Sensors of Structure

- Matter Waves and the deBroglie wavelength
- Heisenberg uncertainty principle
- Electron diffraction
- Transmission electron microscopy
- Atomic-resolution sensors

deBroglie

- Postulated that all objects have a wavelength given by
  - $\lambda=h/p$
    - λ=wavelength
    - h=Planck's constant
    - p=momentum of object
- In practice, only really small objects have a sensible wavelength

Wave-Particle duality

- A consequence of the deBroglie hypothesis is that all objects can be thought of as "wavicles": both particles and waves
- This has troubled many philosophically-minded scientists over the years.
- Inescapable if we want to build atomic-resolution sensors.

Heisenberg Uncertantity Principle

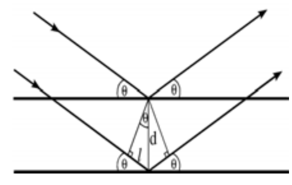
- Cannot simultaneously measure an object's momentum and position to a better accuracy than $\hbar/2$
  - $\Delta p_x \Delta x \geq \hbar/2$
- Direct consequence of wave-particle duality
- Places limitations on sensor accuracy

Electron Diffraction

- Accelerated electrons have wavelength of order 1 Angstrom=1e-10m
- Same order as atomic spacing
- Electrons undergo Bragg diffraction at atomic surfaces if the atoms are lined up in planes, ie a crystal

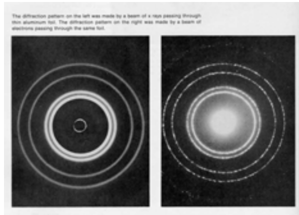
Bragg reflection

- Constructive interference when the path length difference is a integer multiple of the wavelengths
- $n\lambda=2d \sin\theta$
- Detailed description requires heavy (mathematical) QM.



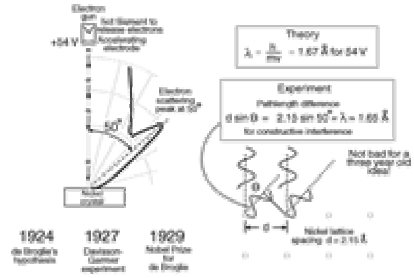
Diffraction Patterns

- Only certain angles of reflection are allowed.
- The diffracted electrons form patterns.
- In polycrystalline material, these are rings



X-rays on left, electrons on right.

Davisson-Germer experiment



- Application of diffraction to measure atomic spacing
- Single crystal Ni target
- Proved deBroglie hypothesis that $\lambda=h/p$

Proof that $\lambda=h/p$

Accelerated electrons have energy eV:

$$eV= \tfrac{1}{2} mv^2 \Rightarrow v = (2Ve/m)^{1/2}$$

de Broglie said:

$$\lambda=h/p=h/(mv)=h/(2mVe)^{1/2}=1.67\ \text{Å}$$

Davisson-Germer found lattice spacing:

$$\lambda=d\sin\theta=1.65\ \text{Å}$$

Excellent agreement between theory and experiment!

Pressure sensing

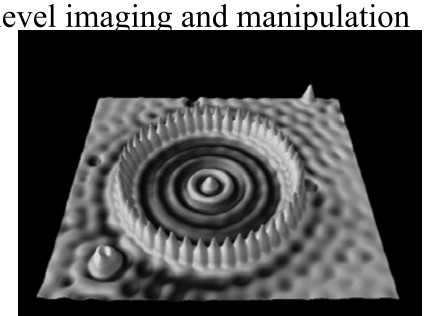
- Atomic spacing changes with pressure:
  - Pressure=$E(\Delta L/L)$
    - E=Youngs modulus (N/m^2)
- As d changes, angle of diffraction changes
- Rings move apart or closer together

STM and AFM

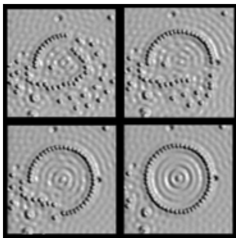
- Electron diffraction can probe atomic lengthscales, but
  - Targets need to be crystalline
  - Need accelerated electrons=>bulky and expensive apparatus.
  - Need alternatives!

Atomic level imaging and manipulation

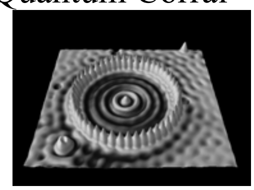
http://www.personal.psu.edu/users/m/m/mmt163/E%20SC%20497E_files/Quantum_Corral.htm



- Scanning Tunnelling Microscopy
- Atomic Force Microscopy



Quantum Corral



- Image shows ‘Quantum corral’ of 48 Fe atoms on a Cu surface
- Low-temp STM used for assembly and imaging
- Can see Schrodinger standing waves
- Colors artificial

Quantum Mechanics

- STM and AFM inherently quantum-mechanical in operation
- Need to understand the electron wavefunction to understand their operation
- We need some QM first

The wavefunction

- The electrons of an atom are described by their wavefunction:
  - $\Psi = \Psi_0 e^{i/\hbar\,(px-Et)}$
  - Contains all information about electron
    - Eg probability of electron being in a certain region is $P(x)=\int \Psi^*\Psi dx$

Schrodinger’s Eqn

- $-\hbar/2m\ d^2\Psi/dx^2 + U(x)\Psi = i\hbar\ d\Psi/dt$
- All ‘waveicles’ must obey this eqn
- U(x) is the potential well
  - In the case of atoms, it can be approximated by a square well

The square well

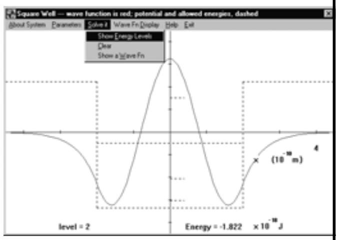
- Solve Schrodinger’s eqn for a potential
  - $U(x)=0$ between $x=0$ and $x=L$
  - $U(x)=U_0$ everywhere else.
- Assume that the solutions do not vary with time (stationary states)
  - $\Psi = \Psi(x)$

Solutions for a square well

- $\Psi(x)=A\sin(n*pi*x/L)$ inside the well
  - These are simply standing waves in a cavity, with n denoting the mode number
- Same as solution from classical physics

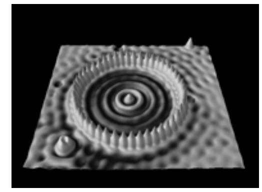
Wavefunction trails

- $\Psi(x)=Ae^{\pm ax}$ outside the well
  - This is the important bit for STM and AFM
  - Means that the wavefunction extends beyond the atomic surface



Atomic level imaging and manipulation

- Scanning Tunnelling Microscopy
- Atomic Force Microscopy



ELASTIC TUNNELLING through 1D Potential Barrier

(1). de Broglie → Matter waves ($\lambda = h/p$)

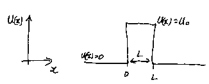
(2) Heisenberg Uncertainty Principle ($\Delta x \Delta p_x \geq \hbar/2$)

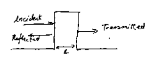
(3) Wavelike behaviour of free particles described by wavefunction ($\Psi = \psi_0 e^{i(kx-\omega t)}$)

(4) Probability density ⇒ Probability of finding particle
$$P = \int_x^{x+dx} |\Psi(x)|^2 dx$$

(5) Schrodinger's Wave equation (1-D, time independent)
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)$$

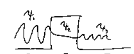
→ Consider particle incident on potential barrier





The transmission probability for a particle through a potential barrier is given by the ratio of the transmitted probability density to the incident probability density i.e.
$$T(E) = \frac{|\psi_{transmitted}|^2}{|\psi_{incident}|^2}$$

→ To determine the probability of transmission need to consider the S.W.E in each of the three regions



The 1-D, time independent SWE is
$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

in Region I & III $U(x) = 0$
$$\Rightarrow \frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) = -k^2\psi(x)$$

where $k^2 = \frac{2mE}{\hbar^2}$

So we need a solution for $\psi(x)$ that satisfies
$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$
, which can have soln of $e^{\pm ikx}$

For I The soln. is $\psi_I(x) = Ae^{ikx} + Be^{-ikx} \rightarrow \psi_I$ (Incident; Reflected)

For III the complete wavefunction is
$$\psi_{III}(x) = Fe^{ikx} + Ge^{-ikx}$$
(G → 0, no reflected component)

In region II, $U(x) = U_0$
$$\Rightarrow \frac{d^2\psi(x)}{dx^2} = \frac{2m(U_0-E)}{\hbar^2}\psi(x) = \alpha^2\psi(x)$$
$$\alpha^2 = \frac{2m(U_0-E)}{\hbar^2}$$

Since α^2 is positive the solns will be of the form $e^{\pm\alpha x}$

so the wavefunction is
$$\psi_{II}(x) = Ce^{\alpha x} + De^{-\alpha x} \quad \text{in region II}$$

The coefficients of the wavefunction C and D are fixed by the requirement that the wavefunction is continuous at the boundaries, i.e. at $x=0$ $\psi_I = \psi_{II}$, & $\frac{d\psi_I}{dx} = \frac{d\psi_{II}}{dx}$
& similarly at $x=L$, $\psi_{II} = \psi_{III}$ & $\frac{d\psi_{II}}{dx} = \frac{d\psi_{III}}{dx}$

This gives

at $x=0$ $A+B = C+D$ for $\psi_I(x) = \psi_{II}(x)$
$ikA - ikB = \alpha C - \alpha D$ for $\frac{d\psi_I}{dx} = \frac{d\psi_{II}}{dx}$

& at $x=L$
$$Ce^{\alpha L} + De^{-\alpha L} = Fe^{ikL}$$
$$\alpha Ce^{\alpha L} - \alpha De^{-\alpha L} = ikFe^{ikL}$$

These can be solved to obtain an expression for the transmission probability i.e $T(E) = \frac{|\psi_{I}|^2}{|\psi_{III}|^2}$

for which we obtain
$$T(E) = \left\{1 + \frac{1}{4}\frac{U_0^2}{E(U_0-E)}\sinh^2\alpha L\right\}^{-1}$$

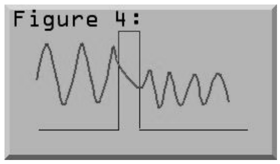
but $\sinh^2(\alpha s) = \left[\frac{1}{2}(e^{\alpha s} - e^{-\alpha s})\right]^2$

for $\alpha s \gg 1$
$$\Rightarrow T(E) \approx \frac{16E(U_0-E)}{V^2}e^{-2\alpha L}$$

$$T(E) \propto \exp(-2\alpha L)$$

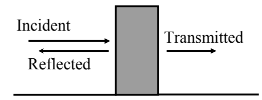
Tunnelling phenomena

- If another atom is brought close enough to the first, the wavefunction from the first atom can overlap into the second
- Means the electron has probability of being found in second atom
- Electron has tunnelled through the potential barrier



Transmitted intensity proportional to $e^{-2\alpha s}$

Where $\alpha = \frac{\sqrt{2m(U-E)}}{\hbar}$



Characteristic scale of tunnelling is $\delta=1/\alpha$

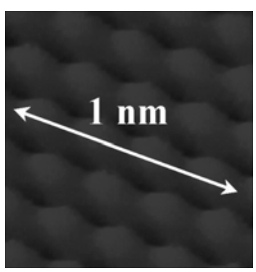
If U-E =4 eV (typical value of metal work function), then for an electron:

$$\delta=(1.05*10^{-34})/[(2(9.1*10^{-31})(4*1.6*10^{-19}))]^{1/2}$$

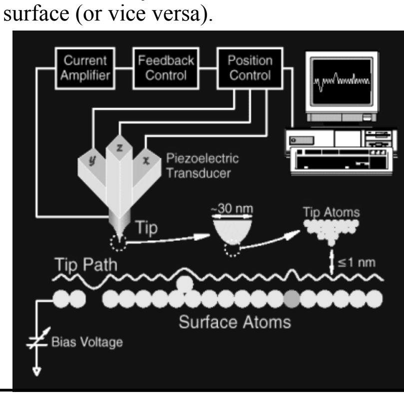
which is about 1 Å

STM Principles

- "Scanning Tunnelling Microscope"
- Tunnelling current depends exponentially on distance from surface
  - Move tip across surface, and the current changes as the tip "feels" the "bumps" caused by valence electron wave functions
- Image shows individual atoms of a sample of Highly Oriented Pyrolytic Graphite.

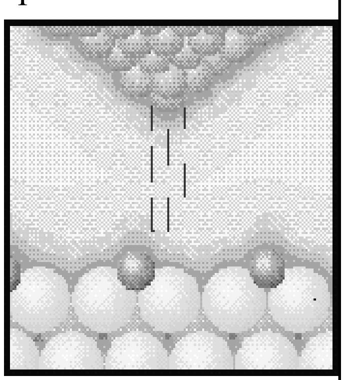


In STM, a tip is brought in very close proximity to a surface to be analysed: the electrons can tunnel from tip to surface (or vice versa).



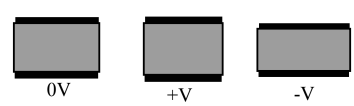
STM operation

Tunnelling current very sensitive function of separation
Keep tip current constant, and measure variations in height with a piezoelectric crystal

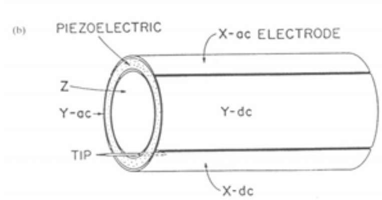


STM and piezos

- Piezoelectric bar
- Application of bias causes expansion contraction of crystal

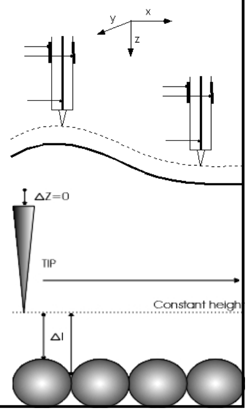


- Tube scanner – 2-D scanning



STM Operating Modes

- Const. current mode:
  - Move tip over surface and measure changes in height with piezo.
- Const. height mode:
  - Keep tip-surface separation const, and measure changes in current.
  - Need very flat samples to avoid tip crash!

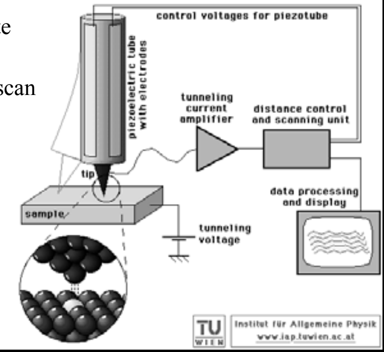


Scanning issues

Raster Scanning over area from .1X.1mm to 10X10 nm

Scan rates can be quite fast

Resolution/scan size/scan rate tradeoff

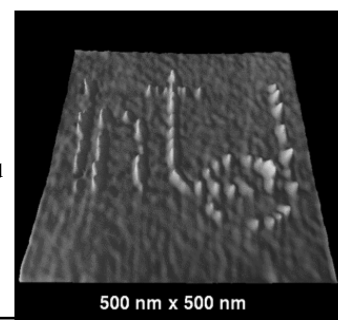


Vacuum Operation

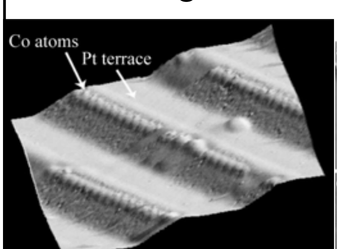
- Needs Ultra High vacuum
  - Prevents unwanted gases adsorbing onto surface
  - Lots of turbo pumps and stainless steel
  - Bakeout and surgical handling procedures

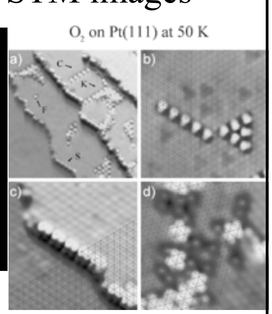
Atomic manipulation using STM

- Can move or desorb atoms as well as image.
- Adsorb=stick to surface
- Desorb=unstick from surface
- Absorb=diffuse into bulk
- Put high voltage on tip to draw current and “arc weld surface”
- Use small bias to pick up atoms and assemble them into cheesy logo



Some gratuitous STM images

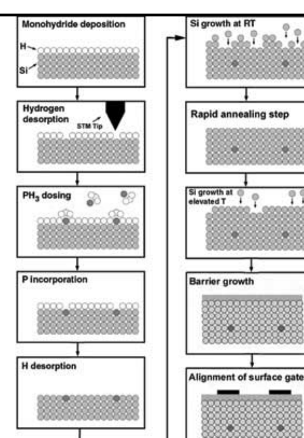




- Great for grant applications and press releases!

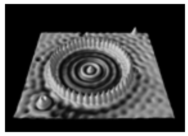
Nanoscale Lithography

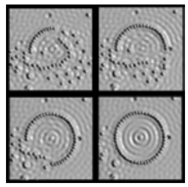
- Selective oxidation of semiconductor surfaces
- Positioning of single atoms



The STM image

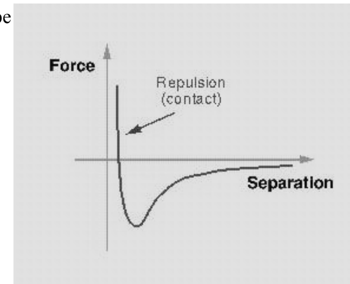
- The STM image is a file of (x,y,height) co-ords
- It can be manipulated to produce all sorts of images
  - Fantastic colour schemes of dubious taste
  - Animation and fly-by videos
- Quantum corrals; can image e- wavefunction
  - See the ripples
  - Spiles are Fe d-orbitals
  - Yellow atoms are Cu





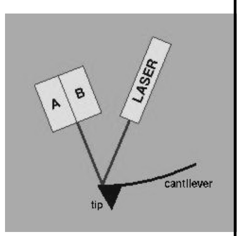
The Atomic Force Microscope

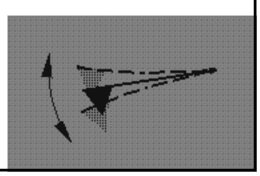
- Atomic Force Microscope (AFM)
- STM measures tunelling current; but AFM measures van der waals forces directly
- Van der Vaals force attractive with $F_{VDW} \propto 1/s^7$



The AFM

- Detect minute movements in cantilever by bouncing laser off and using interferometry (remember laser sensors)
- Photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts to voltage.
- Feedback from photodiode signals, enables the tip to maintain either a constant force or constant height above the sample.
- Atomic resolution
- Sample need not be electrically conductive



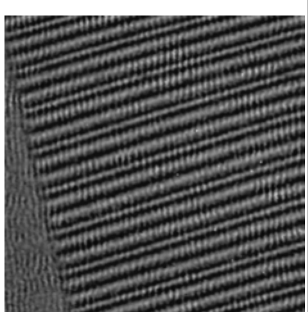


The AFM cantilever

- Most critical component.
- Low spring constant for detection of small forces (Hookes law $F=-kx$)
- High resonant frequency to minimise sensitivity to mechanical vibrations ($\omega_o^2=k/m_c$)
- Small radius of curvature for good spatial resolution
- High aspect ratio (for deep structures), can use nanotubes

AFM

- Can get atomic scale resolution, just like STM.
- Still needs UHV and vibration isolation for atomic scale resolution.
- Different Modes:
  - Contact
  - Non-contact (resonant response of cantilever monitored)

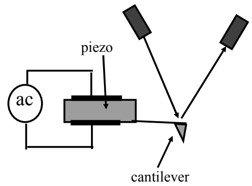


Contact mode

- Responds to short range interatomic forces
  - Variable deflection imaging
    - scan with no feedback, measure force changes across surface
  - Constant Force imaging
    - Force and cantilever deflection kept constant to image surface topography
- Caution is required to ensure cantilever doesn't damage surface

Non-Contact mode

- Responds to long range interatomic forces ⇒ greater sensitivity required
- Instead of monitoring quasi-static cantilever deflections measure changes in resonant response of cantilever
- Cantilever connected to piezoelectric element – bends with applied potential
- Lower probability of inducing damage to surface

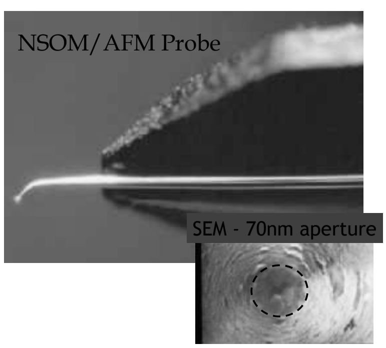


- Cantilever driven close to resonant frequency, ω_o
- If cantilever has spring const, k_o in absence of surface interactions
- Then in presence of force gradient, $F' = dF_z/Dz$
  $K_{eff} = k_o - F'$
- This causes shift in resonant frequency i.e
  $\omega_{eff}^2 = k_{eff}/m_c = (k_o - F')/m_c = (k_o/m_c)(1 - F'/k_o)$
  $\omega_{eff} = \omega_o (1 - F'/k_o)^{1/2}$
- If F' small $\omega_{eff} \sim \omega_o (1 - F'/2k_o)$, hence a force gradient F will shift the resonant frequency

Near field Scanning Optical Microscope (NSOM) Combined with AFM

•Optical resolution determined by diffraction limit (~λ)

•Illuminating a sample with the "near-field" of a small light source.
• Can construct optical images with resolution well beyond usual "diffraction limit", (typically ~50 nm.)



NSOM Setup

Transmission

Ideal for thin films or coatings which are several hundred nm thick on transparent substrates (e.g., a round, glass cover slip).

Photoluminescence emsission

Sample locally illuminated with SNOM, spectrally resolved global photemission measured.