Calculating core-level shifts, surface core-level shifts, STM images

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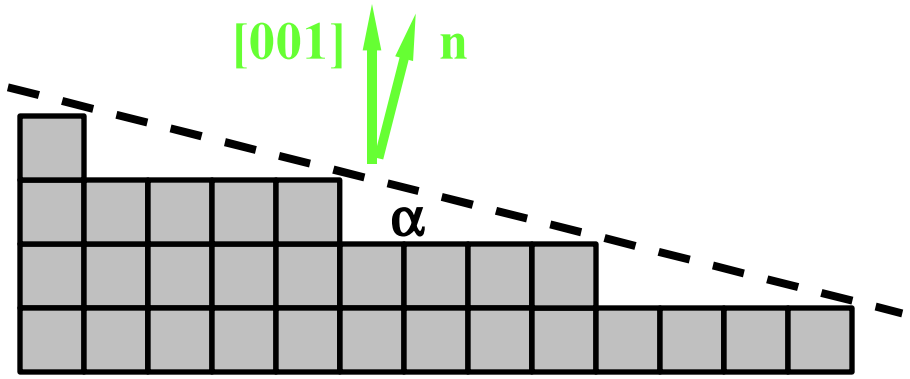
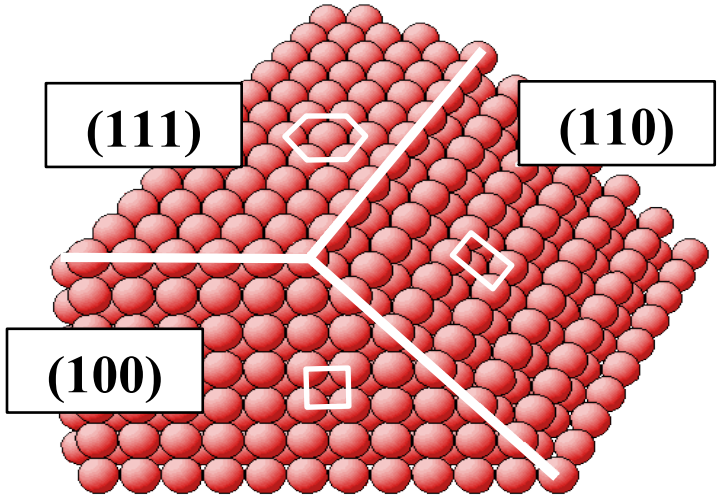
Ideal surfaces_

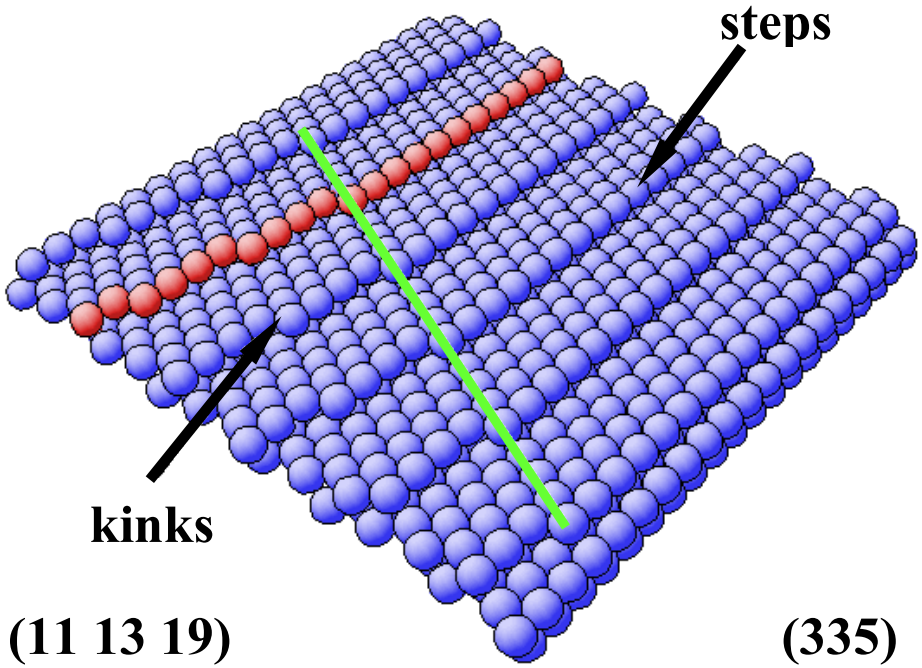


Cutting close-packed materials (fcc/hcp/bcc)

low-index surfaces



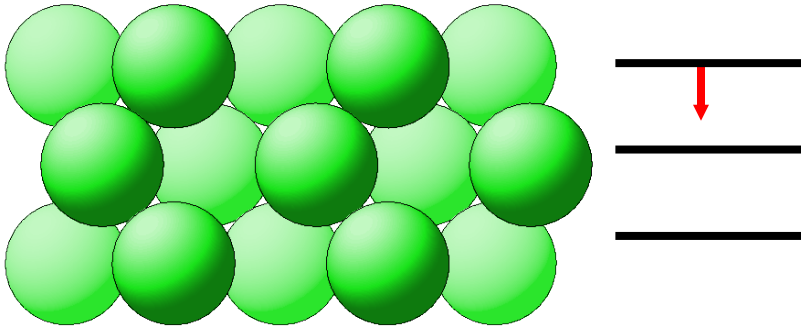
vicinal surfaces



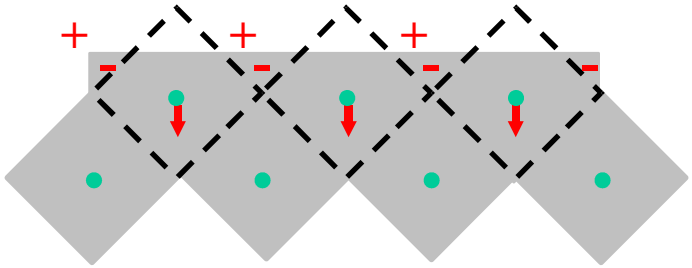
(11 13 19) **(335)**

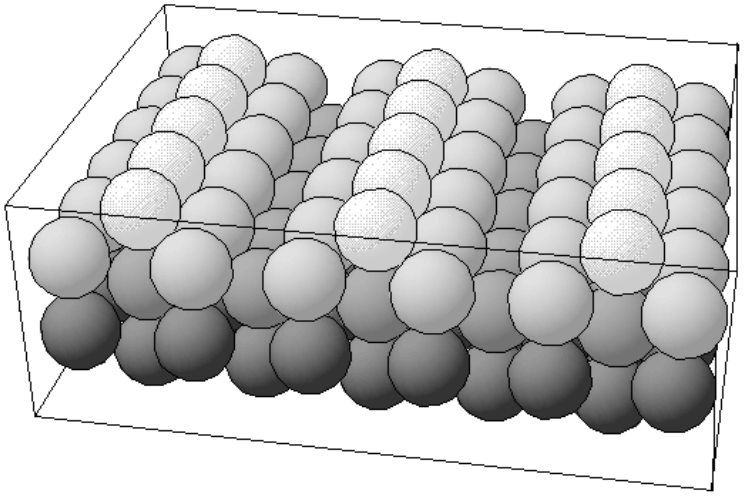
Relaxation and reconstruction: metals_

Layer relaxation

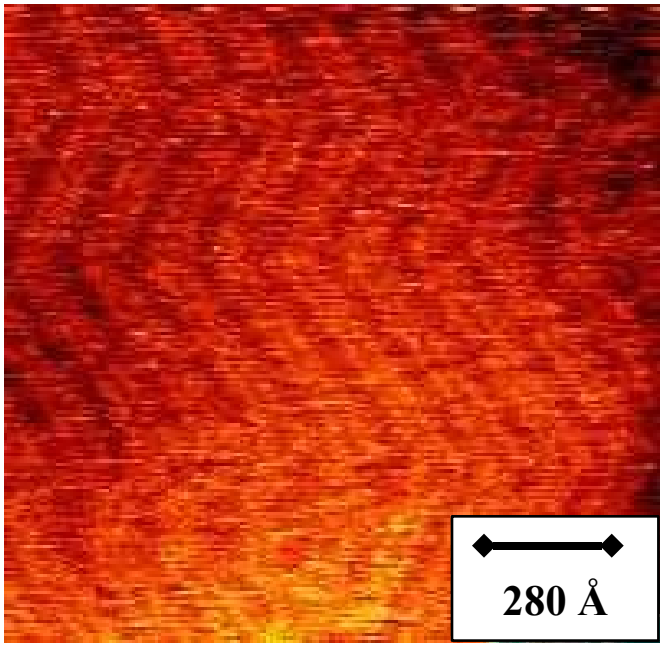


Smoluchowski smoothing



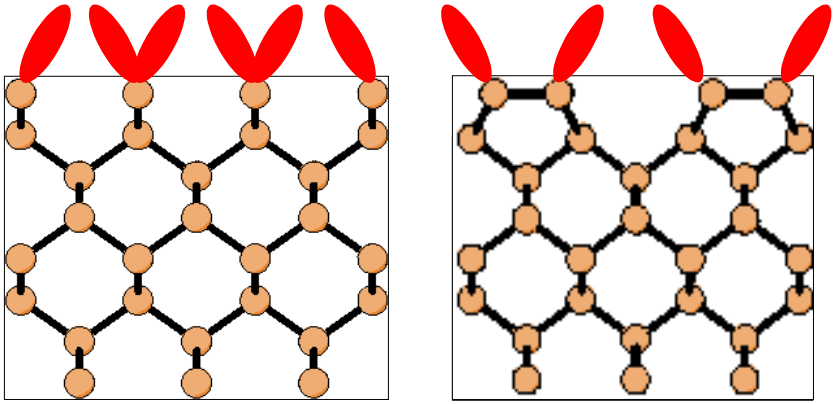


fcc(110)-(1x2) missing row reconstruction

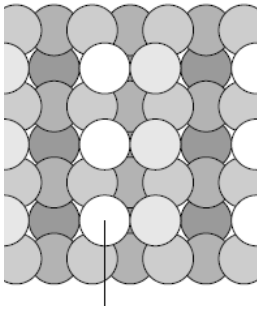


Au(111)-22x√3 herringbone structure

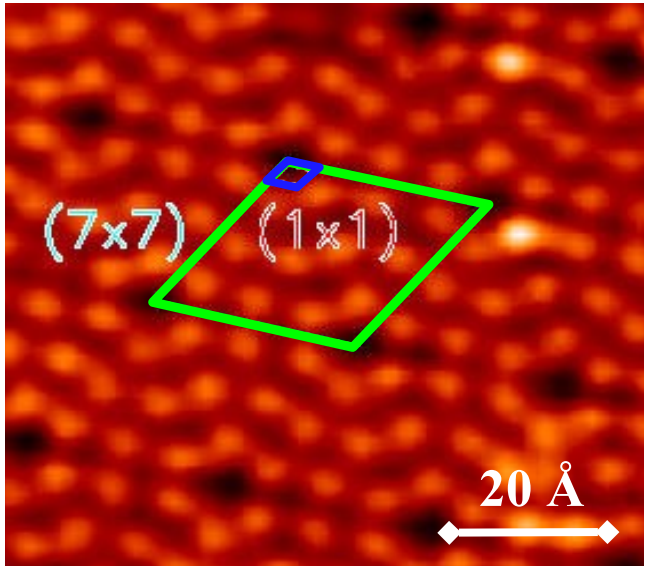
Relaxation and reconstruction: semiconductors



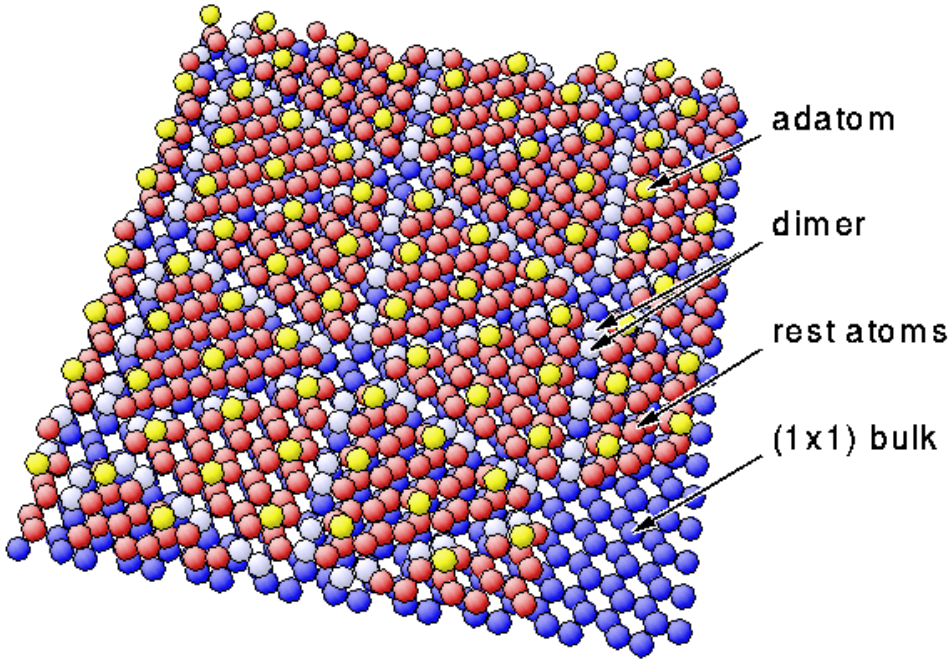
Dimerization at (001) surface of group IV elements



“Dangling bond minimization”

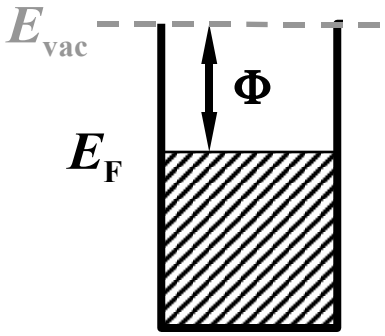


Si(111)-(7x7) DAS-model



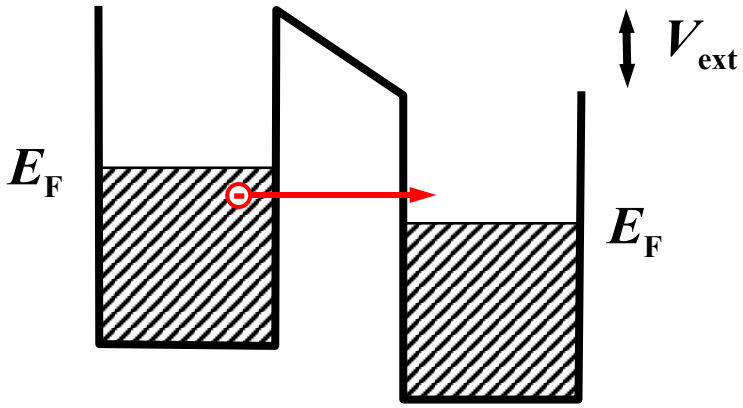
Scanning Tunneling Microscopy (STM)_

Binning, Rohrer, Gerber and Weibel 1982
1986 Nobel Price for Binning and Rohrer

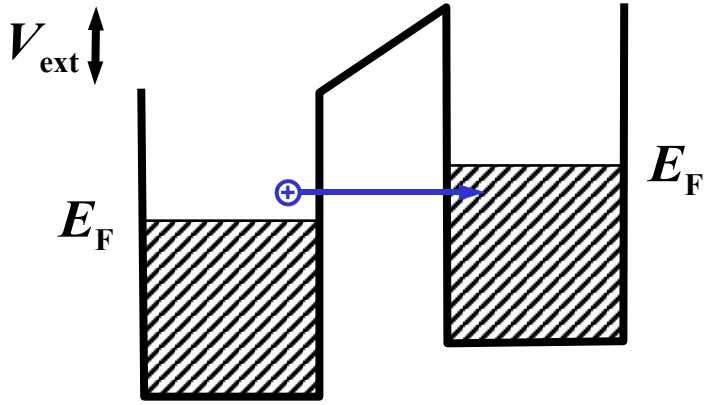


Bring two metals close to each other and measure tunneling current

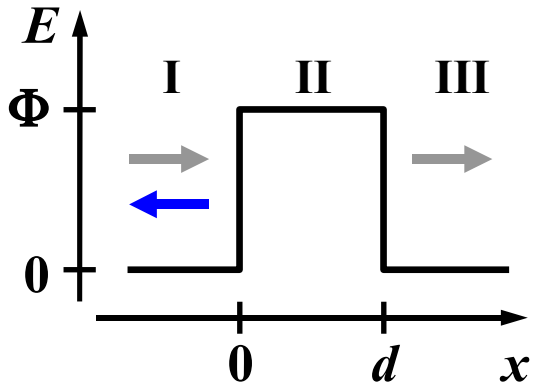
Negative tip bias:
Probe empty substrate states



Positive tip bias:
Probe filled substrate states



The tunneling effect_



- View solid as a 1*D* quantum well with non infinite walls
- Solve the Schrödinger eq. inside and outside the solid

Constant potential V = Φ

Part I: $\Psi_I(x) = e^{ikx} + R\, e^{-ikx}$, $k = (2mE/\hbar)^{1/2}$

Part II: $\Psi_{II}(x) = A\, e^{i\kappa x} + B\, e^{-i\kappa x}$, $\kappa = (2m(\Phi - E)/\hbar)^{1/2}$ $E < \Phi$: damped wave

Part III: $\Psi_{III}(x) = S\, e^{ikx}$

Transmission coefficient: $\mathbf{T = |S|^2 \sim e^{-2\kappa d}}$, for $\kappa d >> 1$

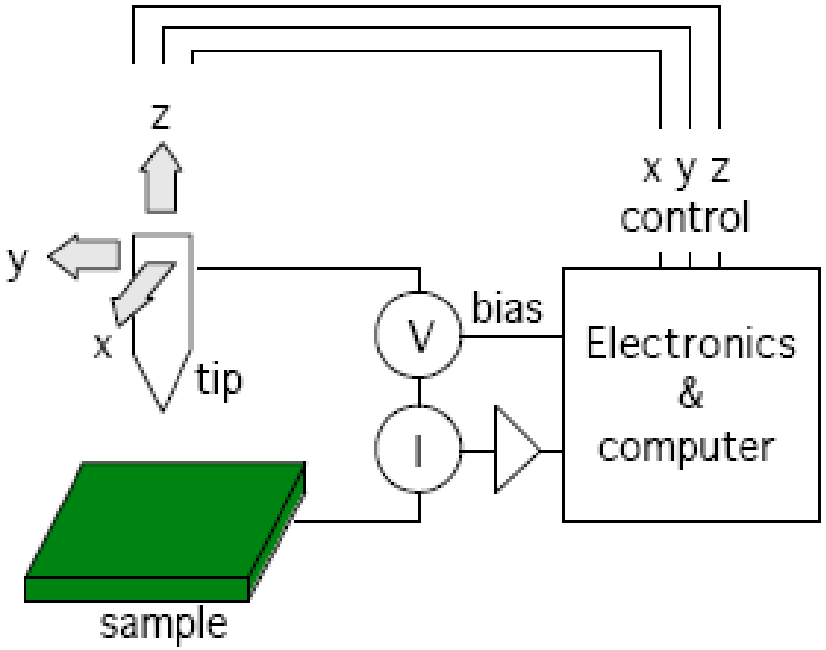
Tunneling is dominated by electrons close to the Fermi-level: $E = 0$

$\kappa = (2m\Phi/\hbar)^{1/2} = 0.51\,\Phi^{1/2}$, κ in Å^{-1}, Φ in eV

$\kappa \sim$ 1-2 Å^{-1} for a typical metal

STM: Experimental setup_

A sharp tip is interacting with the surface and a topographic surface image is produced by scanning.



-The movement of the tip over the surface is in raster fashion and computer controlled

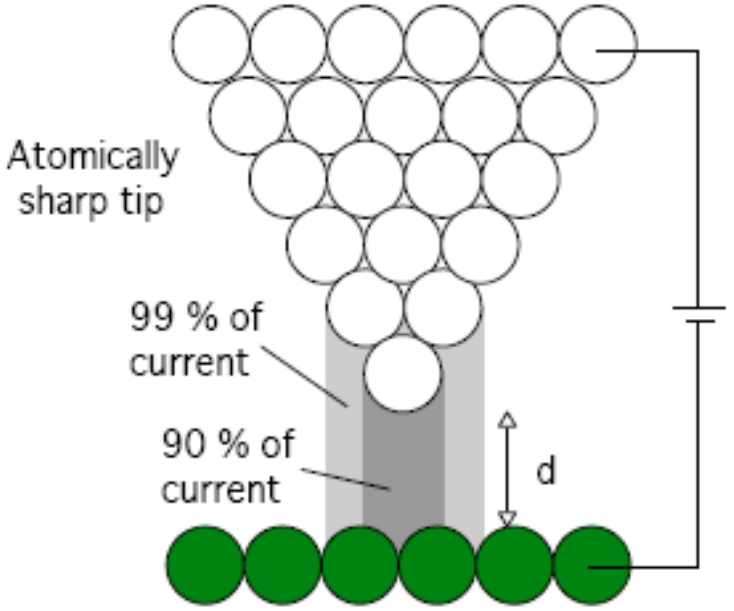
- At each lateral point the measured tunneling current is converted into pixel intensity to generate an image

-Vibrational isolation is crucial

- the only experimental limitation for an STM is the requirement of conducting surfaces.

The STM tip_

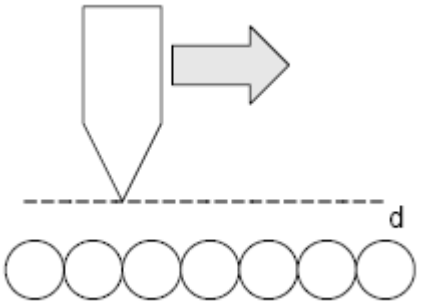
- Tip materials: often pure metals or metal alloys (e.g. W, PtIr)
- sharp tips are produces by mechanical cutting, ion beam milling or electrochemical etching
- exact geometry is commonly unknown



- sufficiently sharp tip: most of the tunneling current, I_t, will go through the pinnacle atom.
- STM precision: due to high sensitivity of the current to the electronic environment of a very small area.
- good vertical resolution due to rapid decay of I_t with distance

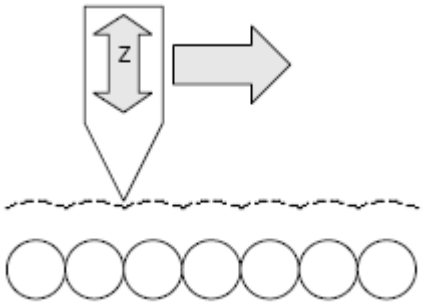
STM: Modes of operation_

Constant height



- Fixed tip-sample distance
- the image is formed by variations in the tunneling current
- fast, but works only for flat surfaces

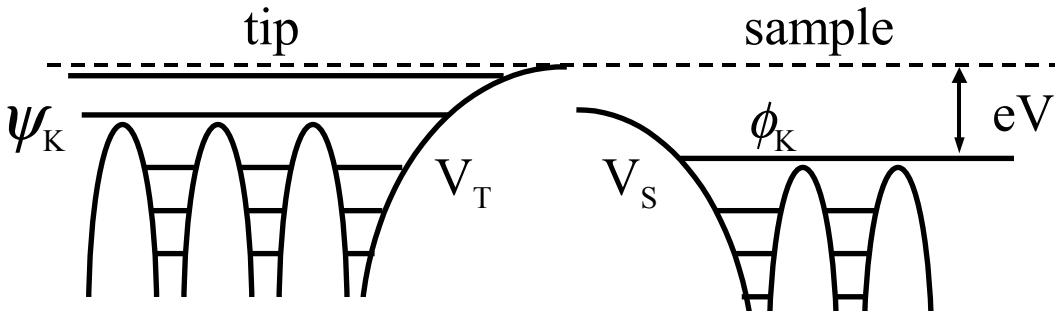
Constant current



- the tunneling current is kept constant by moving the tip up and down
-the movement in z-direction becomes the image
- slower, but works for rough surfaces

Bardeen transfer hamiltonian_

Inherently non-equilibrium situation!



Trick:

- Assume two decoupled subsystems, each itself in equilibrium
  H = -ħ2Δ/(2m) + V_S + V_T

- Tip is only a small perturbation of the sample hamiltonian

Fermi golden rule $$I = 2e\sum_{k=occ}^{k'=empty} T_{kk'} = 2e\sum_{k=\mathrm{occ}}^{k'=\mathrm{empty}} \frac{2\pi}{\hbar}\left|M_{kk'}\right|^2 \delta\left(\varepsilon_k - \varepsilon_{k'}\right)$$

$M_{kk'} = \langle\psi_k \mid V_T \mid \varphi_{k'}\rangle$ is the Bardeen matrix element

$T \to 0$ K: $$I = \frac{4\pi e}{\hbar}\int_0^{eV} d\varepsilon \iint d^2k \Big/ (2\pi)^2 \, d^2k' \Big/ (2\pi)^2 \left|M_{kk'}\right|^2 n_k^{tip}(\varepsilon) n_{k'}^{sample}(\varepsilon)$$

Tersoff-Hamann approximation_

Constant current contours are modeled from the electronic structure of the surface alone

- Limit of low bias => constant matrix element
- Tip with *s*-like character at R_0

$$I \sim \int_{E_F}^{E_F+eV} d\varepsilon \, n^{sample}(\varepsilon, R_0)$$

Tunneling current is proportional to the local density of states at the position of the STM tip

$$I \propto \sum_{E_n > E_F - eV_{bias}}^{E_n < E_F} \left|\phi(R_0, E_n)\right|^2 = n(R_0, V_{bias})$$

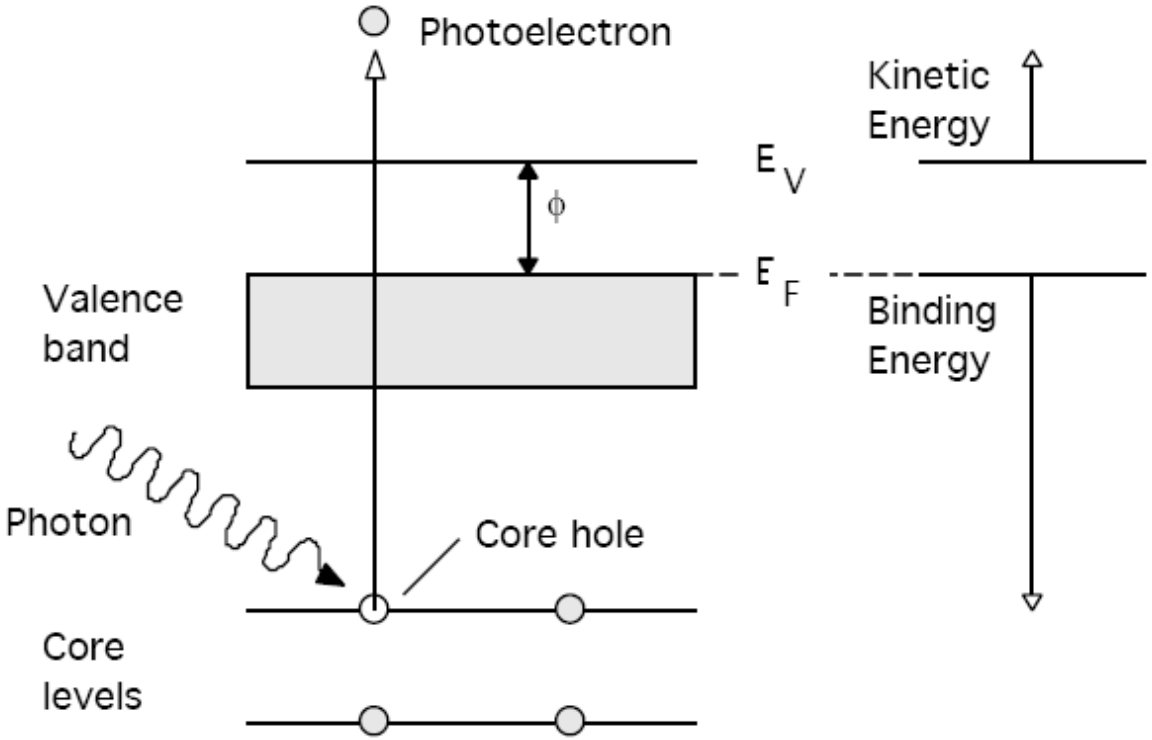
Practical evaluation:

- Compute $n_{tot}(x,y,z)$
- Solve $n_{tot}(x,y,R_0) = n_0$
- Plot $n_0(x,y)$ to simulate a constant current mode

J. Tersoff and D.R. Hamann,
Phys. Rev. Lett. ***50****, 1998 (1985)*
Phys. Rev. B ***31****, 805 (1985)*

X-ray Photoelectron Spectroscopy (XPS)

- monochromatized X-ray beam => synchrotron radioation is used often
- only levels with E_B<hν can be ionised

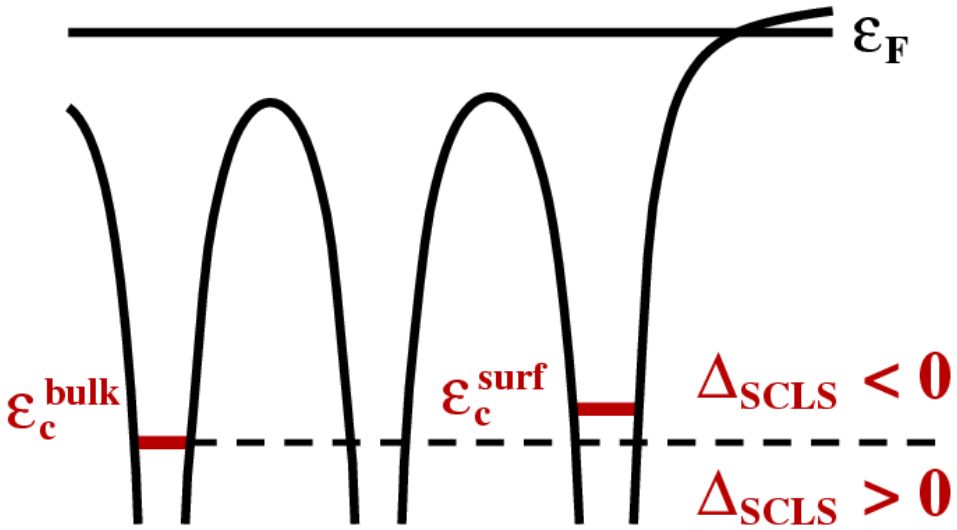


$$E_{kin} = h\nu - E_B - \Phi$$

XPS or ESCA: compositional analysis
HRCLS: chemical and bonding environment of emitting atom

Surface core-level shifts and how to calculate them

$$\Delta_{SCLS} = [\, E^{surf}(n_c - 1) - E^{surf}(n_c) \,] - [\, E^{bulk}(n_c - 1) - E^{bulk}(n_c) \,]$$



Initial-state approximation:

$$\Rightarrow \Delta_{SCLS}^{initial} \approx -[\, \varepsilon_c^{surf}(n_c) - \varepsilon_c^{bulk}(n_c) \,]$$

$$\Delta_{screen} = \Delta_{SCLS} - \Delta_{SCLS}^{initial}$$

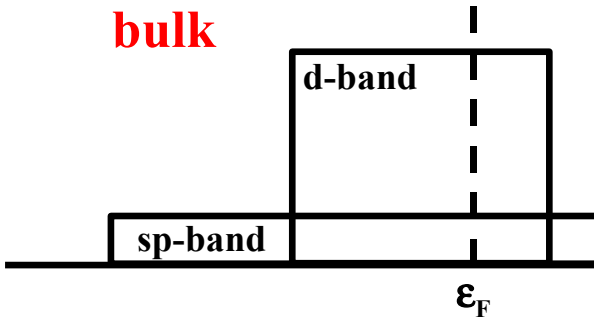
$$E(n_c - 1) - E(n_c) =$$

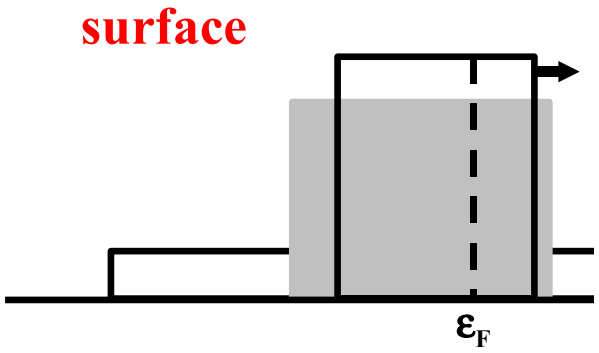
$$= \int_{n_c}^{n_c - 1} \frac{\partial E(n')}{\partial n'} dn' \approx -\varepsilon_c(n_c - \tfrac{1}{2})$$

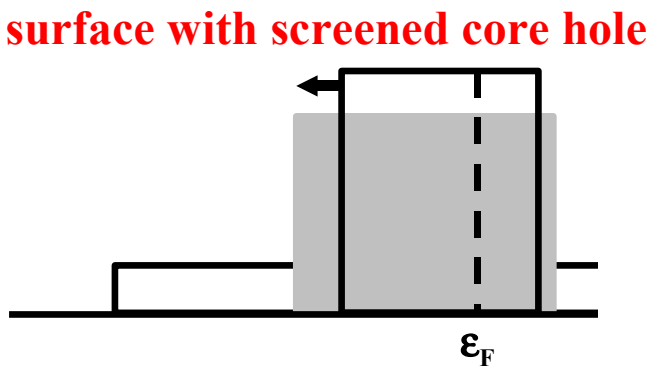
Final-state calculation:

$$\Rightarrow \Delta_{SCLS} \approx -[\, \varepsilon_c^{surf}(n_c - \tfrac{1}{2}) - \varepsilon_c^{bulk}(n_c - \tfrac{1}{2}) \,]$$

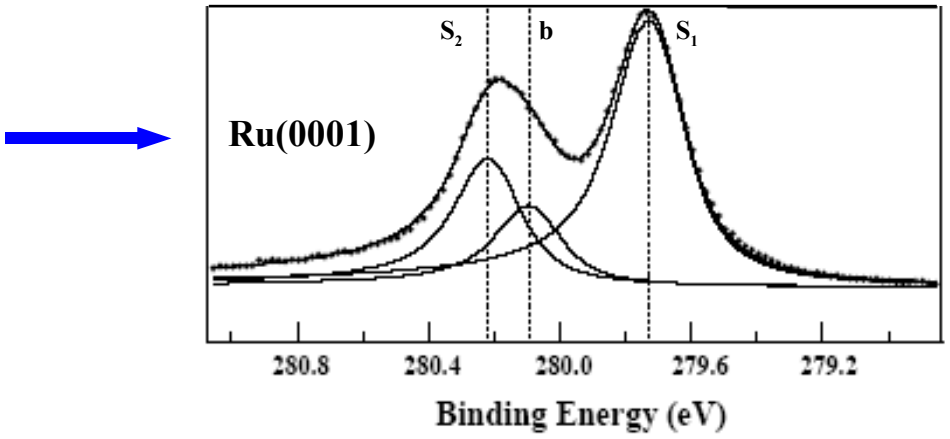
Screening at a transition metal surface





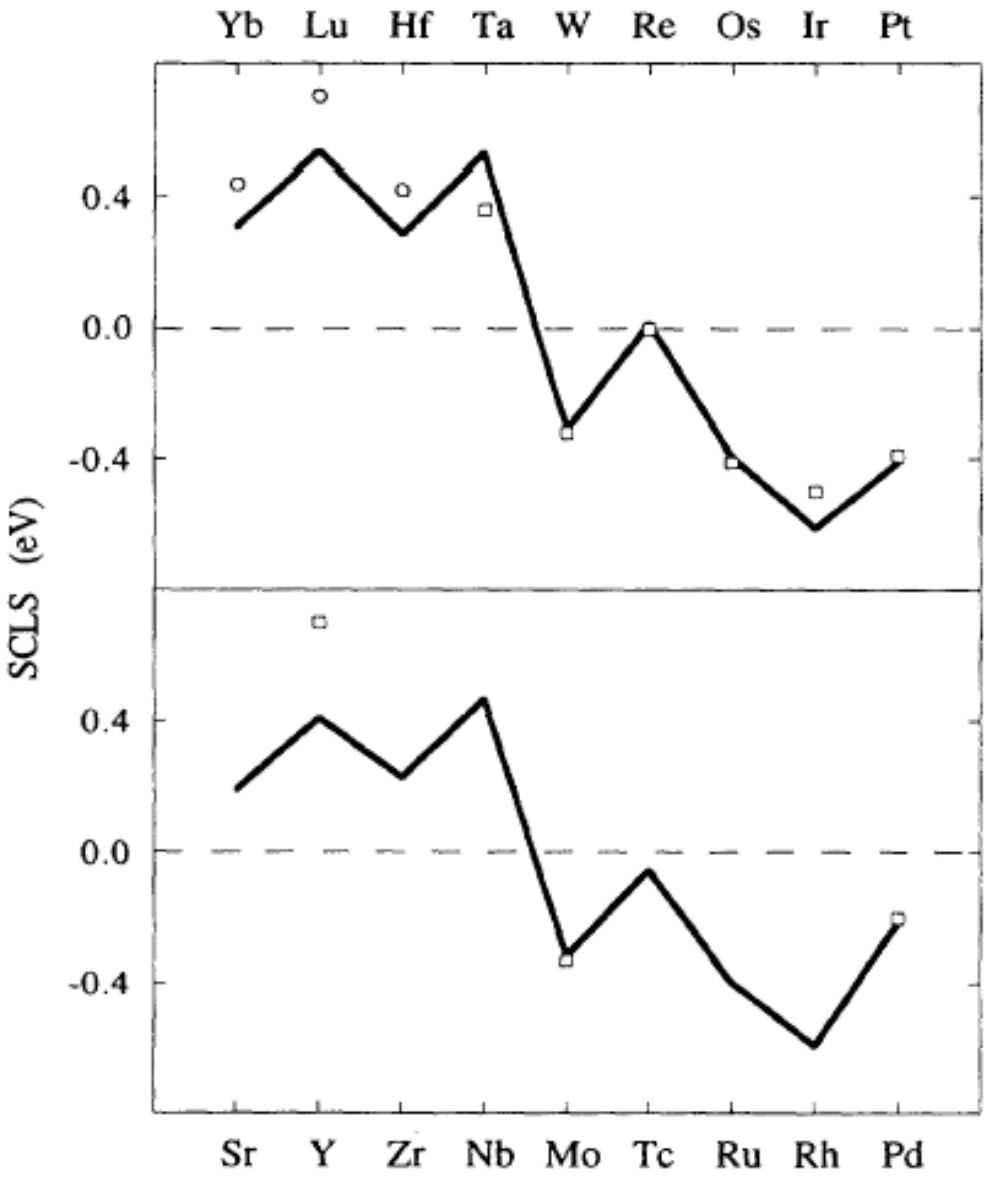


Center of gravity shifts primarily to achieve local charge neutrality



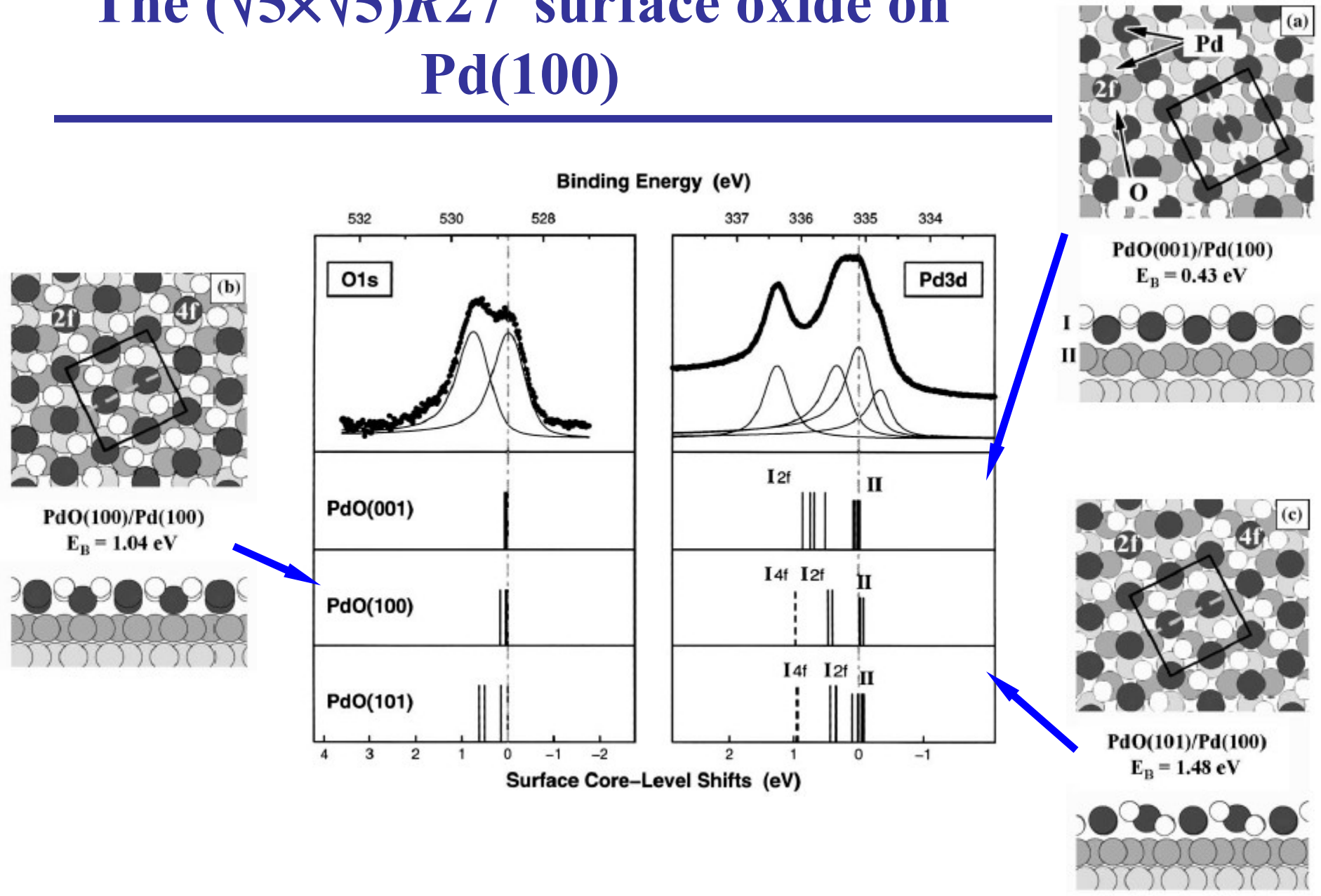
S. Lizzit *et al.*, Phys. Rev. B **63**, 205419 (2001)

Screening at a transition metal surface



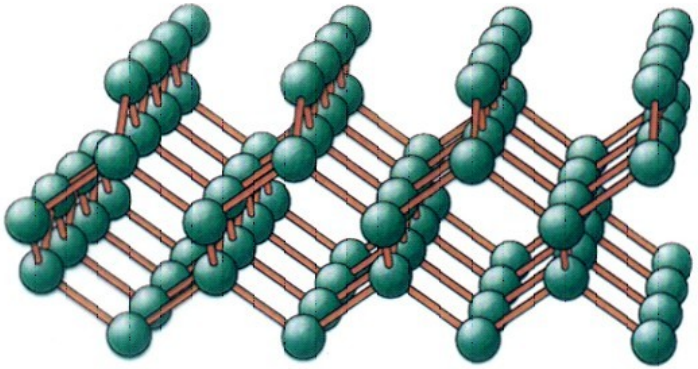
M. Aldén *et al.*,
Phys. Rev. Lett. **71**, 2449 (1993)

The (√5×√5)*R*27° surface oxide on Pd(100)

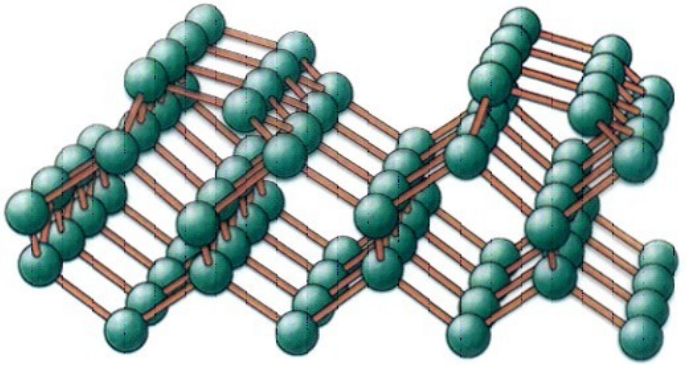


M. Todorova *et al*., Surf. Sci. **541**, 101 (2003)

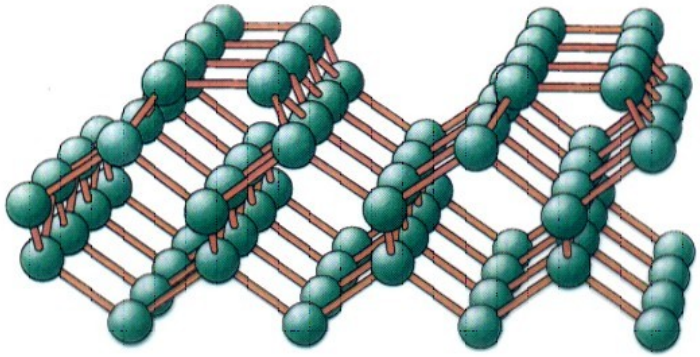
Dimerization and dimer buckling at Si(001)



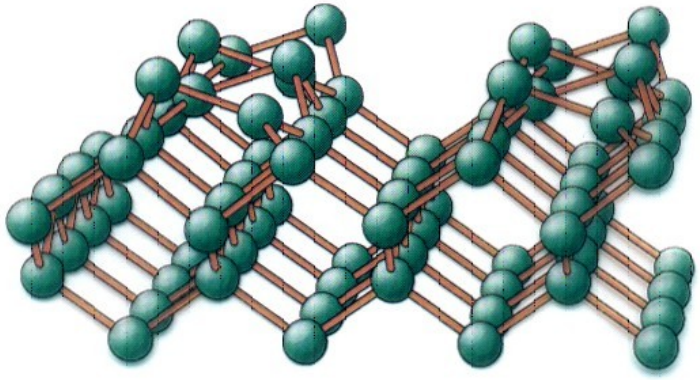
truncated bulk geometry



dimer buckling



formation of dimers

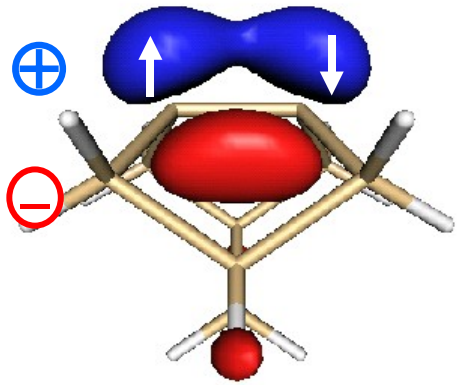


alternating buckling

Buckling at the clean Si(001) surface is sensitive to electron correlation and electron-lattice coupling

"A negative U system" ?

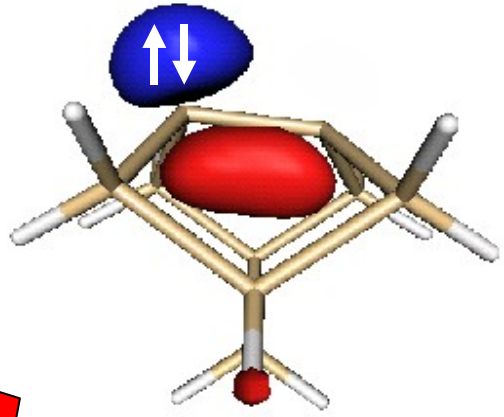
HOMO of symmetric dimer



favored by MCSCF (clusters)

Which configuration is the ground state ?

HOMO of buckled dimer



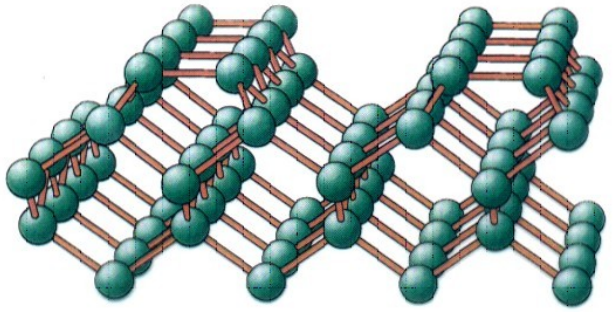
favored by DFT (slabs)

this one

Clean Si(001): experimental Results

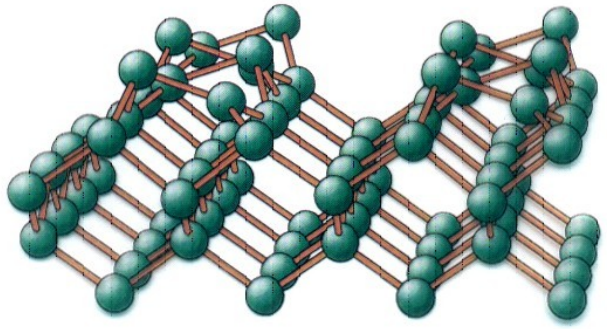
STM

- **Room temperature: symmetric dimers**

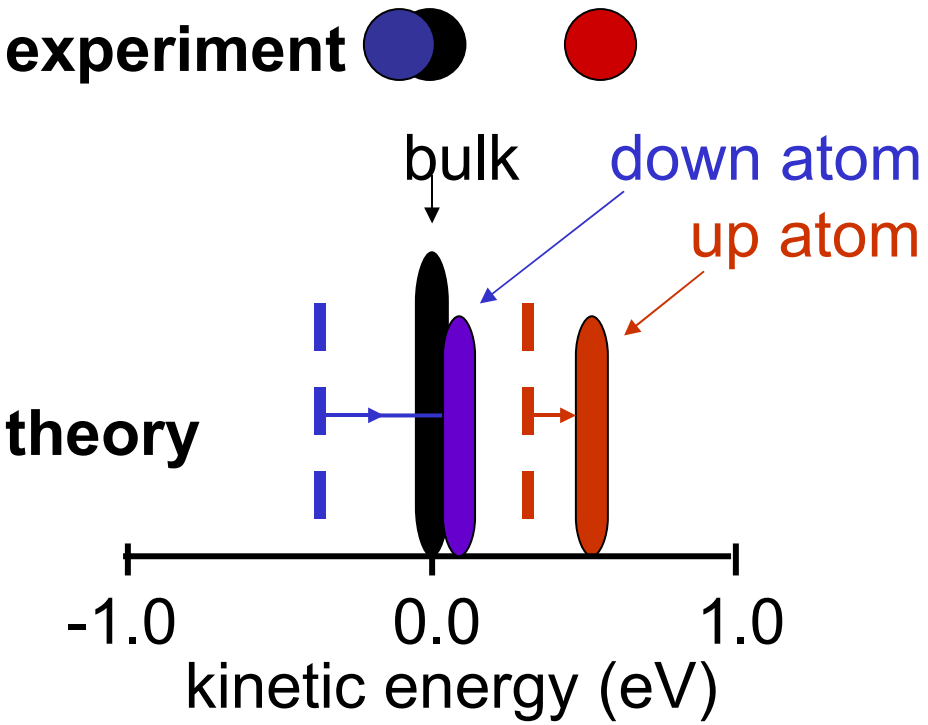


SCLS

- **buckled dimers**



Si 2*p* SCLS for Si(001) p(2x2)



Theory

dashed: initial-state effect only

bars: including also final-state screening (by total-energy differences or transition-state theory)

E. Pehlke and M.Scheffler, PRL 71, 2338 (1993).

For this system: screening at the surface is better than in the bulk

Two peaks = clear proof for the buckling

Further reading

W. Hofer, *"Theories of scanning probe microscopes at the atomic scale"*, Rev. Mod. Phys. **75**, 1287 (2003)

J.C. Chen, *"Introduction to Scanning Tunneling Microscopy"*, Oxford series in optical and imaging science, Oxford University Press, New York, 1993

S. Lizzit *et al*., *"Surface core-level shifts of clean and oxygen-covered Ru(0001)"*, Phys. Rev. B **63**, 205419 (2001)

D.Spanjaard *et al*., *"Surface core level spectroscopy of transition metas: A new tool for the determination of their surface structure"*, Surf. Sci. Rep. 5, 1 (1985)

W.F. Engelhoff, Jr., *"Core-level binding-energy shifts at surfaces and in solids"*, Surf. Sci. Rep. 6, 253 (1987)