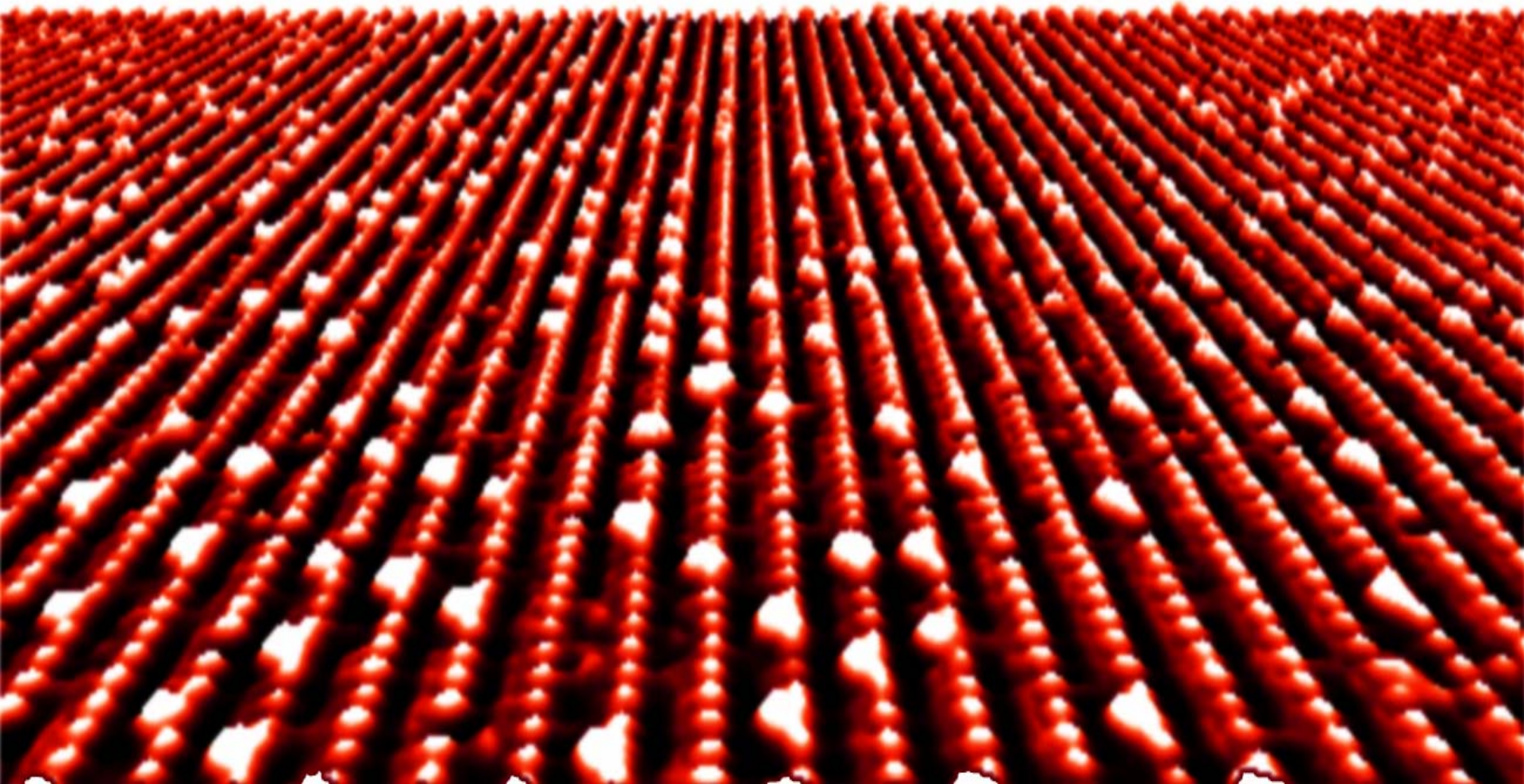
Electronic Properties of Atomic Wires: from Semiconductor Surfaces to Organic Chains and DNA

F. J. Himpsel



- **One-dimensional phenomena**
- **Ultimate limit of nanowires, electronics**
- **Single chain of overlapping orbitals (channel)**
- **Fabrication of atomic/molecular wires**

Combine spectroscopic methods

- Angle-resolved photoemission
- Two-photon photoemission
- Scanning tunneling spectroscopy

(Filled vs. empty states, real space vs. momentum space)

Physics in one dimension

- **Elegant and simple**
- **Lowest dimension containing translational motion**
- **Electrons cannot avoid each other**
- **No such thing as an individual electron or hole**
- **Spinons and holons instead**

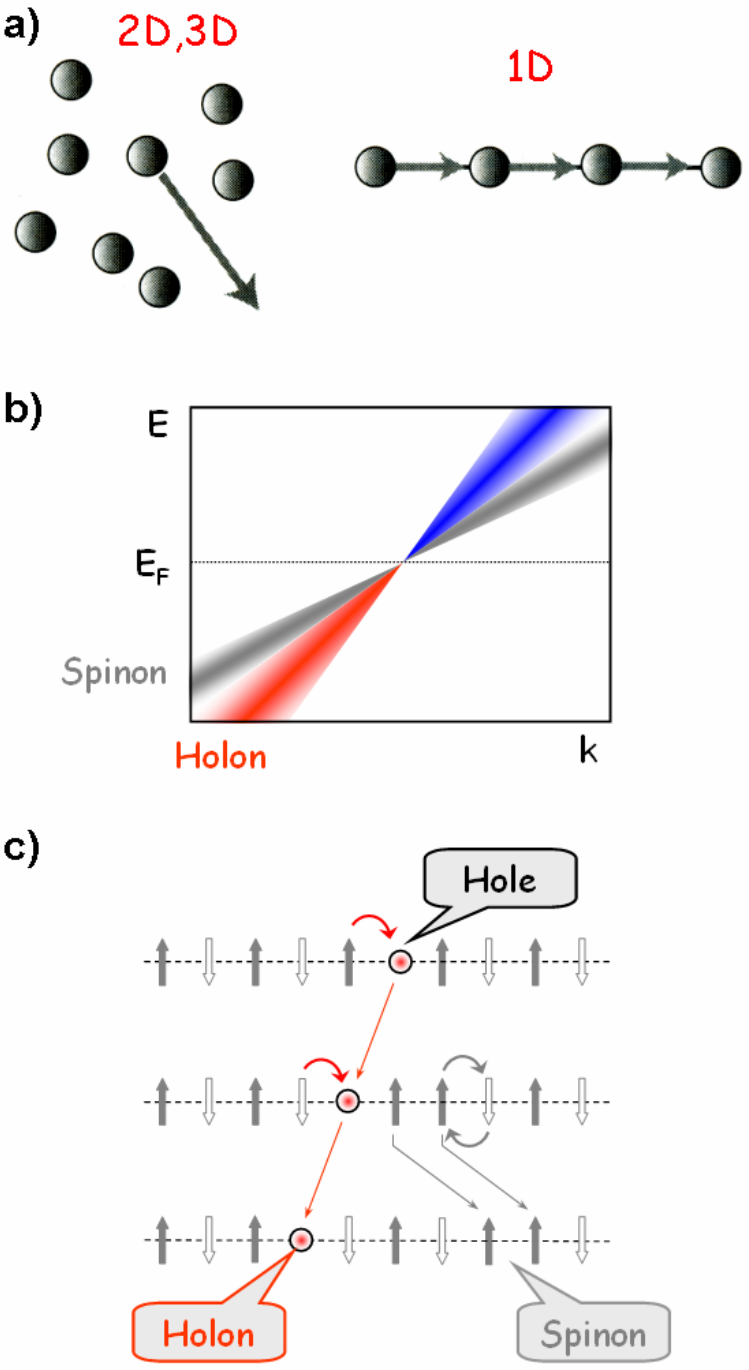
Electrons cannot avoid each other in 1D

Delocalized electrons:

⇒ **Momentum space**
Tomonaga-Luttinger model

Localized electrons:

⇒ **Real space**
Hubbard model



Collective excitations in 1D

Strictly-speaking, one should consider only collective excitations in 1D, not single-electron energy bands. (I used to ask theorists how many electrons/atoms are involved but they tended to hedge.)

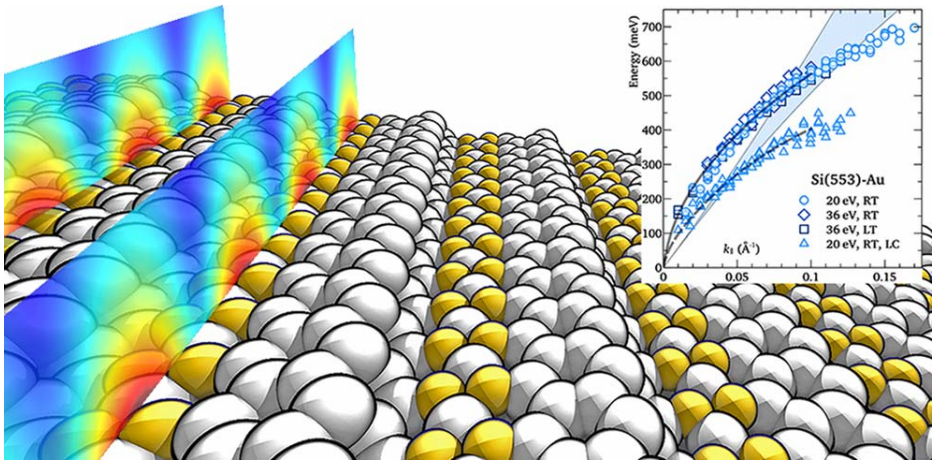
Spinons and holons are groups of electrons and holes which act like a spin without charge or a charge without spin.

Can this concept be tested? What identifies spinons vs. holons? Photons interact mainly with charge. Neutrons probe the bulk.

To get started, study known collective excitations ⇒ plasmons!

Lichtenstein,…,**Pfnür**, PRB **97**, 165421 (2018).

Sanna,…,**Pfnür**, JPCC **122**, 25580 (2018).



Limits of electronics from information theory

Conductance/Channel: $G = 2e^2/h \cdot T \qquad T \leq 1$

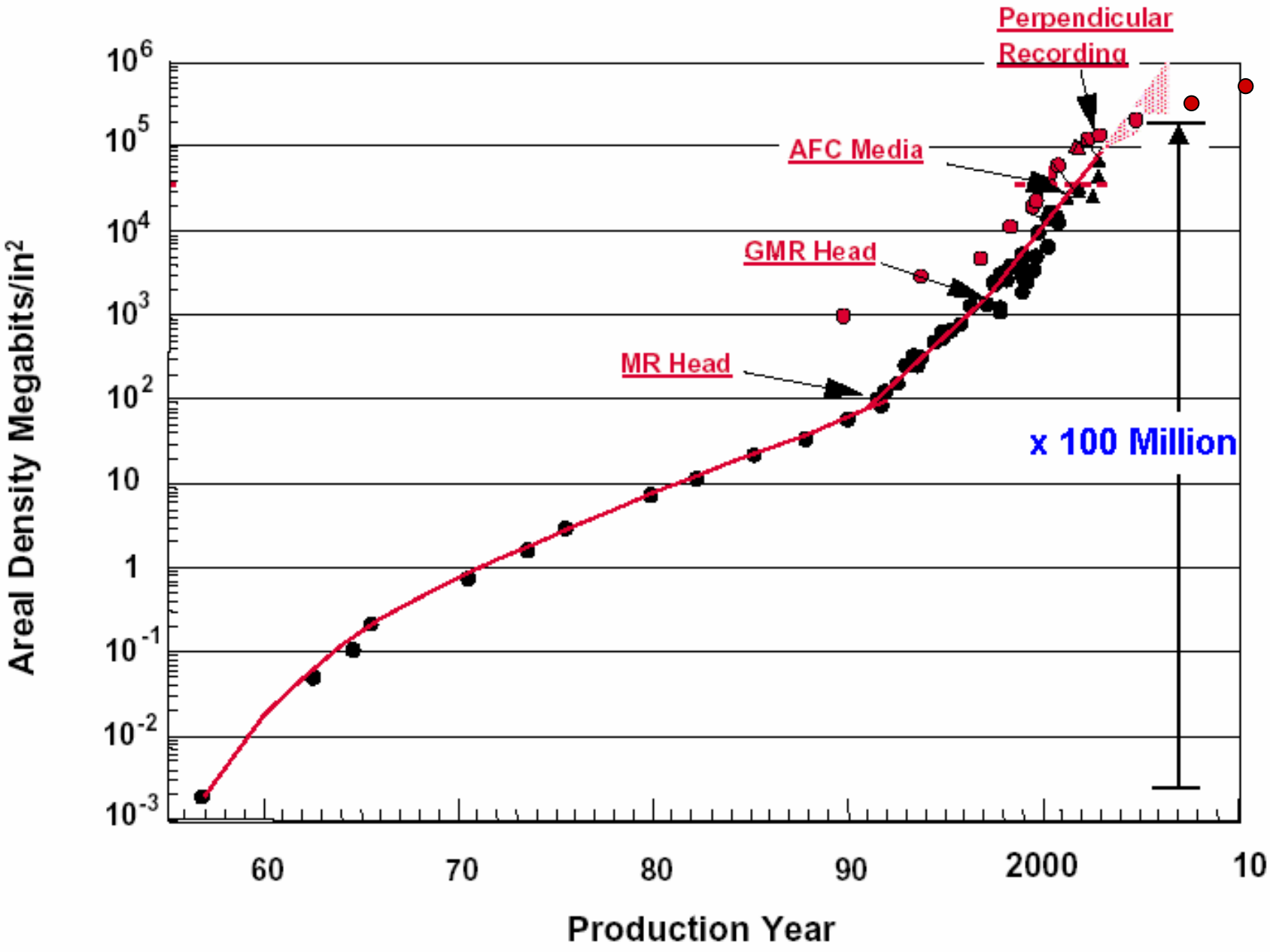
Energy to switch a bit: $E = k_B T \cdot \ln 2$

Time to switch one bit: $t = h / E$

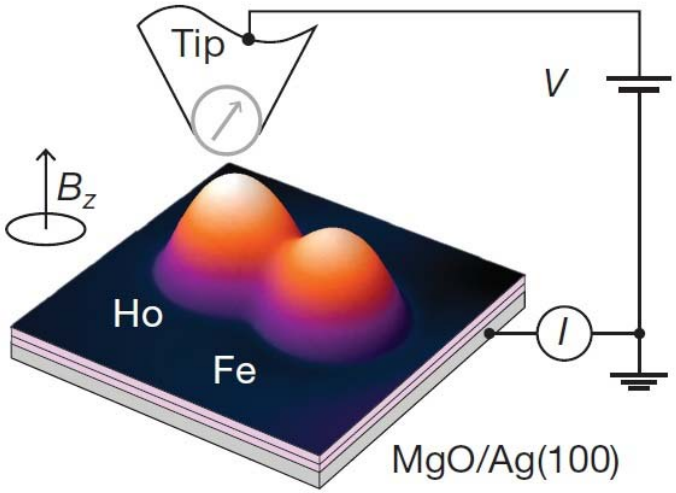
Energy to transport a bit: $E = k_B T \cdot \nu/c \cdot d$

Data storage

Magnetic is densest, but still needs 10^6 Spins/Bit



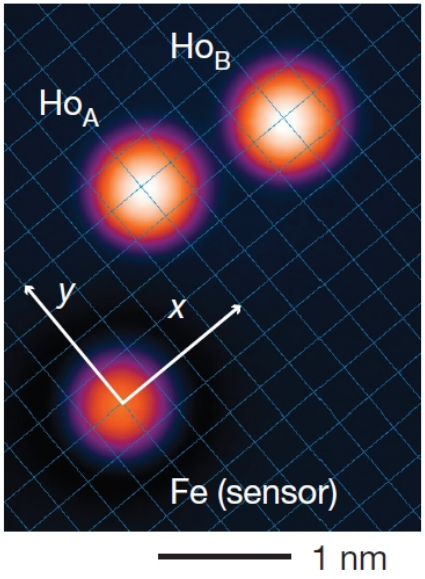
Reading and writing single-atom magnetic bits

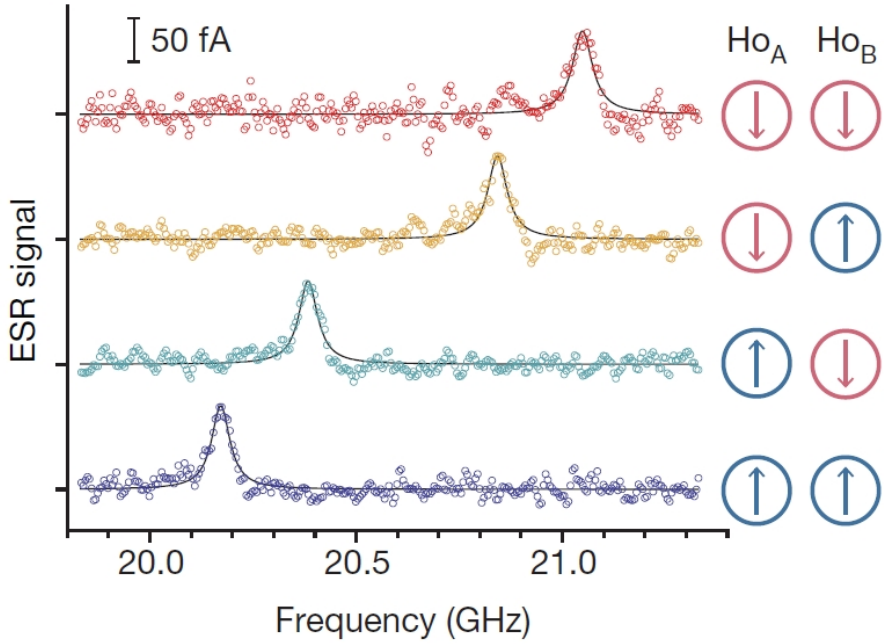


Reading via tunneling magnetoresistance

Writing via current pulse at the Ho atom

Magnetic state of the Ho from ESR at the Fe





Natterer et al.,
Nature **543**, 226 (2017).

Futuristic transistor, made of graphene ribbons

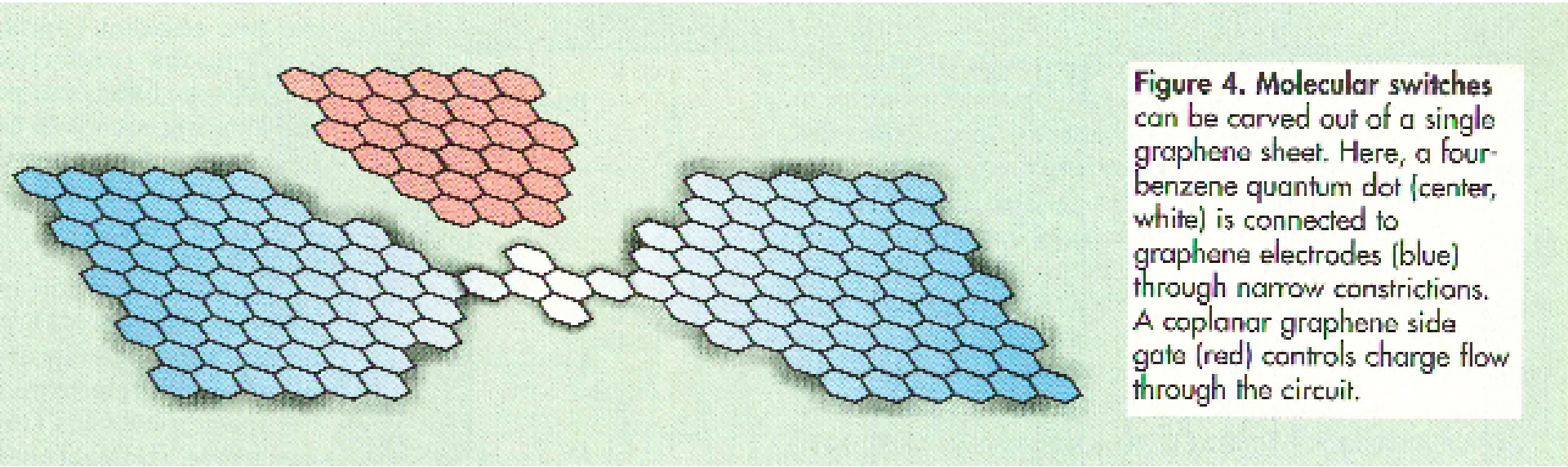


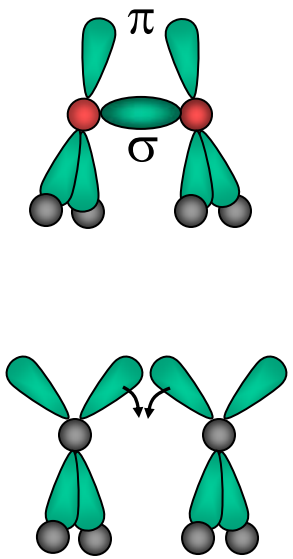
Figure 4. Molecular switches can be carved out of a single graphene sheet. Here, a four-benzene quantum dot (center, white) is connected to graphene electrodes (blue) through narrow constrictions. A coplanar graphene side gate (red) controls charge flow through the circuit.

Geim and MacDonald, Physics Today, August 2007

Silicon ribbons instead ?

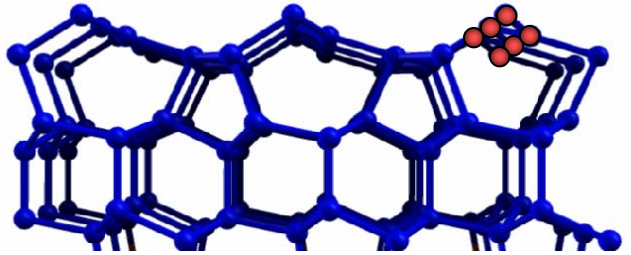
Self-assembled atom chains on silicon

Si=Si dimers



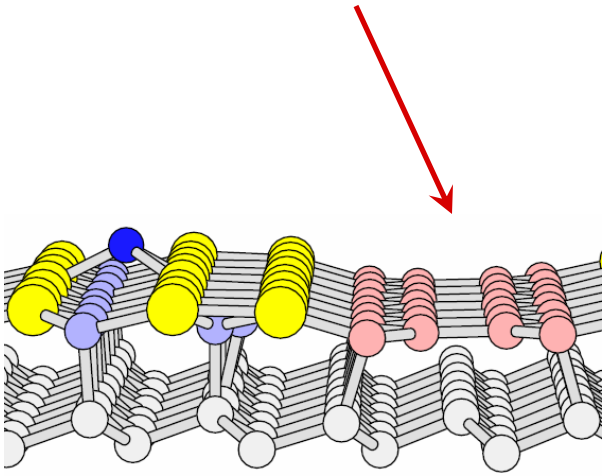
Si(100)2x1

π-bonded Si chain



Si(111)2x1
(cleaved)

graphitic Si ribbon



Si(111)5x2-Au

Conventional wisdom says that π-bonds form only in carbon.

Silicon surfaces break this rule to avoid broken bonds.

Si(111)5x2-Au, found in 1969

BRIT. J. APPL. PHYS. (J. PHYS. D), 1969, SER. 2, VOL. 2. PRINTED IN GREAT BRITAIN

Segregation of gold to the silicon (111) surface observed by Auger emission spectroscopy and by LEED

H. E. BISHOP and J. C. RIVIÈRE

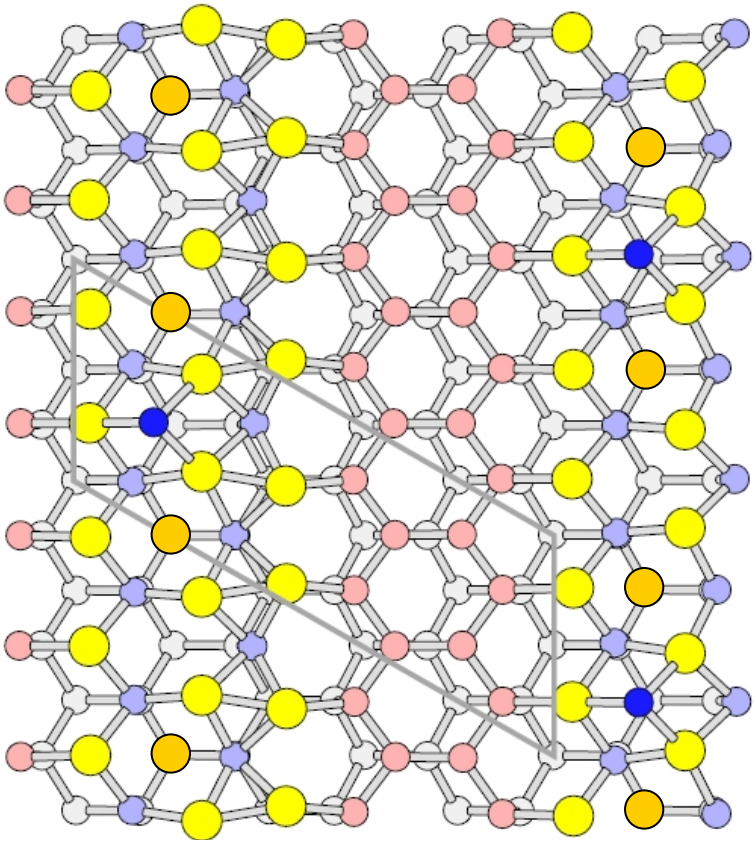
Solid State Division, U.K.A.E.A. Research Group, Atomic Energy Research Establishment, Harwell

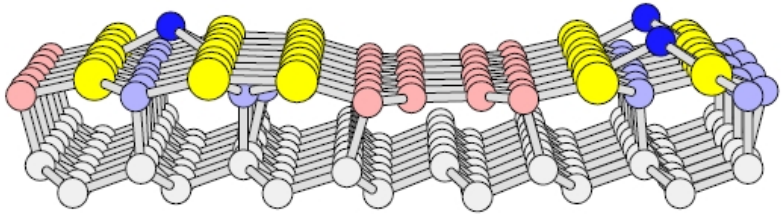
MS. received 21*st July* 1969

Abstract. A silicon crystal implanted with gold was heated to successively higher temperatures, reaching a maximum of 1250 °C, and its surface examined by Auger emission spectroscopy (AES) and LEED at each stage. No recrystallization was observed until the crystal had been heated to 740 °C, at which point the AES analysis could be interpreted in terms of the appearance of gold atoms at the surface. At 810 °C the Auger peaks from gold were considerably larger than those from silicon, but decreased progressively thereafter as the temperature was raised until, at over 1000 °C, the differential distribution was indistinguishable from that of clean silicon. The first LEED pattern observed, at 740 °C, was not the Si(111)-7 pattern, but another familiar one, the Si(111)-($\sqrt{3} \times \sqrt{3}$)-R30 ° pattern. With increasing temperature, the $\frac{1}{3}$rd-order pattern spread over the whole surface and, above 900 °C, was joined by another, a $\frac{1}{5}$th-order pattern, probably based on a domain structure. At the highest

a 1/5th-order pattern

Si(111)5x2-Au, refined structure





The basic structure is 5x1:

3 Au atom chains
Graphitic Si ribbon

plus Si adatoms (dopants)

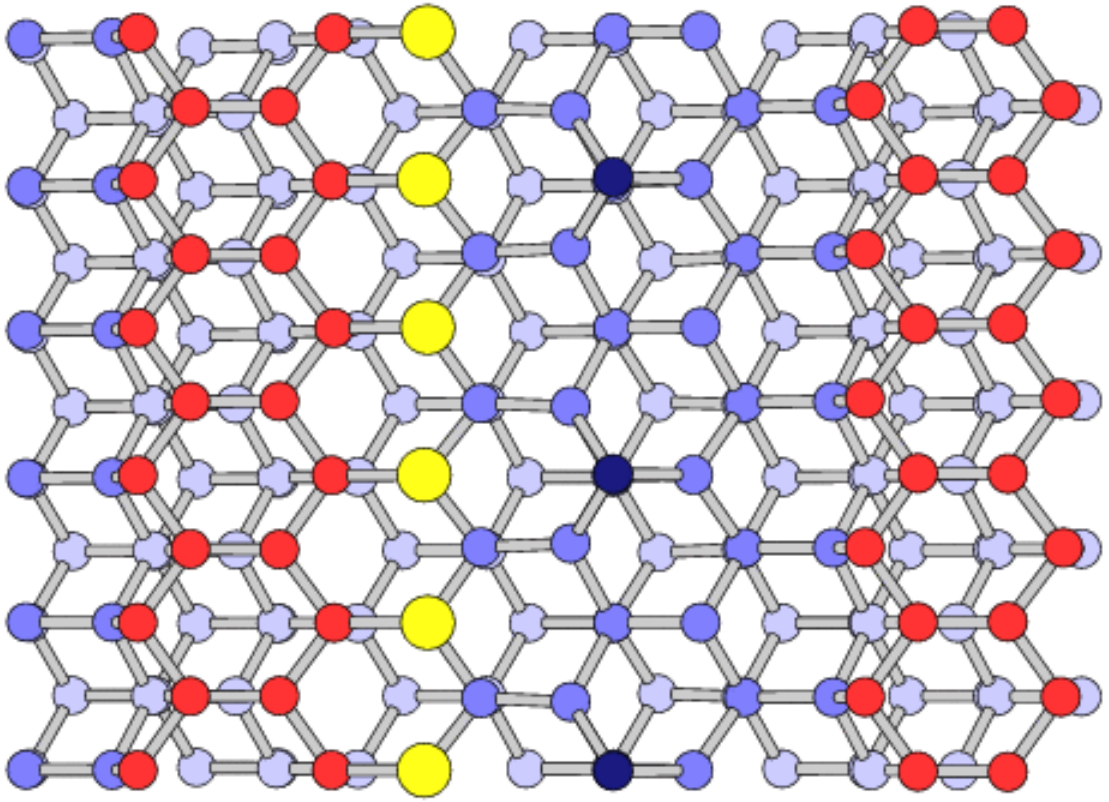
plus extra Au atoms

Erwin et al., PRB **80**, 155409 (2009).

Kwon, Kang, PRL **113**, 086101 (2014).

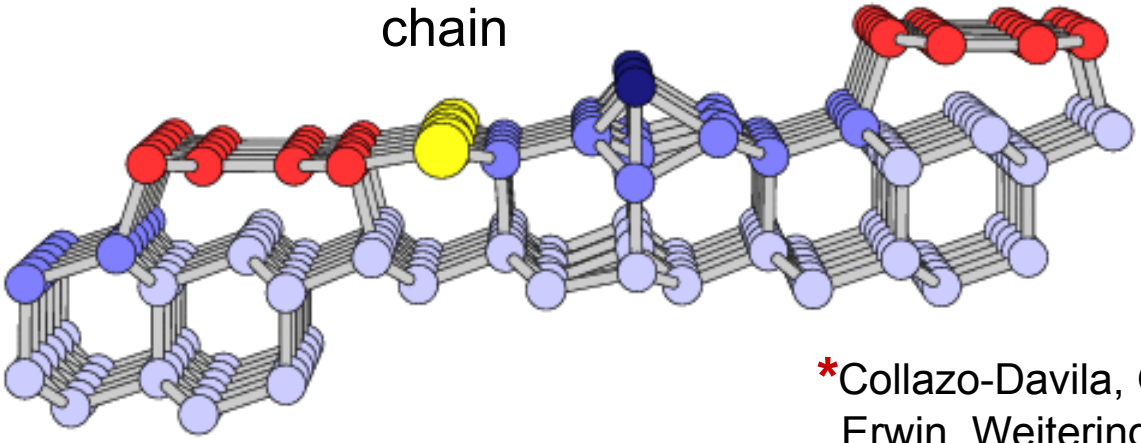
A simpler structure:

Si(557)-Au



Au
chain

Graphitic ribbon*

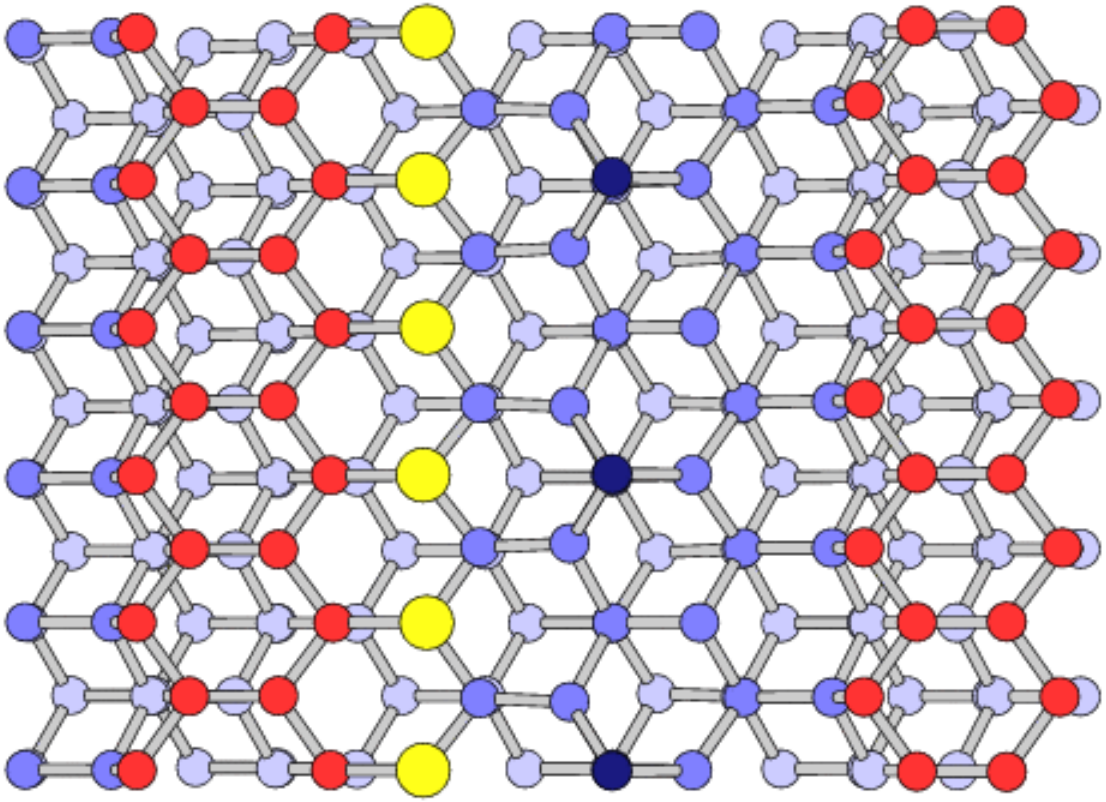


Discovered by RHEED:
Jalochowski et al.,
Surf. Sci. **375**, 203 (1997)

Calculated structure:
Sanchez-Portal et al.,
PRB **65**, 081401 (2002)
Crain, Erwin, et al.,
PRB **69**, 125401 (2004)

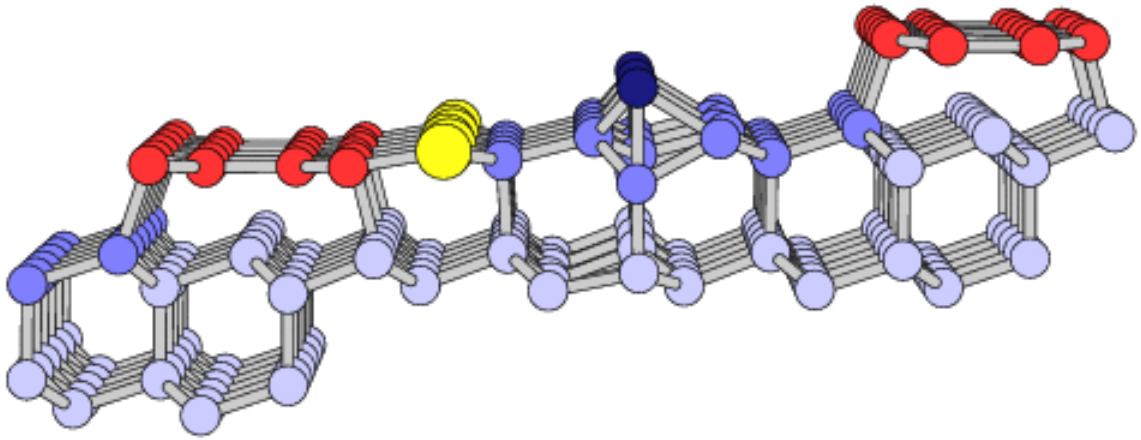
X-Ray diffraction:
Robinson et al.,
PRL **88**, 096104 (2002)

*Collazo-Davila, Grozea, Marks, PRL **80**, 1678 (1998).
Erwin, Weitering, PRL **81**, 2296 (1998).

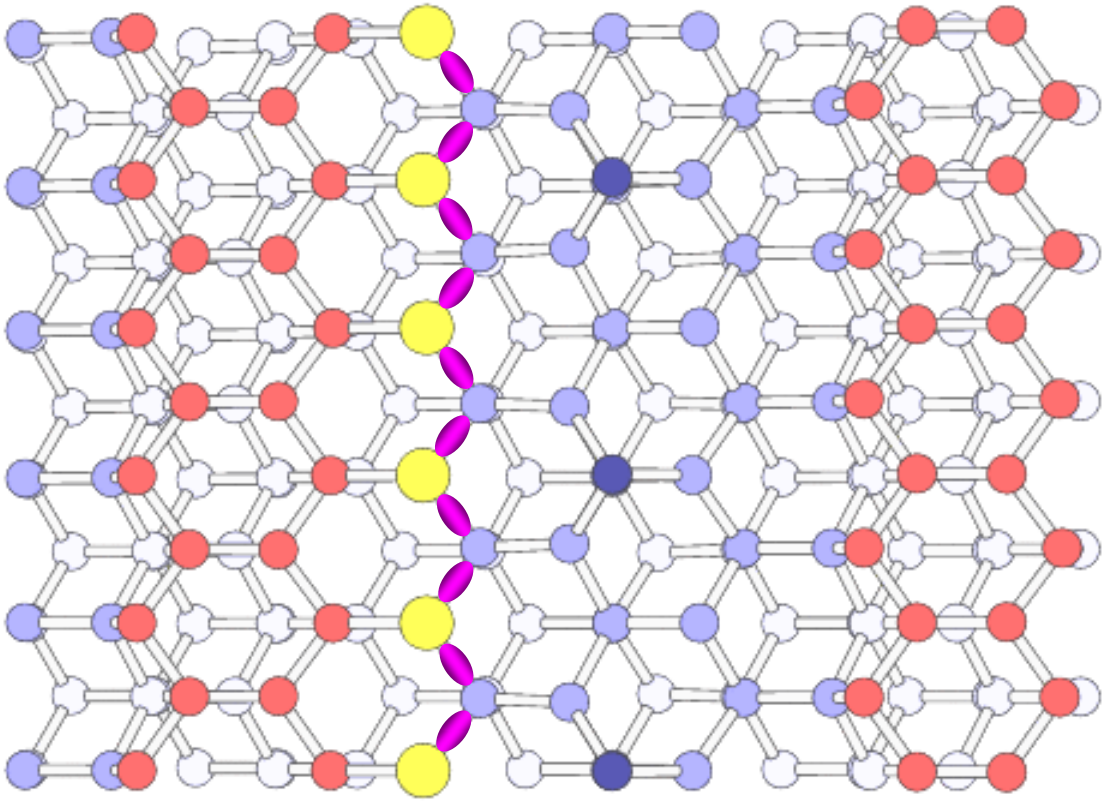


What drives the surface 1D ?

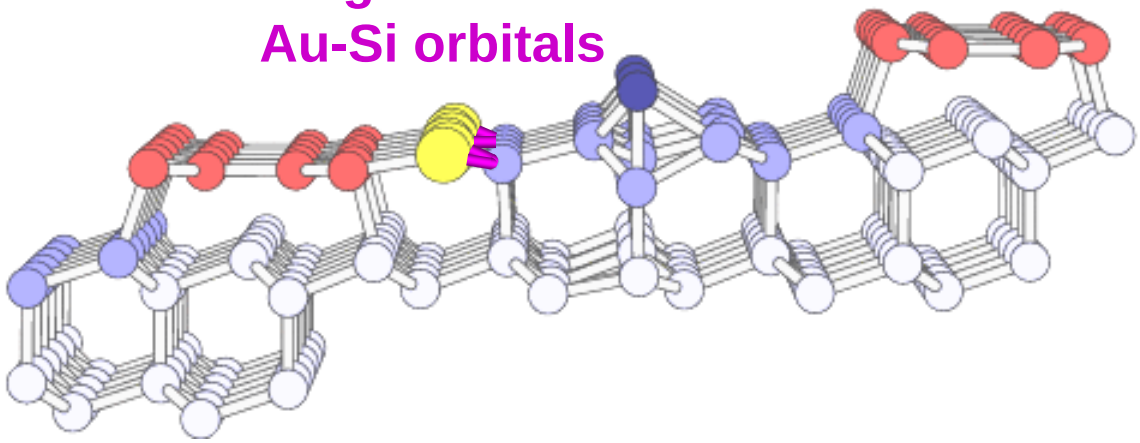
Perfect lattice match along the ribbon



Complete mismatch perpendicular to it



Single chain of
Au-Si orbitals



The ultimate nanowire

Metal atoms that produce 1D chains on vicinal Si(111):

I: Li, Na,…
II: Ca, Ba,…
III: In
IV: Pb
NM: Ag, Au
TM: Pt
RE: Gd, Dy,…

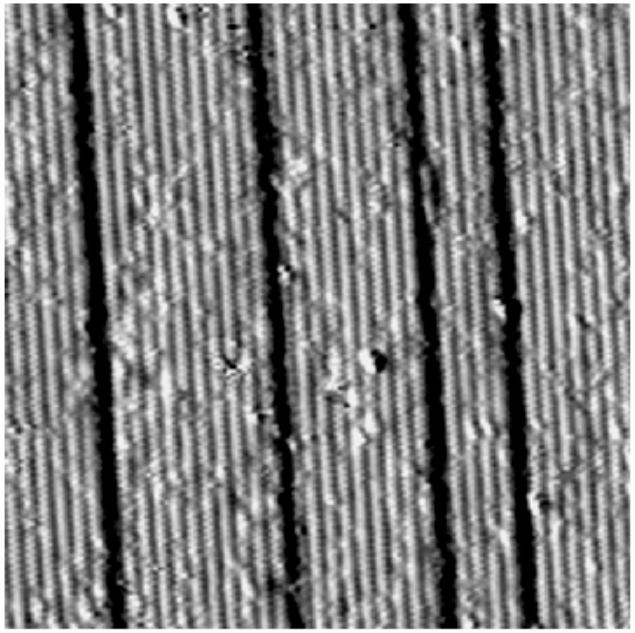
on Si(100):

III: Bi
TM: Ir

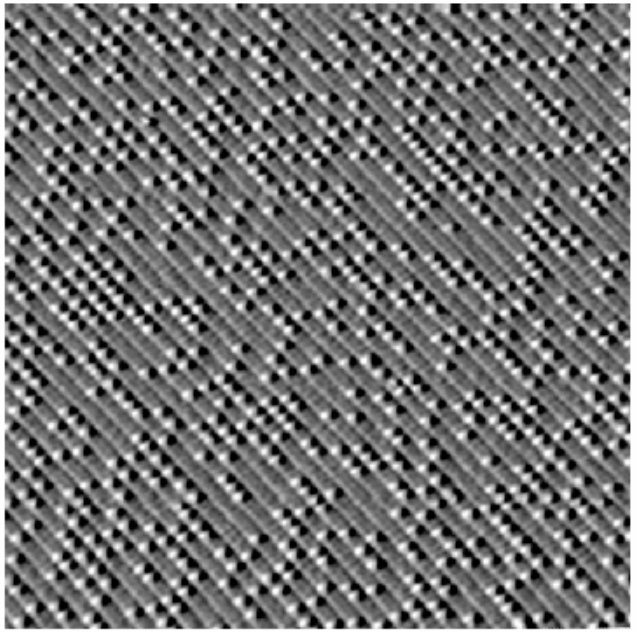
on Ge(100):

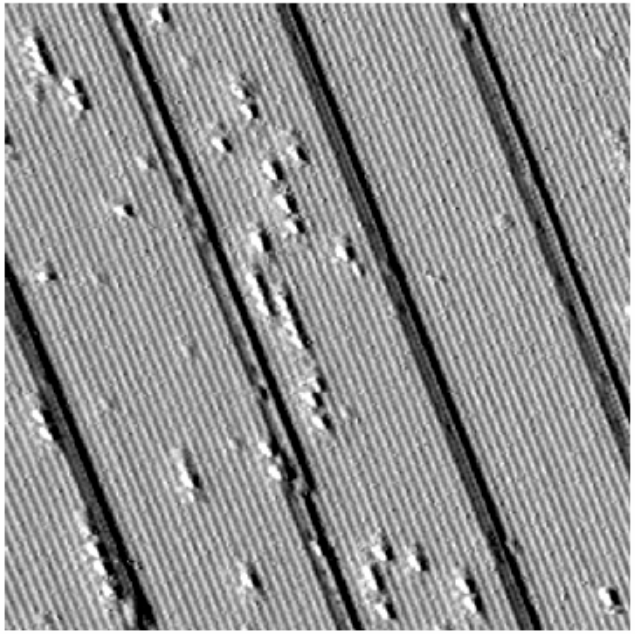
NM: Au
TM: Pt

Si(111) 5×2 - Gd



Si(111) 5×2 - Au





Si(111) 3×1 - Ag

Si(557) - Au

Mapping electrons at surfaces

Angle-resolved photoemission

measures all quantum numbers: E, k_x, k_y

Fermi surface: $I(k_y, k_x)$

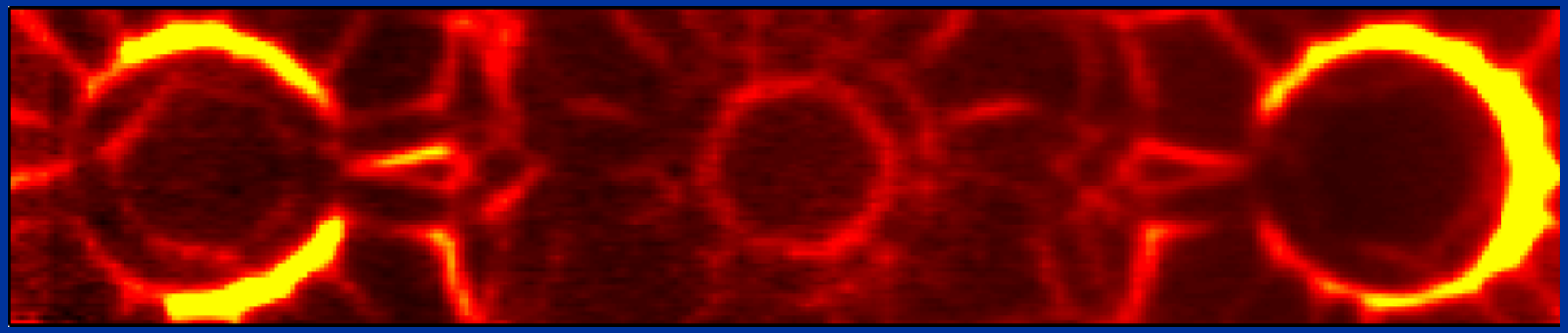
Band dispersion: $I(E, k_x)$

Phil Anderson: Photoemission data will provide the “smoking gun” for solving HiTc superconductivity.

Fermi surfaces between 2D and 1D

2D

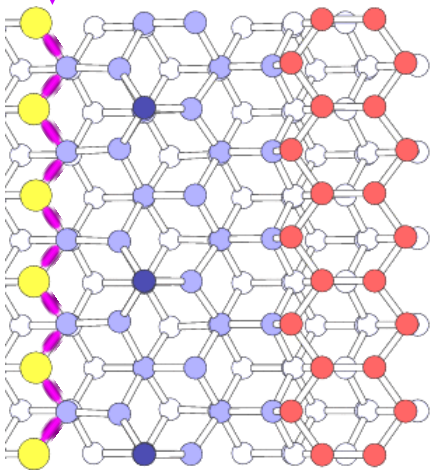
2D + super-lattice



Toward 1D

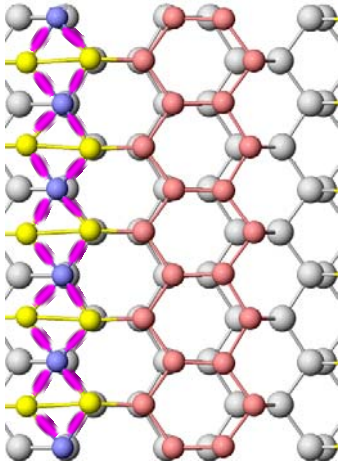
Band dispersions of atom chains

Single Chain



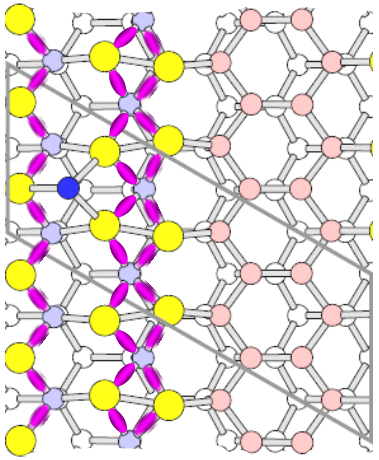
Si(557) -Au

Double Chain

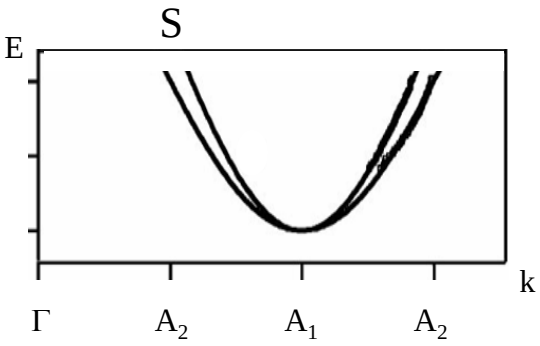


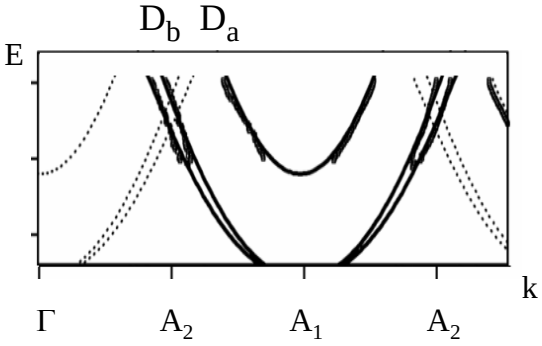
Si(553) –Au

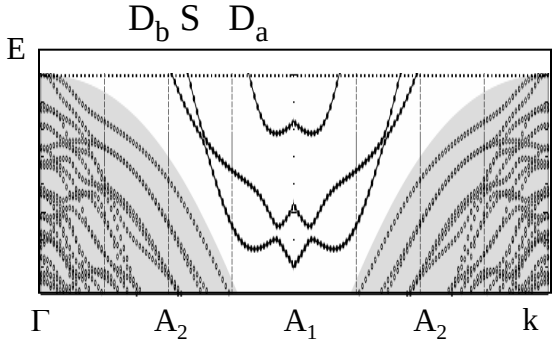
Three Chains



Si(111) -Au

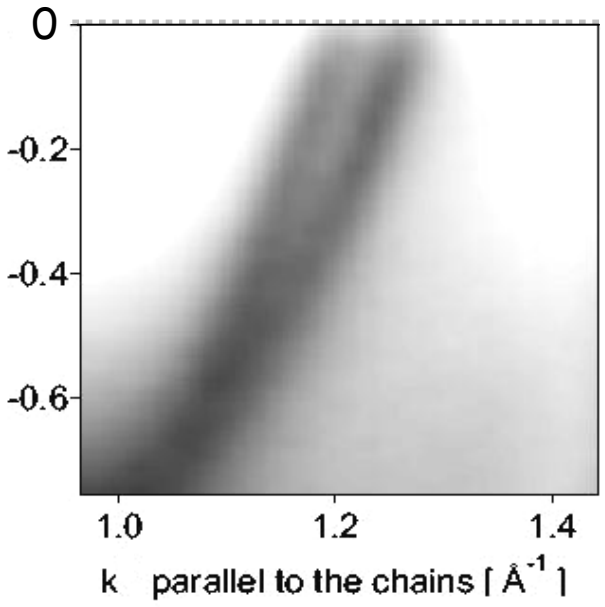




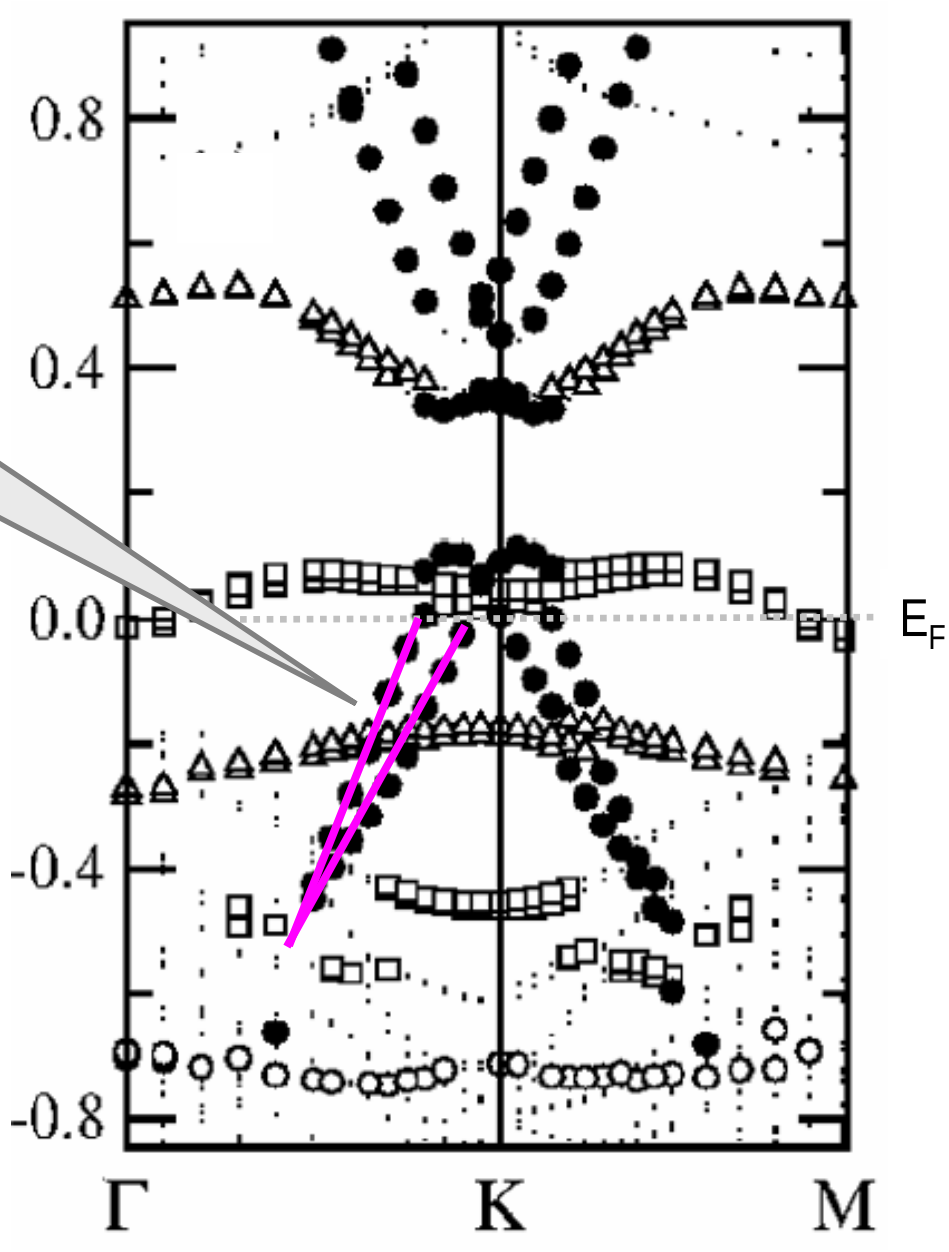


S = Single Chain, D_b = Double chain (bonding), D_a = Double chain (antibonding), S. Erwin (unpublished)

What about the splitting?
Prediction: It is magnetic!

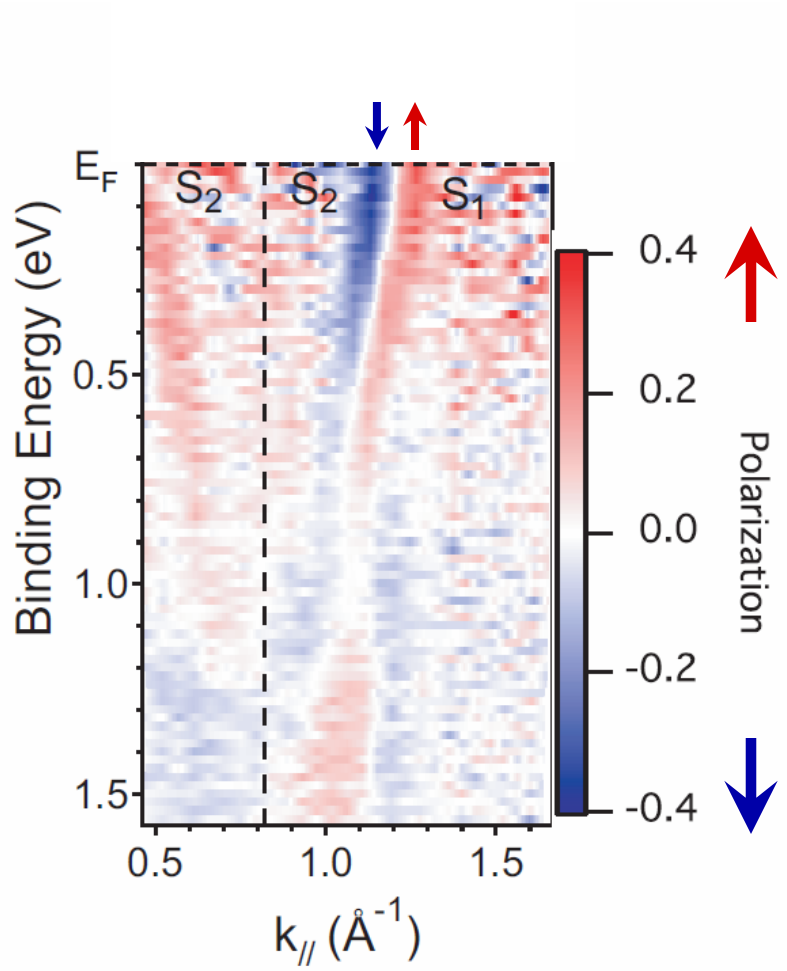


Crain et al., PRB **69**, 125401 (2004).



Sanchez-Portal et al., PRL **93**, 146803 (2004).

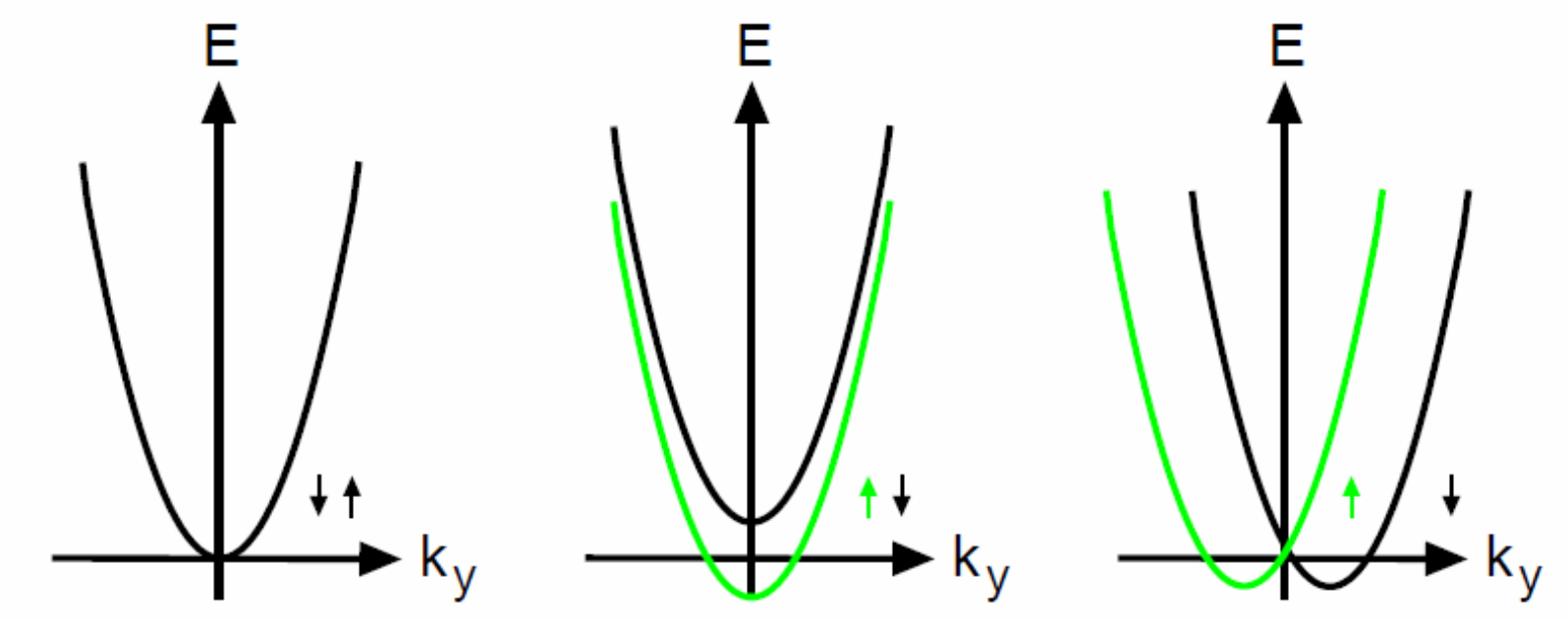
Evidence for a magnetic splitting



Spin-polarized, angle-resolved photoemission

Okuda et al. PRB **82**, 161410(R) (2010).

Various spin splittings



Non-magnetic

Exchange Splitting

ΔE

vertical shift

Rashba Splitting

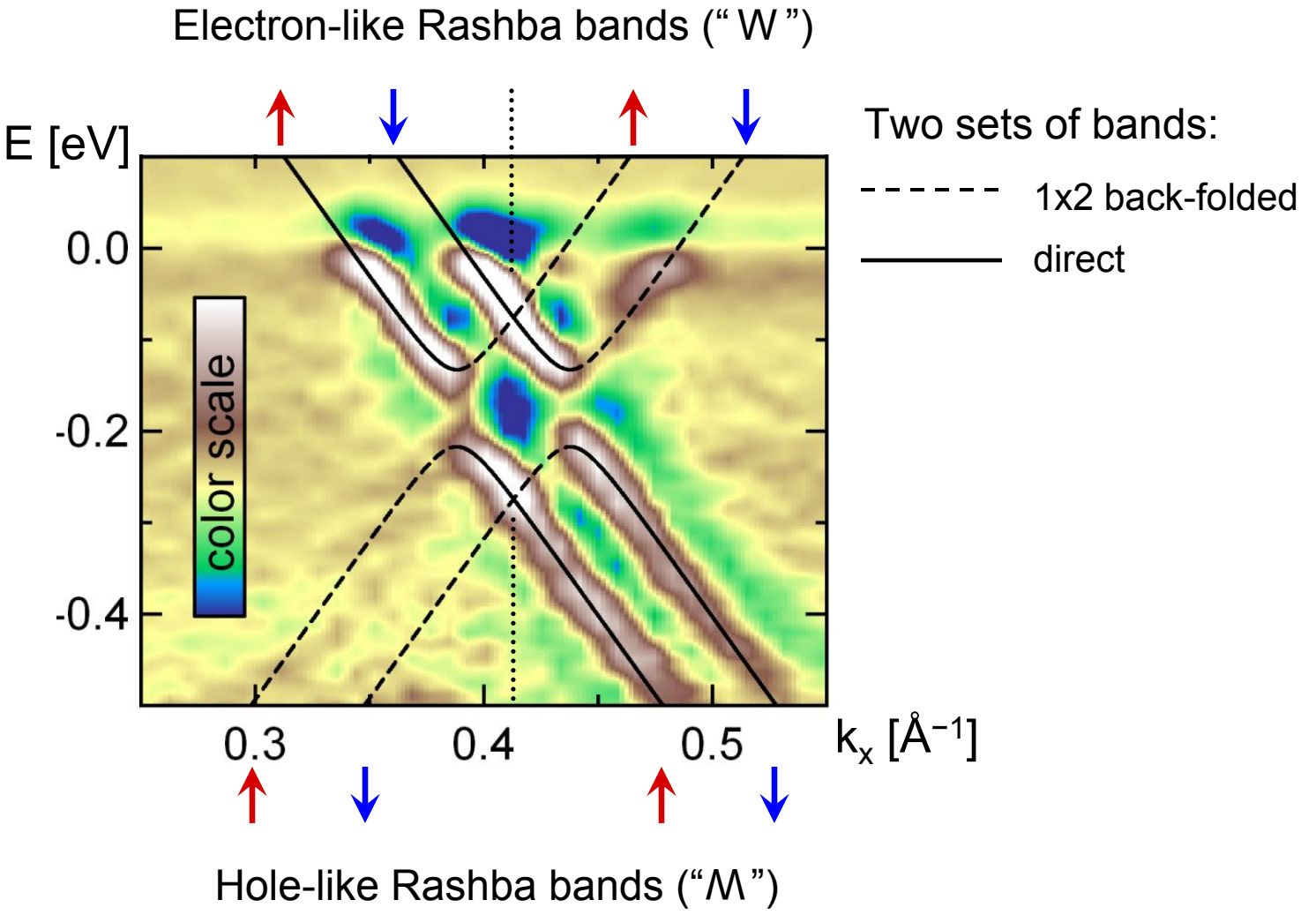
Δk

horizontal shift

"W" shape

Rashba (spin-orbit) Hamiltonian: $H \propto (\vec{k} \times \vec{\nabla} V) \cdot \vec{s}$

Evidence for Rashba splitting (Δk)



Barke et al., PRL **97**, 226405 (2006).

Spin-polarization of broken bonds?

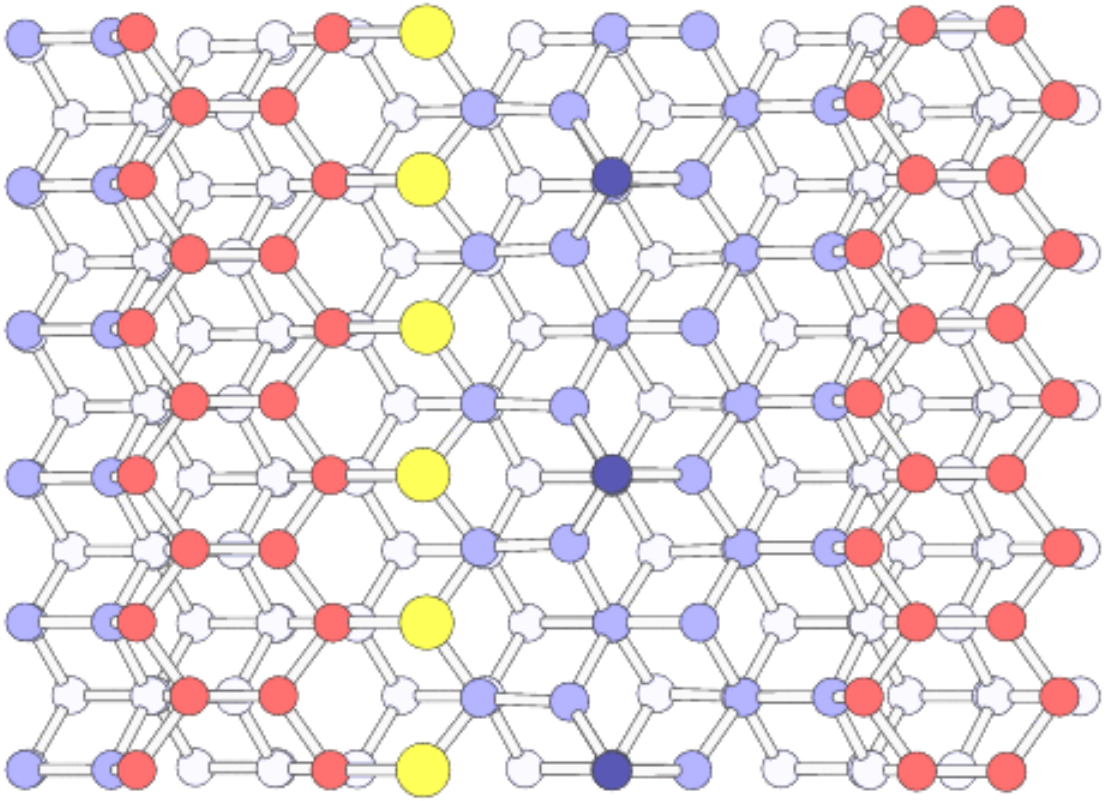
3D: No **Spin-paired electrons in σ-bonds**

2D: No **Spin-paired electrons in π-bonds**

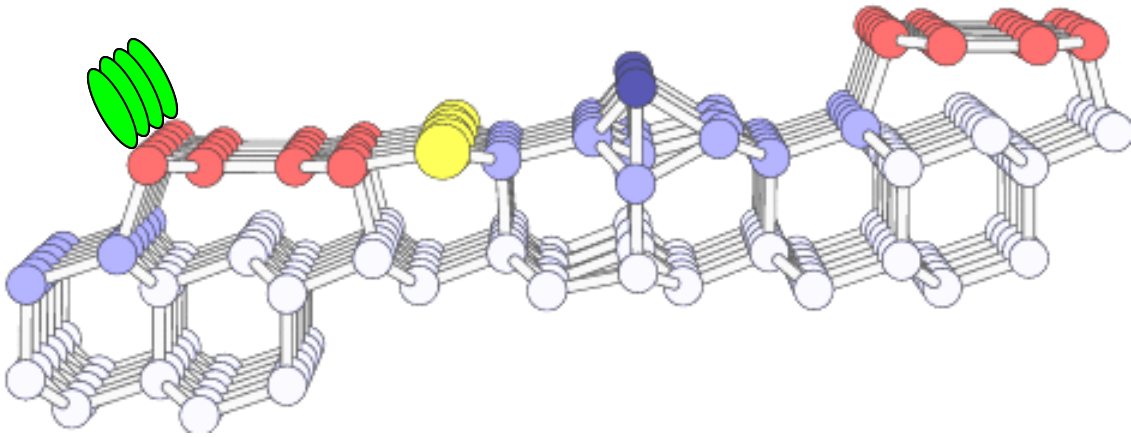
1D: ??

0D: Yes **Isolated broken bond electrons: P_b-center at the Si/SiO_2 interface, observed by ESR**

Look for isolated broken bonds



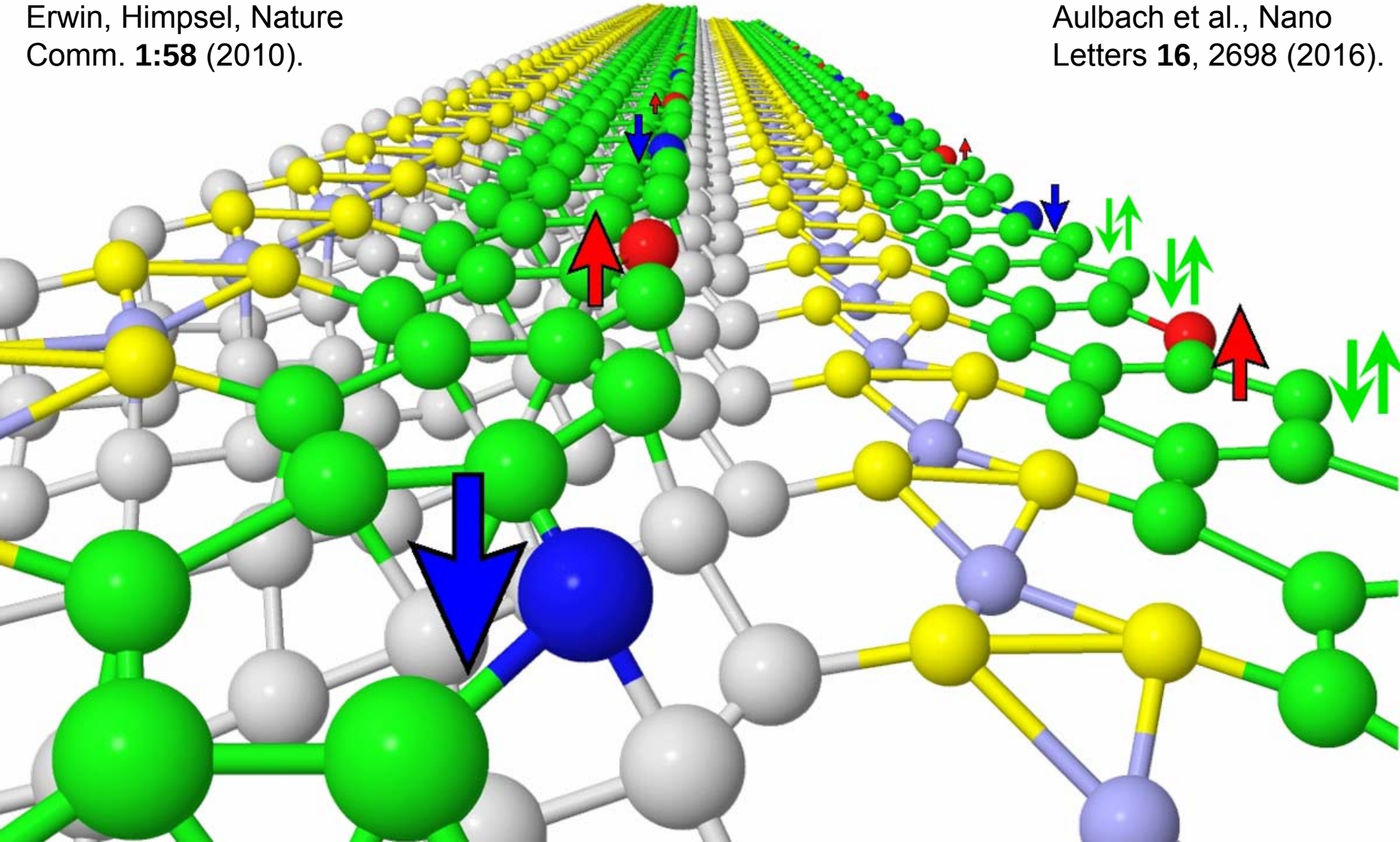
Focus on the step edge



Si edge atoms with an unpaired electron may become spin-polarized

Erwin, Himpsel, Nature Comm. **1:58** (2010).

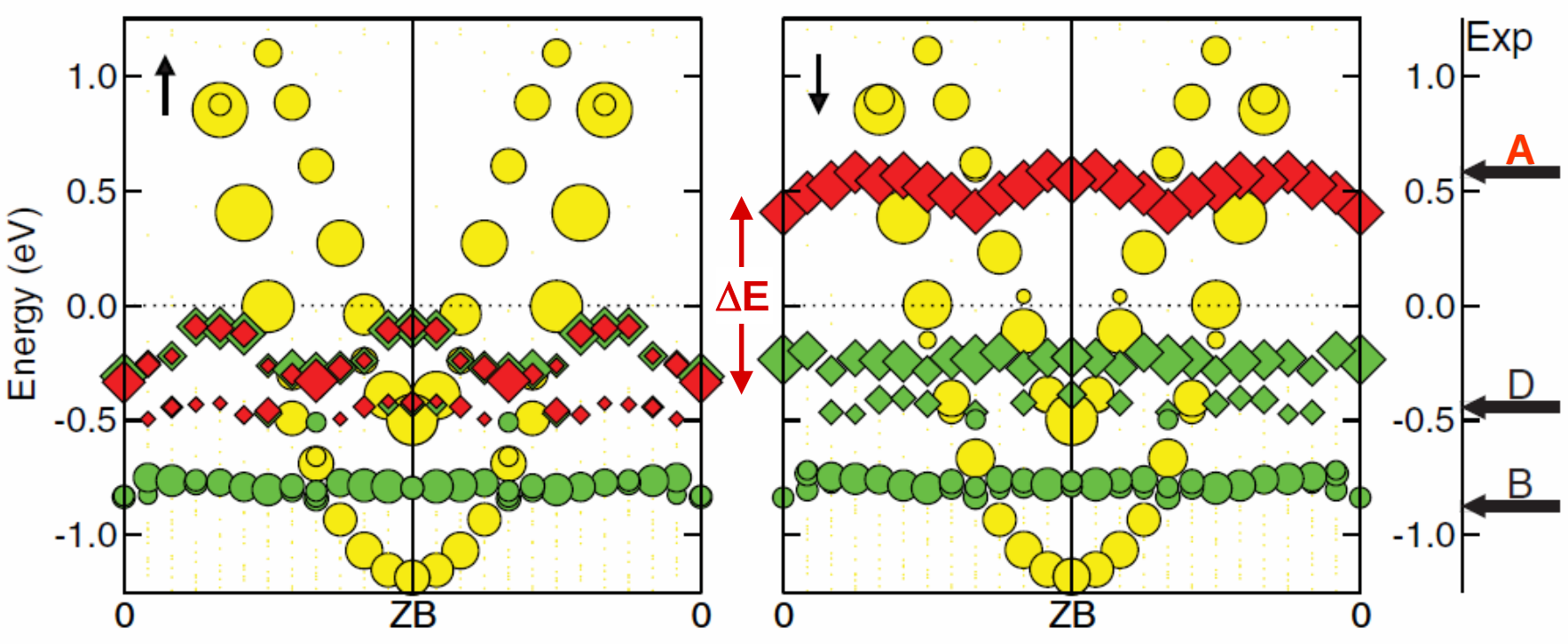
Aulbach et al., Nano Letters **16**, 2698 (2016).



Magnetic band structure

Empty minority spin state characterizes polarized edge atoms

(absent for unpolarized edge atoms)

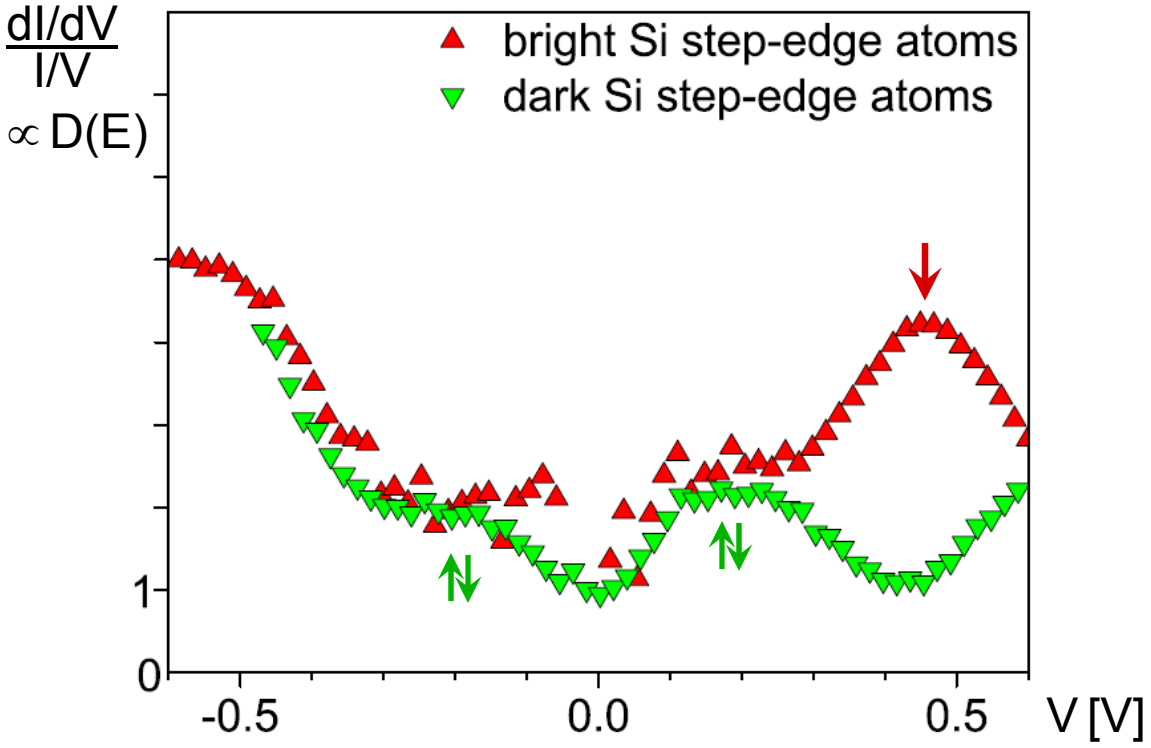


Two-photon photoemission results

Biedermann et al., PRB **85**, 245413 (2012).

Snijders, Erwin, et al., New Journal of Physics **14**, 103004 (2012).

Scanning tunneling spectroscopy of edge states

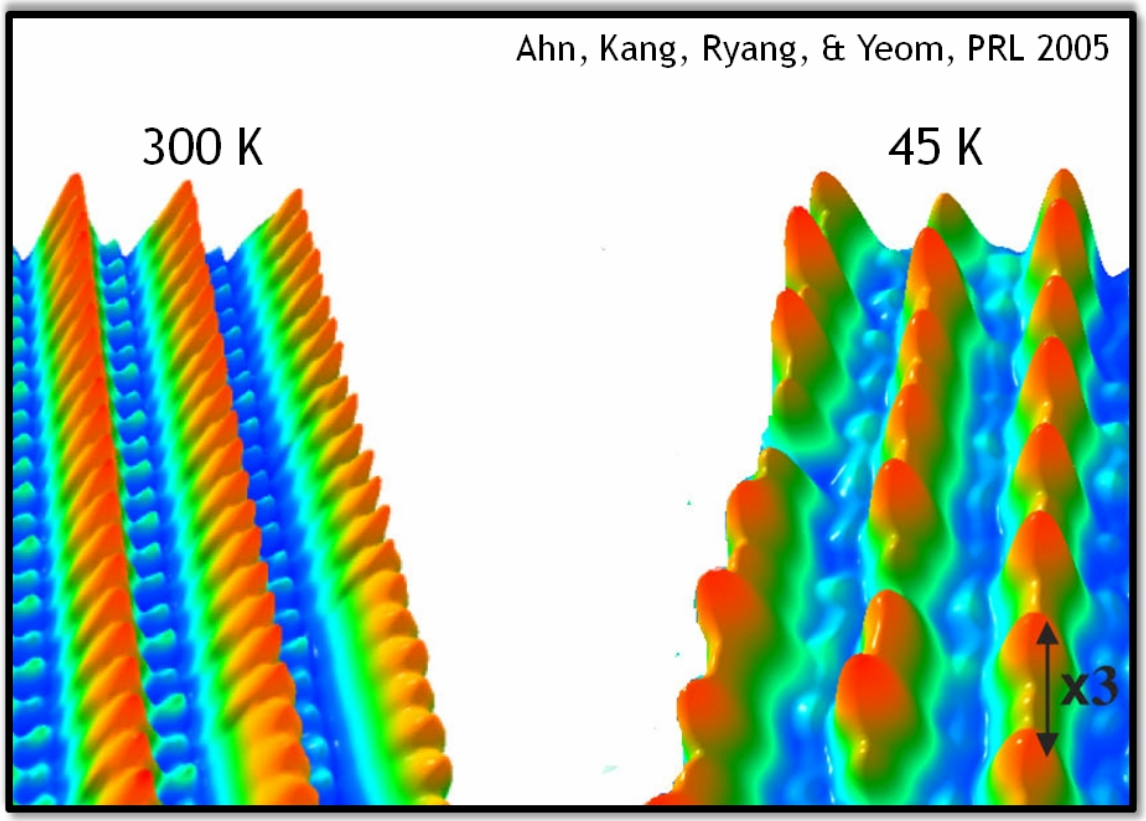


The high density of states (arrow) is consistent with an empty minority spin state of polarized edge atoms.

Needs to be tested by local ESR or spin-polarized STM.

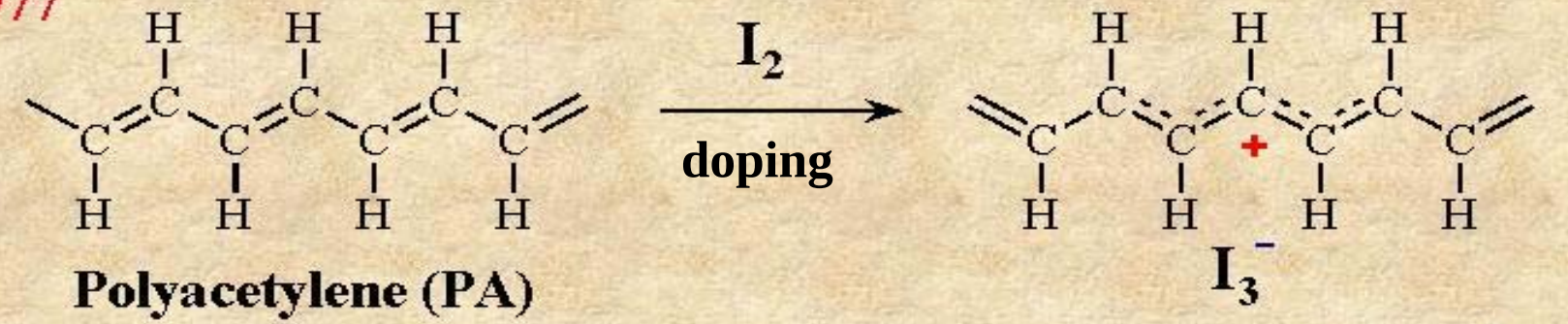
1D superlattice at steps below 50K

Atoms?	Reconstruction	Braun … PRB **98**, 121402(R) (2018).
Charges?	Charge density wave	Shin … PRB **85**, 073401 (2012).
Spins?	Spin density wave	Aulbach … PRL **111**, 137203 (2013).
	All of the above?	Compare complex oxides.



Molecular wires from doped polymers

1977



Polyacetylene (PA)

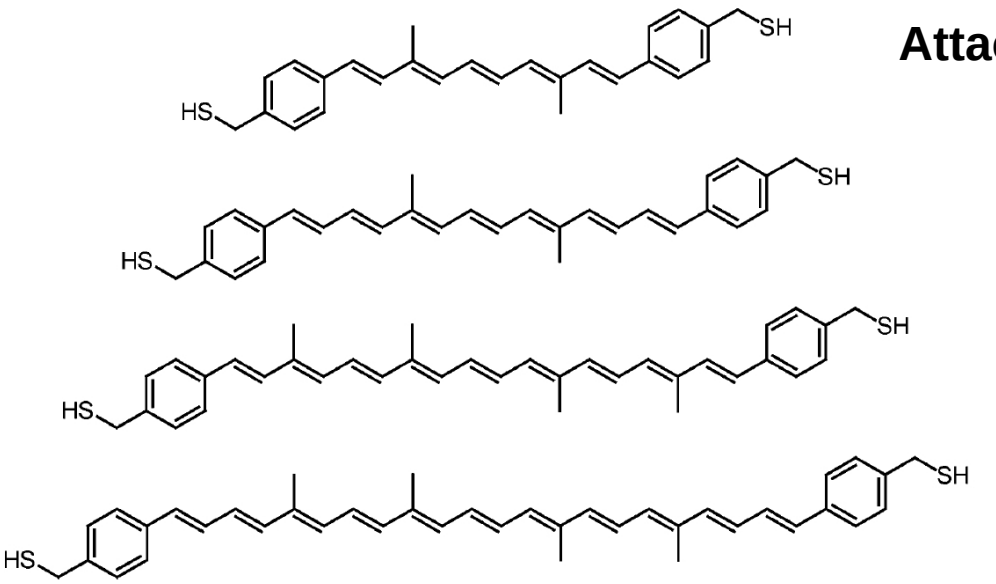
$\sigma = 10^{-9}$ S/cm

$\sigma = 38$ S/cm $= 38 \frac{1}{\Omega cm}$

σ = Conductivity

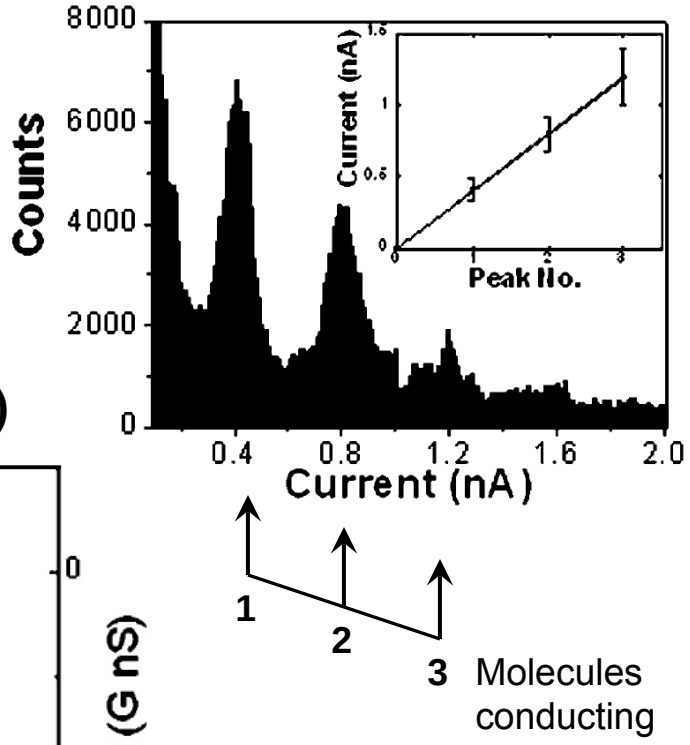
Nobel Prize in Chemistry 2000
Shirakawa, McDiarmid, Heeger

Electrical measurements of individual molecular wires

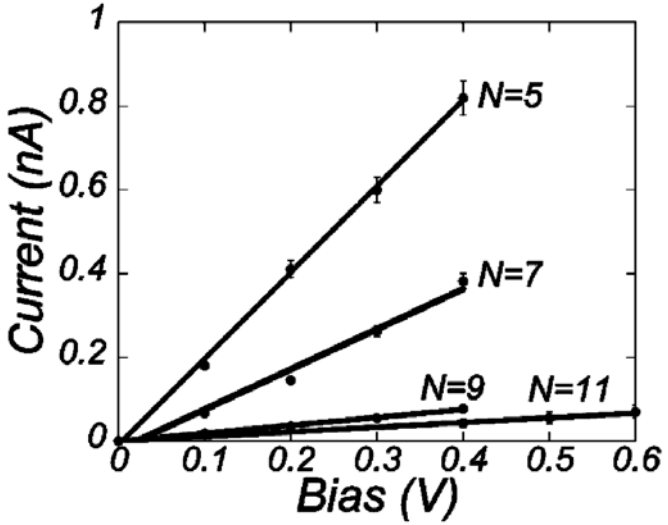


Attachment to Au electrodes via thiol (SH)

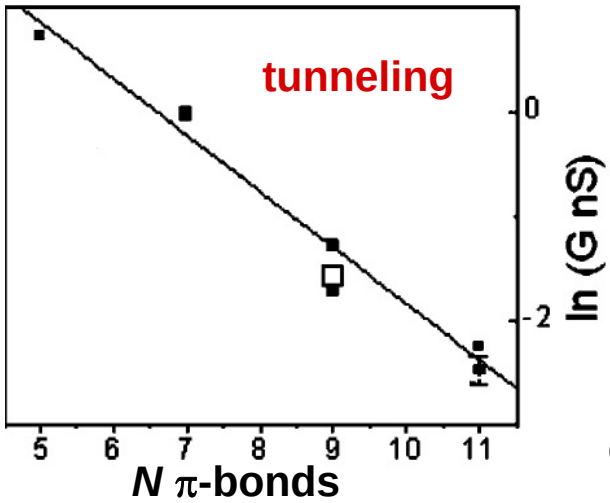
Address individual molecules by AFM/STM or break junction:



Ohmic I(V)



Exponential R(*N*)

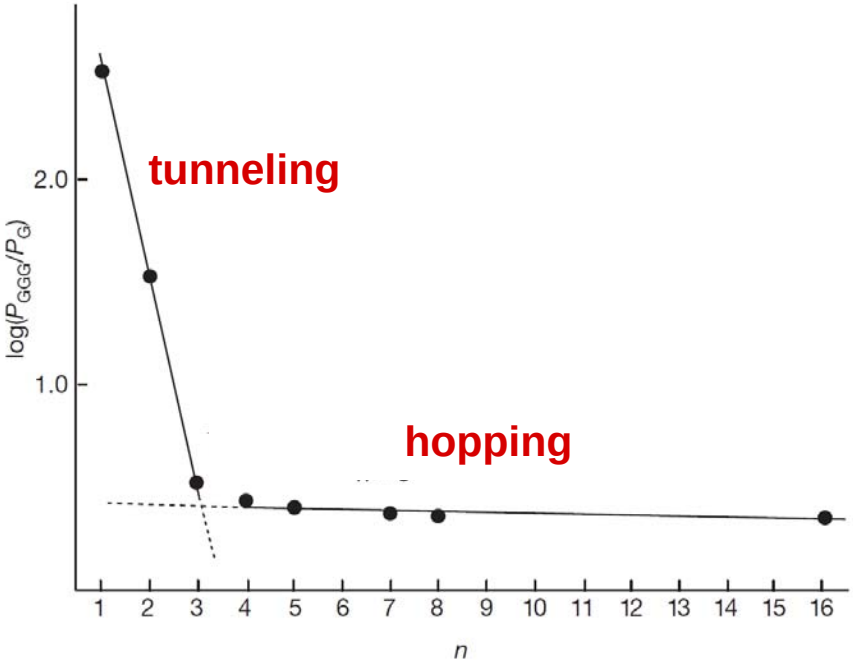


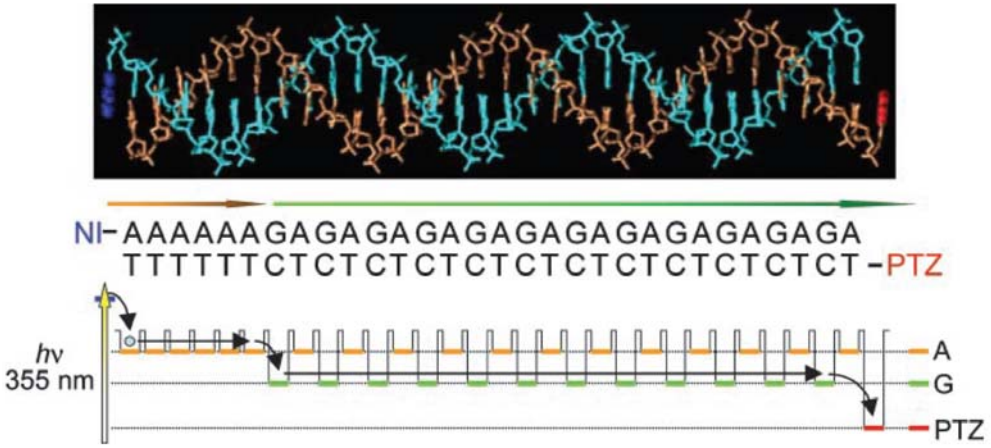
He et al., JACS **127**, 1384 (2005)

Choi et al., Science **320**, 1482 (2008)

DNA as (super)-conducting wire ??

- **Superconductivity induced by proximity to metallic contacts.**
- **The hydration shell and the counter-ions conduct.**
  Without them DNA would degrade.
- **Pump-probe measurements find tunneling up to 2 base pairs and hopping of holes between adenine bases for longer DNA.**



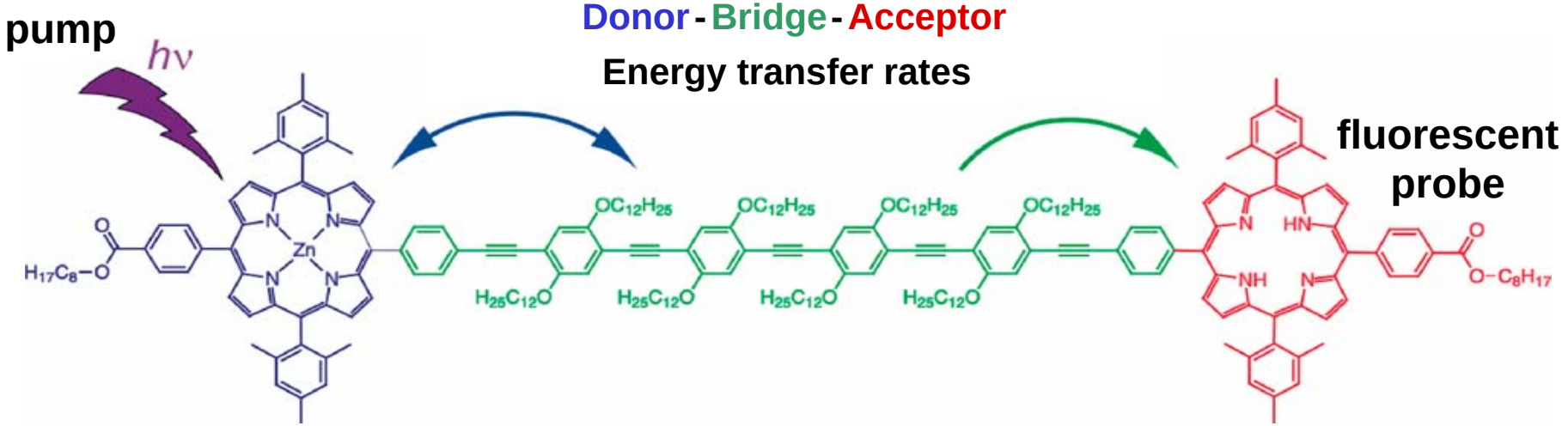


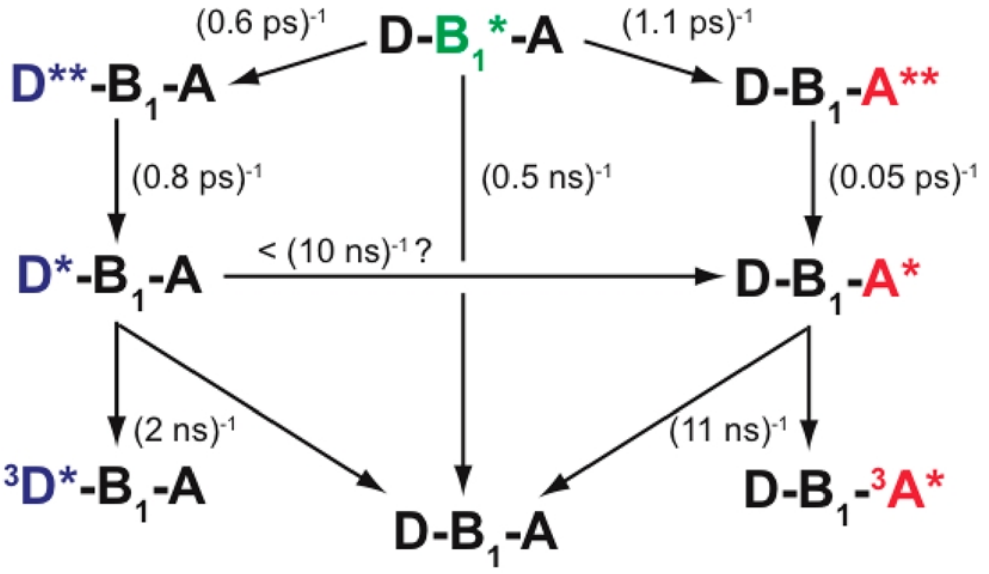
Giese et al., Nature **412**, 318 (2001).

Takada et al., PNAS **101**, 14002 (2004).

Endres, Cox, Singh, Rev. Mod. Phys. **76**, 195 (2004).

Propagation of carriers along a molecular wire

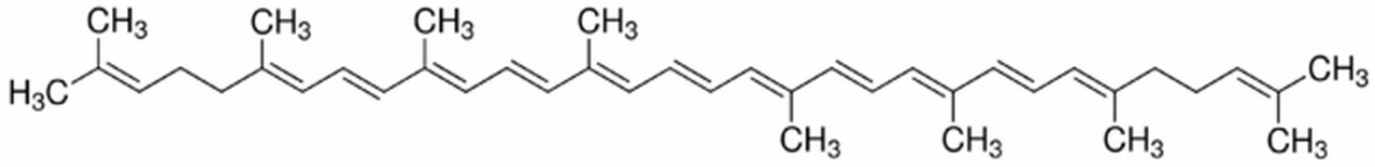




Duvanel, Grilj, Vauthey, J. Phys. Chem. A **117**, 918 (2013).

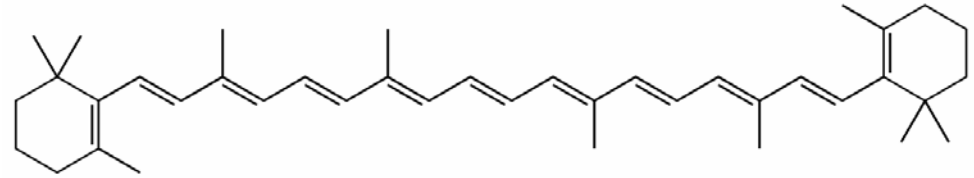
Spectroscopy of π-chains

A chain of overlapping π-orbitals forms a molecular wire



Lycopene

(makes tomatoes red)

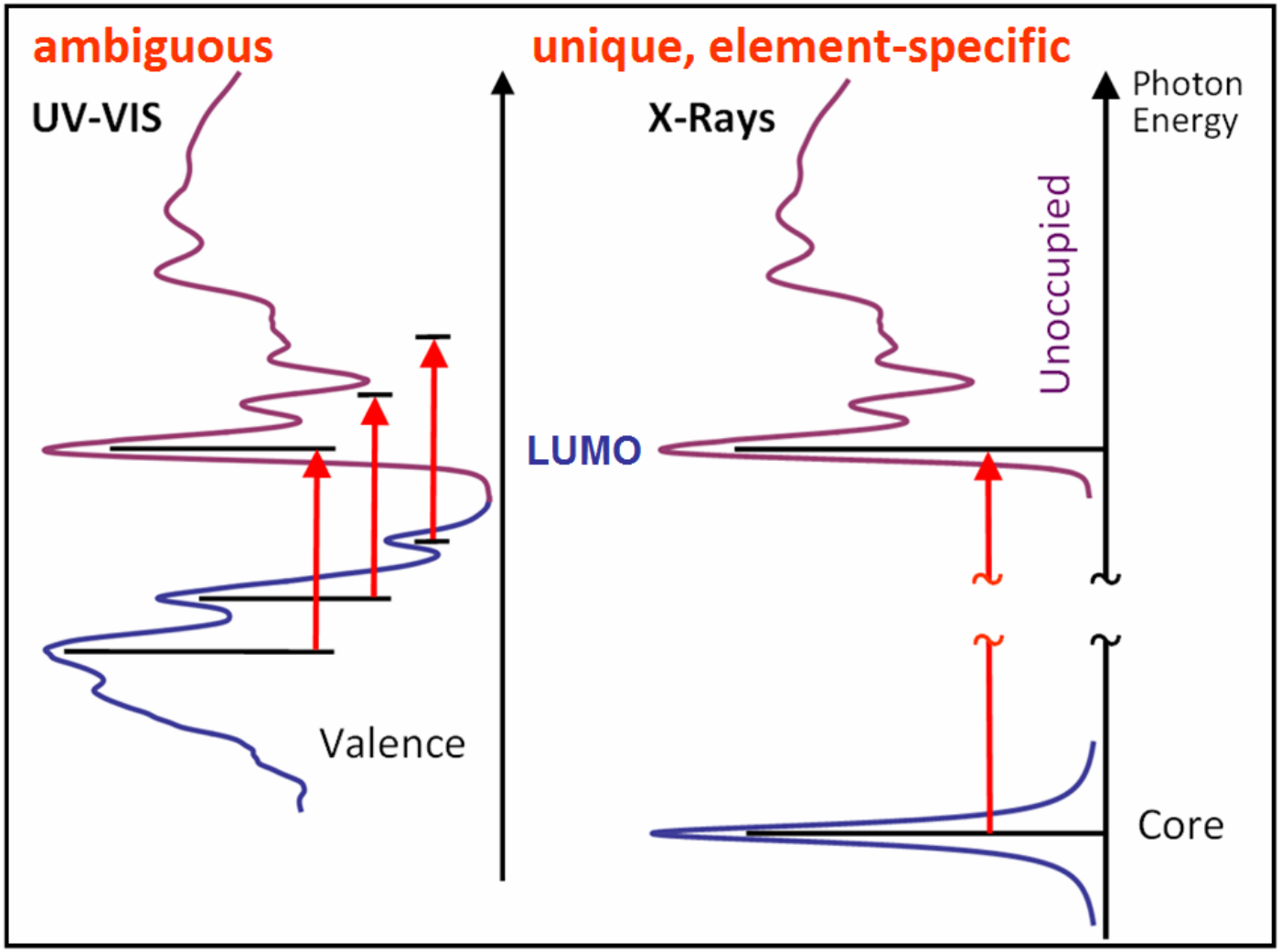


Beta Carotene

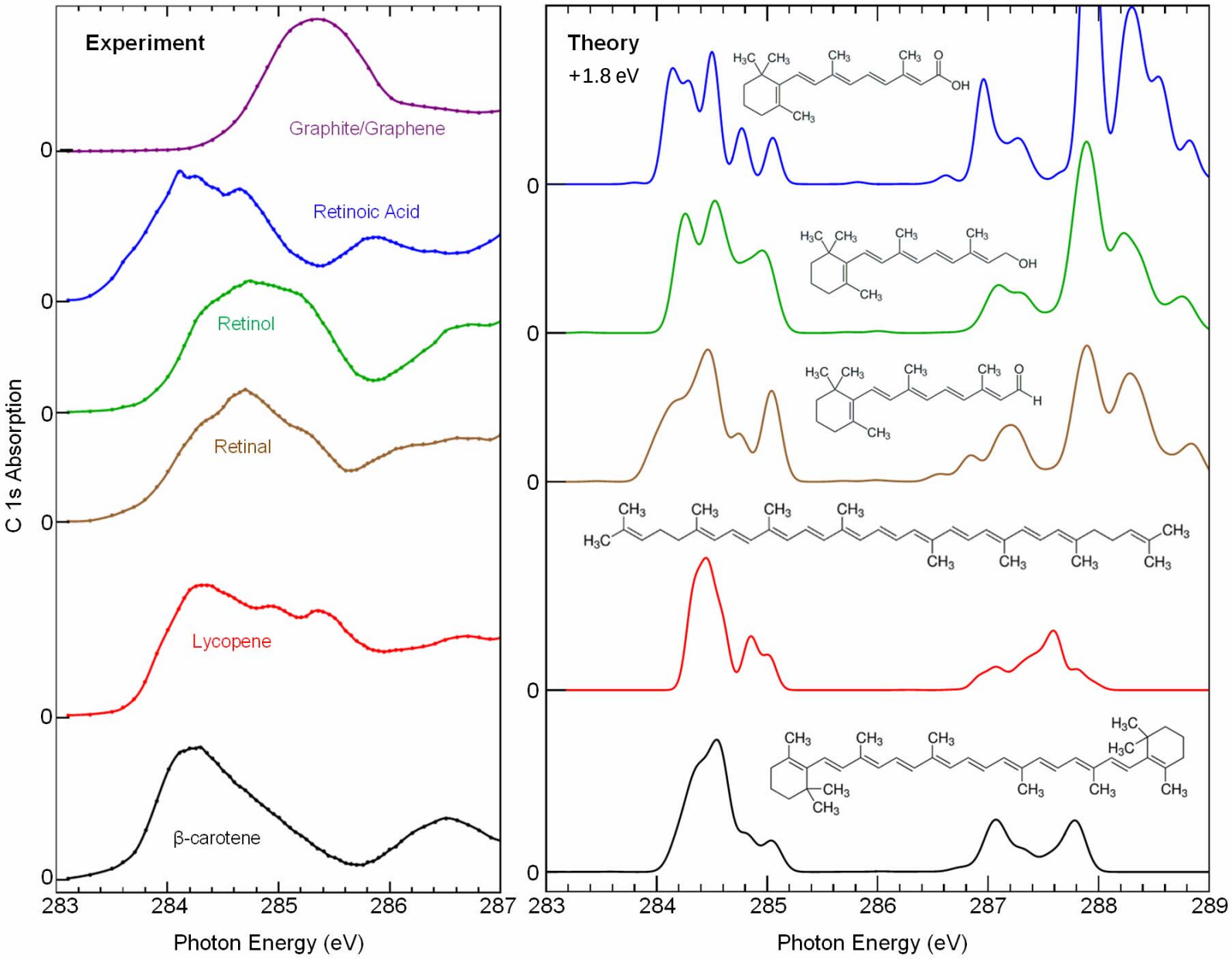
(makes carrots orange)

Garcia-Lastra et al., J. Phys. Chem. C **120**, 12362 (2016)

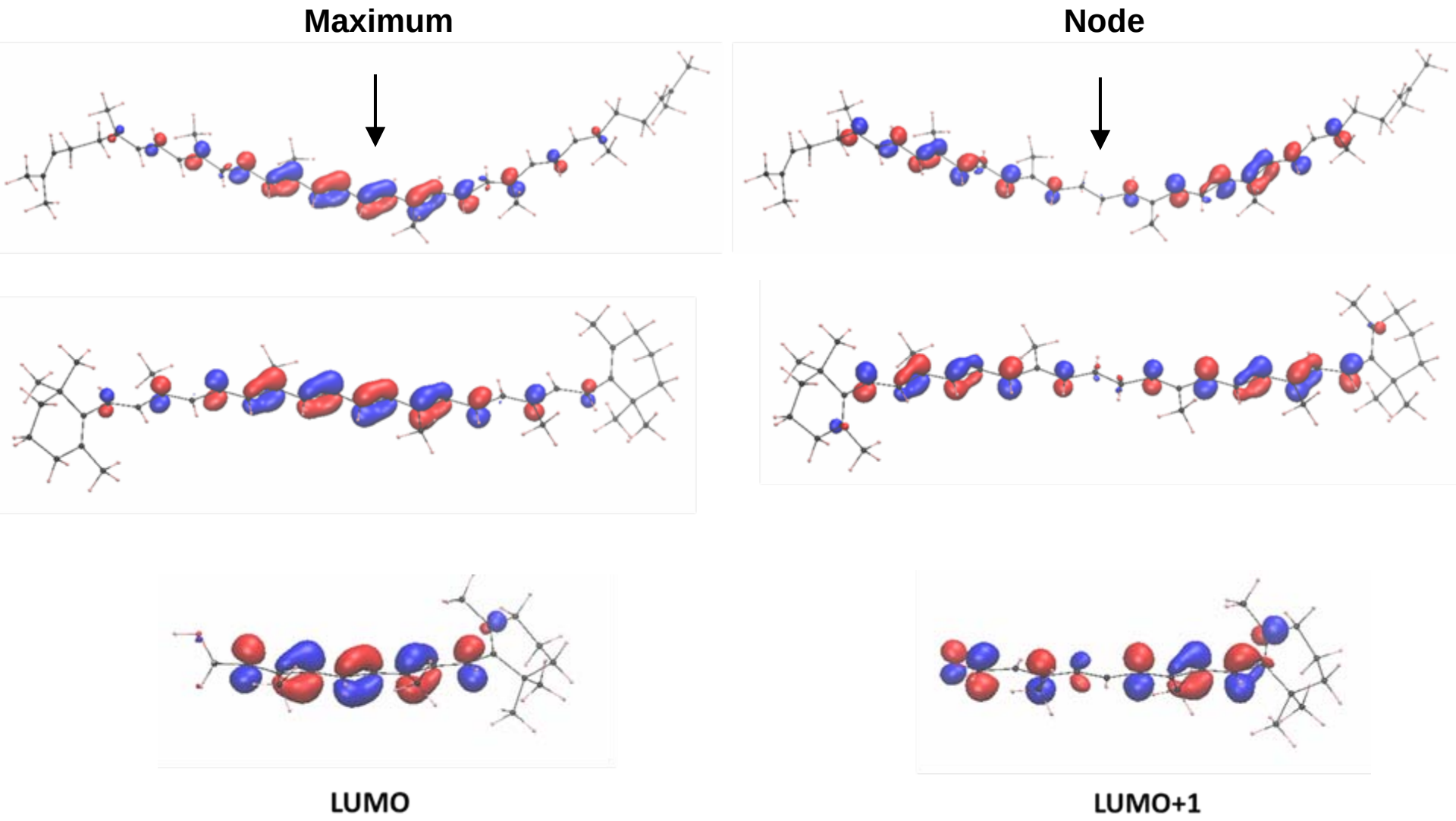
Energy levels from absorption spectroscopy



Transitions from the C1s level into the lowest π* (=LUMO)



Wave functions of molecular wires: vibrating strings



Garcia-Lastra et al., J. Phys. Chem. C **120**, 12362 (2016)

- **Atomic/molecular wires by self-assembly**
- **Single chain of overlapping orbitals (=channel)**
- **Alternating spins or charges at step edges**