Nanostructures

1. Effects for Electrons at Nanometer Scale
2. Microscopy and Spectroscopy of Nanostructures
    - A. Electron Microscopy (EM)
    - B. Scanning Tunneling Microscopy (STM)
    - C. Scanning Probe Microscopy (SPM)
3. Quantum Dots
4. Coulomb Blockade
5. Single Electron Transistor

Effects for Electrons in Nanostructures

- Quantum confinement effect
- Tunneling effects
- Charge discreteness and strong electron-electron Coulomb interaction effects
- Strong electric field effects
- Ballistic transport effects

Important Length Scales

Elastic mean free path (l_e): average distance the electrons travel without being elastically scattered

$l_e = v_F\tau_e$. v_F denotes the Fermi velocity of the electrons

Phase coherent length (l_Φ): average distance the electrons travel before their phase is randomized

$l_\Phi = v_F\tau_\Phi$. τ_Φ denotes the dephasing time of the electrons

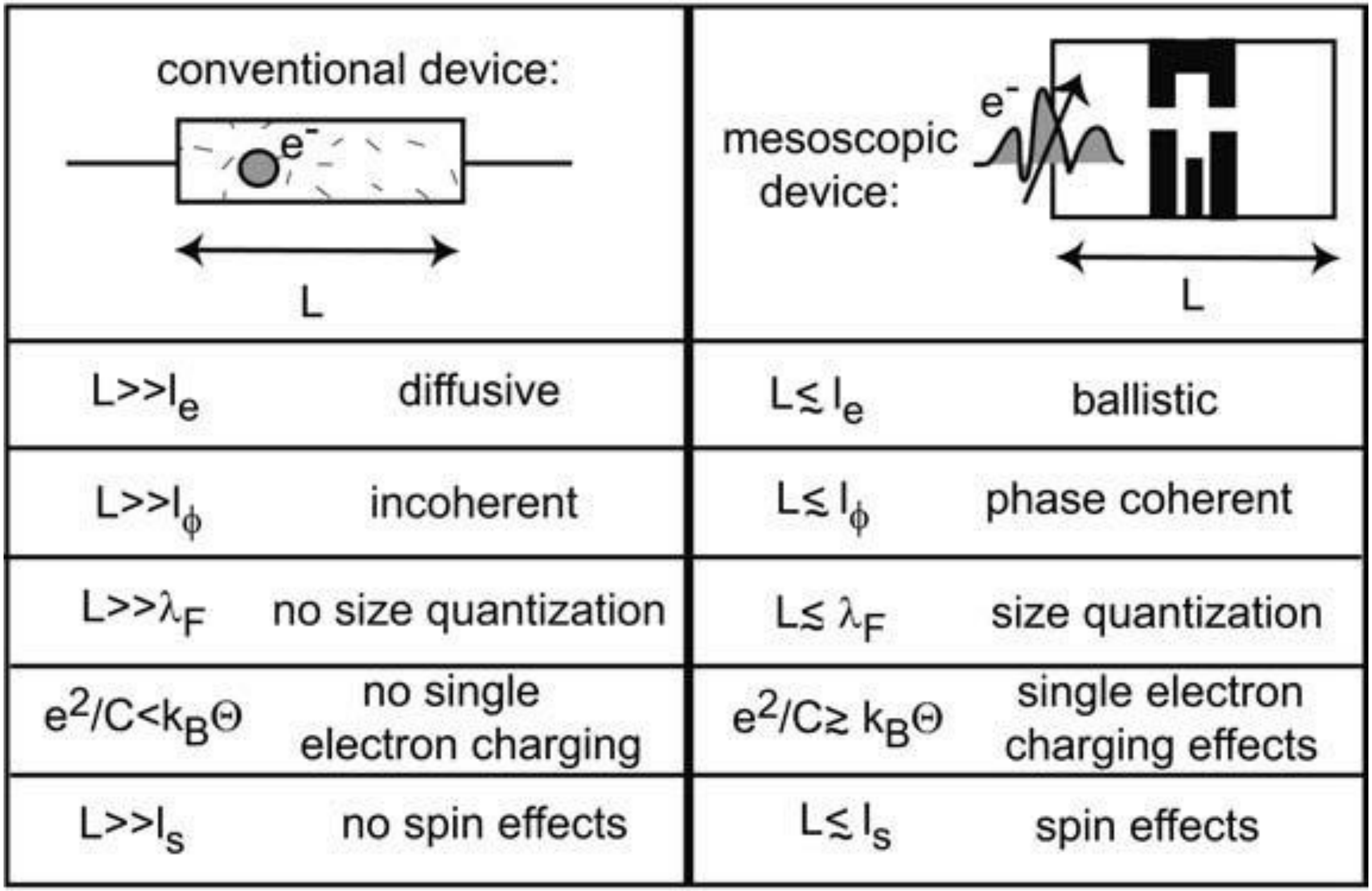
Fermi wavelength (λ_F): de Broglie wavelength of Fermi electrons

in $d = 3$: $\lambda_F = 2^{3/2}(\pi/3n)^{1/3}$

in $d = 2$: $\lambda_F = (2\pi/n)^{1/2}$

in $d = 1$: $\lambda_F = 4/n$

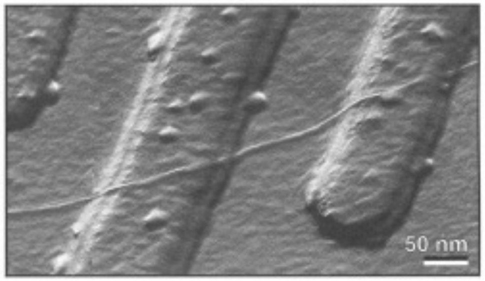
Important Mesoscopic Regimes



conventional device:		mesoscopic device:	
$L>>l_e$	diffusive	$L \lesssim l_e$	ballistic
$L>>l_\phi$	incoherent	$L \lesssim l_\phi$	phase coherent
$L>>\lambda_F$	no size quantization	$L \lesssim \lambda_F$	size quantization
$e^2/C<k_B\Theta$	no single electron charging	$e^2/C \gtrsim k_B\Theta$	single electron charging effects
$L>>l_s$	no spin effects	$L \lesssim l_s$	spin effects

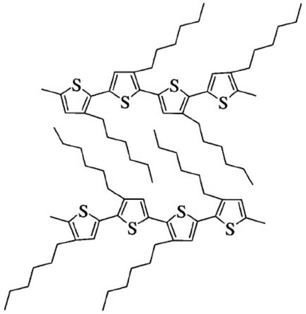
Nanoscale Electronics

Nanotubes/wires

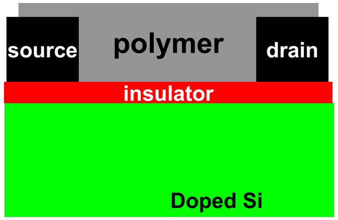


Tans *et al.* (1997)

Organic electronics

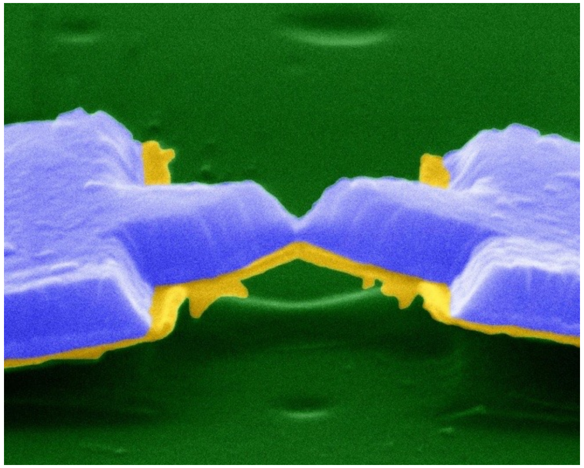


Poly(3-hexylthiophene)

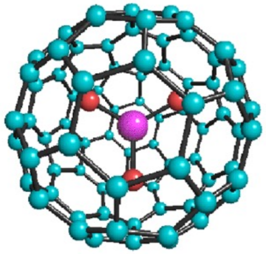


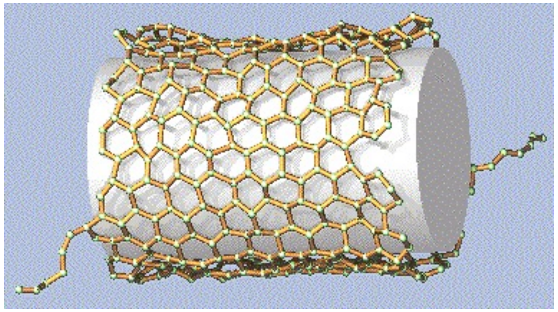
Z.Q. Li *et al.* (2006)

Atomic point contacts

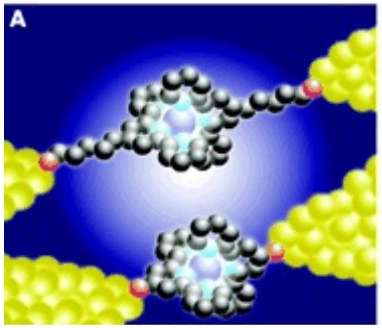


Scheer *et al.* (1998)



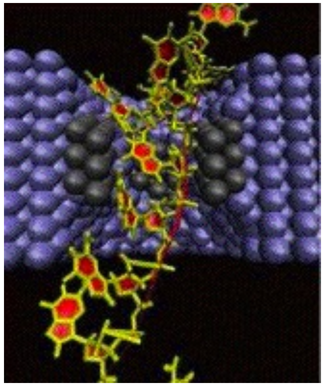


Molecular junctions



from Nitzan *et al.* (2003)

Fast DNA sequencing



Lagerqvist *et al.* (2006)

Electron Microscopy and Microanalysis

- Microscopies: morphologies in small scales (micrometer or nanometer)

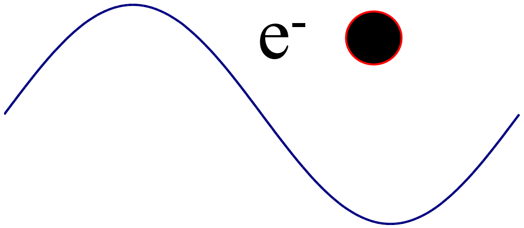
  Optical microscopy, Electron microscopy, Ion microscopy, Scanning probe microscopy….., offer images only.

- Microanalyses: composition and/or structures in small scales (micrometer or nanometer)

  Energy Dispersive Spectroscopy, Wave-length Dispersive Spectroscopy, Electron Energy Loss Spectroscopy, Auger Electron Spectroscopy, Convergent Beam Electron Diffraction, Select Area Diffraction….., offer spectra and/or diffraction patterns

Why electrons?

- Wave Behaviours
  - images and diffraction patterns
  - wavelength can be tuned by energies
- Charged Particle Behaviours
  - strong electron-specimen interactions
  - chemical analysis is possible



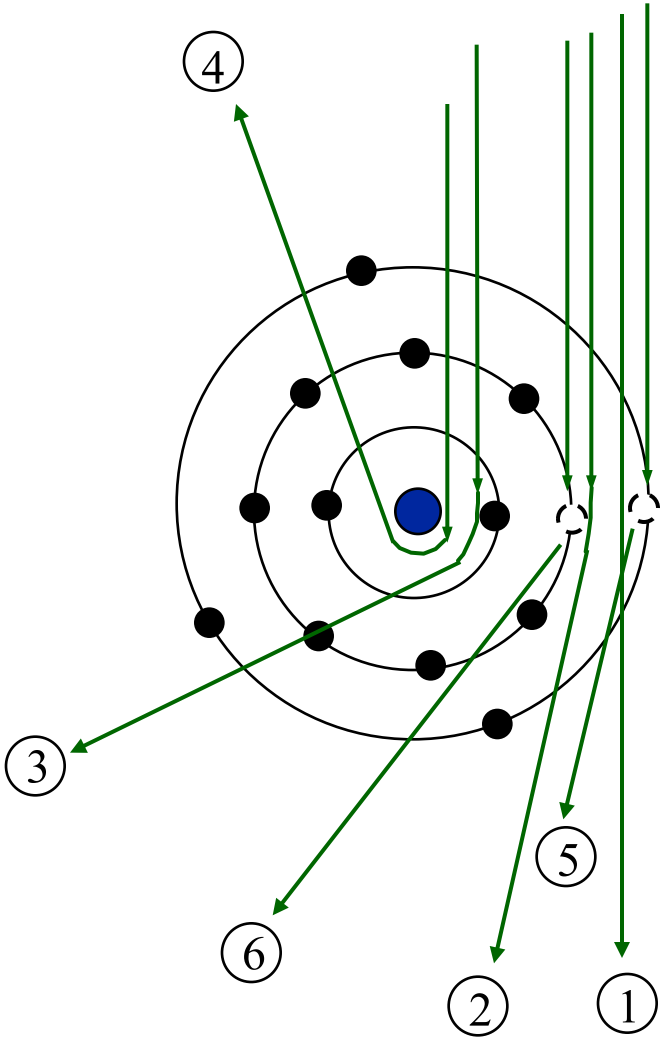
de Broglie's wavelength

$$\lambda \sim \frac{1.22}{E^{½}}$$

E (kev)	λ(Å)
100	0.037
200	0.025
300	0.0196
400	0.0169

Interaction of Energetic Electrons with Materials

Interaction with an Atom



① Unscattered

② Low angle elastically scattered

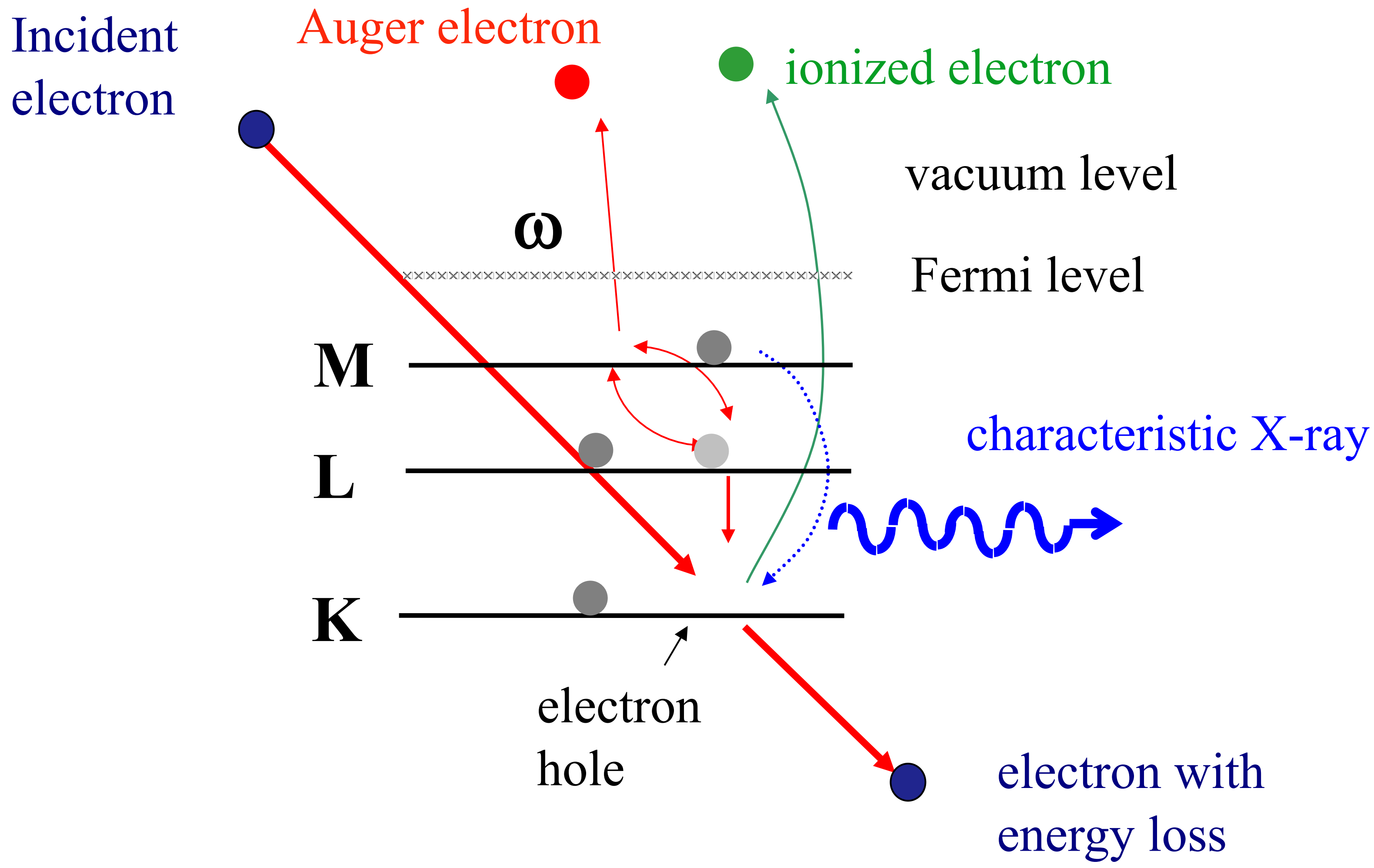
③ High angle elastically scattered

④ Back scattered

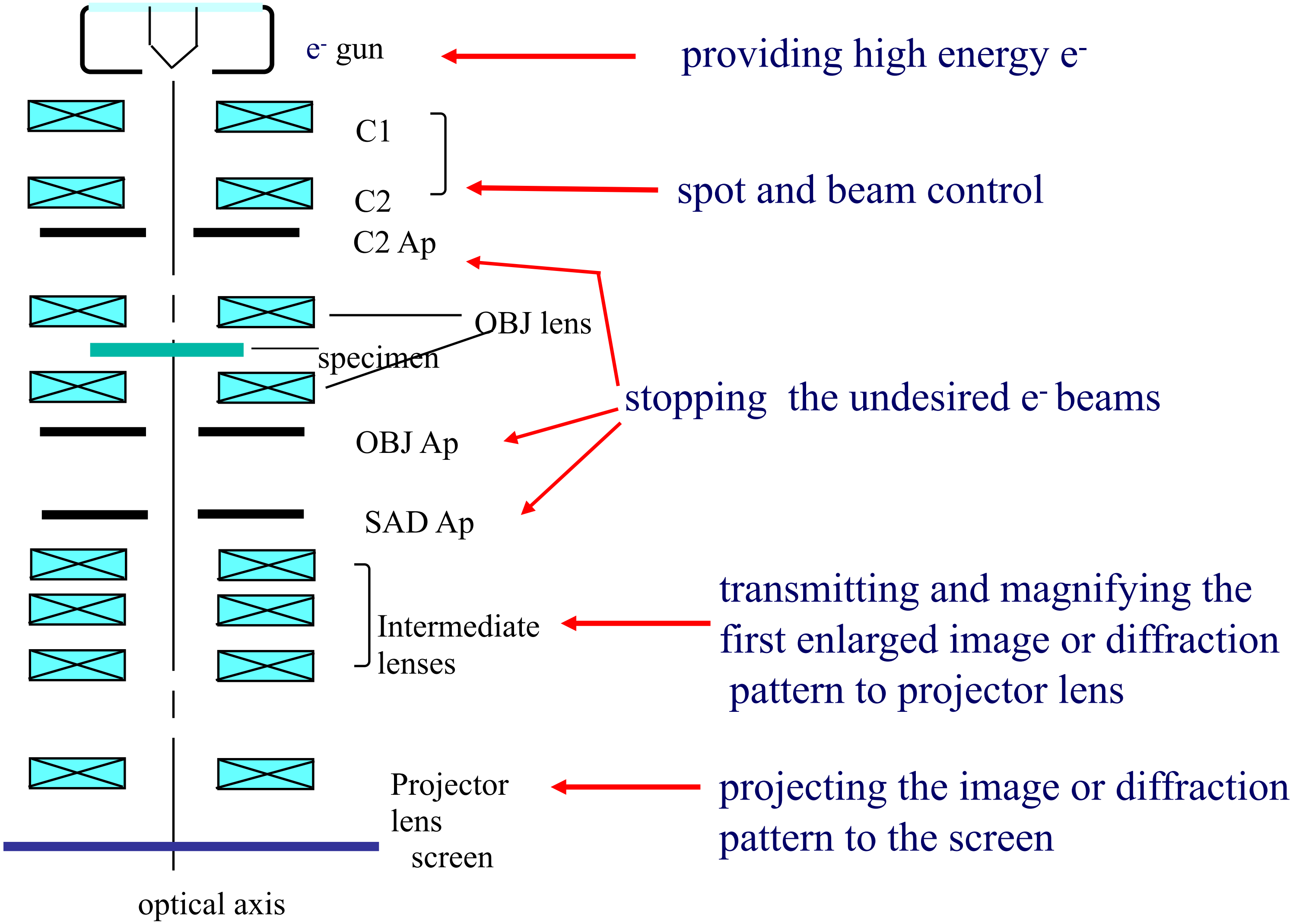
⑤ Outer shell inelastically scattered

⑥ Inner shell inelastically scattered

Interaction of Energetic Electrons with Materials



Lens System of TEM



providing high energy e^-

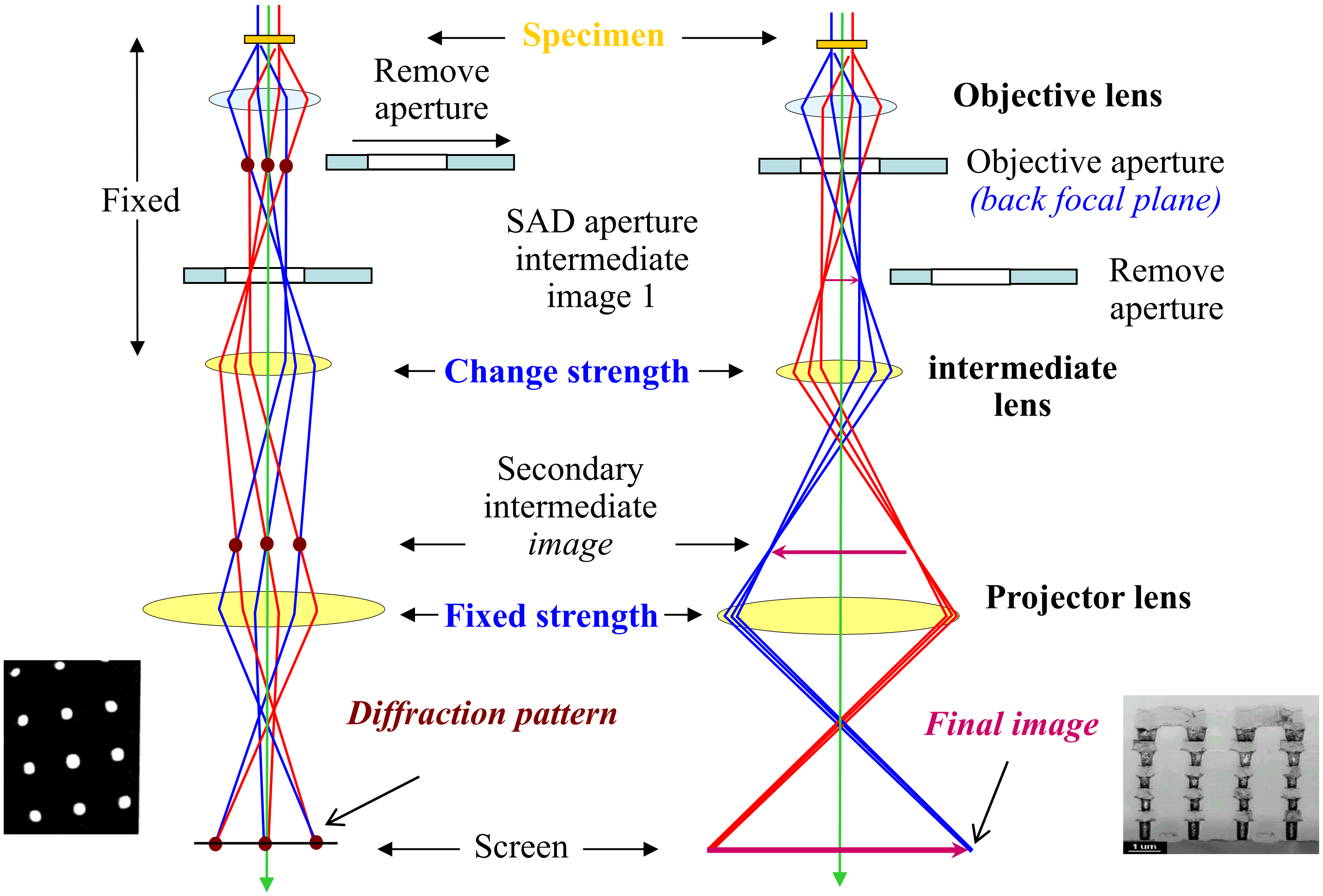
spot and beam control

stopping the undesired e^- beams

transmitting and magnifying the first enlarged image or diffraction pattern to projector lens

projecting the image or diffraction pattern to the screen

Operational Modes of TEM



Diffraction mode

Image mode

Specimen

Remove aperture

Objective lens

Objective aperture *(back focal plane)*

Fixed

SAD aperture intermediate image 1

Remove aperture

Change strength

intermediate lens

Secondary intermediate *image*

Fixed strength

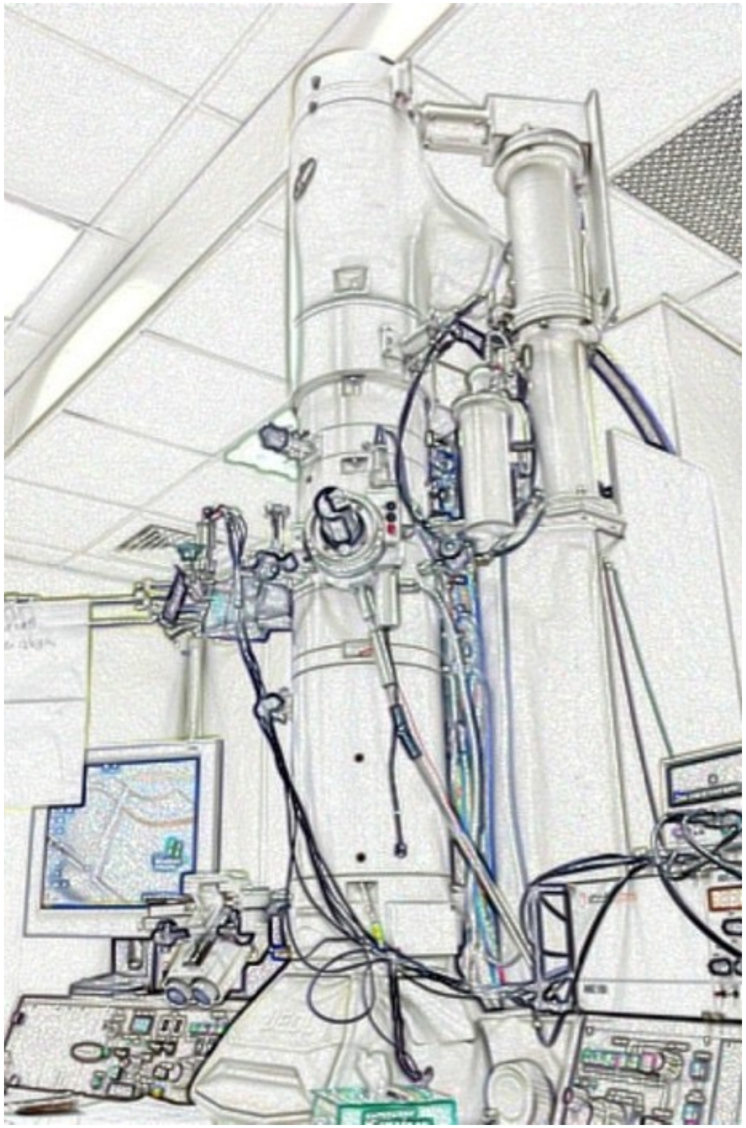
Projector lens

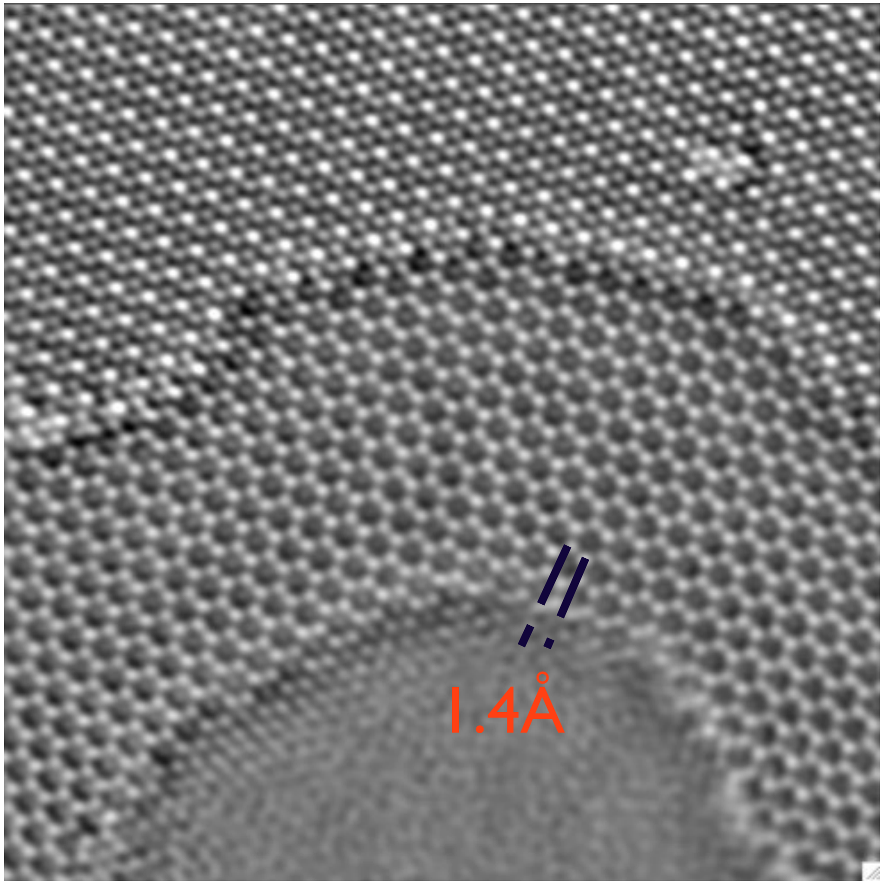
Diffraction pattern

Final image

Screen

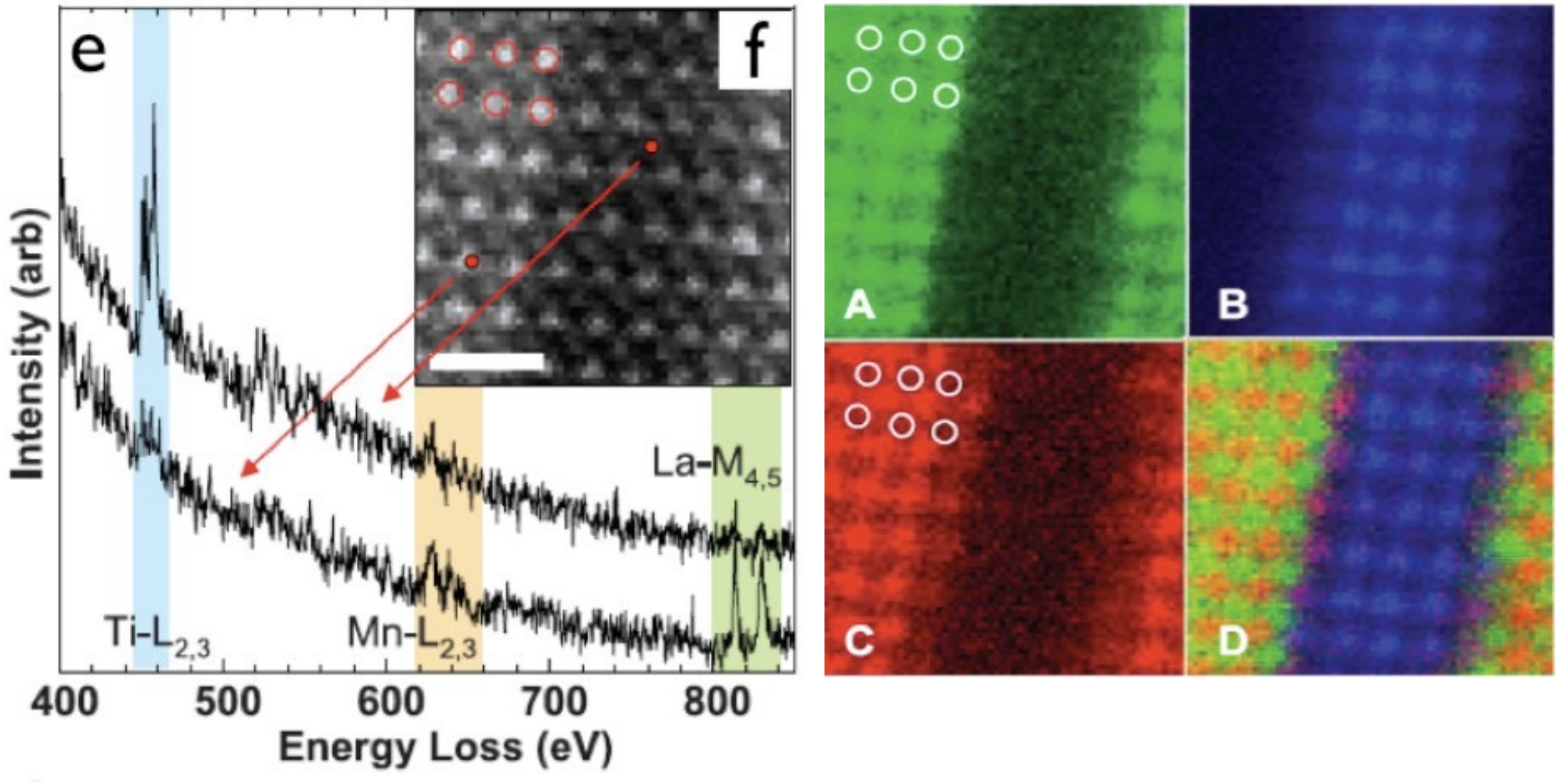
Imaging by C_s-corrected TEM





Atomic Resolution

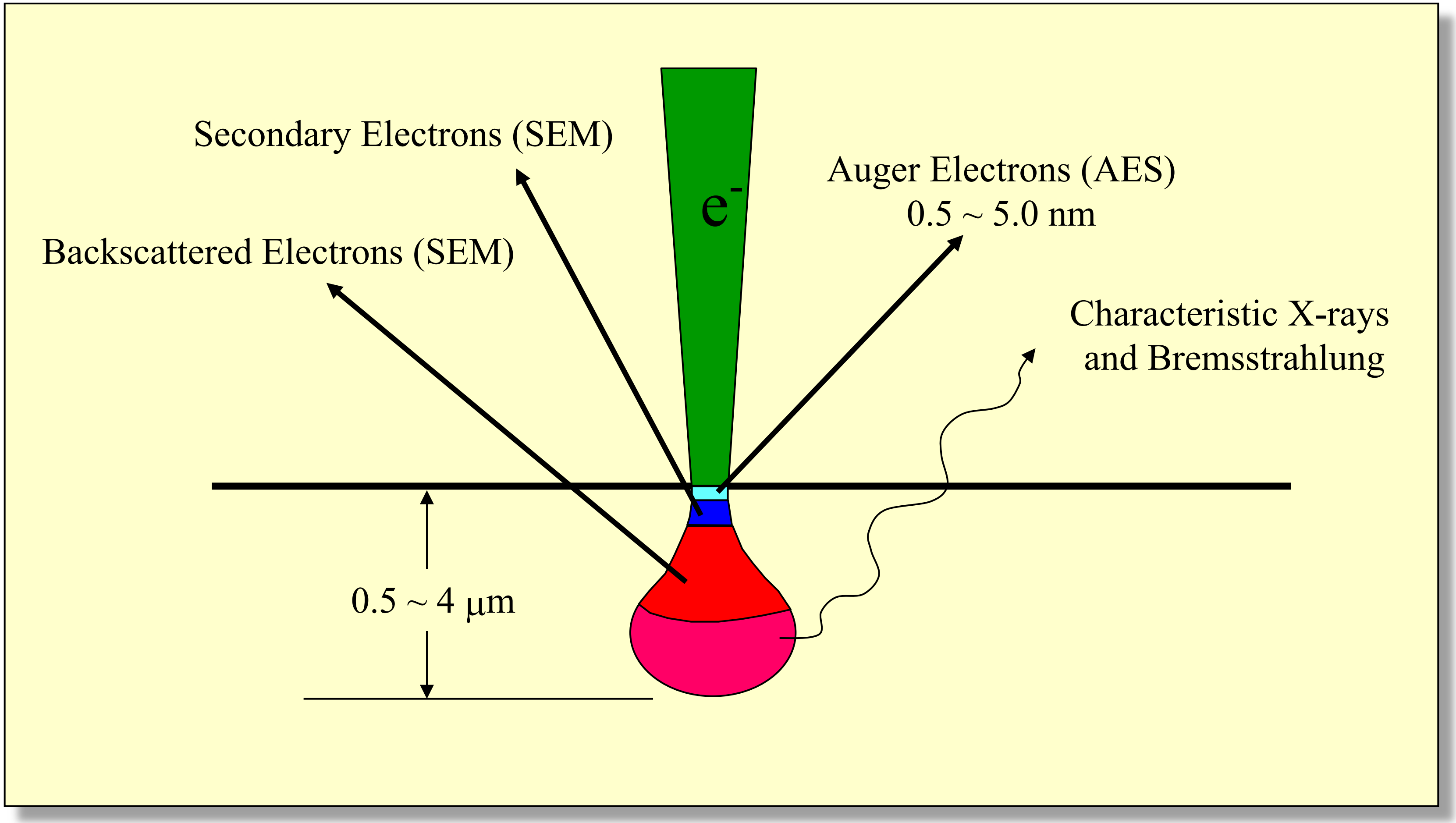
Spectroscopy by STEM



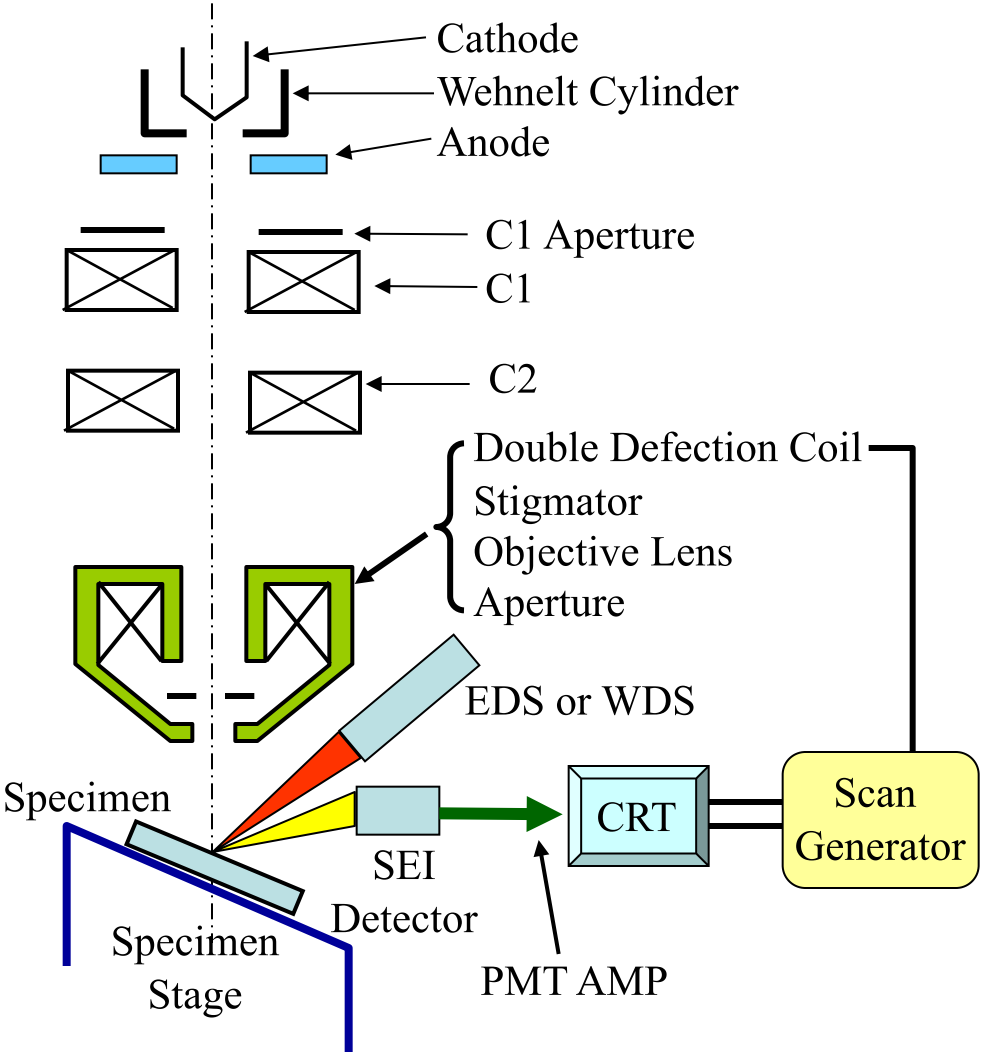
Atomic resolution of EELS of $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ multilayer
- D. A. Muller, et al, SCIENCE **319** 1073-1075 (2008)

Interaction of Energetic Electrons with Materials

Interaction with a thick specimen (SEM)



Lens System of SEM



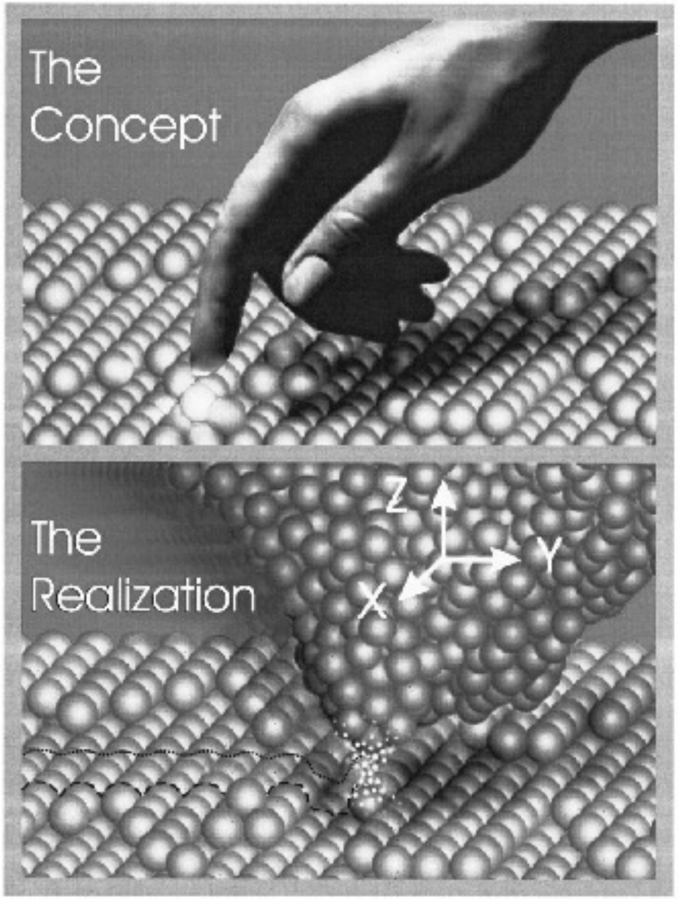
Scanning Tunneling Microscopy

A scanning tunneling microscope (STM) is an instrument for imaging surfaces at the atomic level. Its development in 1981 earned its inventors, Gerd Binnig and Heinrich Rohrer (at IBM Zürich), the Nobel Prize in Physics in 1986. For a STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm (10 pm) depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra-high vacuum but also in air, water, and various other liquid or gas ambients, and at temperatures ranging from near zero kelvin to over 1000°C.

References:

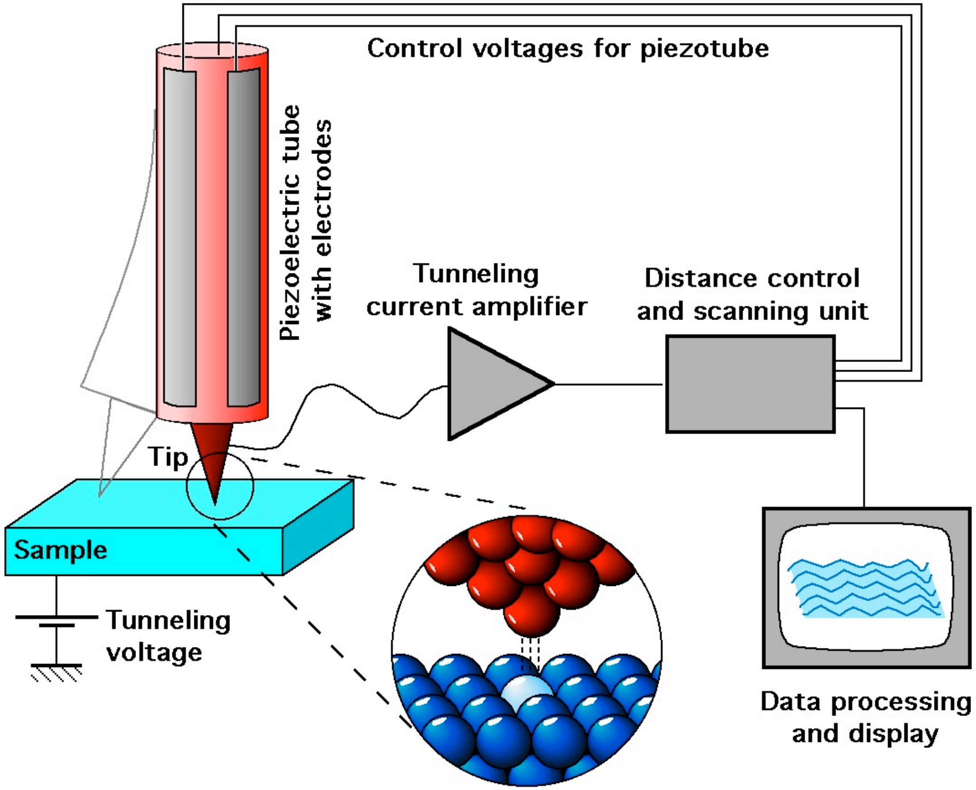
1. G. Binnig, H. Rohrer, C. Gerber, and Weibel, Phys. Rev. Lett. **49**, 57 (1982); and ibid **50**, 120 (1983).
2. J. Chen, *Introduction to Scanning Tunneling Microscopy*, New York, Oxford Univ. Press (1993).

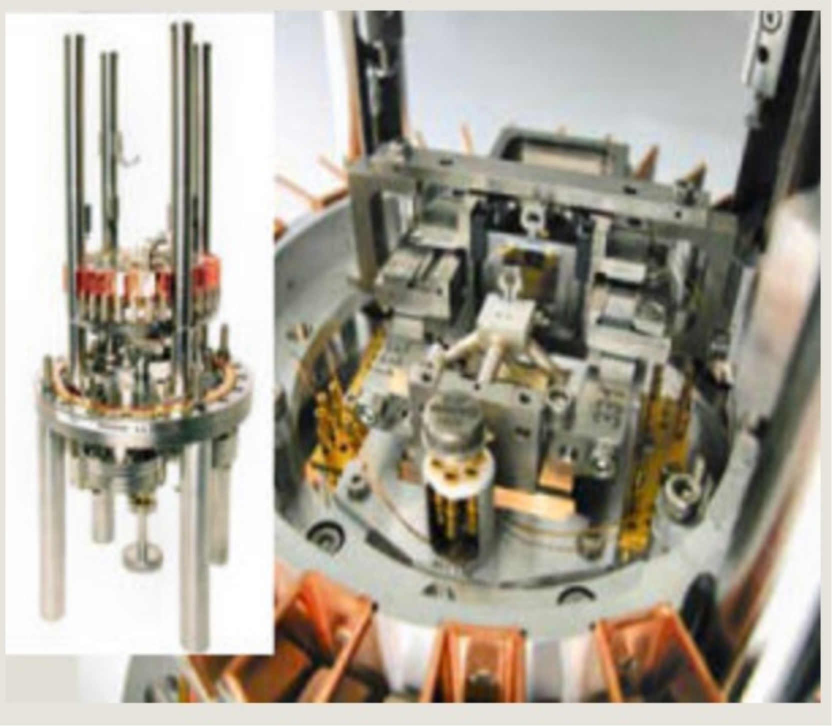
Concept: Eye and Finger



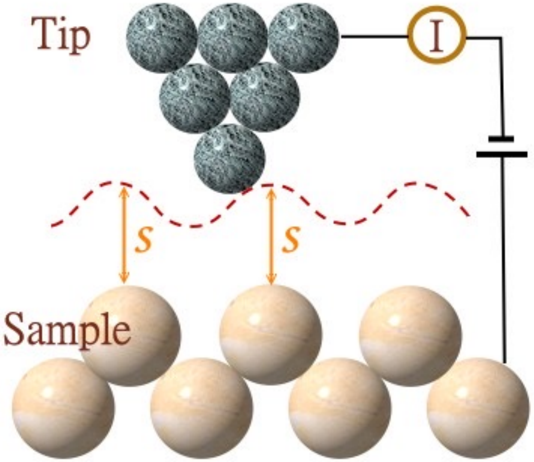
G. Binnig and and H. Rohrer, *Rev. of Mod. Phys.* **71**, S324-S330 (1999).

Scanning Tunneling Microscopy

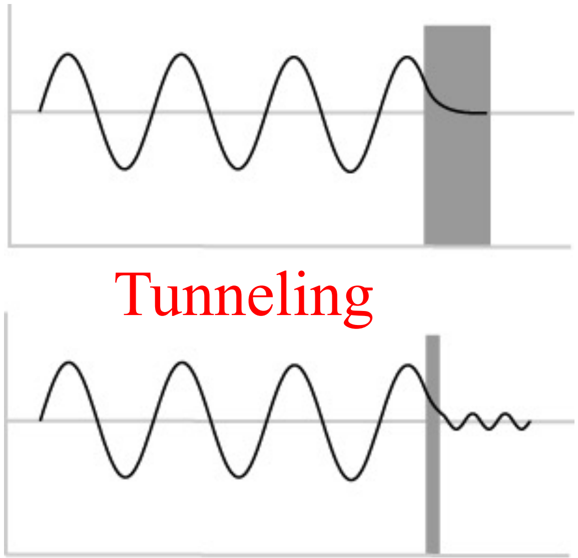


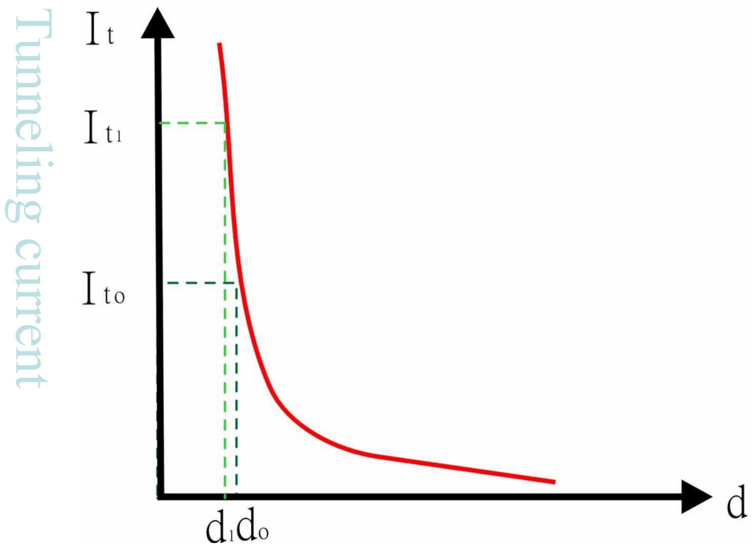


Theory of STM



Constant Current Mode





Tunneling current I_t

$I_t \propto (V/d)\exp(-A\phi^{1/2}d)$

$A = 1.025\ (\mathrm{eV})^{-1/2}\text{Å}^{-1}$

$\phi \sim 4 - 5$ eV

d decreases by 1 Å,

I_t will be increased by ~10 times.

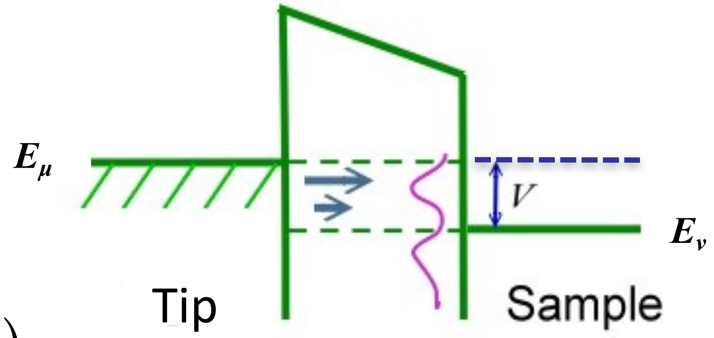
Tunneling Current

$$I_{T\to S} = \frac{2\pi e}{\hbar}\sum_{\mu\nu} f\left(E_\mu\right)\left[1-f\left(E_\nu+eV\right)\right]\left|M_{\mu\nu}\right|^2 \delta\left(E_\mu - E_\nu - eV\right)$$

where $f(\mathrm{E})$ is Fermi function,

$E_{\mu,\nu}$ is the energy of state, where μ and ν run over all the states of the tip and surface,

$M_{\mu\nu}$ is tunneling matrix element.



$$M_{\mu\nu} \equiv \frac{\hbar^2}{2m}\int d\vec{s}\left(\psi_\mu{}^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu{}^*\right)$$

where ψ_μ is the wave function, and the integral is over any plane in the barrier region.

$$I = I_{T\to S} - I_{S\to T}$$

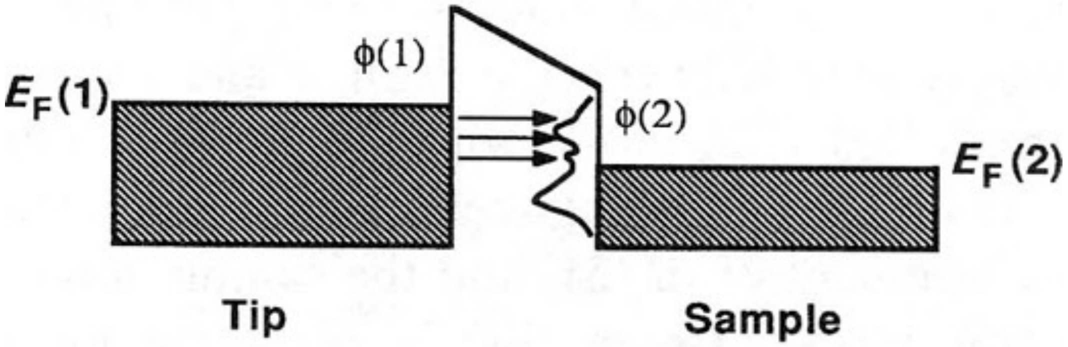
Transmission probability ≡ $M\left(E\right) = \exp\left[-A\phi^{\frac{1}{2}}S\right]$

$$= A'\int_{-\infty}^{\infty} \rho_T\left(E\right)\rho_S\left(E+eV\right)\left|M\left(E\right)\right|^2\left[f\left(E\right)-f\left(E+eV\right)\right]dE$$

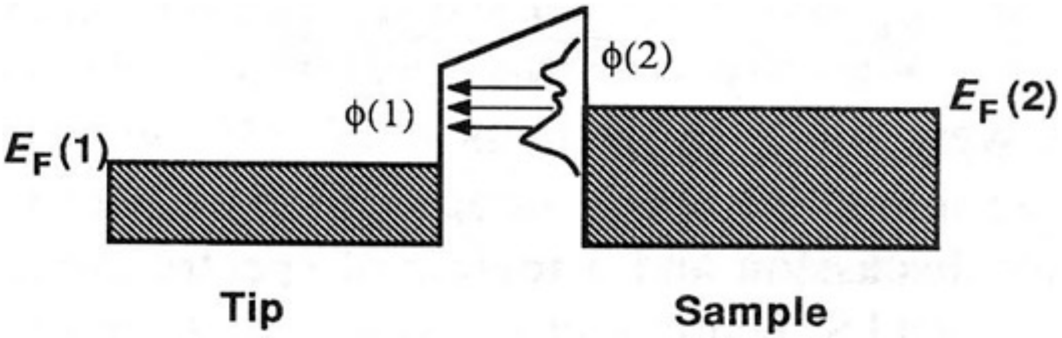
where ρ_S and ρ_T are the densities of states in the sample and the tip, respectively.

Electronic Structures at Surfaces

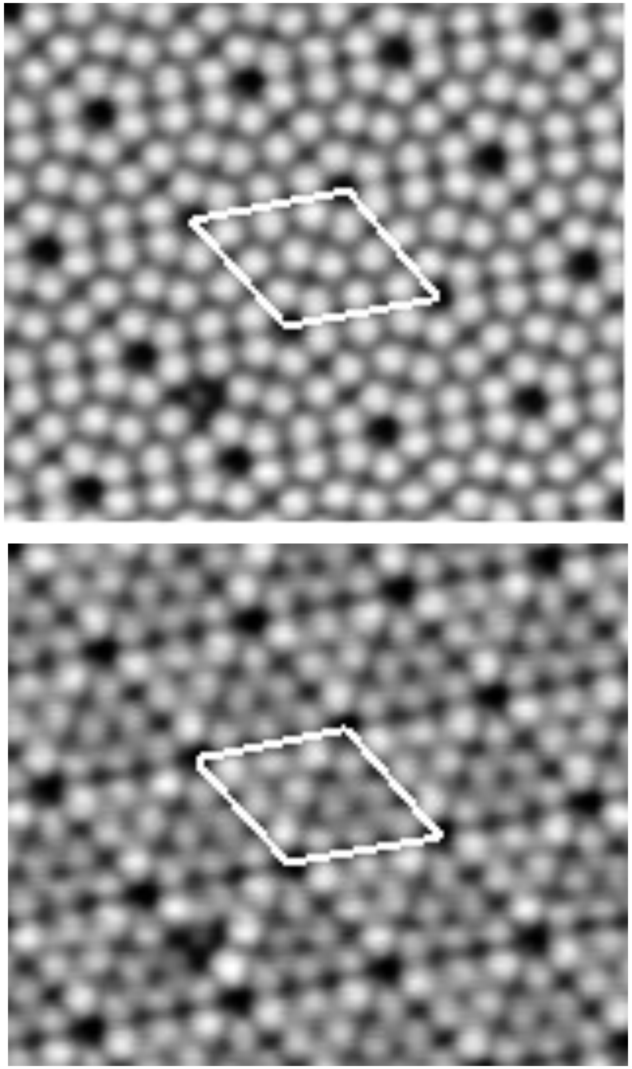
Empty-State Imaging



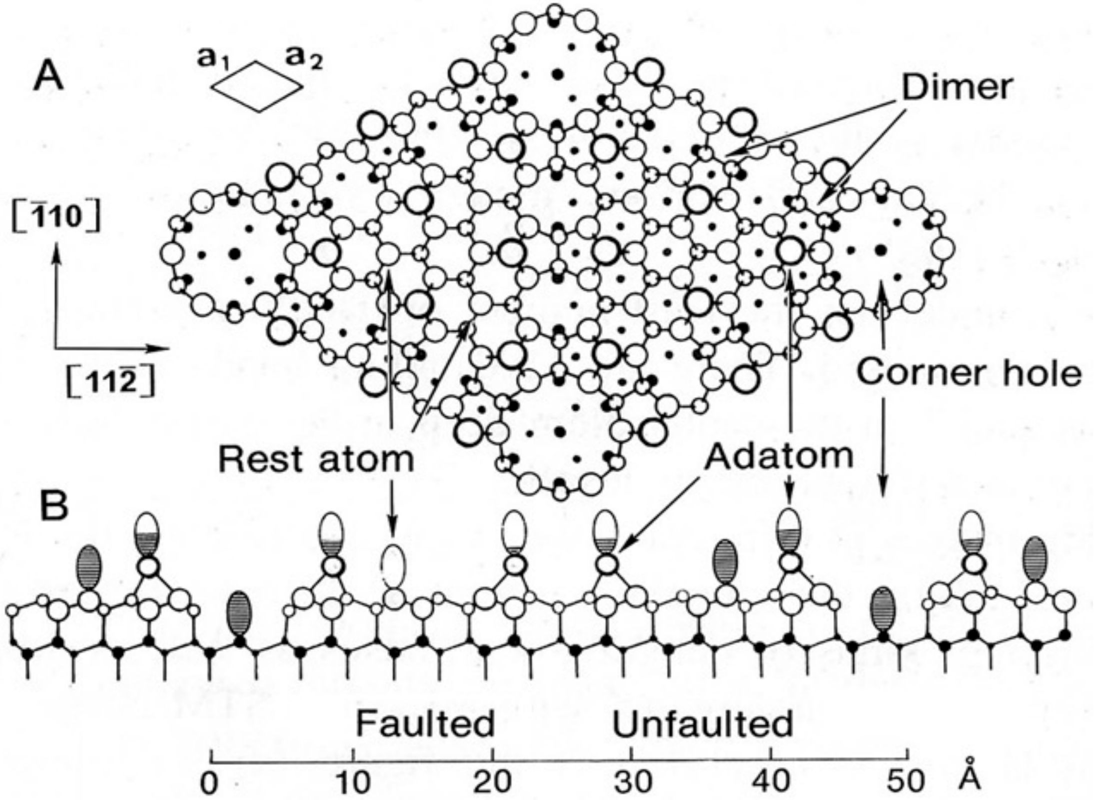
Filled-State Imaging



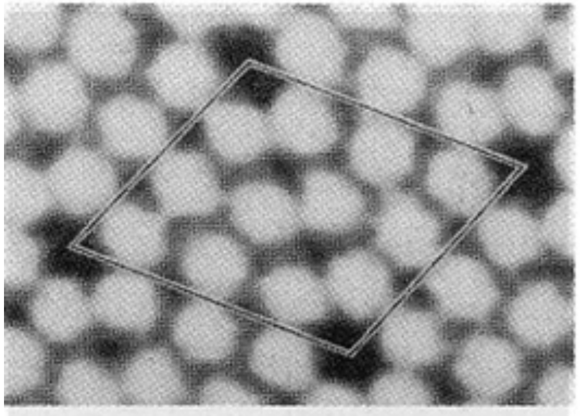
STM Images of Si(111)-(7×7)



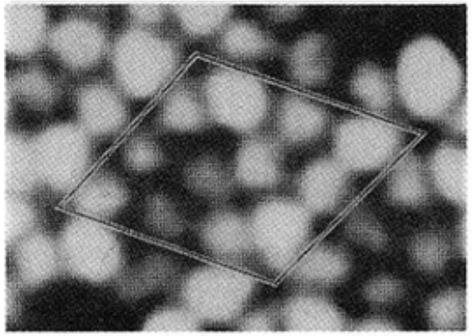
STS of Si(111)-(7x7)



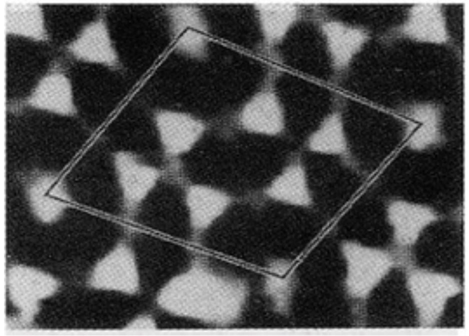
Topograph



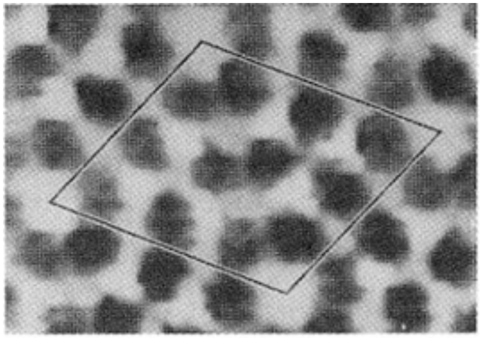
+2 V



-0.35 V

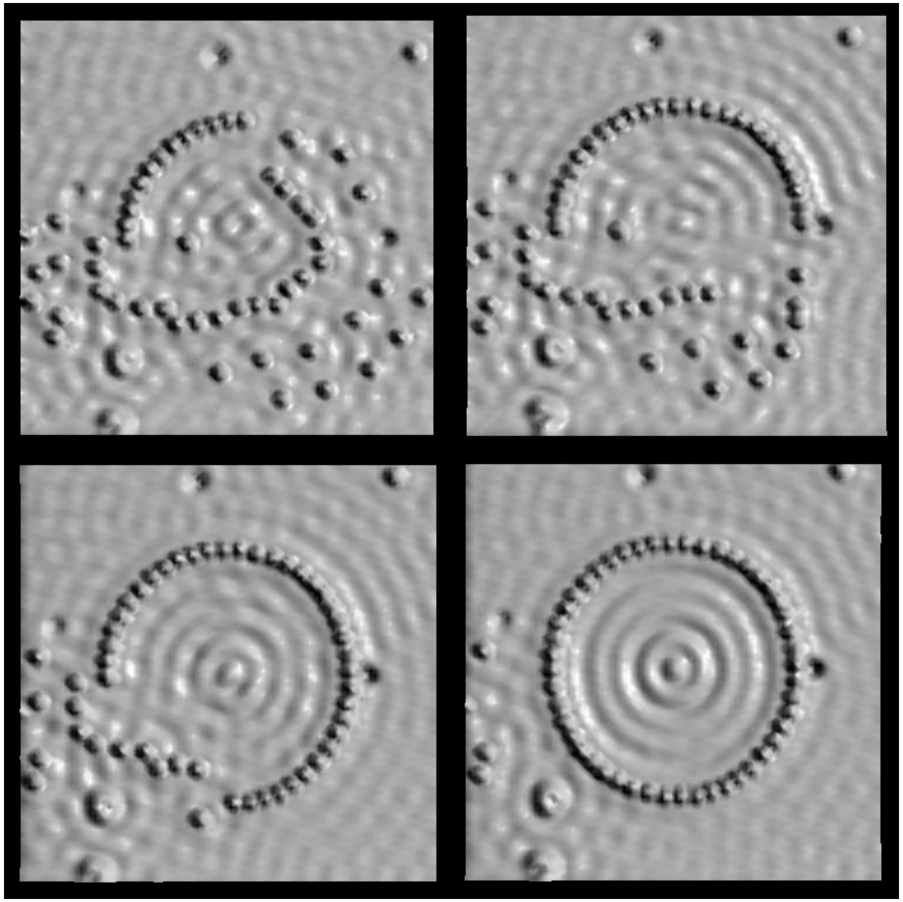


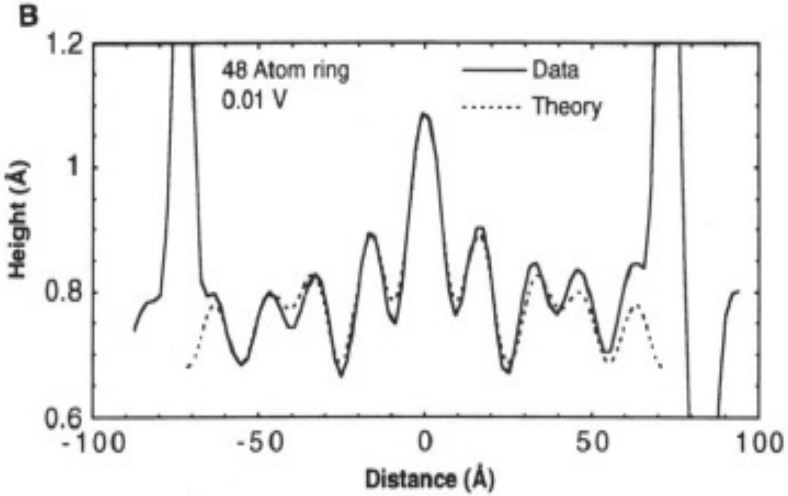
-0.8 V



-1.8 V

Quantum Corral





Exp.-theory:

B) Solid line: cross section of the above data. Dashed line: fit to cross section using a linear combination of $|5,0\rangle$, $|4,2\rangle$, and $|2,7\rangle$ eigenstate densities.

Fe on Cu(111) at 4.5K

M. Crommie et al, *Science* **262**, 218 (1993)

Scanning Probe Microscopy (SPM)

Scanning Tunneling Microscopy (STM)

--- G. Binnig, H. Rohrer et al, (1982)

Near-Field Scanning Optical Microscopy (NSOM)

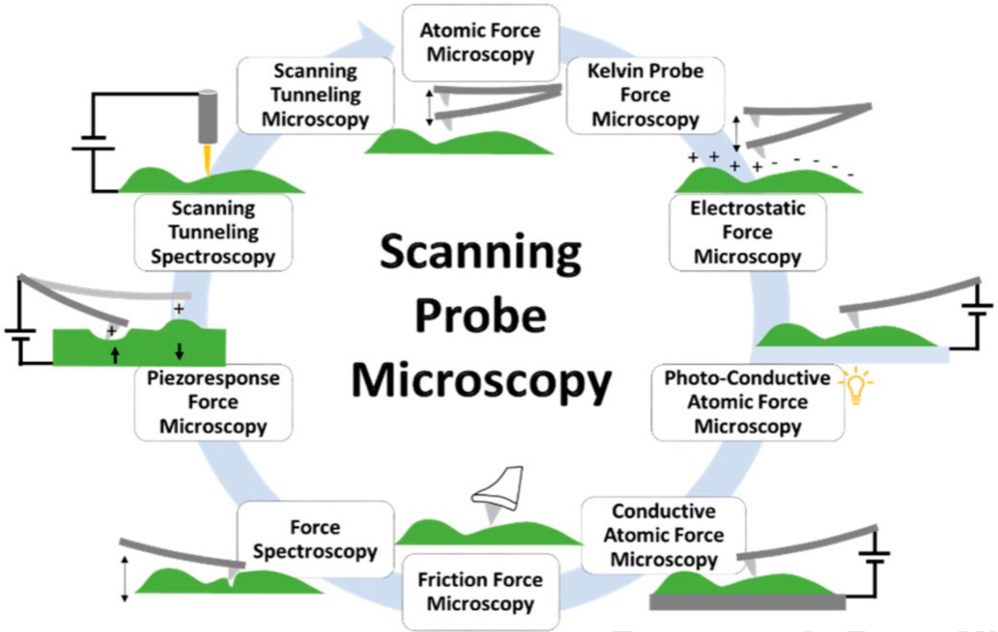
--- D. W. Pohl (1982)

Atomic Force Microscopy (AFM)

--- G. Binnig, C. F. Quate, C. Gerber (1986)

Scanning Thermal Microscopy (SThM)

--- C. C. Williams, H. Wickramasinghe (1986))



Magnetic Force Microscopy (MFM)

--- Y. Martin, H. K. Wickramasinghe (1987)

Friction Force Microscopy (FFM or LFM)

--- C. M. Mate et al (1987)

Electrostatic Force Microscopy (EFM)

--- Y. Martin, D. W. Abraham et al (1988)

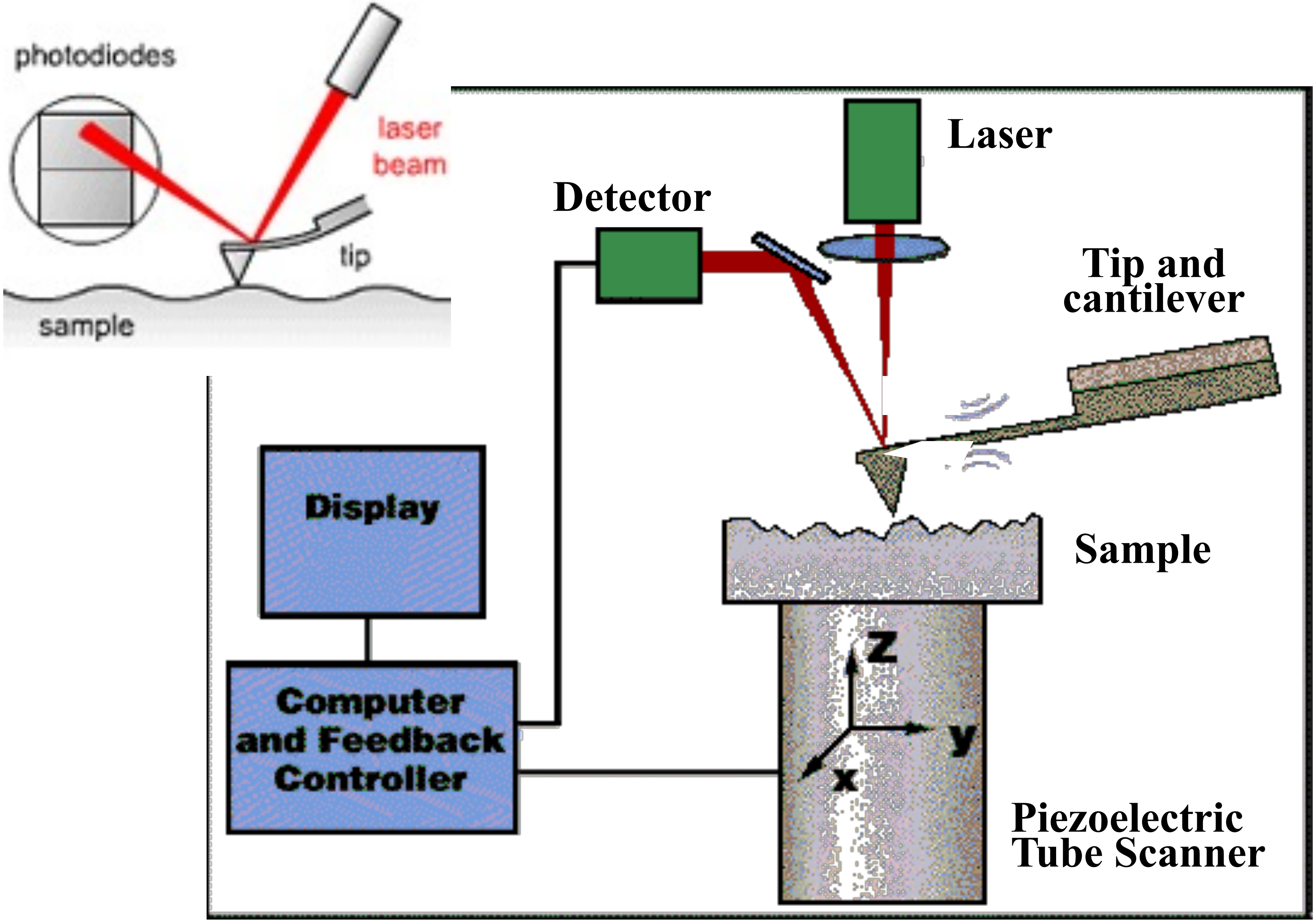
Scanning Capacitance Microscopy (SCM)

--- C. C. Williams, J. Slinkman et al (1989)

Force Modulation Microscopy (FMM)

--- P. Maivald et al (1991)

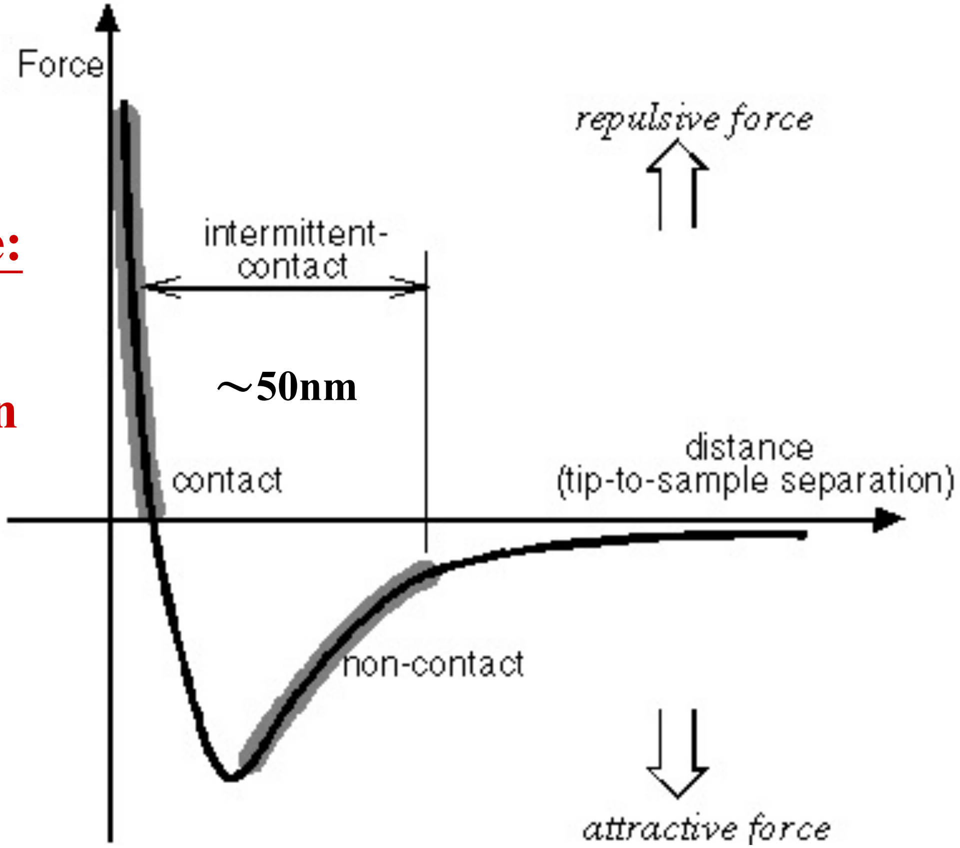
Atomic Force Microscopy (AFM)



Interaction between Probe and Sample

Short-range:

1) **Bonding**
2) **Repulsion**

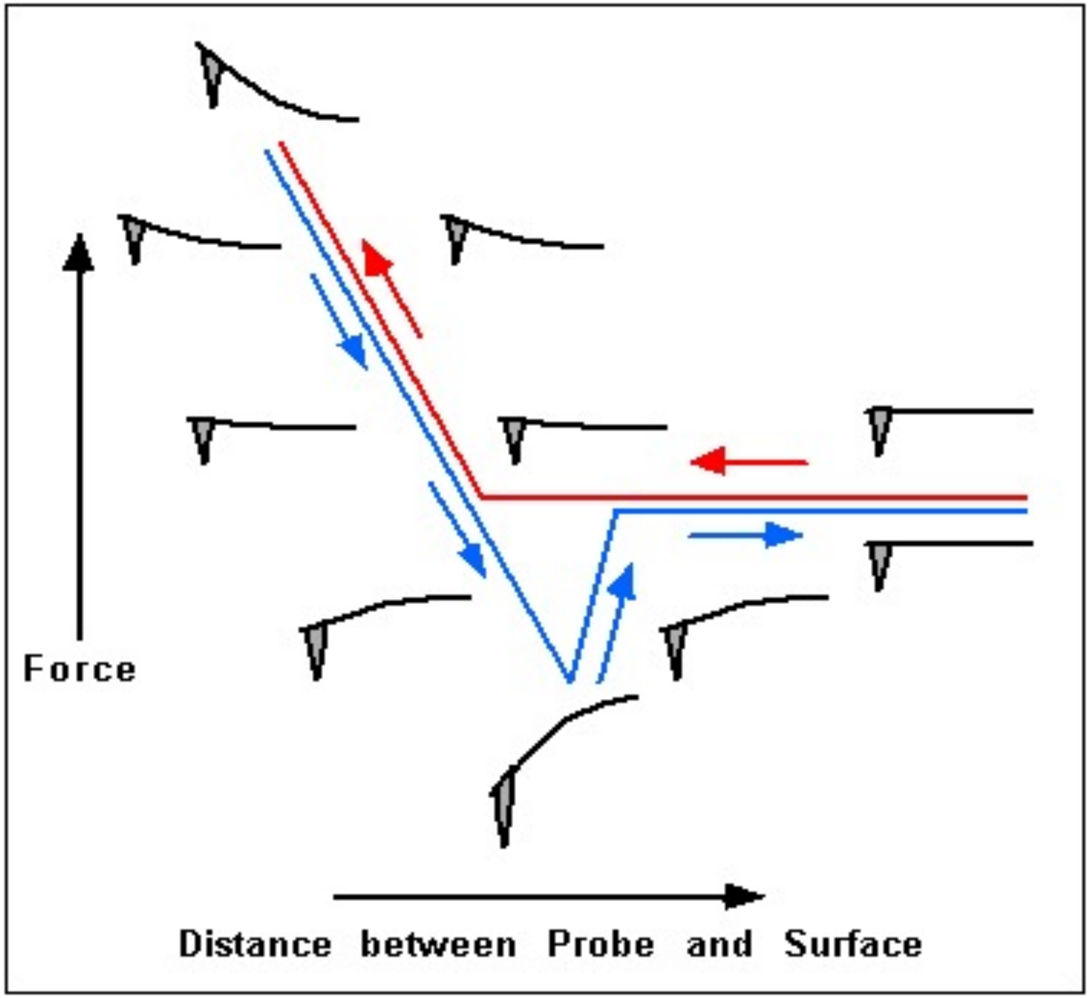


Long-range:

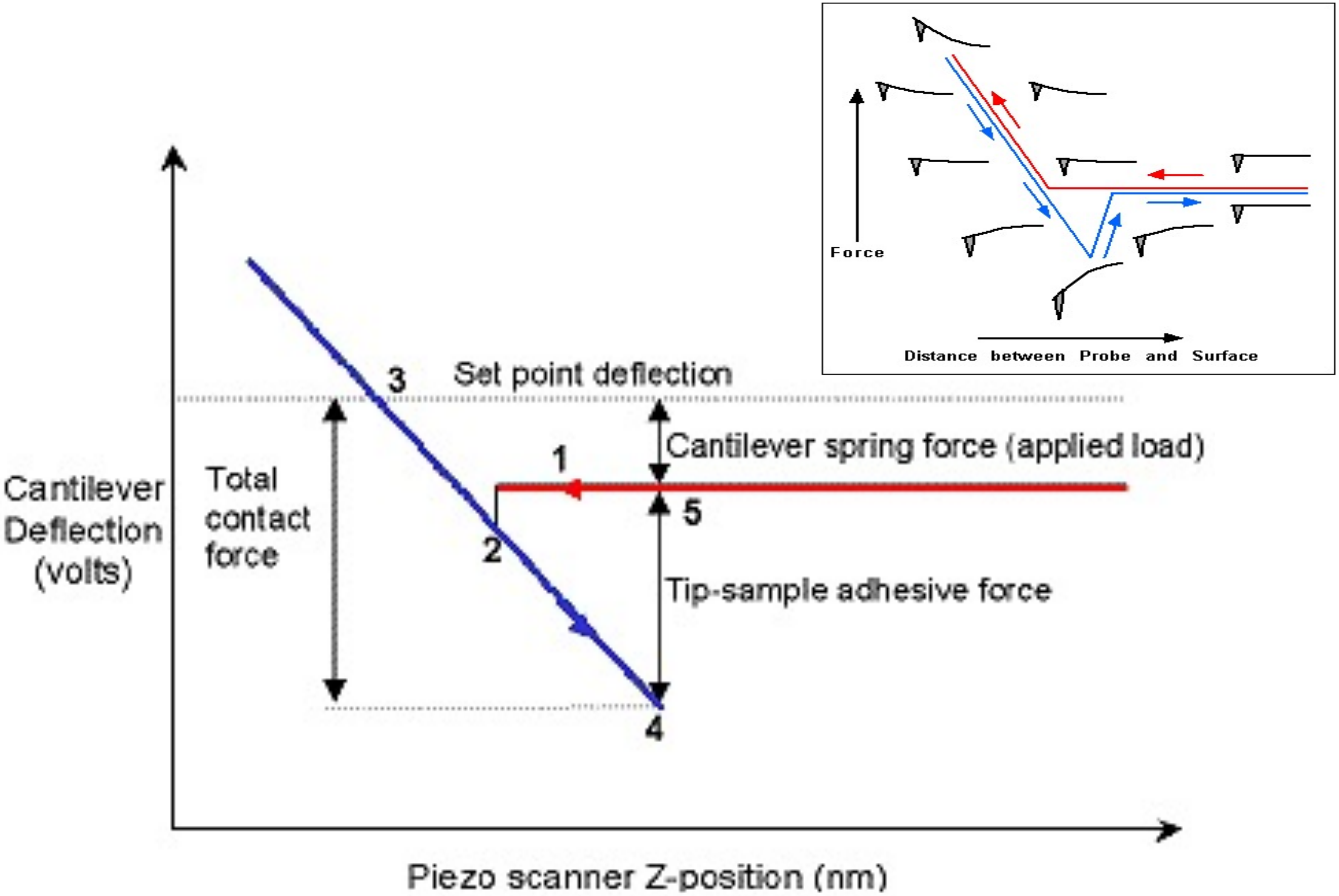
1) **Van der Waal**
2) **Capillary**
3) **Magnetic**
4) **Electrostatic**

Lennard-Jones potential $\phi(r) = - A/r^6 + B/r^{12}$

Reaction of the probe to the force

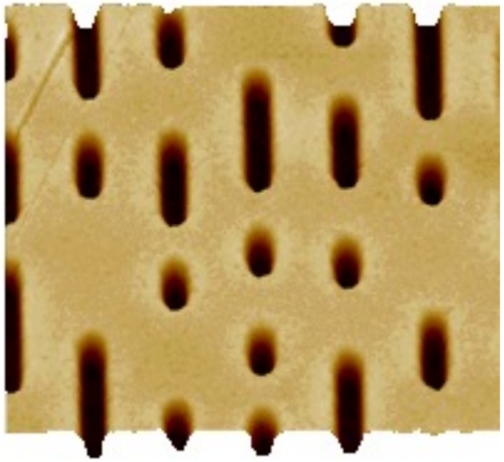


Deflection of Cantilever vs Piezo displacement

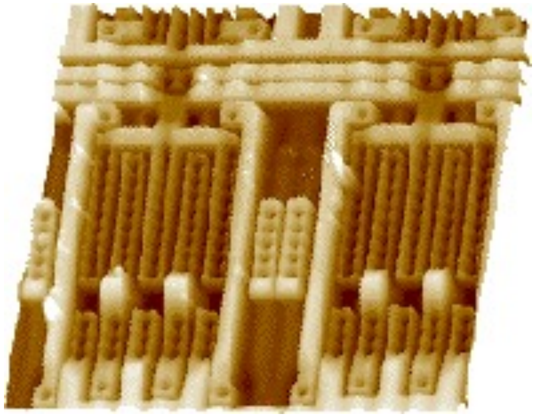


AFM Images

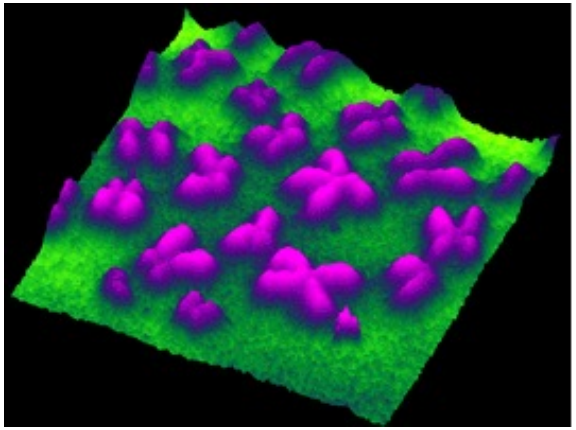
CD pits



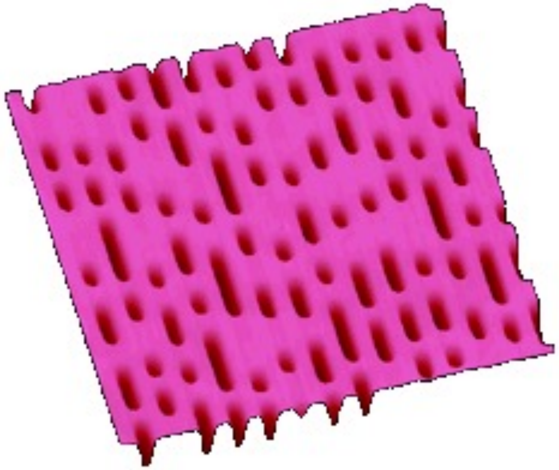
Integrated circuit



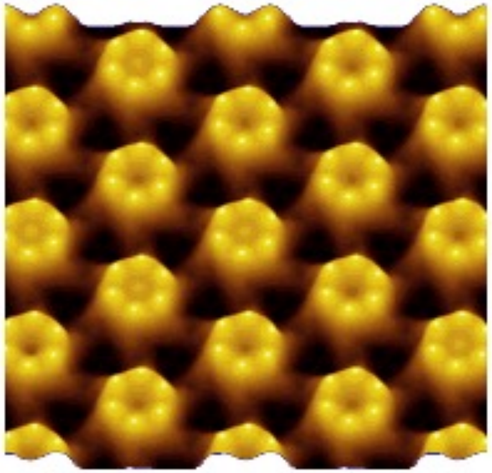
Chromosomes



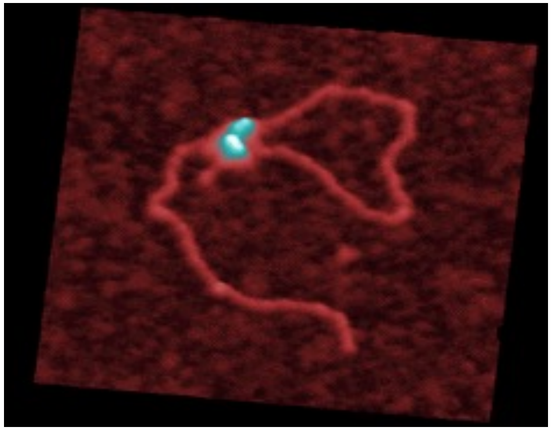
DVD pits



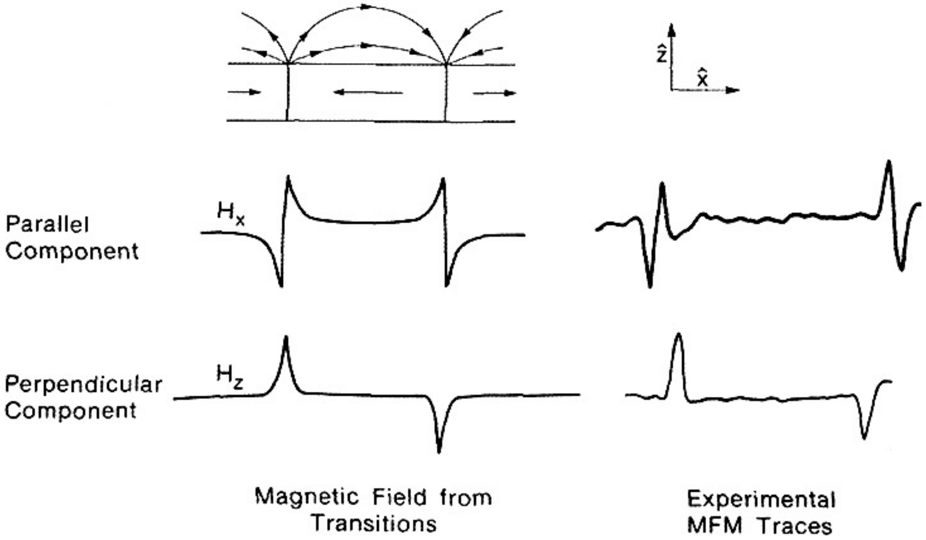
Bacteria

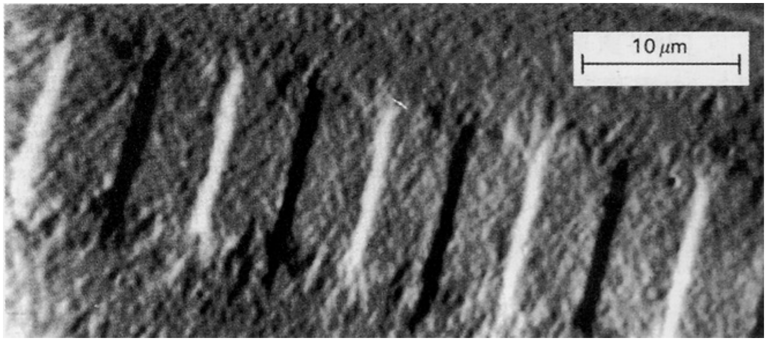


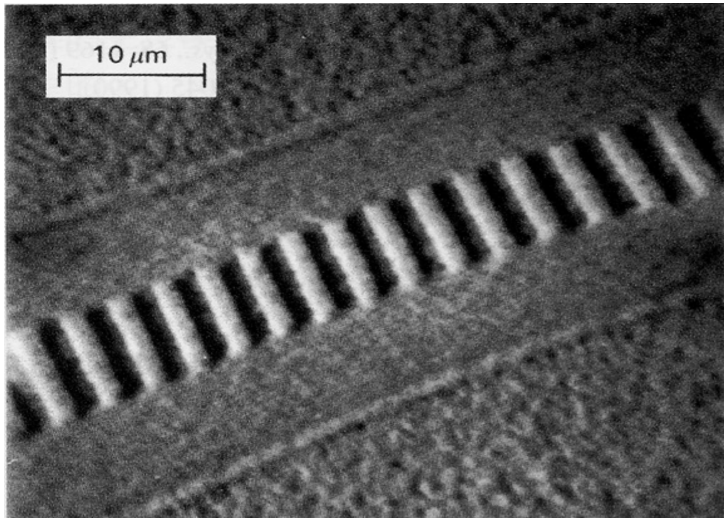
DNA



MFM Images







Tip as a point dipole

$$F_z = \partial(m_xH_x + m_yH_y + m_zH_z)/\partial z$$

Tip as a long rod

$$F_z = m_zH_z$$

2-D nanostructures:

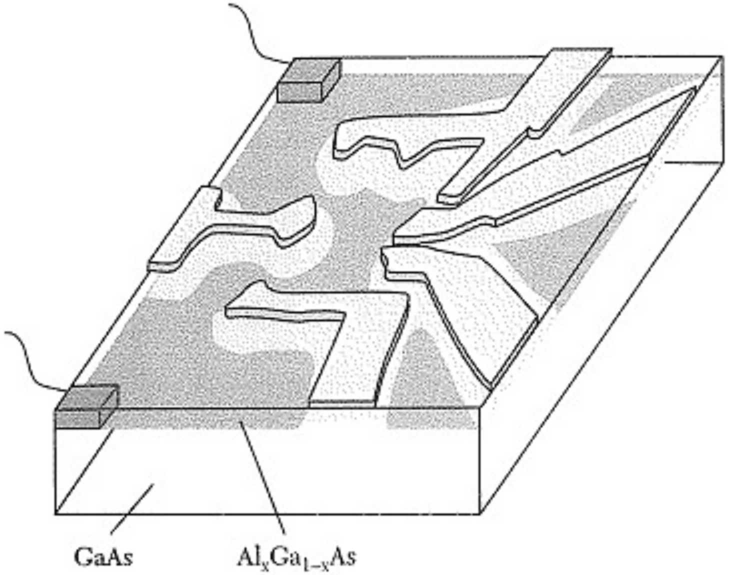
graphene, metallic thin films, superlattices, … .

1-D nanostructures:

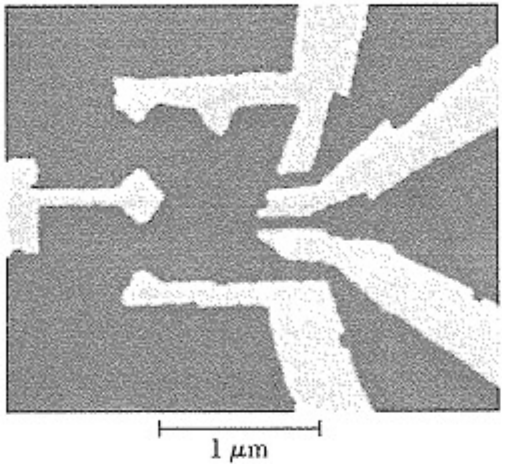
carbon nanotubes, quantum wires, conducting polymers, … .

0-D nanostructures:

semiconductor nanocrystals, metal nanoparticles,
lithographically patterned quantum dots, … .

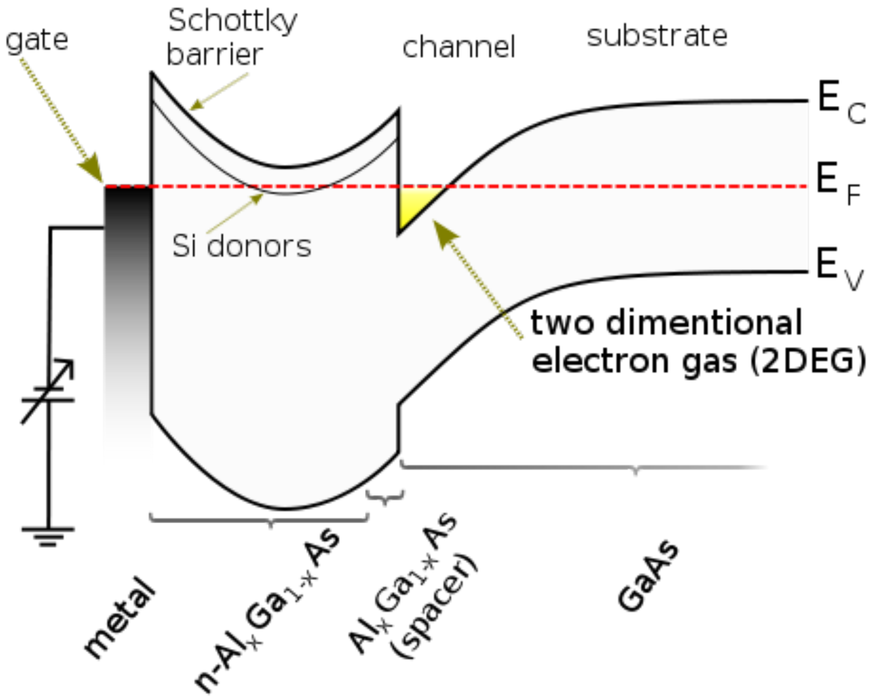


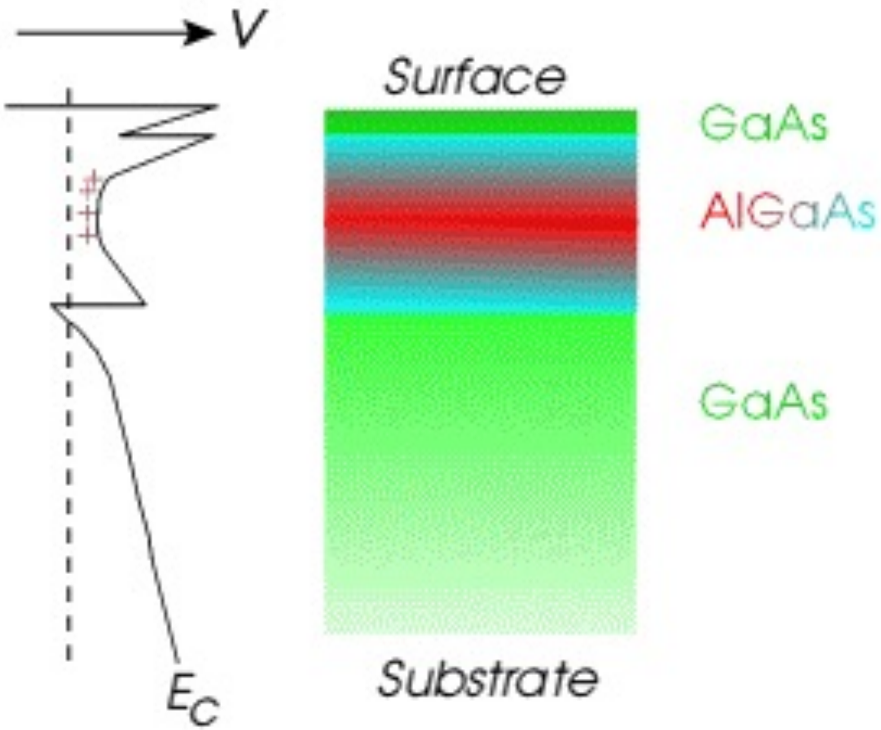
Gate electrode pattern of
a quantum dot on 2DEG



SEM image

2D electron gas (2DEG)





Electronic Structure of 0-D Systems

Quantum dots: Quantized energy levels.

e in spherical potential well: $\varepsilon_{n,l,m} = \varepsilon_{n,l}$ $\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\,Y_{l,m}(\theta,\phi)$

For an infinite well with $V = 0$ for $r < R$:

$$\varepsilon_{n,l} = \frac{\hbar^2 \beta_{n,l}^2}{2m^* R^2} \qquad R_{n,l}(r) = j_l\left(\frac{\beta_{n,l}\, r}{R}\right) \qquad \text{for } r < R$$

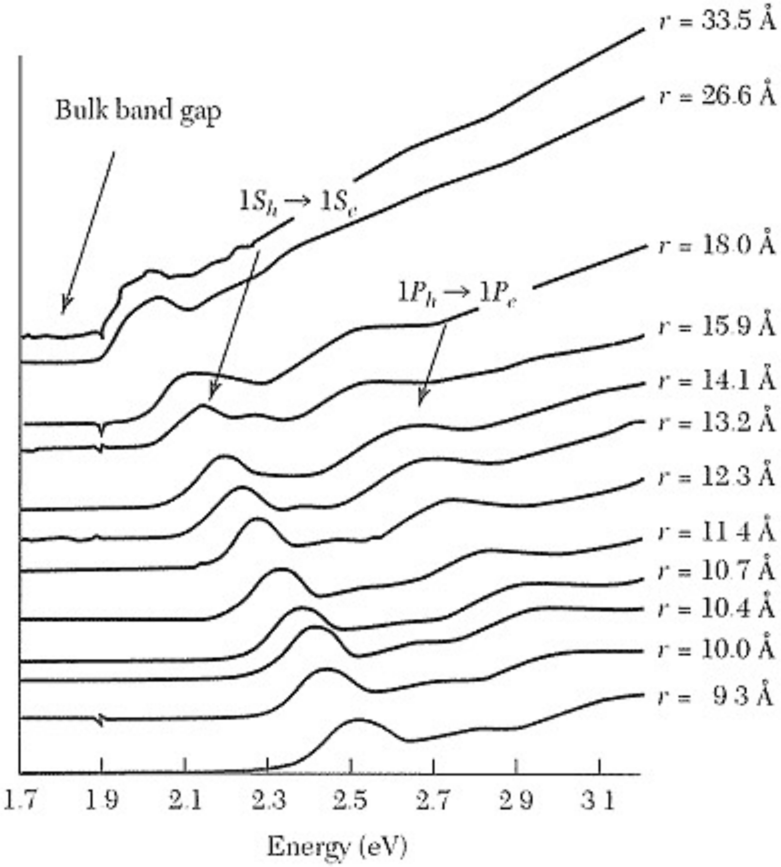
$\beta_{n,l}$ = n^{th} root of $j_l(x)$. $j_l(\beta_{n,l}) = 0$

$\beta_{0,0} = \pi$ (1S), $\beta_{0,1} = 4.5$ (1P), $\beta_{0,2} = 5.8$ (1D)

$\beta_{1,0} = 2\pi$ (2S), $\beta_{1,1} = 7.7$ (2P)

Semiconductor Nanocrystals

CdSe nanocrystals



For CdSe:

$$m_c{}^* = 0.13\,m \qquad \varepsilon_{n,l} = \left(\frac{\beta_{n,l}}{\beta_{0,0}}\right)^2 \left(\frac{2.9eV}{R^2}\right)$$

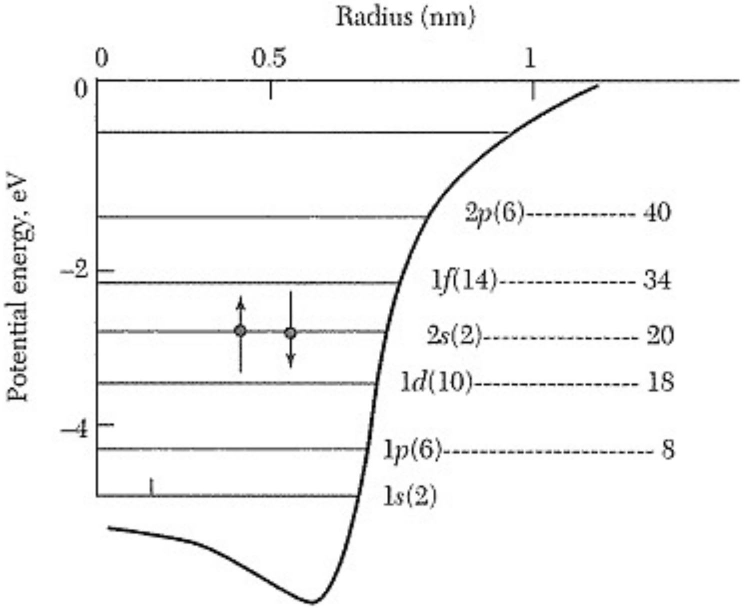
For $R = 2$ nm, $\varepsilon_{0,1} - \varepsilon_{0,0} = 0.76\,eV$

For *e*, $\varepsilon_{0,0}$ increases as *R* decreases.
For *h*, $\varepsilon_{0,0}$ decreases as *R* decreases.
→ E_g increases as *R* decreases.

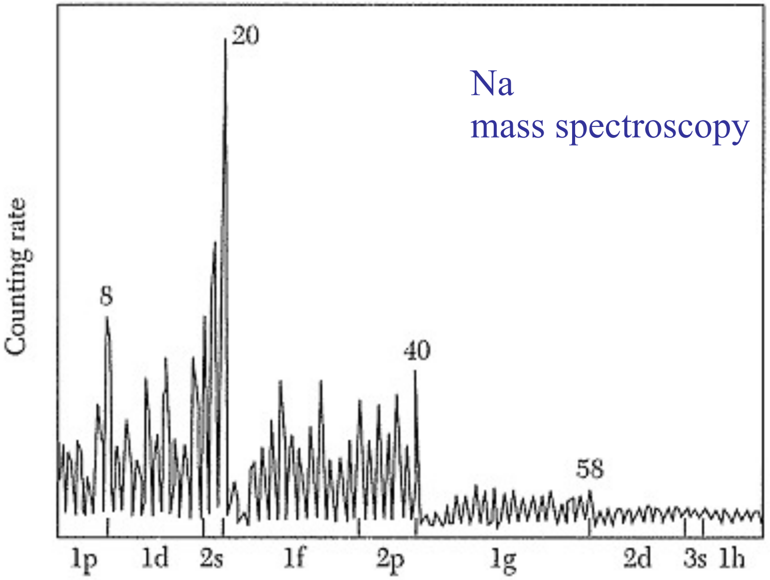
Optical spectra of nanocrystals can be tuned continuously in visible region.

Applications: fluorescent labeling, LED.

Metallic Dots



Small spherical alkali metallic cluster



Mass spectroscopy (abundance spectra):
Large abundance at cluster size of magic numbers (8, 20, 40, 58, …)
→ enhanced stability for filled *e*-shells.

Average level spacing at ε_F :

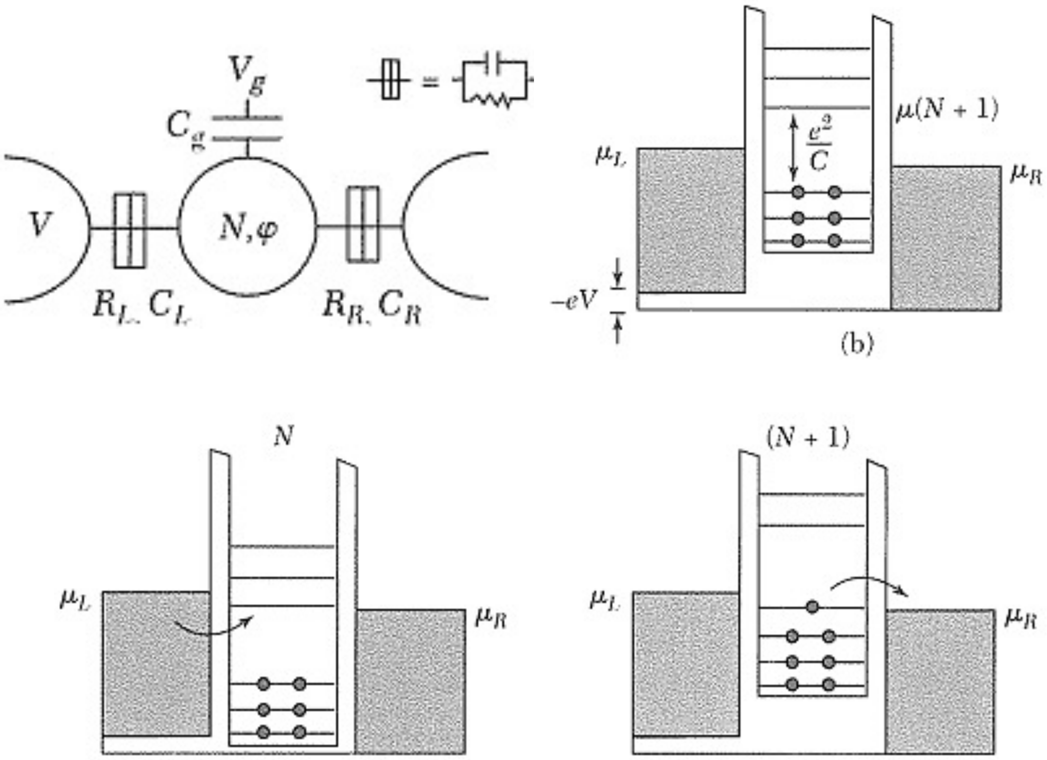
$$\Delta\varepsilon \approx \frac{1}{D(\varepsilon_F)} = \frac{2\varepsilon_F}{3N}$$

For Au nanoparticles with $R = 2$ nm,
$\Delta\varepsilon \approx 2$ meV.
whereas CdSe gives $\Delta\varepsilon \approx 0.76$ eV.
→ ε quantization more influential in semiconductor.

Discrete Charge States

Thomas-Fermi approximation: $\mu_{N+1} = \varepsilon_{N+1} - e\,\varphi \;= \varepsilon_{N+1} + NU - \alpha\, e\, V_g$

U = interaction between 2 e's on the dot = charging energy.
α = rate at which a nearby gate voltage V_g shifts φ of the dot.



Neglecting its dependence on state,

$$U = \frac{e^2}{C} \qquad \alpha = \frac{C_g}{C}$$

C = capacitance of dot.
C_g = capacitance between gate & dot

If dot is in weak contact with reservoir, e's will tunnel into it until the μ's are equalized.

Change in V_g required to add an e is

$$\Delta V_g = \frac{1}{\alpha\, e}\left(\varepsilon_{N+1} - \varepsilon_N + \frac{e^2}{C} \right)$$

U depends on size &shape of dot & its local environment.

For a spherical dot of radius R surrounded by a spherical metal shell of radius $R + d$,

$$U = \frac{e^2}{\varepsilon R} \frac{d}{R+d}$$

For $R = 2$ nm, $d = 1$ nm & $\varepsilon = 1$, we have

$$U = 0.24 \text{ eV} \quad >> \quad k_B T = 0.026\text{eV} \quad \text{at } T = 300\text{K}$$

→ Thermal fluctuation strongly supressed.

For metallic dots of 2nm radius, $\Delta\varepsilon \approx 2\text{meV} \rightarrow \Delta V_g$ due mostly to U.
For semiC dots, e.g., CdSe, $\Delta\varepsilon \approx 0.76$ eV $\rightarrow \Delta V_g$ due both to $\Delta\varepsilon$ & U.

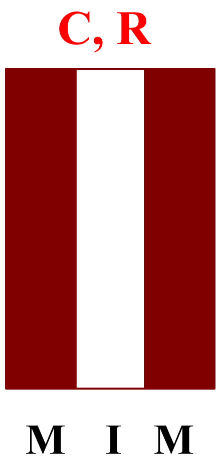
Charging effect is destroyed if tunneling rate is too great.
Charge resides in dot for time $\delta t \approx RC$. (R = resistance)

$$\rightarrow \qquad \delta\varepsilon \approx \frac{h}{\delta t} \approx \frac{h}{RC} = \frac{e^2}{C} \frac{h}{e^2} \frac{1}{R}$$

Quantum fluctuation smears out charging effect when $\delta\varepsilon \approx U$, i.e., when $R \sim h / e^2$.

Conditions for a Coulomb Blockade

1) The Coulomb energy e^2/C needs to exceed the thermal energy k_BT.
Otherwise an extra electron can get onto the dot with thermal energy instead of being blocked by the Coulomb energy. A dot needs to be either small (<10 nm at 300K) or cold (< 1K for a μm sized dot).



2) The residence time $\Delta t = RC$ of an electron on the dot needs to be so long that the corresponding energy uncertainty $\Delta E = h/\Delta t = h/RC$ is less than the Coulomb energy e^2/C . That leads to a condition for the tunnel resistance between the dot and source/drain: $R > h/e^2 \approx 26\ \mathrm{k}\Omega$

$$\langle R + dR \rangle = \langle R \rangle \left(1 + 2 \frac{dL}{l_e} \right) \quad \rightarrow \quad \langle dR \rangle = \langle R \rangle \frac{2dL}{l_e}$$

$$\therefore \quad \ln \frac{\langle R \rangle}{\langle R \rangle_0} = \frac{2L}{l_e} \quad \text{where} \quad \langle R \rangle_0 = \langle R \rangle \big|_{L=0} = R_Q = \frac{h}{2e^2}$$

$$\langle R \rangle = \frac{h}{2e^2} \exp\left(\frac{2L}{l_e} \right) \qquad \text{C.f. Ohm's law } R \propto L$$

For a 1-D system with disorder, all states become localized to some length ξ .
Absence of extended states → $R \propto \exp(a\, L / \xi)$, a = some constant.
For quasi-1-D systems, one finds $\xi \sim N\, l_e$, where N = number of occupied subbands.

For $T > 0$, interactions with phonons or other e's reduce phase coherence to length $l_\varphi = A\, T^{-\alpha}$.

$$\therefore \quad \langle R \rangle \approx \frac{h}{2e^2} \exp\left(\frac{2l_\varphi}{l_e} \right) \qquad \text{for each coherent segment.}$$

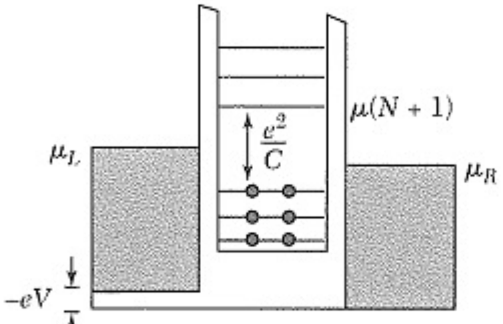
Overall $\langle R \rangle \approx$ incoherent addition of L / l_φ such segments.

For sufficiently high T, $l_\varphi \le l_e$, coherence is effectively destroyed & ohmic law is recovered.

All states in disordered 2-D systems are also localized.
Only some states (near band edges) in disordered 3-D systems are localized.

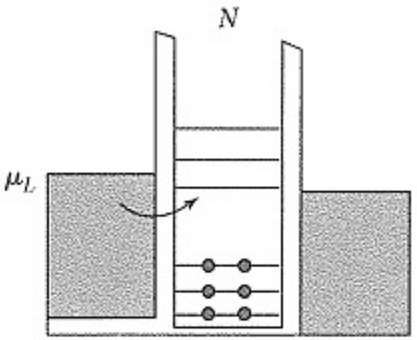
Electrical Transport in 0-D

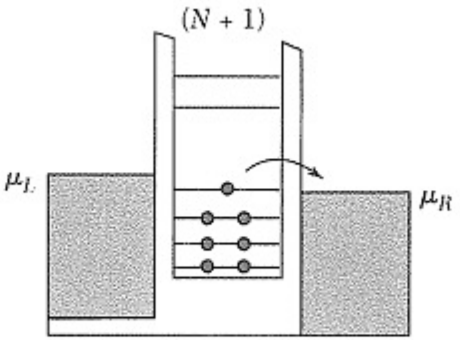
For $T < (U + \Delta\varepsilon) / k_B$, U & $\Delta\varepsilon$ control e flow thru dot.



(b)

Transport thru dot is suppressed when μ_L & μ_R of leads lie between μ_N & μ_{N+1} (Coulomb blockade)





Transport is possible only when μ_{N+1} lies between μ_L & μ_R .

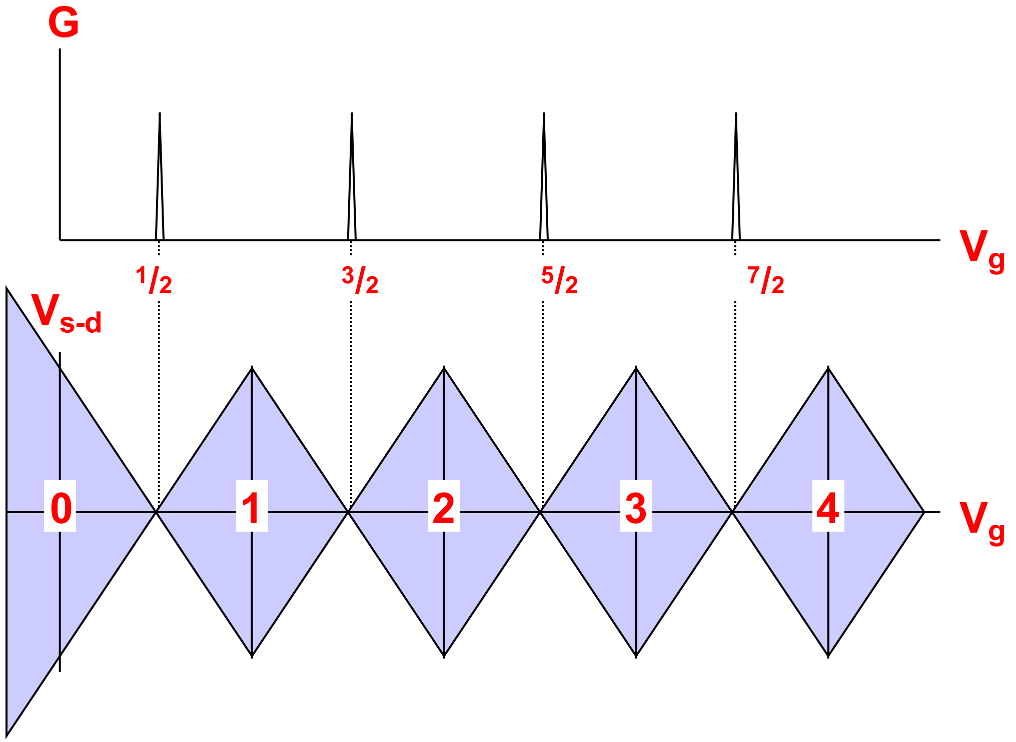
→ Coulomb oscillations of $G(V_g)$.

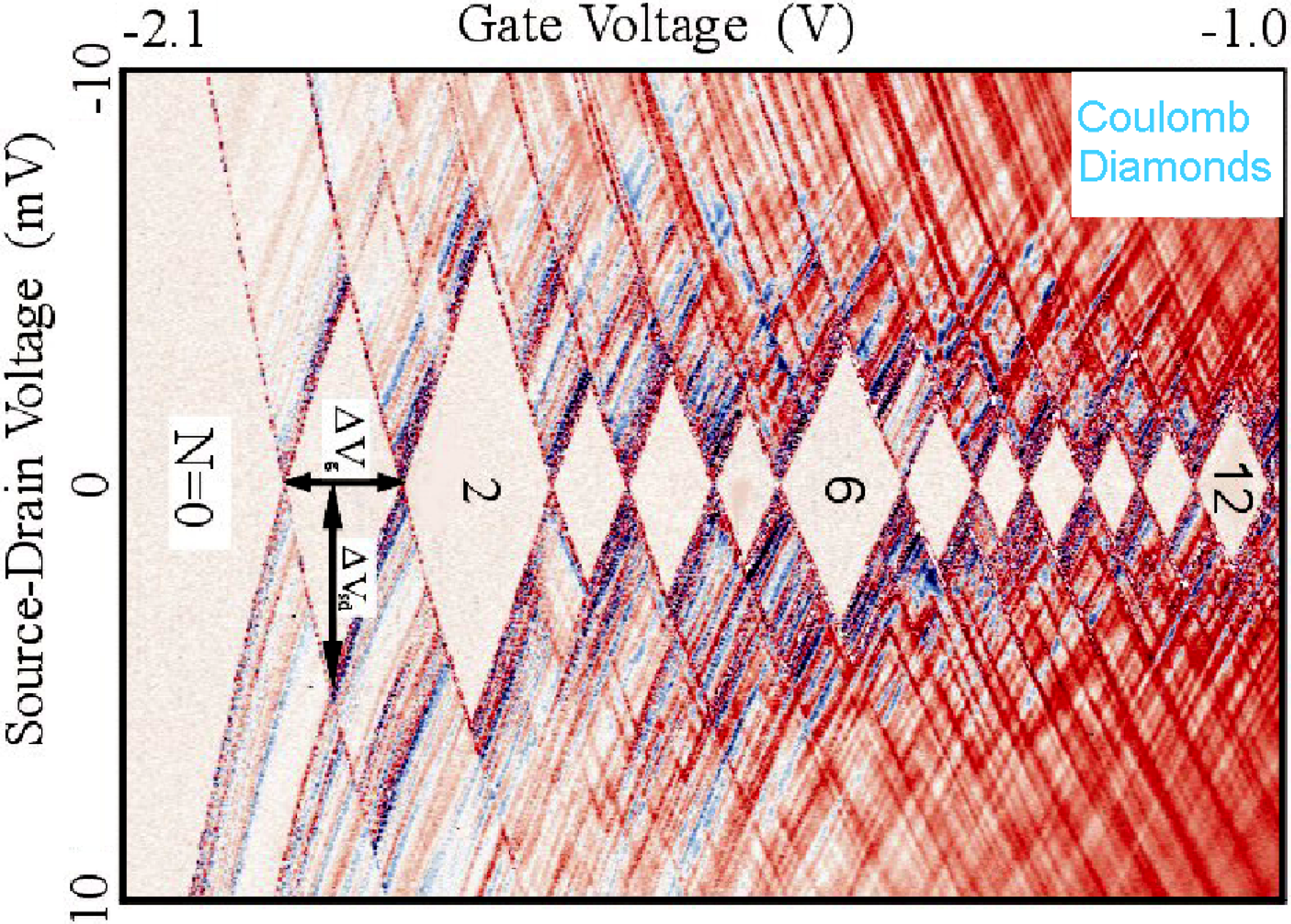
Gate Voltage versus Source-Drain Voltage

The situation gets a bit confusing, because there are two voltages that can be varied, the gate voltage V_g and the source-drain voltage $V_{s\text{-}d}$.

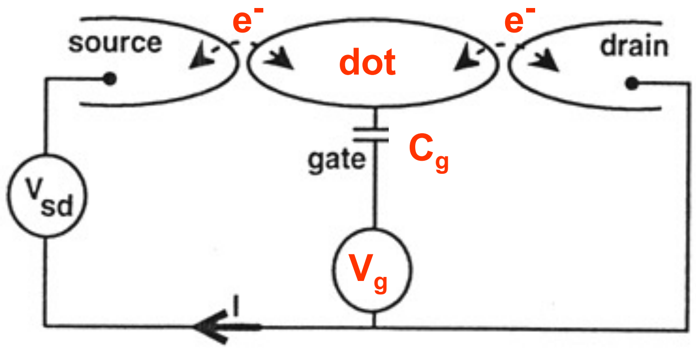
Both affect the conductance. Therefore, one often plots the conductance G against both voltages (see the next slide for data).

Schematically, one obtains "Coulomb diamonds", which are regions with a stable electron number N on the dot (and consequently zero conductance).




Gate Voltage (V)
-2.1
-1.0
Source-Drain Voltage (mV)
-10
0
10
Coulomb Diamonds
N=0
2
6
12
ΔV_g
ΔV_sd

Single Electron Transistor (SET)



A single electron transistor is similar to a normal transistor (below), except

1) the channel is replaced by a small dot.

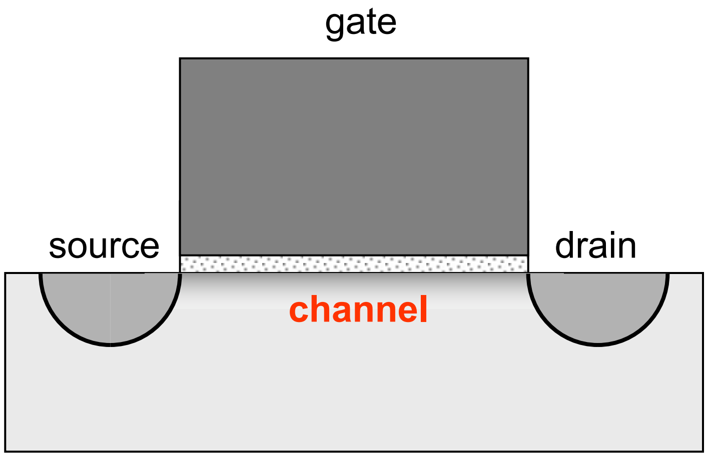
2) the dot is separated from source and drain by thin insulators.

An electron tunnels in two steps:

source → dot → drain

The gate voltage V_g is used to control the charge on the gate-dot capacitor C_g .

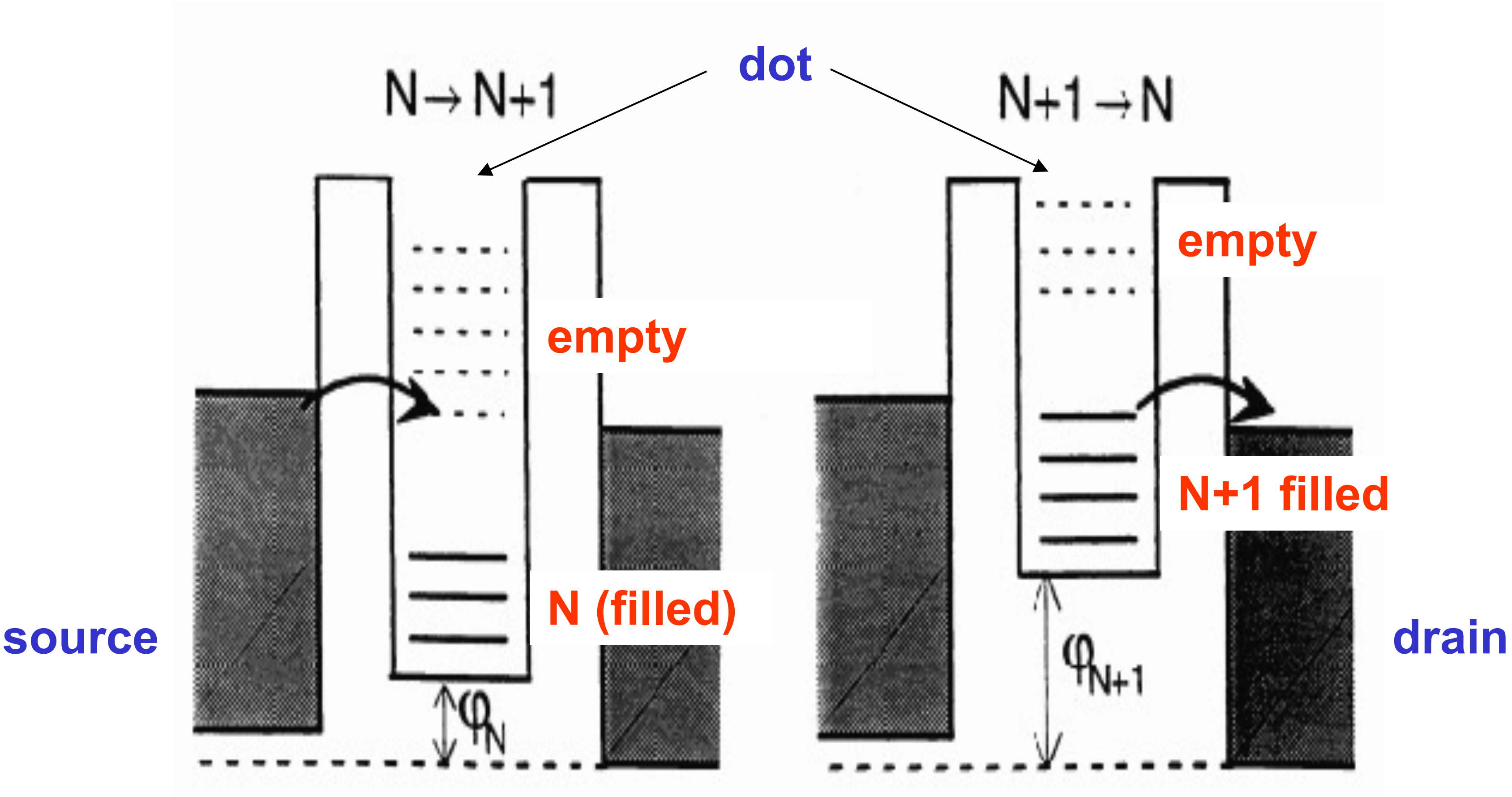
How can the charge be controlled with the precision of a single electron?



Kouwenhoven et al., *Few Electron Quantum Dots*, Rep. Prog. Phys. **64**, 701 (2001).

Two Step Tunneling

source → dot → drain



dot

empty

N (filled)

empty

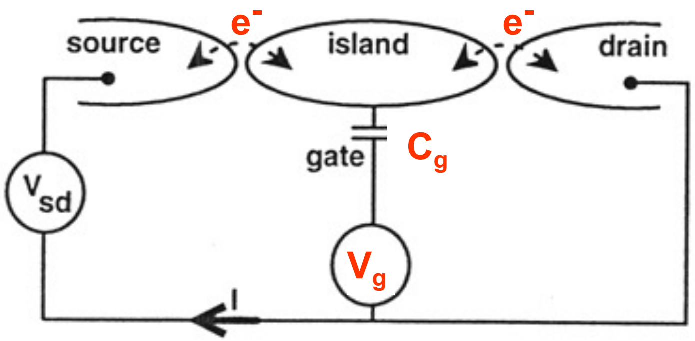
N+1 filled

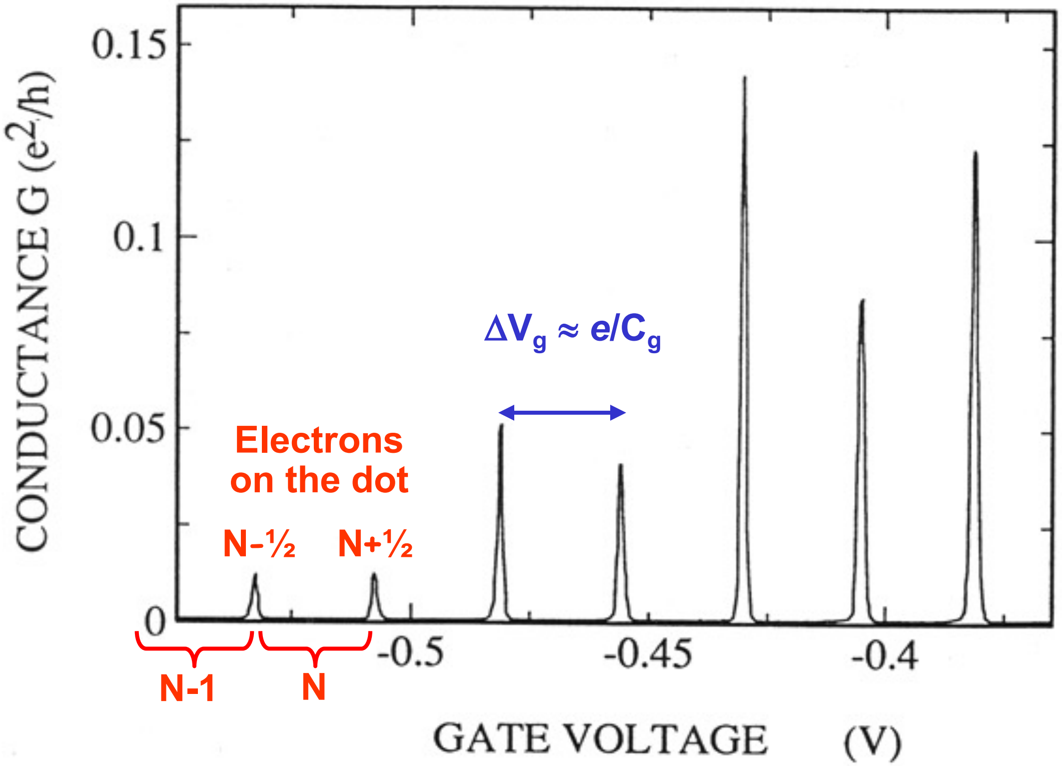
source

drain

(For a detailed explanation see the annotation in the .ppt version.)

Charging a Dot, One Electron at a Time





Sweeping the gate voltage V_g changes the charge Q_g on the gate-dot capacitor C_g . To add one electron requires the voltage $\Delta V_g \approx e/C_g$ since $C_g = Q_g/V_g$.

The source-drain conductance **G** is zero for most gate voltages, because putting even one extra electron onto the dot would cost too much Coulomb energy. This is called **Coulomb blockade**.

Electrons can hop onto the dot only at a gate voltage where the number of electrons on the dot flip-flops between **N** and **N+1**. Their time-averaged number is **N+½** in that case.

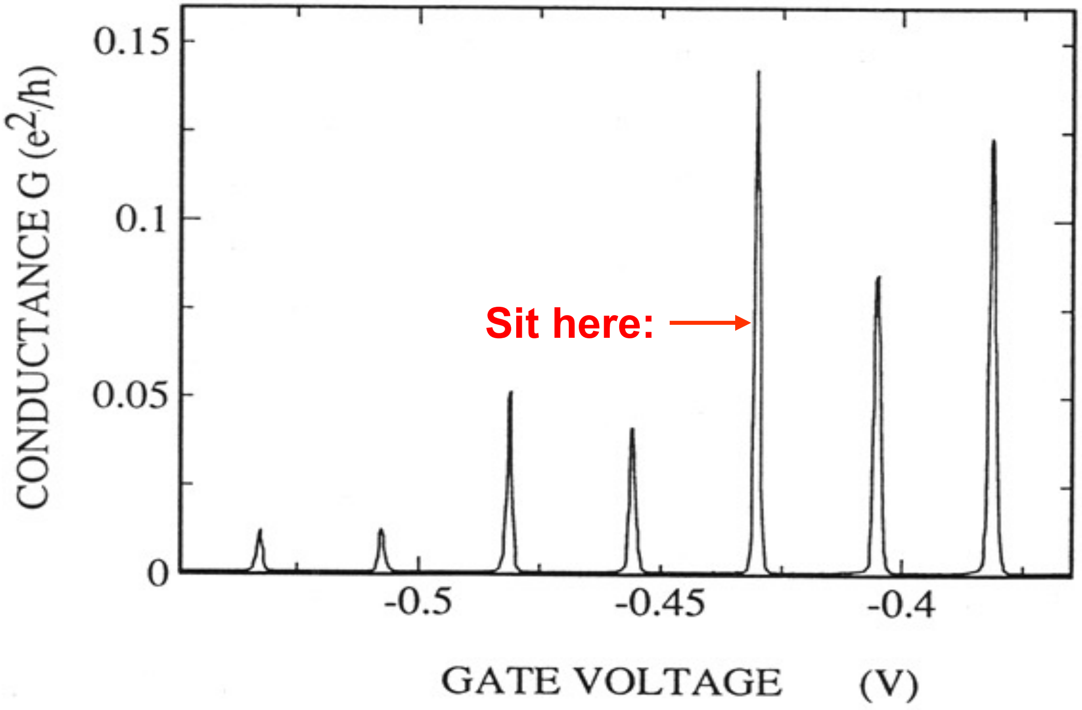
The spacing between these half-integer conductance peaks is an integer.

SET as Extremely Sensitive Charge Detector

At low temperature, the conductance peaks in a SET become very sharp.

Consequently, a very small change in the gate voltage half-way up a peak produces a large current change, i.e. a large amplification. That makes the SET extremely sensitive to tiny charges.

The flip side of this sensitivity is that a SET detects every nearby electron. When it hops from one trap to another, the SET produces a noise peak.

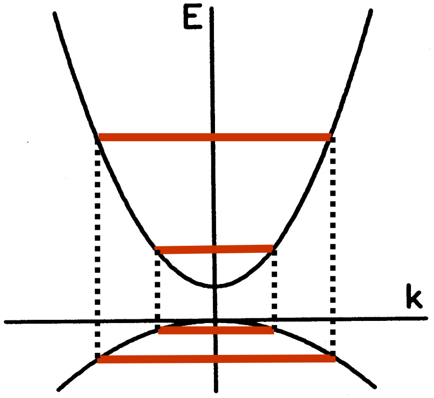


Sit here:

Including the Energy Levels of a Quantum Dot

Contrary to the Coulomb blockade model, the data show Coulomb diamonds with uneven size. Some electron numbers have particularly large diamonds, indicating that the corresponding electron number is particularly stable.

This is reminiscent of the closed electron shells in atoms. Small dots behave like artificial atoms when their size shrinks down to the electron wavelength. Continuous energy bands become quantized (see Lecture 8). Adding one electron requires the Coulomb energy U plus the difference ΔE between two quantum levels. If a second electron is added to the same quantum level (the same shell in an atom), ΔE vanishes and only the Coulomb energy U is needed.



The quantum energy levels can be extracted from the spacing between the conductance peaks by subtracting the Coulomb energy $U = e^2/C$.

Precision Standards from “Single” Electronics

Count individual electrons, pairs, flux quanta

Current I
Coulomb
Blockade

$I = e\,f$

Voltage V
Josephson
Effect

$V = h/2e \cdot f$

$V/I = R = h/e^2$

Resistance R
Quantum Hall
Effect

(f = frequency)

Problems

1. ***Energies of a spherical quantum dot.*** Consider a spherical dot of radius *R* surrounded by a spherical metal shell of radius *R* + *d*.
   (a) Derive the formula $U = \frac{e^2}{\varepsilon R}\frac{d}{R+d}$ for the charging energy. (b) Show that, for $d \ll R$, the result is the same as that obtained using the parallel plate capacitor result, $C = \varepsilon\varepsilon_0 A/d$. (c) For the case of an isolated dot, $d \rightarrow \infty$, find the ratio of the charging energy to lowest quantized energy level. Express your answer in terms of the radius *R* of the dot and the effective Bohr radius a_B^*.

2. ***Pair tunneling.*** Superconductivity adds a new and exciting twist to single electron tunneling. Work out the basic modifications due to superconductivity.

3. ***Carbon nanotube band structure*.** Figure at the right shows the graphene lattice with the primitive lattice translation vectors of length a = 0.246 nm, along with the first Brillouin zone. (a) Find the set of reciprocal lattice vectors G associated with the lattice. (b) Find the length of the vectors K and K’ shown in the figure in terms of a.

For energies near the Fermi energy and wavevectors near the K point, the 2D band structure can be approximated as

$$\varepsilon = \pm\hbar v_F|\Delta\mathbf{k}| \qquad \Delta\mathbf{k} = \mathbf{k} - \mathbf{K}\ ,$$

where $v_F = 8 \times 10^5$ m/s. A similar approximation holds near the K' point. Consider a tube rolled up along the x-axis with a circumference na. By applying periodic boundary conditions along the rolled up direction, the dispersions of the 1D sub- bands near the K point can be found. (c) Show that, if n is divisible by 3, there exists a "massless" subband whose energy is linear in Δk_y. Sketch this subband. These nanotubes are 1D metals. (d) For the case of $n = 10$, find the magnitude of the semiconducting bandgap ε_{11} in eV and show that $\varepsilon_{22}/\varepsilon_{11} = 2$. (e) Again for the $n = 10$ case, show that the dispersion relation of the lowest electron subband is of the form of a relativistic particle, $\varepsilon^2 = (m^*c^2)^2 + (pc)^2$, where v_F plays the role of the speed of light, and find the ratio of effective mass m^* to the free electron mass m.