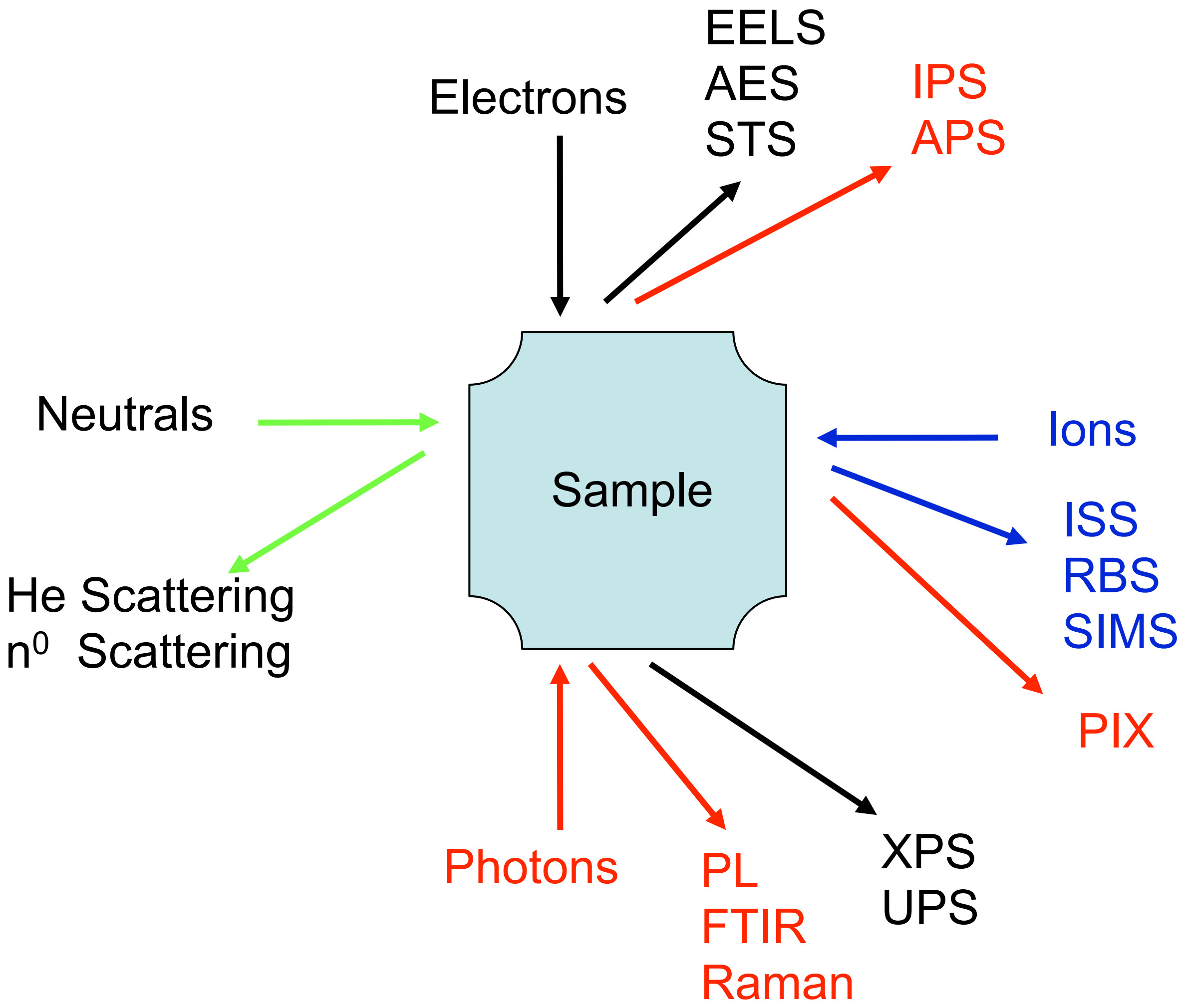
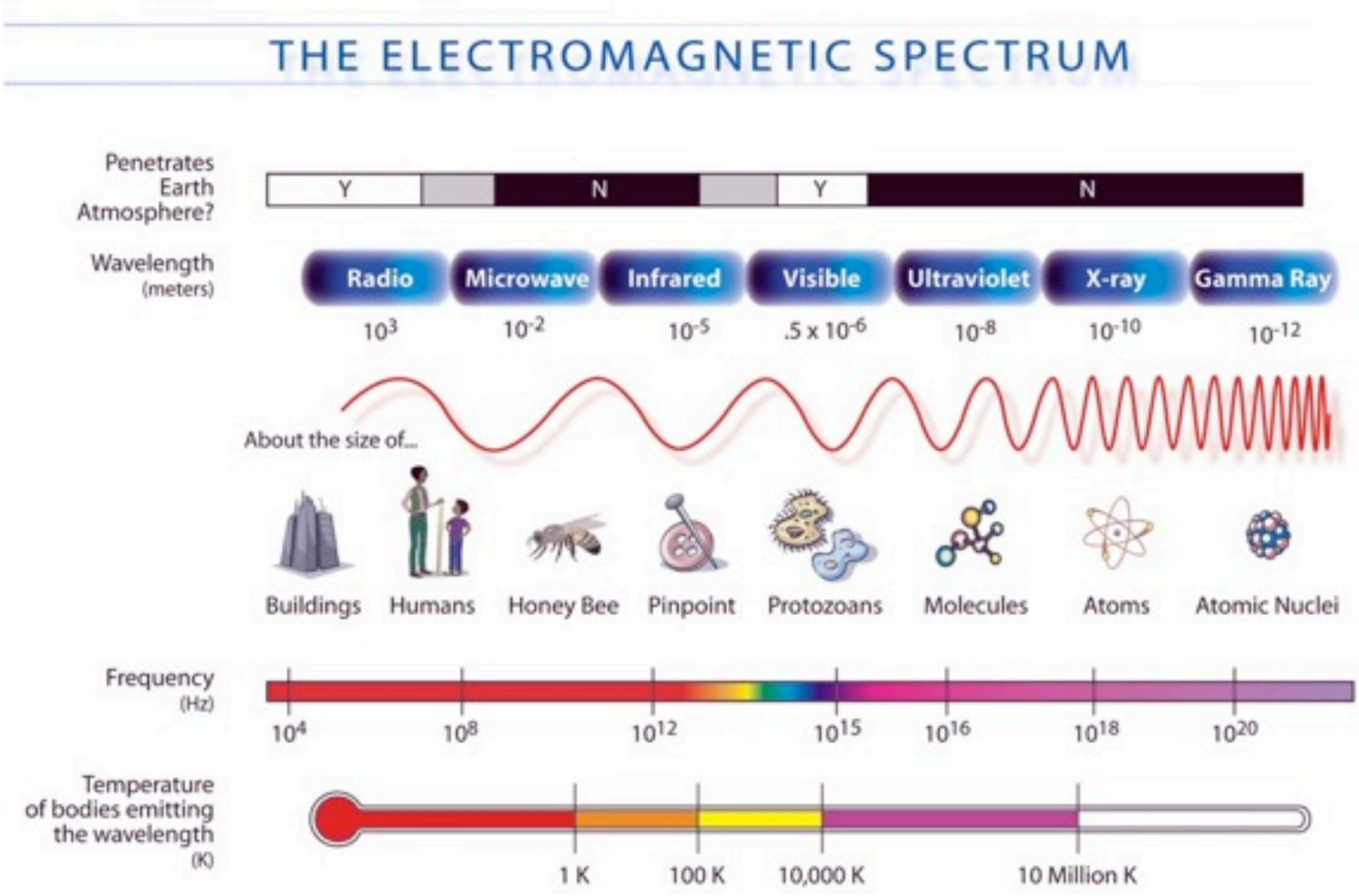
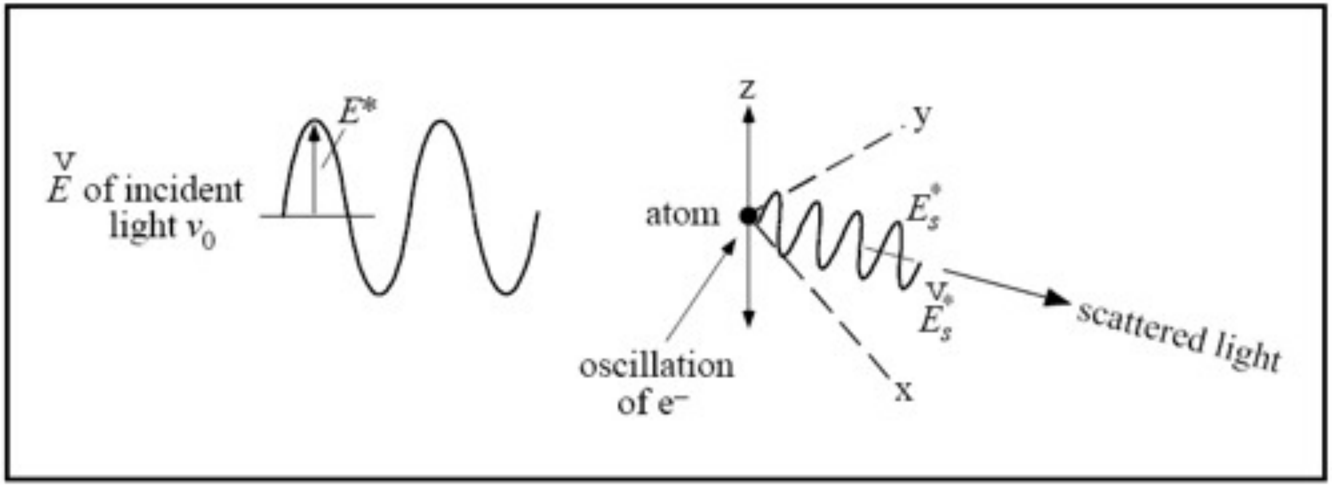
Various spectroscopic methods

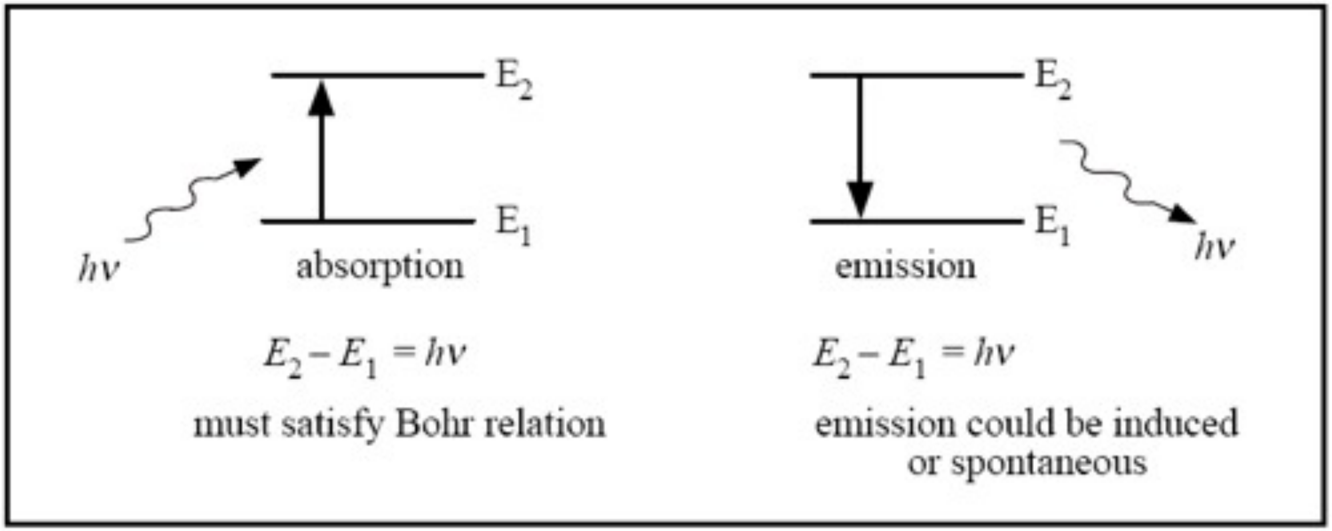


Interaction between light and matter



Scattering and absorption/emission of light





We can use light scattering and absorption to probe the dynamics of atoms and molecules in a matter because:

- Light is an electromagnetic wave consisting of oscillating electric and magnetic fields.
- Electrons and nuclei are charged particles, and their motions in atoms, molecules, and lattices generate oscillating electric fields.
- A matter can absorb energy from light if the frequency of the light oscillation and the frequency of the electron or lattice "transition motion" match. Unless these frequencies match, light absorption cannot occur. The "transition motion" frequency is related to the frequencies of motion in the higher and lower energy states.
- By measuring the frequencies of light absorbed by a matter, we can determine the frequencies of the various transition motions within the matter.

Phenomena due to light scattering

(a) Reflection : Light scattered in the opposite direction of incident light.
(b) Refraction : Light scattered in the forward direction combines with the incident beam to give rise to the phenomenon of refraction. The physical effect of this combination is to make the transmitted light appear as though it has travelled more slowly through the sample than through a vacuum.

$$\text{index of refraction} \quad n \equiv \frac{\text{velocity of light in vacuum}}{\text{velocity of light in substance}}$$

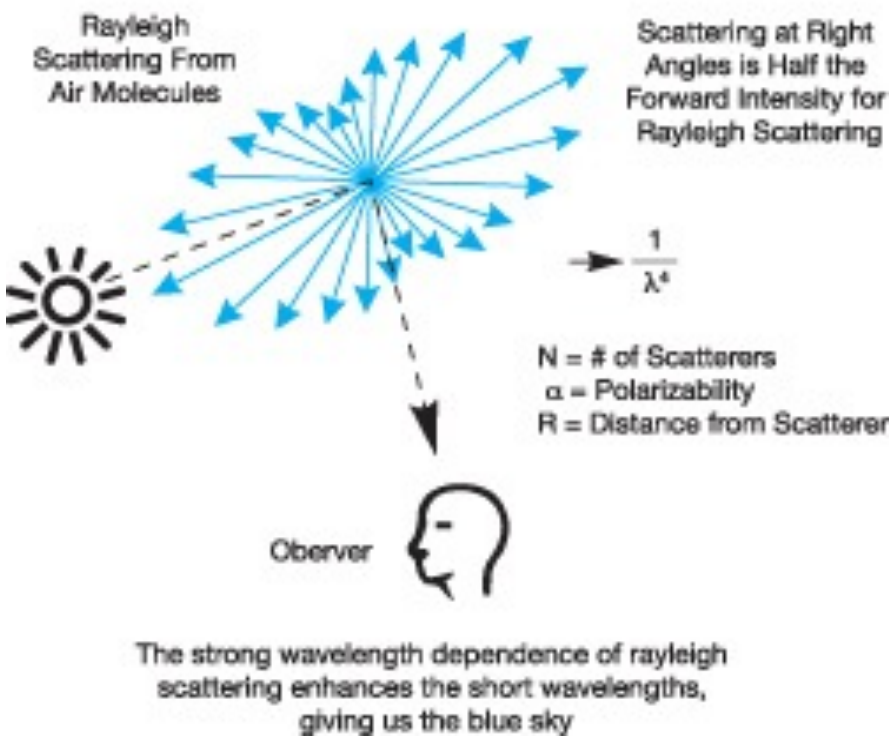
(c) Diffraction : Superposition of scattered waves from individual atoms or molecules in the sample. If the sample is highly ordered, diffraction pattern periodicity in the distribution of atoms and molecules in the sample can be used to deduce or infer the relative positions of atoms in a sample.

Rayleigh scattering

Rayleigh scattering is the elastic scattering of light (electromagnetic radiation) by particles much smaller than the wavelength of the light, which may be individual atoms or molecules. It can occur when light travels in transparent solids and liquids, but is most prominently seen in gases.

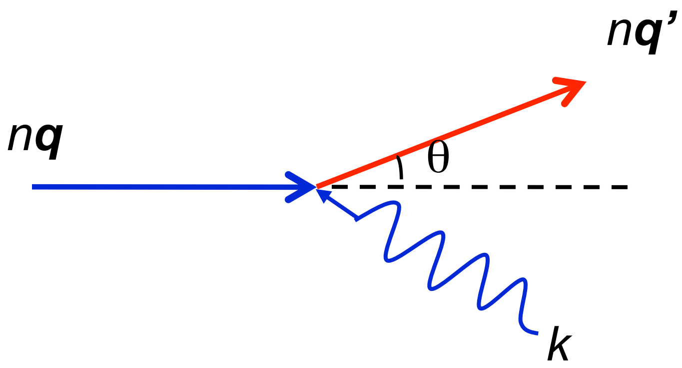
Rayleigh scattering is a function of the electric polarizability (α) of the particles:

$$I = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 R^2}(1 + \cos^2\theta).$$



Brillouin scattering

Brillouin scattering occurs when light in a medium (such as water or a crystal) interacts with time dependent optical density variations and changes its energy (frequency) and path. The density variations may be due to acoustic modes, such as phonons, magnetic modes, such as magnons. As described in classical physics, when the medium is compressed, its index (*n*) of refraction changes and the light's path necessarily bends.

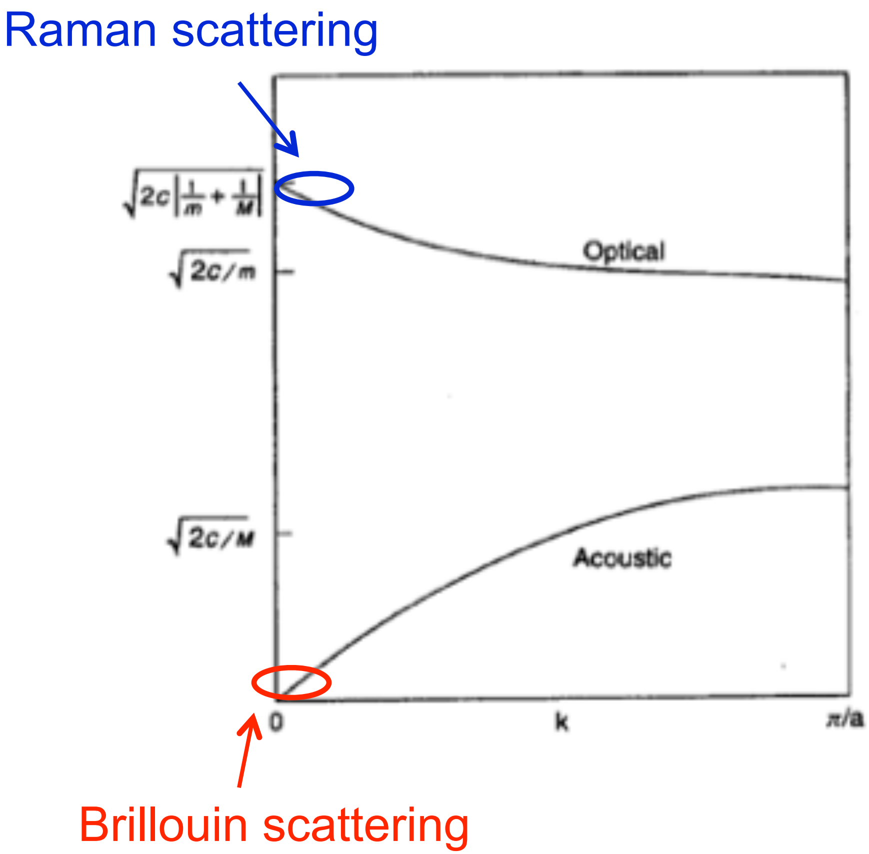


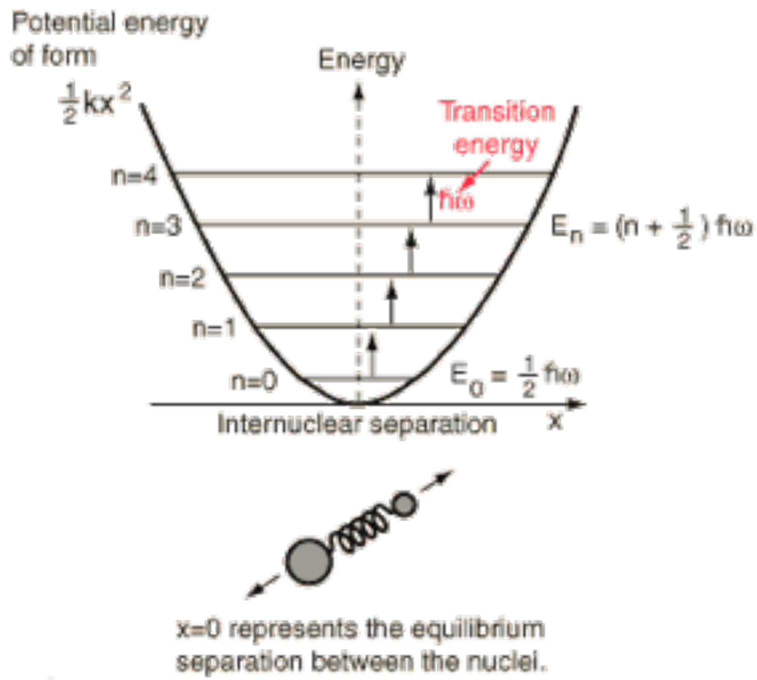
q is small in the Brillouin zone

$$k = (2n\omega/c)\sin(\theta/2)$$

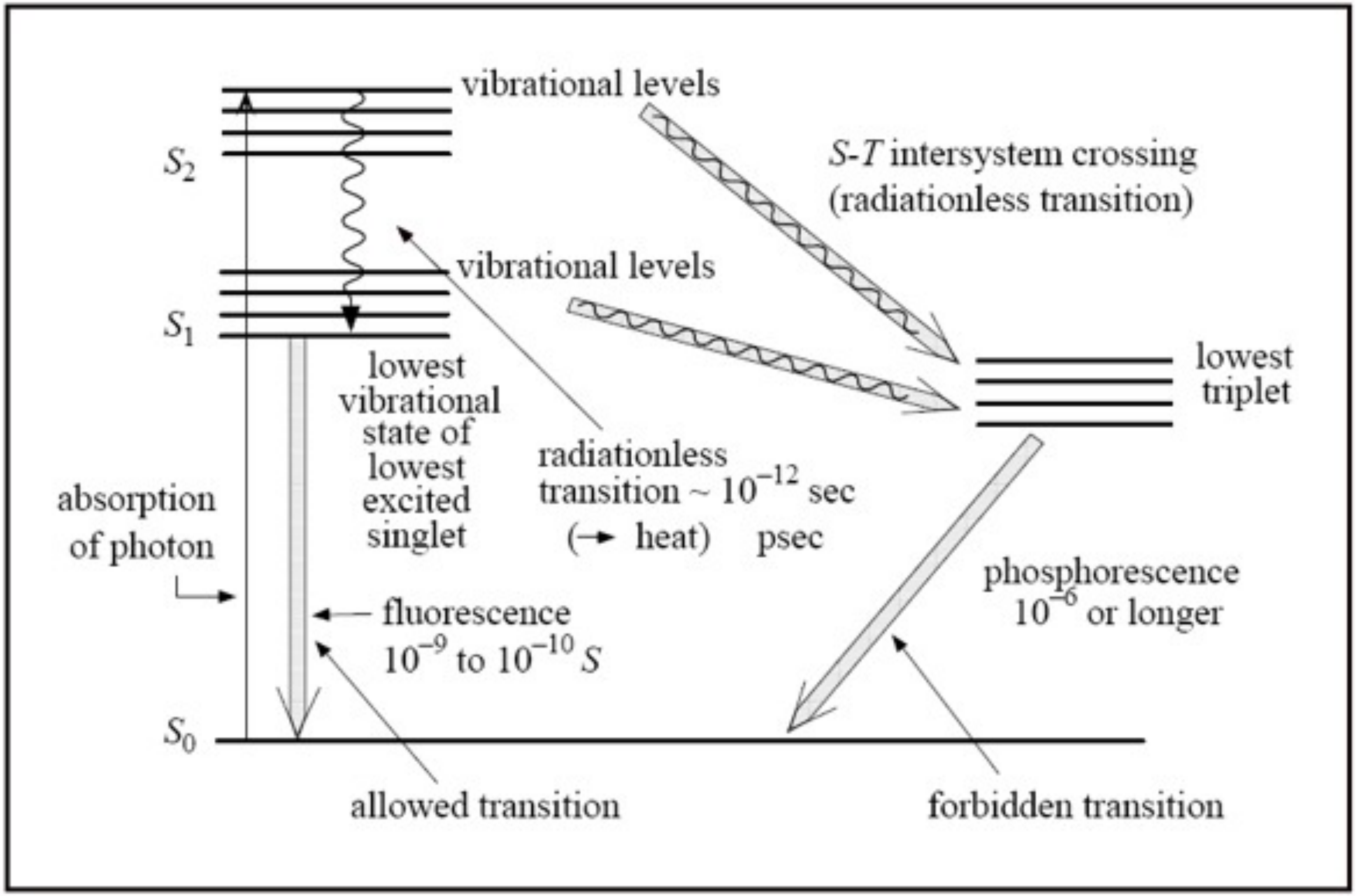
$$c_s(k) = \Delta\omega / k = (\Delta\omega/2\omega)(c/n)\csc(\theta/2)$$

Vibrational Spectroscopy

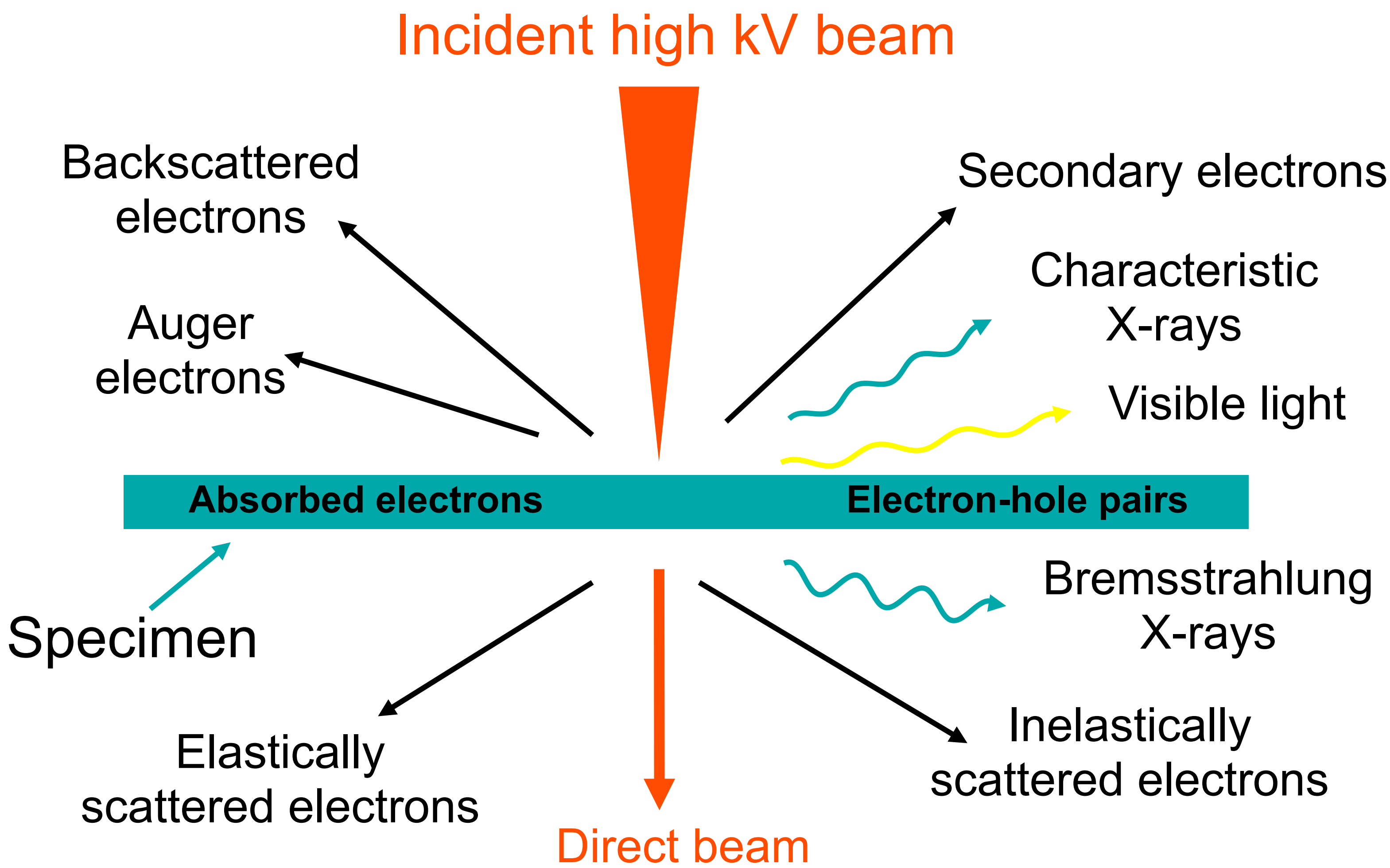




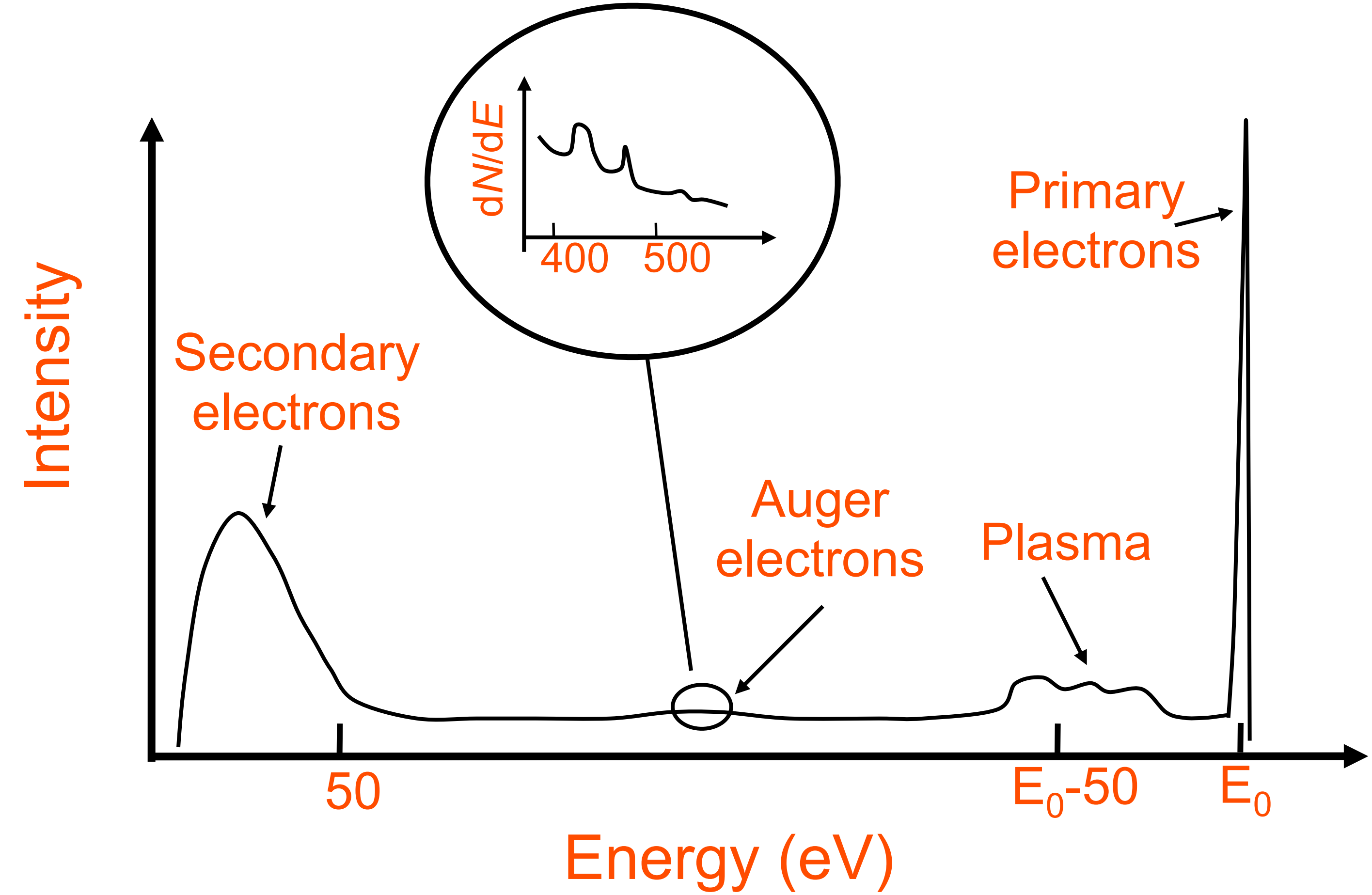
Fluorescence and phosphorescence



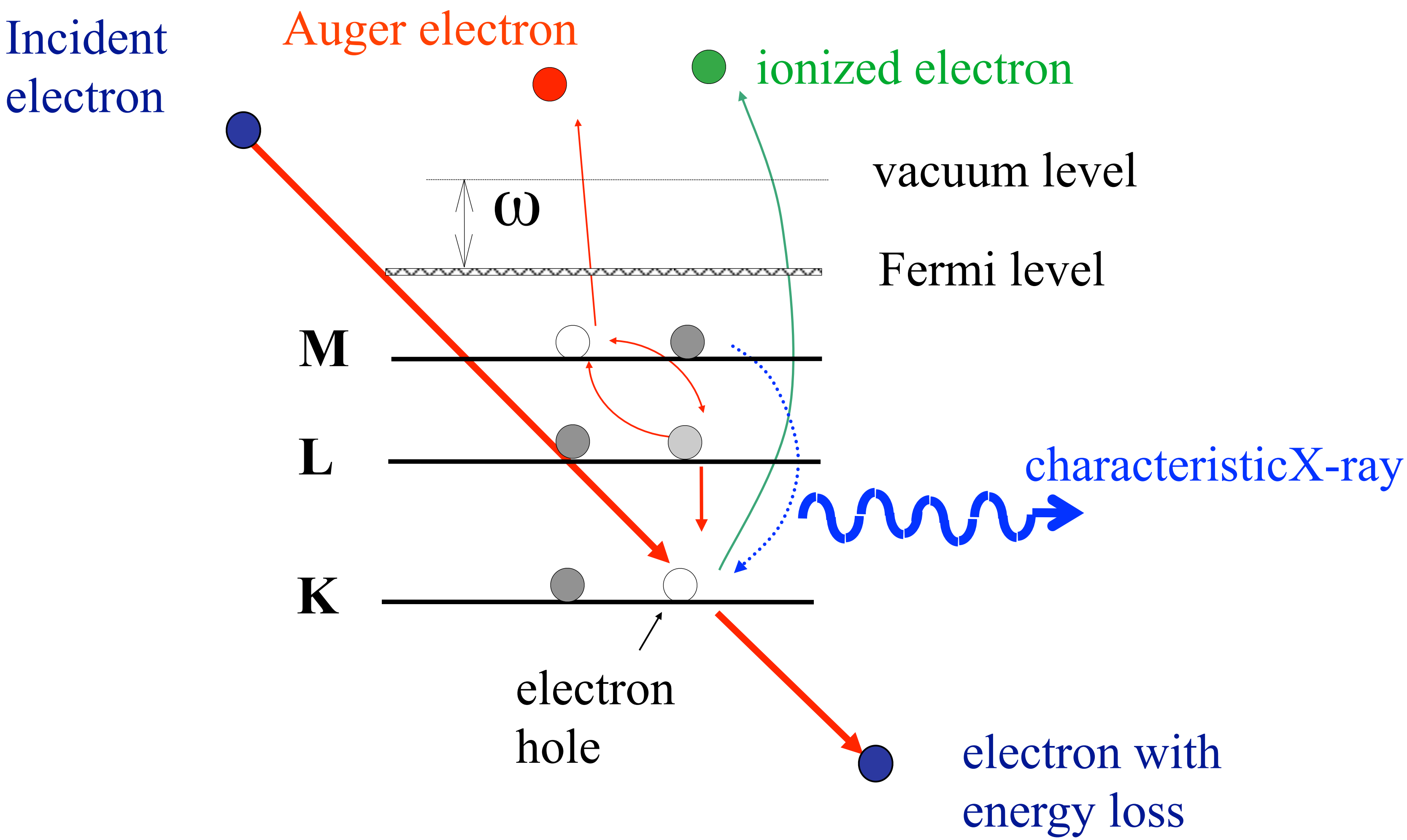
Interaction of electron beam with solid



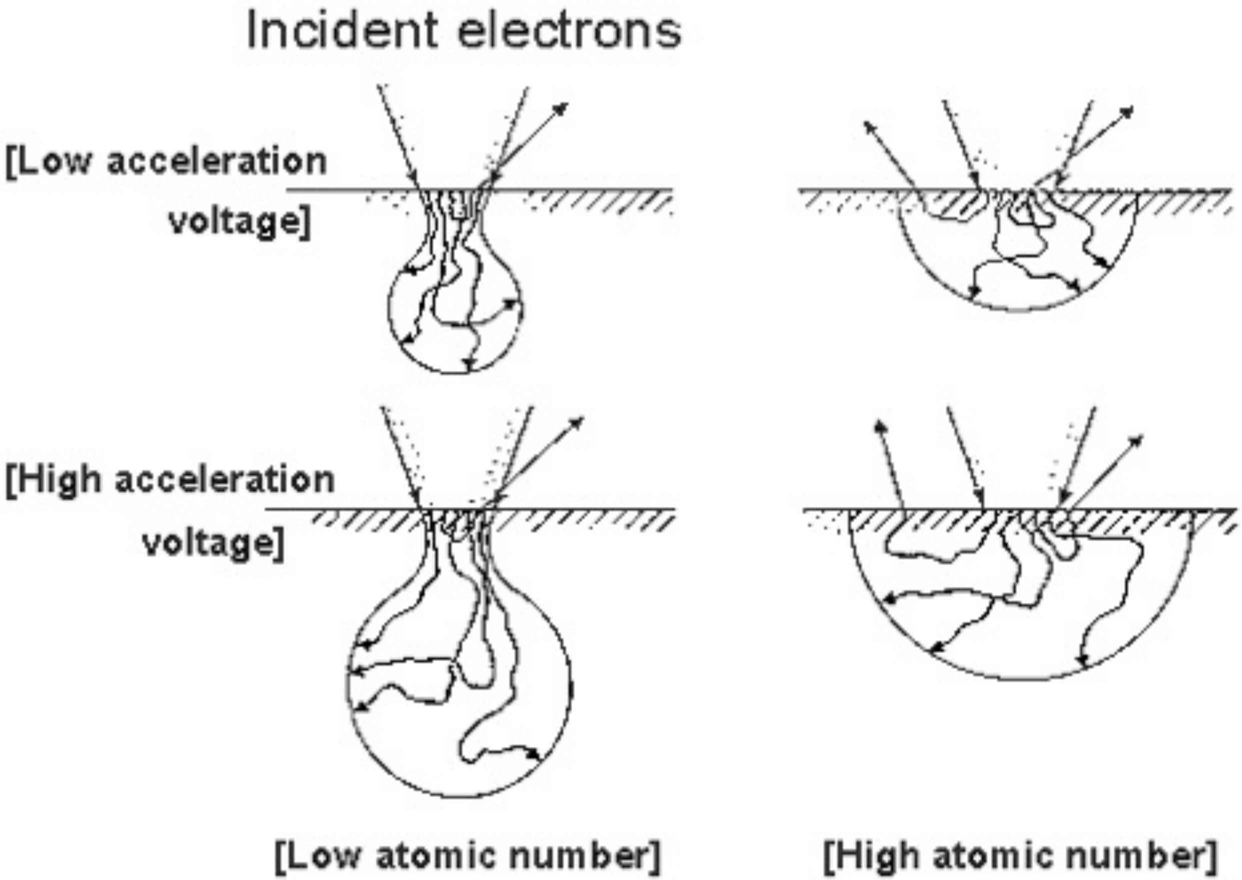
Energy distribution of detected electrons



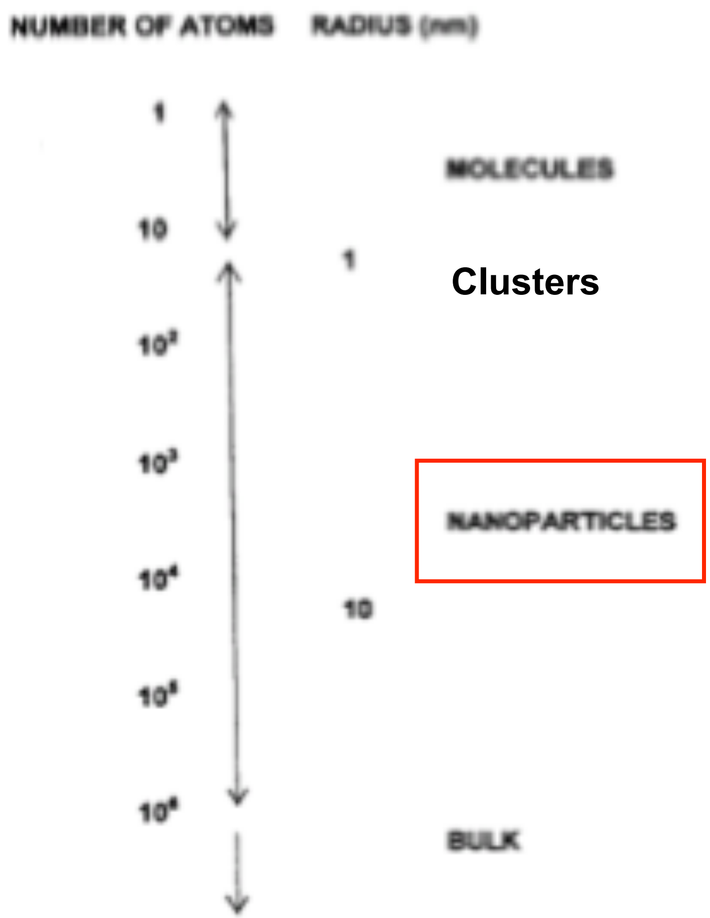
Interaction of high energy (~kV) electrons with (solid) materials-I, cont.



Penetration power of e-beam



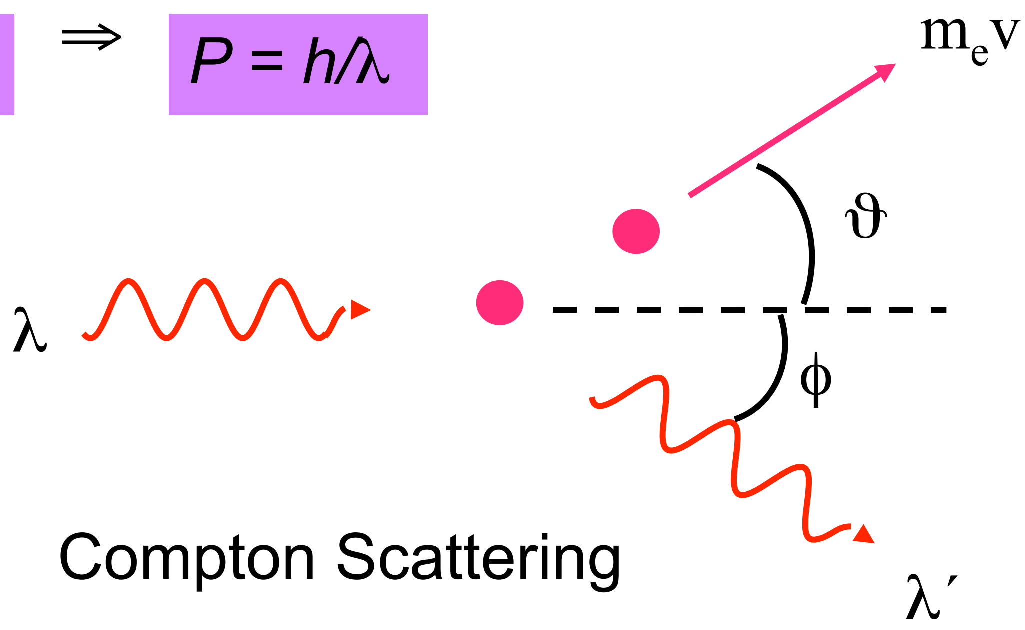
Properties of individual nanoparticles



Particle nature of photons

Einstein's proposal:

$E = h\nu$ $\Rightarrow$ $P = h/\lambda$



Compton Scattering

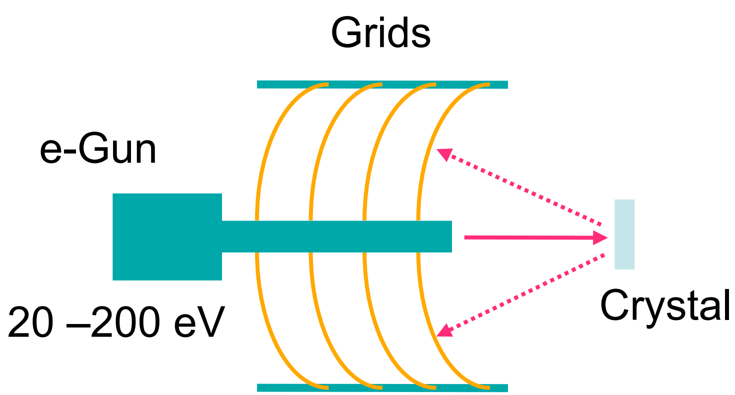
Wave nature of electrons

de Broglie's proposal:

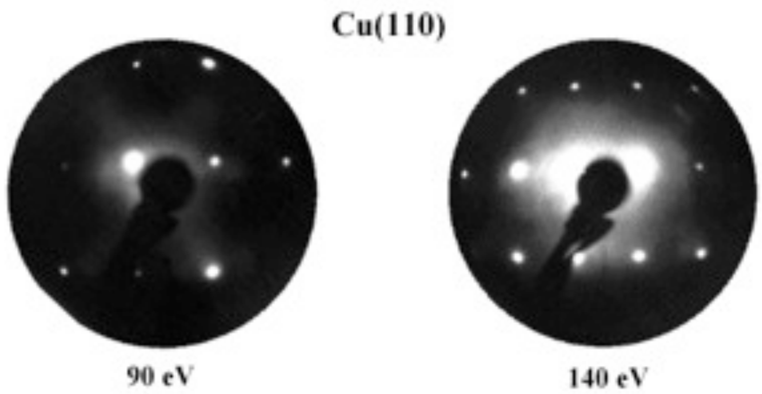
$\lambda = h/P$ $\Rightarrow$ $\nu = h/E$

For electrons:

$\lambda\ (nm) = 1.22/E^{1/2}(eV)$



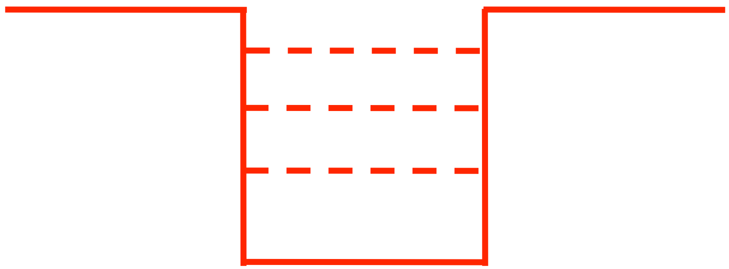
LEED



Fundamentals of quantum mechanics

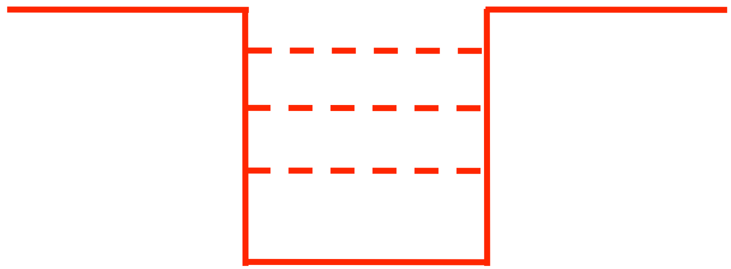
Fundamentals of quantum mechanics

1. Quantization

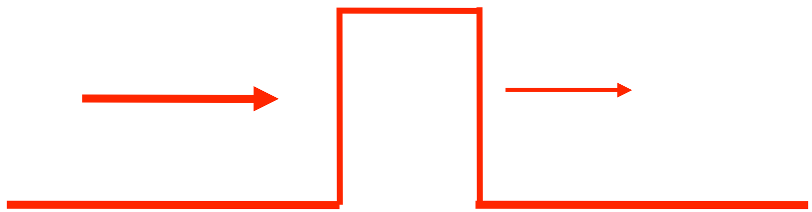


Fundamentals of quantum mechanics

1. Quantization



2. Tunneling



Fundamentals of quantum mechanics

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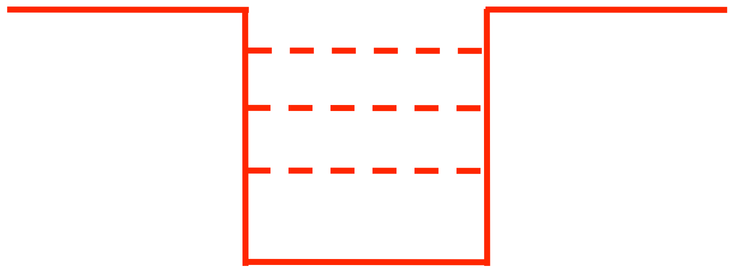

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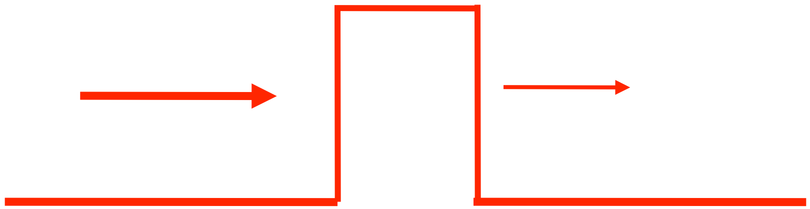
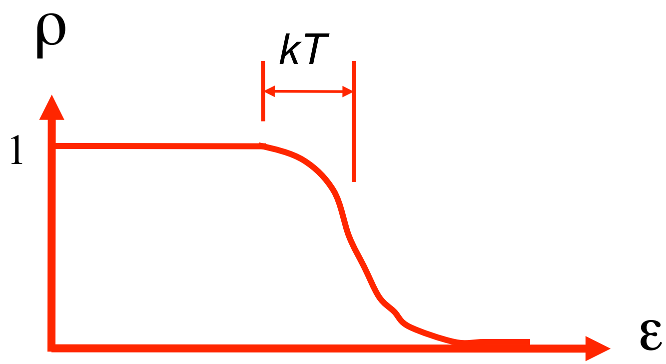
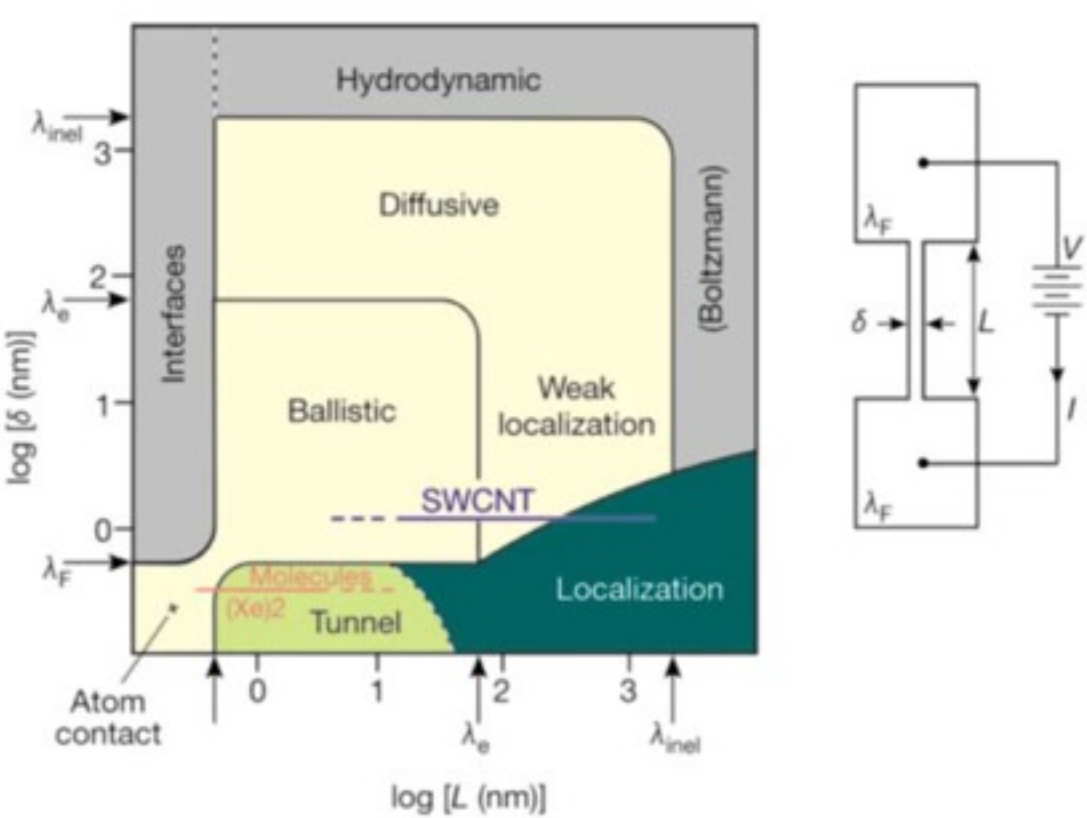


3. Statistics

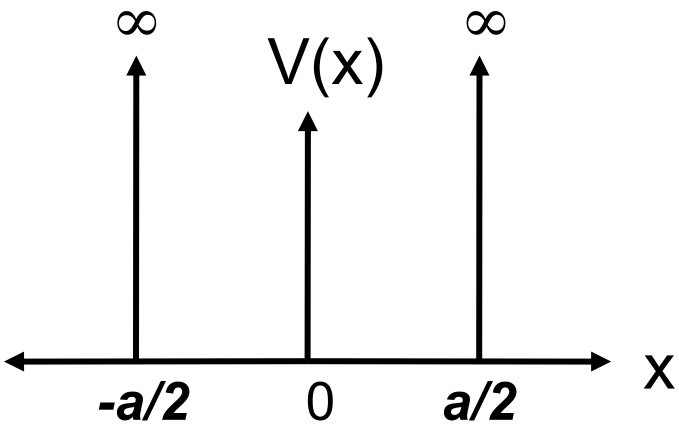


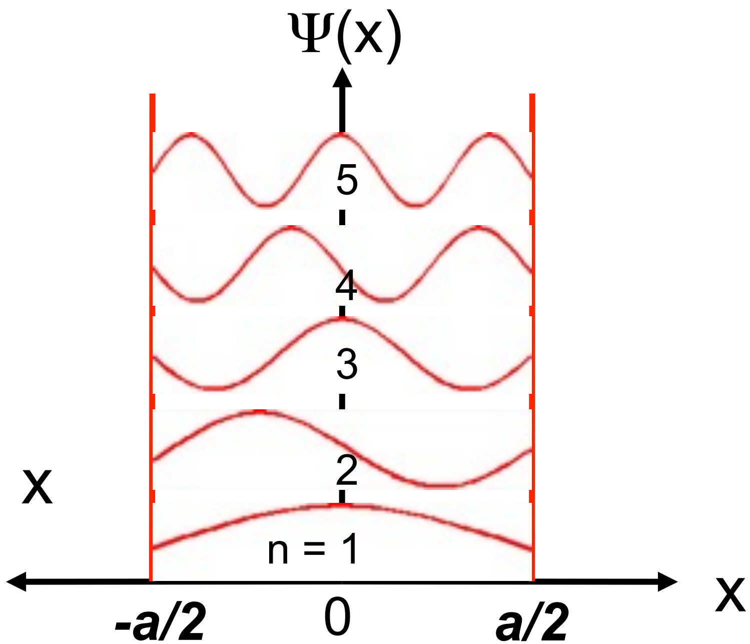
Critical Length scale

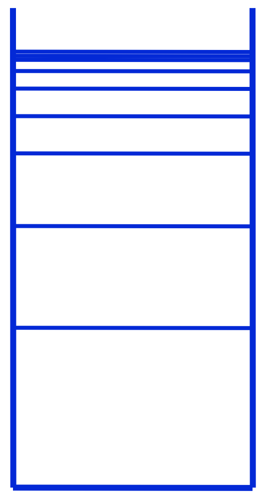


C. Joachim *et al., Nature* 408, 541 (2000).

One dimensional size effect





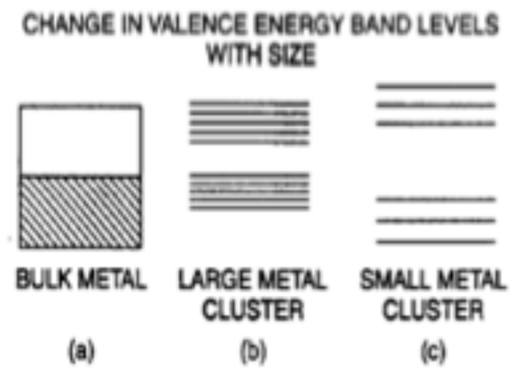


Atomic Levels

$$\Psi(x) = \begin{cases} \sin(n\pi x/a), \text{ n even} \\ \cos(n\pi x/a), \text{ n odd} \end{cases}$$

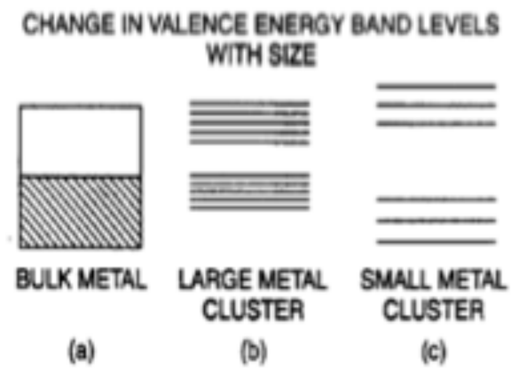
$$E = n^2\pi^2h^2/2ma^2, \ n = 1,2,3\ldots$$

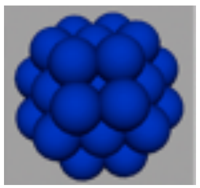
Size effect



Size →

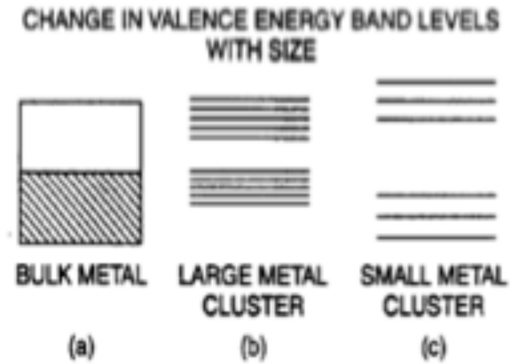
Size effect

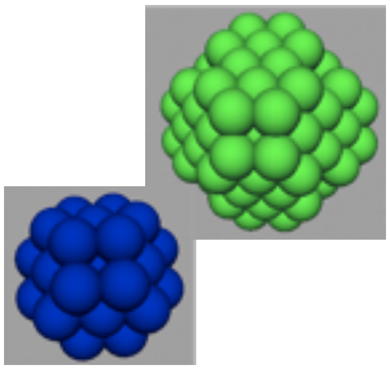




Size →

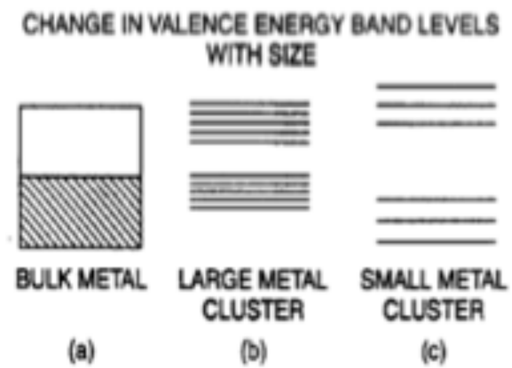
Size effect

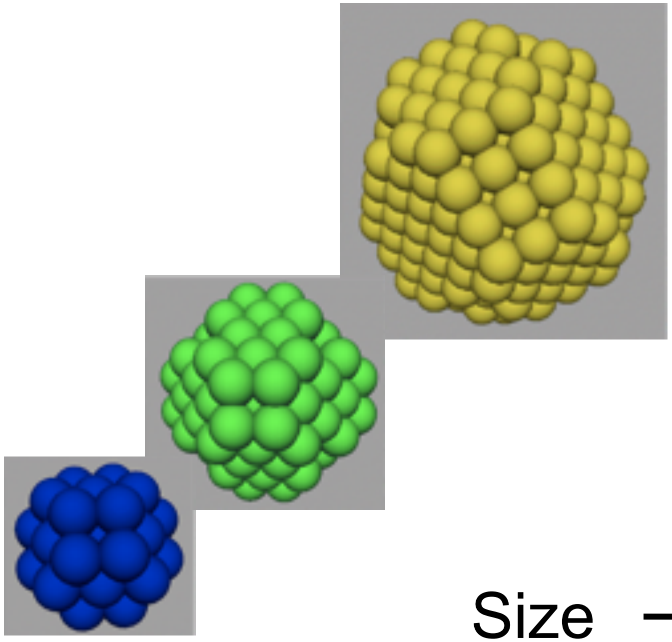




Size →

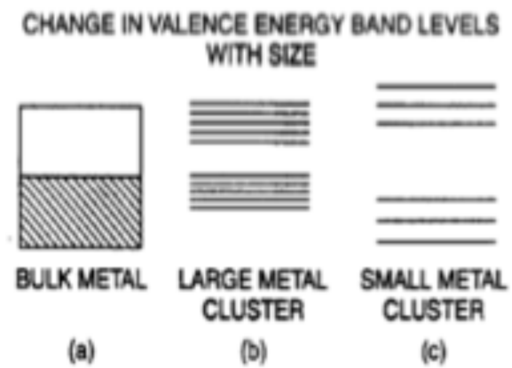
Size effect

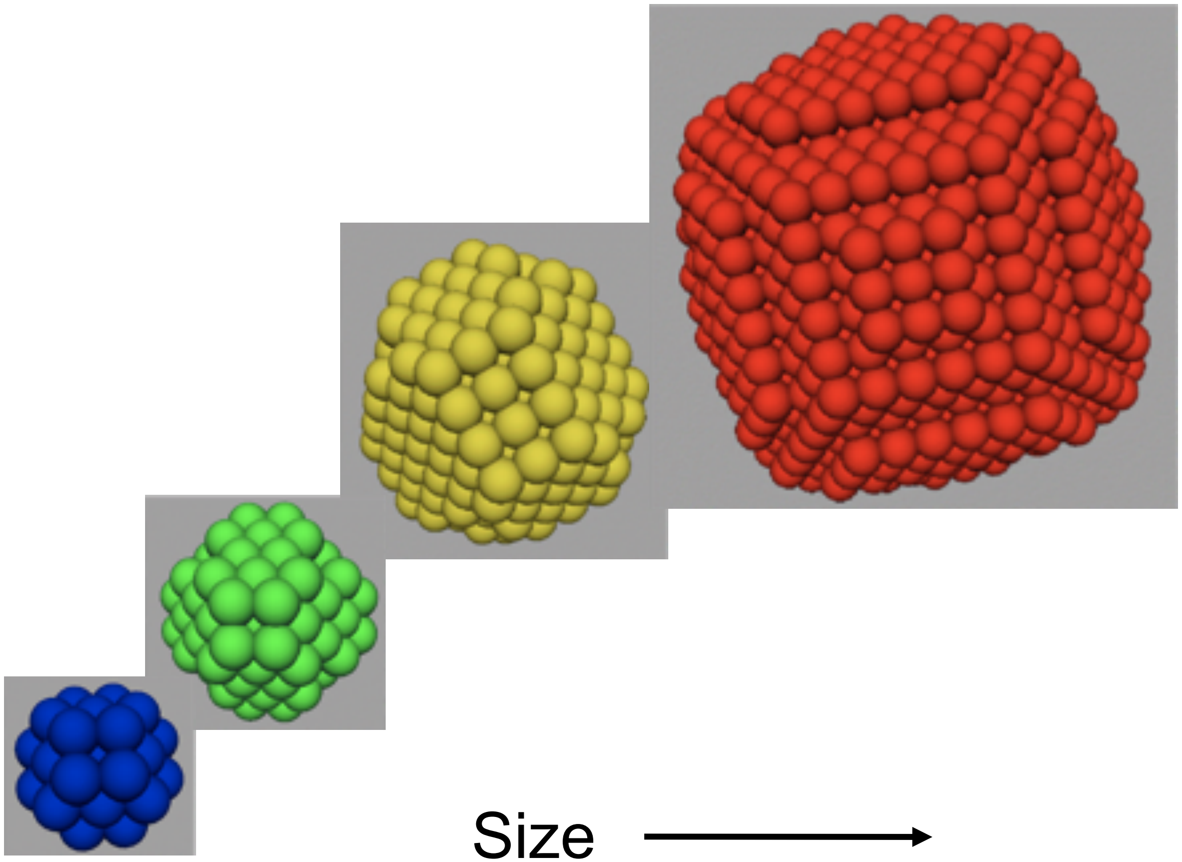




Size →

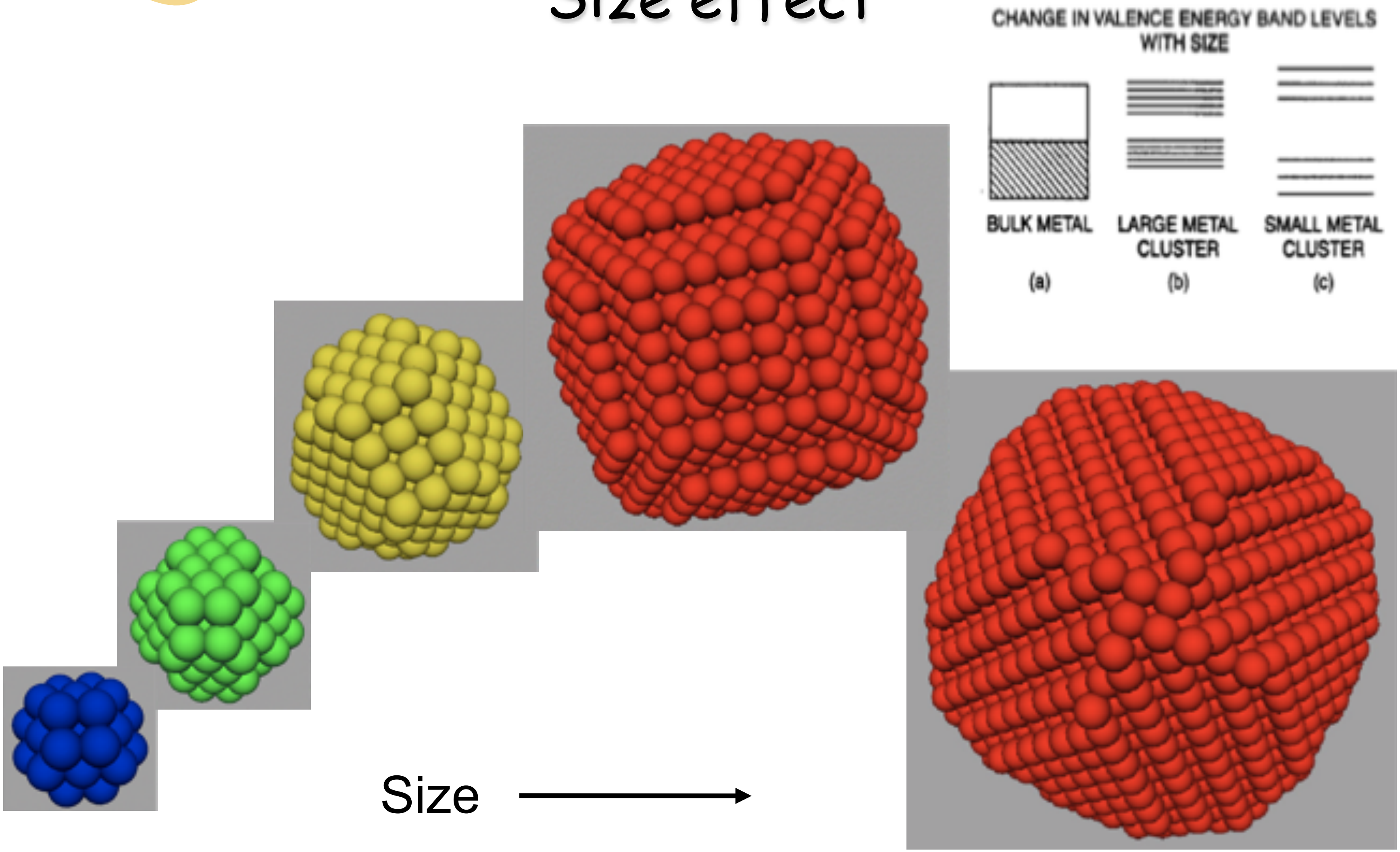
Size effect





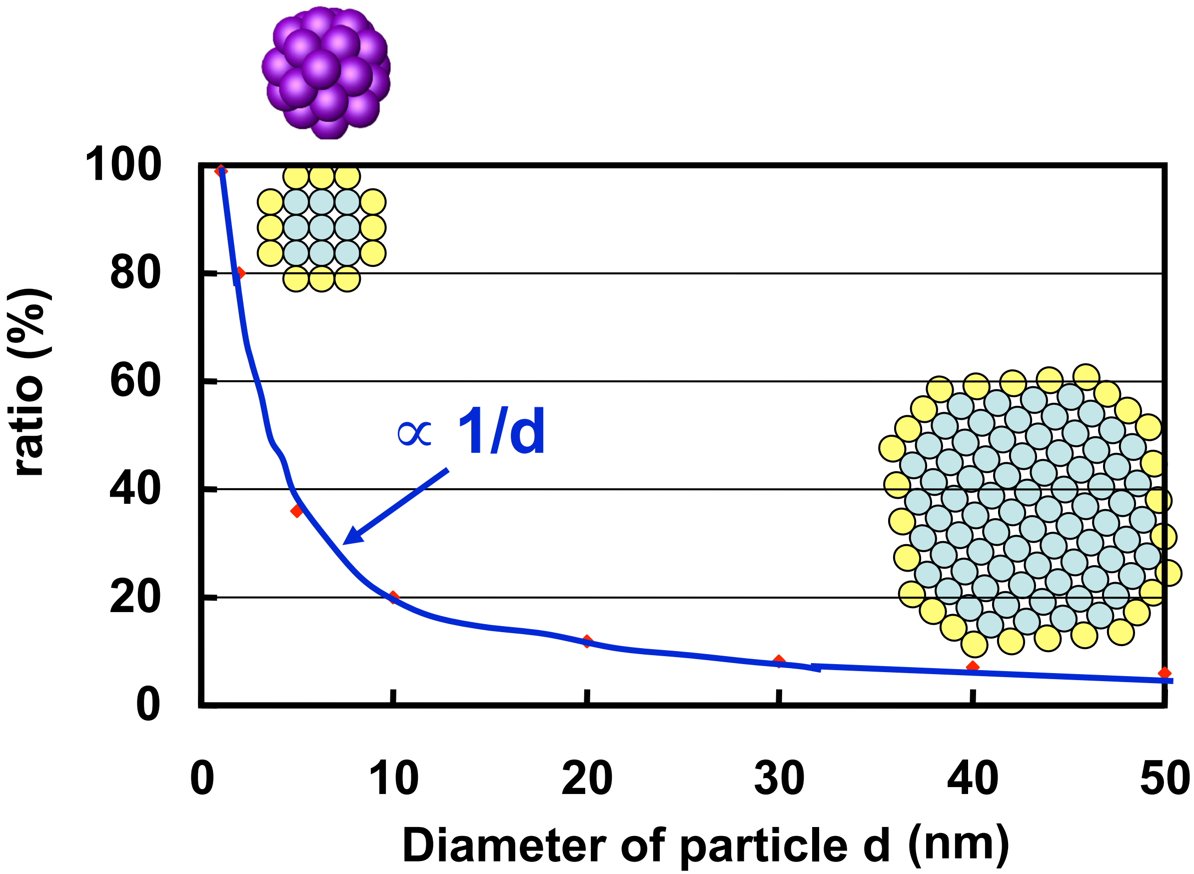
Size →

Size effect

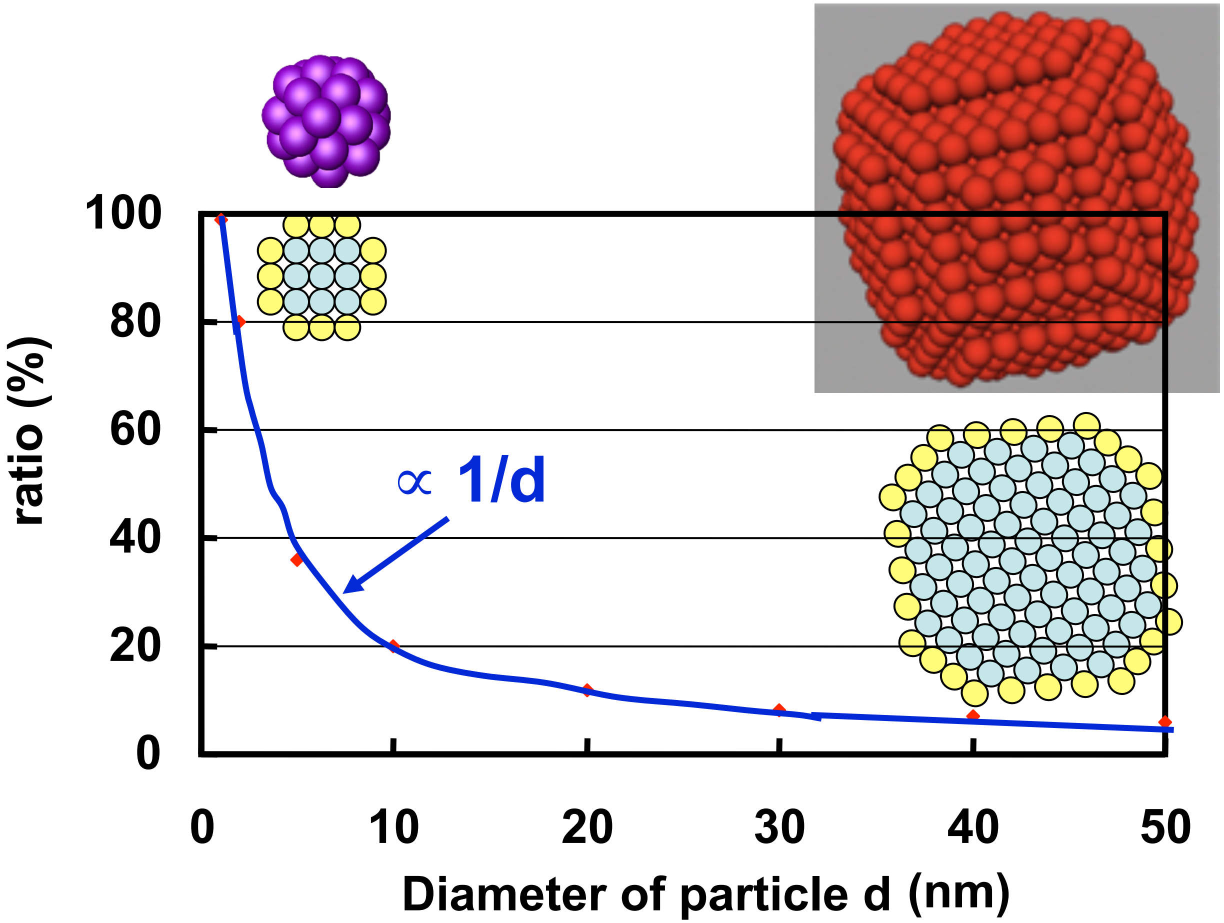


Size →

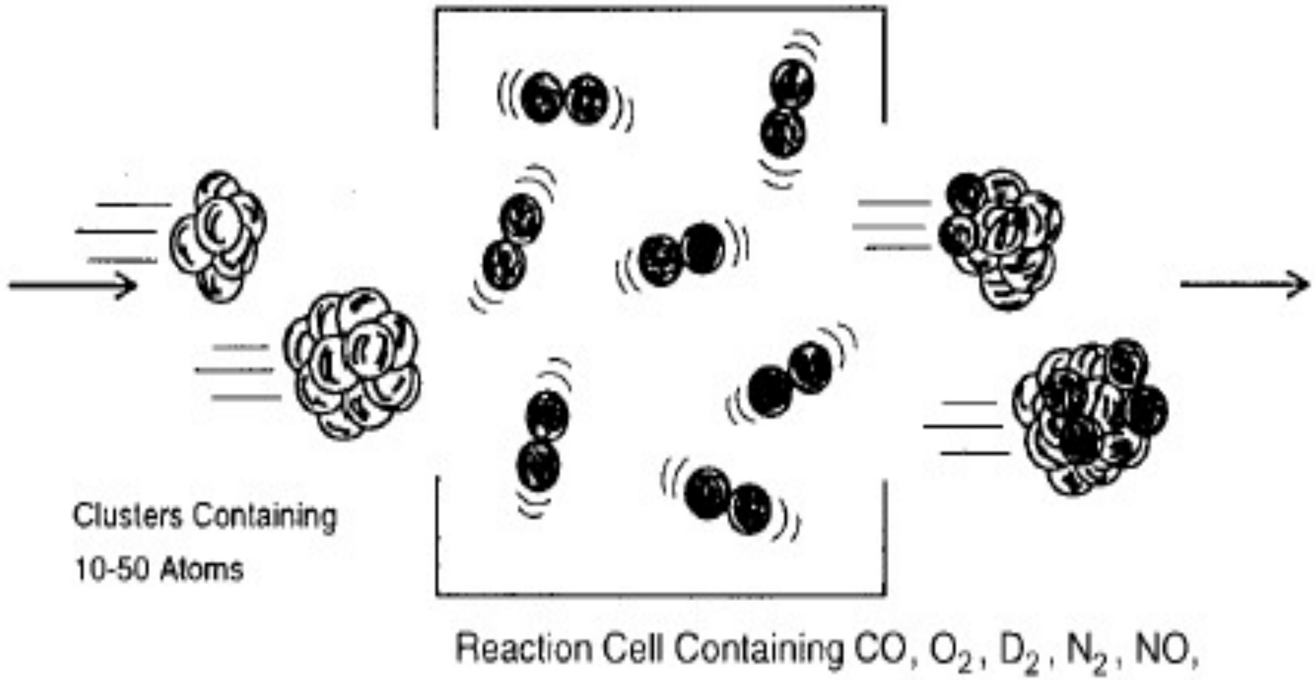
Ratio of surface atoms



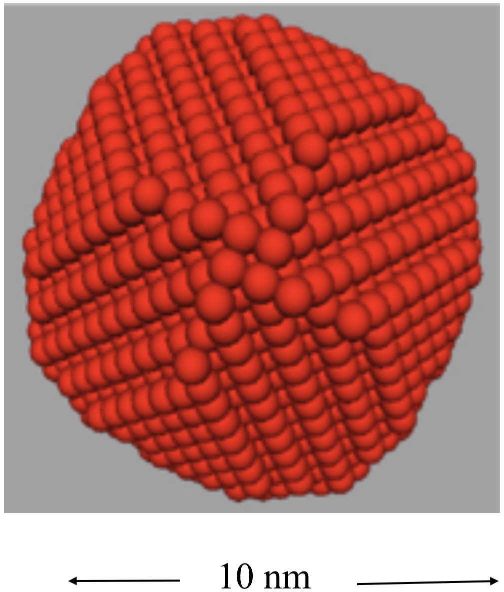
Ratio of surface atoms



Enhanced catalytic effect



Au nanoparticle as an example



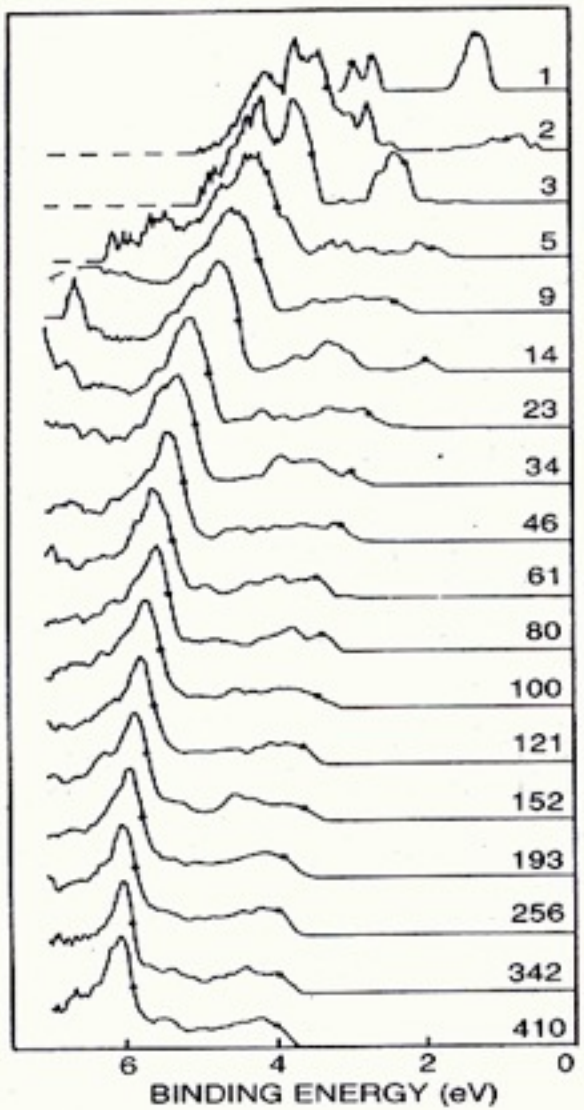
$$E_F = (\hbar^2/2m)\,(3\pi^2 n)^{2/3}$$

$$g(E_F) = (3/2)\,(n/E_F)$$

$$\delta = 2/[g(E_F)V] = (4/3)\,(E_F/N)$$

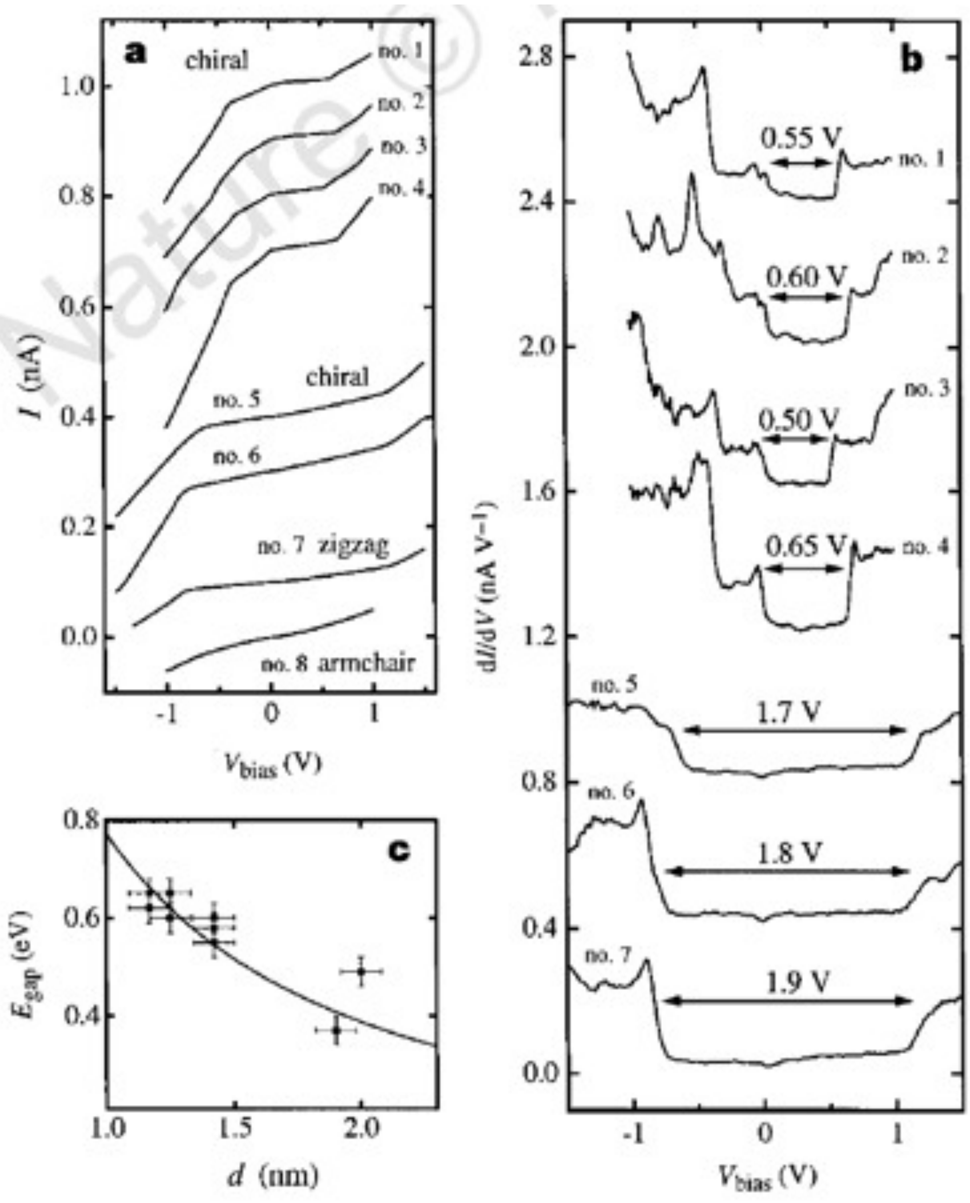
Number of valence electrons (N) contained in the particles is roughly 40,000. Assume the Fermi energy (E_F) is about 7 eV for Au, then

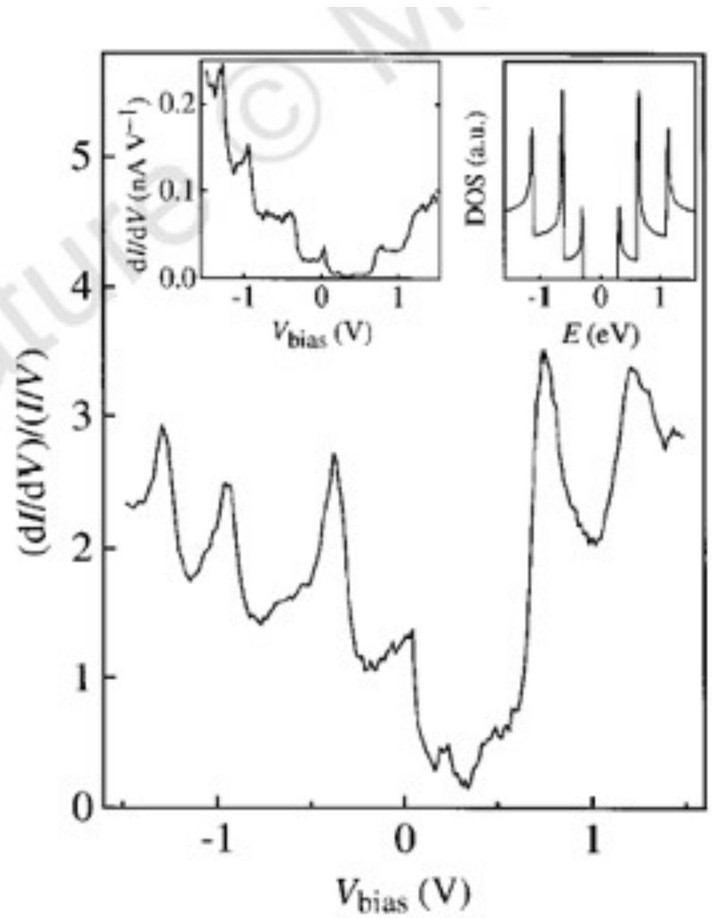
$$\delta \sim 0.22 \text{ meV} \sim 2.5 \text{ K}$$



Ultraviolet photoemission spectra of ionized copper clusters Cu_N^- ranging in size from N of 1 to 410 show the energy distribution versus binding energy of photoemitted electrons. These photoemission patterns show the evolution of the 3d band of Cu as a function of cluster size. As the cluster size increases, the electron affinity approaches the value of the bulk metal work function. (Adapted from ref. 10.) **Figure 5**

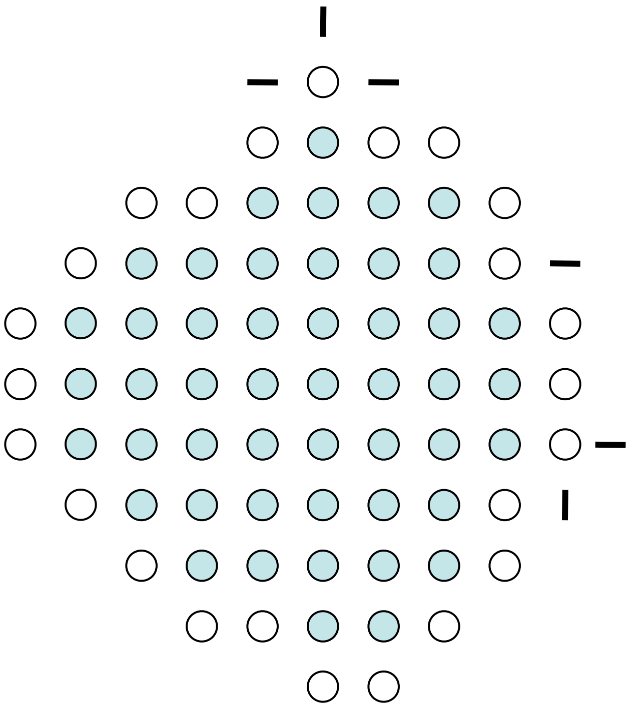
Electronic Structure of Single-wall Nanotubes





Nature **391**, 59 (1998).

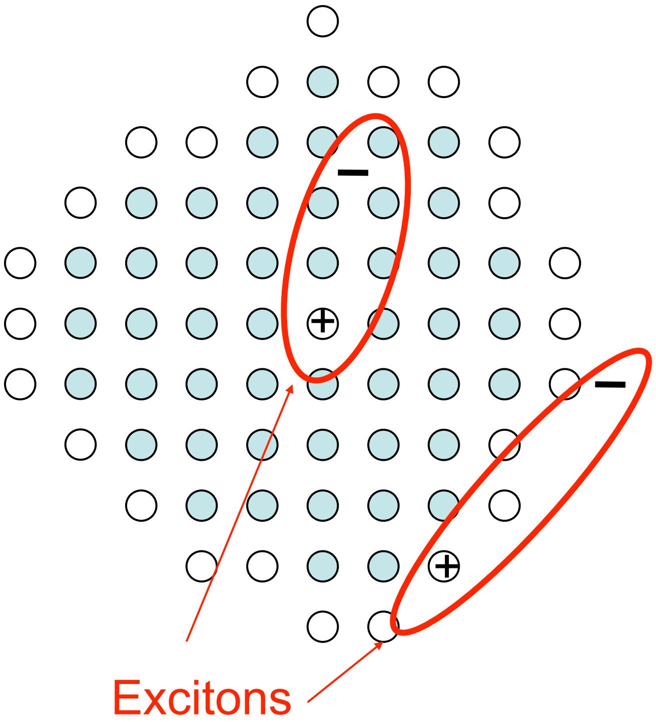
Optical properties of nanoparticles (in the infrared range)



(1) Broad-band absorption:
Due mainly to the increased normal modes at the surface.

(2) Blue shift:
Due mainly to the bond shortening resulted from surface tension.

Optical properties of nanoparticles (in the visible light range)



(1) Blue shift:
Due mainly to the energy-gap widening because of the size effect.

(2) Red shift:
Bond shortening resulted from surface tension causes more overlap between neighboring electron wavefunctions. Valence bands will be broadened and the gap becomes narrower.

(3) Enhanced exciton absorption:
Due mainly to the increased probability of exciton formation because of the confining effect.

Plasma oscillation of free electron gas

Drude Model (free electron gas model)

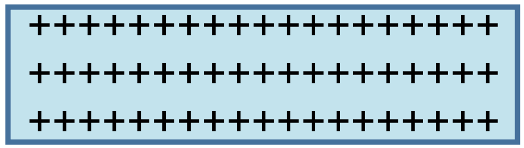
1. Electronic equation of motion

$$\frac{d}{dt}\mathbf{p}(t) = q\mathbf{E} - \frac{\mathbf{p}(t)}{\tau},$$

2. Ohm's law

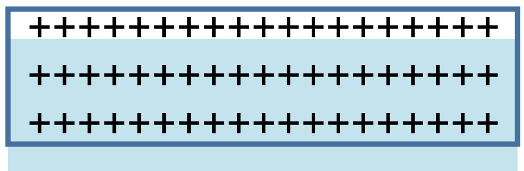
$$\mathbf{J} = \left(\frac{nq^2\tau}{m}\right)\mathbf{E} = \sigma E$$

$$nmx'' + (n^2e^2/\sigma)x' = -neE$$



Fourier transformed

$$\Rightarrow [-nm\omega^2 - i(n^2e^2\omega/\sigma(\omega)]x(\omega) = -neE(\omega)$$



$$\epsilon(\omega) \equiv 1 + 4\pi\frac{P(\omega)}{E(\omega)}, \quad P(\omega) = -nex(\omega)$$

$$\epsilon(\omega) \equiv 1 - \frac{\omega_p{}^2}{\omega^2 + i\omega\omega_p{}^2/(4\pi\sigma(\omega))}, \quad \omega_p{}^2 = 4\pi ne^2/m$$

Optical properties

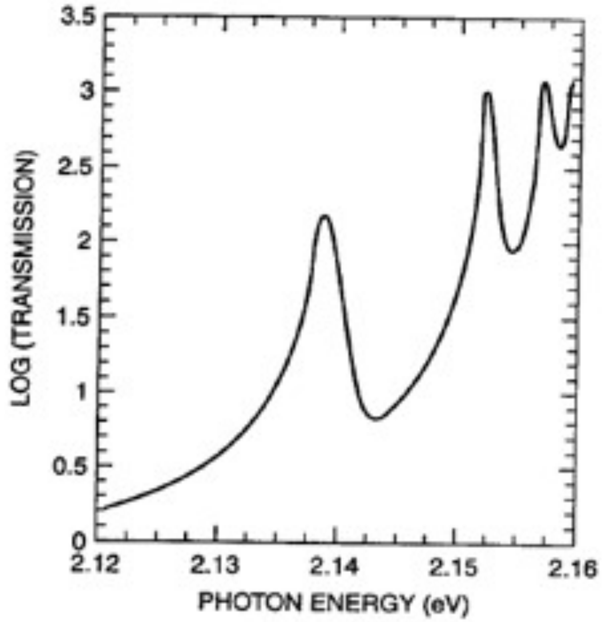


Figure 4.19. Optical absorption spectrum of hydrogen-like transitions of excitons in Cu_2O. [Adapted from P. W. Baumeister, *Phys. Rev.* **121**, 359 (1961).]

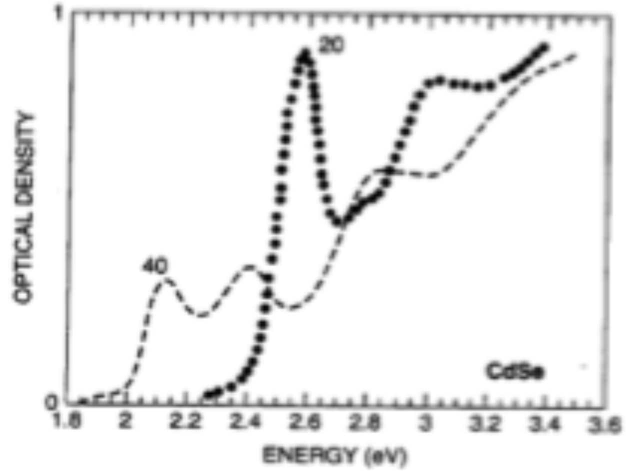
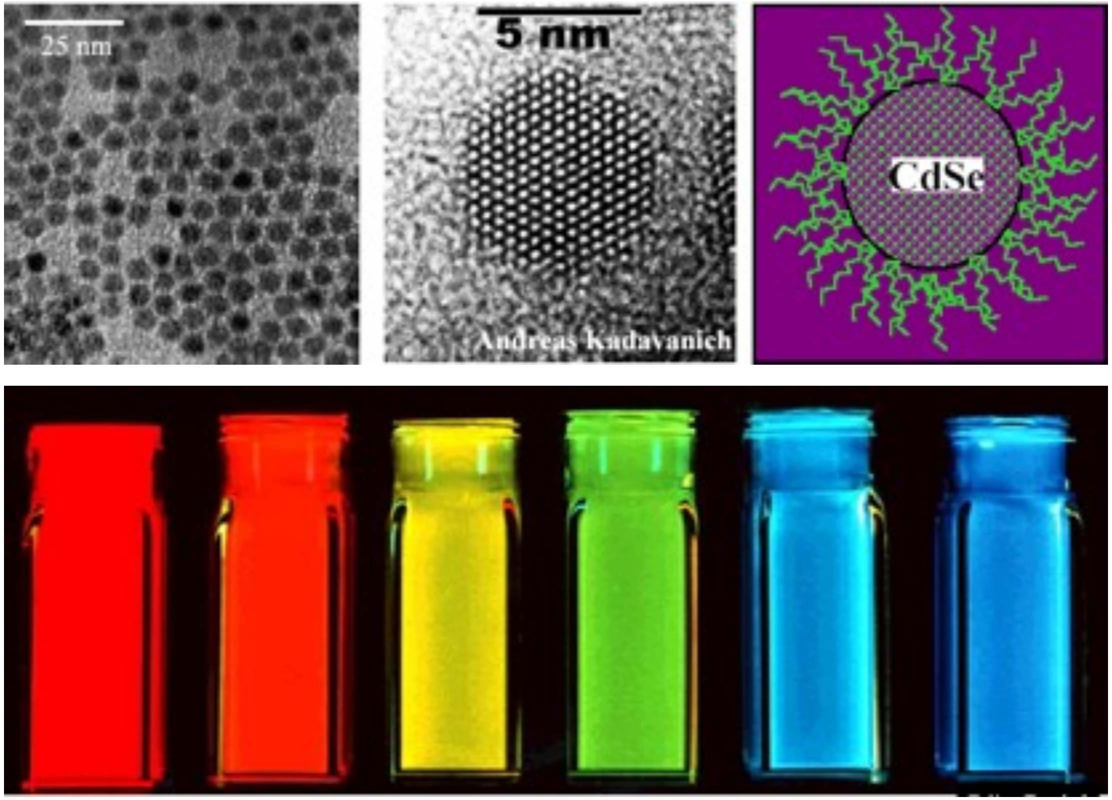


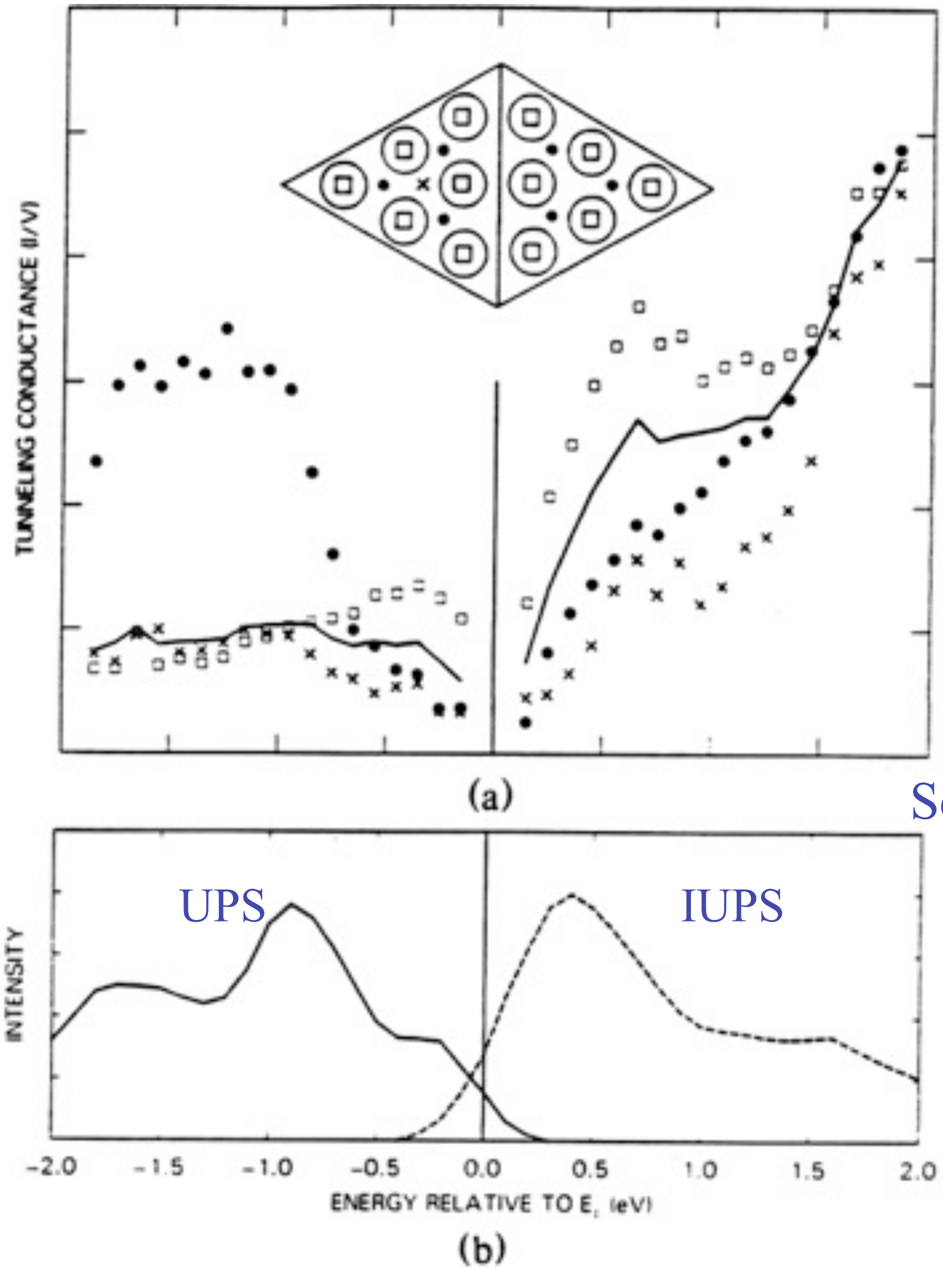
Figure 4.20. Optical absorption spectrum of CdSe for two nanoparticles having sizes 20 Å and 40 Å, respectively. [Adapted from D. M. Mittleman, *Phys. Rev.* **B49**, 14435 (1994).]

Semiconductor quantum dots



(Reproduced from Quantum Dot Co.)

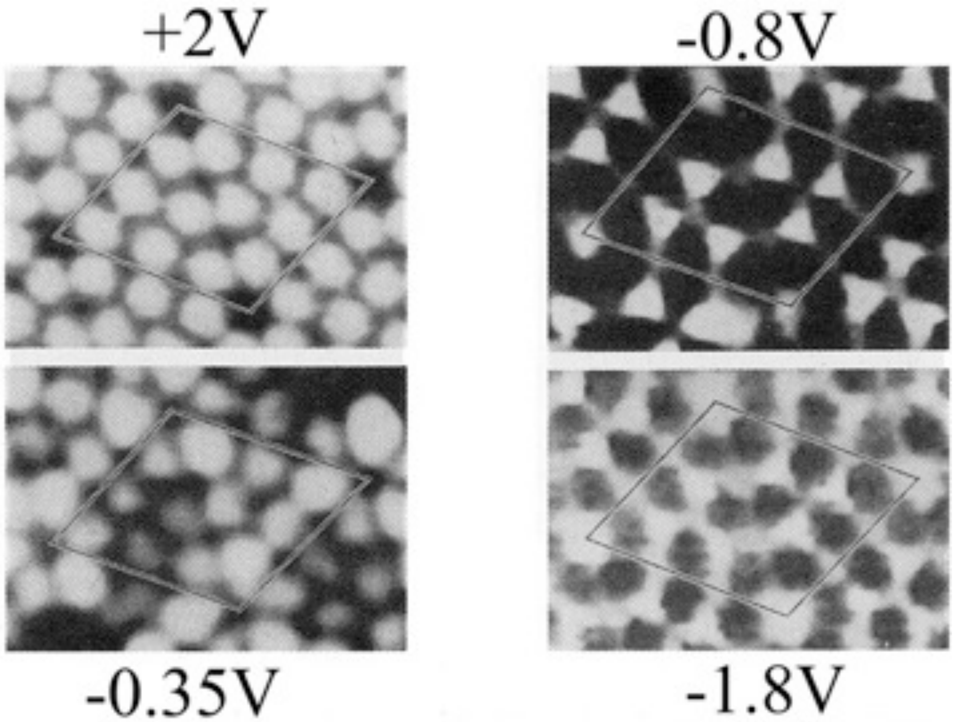
STS of Si(111)-(7x7)

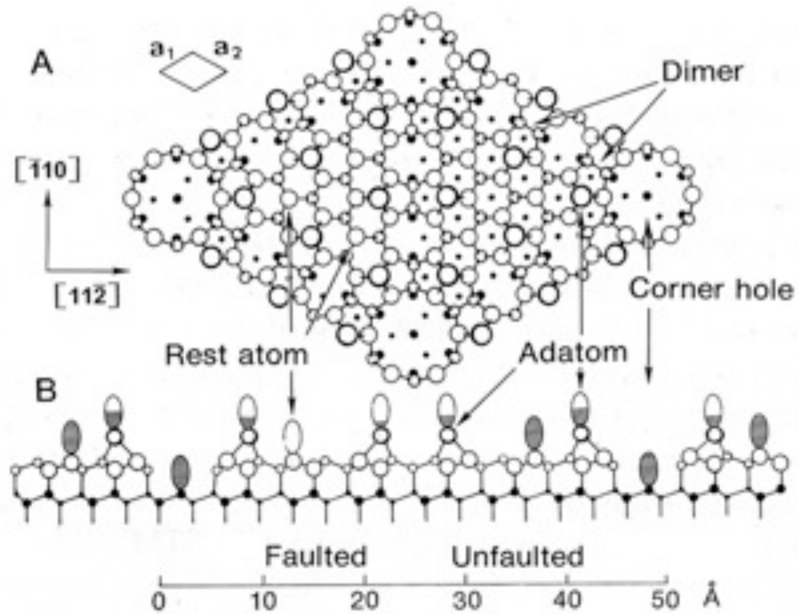


Science **234**, 304 (1986).

STS of Si(111)-(7x7)

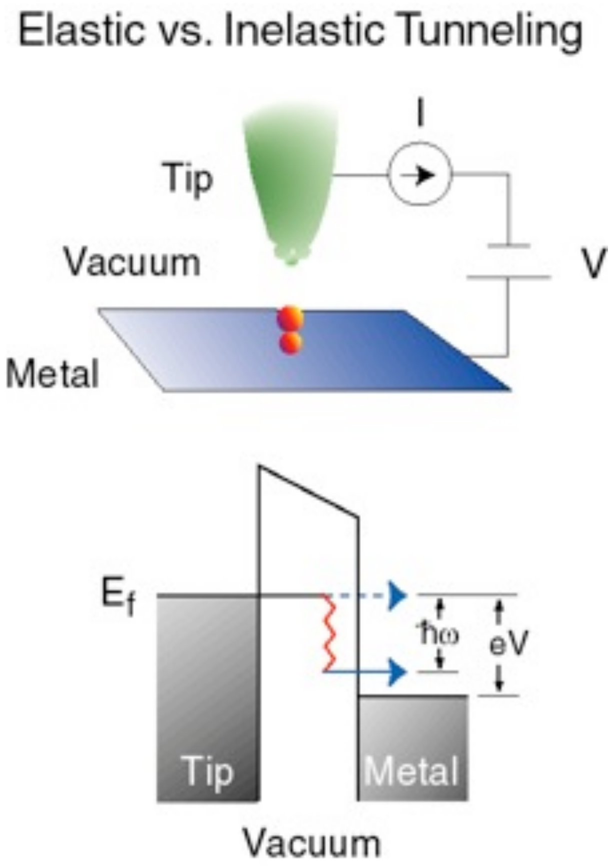
topograph

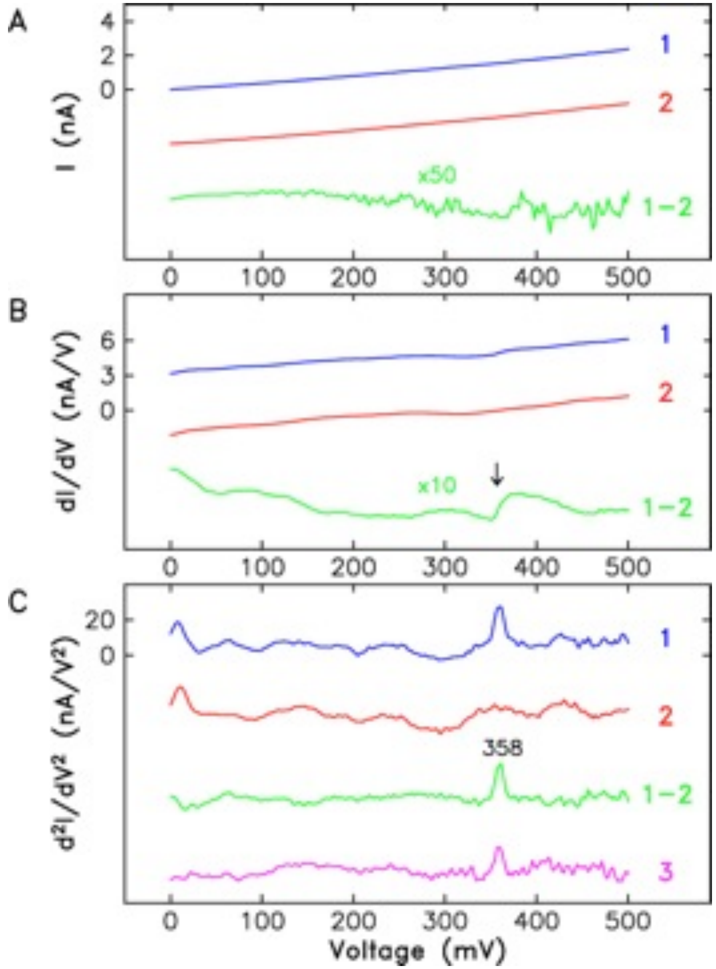




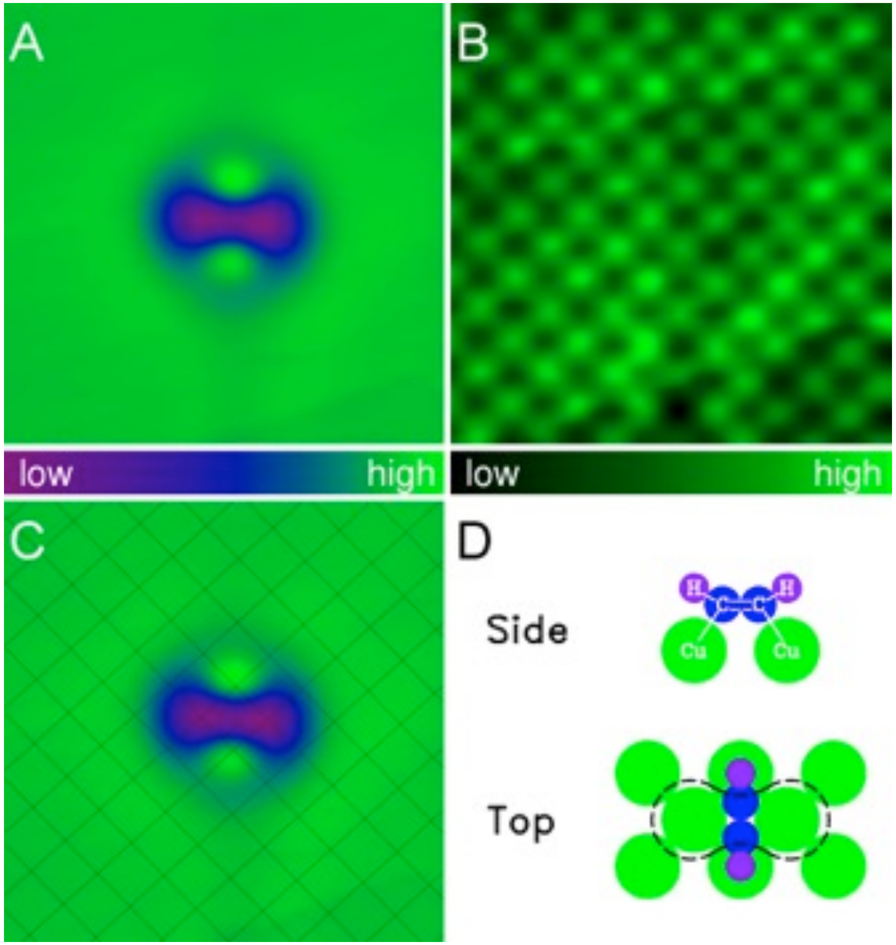
1. Science **234**, 304-309 (1986).
2. Phys. Rev. Lett. **56**, 1972-1975 (1986).

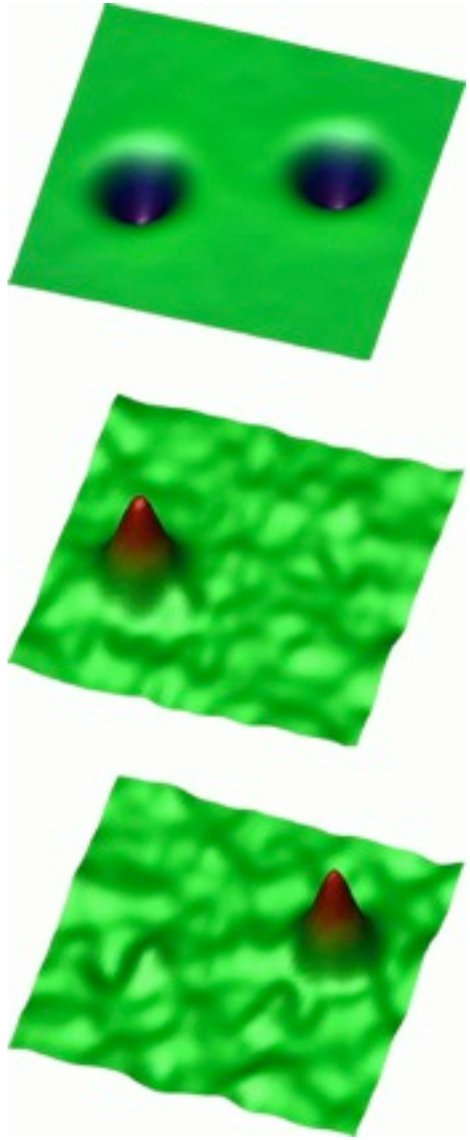
Inelastic Tunneling





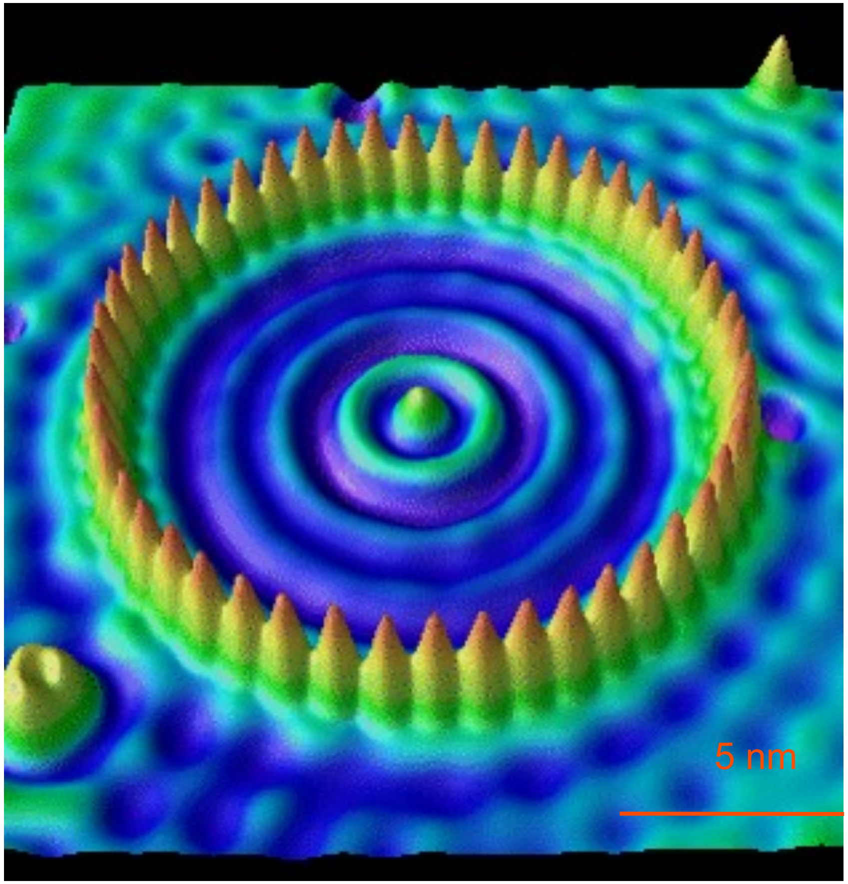
Single Molecule Vibrational Spectroscopy and Microscopy





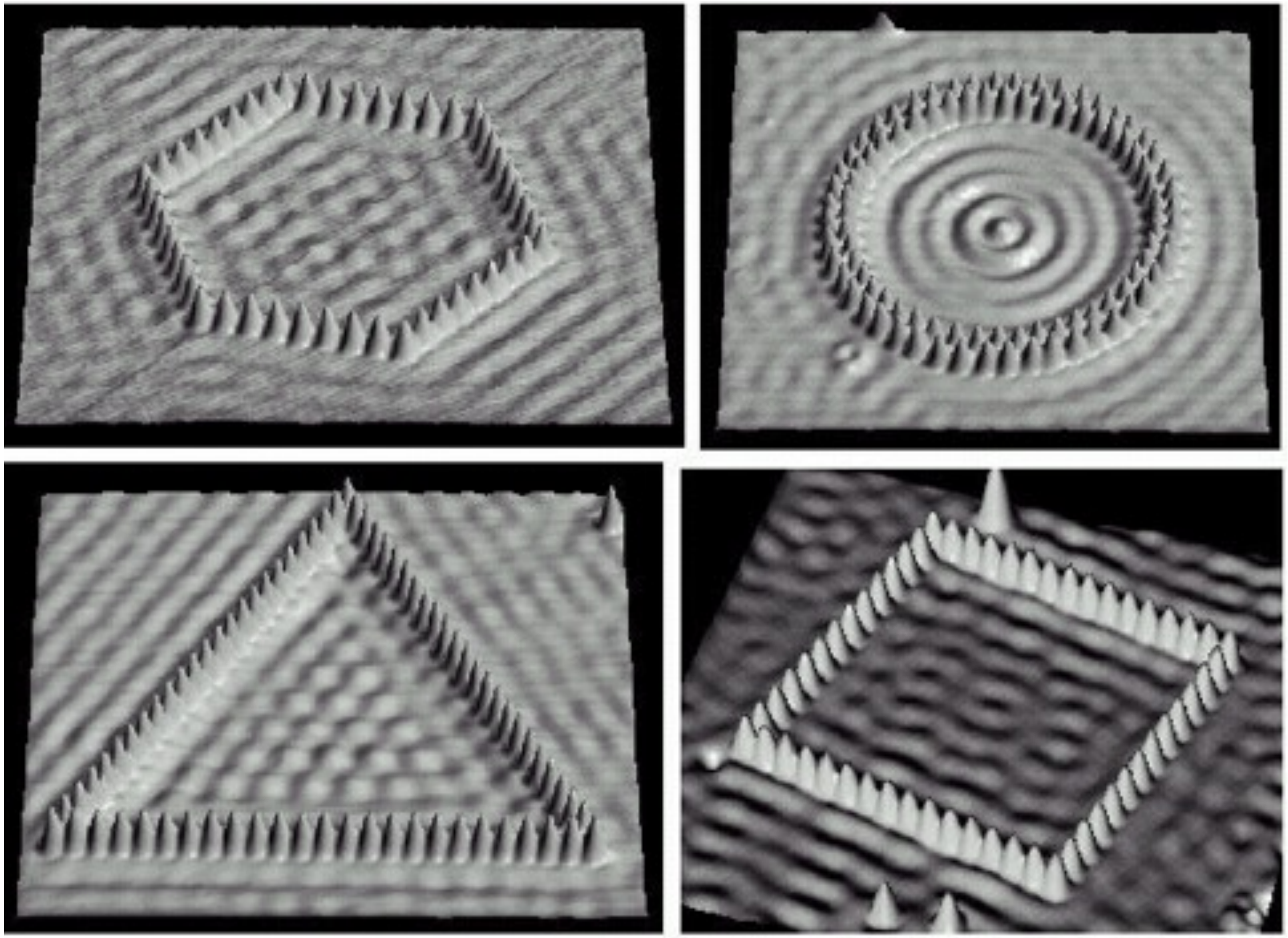
B.C. Stipe, M.A. Rezaei, and W. Ho,
Science **280**, 1732-1735 (1998).

Quantum corral



D.M. Eigler, IBM, Amaden

Quantum corral



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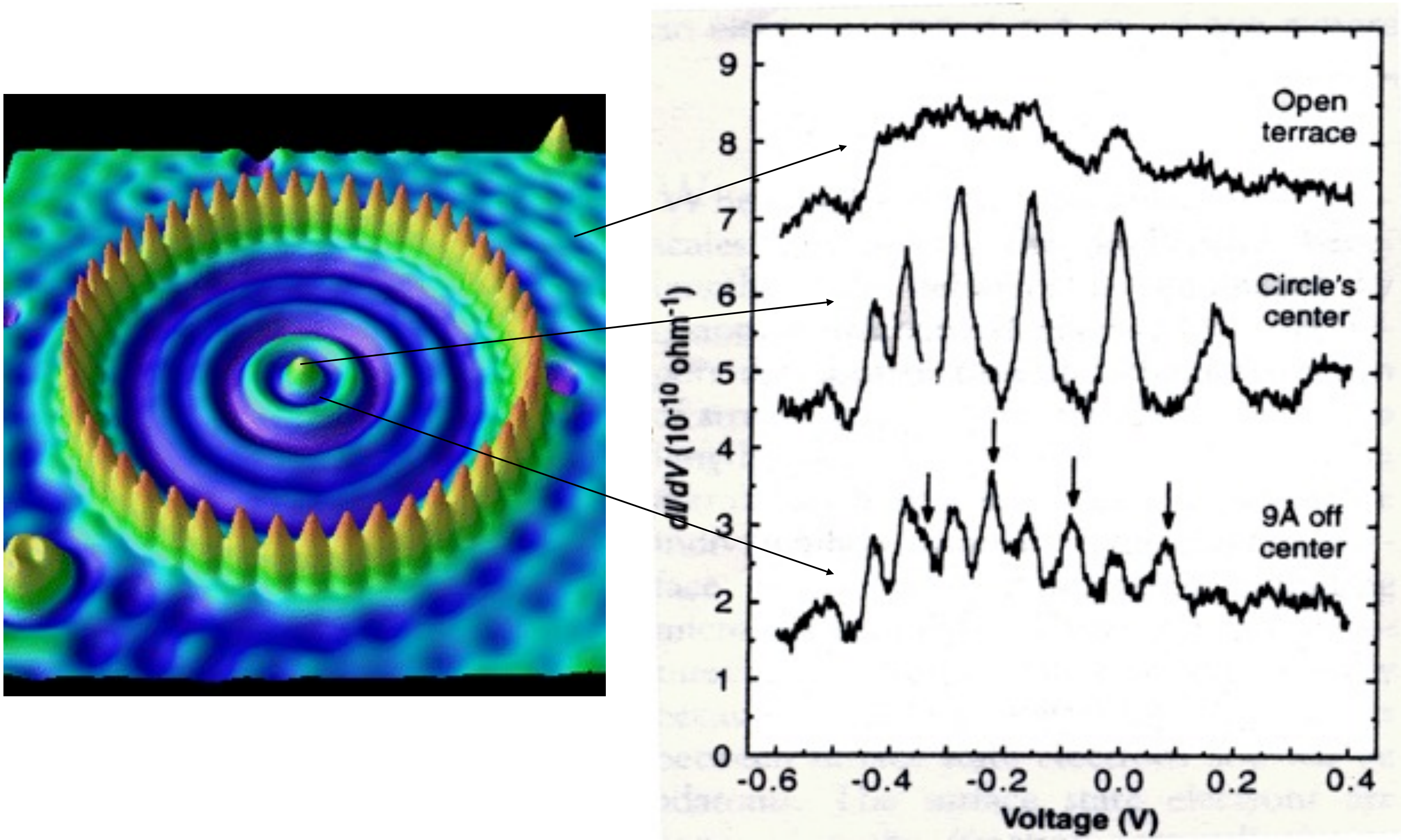
Artificial atom



Homework#16 (Jan. 3, 2011):

(a) When the electronic properties of a nanoparticle are measured by optical spectroscopy, both blue and red shifts, comparing to its bulk counterpart, can occur. Please explain the causes of the blue and red shifts, respectively.

(b) The vibrational properties of a nanoparticle, when measured by optical spectroscopy, can result in a blue shift in reference to its bulk counterpart. Please explain the cause.