STM, NC-AFM, and Atom Manipulation: From Personal Art to Exact Science

C. Julian Chen

Institut für Angewandte Physik und Zentrum für Mikrostrukturforschung

Universität Hamburg, Jungiusstrasse 11, Hamburg

Much of the research work presented here was done at IBM TJ Watson Research Center, Yorktown Heights, New York, USA

Outline

Atomic resolution in STM and NC-AFM

- The art of tip sharpening
- The mystery of spontaneous tip restructuring

Understand and characterize tip states

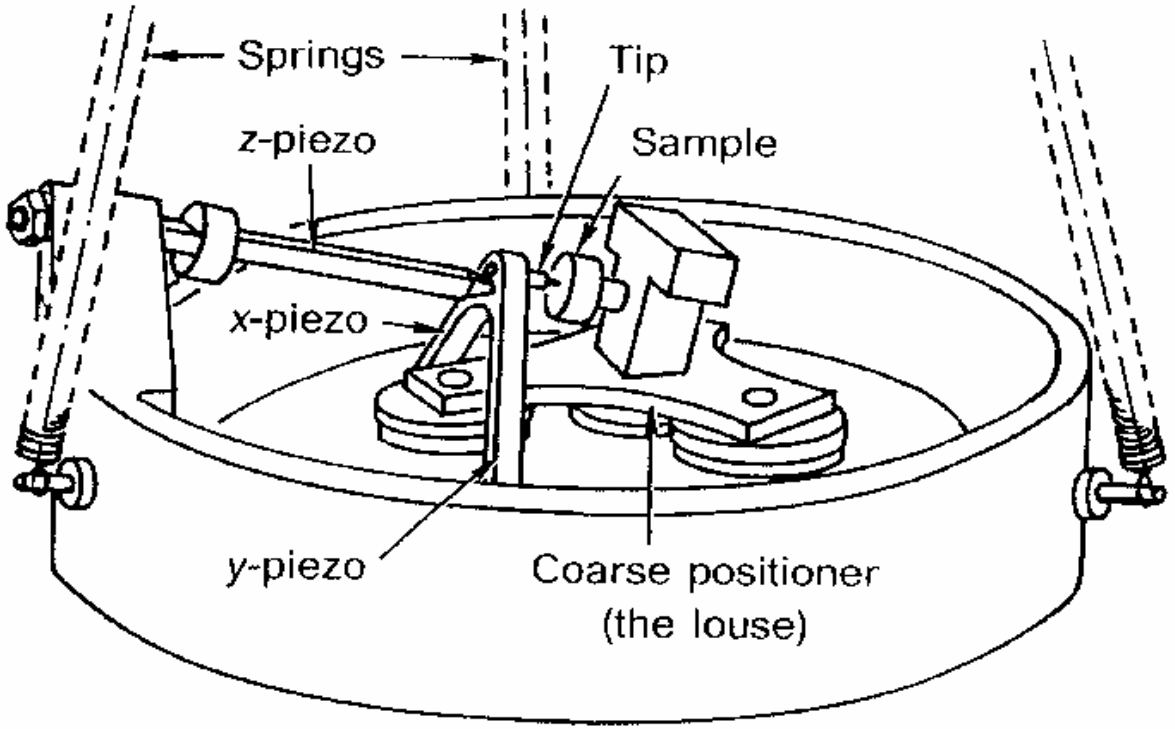
- Existence and manifestation of various tip states
- Experimental determination of various tip states
- Case of spin-polarized STM

Spin-polarized non-contact AFM

- A unified view of tunneling, chemical bond, and magnetism
- Probe chemical bonds through tunneling measurements
- Probe exchange coupling by force and tunneling measurements
- Atom manipulation: from personal art to exact science

The Scanning Tunneling Microscope

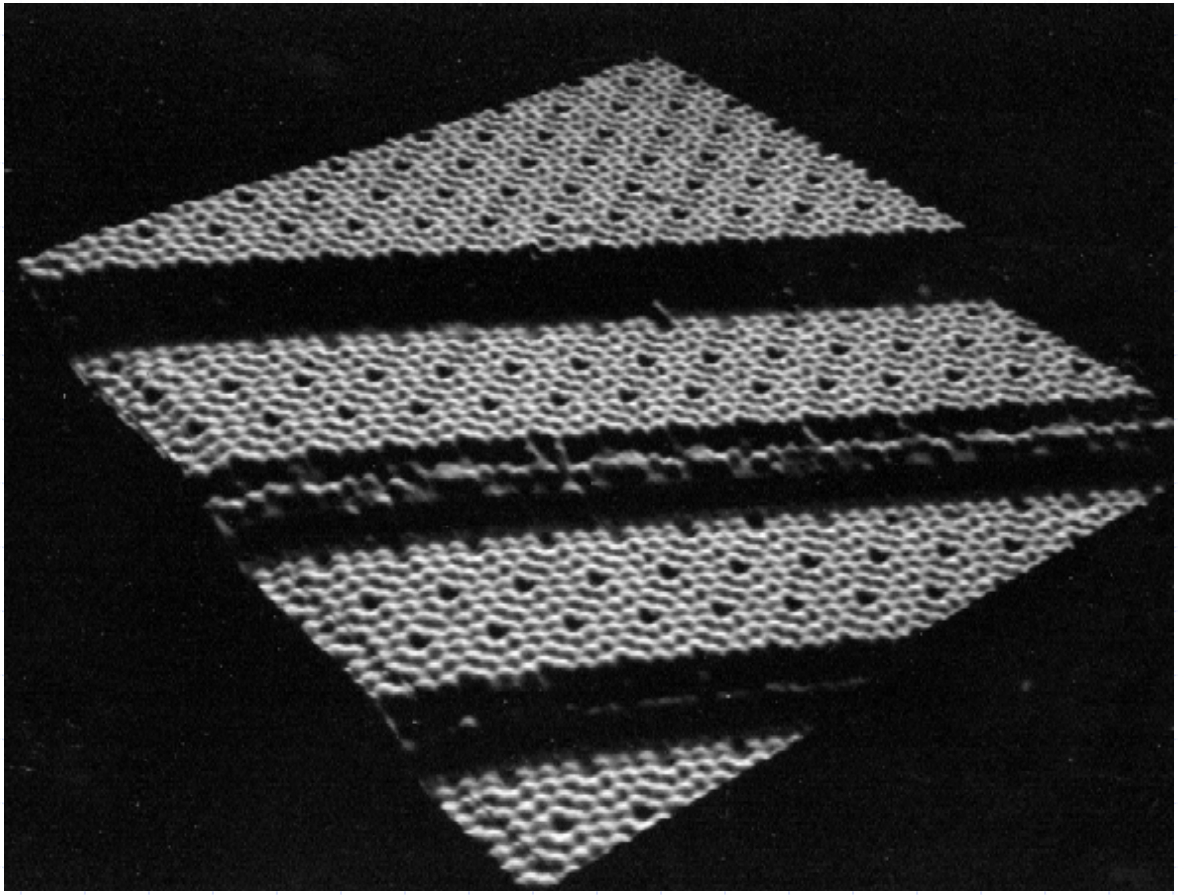
A humble gadget that shocked the science community.



Binnig, Rohrer, Gerber and Weibel, ***Phys. Rev. Lett.*** **49** 57 (1982).

Nobel Prize in Physics 1986: Binnig and Rohrer

Stairway to Heaven to Touch Atoms



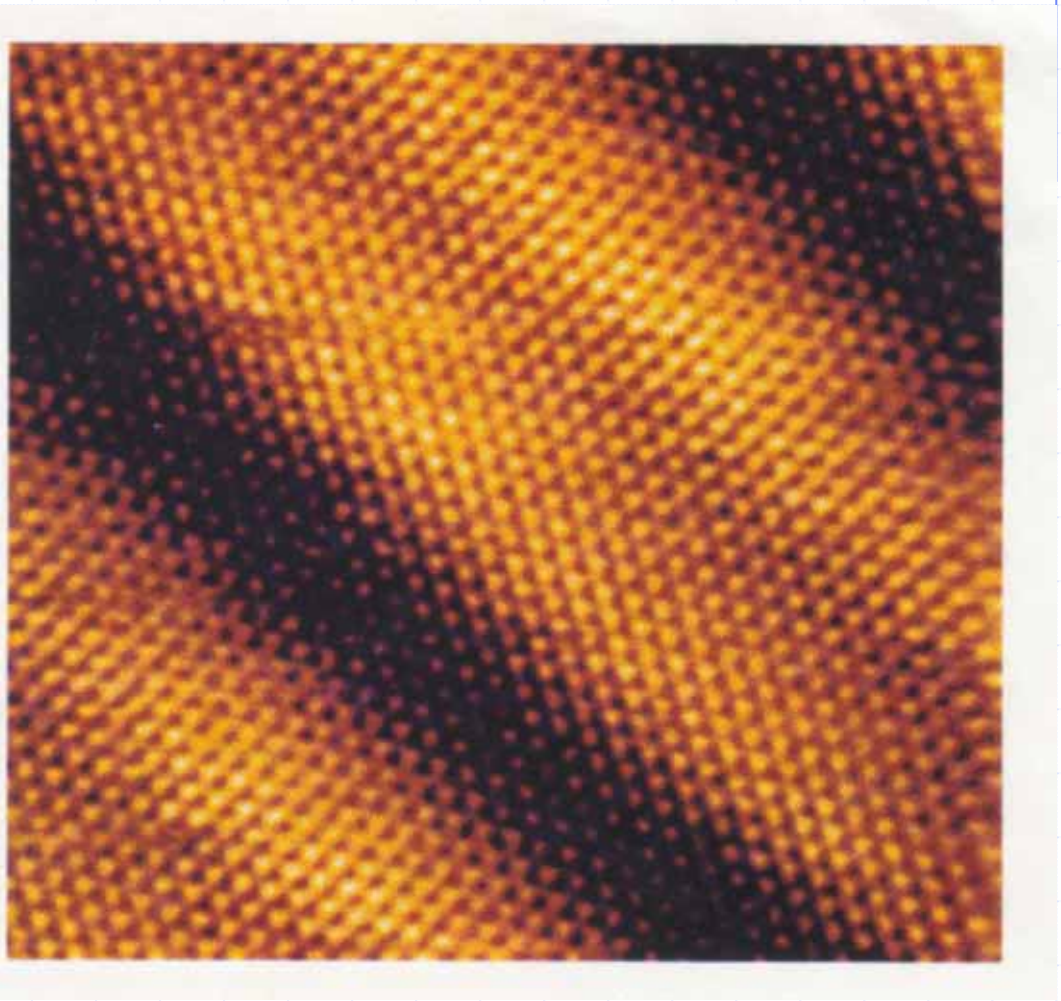
Wiesendanger et al., ***Phys. Rev. Lett.*** **65,** 247 (1990).

Atomic Resolution on Metal Surfaces

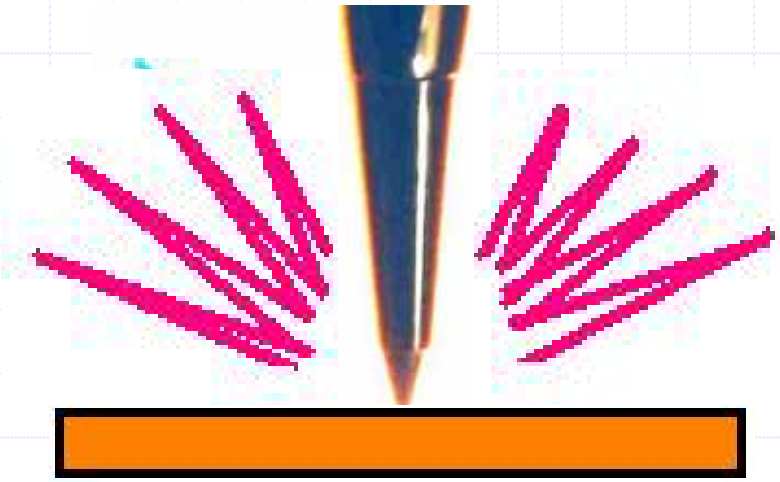
Using STM, individual atoms are routinely resolved on all metal surfaces, with typical interatomic distance of 2.5-3.5 A (0.25-0.35 nm).

Figure: An STM image of Au(111) surface, showing both large reconstruction and small atomic details.

Barth et al., ***Phys. Rev.*** **B 42,** 9307 (1990).



The Art of STM tip sharpening



? ? ?

(1) Even with a carefully made tip, atom resolution would not occur immediately.

(2) By treat the tip with a controlled collision,

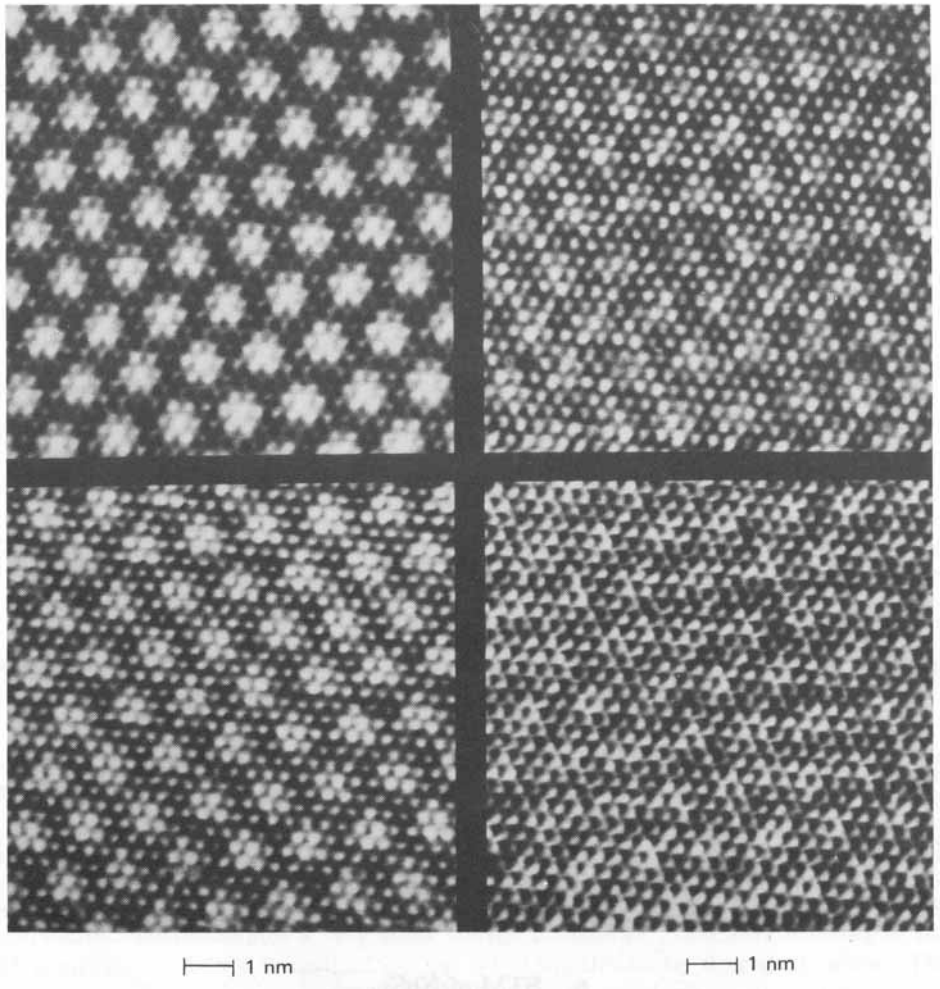
(3) or, treat the tip with an electrical pulse, atomic resolution may suddenly show up.

(4) Often, spontaneous tip restructuring could change the resolution dramatically (for good or for bad).

Tip-State Dependence of STM Images

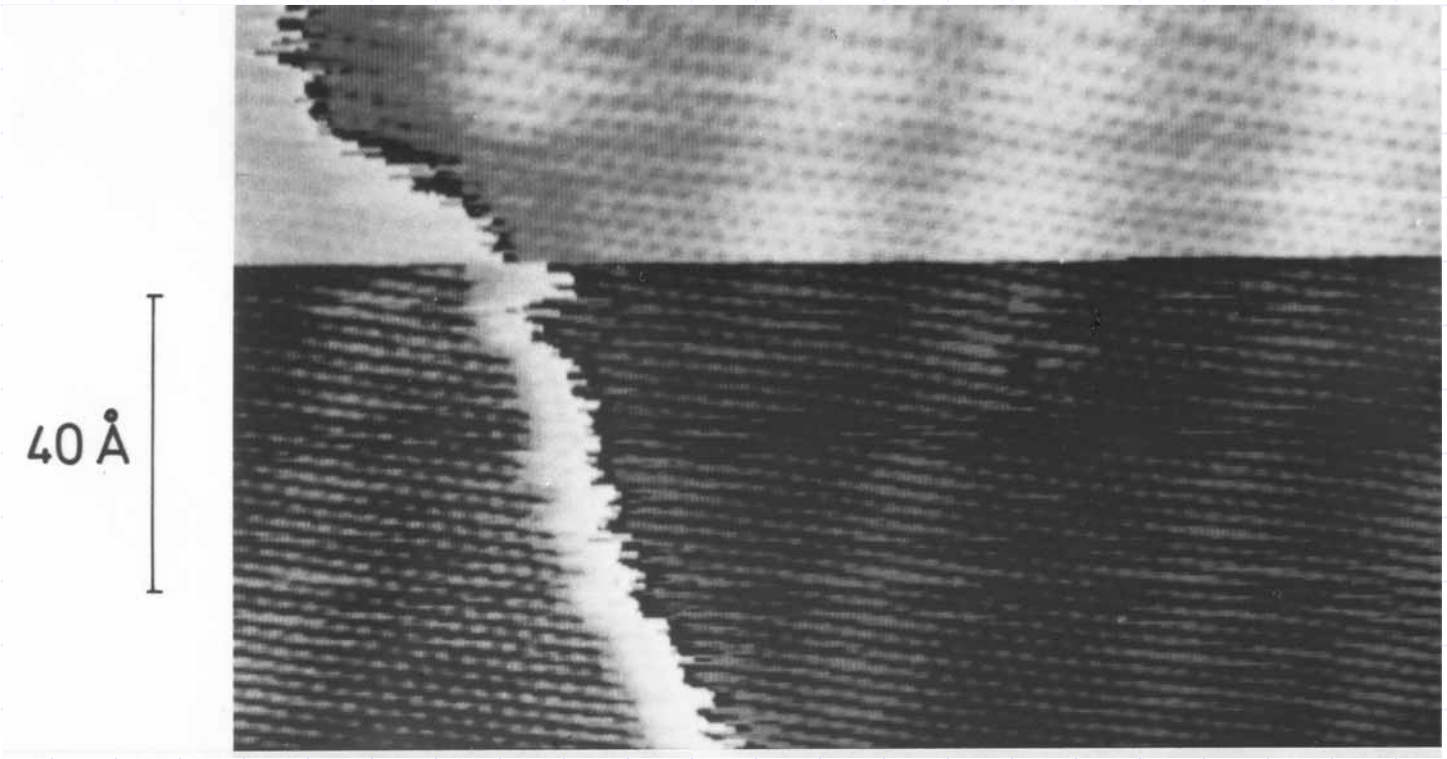
Several images of the same sample taken within 2 hours under identical conditions, showing dramatic differences due to changes in tip states.

R. V. Coleman et al., Adv. Phys. *37*, p.607, (1988).



Spontaneous Corrugation Reversal

After a spontaneous tip restructuring, under identical tunneling conditions, atomic corrugation reversed.



Barth, Burne, Ertl and Behm, ***Phys Rev*** **B 42,** 9307 (1990).

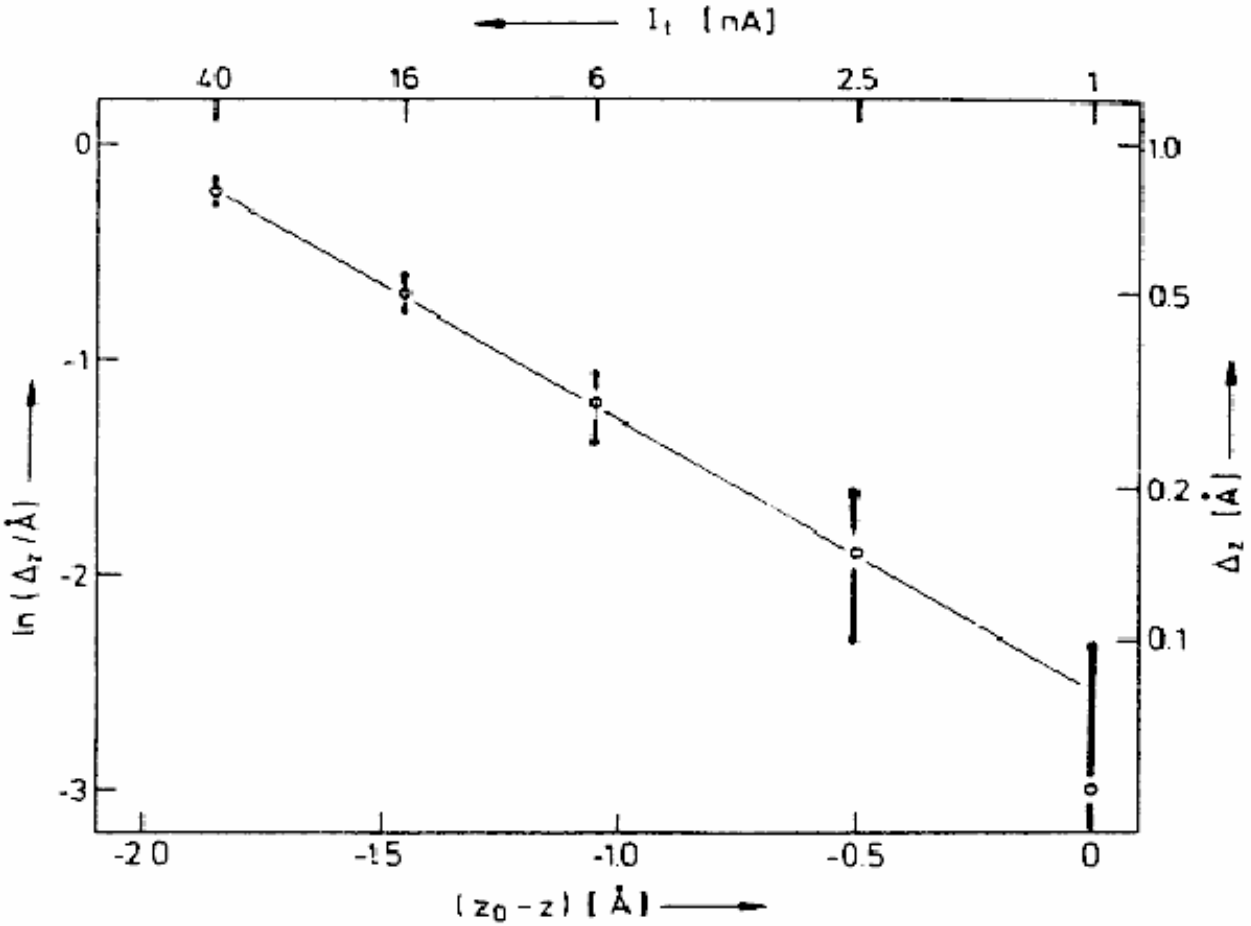
Corrugation amplitude observed on Al(111)

As large as 0.6 Å, more than 10 times greater than that of LDOS contour.

Critically depends on tip status.

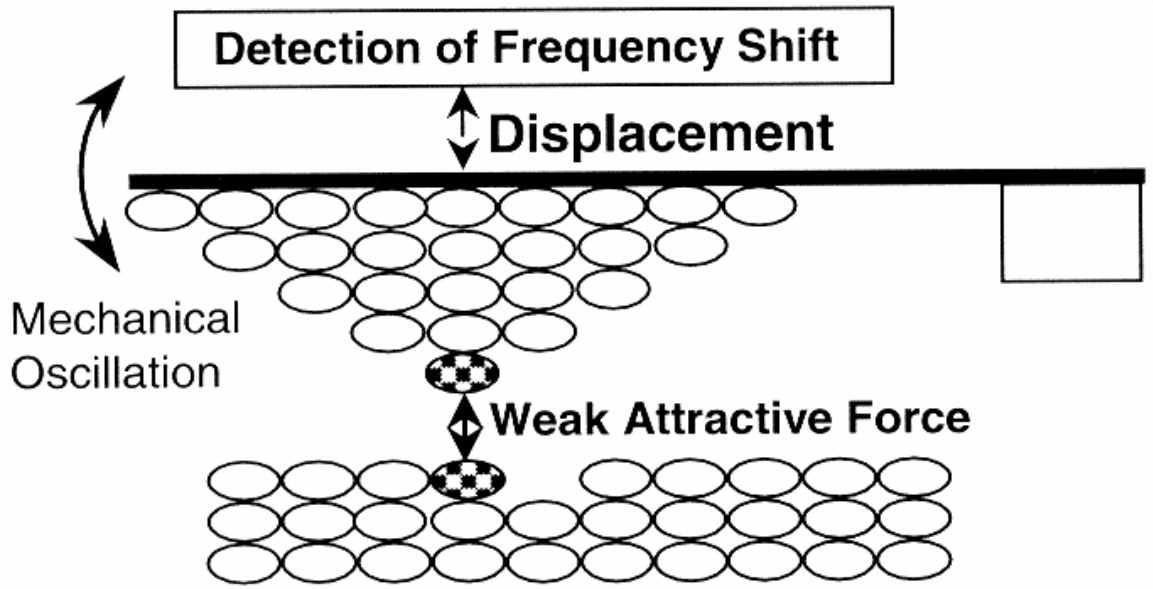
Exponentially depends on tip-sample distance.

Wintterlin et al., ***Phys. Rev. Lett.*** **62,** 59 (1989).



Non-Contact Atomic Force Microscopy (NC-AFM)

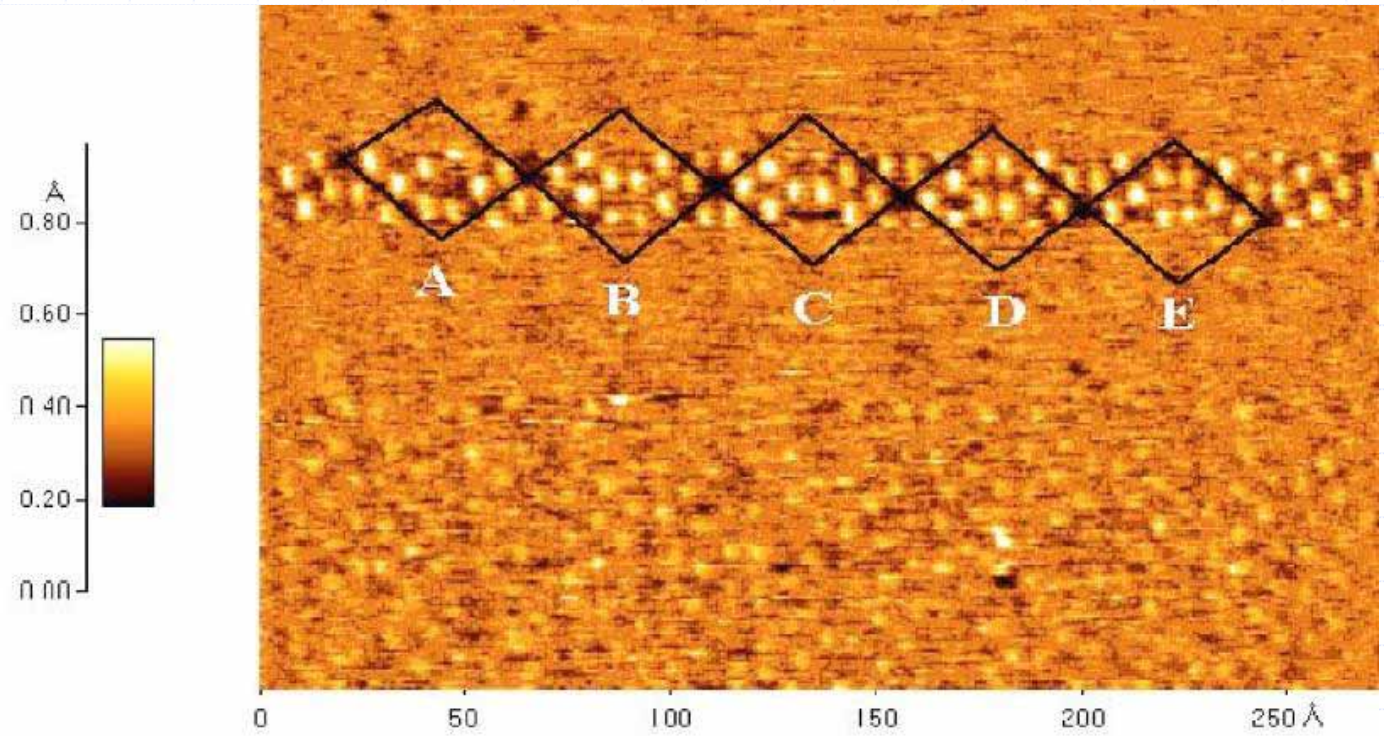
Using frequency-modulation method to detect weak attractive atomic force thus to obtain atomic images.



Noncontact Atomic Force Microscopy, **Eds. Morita, Wiesendanger, and Meyer, Springer 2002, page 3.**

Atom-resolved NC-AFM image of Si(111)7x7

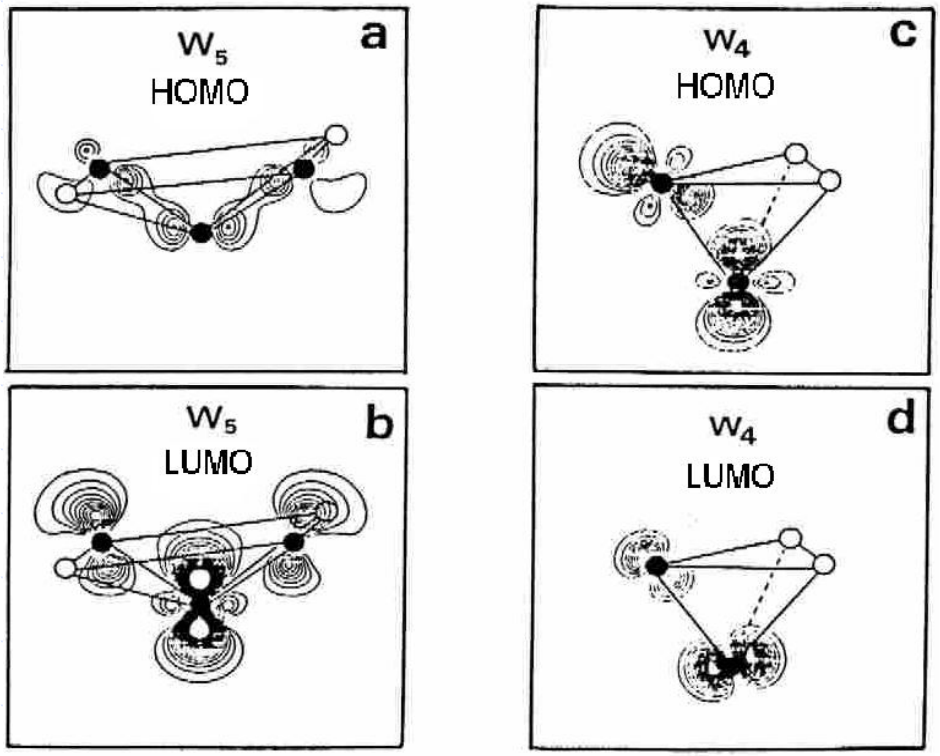
The image changes abruptly from time to time, showing the effect of tip condition changes.



F. Giessibl, Science, Vol 267, 68 (1995).

Tip states: First-principle computations

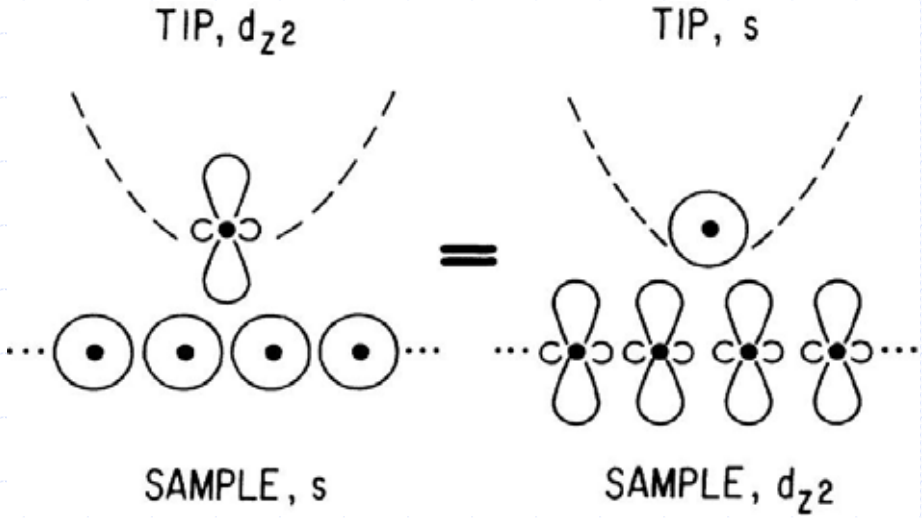
By modeling the tip as W clusters, Ohnishi and Tsukada found that the tip states near Fermi level are dominated by *d*-type wavefunctions.



Ohnishi and Tsukada, Solid State Commun. 71, 391 (1989).

Effect of atomic-scale tip electronic states

Conceptually, the effect of tip states can be understood in light of the *reciprocity principle* : At microscopic scale, an image may be interpreted either as probing the sample state with a tip state, or as probing the tip state with a sample state.



Tunneling matrix elements: the derivative rule

The tunneling matrix elements, needed to compute tunneling current, follow a very simple derivative rule:

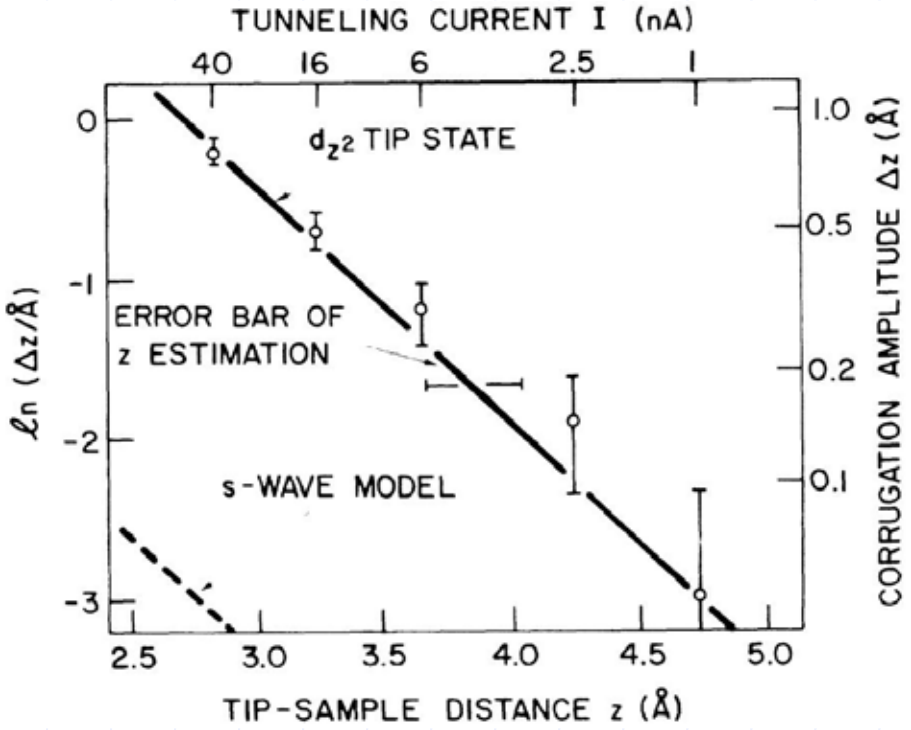
Tip state	Matrix element
s	$\frac{2\pi C\hbar^2}{\kappa m}\psi(\mathbf{r}_0)$
p_z	$\frac{2\pi C\hbar^2}{\kappa m}\frac{\partial\psi}{\partial z}(\mathbf{r}_0)$
p_x	$\frac{2\pi C\hbar^2}{\kappa m}\frac{\partial\psi}{\partial x}(\mathbf{r}_0)$
p_y	$\frac{2\pi C\hbar^2}{\kappa m}\frac{\partial\psi}{\partial y}(\mathbf{r}_0)$
d_{zx}	$\frac{2\pi C\hbar^2}{\kappa m}\frac{\partial^2\psi}{\partial z\,\partial x}(\mathbf{r}_0)$
d_{zy}	$\frac{2\pi C\hbar^2}{\kappa m}\frac{\partial^2\psi}{\partial z\,\partial y}(\mathbf{r}_0)$
d_{xy}	$\frac{2\pi C\hbar^2}{\kappa m}\frac{\partial^2\psi}{\partial x\,\partial y}(\mathbf{r}_0)$
$d_{z^2-\frac{1}{3}r^2}$	$\frac{2\pi C\hbar^2}{\kappa m}\left(\frac{\partial^2\psi}{\partial z^2}-\frac{1}{3}\kappa^2\psi\right)(\mathbf{r}_0)$
$d_{x^2-y^2}$	$\frac{2\pi C\hbar^2}{\kappa m}\left(\frac{\partial^2\psi}{\partial x^2}-\frac{\partial^2\psi}{\partial y^2}\right)(\mathbf{r}_0)$

Quantitative analysis of Al(111) STM images

By assuming a d_{z^2} atomic state on a W tip, the experimental data of corrugation vs. distance is recovered with no adjustable parameters.

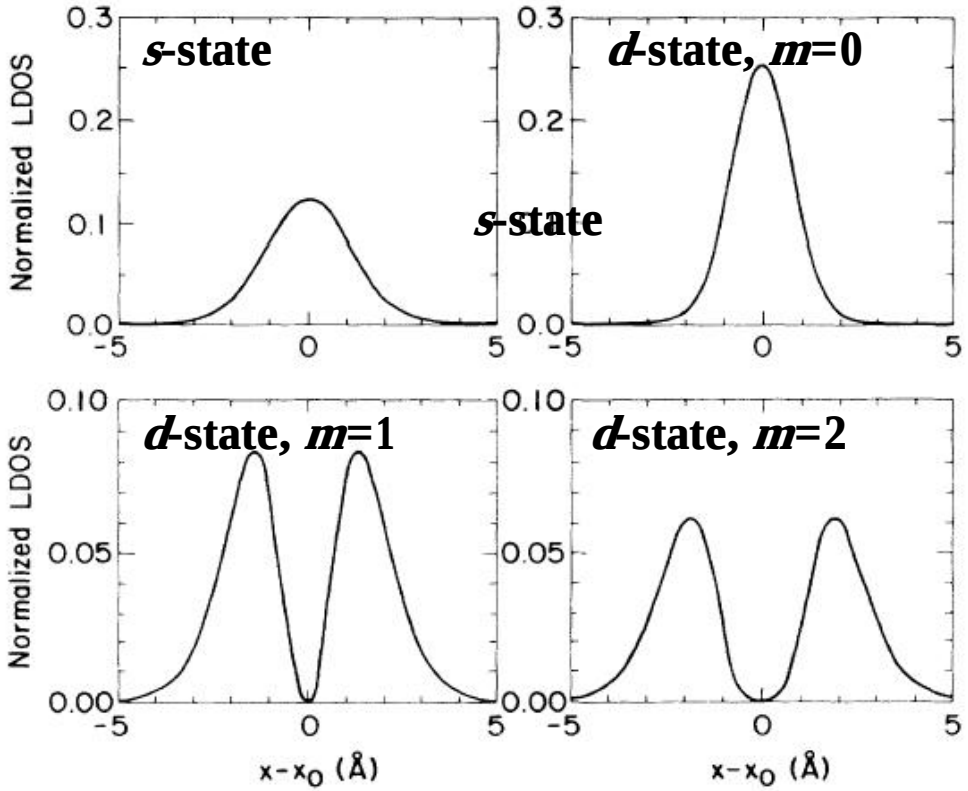
The d_{z^2} tip state enhances the corrugation amplitude by a factor of 20 over LDOS corrugation.

Exponential dependence of corrugation amplitude on tip-sample distance fully explained.



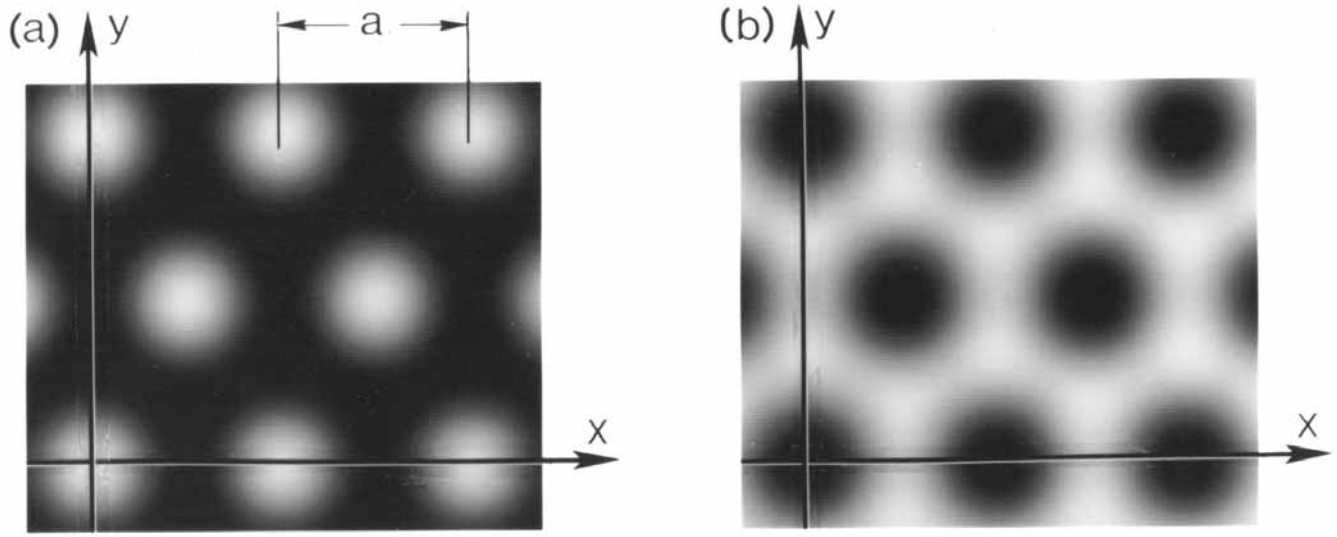
Effect of $m \neq 0$ tip states: Corrugation reversal

Near the Fermi level, if one of the *d*-states dominates, the image can be positive or reversed.



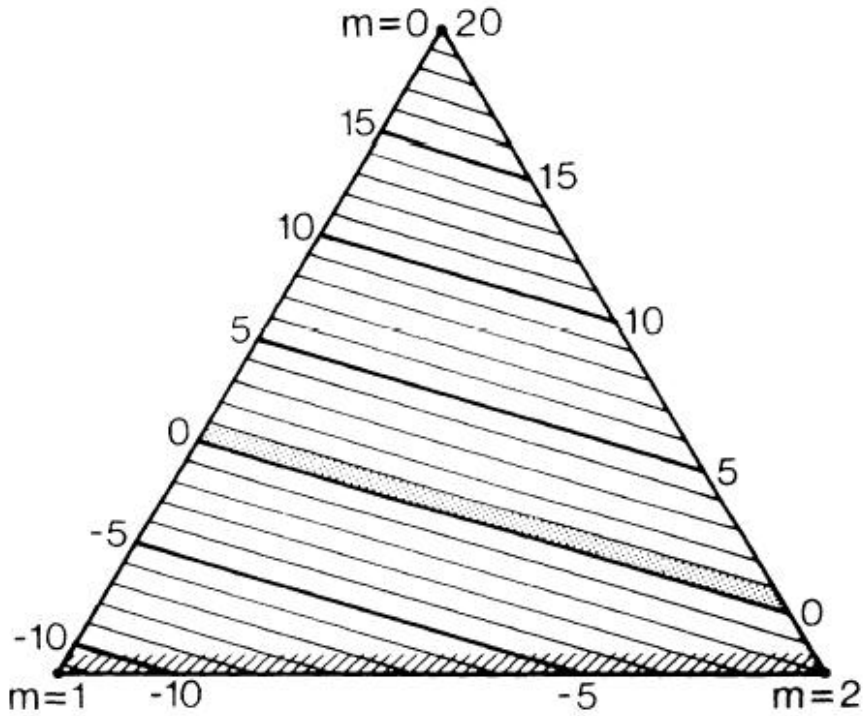
Effect of $m \neq 0$ tip states: Corrugation reversal

Mathematically, the phenomena of corrugation reversal can be described by hexagonal cosine functions,



Effect of $m \neq 0$ tip states: Corrugation reversal

According to the composition of the tip states near the Fermi level, various corrugation enhancements (positive or negative) can occur.



Theoretical and experimental verifications

First-principle computation of tip electronic states.

First-principle computation of surfaces electronic structures and STM images with regard to tip states.

Experimental verifications of the theoretical STM images computed with different tip electronic states.

Experimental observations of tip electronic states by NC-AFM and STM.

First-Principle Computation of STM Tip Electronic States (1)

J. Phys.: Condens. Matter 7 (1995) 6625–6640.

The electronic structure and stability of transition metal nanotips—part I

H Ness† and F Gautier‡

† Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK
‡ IPCMS–GEMME, Bâtiment 69, 23 rue du Loess, 67037 Strasbourg, France

The roles of the atomic and electronic structure of nanotips on STM images were first pointed out by Ohnishi and Tsukuda [12]. They find that the current is primarily generated by the d_{z^2} tip state considered above.

On the other hand, Chen has calculated explicitly the tunnelling matrix elements, used in the Bardeen approach, for different tip states [14]. These matrix elements are found to be proportional to the partial derivatives of the unperturbed sample wave functions taken at the position r_0 of the tip. Using his 'derivative rule' for model simple metals, Chen has found that the contribution of p_z and d_{z^2} tip orbitals yields an enhancement of the corrugation compared to s states [14]. This is assumed to be a possible explanation for the high corrugation observed on compact metal surfaces. Within his framework, Chen also obtains, as observed in some STM images, a contrast inversion when an $m \neq 0$ state dominates the tip states near ε_F over $m = 0$ (p_z of d_{z^2}) state [15].

These two last models emphasize the importance of the electronic structure of nanotips for the understanding of STM images.

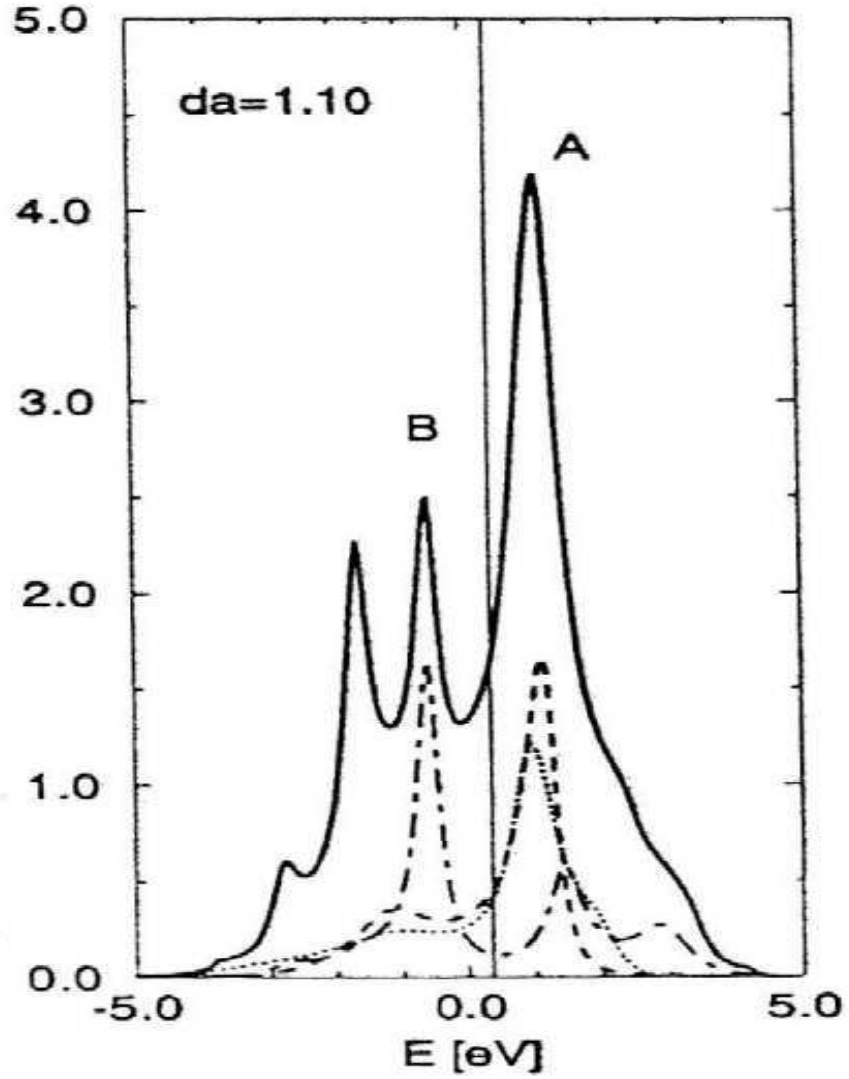
First-Principle Computation of STM Tip Electronic States (1)

J. Phys.: Condens. Matter 7 (1995) 6625–6640. H Ness† and F Gautier‡

DOS of a W(100) tip:

Peak A comes mainly from
d_{z2} and d_{x2-y2} states,
….. d_{z2}
----- d_{x2-y2}

Peak B comes mainly from
d_{xy} orbital
-.-.- d_{xy}



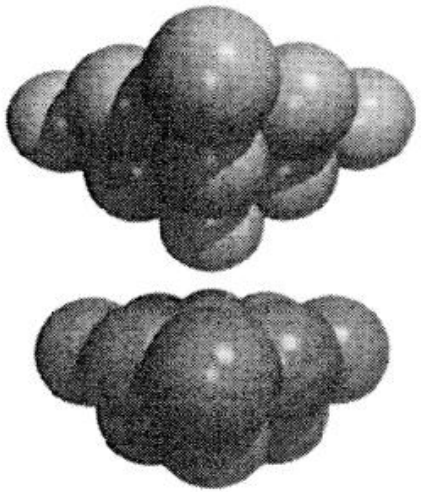
First-Principle Computation of STM Tip Electronic States (2)

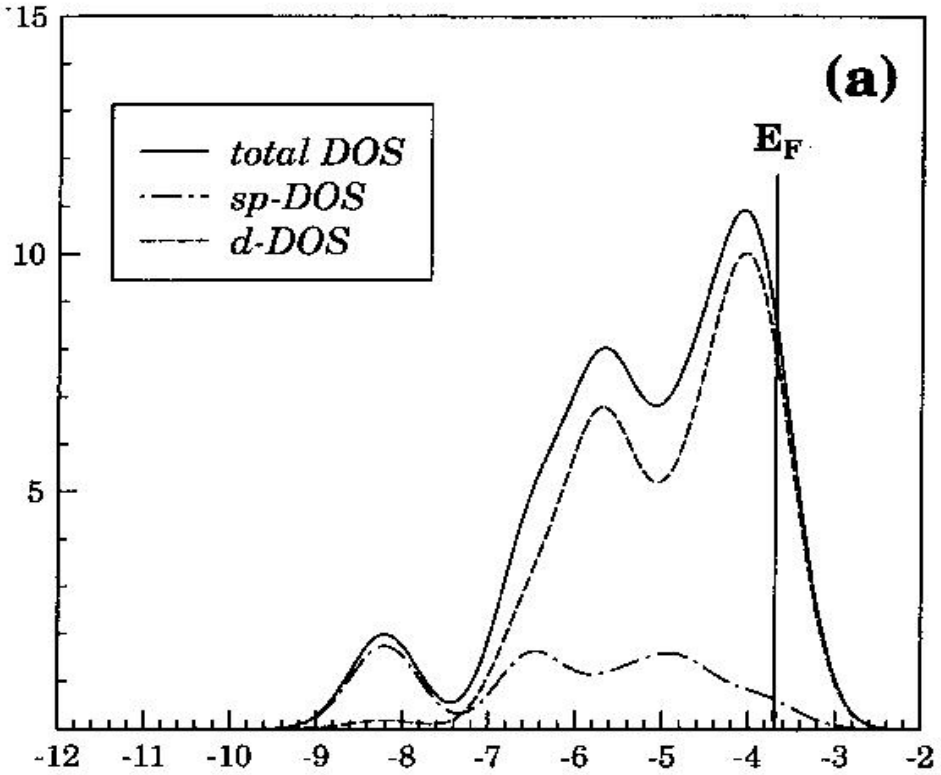
ELSEVIER

Journal of Physics and Chemistry of Solids 60 (1999) 681–688

Cluster-model density functional study of a W–Cu(1 0 0) STM junction

L. Lamare[a,*], H. Aourag[b], J.-P. Dufour[a]





First-Principle Computation of STM Tip Electronic States (2)

ELSEVIER

Journal of Physics and Chemistry of Solids 60 (1999) 681–688

Cluster-model density functional study of a W–Cu(1 0 0) STM junction

L. Lamare[a,*], H. Aourag[b], J.-P. Dufour[a]

5. Conclusions

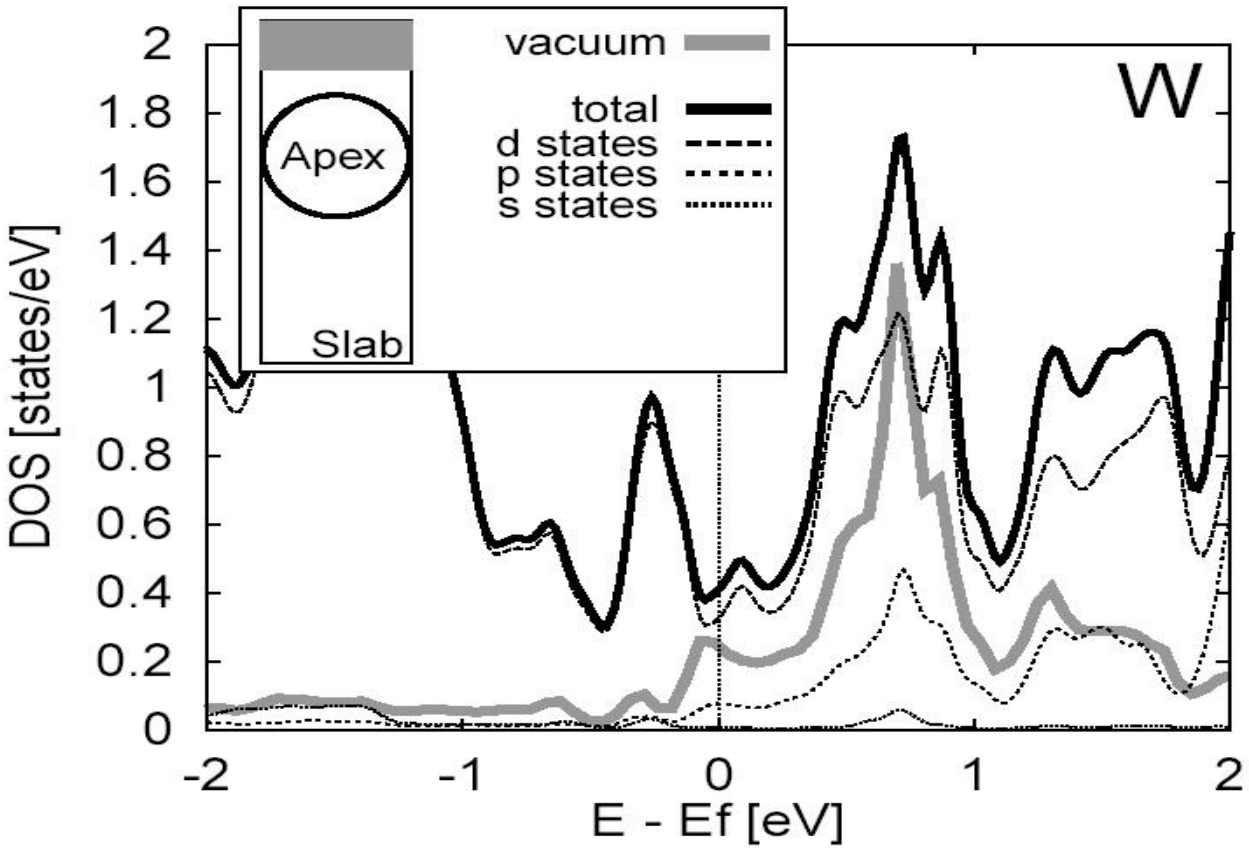
This study shows that the electronic properties of the W and Cu clusters in the W–Cu tip–sample interacting systems are very near of those of the corresponding isolated clusters when the tip–sample separation d is equal to 4 Å, whereas strong electronic coupling effects are observed when d is reduced to 1 Å. In addition, the electronic density analysis emphasizes the major role played by the W-5d atomic tip states, especially the $5d_{z^2}$ state, in the tip–sample interactions and confirms the Chen's results [13].

First-Principle Computation of STM Tip Electronic States (3)

Solid State Communications 113 (2000) 245–250

Modeling STM tips by single absorbed atoms on W(100) films: 5d transition metal atoms

W.A. Hofer[a,*], J. Redinger[a], P. Varga[b]



First-Principle Computation of STM Tip Electronic States (3)

Solid State Communications 113 (2000) 245–250

Modeling STM tips by single absorbed atoms on W(100) films: 5d transition metal atoms

W.A. Hofer[a,*], J. Redinger[a], P. Varga[b]

It has long been suspected that the contamination of a scanning tunneling microscope (STM) tip with single atoms of the sample surface or adsorbates may play a key role in STM imaging. However, till recently the theoretical models used, e.g. the Tersoff–Hamann model [1], rather simple models of the STM tip. The first step towards more realistic models of the tip was due to Chen [2], who demonstrated the effect of p-and d-like tip states on the corrugation of sample surfaces.

In all cases the contributions of the s-band were fairly insignificant. The result suggests that STM tips contaminated with a 5d transition metal atom will measure currents and corrugations that deviate from the usual results calculated with the Tersoff–Hamann model.

First-Principle Computation of STM Tip Electronic States (4)

PHYSICAL REVIEW B, VOLUME 64, 125108

Modeling STM tips by single absorbed atoms on W(100) films: 3*d* and 4*d* transition-metal atoms

W. A. Hofer* J. Redinger R. Podloucky

(Received 9 March 2001; published 6 September 2001)

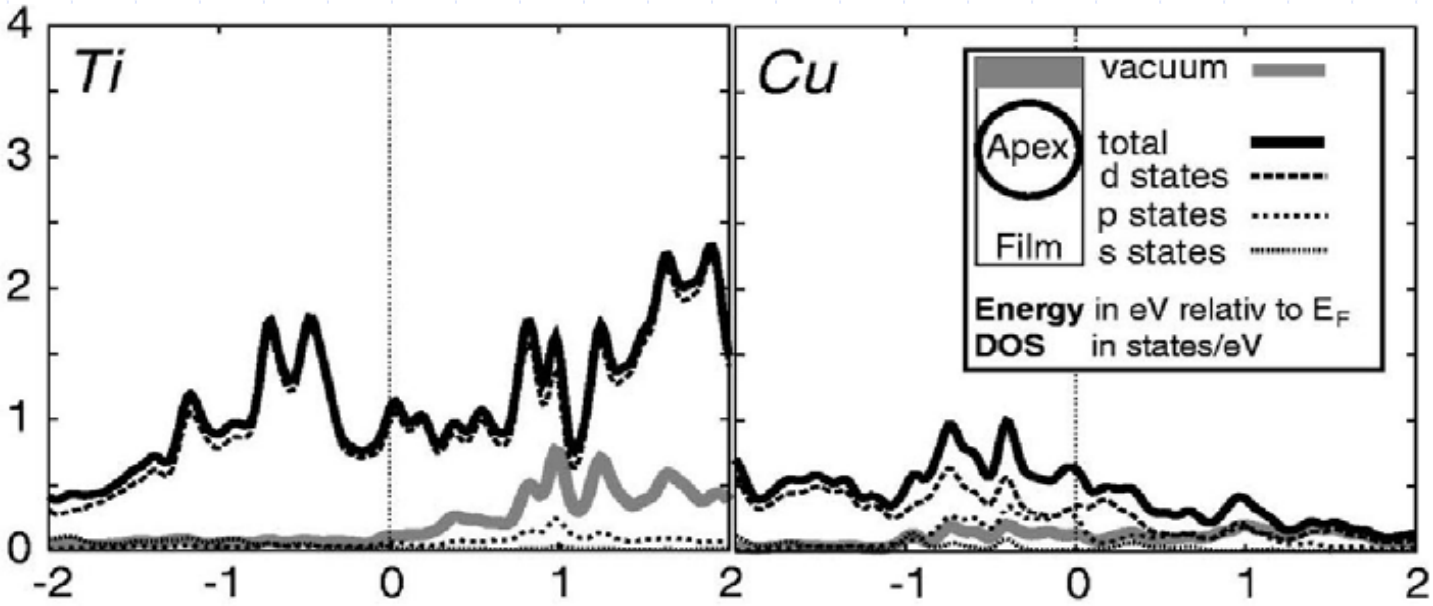


FIG. 1. 3*d* elements, paramagnetic apex atoms: DOS in the apex atom and in the vacuum. The contributions in the apex atom are given for the Kohn-Sham *s*, *p*, and *d* states; we observe predominant *d* contributions for all atoms.

First-Principle Computation of STM Tip Electronic States (4)

PHYSICAL REVIEW B, VOLUME 64, 125108

Modeling STM tips by single absorbed atoms on W(100) films: 3*d* and 4*d* transition-metal atoms

W. A. Hofer* J. Redinger R. Podloucky

(Received 9 March 2001; published 6 September 2001)

In all cases we found a dominance of *d* states in the apex atom for the energy range considered (−2 eV to +2 eV). In contrast to the simple Tersoff-Hamann model the LDOS of the tip in the vacuum region above the sample surface depends on the energy interval considered as well as the specific tip atom. In most cases we found a composition of p_z and d_{z^2} like states dangling out of the tip atom and decaying exponentially for larger vertical distances.

Non-perturbative Theory of STM Images wrt Tip States

PHYSICAL REVIEW B VOLUME 61, NUMBER 11 15 MARCH 2000-I

Tip orbitals and the atomic corrugation of metal surfaces in scanning tunneling microscopy

William Sacks
Groupe de Physique des Solides, Universités Paris 7 et Paris 6, Unité Mixte de Recherche C.N.R.S. (UMR 75 88), 2 place Jussieu, 75251 Paris Cedex 5, France
(Received 27 July 1999)

When atomic resolution is achieved, the scanning tunneling microscope (STM) image of a dense metal surface shows a giant amplitude, i.e., between one and two orders of magnitude larger than expected from an *s*-wave tip. To date, no satisfactory explanation has been given. Using our earlier nonperturbative formalism for the tunnel current, we reconsider the corrugation problem with a single atom tip having *s*, *p*, or *d* orbitals, or a combination. Particular emphasis is on the value of the corrugation as a function of the tunnel resistance $\Delta_{l,m}(R)$. Results show that the corrugation, observed over the wide range $(10^5-10^8\Omega)$, is inconsistent by nearly two orders of magnitude with the *s*-orbital theory, and by one order of magnitude with the d_{z^2} one. We also can put aside tip-surface interactions. Tip states, such as p_z and d_{z^2}, give basically *s*-wave behavior in $\Delta_{l,m}(R)$. However, those with axial symmetry, such as $d_{xz}+id_{yz}$ and having a nodal line orthogonal to the surface, give an enhanced corrugation. Finally, in tip states with a nodal plane, such as $d_{x^2-y^2}$, the enhancement effect is much more pronounced. Identical results are obtained by considering separately the nearly free electron model, and a new method of atomic orbital superposition, for the metal surface.

Non-perturbative Theory of STM Images wrt Tip States

PHYSICAL REVIEW B VOLUME 61, NUMBER 11 15 MARCH 2000-I

Tip orbitals and the atomic corrugation of metal surfaces in scanning tunneling microscopy

William Sacks

tip state	$\hat{\mathcal{D}}_{l,m}$	$\lvert f_{l,m}(\mathbf{k})\rvert^2$	$a_{l,m}(z)$
s	$\sqrt{4\pi}$	4π	$\frac{1}{\kappa z}$
d_{z^2}	$-\frac{\sqrt{5\pi}}{\kappa^2}\left(3\frac{\partial^2}{\partial z^2}-\kappa^2\right)$	$\frac{5\pi}{\kappa^4}(3\alpha_k^2-\kappa^2)$	$\frac{5}{\kappa z}$
$d_{xz}+id_{yz}$	$\frac{\sqrt{30\pi}}{\kappa^2}\left(\frac{\partial}{\partial x}-i\frac{\partial}{\partial y}\right)\frac{\partial}{\partial z}$	$\frac{30\pi}{\kappa^4}k^2\alpha_k^2$	$\frac{15}{2}\frac{1}{(\kappa z)^2}$
d_{xy}	$2\frac{\sqrt{15\pi}}{\kappa^2}\frac{\partial^2}{\partial x\,\partial y}$	$\frac{60\pi}{\kappa^4}k_x^2k_y^2$	$\frac{15}{4}\frac{1}{(\kappa z)^3}$
$d_{x^2-y^2}$	$\frac{\sqrt{15\pi}}{\kappa^2}\left(\frac{\partial^2}{\partial x^2}-\frac{\partial^2}{\partial y^2}\right)$	$\frac{15\pi}{\kappa^4}(k_x^2-k_y^2)^2$	$\frac{15}{4}\frac{1}{(\kappa z)^3}$

First-Principle Computation of STM Images wrt Tip States (1)

PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

Charge-density oscillations on Be($10\bar{1}0$): Screening in a non-free two-dimensional electron gas

B. G. Briner
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

Ph. Hofmann*
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin;
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37888;
and Oak Ridge National Laboratories, Oak Ridge, Tennessee 37800-1501

M. Doering and H.-P. Rust
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

E. W. Plummer
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37888
and Oak Ridge National Laboratories, Oak Ridge, Tennessee 37800-1501

A. M. Bradshaw
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin
(Received 30 April 1998)

First-Principle Computation of STM Images wrt Tip States (1)

PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

The *s*-wave approximation predicts a strong suppression of higher-order Bloch components in STM images. It cannot explain that the atomic lattice corrugation on metals is resolved in the STM. This shortcoming has led Chen to propose that the probe tip should rather be described by a *p* or a *d* orbital.[43] In the following we shall use Chen's expression for a *d* wave tip,

$$I_{T,d}(\mathbf{r}_\parallel, z_0) = \text{const} \times \int |M_{d_z}|^2 d^2\mathbf{k}_{||}$$

$$= \text{const} \times \int \left| \frac{\partial^2 \psi(\mathbf{r}_\parallel, z_0)}{\kappa^2 \partial z^2} - \frac{1}{3}\psi(\mathbf{r}_\parallel, z_0) \right|^2 d^2\mathbf{k}_{||} \,. \tag{12}$$

A tunnel current image is finally obtained by numerically evaluating Eq. (12). Typical results of such model calculations are displayed in Fig. 9. Considering the simplicity of our model the overall agreement between theory and experiment is very satisfactory.

First-Principle Computation of STM Images wrt Tip States (2)

PHYSICAL REVIEW B VOLUME 58, NUMBER 24 15 DECEMBER 1998-II

Prediction of bias-voltage-dependent corrugation reversal for STM images of bcc (110) surfaces: W(110), Ta(110), and Fe(110)

S. Heinze
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany
and Zentrum für Mikrostrukturforschung, Universität Hamburg, D-20355 Hamburg, Germany

S. Blügel*
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

R. Pascal, M. Bode, and R. Wiesendanger
Zentrum für Mikrostrukturforschung, Universität Hamburg, D-20355 Hamburg, Germany
(Received 15 July 1998)

The STM analysis is carried out within the *s*-orbital tip-model of Tersoff and Hamann. The enhancement of the corrugation amplitude due to p_z- and d_{z^2}-type tip-orbitals are determined. We show that the enhancement factors calculated are close to the analytic factors given by Chen. [S0163-1829(98)04347-1]

First-Principle Computation of STM Images wrt Tip States (2)

PHYSICAL REVIEW B VOLUME 58, NUMBER 24 15 DECEMBER 1998-II

S. Heinze S. Blügel R. Pascal, M. Bode, and R. Wiesendanger

Although we think that the *s*-orbital tip model is sufficient for the qualitative understanding of the STM image on the basis of the electronic structure it fails, however, to explain the experimentally observed corrugation amplitude quantitatively. Chen[19] has generalized the *s*-orbital tip model to arbitrary orbital symmetries. He derived the so-called *derivative rule* (see below). We apply the derivative rules directly in *ab initio* calculations in order to estimate the influence of the tip states on the STM image and to compare the calculated corrugation amplitude quantitatively with the experiment.

First-Principle Computation of STM Images wrt Tip States (2)

PHYSICAL REVIEW B VOLUME 58, NUMBER 24 15 DECEMBER 1998-II

S. Heinze S. Blügel R. Pascal, M. Bode, and R. Wiesendanger

Tip-state enhancement according to first-Principle computation

Tip-state enhancement according to analytical formulae.

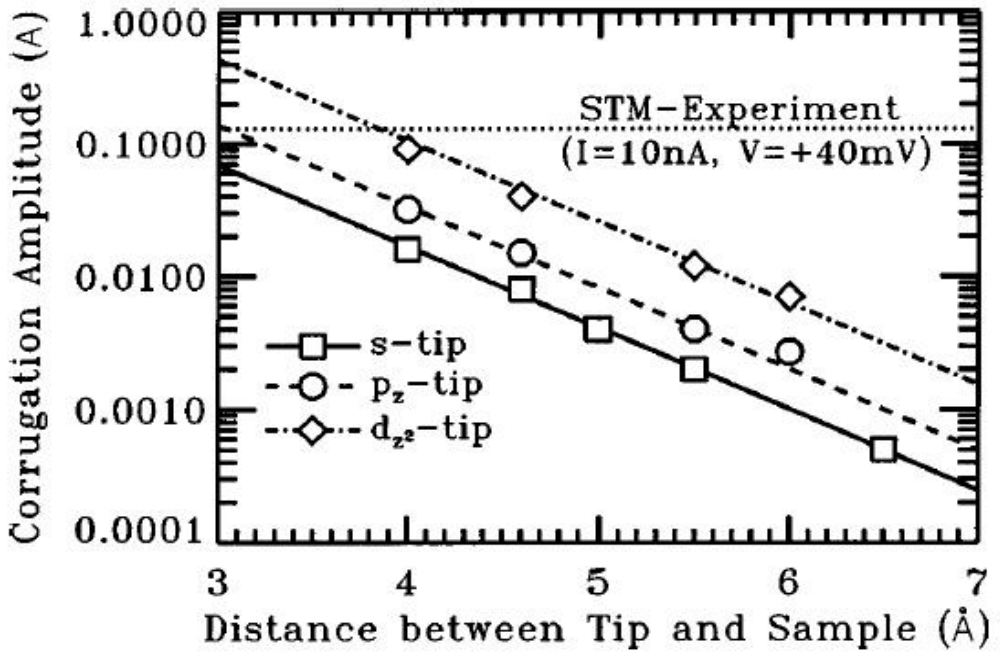
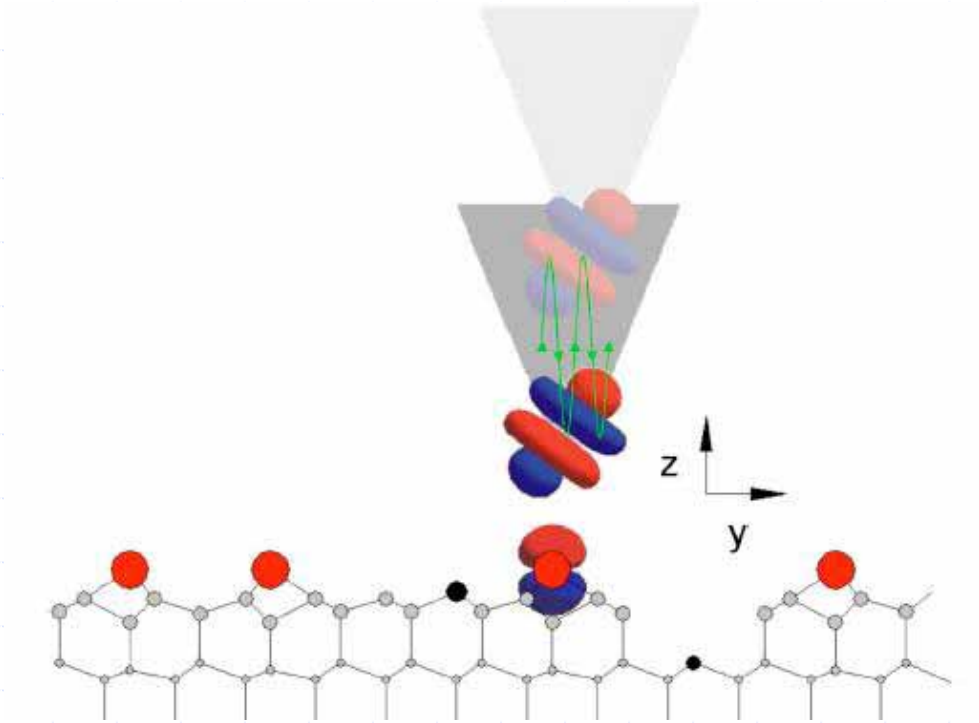


FIG. 4. Corrugation amplitude as function of the tip-sample distance for three different orbital symmetries of the tip state. Using Chen's derivative rule (Ref. 19) the corrugation amplitudes for *s*-, p_z-, and d_{z^2}-type tip orbitals have been calculated. The dashed and dotted-dashed lines are given by the interpolated values of the *s*-type tip multiplied by Chen's enhancement factors (Ref. 19) for a p_z and d_{z^2} tip, respectively.

Tip Electronic States Imaged by STM (1)

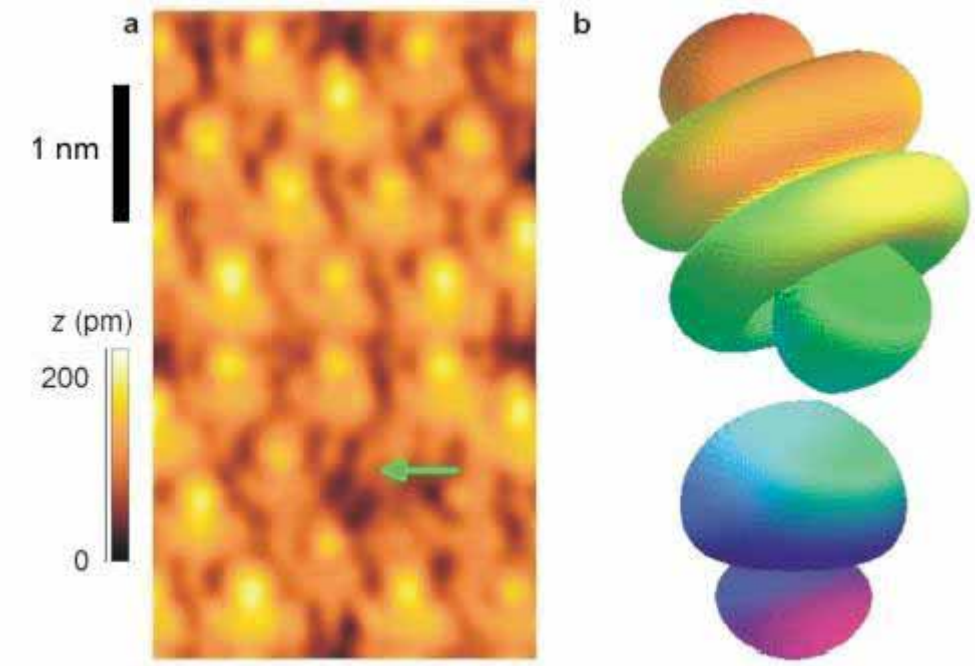
Using a vibrating STM tip to prevent tip crashing, STM can image tip electronic states in great details.



Herz, Giessibl, and Mannhart, Phys. Rev. B 68, 045301 (2003).

Tip Electronic States Imaged by STM (2)

Using Si(111)7X7 as sample, Co_6Fe_3Sm as tip, a 4f orbital of an Sm atom is resolved in real space.



Herz, Giessibl, and Mannhart, Phys. Rev. B 68, 045301 (2003).

Case of spin-polarized STM

SP-STM has achieved great progress recently:

-- Reproducible SP-STM tip production procedures

-- Well-understood systems with surface magnetism

-- Nearly atomic resolution

Some ideas about atom-resolved SP-STM

-- Mathematical formulation of tip states with spin

-- Using the popular tip sharpening procedures

-- Experimental tip-state characterization:

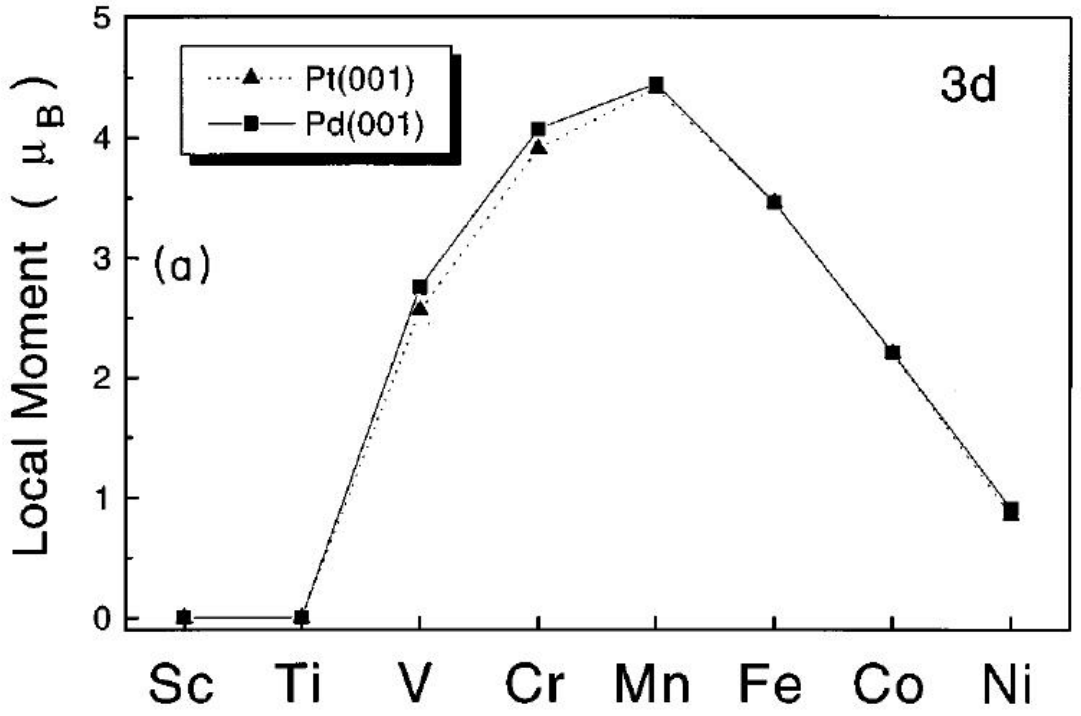
> determine z-component of spin polarization

> determine azimuth of spin polarization

> determine orbital symmetry and type

Single-atom SP-STM tip

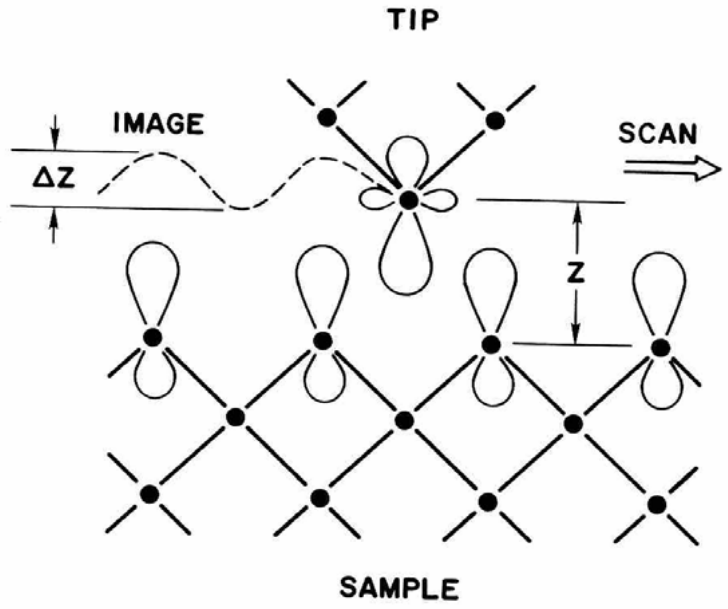
3d transition-metal atoms adsorbed on noble or refractive metal tips often show large local magnetic moments.



Stepanyuk et al., ***Phys Rev B*** **53** 2121 (1996).

A microscopic view of STM

To understand the atom-resolved STM images, we need to take an microscopic view that a single dangling bond on the tip apex is the key its true atomic resolution…



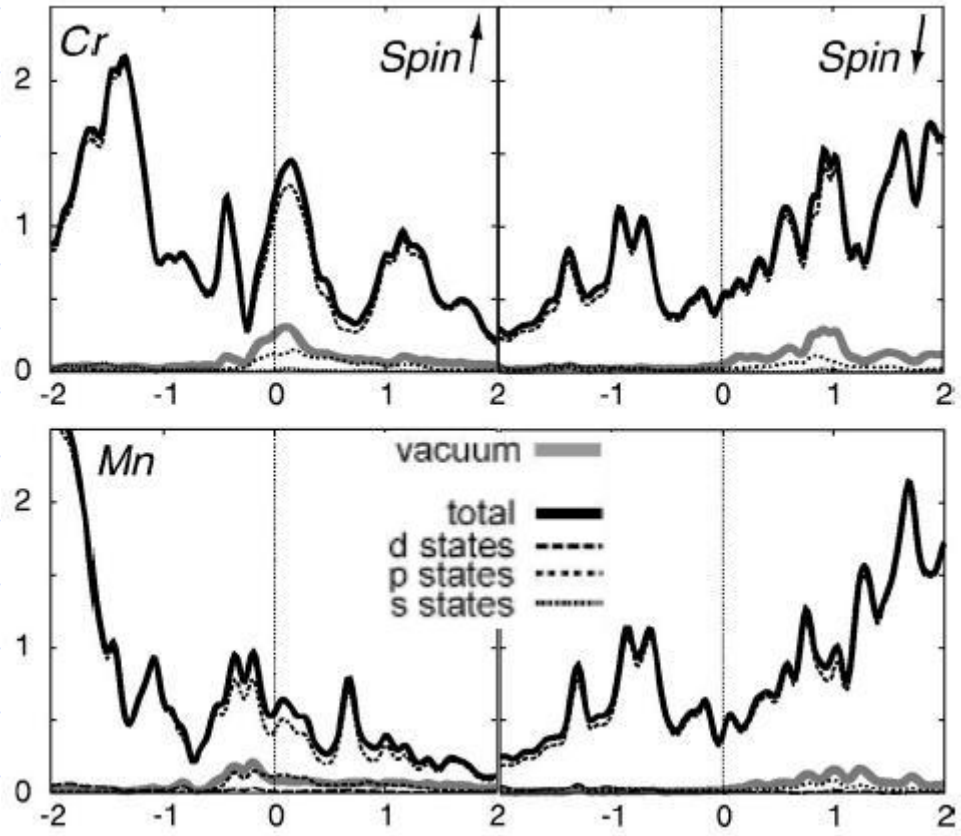
Baratoff (Presentation on Europhysics Conference, March 1983).

Electronic states of W tip with Cr or Mn adsorbed

Electronic states of STM tip: Cr or Mn atom adsorbed on W tip.

3d states dominate tip DOS.

At 0.1 to 0.4 eV below Fermi level, Mn tip state ($3d_{Z^2}$) is highly spin-polarized.

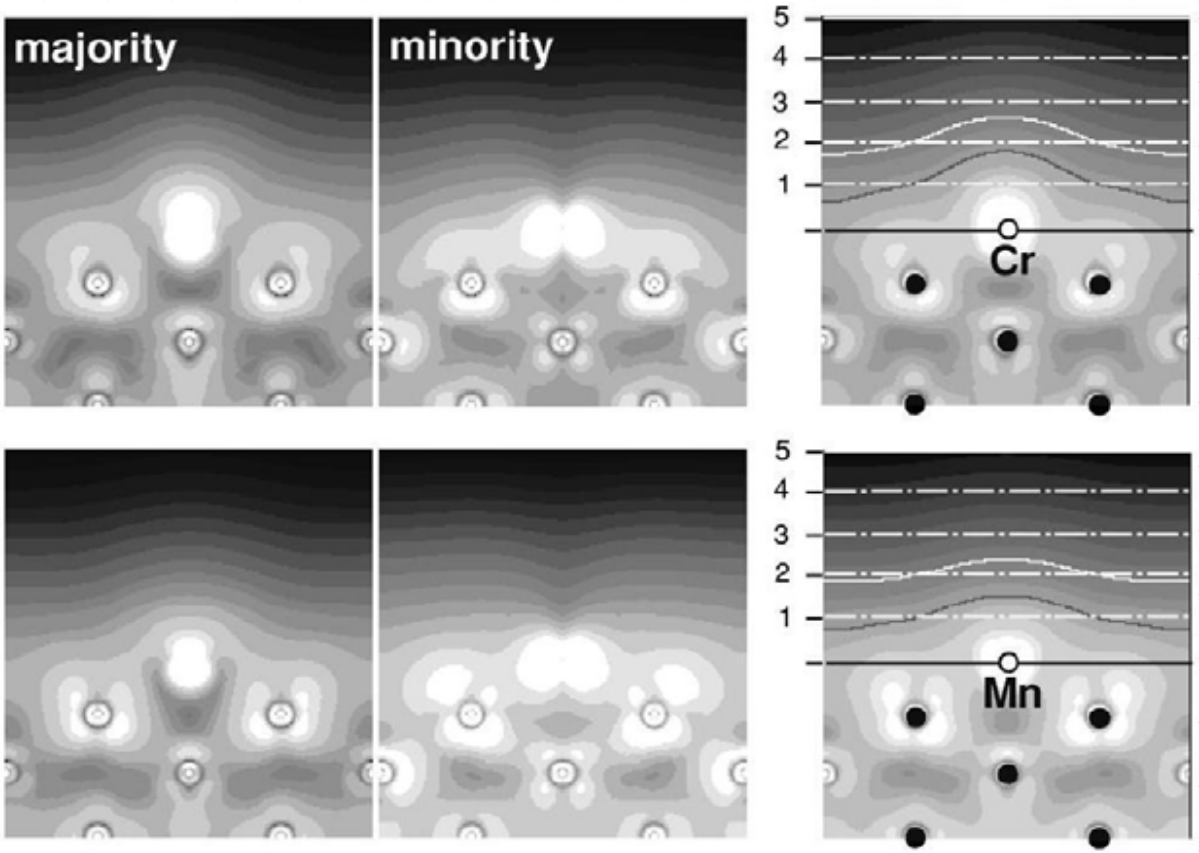


Hofer, Redinger and Podlousky, ***PRB*** **64** 125108 (2001).

Electronic states of W tip with Cr or Mn adsorbed

For both Cr and Mn, the majority tip state is d_{Z^2} type.

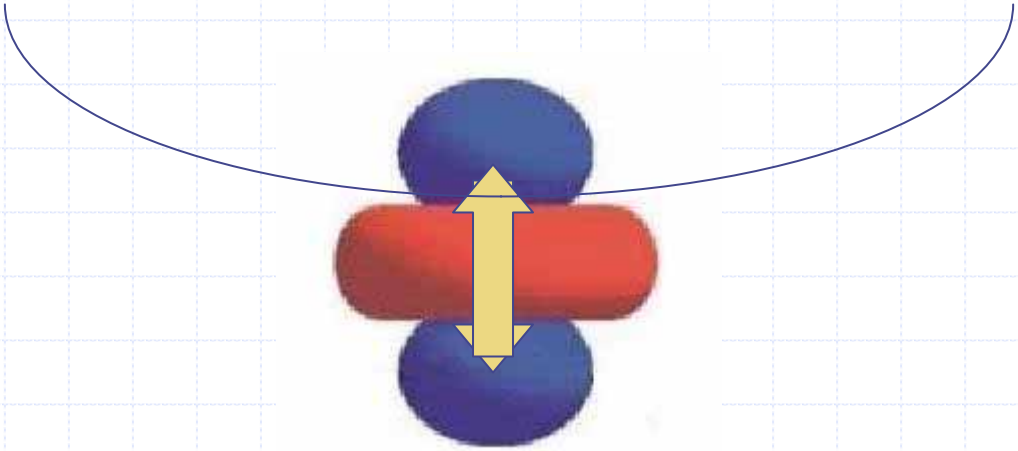
Therefore, it is possible to get spin-polarized information and atomic resolution.



Hofer, Redinger and Podlousky, ***PRB*** **64** 125108 (2001).

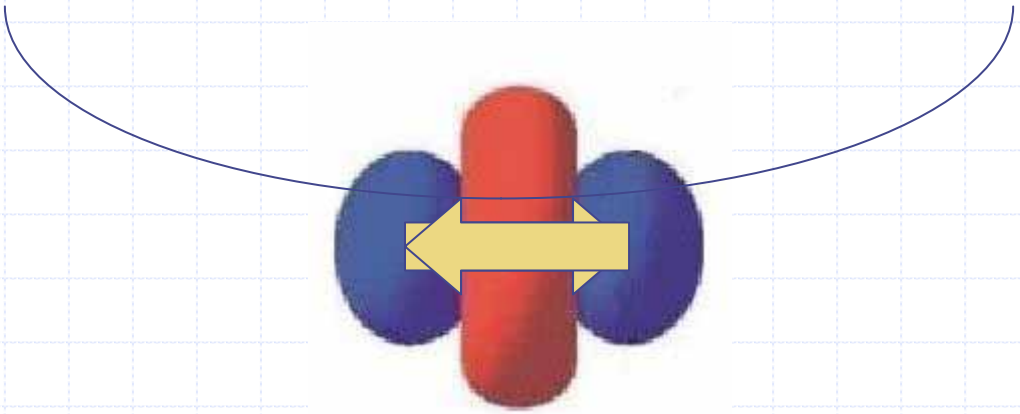
Spin-polarized single-atom STM tip

Typically made of 3d transition metals (Cr, Mn, Fe, Co, Ni), the tip states have a spin degree-of-freedom, in addition to the 5 different 3d states.



Spin-polarized single-atom STM tip

Typically made of 3d transition metals (Cr, Mn, Fe, Co, Ni), the tip states have a spin degree-of-freedom, in addition to the 5 different 3d states.



Spin-polarized single-atom STM tip

- **Typically a 3*d* atom (Cr, Mn, Fe, Co, Ni).**
- **The *d*-shell has 5 different orbital wavefunctions.**
- **Each of those has two spin-polarizations.**
- **Each of the 10 states has its energy level and spectral broadenings.**
- **Some are filled states, some are empty states.**
- **If different spin-polarized state has different energy levels, a net spin polarization exists.**
- **With a well-characterized sample, the tip states can be determined experimentally.**

Spin-polarized single-atom STM tip

A spin-polarized *d*-type tip wavefunction in the vacuum region has the general form:

$$\Psi_\sigma(\mathbf{r}) = k_2(\kappa r)\sum_{m=-2}^{2} C_{m\sigma} Y_{2m}(\theta,\varphi),$$

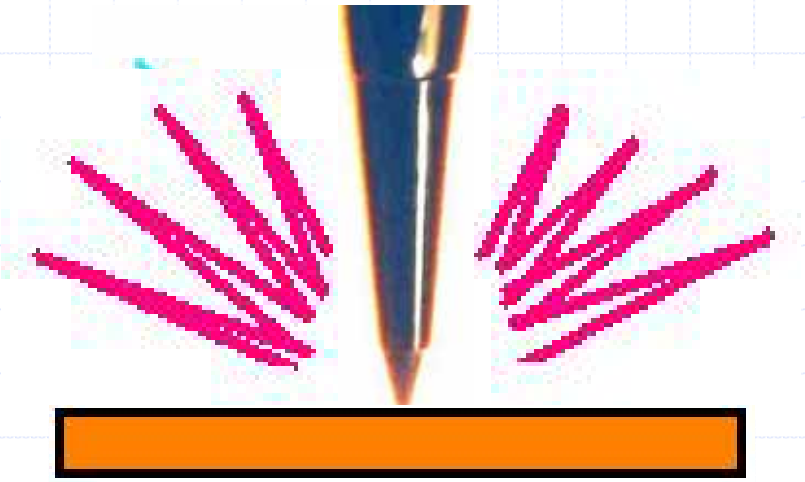
$\Psi_\sigma(\mathbf{r})$ **: a component of the spinor with spin index** σ**.**

$k_2(\kappa r)$ **: spherical modified Bessel wavefunction**

κ **: decay constant in vacuum**

$Y_{2m}(\theta,\varphi)$ **: spherical harmonics**

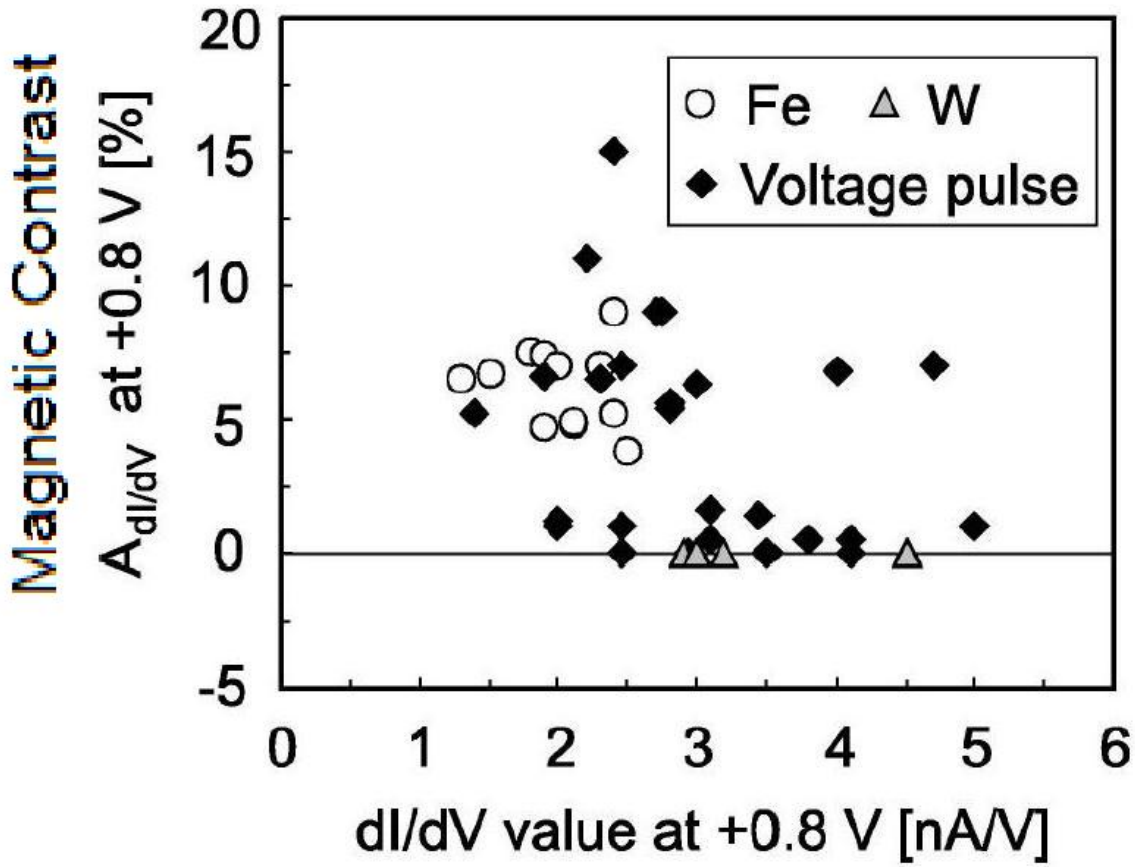
Generating spin-polarized tip using controlled collision and electrical pulses



(1) Start with a magnetic material, Cr, Mn, Fe, Gd, etc.
(2) Using a non-magnetic tip, for example W.
(3) By treat the tip with a controlled collision,
(4) or, treat the tip with an electrical pulse, a variety of magnetic contrasts can be generated.

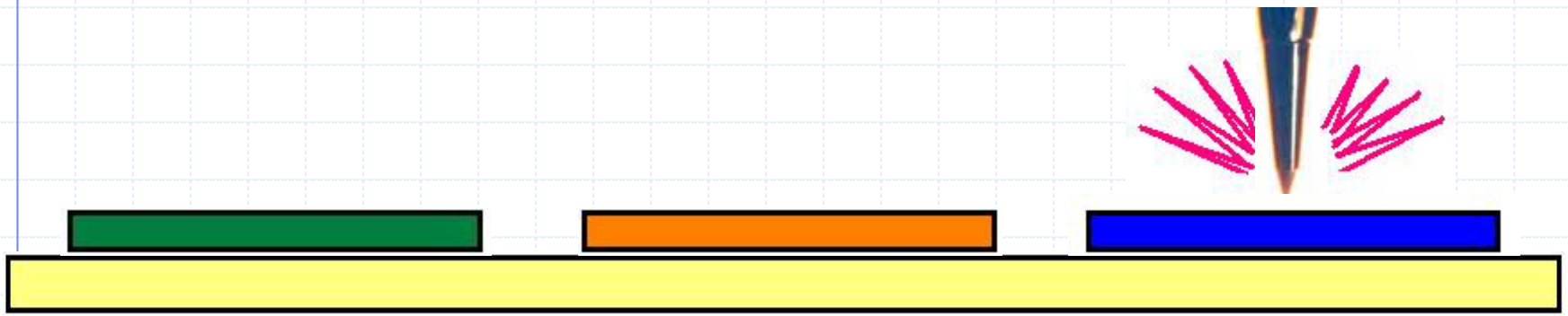
Yamada, Bishoff, Mizoguchi and van Kempen, ***Appl. Phys. Lett.*** **82** 1437 (2003).

Generating spin-polarized tip using controlled collision and electrical pulses



Yamada, Bishoff, Mizoguchi and van Kempen, ***Appl. Phys. Lett.*** **82** 1437 (2003).

SP-STM with tip characterization



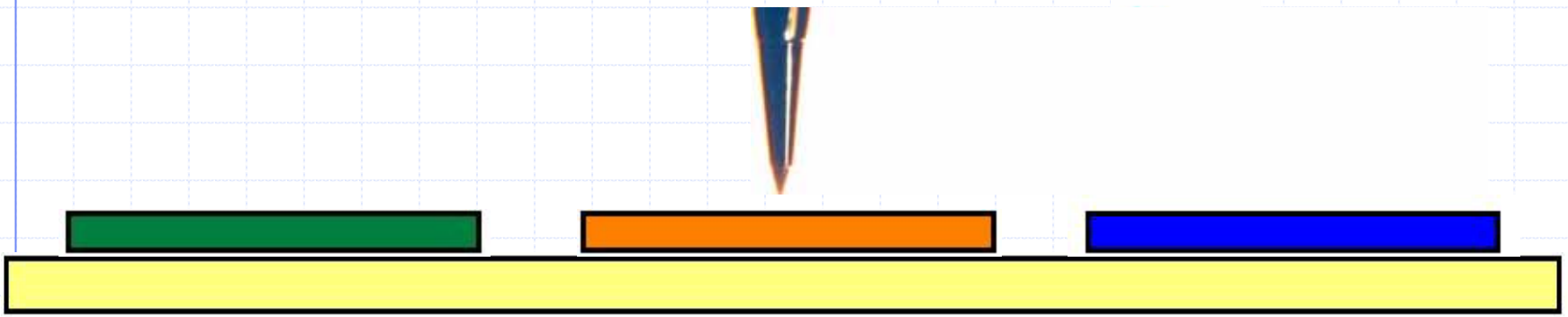
Target-sample imaging stage

Tip-characterization stage: Fe/W(110), Si(111)7X7

Tip-treatment stage: Cr, Mn, …

(1). Bring the tip to the tip-treatment stage.
(2). Treat the tip with a controlled collision.
(3). Or, treat the tip with an electrical pulse.

SP-STM with tip characterization



Target-sample imaging stage

Tip-characterization stage: Fe/W(110), Si(111)7X7

Tip-treatment stage: Cr, Mn, …

(4). Characterize the tip with a standard surface.

SP-STM with tip characterization

Target-sample imaging stage

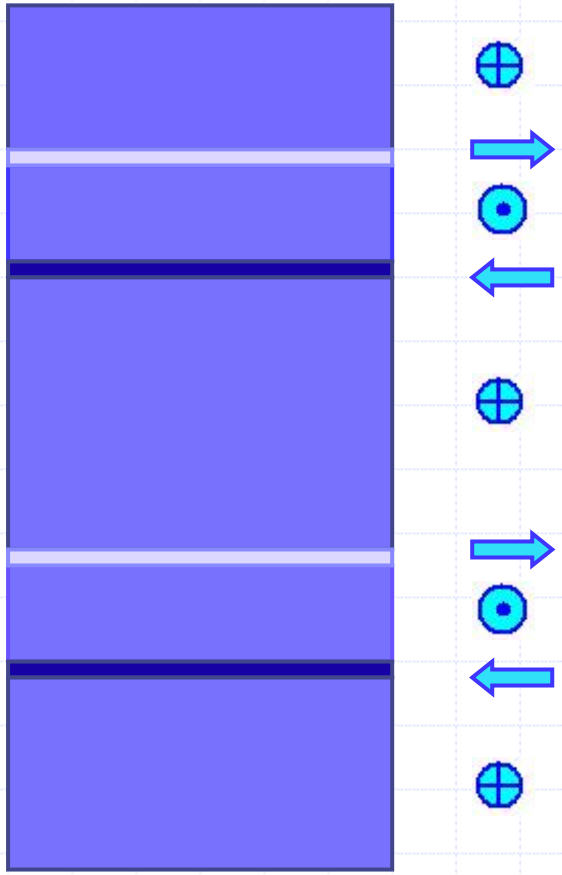
Tip-characterization stage: Fe/W(110), Si(111)7X7

Tip-treatment stage: Cr, Mn, …

(5). Using the characterized tip to probe a sample.

SP-STM tip characterization

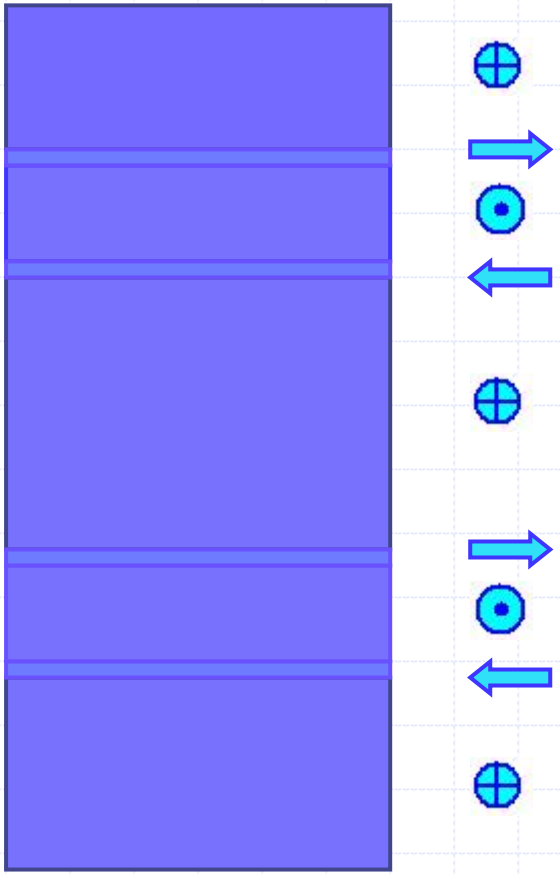
Using Fe/W(110) to determine spin polarization of tip states, with a rotating-tip STM.



Pietzsch, Kubetzka, Bode, and Wiesendanger, ***Phys. Rev. Lett.*** **84** 5212 (2000).

SP-STM tip characterization

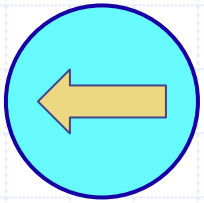
Using Fe/W(110) to determine spin polarization of tip states, with a rotating-tip STM.

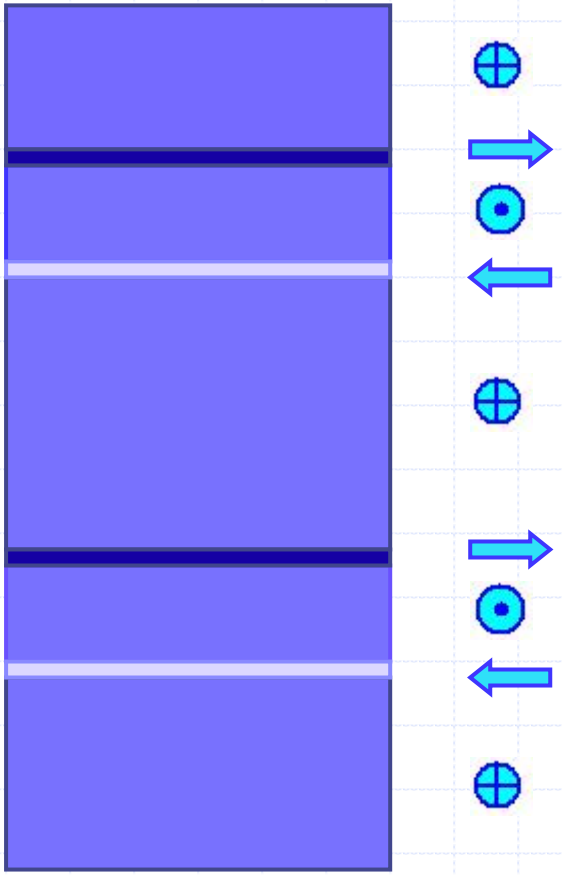


Pietzsch, Kubetzka, Bode, and Wiesendanger, ***Phys. Rev. Lett.*** **84** 5212 (2000).

SP-STM tip characterization

Using Fe/W(110) to determine spin polarization of tip states, with a rotating-tip STM.

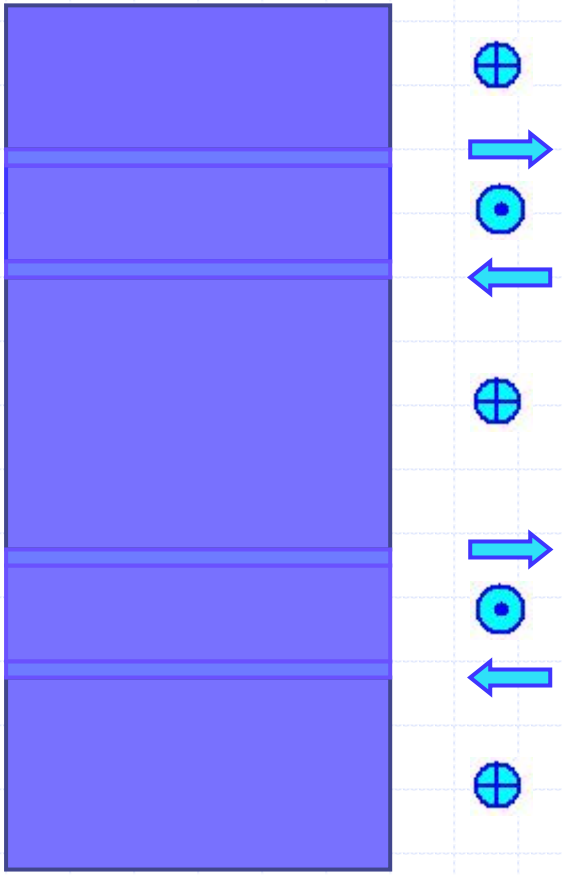




Pietzsch, Kubetzka, Bode, and Wiesendanger, ***Phys. Rev. Lett.*** **84** 5212 (2000).

SP-STM tip characterization

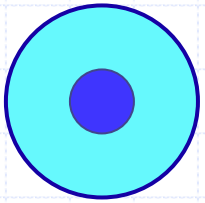
Using Fe/W(110) to determine spin polarization of tip states, with a rotating-tip STM.

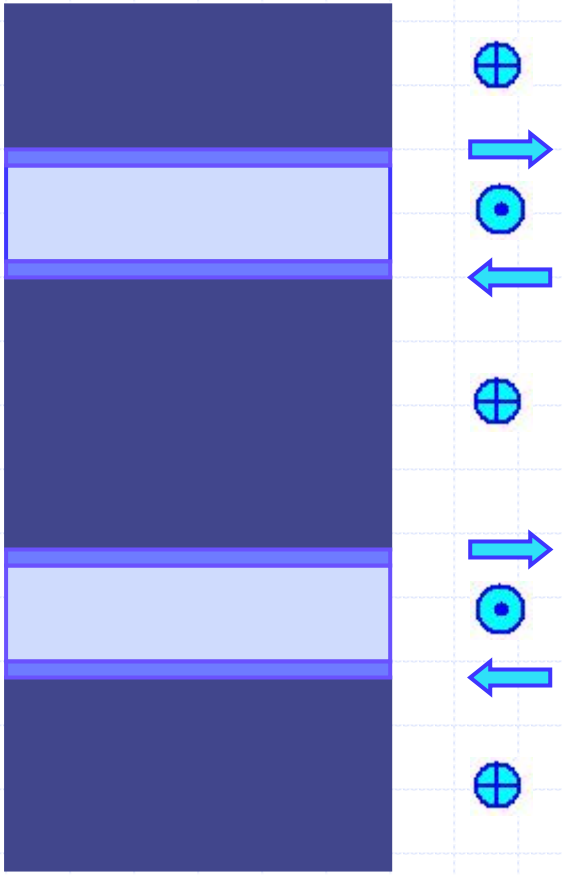


Pietzsch, Kubetzka, Bode, and Wiesendanger, ***Phys. Rev. Lett.*** **84** 5212 (2000).

SP-STM tip characterization

Using Fe/W(110) to determine spin polarization of tip states, with a rotating-tip STM.

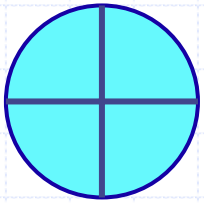


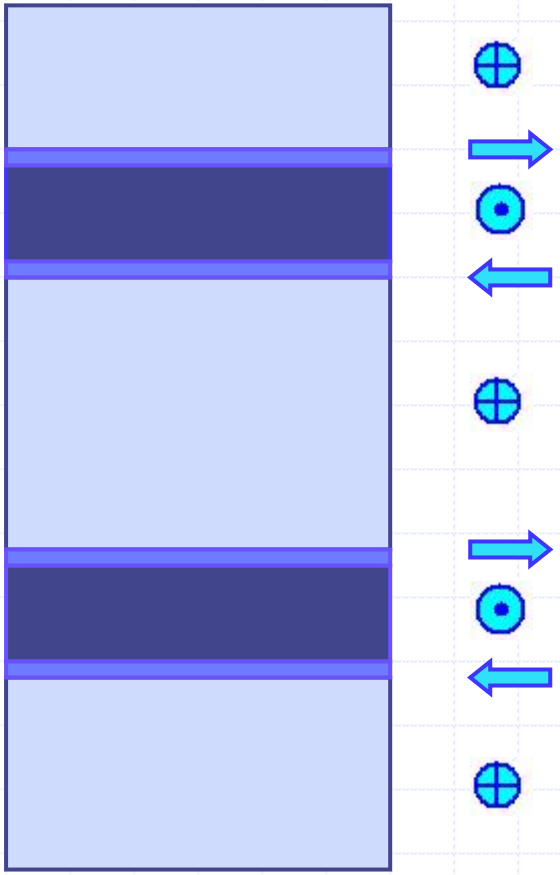


Pietzsch, Kubetzka, Bode, and Wiesendanger, ***Phys. Rev. Lett.*** **84** 5212 (2000).

SP-STM tip characterization

Using Fe/W(110) to determine spin polarization of tip states, with a rotating-tip STM.

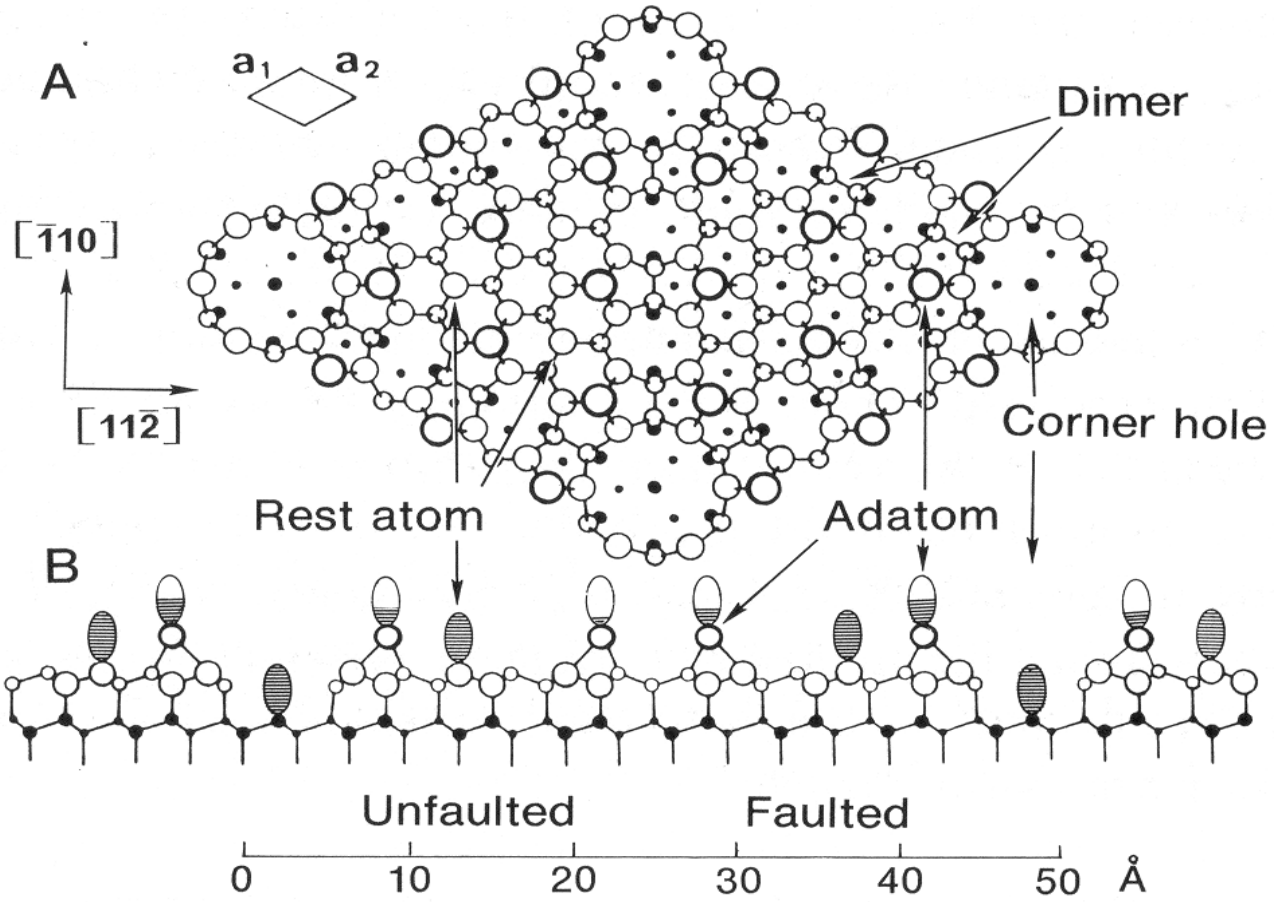




Pietzsch, Kubetzka, Bode, and Wiesendanger, ***Phys. Rev. Lett.*** **84** 5212 (2000).

The Si(111)7X7 Surface Structure

The distance between adjacent adatoms is 7 Å. Its electronic structure is well-understood. Therefore, it is ideal for tip-state determination.



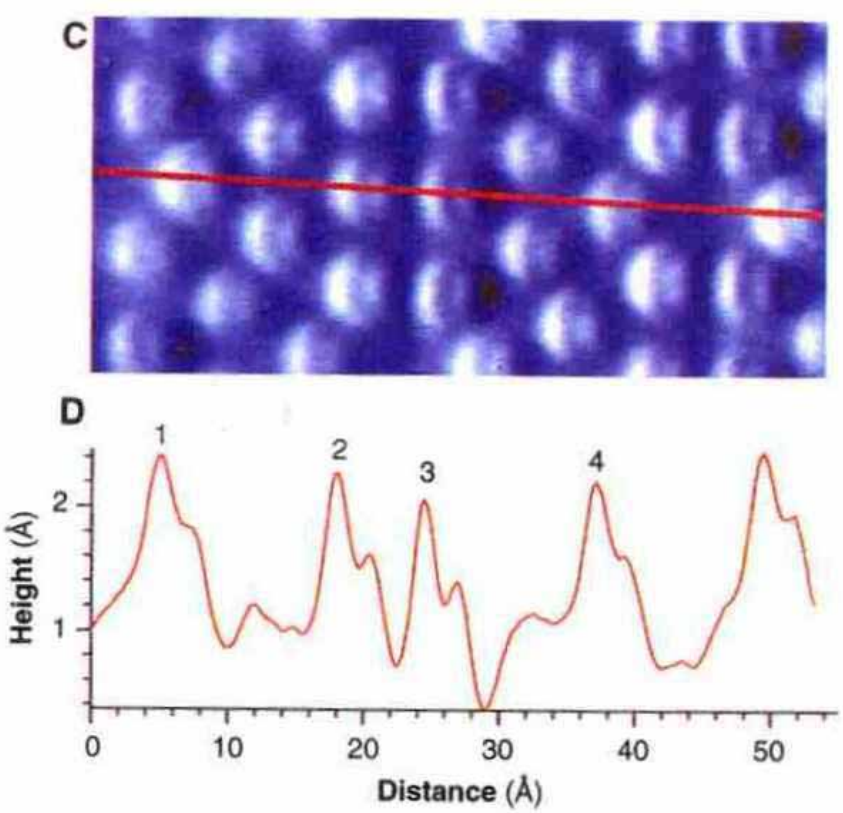
Tip Electronic States Imaged by NC-AFM

Franz J. Giessibl et al., *Science,* Vol. 289, p 422 – p 425, July 21, 2000.

Each image of an adatom on Si(111)7X7 is split into two.
The topography of each group is very similar.

The only possible interpretation:
Each group is an image of the tip electronic states, probed by an adatom on Si(111)7X7 sample.

A manifestation of *reciprocity principle* in STM imaging.
An example of *inversed STM:* imaging the tip with a "sample".



Spin-polarized NC-AFM

Studying magnetism in insulators

-- Tunneling experiment cannot be conducted. NC-AFM works.

Force measurement complements tunneling

-- Valuable also for magnetic properties of conductors.

Direct measurement of exchange interactions

-- visualize the origin of Heisenberg's exchange coupling.

Related issues:

-- A universal relation between tunneling conductance, chemical bond, and exchange coupling as the origin of magnetism.

-- Basic physics of atom manipulation (pulling and sliding).

Heisenberg Hamiltonian (1928)

$$H_{eff} = -2\sum_{i>j} J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j .$$

$\mathbf{S}_i$ **Spin vector of the *i* th atom**

$\mathbf{S}_j$ **Spin vector of the *j* th atom**

J_{ij} **Coefficients depending on the displacement between the *i* th atom and the *j* th atom.**

-- decaying with distance (a few atoms away)

-- orientation dependent (magnetic anisotropy)

Origin of exchange coupling coefficients J_{ij}

The initial idea of exchange coupling came from Heitler and London's treatment of hydrogen molecule (1927).

However, the Heitler -London treatment diverges at large distances, and does not give the correct initial states.

An asymptotically correct treatment (Holstein, Landau, and Herring) is based on first-order perturbation theory.

An extension to time-dependent perturbation theory provides a unified view of tunneling, chemical bond, and exchange coupling in magnetism.

C. Herring, **Direct Exchange between Well-Separated Atoms,** in ***Magnetism,*** Vol. **IIB,** Eds. Rado and Suhl, 1966.

A related issue:
Relation between STM and NC-AFM

What is the physical origin of atomic resolution in STM and NC-AFM?

What kind of scientific knowledge can we extract from the atom-resolved STM and NC-AFM images, and how?

What is the relation between tunneling conductance and attractive atomic force in STM and NC-AFM?

What can we do to improve the experimental conditions of STM and NC-AFM to enlarge the information channel to Mother Nature?

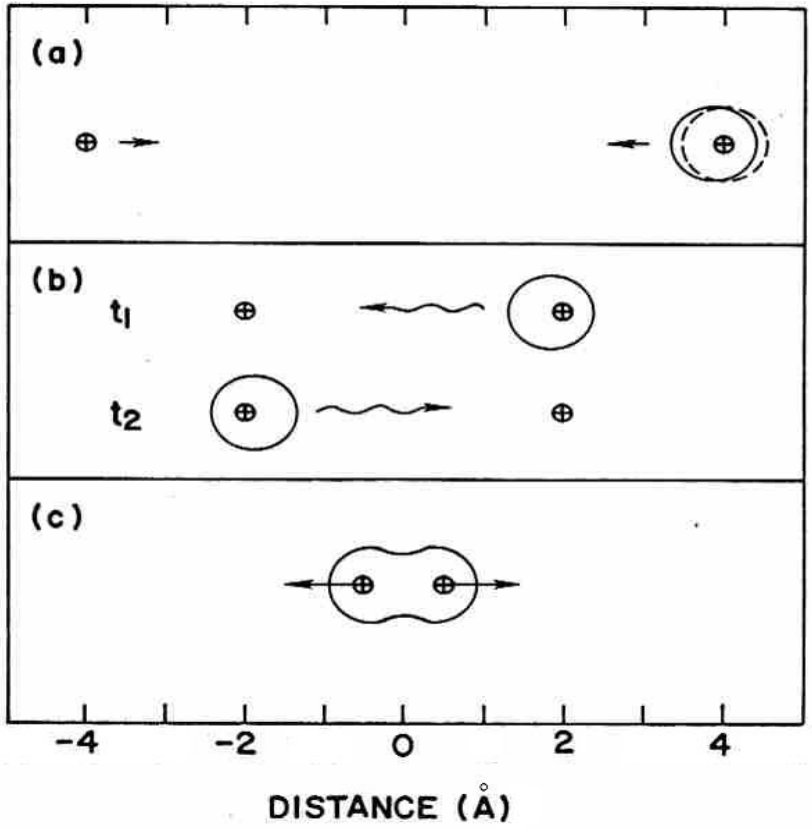
Covalent bond and tunneling matrix element

The problem of H_2^+

Large distances: r > 6 Å
van del Waals force

Intermediate distances: 2-6 Å
tunneling, covalent bond, and exchange coupling.

Very short distances: r < 2 Å
core-core repulsion



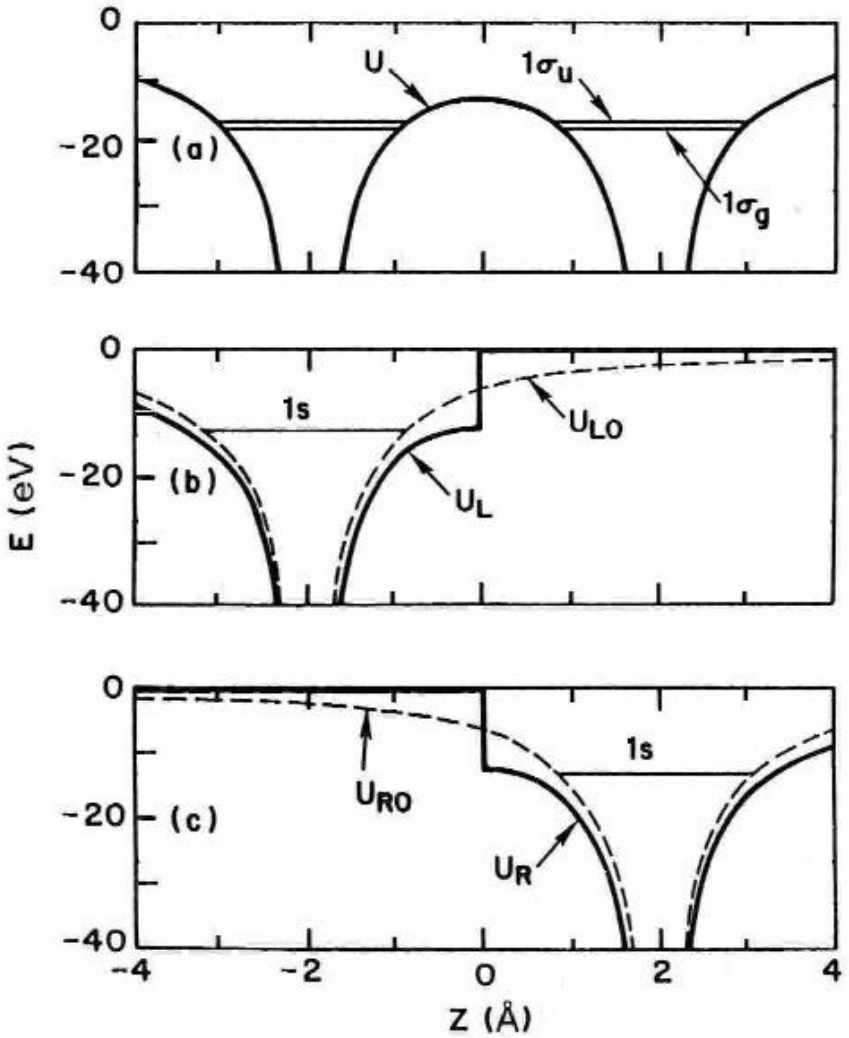
After C. Herring, **Critique of the Heitler-London method of calculating spin couplings at large distances, *Rev. Mod. Phys.*, 34,** 631-645 (1962).

Covalent bond and tunneling matrix element

The problem of H_2^+

By correctly choosing the unperturbed potential for the hydrogen atoms, using first-order perturbation theory, the exchange coupling energy (or the covalent bonding energy) can be accurately evaluated.

After C. Herring, **Critique of the Heitler-London method of calculating spin couplings at large distances, *Rev. Mod. Phys.*, 34,** 631-645 (1962).



Covalent bond and tunneling matrix element

Covalent bond energy in H_2^+: exact solution vs. tunneling evaluation.

$$M = \frac{1}{2}\int \left[\psi_R \nabla \psi_L - \psi_L \nabla \psi_R\right] \cdot d\mathbf{S}$$

$$= -\frac{2}{e} R e^{-R}.$$

The Bardeen tunneling matrix element can be evaluated analytically for the case of hydrogen molecule ion.

Covalent bond and tunneling matrix element

Tunneling evaluation of H_2^+ energy levels

$$\Delta E(1\sigma_g) = -\frac{9}{4R^4} - \frac{2}{e} R e^{-R},$$

$$\Delta E(1\sigma_u) = -\frac{9}{4R^4} + \frac{2}{e} R e^{-R}.$$

Exact solution of H_2^+

$$\Delta E_{\pm} = -\frac{9}{4R^4} - \frac{15}{2R^6} - \frac{213}{4R^7}$$

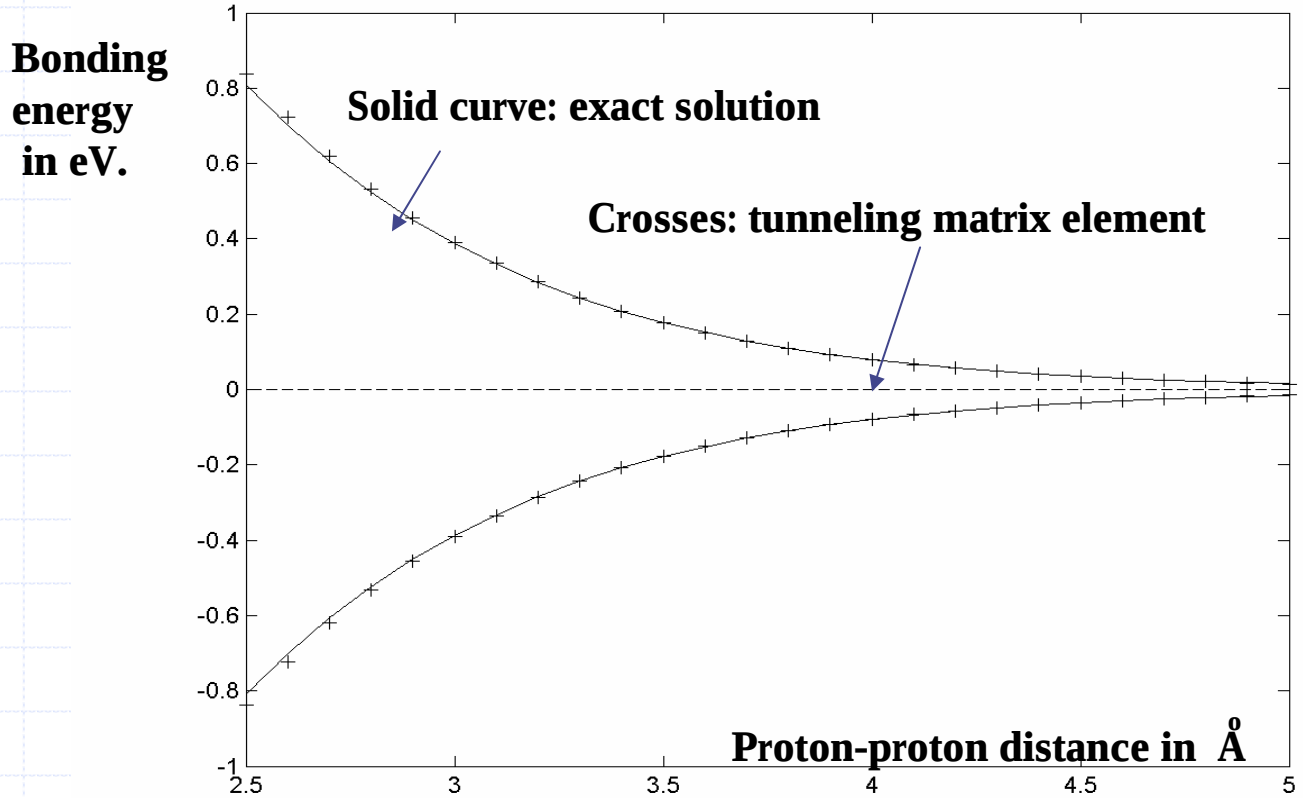
$$\pm \frac{2}{e} R e^{-R} \left(1 + \frac{1}{2R} - \frac{25}{8R^2}\right) + \ldots.$$

Van del Waals

Exchange interaction

Covalent bond and tunneling matrix element

Covalent bond energy in H_2^+: exact solution vs. tunneling evaluation.



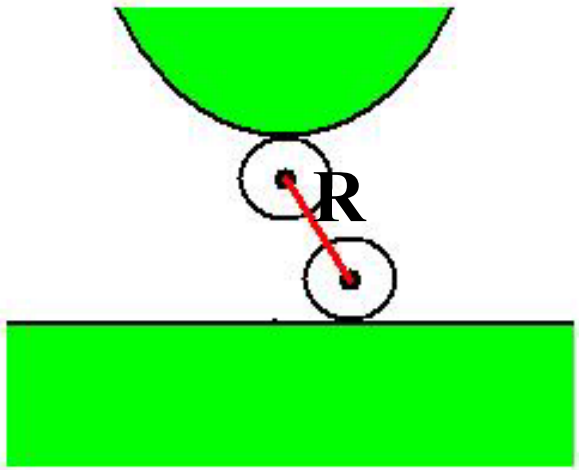
The Bardeen tunneling matrix element almost exactly equals the chemical bonding energy and the exchange coupling energy.

Relation between bonding energy and tunneling

The bonding energy between the tip atom and an atom on the sample is determined by the overlap of the two wavefunctions,

$$E = E(\mathbf{R}),$$

where $\mathbf{R}$ is the vector distance between the nuclei of the two atoms.



The tunneling matrix element between the two atoms is also determined by the overlap of the two wavefunctions, thus

$$M = M(\mathbf{R}).$$

Intuitively, there should be a relation between the two quantities.

A universal relation between attractive atomic force and tunneling conductance

Attractive atomic force (chemical bond force) is

$$F = -\frac{\partial |M|}{\partial z}.$$

Using Fermi golden rule, tunneling conductance is

$$G = \frac{(2\pi)^2}{R_K} \rho_S \rho_T |M|^2 .$$

$R_K = h/e^2 \approx$ **25.812 kΩ: von Klitzing's constant**

ρ_S **: sample DOS at Fermi level**

ρ_T **: tip DOS at Fermi level**

An experimentally verifiable relation

Using time-dependent perturbation theory, a universal relation between tunneling conductance $G = dI/dU$ and attractive atomic force F is derived,

$$F^2 = \frac{f \kappa^2 R_K}{\rho_S \rho_T} G,$$

$R_K \approx 25.812\ \text{k}\Omega$: **von Klitzing's constant**

ρ_S : **sample DOS at Fermi level**

ρ_T : **tip DOS at Fermi level**

$f \approx 1$: **tip geometry form factor**

Chen, J. Phys. Cond. Matter, Vol 3, 1227 (1991); ***Introduction to Scanning Tunneling Microscopy,*** **1993, Chapter 7.**

Experimental verification of $F^2 \sim G$ relation (1)

New Journal of Physics **2** (2000) 29.1–29.10

Metallic adhesion and tunnelling at the atomic scale

A Schirmeisen[1], G Cross[1]†, A Stalder[1]‡, P Grütter[1] and U Dürig[2]

[1] Center for the Physics of Materials, McGill University, Montréal, Canada

[2] IBM Research Division, Zurich Research Laboratory, Switzerland

The first experiments drawing attention to the connection between adhesion forces and tunnelling were performed by Dürig *et al* [9]. Following a suggestion by Herring [20], Chen [21] proposed a model that links force and conductance. The model relies on the idea that the splitting of eigenstates due to the overlap of the electron wavefunctions is well described by the Bardeen integral M, which gives rise to the force $f = -\partial|M|/\partial z$ as well as the tunnelling conductance $G = ((2\pi)^2/R_K)\rho_{tip}\rho_{sample}|M|^2$ (with ρ = local density of states (LDOS)). Using the experimental fact that $G \sim \exp(-2\kappa z)$ where $\kappa = (2m_e\phi)^{1/2}/\hbar$, Chen found that for a metallic contact

$$f = -\frac{\alpha\kappa}{2\pi}\left(\frac{GR_K}{\rho_{tip}\rho_{sample}}\right)^{1/2}.$$

Here α is a geometric shape factor, with $\alpha = 2/\pi$ for a paraboidal tip, and $R_K = h/e^2$ is the von Klitzing constant.

Experimental verification of $F^2 \sim G$ relation (1)

Metallic adhesion and tunnelling at the atomic scale

A Schirmeisen[1], G Cross[1]†, A Stalder[1]‡, P Grütter[1] and U Dürig[2]

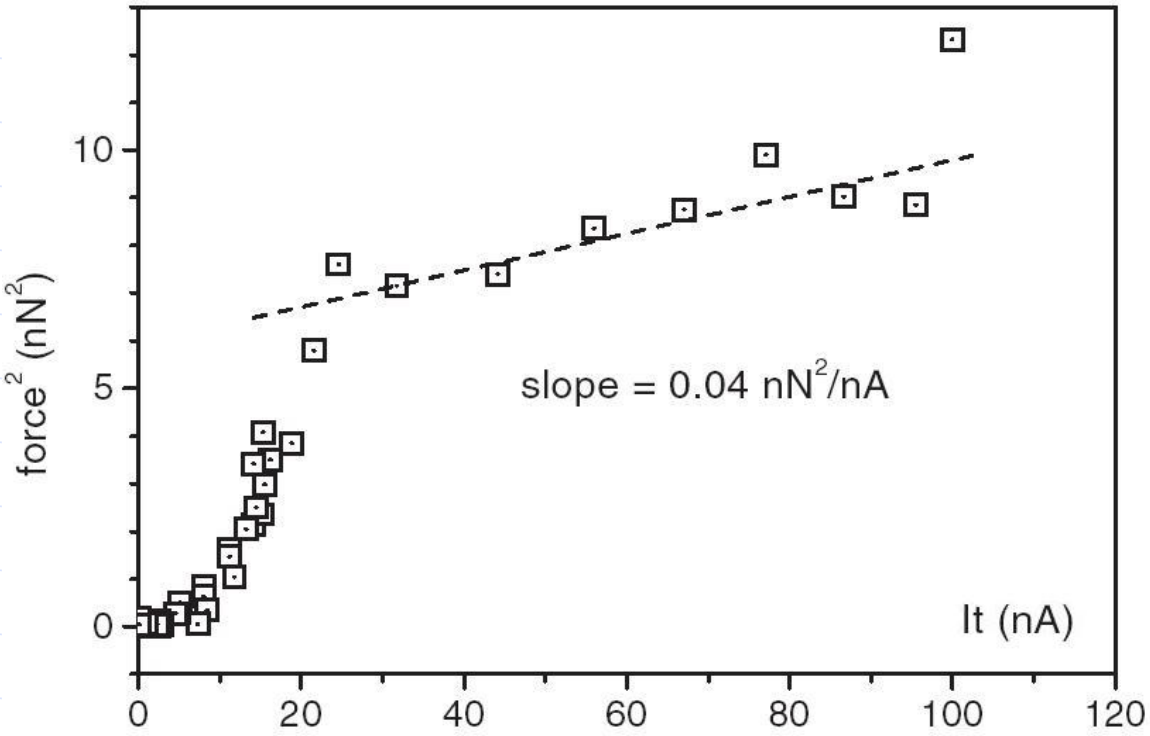


Figure 5. Correlation between force and tunnelling current using Chen's model. The graph shows the square of the force against the current, where an approximately linear relationship can be observed for currents above 20 nA. The slope of the curve of $\Delta f^2/\Delta I_t = 0.04\,\mathrm{nN^2\,nA^{-1}}$ translates to a convoluted LDOS of the tip and the sample of $\rho_{con} = 0.1$ states/eV/atom.

Experimental verification of $F^2 \sim G$ relation (2)

PHYSICAL REVIEW B VOLUME 62, NUMBER 24 15 DECEMBER 2000-II

Dynamic force microscopy of copper surfaces: Atomic resolution and distance dependence of tip-sample interaction and tunneling current

Ch. Loppacher,* M. Bammerlin, M. Guggisberg, S. Schär, R. Bennewitz, A. Baratoff, E. Meyer, and H.-J. Güntherodt
Institute of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland
(Received 15 February 2000; revised manuscript received 30 June 2000)

III. DISCUSSION

The most striking observations of our study are as follows:

(i) The achievement of true atomic resolution on the two most close-packed surfaces of a fcc metal in two dynamic modes possible with a combined AFM/STM,

(ii) The exponential decay of the short-range attractive tip-sample interaction and of the time-averaged tunneling current with respective decay lengths satisfying $\lambda_F = 2\lambda_T$ down to distances where atomic resolution is possible,

Experimental verification of $F^2 \sim G$ relation (2)

PHYSICAL REVIEW B VOLUME 62, NUMBER 24 15 DECEMBER 2000-II

Dynamic force microscopy of copper surfaces: Atomic resolution and distance dependence of tip-sample interaction and tunneling current

The relation mentioned under item (ii) has been proposed by Chen[29] by analogy with the molecular orbital picture of molecular bonding. As a result, the force due to electronic overlap,

$$F = -\frac{\partial \Delta E}{\partial s} = \frac{\partial M}{\partial d} \tag{3.1}$$

is attractive and has an exponential dependence with the same decay length λ_F. On the other hand, in the same range, the tunneling current I_t is proportional to a weighted average of $|M|^2$ over the energy window defined by the voltage drop across the barrier.[30,4] Thus one expects $\lambda_F = 2\lambda_T$.

Suggested experiments

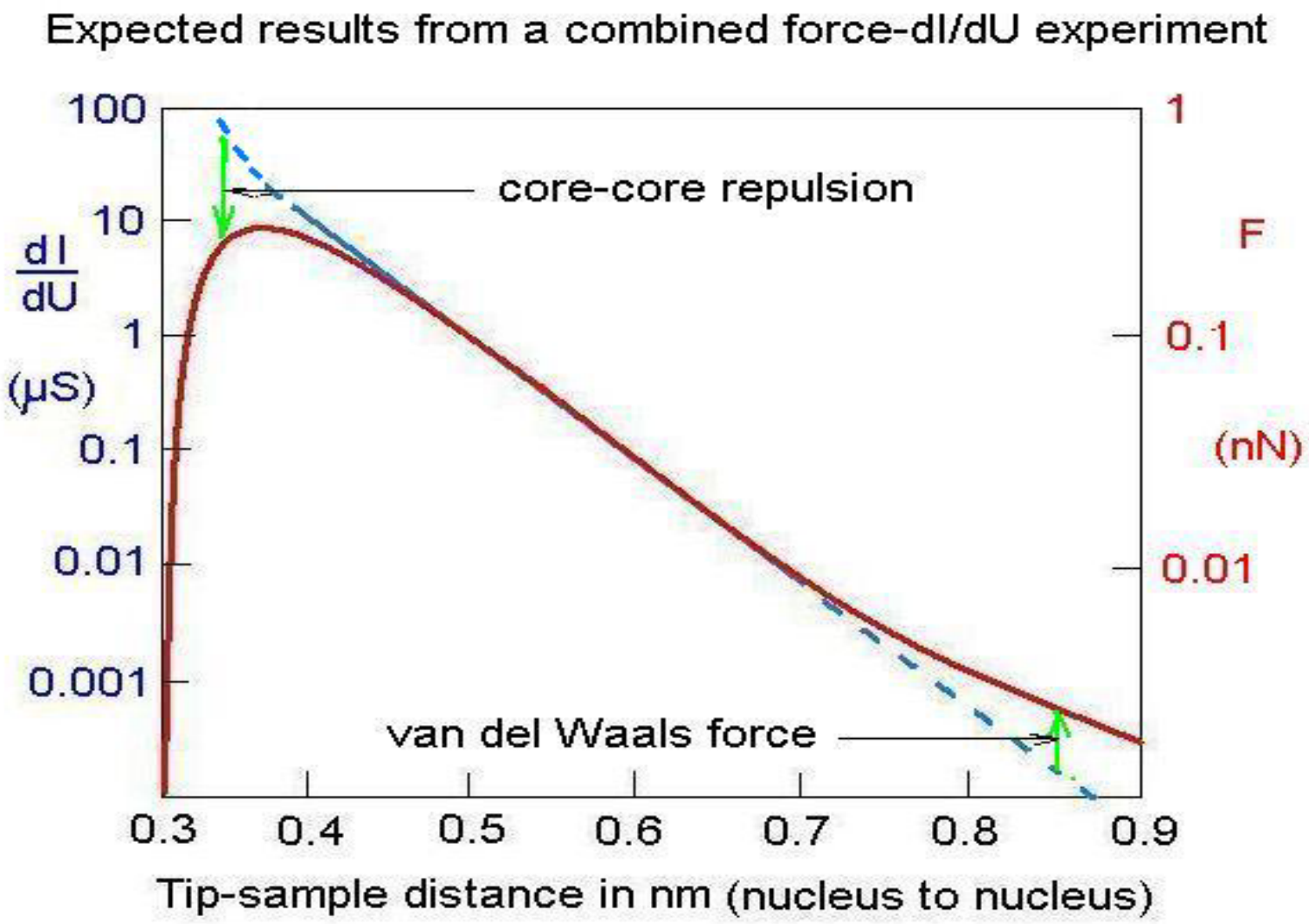
Simultaneous measurement of attractive atomic force and tunneling conductance

- Verify the equivalence of tunneling and chemical bond.
- Extract tip and sample electronic information

Conduct spin-polarized NC-AFM experiments

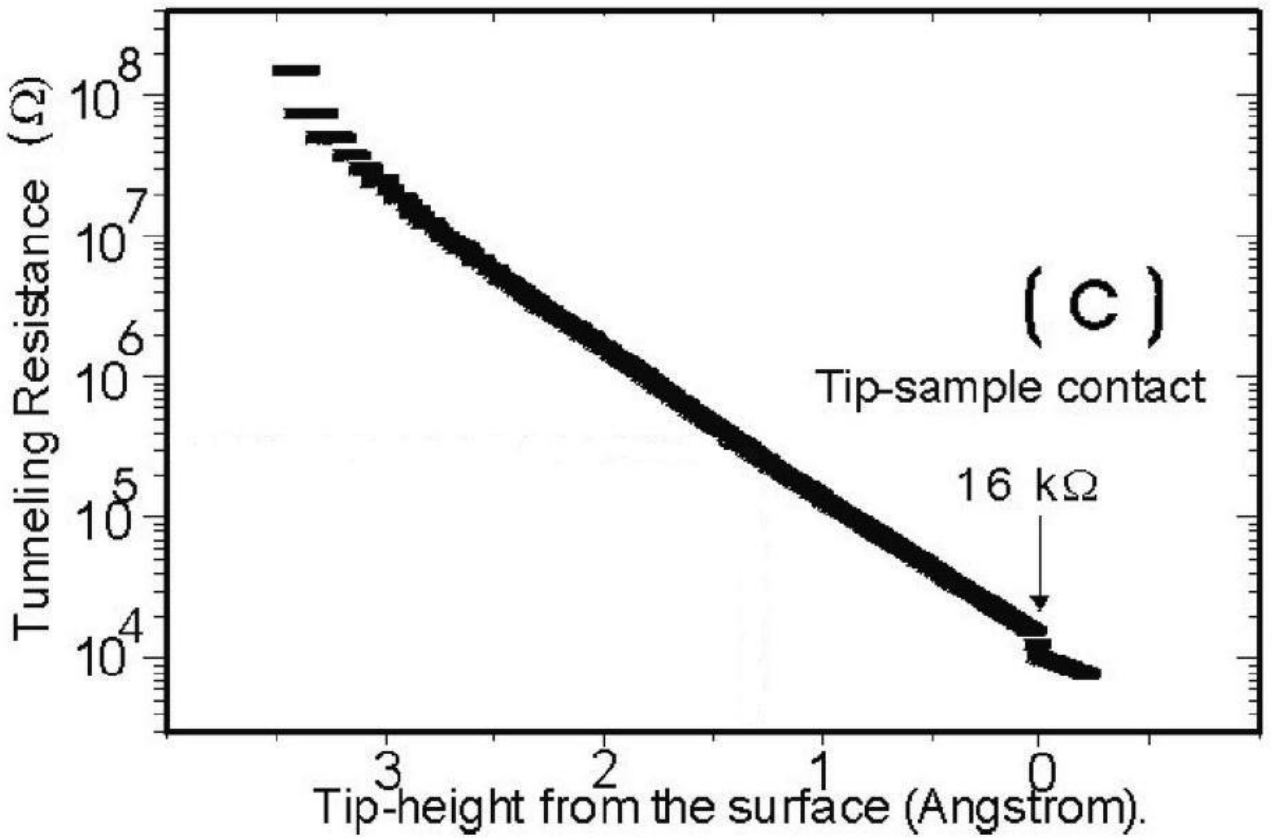
- Main difficulty: tip formation and tip characterization
- Tip formation by controlled collision and electrical pulse
- Using SP-STM to characterize SP-AFM tip

Experimental verification of $F^2 \sim G$ relation



Example of a recent measurement of I-Z relation

W tip on Ag(111) sample, ~6K.



Hla, Braun and Rieder, ***PRB* 67** 201402 R (2003).

Spin-polarized NC-AFM: possible contrast mechanisms

Tip with in-plane spin polarization, rotating tip.

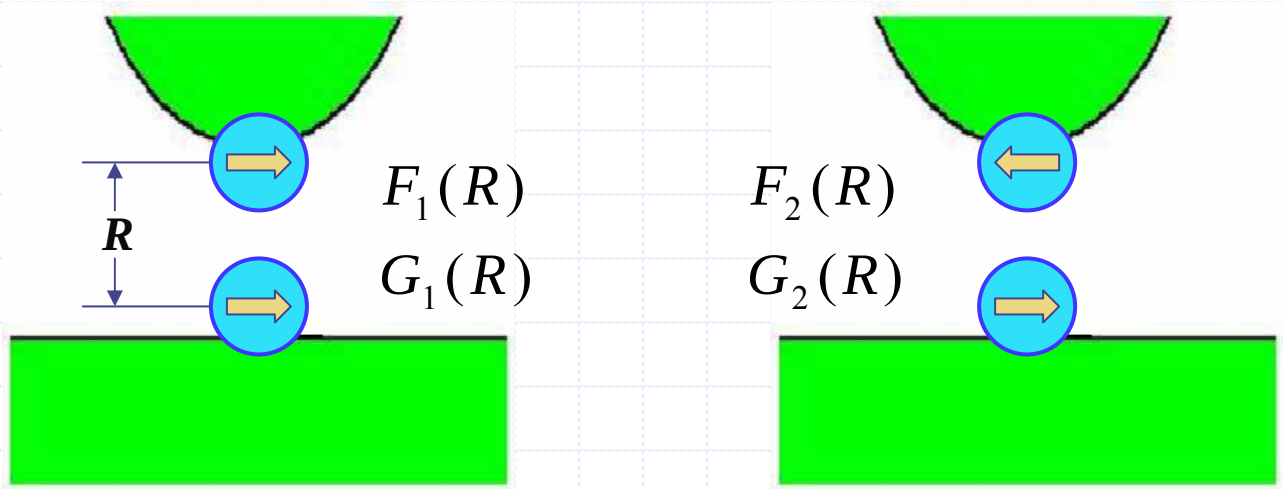
Tip with perpendicular (out-of-plane) spin polarization, exchange tip (or recondition tip).

Tip with in-plane spin polarization, atoms on sample surface has different in-plane spin polarizations.

Tip with out-of-plane spin polarization, atoms on sample surface has different out-of-plane spin polarizations.

Bias-dependent non-contact force effects.

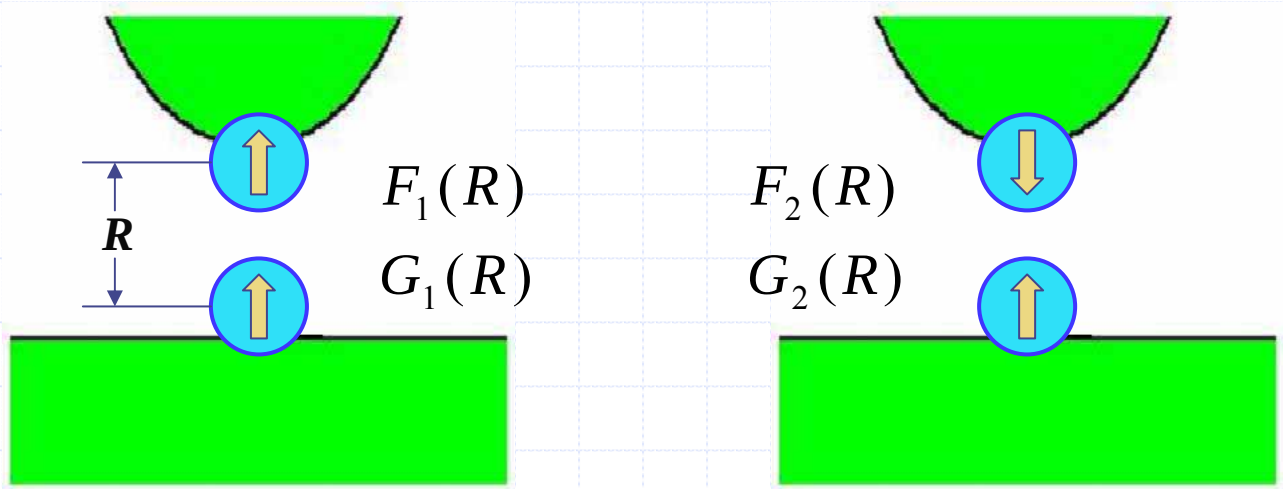
Experimental observation of exchange interactions through atomic force and tunneling measurements



$$J(R) = -\int_{\infty}^{R} \left[F_1(r) - F_2(r) \right] dr,$$

$$\left[J(R) \right]^2 \cong \text{const} \times \left[G_1(R) - G_2(R) \right].$$

Experimental observation of exchange interactions through atomic force and tunneling measurements



$$J(R) = -\int_{\infty}^{R} \left[F_1(r) - F_2(r) \right] dr,$$

$$\left[J(R) \right]^2 \cong \text{const} \times \left[G_1(R) - G_2(R) \right].$$

Experimental problem: Tip characterization

Tip preparation and tip characterization can be follow the same method as in tunneling experiments.

With a tip rotation mechanism, the azimuth of spin polarization can be controlled.

Because tunneling (including STS) can provide complete information about tip states, but with greater ease and greater richness than AFM, the tip can be characterized with tunneling experiments.

Another related issue:
Physical mechanism of atom manipulation

What is the force that moves the atoms?

What is the relation between that force and tunneling?

How to control atom moving precisely?

The Art of Atom Manipulation

Controlled manually.

Each move takes days.

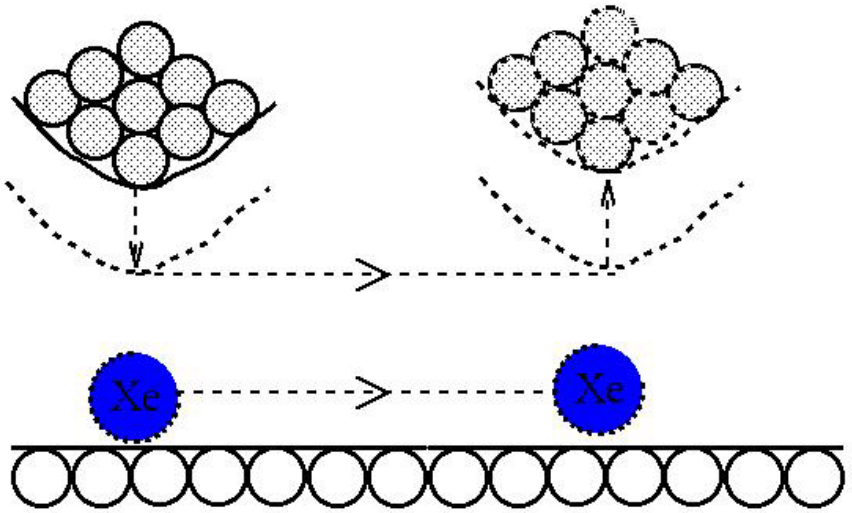
It takes weeks to make an "IBM" pattern.

It made headline news.

No reproducible recipe ever published.

Positioning Atoms with an STM

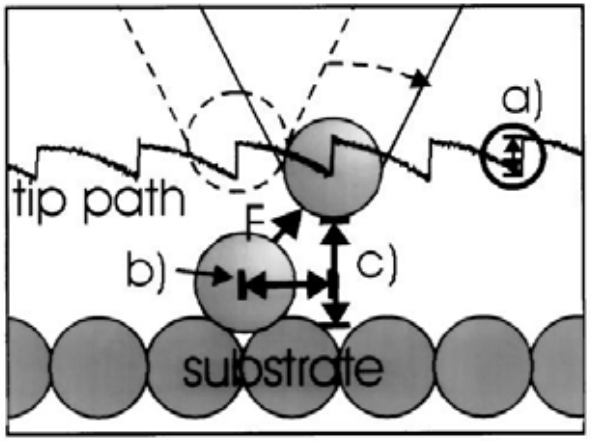
D.M. Eigler & E.K. Schweizer Nature **344** 524 (1990)



The STM tip is brought down near the atom, until the attraction is enough to hold it as the atom is dragged across the surface to a new position.

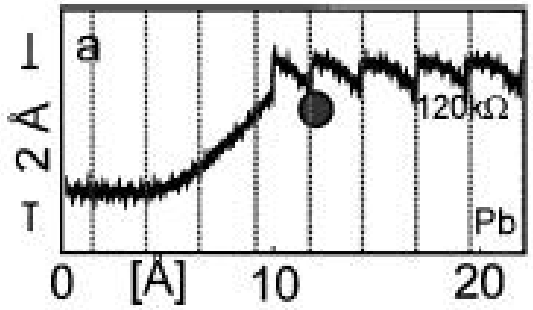
Atom manipulation: Towards an exact science (1)

Basic steps of atom manipulation

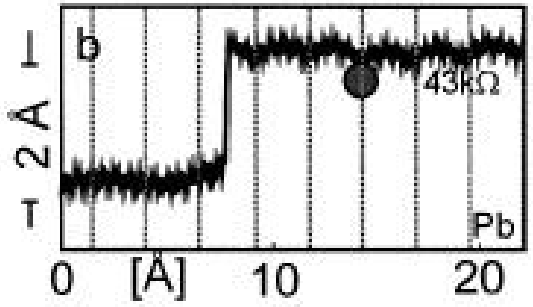


Bartels, Meyer and Rieder, ***PRL* 79** 697 (1997).

pulling



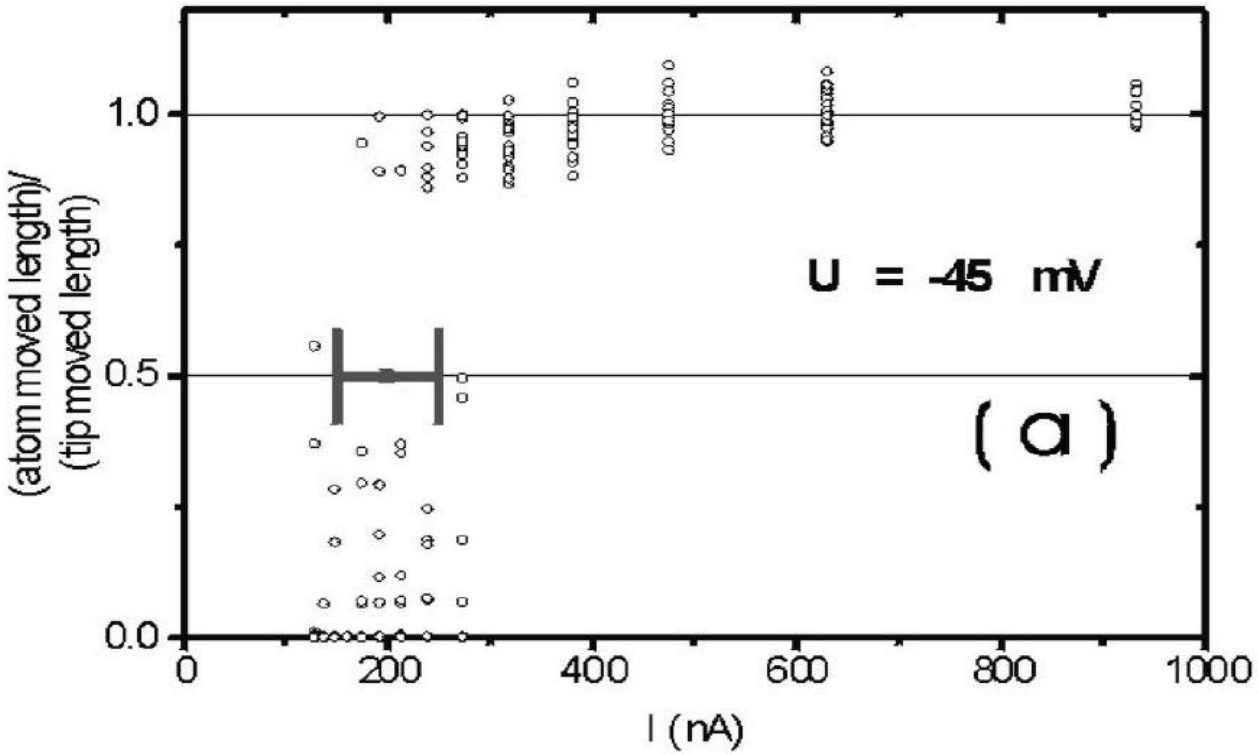
sliding



Meyer, Moresco, Hla, Repp, Foelsch and Rieder, ***JJAP* 40** 4409 (2001).

Atom manipulation: Towards an exact science (2)

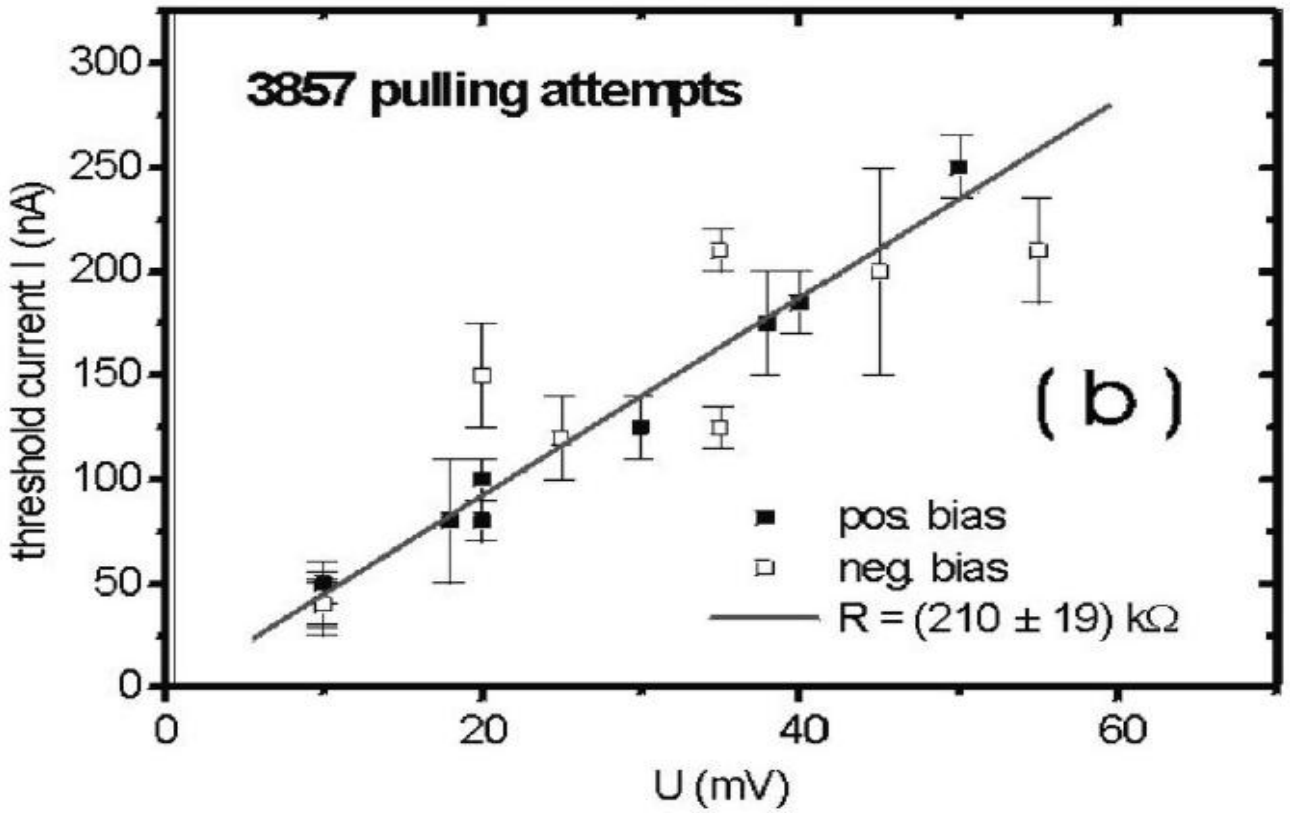
Computer-automated atom-pulling experiments



Hla, Braun and Rieder, ***PRB*** **67** 201402 R (2003).

Atom manipulation: Towards an exact science (3)

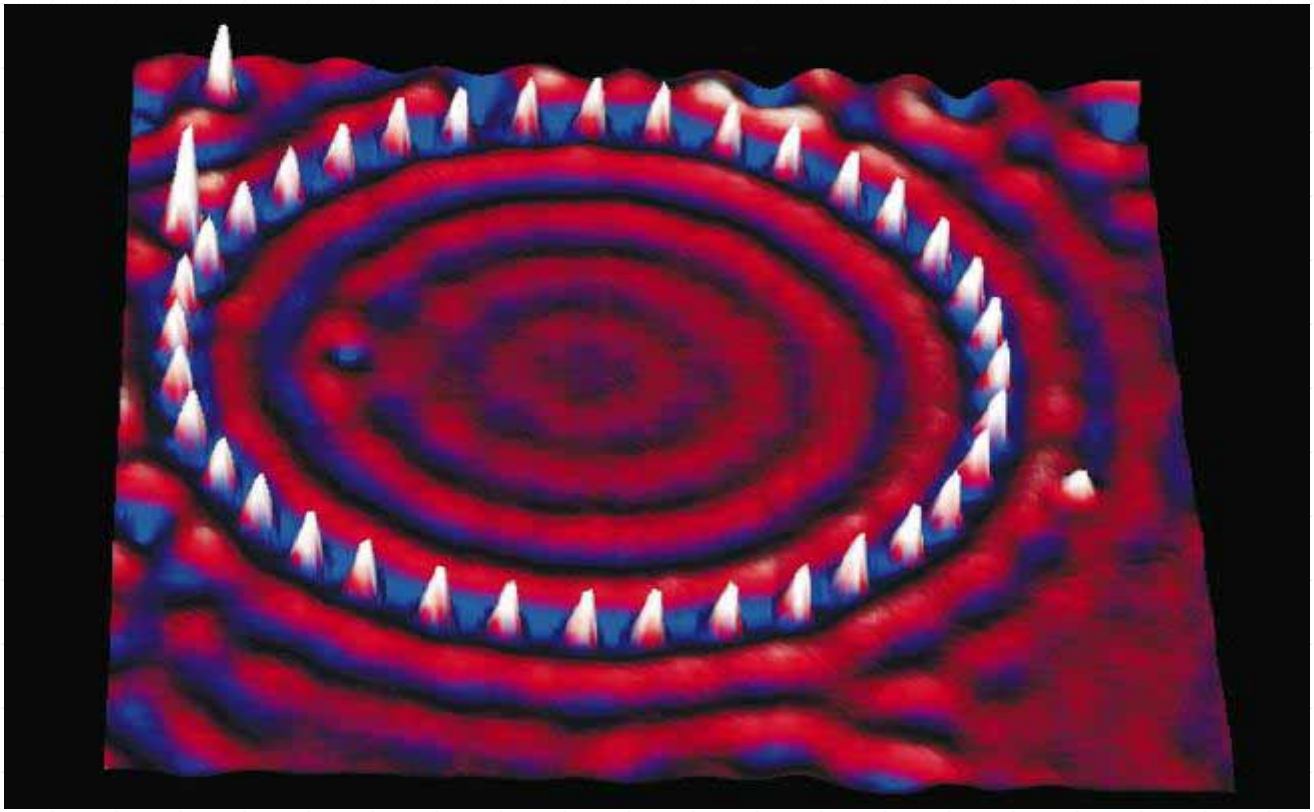
A well-defined threshold tunneling resistance is found.



Hla, Braun and Rieder, ***PRB* 67** 201402 R (2003).

Atom manipulation: Towards an exact science (4)

Complicated patterns can be generated by programming.



Hla, Braun and Rieder, ***PRB* 67** 201402 R (2003).

Atom manipulation:
Towards an exact science (4)

What is the meaning of threshold tunneling resistance?

The force is independent of the magnitude of bias.

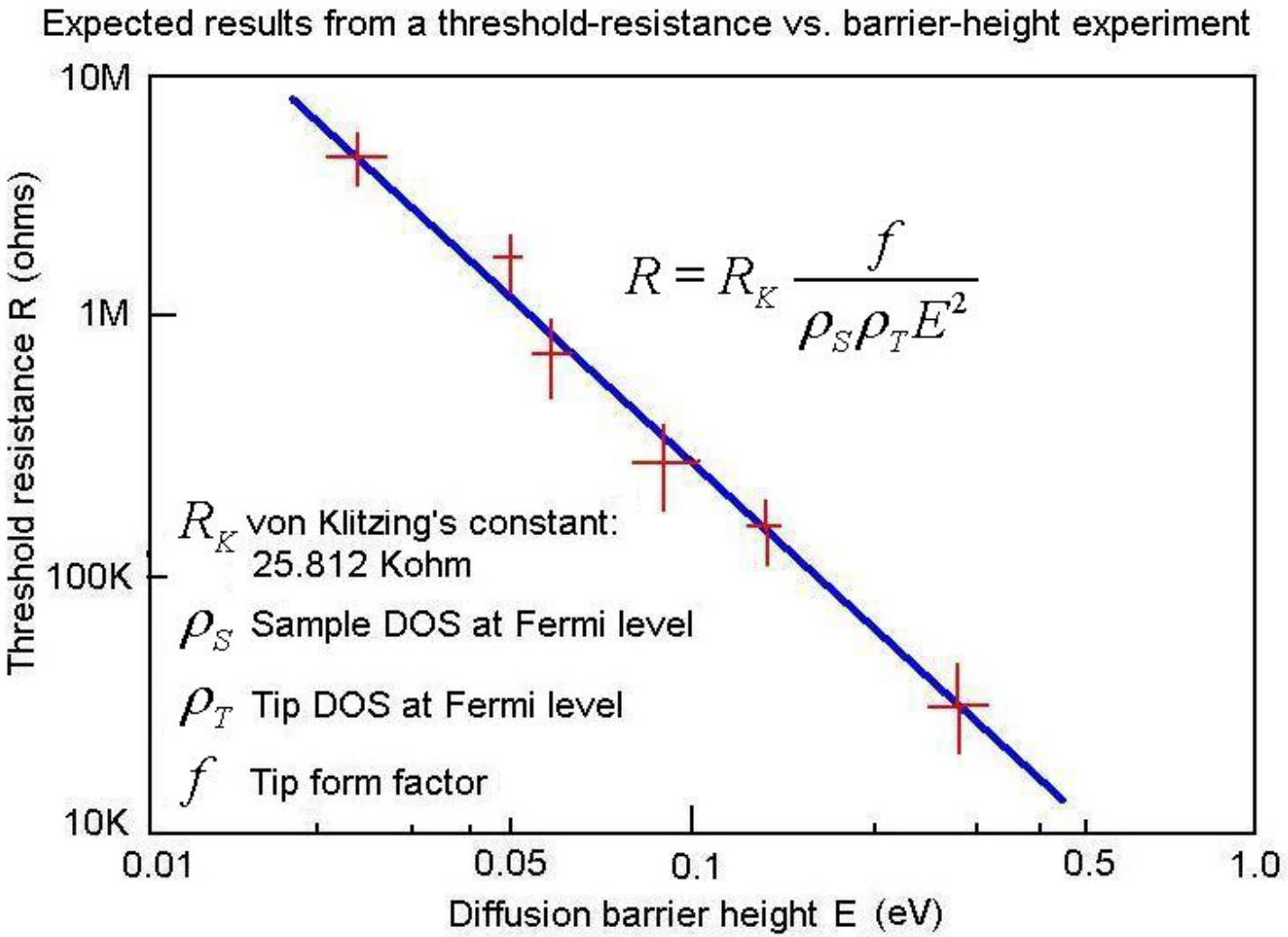
The force is independent of the polarity of bias.

Therefore, it is not related to electrical field or current.

It is the formation of a partial chemical bond.

If this is true, then the threshold tunneling resistance should be directly related to the diffusion barrier height for the atom to move over. And this can be verified experimentally.

Atom manipulation:
A proposed new experiment



Summary

Atomic resolution in STM and NC-AFM

- The art of tip sharpening
- The mystery of spontaneous tip restructuring

Understand and characterize tip states

- Existence and manifestation of various tip states
- Experimental determination of various tip states
- Case of spin-polarized STM

Spin-polarized non-contact AFM

- A unified view of tunneling, chemical bond, and magnetism
- Probe chemical bonds through tunneling measurements
- Probe exchange coupling by force and tunneling measurements
- Atom manipulation: from personal art to exact science