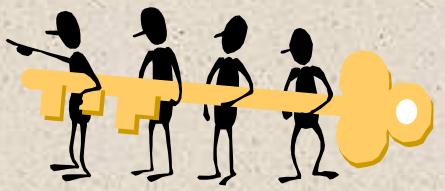
Electron Transport Through Atomic and Molecular Chains. Length Effects



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ORNL

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Molecular devices are basic functional units in nanotechnology

For applications in molecular electronics, for nanosensors …
key issues are networking, self-assembling …

Need to know and control each device in all detail.

Critical knowledge often absent:

-Relation of the device functionality to

-detail of molecule-lead junction

-detail of chemistry of the molecule

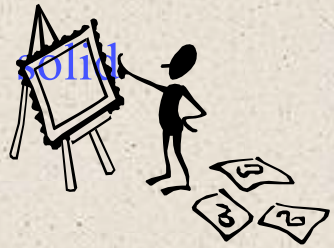
-Response of the device to the temperature, electric bias, chemical dynamics

-Control of various functions (transistor, diode, resistor)

•***"Move" is on theory:***

-Simulations that incorporate quantum mechanics

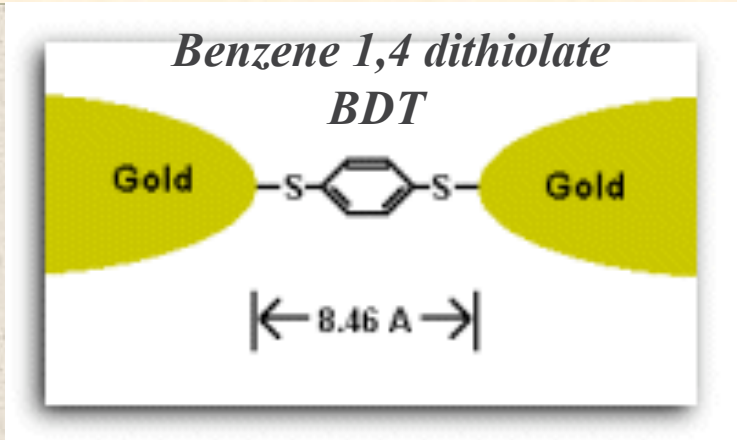
A big challenge for molecular physics, computational chemistry, solid state sciences, nanosciences



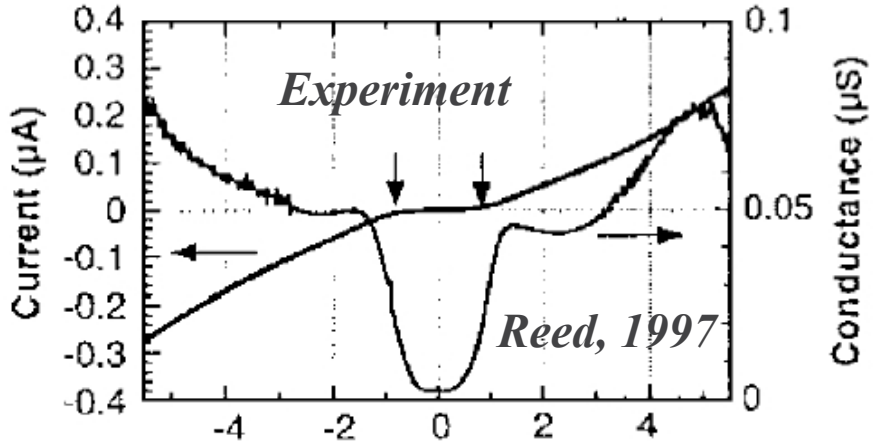
Also a large opportunity, not seen in history of sciences

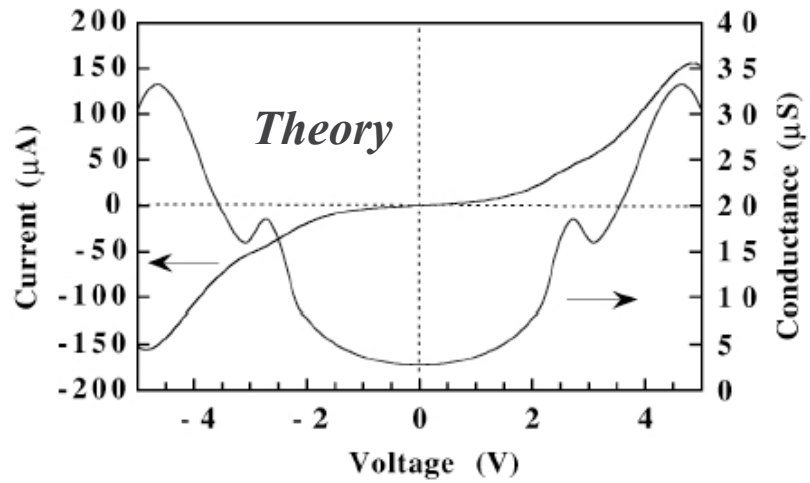
Famous example

Conductance through a molecule



Reed & Tour, Sc. Am. (June, 2000)





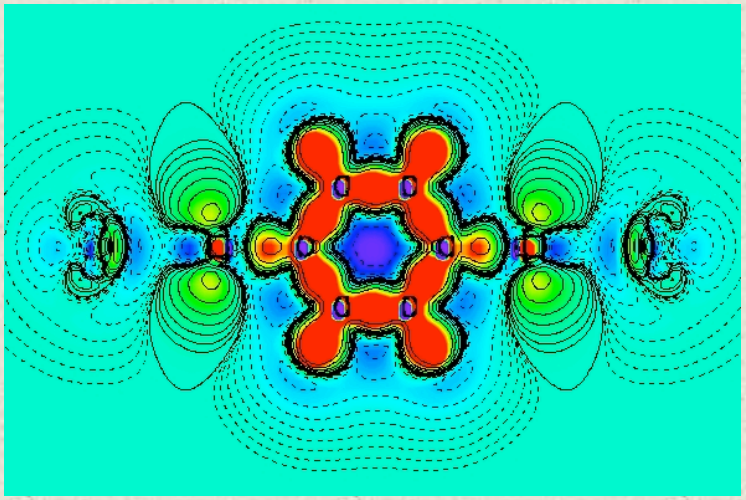
Di Ventra et al., PRL 84, 979 (2000)

Jellium model for leads

Questions:

- ***Why is theoretical result orders of magnitude larger than the experimental one?***
- STM tip-molecule interface?
- Surface-molecule interface?
- Correlations beyond DFT?
- Neighboring molecular strands?
- External electric bias?
- Temperature?

Structural properties



Courtesy of G. Painter

Have interface between organic and inorganic materials!!!

Charge densities:

- ***Recognition of conjugated configs.***
- ***pi-orbitals***
- ***Interaction fields***

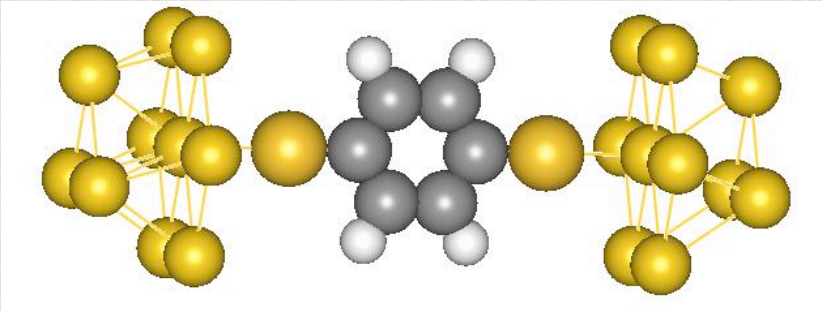
Understanding the role of

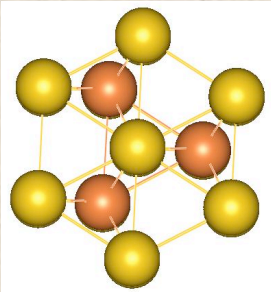
- Size of the basis states
- Choice of Exchange and Correlation Functionals
  (many-body effects beyond DFT)

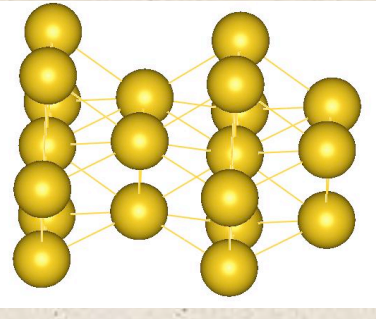
Proficiency:

- NWChem implementation on Eagle
  Significant help from
  D. Bernholdt (ORNL)
  T. Windus, E. Apra (PNNL)
  Trey White (ORNL)

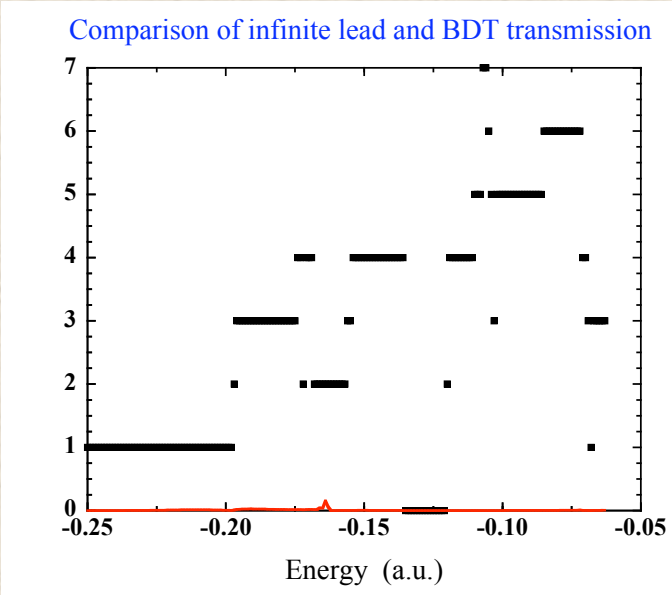
BDT with gold nanowires

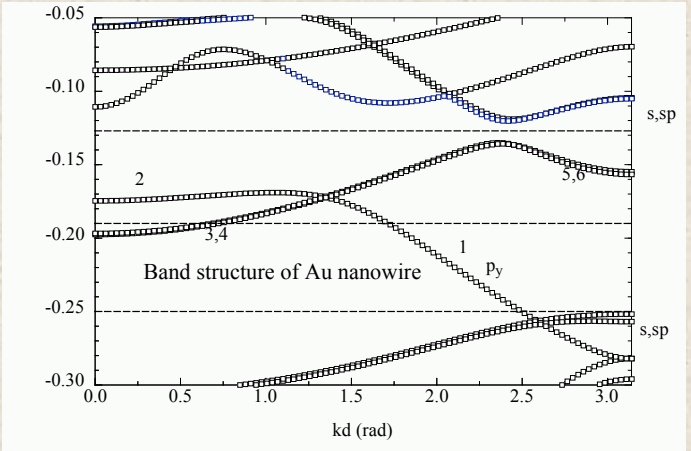






View from the top



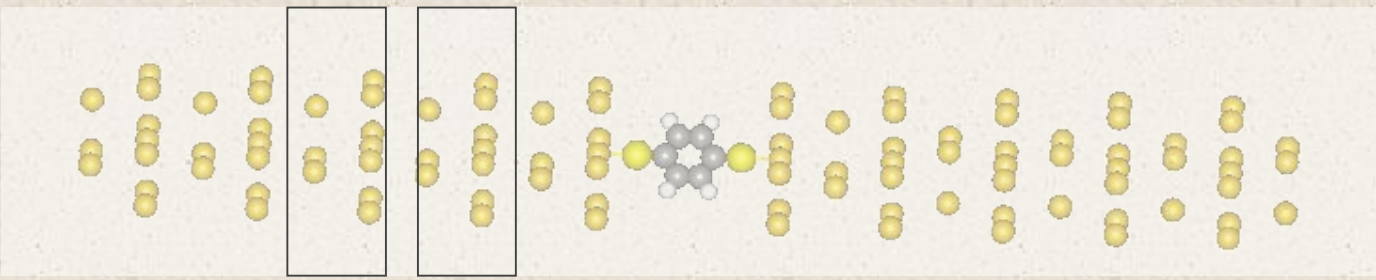


$$\sigma = \frac{e^2}{h} T$$

Landauer formula

Quant of conductance ~ 38 μS

Generalised Tight Binding Model

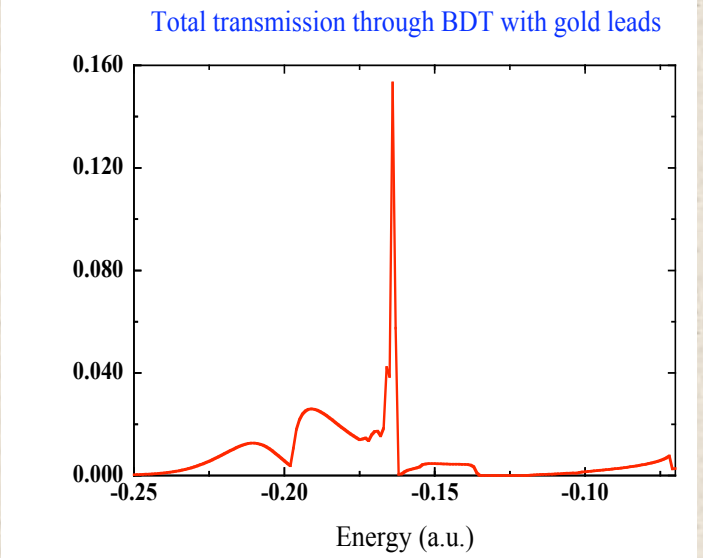


layer

Only adjacent layers coupled

$$T = \mathrm{Tr}(\Gamma_{left} G^{r}_{mol} \Gamma_{right} G^{a}_{mol})$$

G is Green's function of the molecule (in presence of the leads)



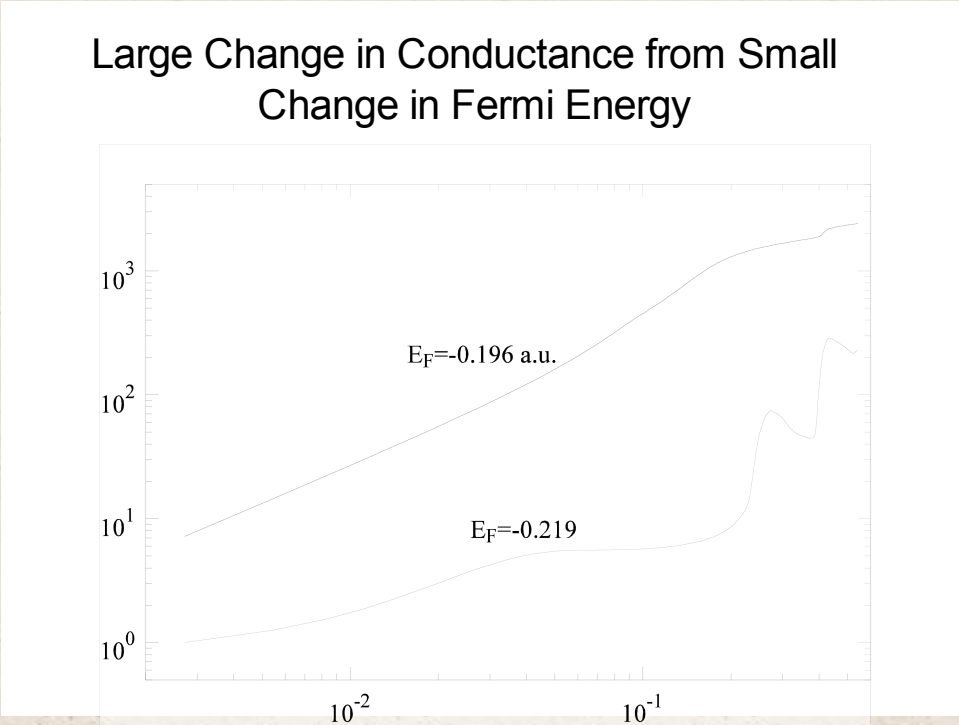
Γ_{left} and Γ_{right}

characterize self-energy of the molecule due to coupling with the leads

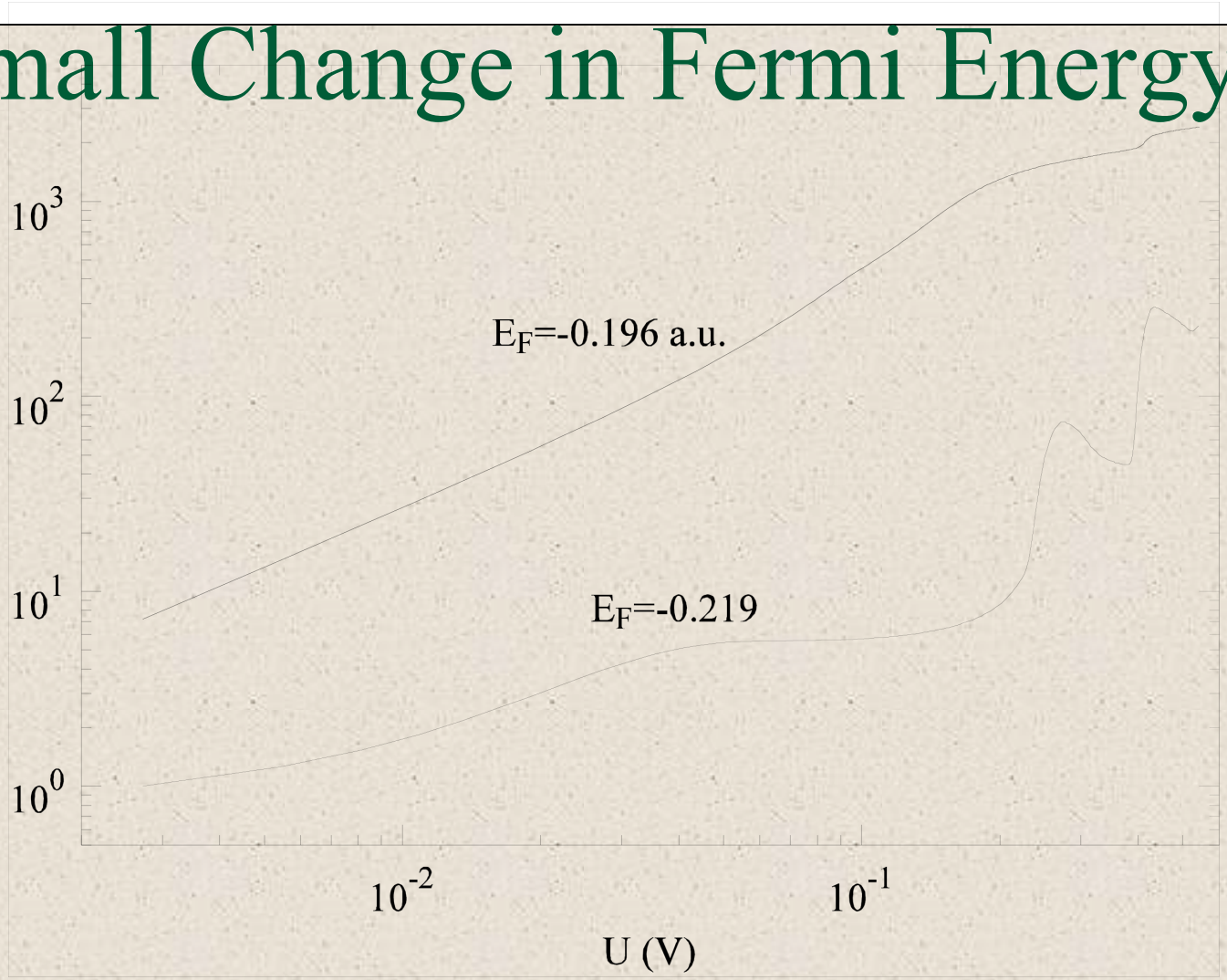
- Fermi energy of the semi-infinite leads is found from the band structure of the TB Hamiltonian
- It differs from the Fermi energy of the cluster calculations from which the TB Hamiltonian of the infinite system is derived
- The electrostatic potential of the lead-molecule-lead system needs to be adjusted so that the integrated density of states below the Fermi energy equals the total number of electrons in the system

- The integrated DOS at zero bias is calculated through a contour integration in the complex energy plane using the Green's function approach

- All of above can be achieved in a nonself-consistent manner in the TB formalism

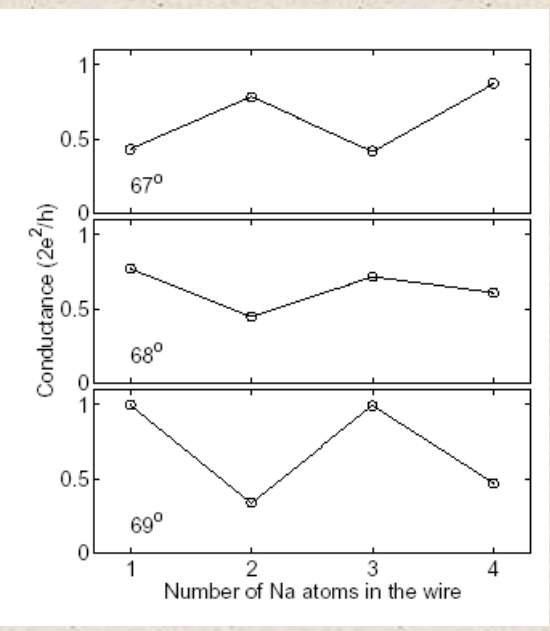


Large Change in Conductance from Small Change in Fermi Energy

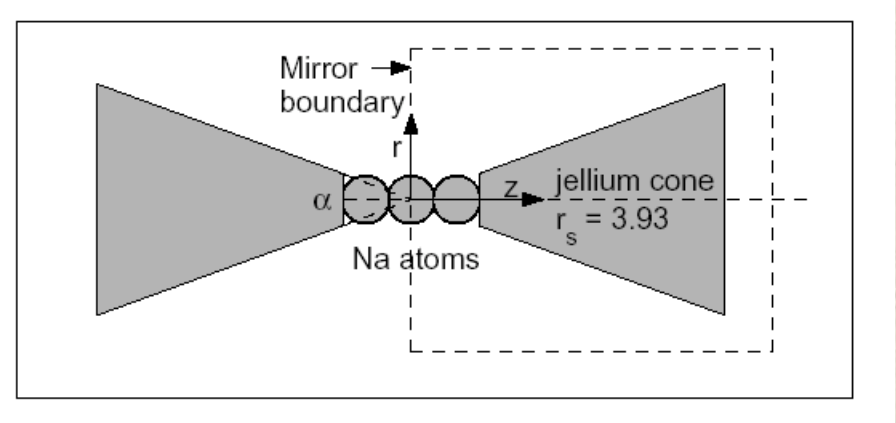


Conductance of organic molecules with metal leads a complex nonlinear phenomena

What happens if the "molecule" is replaced with an 1D chain of metal atoms?



P. Havu et al., Phys. Rev. B 66, 075401 (2002).



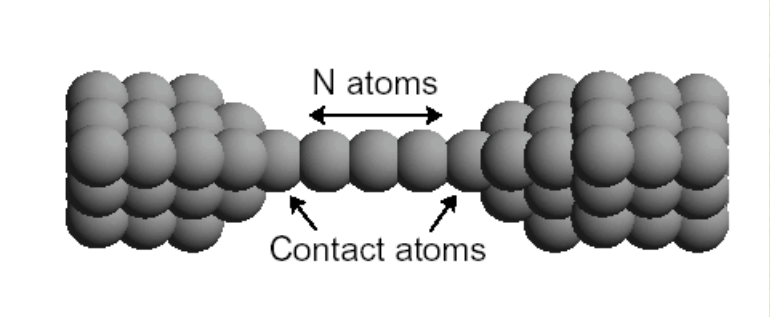
The even-odd oscillations for Na and Au (dependent also on the junction geometry)

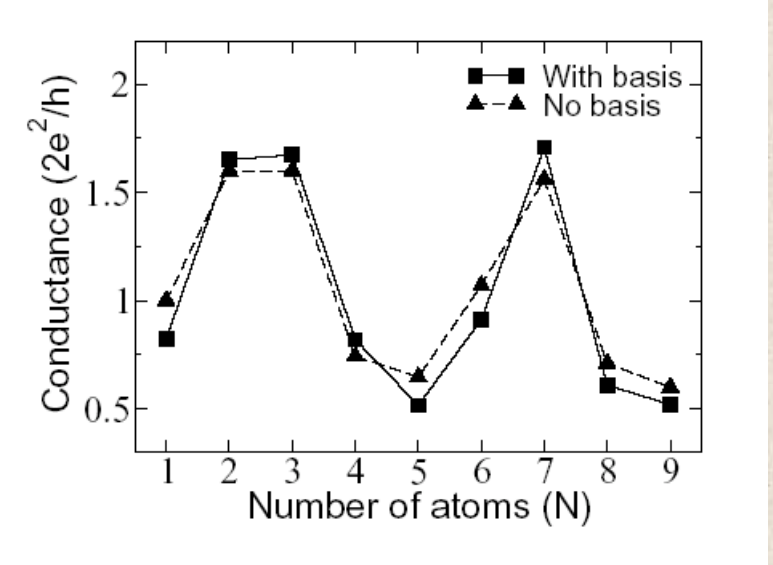
From different wavefunction parity is, and the neutrality requirement

Position of the Fermi energy to a resonance!

Change of FE change the period.

Aluminum chain with aluminum leads



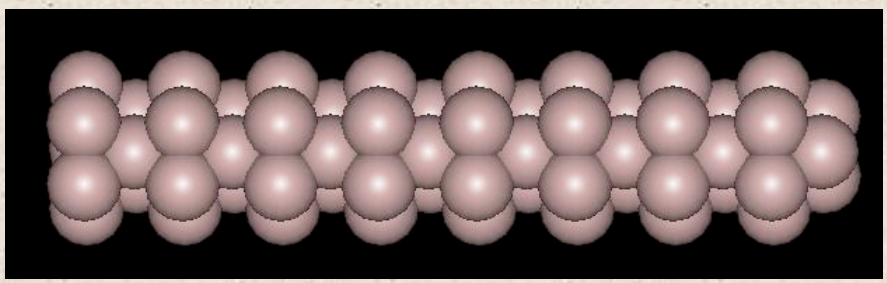


This super-cell repeated infinitely as a period!!!!?

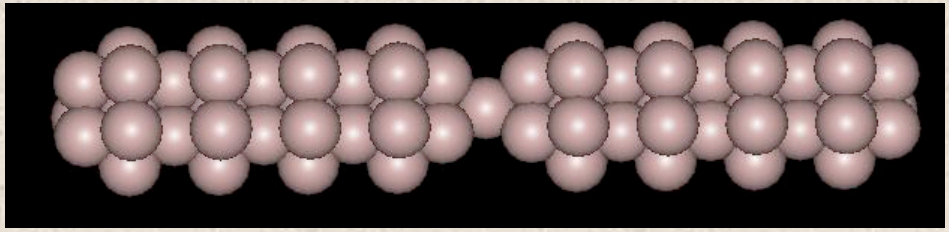
Thygesen et al., PRL 91, 146801 (2003)

4-atom period?

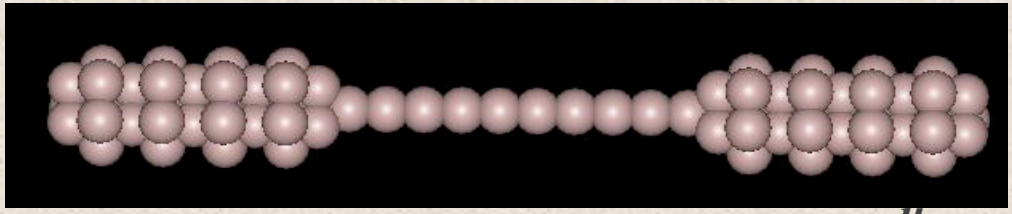
Our calculation for Al chain (1-21 atoms)



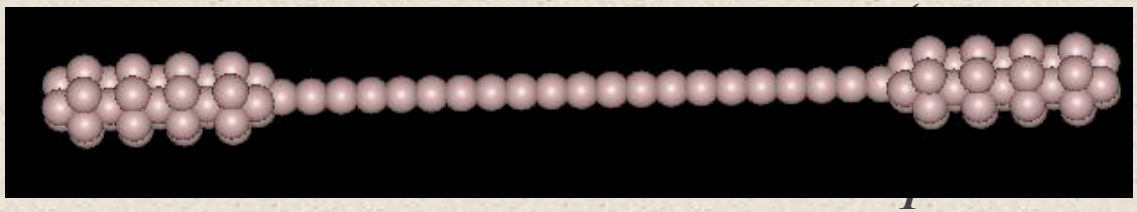
Nanowire-lead periodically extended 40 atoms (4 layers) cell



1-atom "chain"



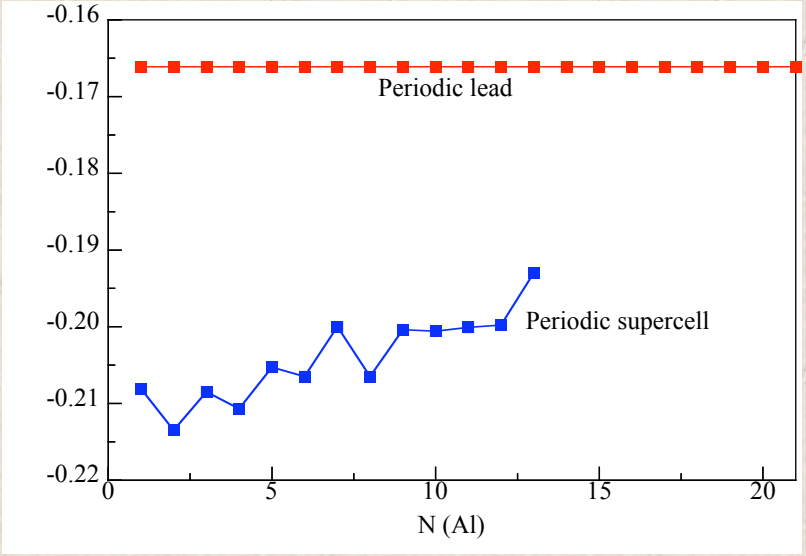
10-atoms chain molecule



21-atoms chain

We consider two cases:

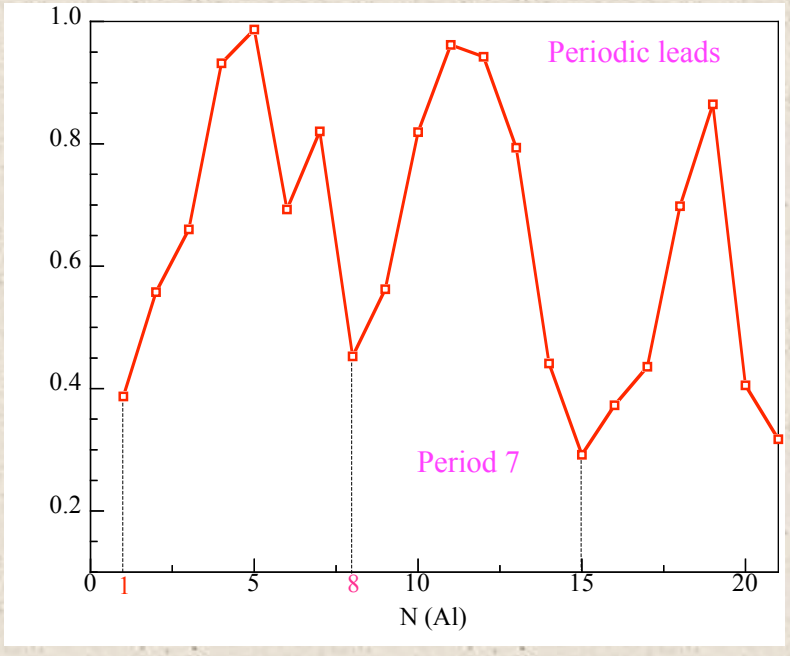
1) Periodic lead (determines Fermi energy)
2) periodic supercell (Fermi energy depends on the chain length

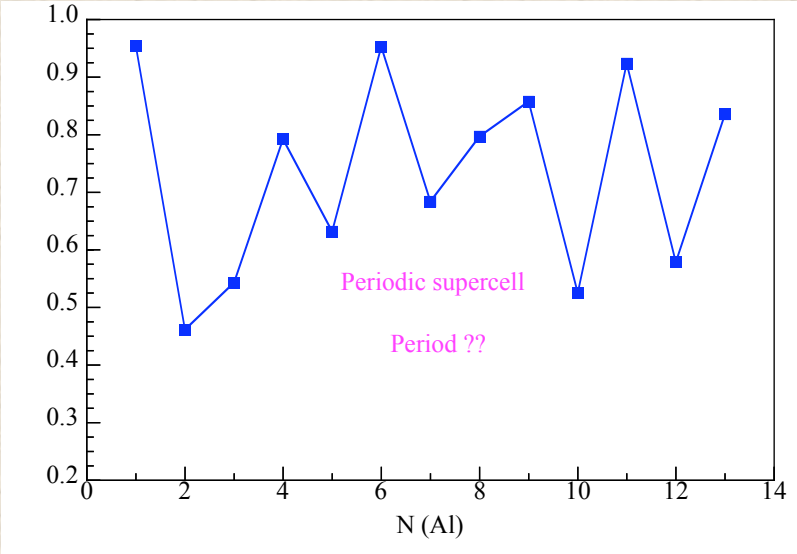


Large effect on Fermi energy

Courtesy of P. Cummings

What is the effect on conductance?





Right!

Wrong?

Conclusions:

•We suspect that the period of conductance oscillations depends on the placement of the Fermi energy.

•The correct Fermi energy is the Fermi energy of the leads!

•Repeating the electrode-molecule ensemble in a super-cell will likely place the Fermi energy incorrectly.

•Our observation is that lower FE tends to produce faster oscillations. Larger supercell would produce faster oscillations.