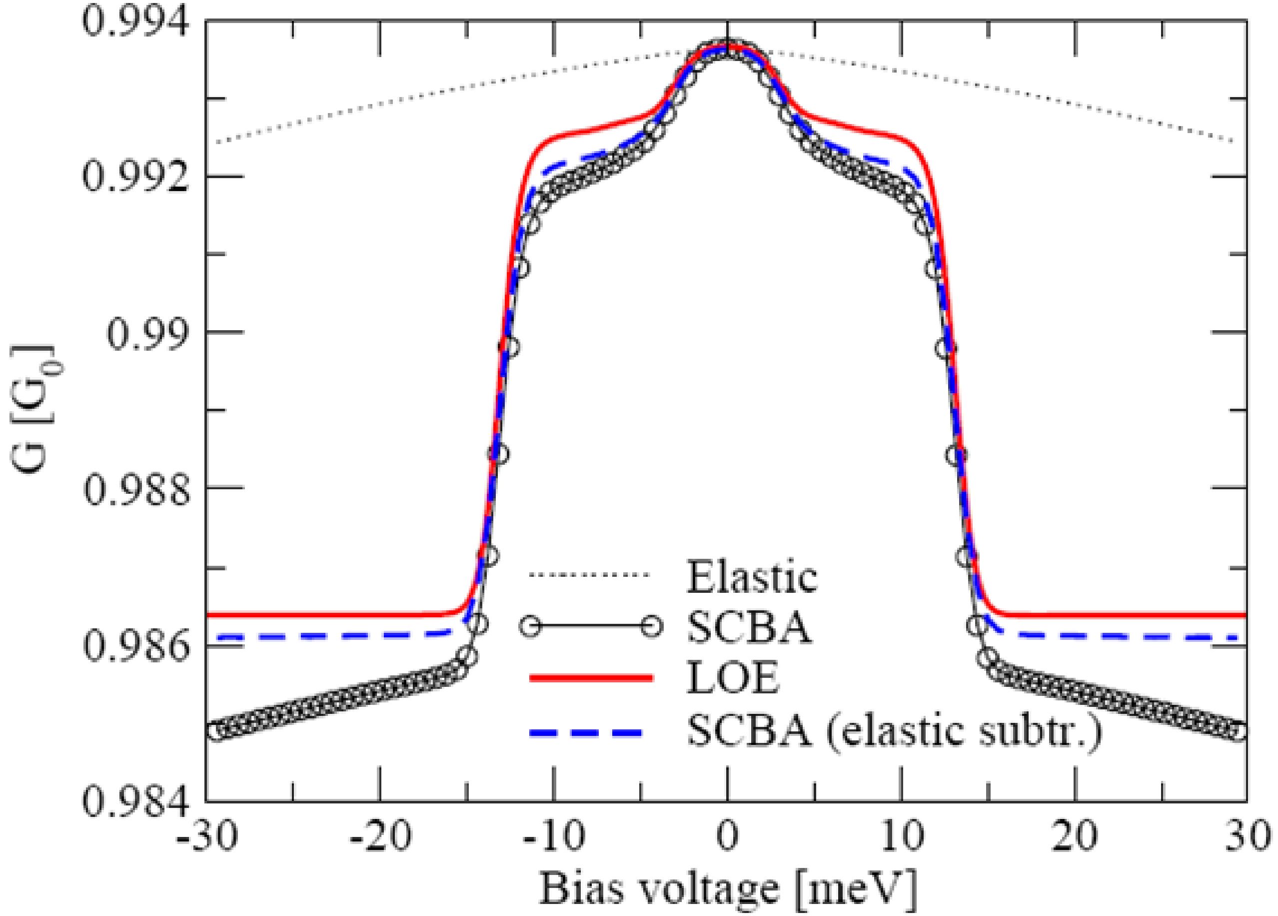
- Device and vibrations limited to molecule
- Only 5 phonon modes
- SZP basis
- SCBA
  - ~40 h on 8 P4 in parallel
- LOE
  - <5 min on 1 P4



Summary/Conclusion

- **DFT-NEGF description of inelastic phonon scattering in transport**
- **Lowest Order Expansion of the SCBA is cheap/fast**
- **Results compares well with experiments:**
  - ✓ Detailed comparison with gold wires
  - ✓ Main features of IETS match experimental data for C_{11}, OPV, OPE

SCBA vs. LOE



G [G_0]
0.994
0.992
0.99
0.988
0.986
0.984
-30
-20
-10
0
10
20
30
Bias voltage [meV]
Elastic
SCBA
LOE
SCBA (elastic subtr.)