Review LEED

"Reflexes"

Real Space

$\vec{a}_1, \vec{a}_2$ – Substrate mesh

$\vec{b}_1, \vec{b}_2$ – adsorbate mesh

$\underset{\approx}{G}$

Inverted Lattice

$\vec{a}_1^* \quad \vec{a}_2^*$ ⊗ ⊗ ⊗ ⊗

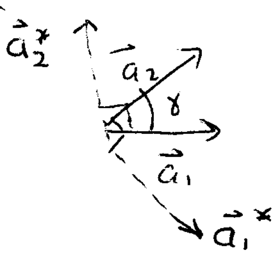
$\vec{b}_1^* \quad \vec{b}_2^*$ × × × ×
(additional)

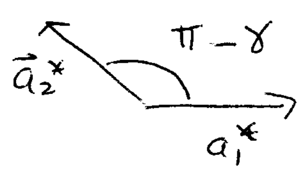
$\underset{\approx}{G}^*$

Inverted Lattice → Real Lattice

$$G = \left((G^*)^{-1}\right)^{+} = \frac{1}{|G^*|}\begin{pmatrix} G_{22}^* & -G_{21}^* \\ -G_{12}^* & G_{11}^* \end{pmatrix}$$

Non-orthogonal Axes



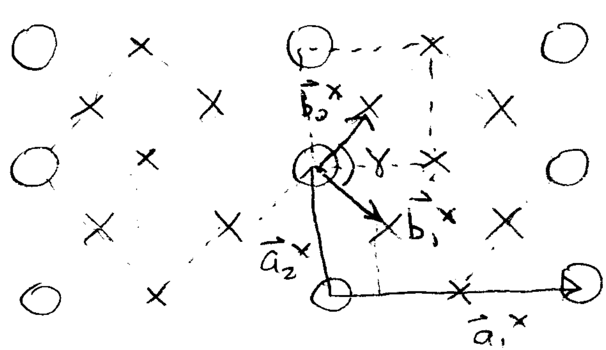


$\gamma = \pi/2$ ∡ same

$$a_i^* = \frac{1}{a_i \sin\gamma}$$

$$b_i^* = \frac{1}{b_i \sin\gamma}$$

Non-orthogonal Problem (LEED → Real surface)

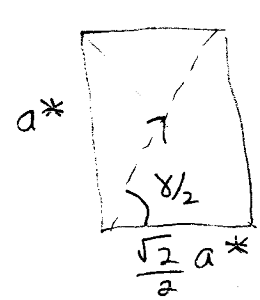


Given $|\vec{a}_1^*| = \sqrt{2}\,|\vec{a}_2^*|$
measured

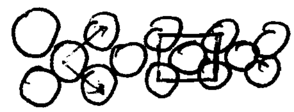
$|\vec{a}_2^*| \equiv a^*$

$|\vec{a}_1^*| = \sqrt{2}\,a^*$

– Focus on upper rectangle:



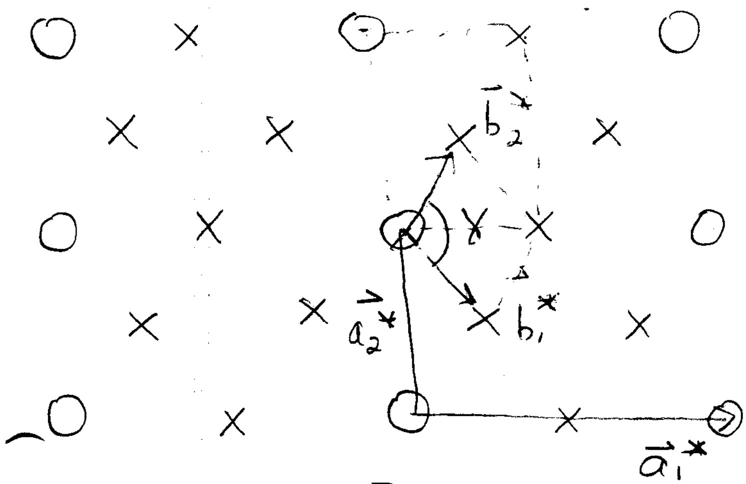
$\vec{b}_1 = \vec{a}_1 + \vec{a}_2$ $\qquad$ $\vec{b}_2 = -\vec{a}_1 + \vec{a}_2$



$100 - \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix}$ $\qquad$ Ask $\theta =$

Inverse + Non-orthogonal

LEED

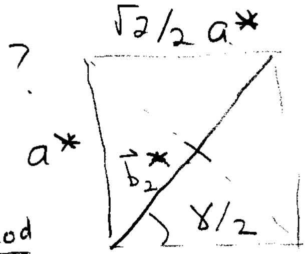


$|\vec{a}_1^*| = \sqrt{2}\,|\vec{a}_2^*|$ measured

$|\vec{a}_1^*| = \sqrt{2}\, a^*$

$|\vec{a}_2^*| = a^*$

$G^* = ?$



$\tan \gamma/2$ $(\gamma^*/2)$ $= \dfrac{1}{\sqrt{2}/2}$

$\gamma/2 = \tan^{-1}\sqrt{2} = 54.74^\circ$

$\gamma = 109.47^\circ$

$\pi - \gamma = 70.53^\circ$

Matrix Method

$\vec{b}_1^* = +\dfrac{\sqrt{2}}{4} a^* \vec{i} - \dfrac{1}{2} a^* \vec{j}$

$\vec{b}_1^* = \dfrac{1}{4}\vec{a}_1^* - \dfrac{1}{2}\vec{a}_2^*$

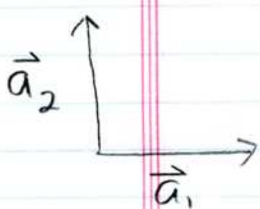
$\vec{b}_2^* = \dfrac{1}{4}\vec{a}_1^* + \dfrac{1}{2}\vec{a}_2^*$

$G^* = \begin{pmatrix} 1/4 & -1/2 \\ 1/4 & 1/2 \end{pmatrix}$

$G = \dfrac{1}{|G^*|}\begin{pmatrix} 1/2 & -1/4 \\ 1/2 & 1/4 \end{pmatrix}$ $\qquad$ $|G^*| = \dfrac{1}{8} - \left(-\dfrac{1}{8}\right) = \dfrac{1}{4}$

$$G = 4\begin{pmatrix} 1/2 & -1/4 \\ 1/2 & +1/4 \end{pmatrix} = \begin{pmatrix} 2 & -1 \\ 2 & 1 \end{pmatrix}$$

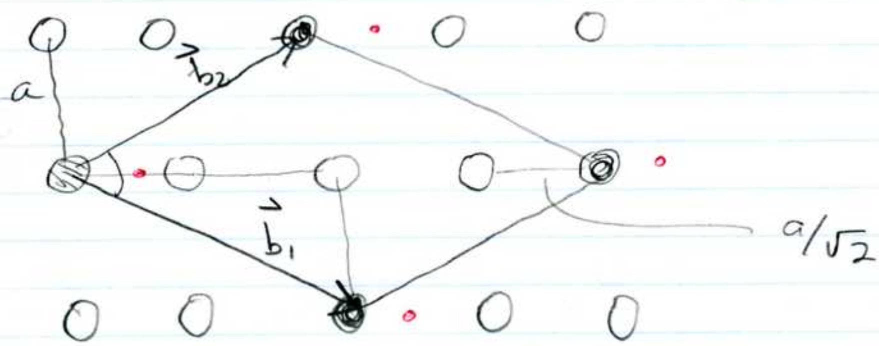
But what does $\vec{a}_1, \vec{a}_2$ net look like?



$|\vec{a}_1| = a/\sqrt{2}$ $\quad |\vec{a}_2| = a$ $\quad \perp$ so no $\sin\gamma$ problem

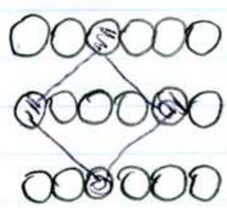
$$\vec{b}_1 = 2\vec{a}_1 - \vec{a}_2$$
$$\vec{b}_2 = 2\vec{a}_1 + \vec{a}_2$$

OR



$\pi - \gamma = 70.53^\circ$ ✓ $\qquad 110 - \begin{pmatrix} 2 & -1 \\ 2 & 1 \end{pmatrix}$

Check $\quad b_2 = \dfrac{1}{b_2^* \sin\gamma}$



LEED   Additional Points

We have studied how reflex positions from both adsorbate and substrate determine the unit surface cell and the overlayer structure.

We have not studied what can be learned from intensities. With luck & fortitude, one can determine exact atomic coordinates:

 vs 

Loss of Order

LEED diffraction patterns arise from periodic order.

No order ⇒ diffuse background only

1-D order ⇒ ~~order~~ diffraction pattern in 1-D only

Reduced Order 

Increasing surface temperature ⇒ increased vibrational motion ⇒ increased diffuse scattering; broader reflexes

Diffusion ⇒ diffuse scattering

Width of Reflex : ROUGH SURFACE

$$\delta\beta = \frac{\lambda}{2d\cos\beta} \quad \text{if } \lambda \text{ known precisely}$$

angular divergence of beam

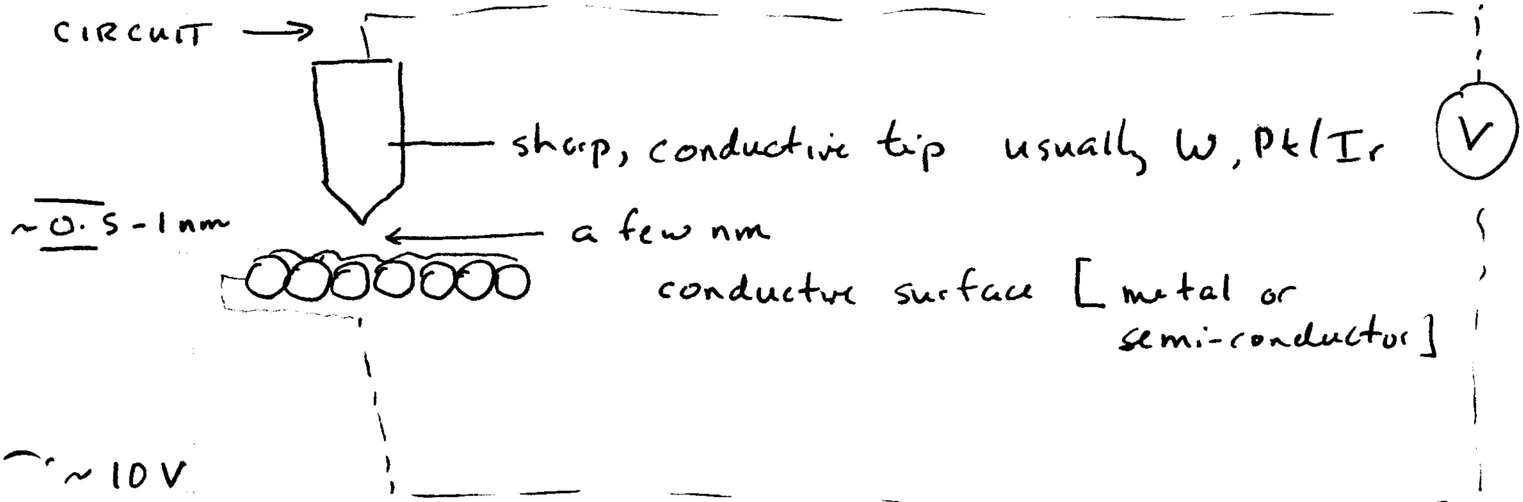
diameter of ordered region (e.g. island)

$\delta\lambda$ adds to width

MICROSCOPIES

Basis: sharp tip is brought close to surface and a measurement is made of some property that depends on distance to surface. Scanning the tip maps out the surface in some sense.

Scanning Tunneling Microscopy (STM)



Voltage difference applied. Can do measurement by:

(a) current at constant voltage (smooth surface)

(b) voltage needed to maintain current while scanning. (rough surface)

What is happening? Electrons tunnel from tip to surface or reverse, depending on polarity $(- \to +)$

$I \propto \exp(-2Kd)$ d: tunneling distance

$$K^2 \cong \frac{2m_e}{\hbar^2}\left(V_{barrier} - E\right) \qquad K \sim 1\ \text{Å}^{-1}$$

$V_{barrier}$: barrier

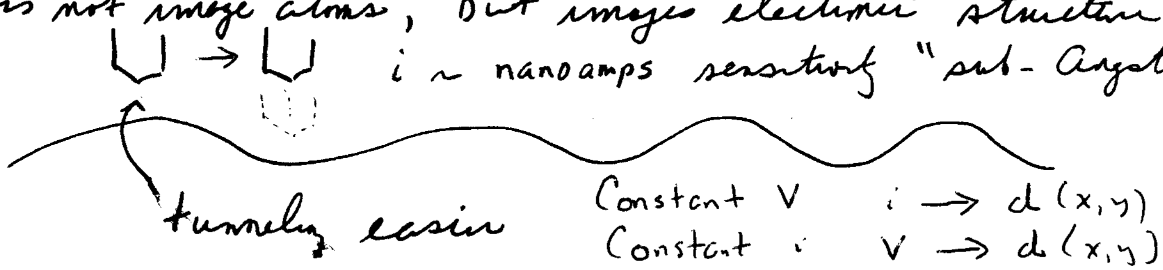
E: electron energy? (state energy)

very sensitive to d

STM does not image atoms, but images electronic structure:

$i \sim$ nanoamps   sensitivity "sub-Angstrom"

$|\psi|^2$



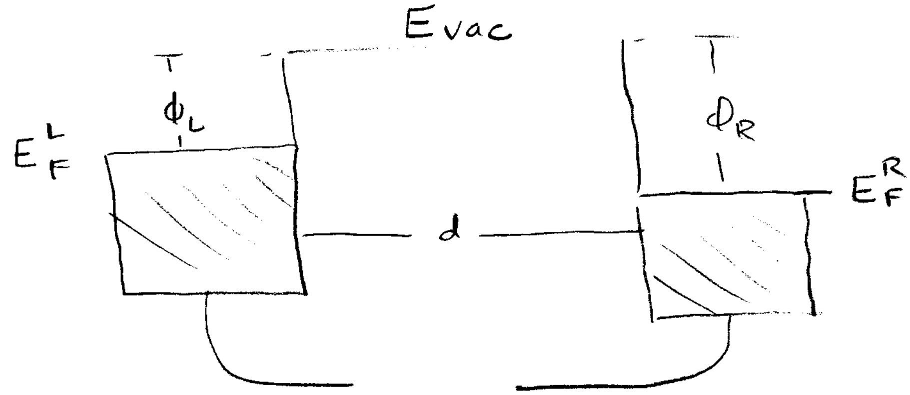
Constant V $i \to d(x,y)$

Constant i $V \to d(x,y)$

– More detail (still oversimplified)

a) <u>Open Circuit</u>:

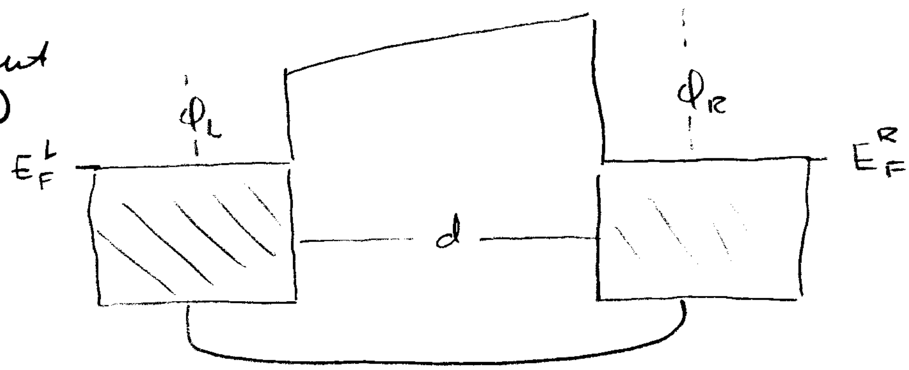
L = surface or tip

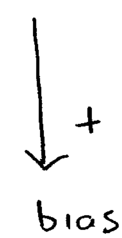


b) Closed Circuit (no voltage)

$\mu_L = \mu_R$

$E_F^L = E_F^R$

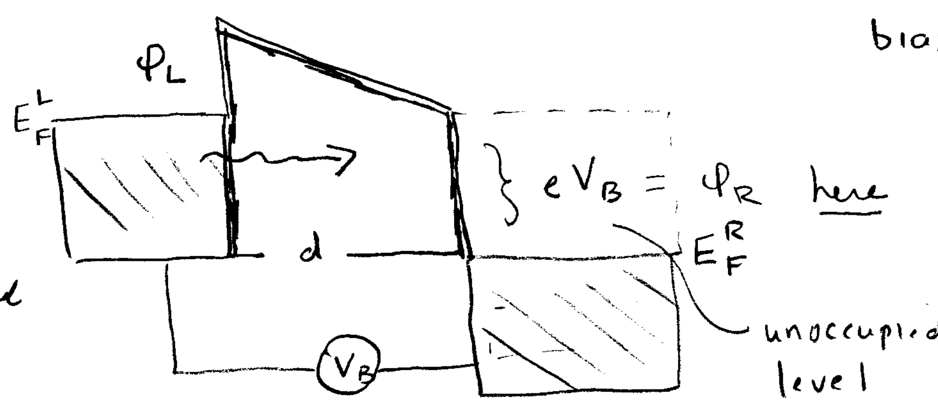




c) + Bias applied to right

$eV_B = E_F^L - E_F^R$

occupied → unoccupied via tunneling



STM images represent a convolution of the density of states, both occupied & unoccupied, between tip & surface.

<u>THUS</u>, surface electronic features can represent occupied or unoccupied states depending on polarity.

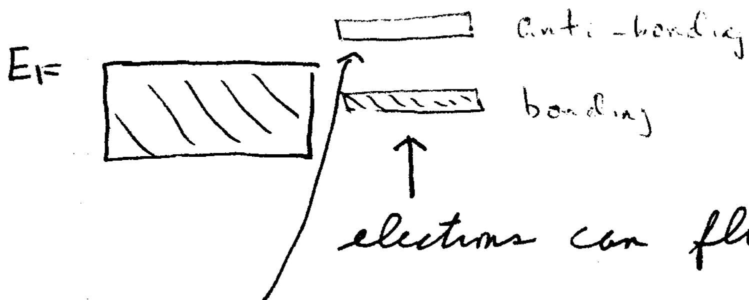
L: occupied states of surface

R: unoccupied states of surface

— Depending on polarity & voltage, both occupied and unoccupied surface bands can be imaged.

Adsorbates

Detection depends on MO - band interactions. Bonding Orbitals lie lower than antibonding ones & so need voltages different. Images may be different too.



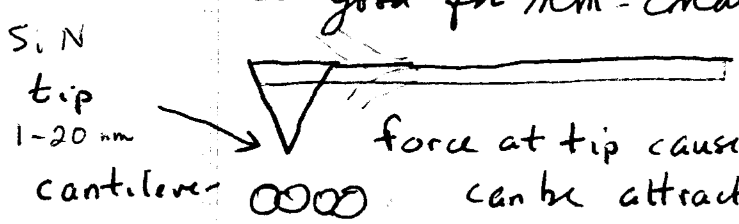
electrons can flow to tip if more (+).

need electrons to flow here, so tip must be more (−).

SHOW PICTURES

Atomic Force Microscopy (Scanning Force Microscopy)

— good for non-conductors as well as conductors



← deflection can be detected by laser

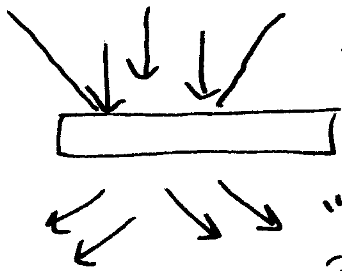
force at tip causes bending

can be attractive or repulsive

Force	Range (nm)	(Kolasinsk.)
van der Waals	≤ 10	
H- bonding	0.2	
Contact	0.1	

— Forces typically at longer range than tunneling current so that resolution < STM 2-10 nm although in exceptional cases atomic resolution can be achieved.

Near-Field Scanning Optical Microscopy (NSOM)



Aperture $< \lambda$

thin film

"near field" of small light source.

aperture $\sim$ Resolution $\ll$ "diffraction limit" ($\sim \lambda/2$)

$\sim$ 50 nm