



2145-40

Spring College on Computational Nanoscience

17 - 28 May 2010

Metal Nanocontacts (Nanofriction): Physics, Theory, Simulation

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# PHYSICS, THEORY, SIMULATION OF METAL NANOCONTACTS

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ICTP Nanocollege, Trieste, 19 May 2010

#### MAKING AND BREAKING METAL-METAL CONTACTS





Rodrigues et al. (2000)

### METAL NANOCONTACTS

(Au)



FIG. 2. HRTEM images of gold NWs; atomic positions appear dark. (a) [100] atom-chain NW; (b) rodlike [110] NW; (c)–(e) temporal evolution of a NW formed when the apexes are sliding: 0, 17:12, and 24:15 min, respectively.

# Fabrication of atomic-size contacts



#### mechanically controllable break junction



- 1 notched wire
- 2 fixed counter supports
- 3 bending beam
- 4 drops of epoxy adhesive
- 5 stacked piezo element

N. Agraït et al., Phys. Repts. 377, 81 (2003)

## METAL NANOCONTACTS

- 1. STRUCTURE? EVOLUTION IN TIME?
- 2. CONDUCTANCE?
- 3. MAGNETISM? WHAT EFFECT ON CONDUCTANCE?
- 4. NANOMAGNETISM IN A NONMAGNETIC METAL CONTACT?

5. KONDO: A MANY-BODY EFFECT IN A NANOCONTACT

# COMPUTATIONAL METHODS

- -- CLASSICAL (MOLECULAR DYNAMICS) SIMULATION OF NANOWIRES AND NANOCONTACT STRUCTURE + BREAKING
- -- AB INITIO DENSITY FUNCTIONAL ELECTRONIC STRUCTURE CALCULATIONS . CODES: MOSTLY PWSCF (QUANTUM ESPRESSO). EX-CORREL. FUNCTIONALS: LDA, GGA, (LDA+U)
- -- BALLISTIC CONDUCTANCE CALCULATIONS: IHM-CHOI METHOD (COMPLEX BAND STRUCTURE, PLANE WAVES) GENERALIZED TO ULTRASOFT PSEUDOPOTENTIALS. (SPIN-ORBIT INTERACTION INCLUDED: EFFECTS ON SPIN + ORBITAL NANOMAGNETISM, CONDUCTANCE)
- -- MANY BODY METHODS (NUMERICAL RENORMALIZATION GROUP) FOR KONDO EFFECT IN TRANSITION METAL ATOMIC NANOCONTACTS

# STRUCTURE

# TIME SCALES IN THE STRUCTURAL EVOLUTION OF NANOCONTACTS

# **τ**<sub>1</sub>. FAST PLASTIC FLOW AND THINNING



**T**<sub>2</sub>. QUASI-EQUILIBRIUM LONG LIVED (MAGIC) "NANOWIRE" STRUCTURES

# **T**<sub>3</sub>. FINAL BREAKING

# IDEAL ULTRATHIN NANOWIRES (THEORY): EXPECT NEW OPTIMALLY PACKED STRUCTURES

# CRYSTALLINE, ICOSAHEDRAL, HELICAL

GULSEREN ERCOLESSI, TOSATTI, PRL 80, 3775 (1998)

METHOD: MOLECULAR DYNAMICS SIMULATIONS. POTENTIAL: EMPIRICAL MANY BODY FORCES (ERCOLESSI, ONG (1992))



# EXPERIMENT:

Au

Takayanagi et al (2000)

# MAGIC GOLD NANOWIRES





Fig. 1. TEM images of stable gold nanowires observed during one thinning process. The diameters of the wires in (A), (B), (C), and (D) are 1.3, 1.1, 0.8, and 0.6 nm, respectively. The dark dots represent positions of atoms projected on the image plane. The dark dots are aligned on atom rows along the wire axis. These wire images are wavy, particularly in (D).

# Au: tem results analysed



Model pict. TEM pict.

1 nm -

Takayanagi et al (2000)

**HELICAL!?** 

 $\Delta N = 7 !?$ 

15-8

14-7

7-1

11-4

13-6

# AB INITIO THEORY OF MAGIC NANOWIRE STRUCTURES: CALCULATE (AND MINIMIZE) WHAT?

# MAGIC NANOWIRES = MINIMA OF FREE ENERGY F? NO:

-- F (N)/N decreases as N grows: wires should thicken.... but they thin down!!

-- Reason: wires are tip-suspended, do not exist in isolation

# THE CONCEPT OF STRING TENSION



#### ATOMS ESCAPE JUNCTION TO GO TO THE LEADS

# MAGIC NANOWIRES: AB INITIO THEORY

(Science 291,288(2001))  $f = \frac{F - \mu N}{L}$ 

- 1. BUILD CRUDE WIRE MODEL USING EMPIRICAL FORCES, MOLECULAR DYNAMICS
- 2. OPTIMIZE STRUCTURE BY FIRST PRINCIPLES DENSITY FUNCTIONAL CALCULATIONS
- 3. OBTAIN F (= E AT T=0) AND L OF OPTIMAL ZERO STRESS STRUCTURE
- 4.  $\mu$  = BULK COHESIVE ENERGY (CALC. SEPARATELY)
- 5. CALCULATE STRING TENSION **f**, REOPTIMIZE IN PRESENCE OF STRESS UNTIL SELFCONSISTENT
- 6. BUILD ANOTHER WIRE MODEL, ETC

# MULTISHELL COAXIAL NANOWIRE MODELS



**Fig. 2.** Cylindrical folding of a triangular lattice for an (m, n) tube, with views of several coaxial tube nanowires. Each atom is pictured as a sphere of atomic radius. The (7, 3) gold nanowire (note its chirality) was reported to be magic in (3).







**Fig. 3.** Calculated (22) string tension (1 eV/Å = 1.6 nN) of tip-suspended gold nanowires at zero temperature (only the largest and smallest *n* values are shown). The minimum demonstrates why the (7, 3) nanowire is magic. The calculations were carried out for infinite tip-free wires, with structure relaxed to minimize string tension (Eq. 1), starting from initial wire geometries obtained by Voter's potential;  $\mu$ (Au) = -4.401 eV was obtained from a separate bulk calculation.

#### Science 291,288(2001)



# Monatomic nanowires

TEM = transmission electron microscope





Ohnishi et al., Nature 395, 780 (1998)

Rodrigues et al., Phys. Rev. Lett, 91, 096801 (2003)



# CONDUCTANCE

# Fabrication of atomic-size contacts



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# Break junction conductance histograms: quantization



A. I. Yanson, Ph.D. Thesis, 2001  $G_0 = 2e^2/h = (12.9 \text{ K}\Omega)^{-1}$ 

# **Ballistic Electron Transport**



(Figure from B. Altshuler)

#### **Ballistic conductance**

Landauer-Buttiker formula for ballistic conductance:



 $G < G_{MAX} = (e^2/h) (N_{UP} + N_{DOWN})$ 



#### **RIGHT TIP**





# COMPUTATIONAL APPROACH

- -- ELECTRONIC STRUCTURE CALCULATIONS: DENSITY FUNCTIONAL THEORY (DFT).
- -- BALLISTIC CONDUCTANCE (LANDAUER) CALCULATIONS: COMPLEX BAND STRUCTURE (PLANE WAVES, ULTRASOFT PSEUDOPOTENTIALS, SPIN-ORBIT EFFECTS INCLUDED)

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SMOGUNOV, DAL CORSO, ET, PRB 70, 045417 (2004); PRB 73, 075418 (2006); PRB 78, 014423 (2008); [but also Mertig et al, Bluegel et al, Bagrets et al, Sanvito et al, Tsymbal et al, Barreteau et al, Brandbyge et al, Di Ventra et al, Todorov et al...]

# 

у

- Given the potential in the leads, find propagating (solid) and evanescent (dashed) states  $\psi_i$  making up the so-called *complex band structure* of the lead.
- Given s.c. potential in scattering region, construct the scattering states for each propagating wave  $\psi_j$  and find  $t_{ij}$  and  $r_{ij}$  by simple wavefunction matching
- WFs are expanded in plane waves in the XY plane and in the real space in the Z

<u>Landauer-Büttiker formula</u> (at zero temperature):  $I = \frac{e}{h} \int_{\mu_s}^{\mu_h} T(E) dE$ 

where the total transmission  $T = \sum_{ij} |t_{ij}|^2$ For infinitesimal voltage,  $\mu_i - \mu_g = e \,\delta V$ ,  $G = \frac{I}{\delta V} = \frac{e^2}{h} T(E_F)$ .

#### Complex bands of a Pt monatomic wire



#### **TEST CASE**



# MAGNETISM



image from (Autes et al 2008)

#### HOW **MAGNETISM** INFLUENCES BALLISTIC **CONDUCTANCE**





# CONDUCTANCE CALCULATIONS NICKEL NANOCONTACT



A) ab-initio electronic structure (local spin density)

B) calculate transmission T(E)

C) ballistic conductance  $G/G_0 = 0.5 T(E_F)$ 

SMOGUNOV, DAL CORSO, ET PRB 70, 045417 (2004)

#### Magnetization along the wire direction in the 3-atom Ni nanocontact







T = 4.2 K

# "SPINTRONICS"



#### FERT



#### GRUENBERG

#### MAGNETORESISTANCE EFFECTS AT NANOCONTACTS



ballistic magnetoresistance (BMR)



Fe: BMR ~ 20-70% M. Viret et al., PRB 66, 220401 (2002)



ballistic anisotropic magnetoresistance (BAMR)

 $\mathbf{BAMR} = \frac{\boldsymbol{G}_{\perp} - \boldsymbol{G}_{\parallel}}{\boldsymbol{G}_{\parallel}}$ 

Fe: BAMR ~ 20% M. Viret et al., Eur. Phys. J. B 51, 1 (2006)

# NANOMAGNETISM AT CONTACTS? (speculative)

# CAN THIS BE LOCALLY MAGNETIC (AT T=0)? WHAT IS THE EFFECT ON CONDUCTANCE?



# Pt, Pd, ...



dell'a dell'accion

# Magnetization of Pd 3 atom contact

#### P. Gava et al (2005)

A

CAUTION: A VERY WEAK EFFECT!



0.19 µ<sub>в</sub>

 $0.31 \ \mu_B$ 

0.19 μ<sub>в</sub>

# KONDO EFFECT



SCREENING

# MAGNETIC IMPURITY IN A NONMAGNETIC METAL NANOCONTACT



Au



# $\begin{array}{c} \textbf{IS THIS STILLOK??} \\ \underline{\textbf{Ballistic conductance calculatio}} \\ \underline{\textbf{Scattering region}} \\ Crystalline lead \\ \psi_{j} \\ \underbrace{\textbf{V}_{j}}_{\textbf{V}_{j}} \\ \underbrace{\textbf{V}_{j}}_{\textbf{V}_{j}}$

- Given the potential in the leads, find propagating (solid) and evanescent (dashed) states  $\psi_i$  making up the so-called *complex band structure* of the lead.
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# MANY BODY EFFECT



# t U - Contraction of the second secon

SOLVED BY e.g., NUMERICAL RENORMALIZATION GROUP

# NUMERICAL RENORMALIZATION GROUP

#### R. BULLA et al (2008)





Ken Wilson

# "DFT + NRG" STRATEGY

1. **DFT** ELECTRONIC STRUCTURE CALCULATION:

- -- IDENTIFY NATURE, SYMMETRY OF COND. CHANNELS
- -- MAGNETIZATION, SPIN OF IMPURITY
- -- SYMMETRY OF FILLED + EMPTY MAGNETIC ORBITALS
- -- EXTRACT SCATTERING PHASE SHIFTS OF CONDUCTION ELECTRONS FOR EACH SYMMETRY& BOTH SPINS
- BUILD GENERALIZED ANDERSON MODELS, INCLUDING ALL SCATTERING SYMMETRY CHANNELS
  ADJUST PARAMETERS OF ANDERSON MODEL TO CLOSELY REPRODUCE DFT PHASE SHIFTS WITHIN HARTEE-FOCK APPROX.
- 3. SOLVE ANDERSON MODEL WITH e.g., NUMERICAL RENORMALIZATION GROUP (NRG) TO OBTAIN SPECTRAL DENSITY, CONDUCTANCE.

#### TEST CASE: Au-Ni NANOCONTACT







# DFT ELECTRONIC STRUCTURE CALCULATIONS



Y. MIURA et al. PRB (2008); R. MAZZARELLO et al (2009)

#### SUBSTITUTIONAL



 $E_{ad} = 2.32 \text{ eV}, \text{ magn.} = 1.9-2.0 \mu_B$ 

REFLECTION SYMMETRY: EVEN, ODD RELATIVE TO Ni

DFT CALCULATION: Ni SPIN DEPENDS ON GEOMETRY



#### CALCULATE IMPURITY PHASE SHIFTS BY SPIN ROTATION ANGLE



Simple model Kondo-like hamiltonian:  $H = -\frac{d}{dx^2} + J \delta(x) S_z S_z$   $\longrightarrow \frac{\theta > 0}{\theta < 0}$ , if J > 0 (coupling antiferro)  $\theta < 0$ , if J < 0 (coupling ferro)

	$\delta_{{\scriptscriptstyle e}/{\scriptscriptstyle o}}^{^{\uparrow}}$	$\delta^{\scriptscriptstyle 4}_{s\prime o}$	$\theta_{_{e/o}}$	Coupling
Bridge	1.16/0.96	1.02/1.52	-16° / +64°	F/AF
Subst.	0.74/1.19	0.62/1.13	-14°/-7°	F/F

-- ONLY ONE CASE (Bridge, odd) WHERE COUPLING IS AF REASON : IN MOST CASES SPIN IS A SPECTATOR





#### EXTENDED ANDERSON MODEL



	Bridge $(eV)$	Substitutional $(eV)$
$\epsilon_e$	0	0
$\Gamma_e$	3	3
$\epsilon_o$	-1.5	-2.1
$\Gamma_o$	0.25	
U	$2.2(3.5^*)$	2.12
$J_H$	0.3	0.2
δ	0.38 rad	

Angle (rad)	Bridge DFT (HF-AIM)	Subst. DFT (HF-AIM)
$\theta_e$	-0.28 (-0.28)	-0.19 (-0.19)
$\theta_o$	1.10(1.17)	-0.12 (-0.00)



#### KONDO TEMPERATURE CONTROLLED BY HUBBARD U



#### SUBSTITUTIONAL Ni

#### SPIN 1 IS SPECTATOR, COUPLING IS "FERRO"



$$H = \sum_{kp\sigma} \epsilon_{pk} c^{\dagger}_{kp\sigma} c^{\dagger}_{kp\sigma} + \sum_{k\sigma} V_{ks} \left( c^{\dagger}_{ke\sigma} s^{\dagger}_{\sigma} + H.c. \right)$$
$$+ \sum_{\sigma} \epsilon_{s} s^{\dagger}_{\sigma} s^{\dagger}_{\sigma} + \sum_{\sigma\alpha} \epsilon_{\alpha} d^{\dagger}_{\alpha\sigma} d^{\dagger}_{\alpha\sigma} + U \sum_{\alpha} n_{\alpha\uparrow} n_{\alpha\downarrow} + J_{H} \vec{S}_{s} \cdot \vec{S}_{d_{\alpha}} \qquad \mathsf{J}_{\mathsf{H}} < \mathsf{0}$$

## PREDICT GEOMETRY-DEPENDENT KONDO EFFECTS, DIFFERENT ZERO\_BIAS CONDUCTANCE ANOMALIES



**Experiment?** 

## CONCLUSIONS

UNSUSPECTEDLY RICH PHYSICS AT NANOCONTACTS

QUASI-EQUILIBRIUM MAGIC NANOWIRES

BALLISTIC CONDUCTANCE AND MAGNETISM

LOCAL CONTACT MAGNETISM IN Pt, Pd?

KONDO EFFECT ACROSS MAGNETIC IMPURITIES CALCULABLE IN ATOMISTIC DETAIL SOME GENERAL REFERENCES (mainly experimental)

- -- METAL NANOCONTACTS, BREAK JUNCTIONS N. Agrait et al, Physics Reports 377, 81 (2003)
- -- MAGNETISM AND CONDUCTANCE Various articles by M. Viret, and by A. Fert
- -- KONDO EFFECT AND ZERO BIAS CONDUCTANCE ANOMALIES IN ATOMIC NANOCONTACTS
  - See, e.g., M. Ternes et al, J. Phys.-Cond. Matt. 21, 053001 (2009).

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THANKS TO MY COLLABORATORS

- P. Baruselli (Trieste)
- A. Dal Corso (Trieste)
- A. Delin (Stockholm)
- M. Fabrizio (Trieste)
- P. Gentile (Salerno)
- P.Lucignano (Trieste/Naples)
- R.Mazzarello (Trieste)
- G. Sclauzero (Trieste)
- A. Smogunov (Trieste)
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