Nanotechnology

Nanoscale phenomena

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Nanotechnology

Nanoscale phenomena

Introduction

Scope and Outline

Scope:

- Basic understanding of some physical and chemical phenomena relevant at nanoscale.

Outline:

- Introduction
- Basics of quantum mechanics
- Atomic structure (hydrogen like atoms)
- Molecular structure (linear combination of atomic orbitals)
- Band structure of solids in 0D, 1D, 2D, 3D (electrons in a box and in a periodic potential)
- Intermolecular forces
- Physi- and chemi-absorption,
- Surface tension
- Examples of nanoscale phenomena: tunneling current, conductance quantization, Coulomb blockade, single electron transistor (SET), nanomagnetism, quantum Hall effect, Casimir effect.

References:

Books

K. S. Krane, Modern Physics, John Wiley & Sons Inc, 2012.

P. Atkins, J. de Paula, Atkins' physical chemistry, Oxford Univ. Press, 2006.

J. N. Israelachvily, Intermolecular and surface forces, Academic Press, 2011.

Web resources

IUPAC guide to chemical nomenclature: http://goldbook.iupac.org

E. F. Schubert, Physical foundation of solid state devices, http://homepages.rpi.edu/~schubert/

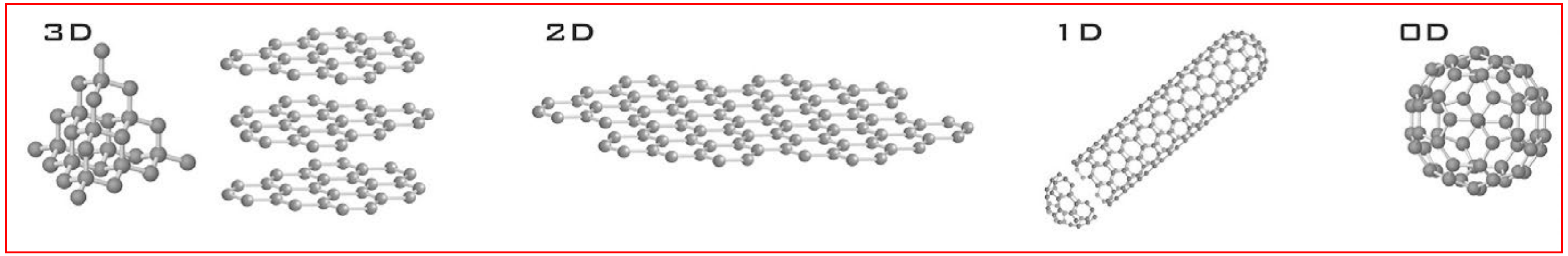
Links to other courses:

Scaling laws (from macro to micro….but not down to nano) are extensively treated in: “Scaling of MEMS”, Ph. Renaud & H. Shea

Nanoscience and nanotechnology: definitions

Nanometer range: from 100 nm down to 0.2 nm in **at least** one dimension.

• Only **one** dimension (2D):	Thin films, thin surface coatings, quantum wells, ..
• Only **two** dimensions (1D):	Nanotubes, nanowires, quantum wires,…
• All **three** dimensions (0D):	Nanoparticles,quantum dots, nanodots….



Nanoscience: study of phenomena and manipulation of materials at the atomic, molecular and macromolecular scale (**nanometer range**), where properties differ significantly from those at larger scale.

Nanotechnologies: design, characterization, production and application of structures, and devices with controlled dimension(s) at the **nanometer range**.

Nanoscience and nanotechnologies: opportunities and uncertainties, The Royal Society & The Royal Academy of Engineering, July 2004, www.nanotech.org.uk

Why it is interesting to study nanoscale «objects» ?

- Nanosized «objects» exhibit **different properties** than larger «objects» of the same material.
- Understanding the behavior of nanoscale «objects» requires **new theories** with respect to those used for the behavior of larger «objects».
- Nanoscale «objects» are **useful** in several fields (fundamental and applied research, medicine, consumer electronics, ….)

Properties of nanoscale «objects»

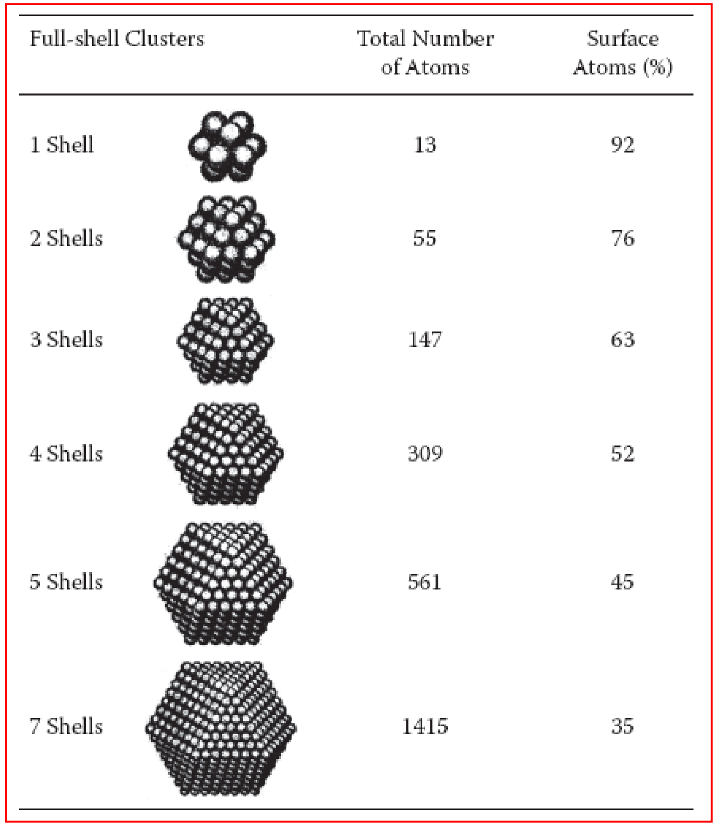
Micrometer scale «objects» have properties typically identical to those of larger «objects» (i.e., they have “bulk” properties).

Which properties might be significantly different in nanoscale «objects» ?

- Optical (color, transparency,….)
- Electrical (conductivity,….)
- Mechanical (hardness,…)
- Thermal (melting point,…)
- Chemical (reactivity, reaction rates, …)
- Magnetic (superparamagnetism,…)

Why properties of nanoscale «objects» are different from those of macroscopic «objects » ?

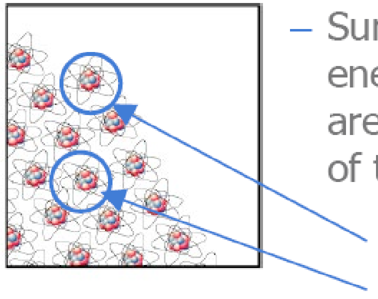
- Surface-to-volume ratios are larger
- Gravitational force is negligible
- Quantum effects might be important
- Random thermal molecular motion is more important
- …



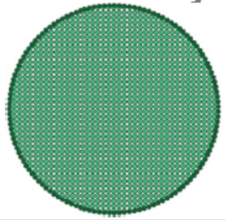
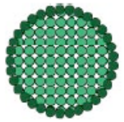
Full-shell Clusters	Total Number of Atoms	Surface Atoms (%)
1 Shell	13	92
2 Shells	55	76
3 Shells	147	63
4 Shells	309	52
5 Shells	561	45
7 Shells	1415	35

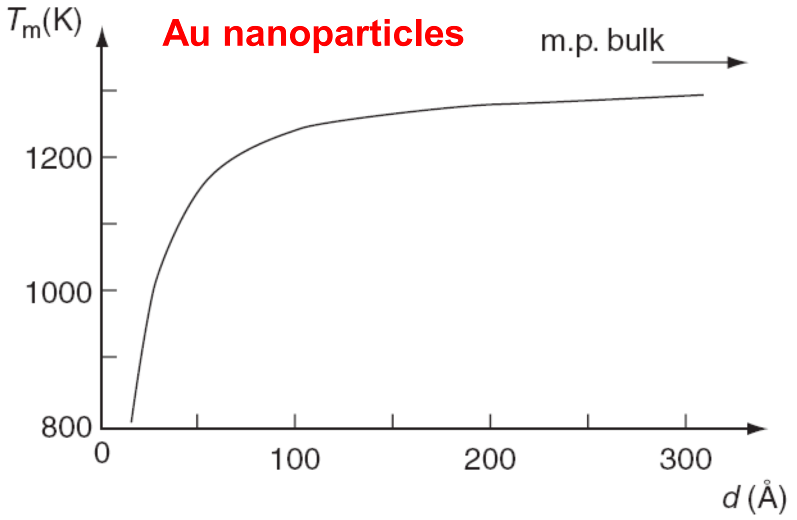
Example: Nanoparticles melting point

- **Melting Point (Microscopic Definition)**
  - Temperature at which the atoms, ions, or molecules in a substance have enough energy to overcome the intermolecular forces that hold the them in a "fixed" position in a solid



  - Surface atoms require *less* energy to move because they are in contact with *fewer* atoms of the substance

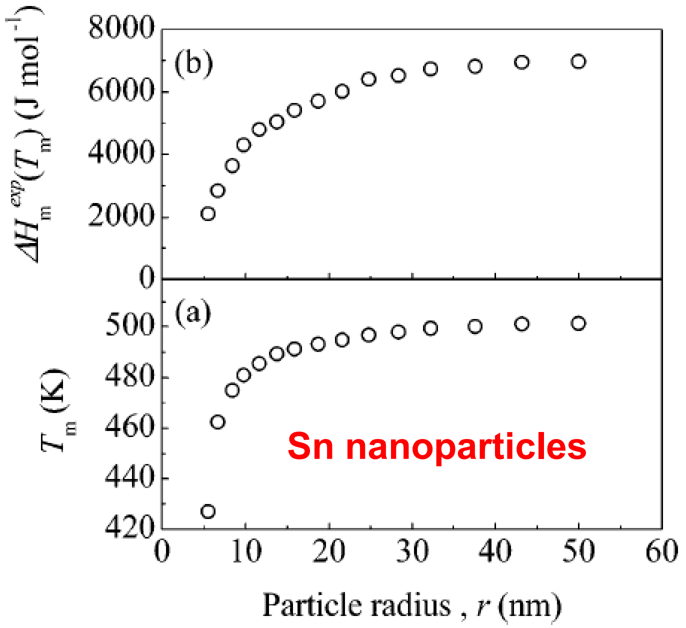
	At the macroscale	**At the nanoscale**
The majority of the atoms are…	**…almost all on the inside of the object** 	**…split between the inside and the surface of the object** 
Changing an object's size…	**…has a very small effect on the percentage of atoms on the surface**	**…has a big effect on the percentage of atoms on the surface**
The melting point…	**…doesn't depend on size**	**… is lower for smaller particles**



Note:

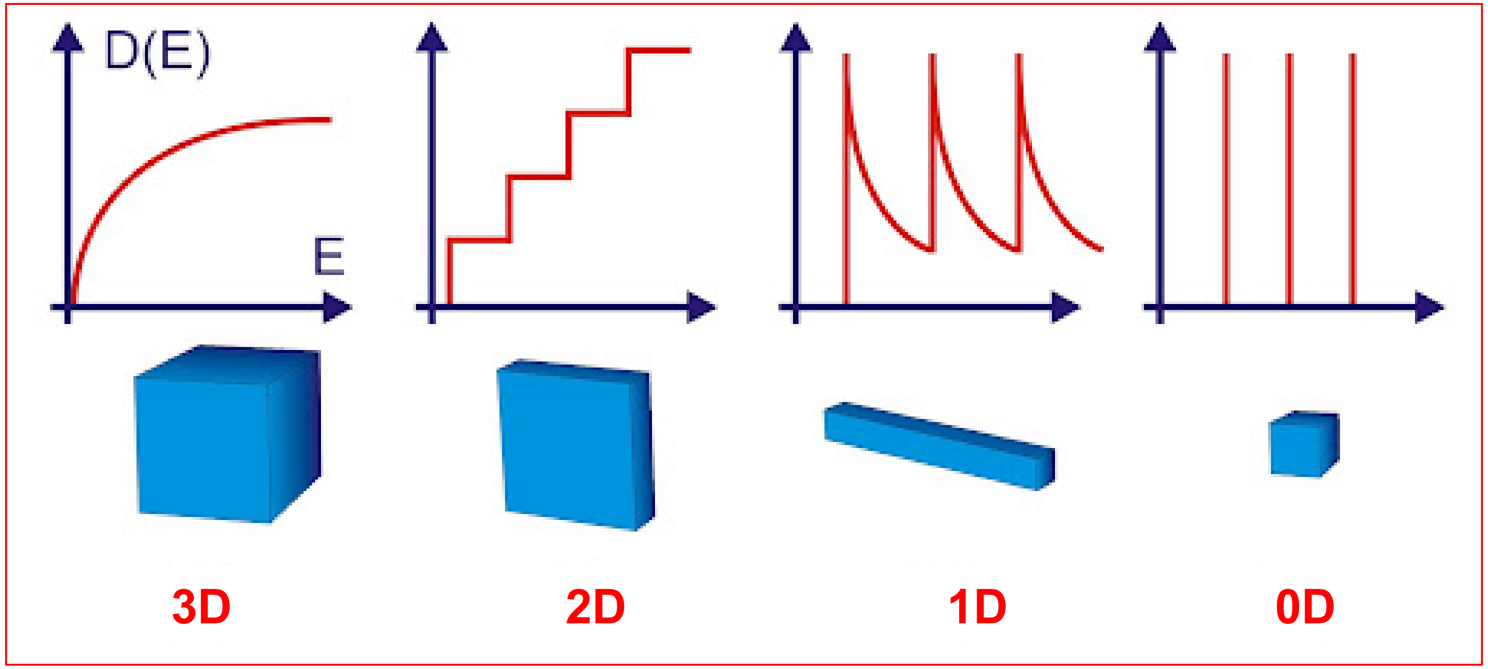
Isolated metallic nanoparticle:
smaller particles have **lower** melting point

Metallic nanocrystals in a continuous matrix:
smaller particles have **higher** melting point



Example: Density of available states for electrons

http://lh6.ggpht.com/-ClHQhVXyMGs/SyQnKaiACVI/AAAAAAAAGP0/oaQUlJY6EPg/dos.jpg



Bulk

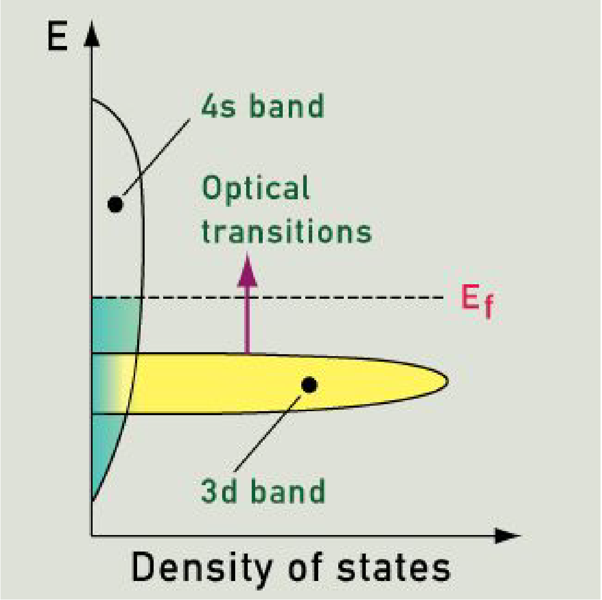
Thin film

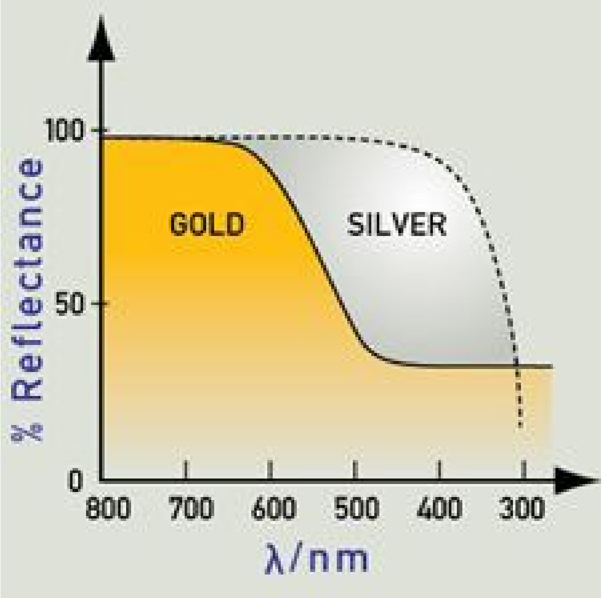
Nanowire

Nanodot

D(E): Density of available states for electrons
E: Energy

Example: Metal nanoparticles optical properties





Macroscopic metallic objects:

Metals are colored because the absorption and re-emission of light are dependent on wavelength.

If the efficiency of absorption and re-emission is equal at all optical energies, then all the different colors under white light illumination will be reflected equally well. Silver has efficiency that does not vary with wavelength within the optical region, and therefore appears close to white. If the efficiency decreases with increasing energy, as is the case for gold and copper, the reduced reflectivity at the blue end of the spectrum produces yellow and reddish colors..

The color of metals can be explained by energy band theory. In metals, empty bands overlap with bands containing electrons. The available electrons fill the bands up the level of the Fermi surface. Silver, gold and copper have similar electron configurations, but we perceive them as having quite distinct colors. The density of states available varies differently as a function of the energy. Electrons absorb energy from incident light, and are excited from lower energy levels to higher, vacant energy levels. The excited electrons can then return to the lower energies and emit the difference of energy as a photon. If an energy level holds many more electrons (than other energy levels) then the excitation of electrons from this highly occupied level to above the Fermi level will become important. Gold has an intense absorption of light with energy of 2.3 eV (from the 3d band to above the Fermi level). The color we see is yellow, as the corresponding wavelengths are re-emitted. Copper has a strong absorption at a slightly lower energy, with orange being most strongly absorbed and re-emitted. In silver, the absorption peak lies in the ultraviolet region, at about 4 eV. As a result, silver maintains high reflectivity evenly across the visible spectrum, and we see it as a pure white. The lower energies (which in this case contain energies corresponding to the entire visible spectrum of color) are equally absorbed and re-emitted.

Example: Metal nanoparticles optical properties

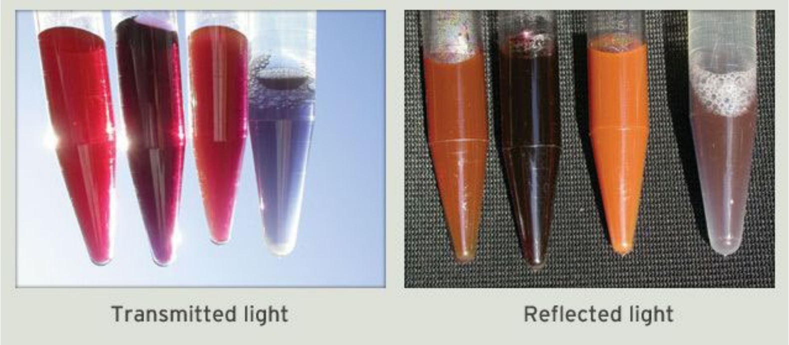
Metallic nanoparticles have size and shape dependent optical properties caused by the surface plasmon resonance (SPR) absorption.

Mie explained this phenomenon theoretically by solving Maxwell's equation for the absorption and scattering of electromagnetic radiation. The developed theory is widely used to calculate the particle extinction spectra of nanoparticles.

The origin of the light absorption by metallic nanoparticles is the coherent oscillation of the conduction band electrons induced by the interaction with the incident electromagnetic wave. This effect is generally known as SPR and it is absent in bulk metals.

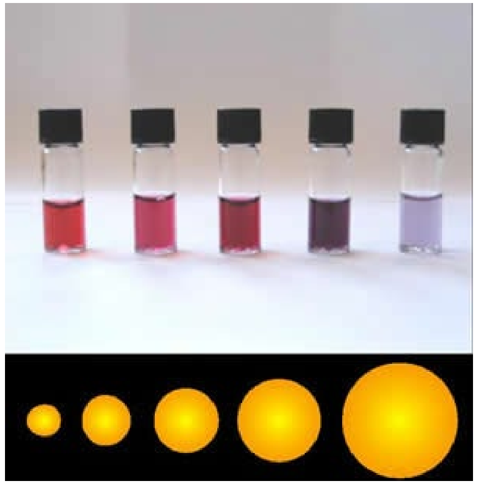
In general, the SPR absorption peak red shifted to longer wavelength with increasing of particle size as predicted by Mie theory.

The SPR frequency of metallic nanoparticles depends on particle **size, shape, dielectric properties**, aggregate morphology, surface modification, and refractive index of the surrounding medium.



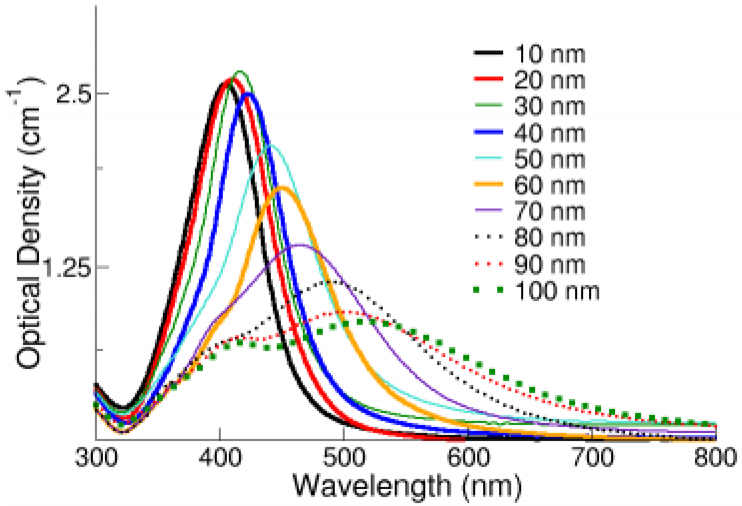
Gold nanoparticles in transparent media. Transmitted light and reflected light.

The Lycurgus Cup, lit from front (reflected light) and behind (transmitted light).

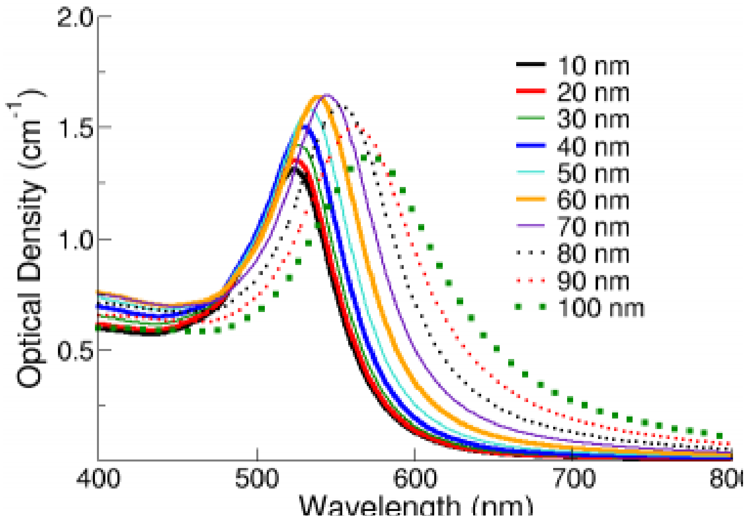


Gold nanoparticles in transparent media. Transmitted light.

Example: Metal nanoparticles optical properties



Absorption (optical density) spectra of silver nanospheres with diameters ranging from 10 - 100 nm at mass concentrations of 0.02 mg/mL.



Absorption (optical density) spectra of gold nanospheres with diameters ranging from 10 to 100 nm at a concentration of 0.05 mg/mL

Metallic nanoparticles have different transmission depending on their size, shape, «medium»,…

These are surface plasmons resonance effects.

The **optical density (*OD*)** quantifies the effect of absorption:

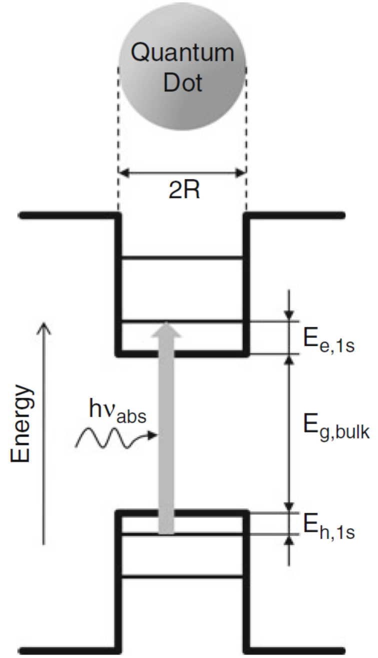
$$OD=\alpha$$

α: absorption coefficient (measure of how much light is absorbed per unit length of the material, and it has usually the units of cm^{-1}).
The transmission through a distance d of the material is

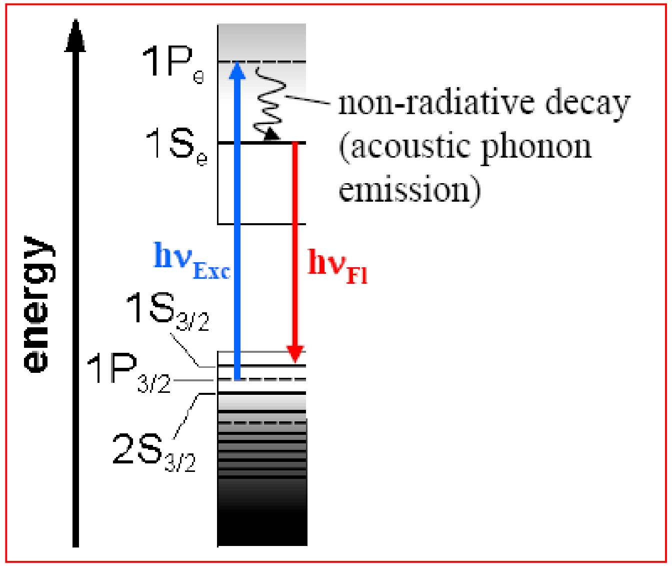
$$T=10^{-OD*d}$$

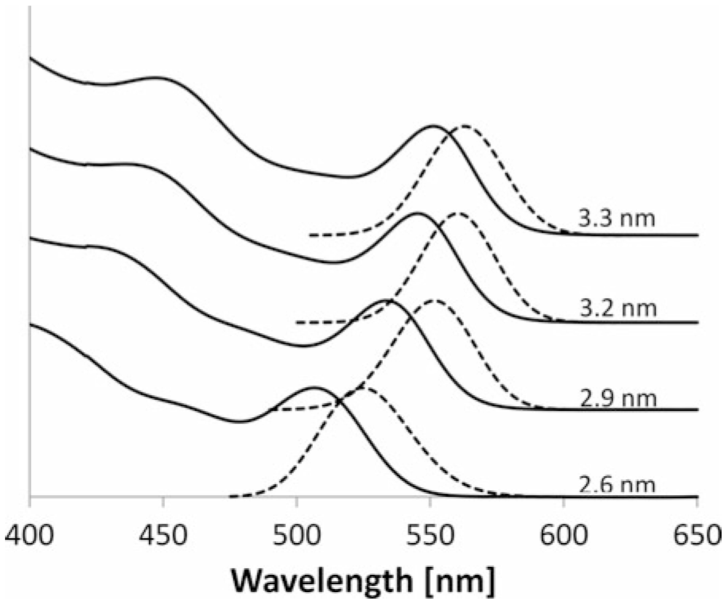
(example: if OD=2 cm^{-1}, the transmission through a distance d=1 cm of the material is T=0.01, i.e., only 1% of the light is transmitted and then 90% of the light is absorbed).

Example: Semiconducting CdSe nanoparticle optical properties



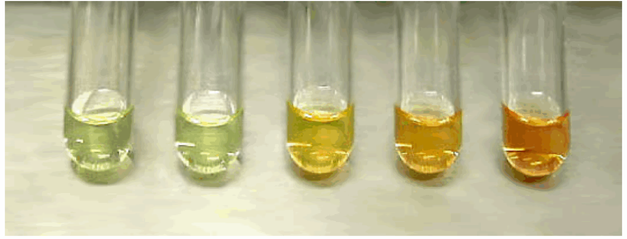
Optical and Electronic Properties, Fig. 3 Schematic of a spherical quantum dot with radius R and of the associated potential profile along any diameter of the sphere. The energy states for electrons and holes are discrete and can be described by the particle-in-a-box model, where the effective masses are used. The *gray arrow* represents the first available exciton state, which in first approximation corresponds to the onset of optical absorption



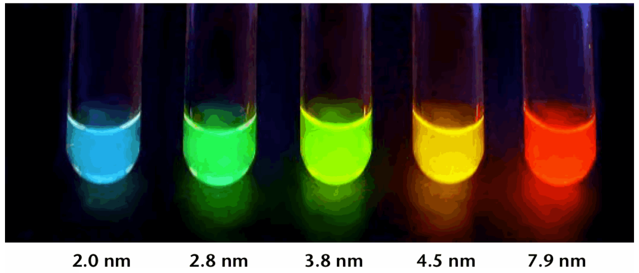


Optical and Electronic Properties, Fig. 4 Typical absorption (*solid line*) and photoluminescence (*dashed line*) spectra of quantum dots. This example shows four CdSe nanocrystals with a radius ranging from 2.6 to 3.3 nm (Data courtesy of Luca Cozzarini)

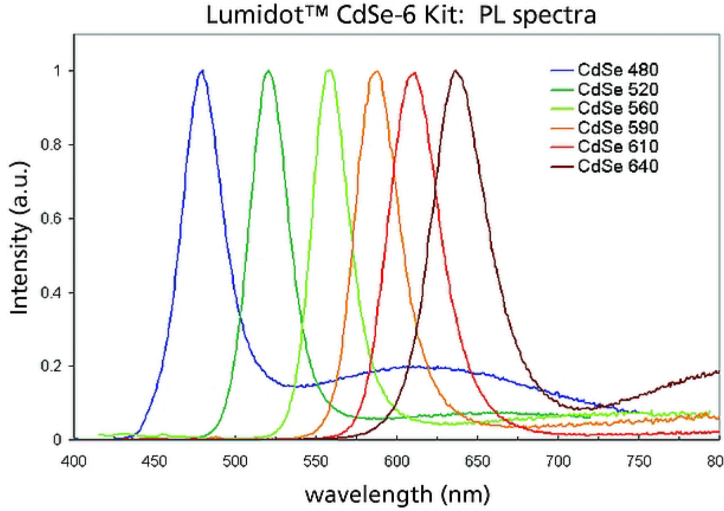
Example: Semiconducting CdSe nanoparticle optical properties



White light illumination

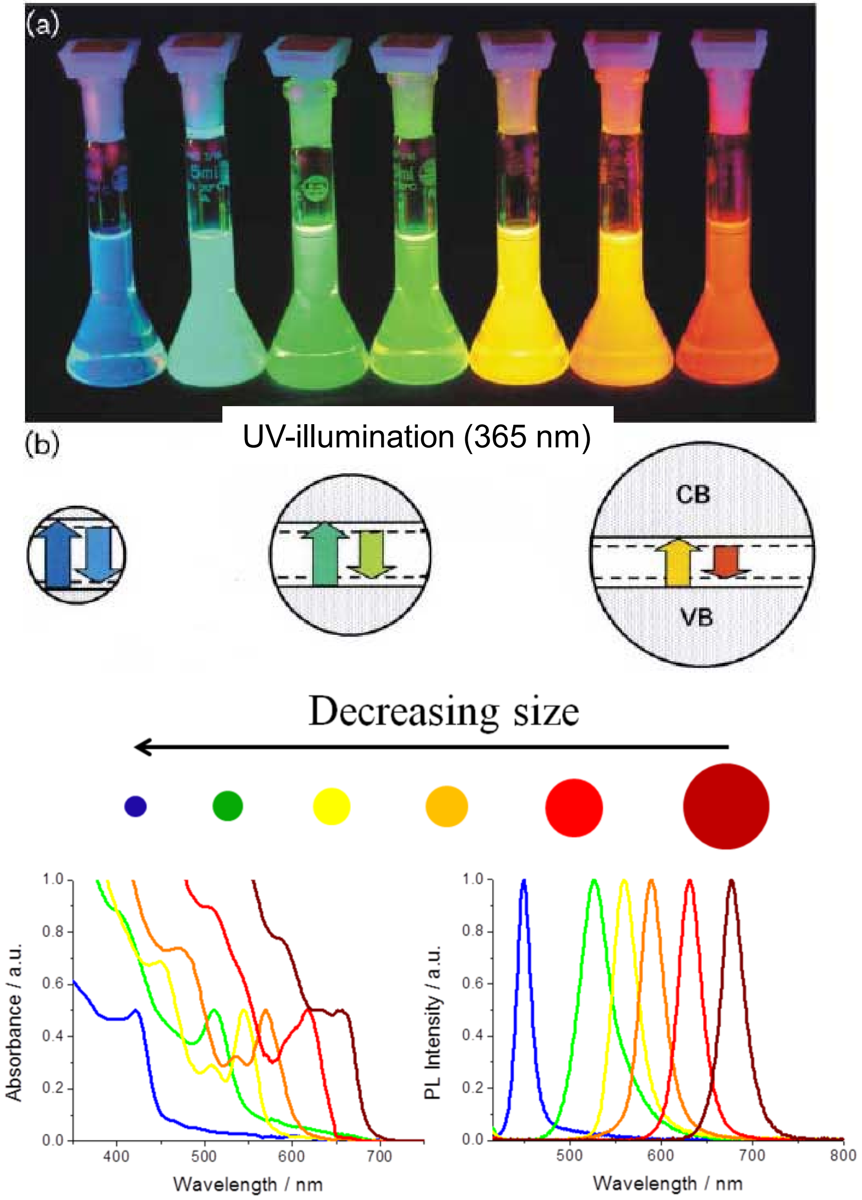


UV-illumination (365 nm)

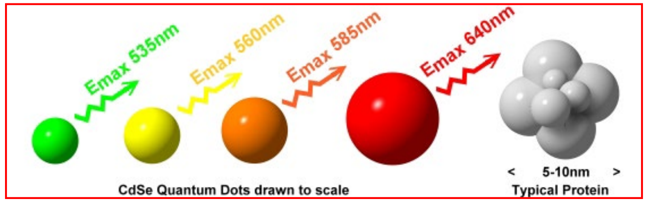


Photoluminescence spectrum of CdSe nanoparticles (Lumidot Sigma-Aldrich) nanocrystal sizes range from 2.5 nm (CdSe 480) to 6.5 nm (CdSe 640).

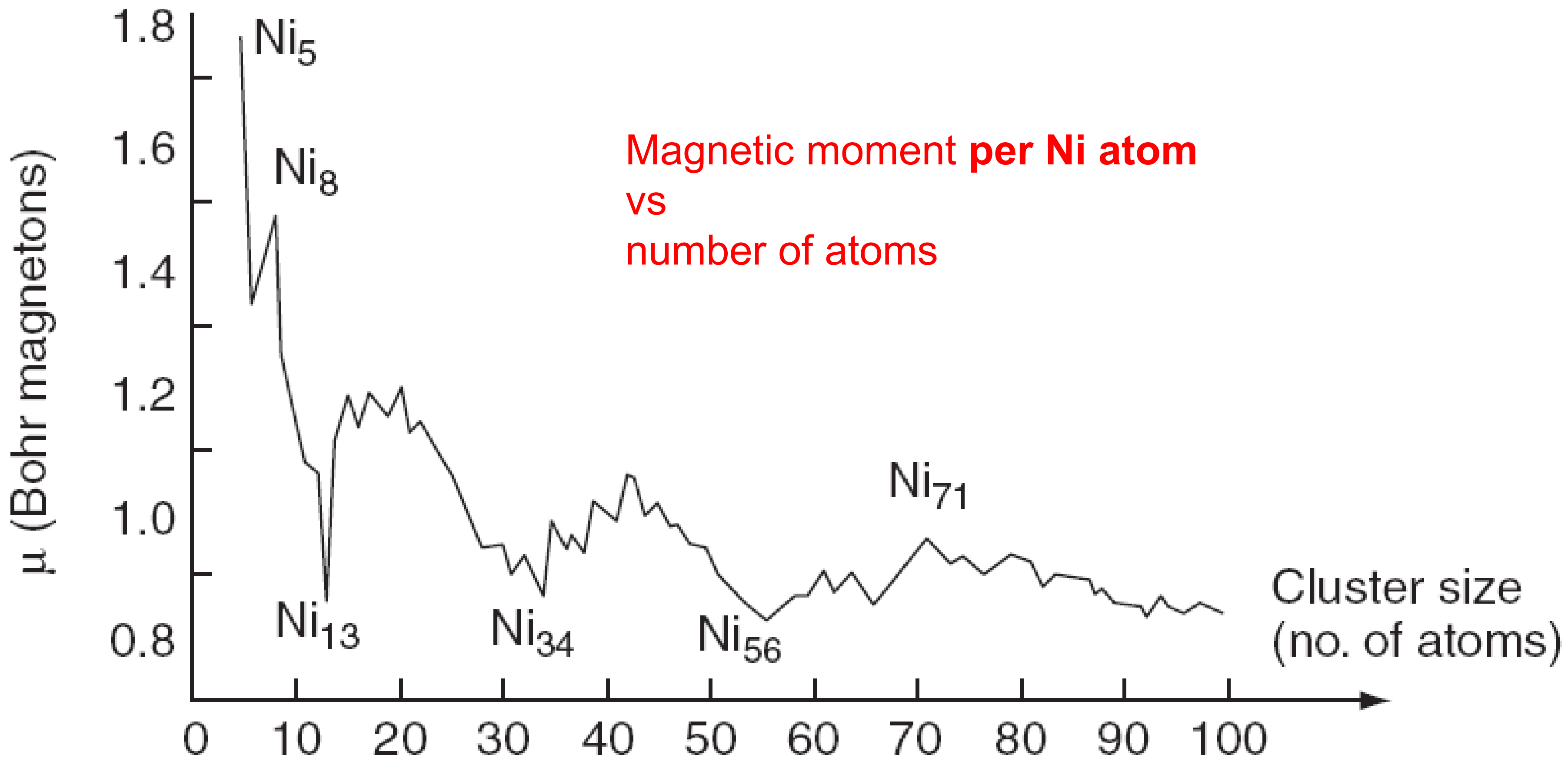
http://nanocluster.mit.edu/wiki/images/f/f2/Synthesis_fig2.jpg



These are «band gap» effects.
Larger CdSe nanoparticles have smaller bandgaps and re-emit light at longer wavelengths.



Example: Magnetic moment of Ni clusters vs cluster size

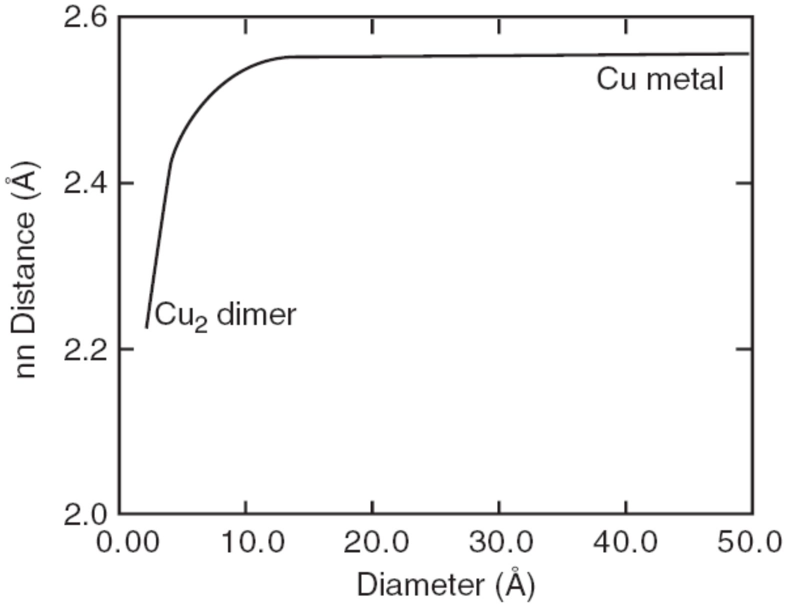


Magnetic moment **per Ni atom**
vs
number of atoms

Example: Structural properties

Interatomic spacing:

- The interatomic spacing of Cu metallic nanoparticles decreases with the decrease of the nanoparticle size.



- The interatomic spacing of semiconductors and metal oxides increases with the decrease of the nanoparticle size.

Shape:

- Large particles have stable shape. Nanoparticles might have shape «fluctuating» over time due to several energy minima located with barrier smaller than thermal energy.

Failures of classical physics

Some failures of classical physics:

- Mercury's orbit → *general relativity*
- Invariance of the speed of light → *special relativity*
- Photoelectric effect → *quantum mechanics*
- Blackbody radiation → *quantum mechanics*
- Wave behaviour of particles → *quantum mechanics*
- Stability of the atoms → *quantum mechanics*
- Emission/absorption lines of the atoms → *quantum mechanics*
- Chemical bonds → *quantum mechanics*

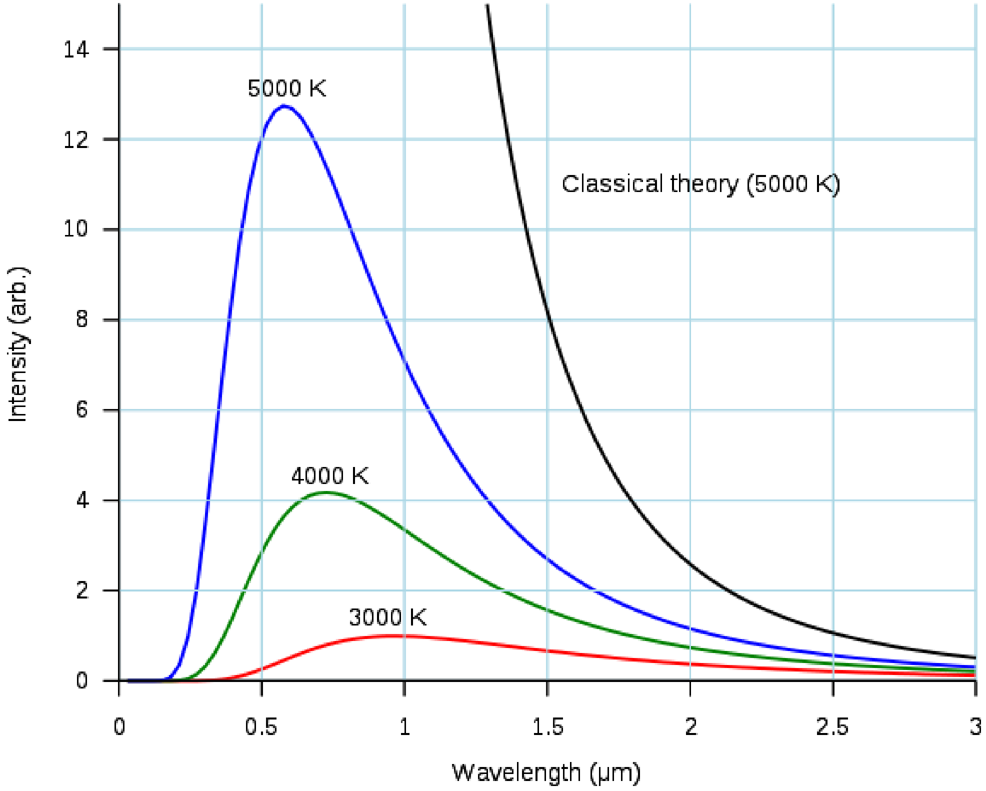
Blackbody radiation

- Classical theory (Rayleigh-Jeans equation):

$$I(\lambda) = \frac{2\pi k T}{\lambda^2}$$

- Quantum theory (Plank equation)

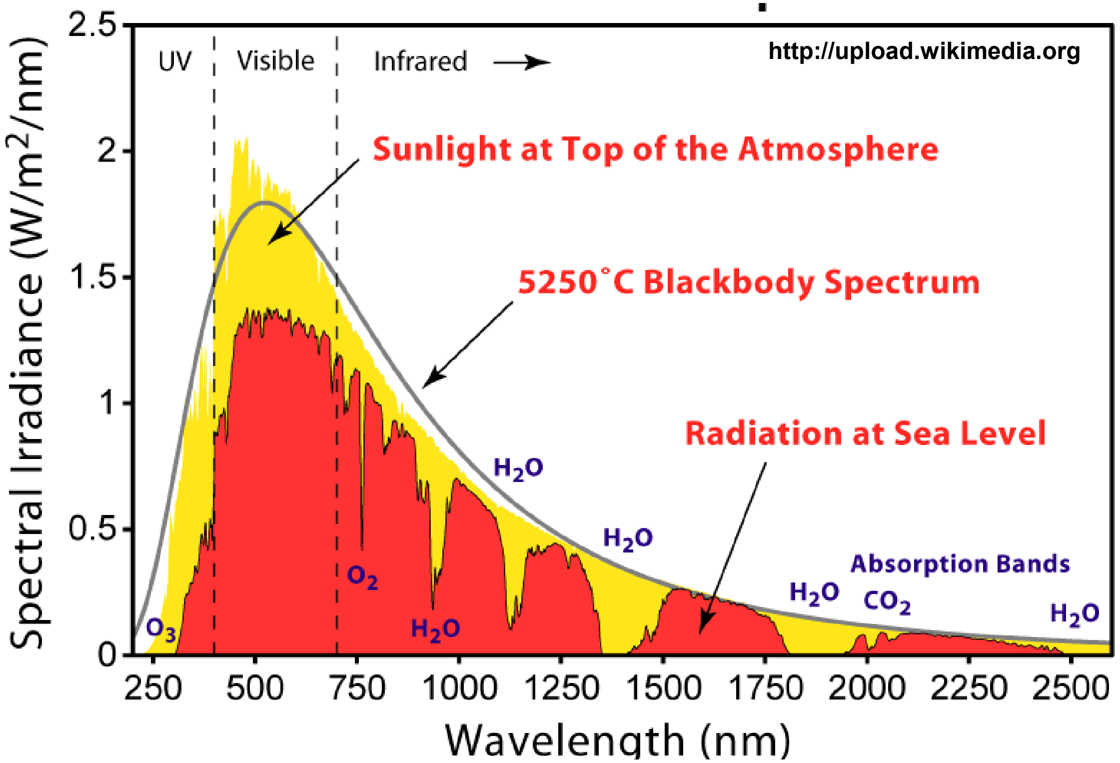
$$I(\lambda) = \frac{4\pi\hbar c^2}{\lambda^5\left[\exp\left(\frac{2\pi\hbar c}{\lambda k T}\right) - 1\right]}$$

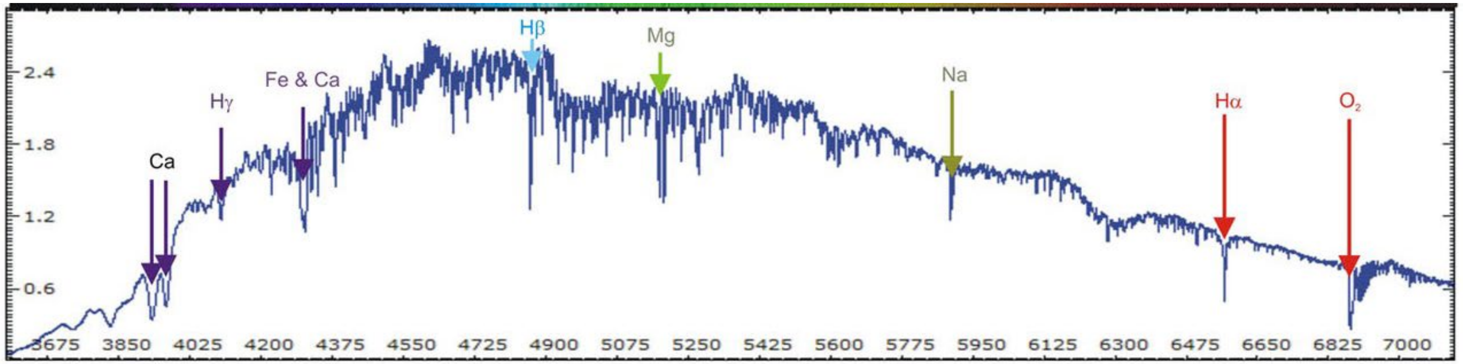


http://4.bp.blogspot.com

Emission/absorption “lines” of the atoms

Sun spectrum is NOT continuous (at the sea level as well as at the top of the atmosphere):
Absorption “lines" due to discrete energy levels of the absorbing molecules/atoms.





Stability of the atoms

^{1}H atom stability

- A “classical physics model” of an ^{1}H atom is a point-like electron rotating around a proton. But “classical physics” predicts that in such accelerated motion the electron emit electromagnetic waves. Hence:

Emission of EM waves → energy loss → electron would "falls" into the nucleus (in about 10^{-11} s)

This is not experimentally observed, hence the “classical physics model” of the ^{1}H atom is not correct.

How long it would take to an electron to collapse on the proton if radiation is taken into account but without considering quantum mechanics ? About 10^{-11} s !

$$F_{Coulomb} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} \qquad F_{Centripetal} = \frac{m_e v^2}{r} \qquad F_{Coulomb} = F_{Centripetal} \quad \Rightarrow \quad \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = \frac{m_e v^2}{r} \quad \Rightarrow v = \sqrt{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{m_e r}}$$

$$E_{Kinetic} = \frac{1}{2} m_e v^2 \qquad E_{Potential} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \quad \Rightarrow \; E_{Total} = E_{Potential} + E_{Potential} = \frac{1}{2} m_e v^2 + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2r}$$

$$P_{Larmor} = \frac{e^2 a^2}{6\pi\varepsilon_0 c^3} \qquad a = \frac{v^2}{r} \quad \Rightarrow \; P_{Larmor} = \frac{e^2}{6\pi\varepsilon_0 c^3}\frac{v^4}{r^2} = \frac{e^2}{6\pi\varepsilon_0 c^3}\frac{1}{r^2}\left(\frac{1}{4\pi\varepsilon_0}\frac{e^2}{m_e r}\right)^2 = \frac{e^5}{96\pi^3\varepsilon_0{}^3 c^3 m_e{}^2 r^4}$$

$$E_{Total} = \int_0^{t_{Collapse}} P_{Larmor}(t)\,dt \quad ......$$

Why do we need quantum mechanics ?

- As shown before, classical physics cannot explain several experimentally observed phenomena.

- We **need** quantum mechanics to explain the following nanoscale «phenomena»:

  - the atomic structure
  - the chemical bonding
  - ….
  - the quantization of the conductance
    - the tunneling effect
    - the Coulomb blockade and the single electron transistor (SET)
    - the quantum Hall effect
    - …

Basics of quantum mechanics

The 5 postulates of quantum mechanics

The postulates of quantum mechanics cannot be proven or deduced.
These postulates are hypotheses, and, if no violation with nature (experiments) is found, they are called ***axioms***, *i.e.* non-provable, true statements.

Postulate 1:

The wave function $\Psi(\boldsymbol{x}, t)$ describes the temporal and spatial evolution of a particle.

Postulate 2:

The product $\Psi^*(\boldsymbol{x}, t)\ \Psi(\boldsymbol{x}, t)$ is the probability density function of a particle. Consequently,

Probability to find the particle "around" the position $\mathbf{x}$ at time t

$$\Psi(\mathbf{x},t)^* \Psi(\mathbf{x},t)\, dxdydz$$

Probability to find the particle in the volume V at time t

$$\int_V \Psi(\mathbf{x},t)^* \Psi(\mathbf{x},t)\, dxdydz$$

Probability to find the particle somewhere in the Universe at time t

$$\int_{Vuniverse} \Psi(\mathbf{x},t)^* \Psi(\mathbf{x},t)\, dxdydz = 1$$

http://homepages.rpi.edu/~schubert/
Physical foundations of solid state devices (free download)

Basics of quantum mechanics

Postulate 3: The wave function Ψ(***x***, *t*) (and its derivative) are continuous in an isotropic medium. The wave function has to be finite and single valued throughout the position space.

Postulate 4: In classical mechanics, variables such as position, momentum, or energy are called *dynamical variables*.In quantum mechanics *operators* rather than *dynamical variables* are employed.

DYNAMICAL VARIABLE		OPERATOR
Position:	x, y, z	x, y, z
Momentum:	p_x, p_y, p_z	$\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}$
Kinetic energy :	$\frac{p^2}{2m}$	$-\frac{\hbar^2}{2m}\nabla^2$
Potential Energy:	$U(x, y, z)$	$U(x, y, z)$
Total Energy:	$\frac{p^2}{2m} + U(x, y, z)$	$-\frac{\hbar^2}{2m}\nabla^2 + U(x, y, z)$ $-\frac{\hbar}{i}\frac{\partial}{\partial t}$

Note:

The total energy is "rappresented" by two operators:

$-\frac{\hbar}{2m}\nabla^2 + U(x, y, z)$ and $-\frac{\hbar}{i}\frac{\partial}{\partial t}$

Basics of quantum mechanics

Postulate 4 (continuation):

Usually the total energy operator is indicated with **H** and called the **hamiltonian operator:**

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{x})$$

The **hamiltonian operator H** represents the **total energy** of a particle represented by the wave function ψ(***x***).

Many problems of quantum mechanics are solved by minimizing the total energy of a particle or a system of particles.

∇^2 : Laplace operator (indicated also with Δ or $\nabla \cdot \nabla$): $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ (cartesian coordinates)

Basics of quantum mechanics

Postulate 4 (continuation):

The Schödinger equation is the key equation in quantum mechanics.

It is formally obtained by making both «total energy operators» acting on the wave function:

$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2+U\left(\mathbf{x},t\right)\right)\Psi\left(\mathbf{x},t\right)=i\hbar\frac{\partial\Psi\left(\mathbf{x},t\right)}{\partial t}}$$

or

$$\boxed{H\Psi\left(\mathbf{x},t\right)=i\hbar\frac{\partial\Psi\left(\mathbf{x},t\right)}{\partial t}}$$

Time-dependent
Schrödinger equation
(linear, 2nd order,
partial differential equation)

Note: In same books the postulates are written differently. In some of them, the Schrödinger equation is considered as one of the postulates and the «total energy operator» is only H.

Basics of quantum mechanics

Postulate 5:

The expectation value, ⟨ξ⟩, of any dynamical variable ξ, is calculated from the wave function according to

$$\langle \xi \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\, \xi_{op} \Psi(x,t)\,\mathrm{dx}$$

where ξ_{op} is the operator of the dynamical variable ξ.

The **expectation value** of a variable is also referred to as **average value** or ensemble average, and is denoted by the triangular brackets ⟨…⟩.

This equation allows one to calculate expectation values of important quantities, such as position, momentum, potential energy, kinetic energy, angular momentum, etc.

Basics of quantum mechanics

- **Time-independent Schrödinger equation**

The Schrödiger equation is partial differential equation → we can write:

$$\Psi\left(\mathbf{x},t\right)=\psi\left(\mathbf{x}\right)f(t)$$

Introducing this equation into the time-dependent Schrödiger equation we have:

$$\frac{1}{\psi\left(\mathbf{x}\right)}H\psi\left(\mathbf{x}\right)=\frac{i\hbar}{f(t)}\frac{\partial}{\partial t}f(t)$$

The left side of this equation depends on **x** only, while the right side depends only on *t*. Because **x** and *t* are independent variables, the equation can be true, only if both sides are constant, i.e.,

$$\frac{i\hbar}{f(t)}\frac{\partial}{\partial t}f(t)=\text{constant}=E \qquad (\Rightarrow f(t)=\exp(-i\frac{E}{\hbar}t))$$

If we denote this constant *E* (the meaning will be clear later), we have

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi\left(\mathbf{x}\right)+U(\mathbf{x})\psi\left(\mathbf{x}\right)=E\psi\left(\mathbf{x}\right)}$$

or

$$\boxed{H\psi\left(\mathbf{x}\right)=E\psi\left(\mathbf{x}\right)}$$

Time-Independent Schrödinger equation
(linear, 2nd order, partial differential equation)

Basics of quantum mechanics

Properties of quantum mechanics operators

- Virtually all operators in quantum mechanics are **linear operators**, i.e.,

$$\xi_{op} c\psi\left(x\right) = c\xi_{op}\psi\left(x\right)$$

where *c* is a constant.

- Quantum mechanics operators, in general, **do not commute**, i.e.,

$$\xi_{op1}\xi_{op2}\psi\left(x\right) \neq \xi_{op2}\xi_{op1}\psi\left(x\right)$$

- Most quantum mechanics operators are **Hermitian operators**, i.e.,

$$\int_{-\infty}^{\infty} \psi_1^*(x)\xi_{op}\psi_2\left(x\right)dx = \int_{-\infty}^{\infty} \psi_2\left(x\right)\ \xi_{op}^*\psi_1^*(x)dx$$

The eigenvalues of Hermitian operators are always **real** numbers.
The eigenfunctions of Hermitian operators corresponding to two unequal eigenvalues are **orthogonal** to each other, i.e.,

$$\int_{-\infty}^{\infty} \psi_1^*(x)\psi_2\left(x\right)dx = 0$$

(see examples and more details in Schubert, Physical foundation of solid state devices, http://homepages.rpi.edu/~schubert/)

Basics of quantum mechanics

- Definition of ***eigenfunctions*** and ***eigenvalues*** of a generic operator:

If the effect of an operator ξ_{op} acting on a function $f(x)$ is that the function $f(x)$ is modified only by the multiplication with a **scalar** constant λ, i.e.

$\xi_{op} f(x) = \lambda f(x)$ Eigenvalue equation

then:
1) $f(x)$ is called ***eigenfunction*** of the operator ξ_{op}
2) λ is called ***eigenvalue*** of the *eigenfunction* $f(\mathrm{x})$ of the operator ξ_{op}

- ***Eigenfunctions*** and ***eigenvalues*** of the energy operator *H*:

H is an Hermitian operator → *E* is a real number → the Schrödinger equation

$$H\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

is an ***eigenvalue equation***, where $\psi(\boldsymbol{x})$ is an eigenfunction of *H* and *E* is an eigenvalue of *H.*

Basics of quantum mechanics

- **Meaning of *E* in the time-independent Schrödinger equation**

The eigenfunctions $\psi_n(\boldsymbol{x})$ and the eigenvalues E_n are found by solving the Schrödinger equation:

$$H\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

Since

$$\langle H\rangle \equiv \int_{-\infty}^{\infty} \psi_n^*(\mathbf{x})\, H\psi_n(\mathbf{x})dx = \int_{-\infty}^{\infty} \psi_n^*(\mathbf{x})E_n\psi_n(\mathbf{x})\,dx = E_n \int_{-\infty}^{\infty} \psi_n^*(\mathbf{x})\psi_n(\mathbf{x})\,dx = E_n$$

$\boldsymbol{E_n}$ are the **expectation values of *H*,** which represent the total energy of the system.

Since the eigenvalues of the Schrödinger equation E_n are *discrete*, only certain energy values are allowed, all other energies are forbidden. The energy eigenvalues are also called *eigenenergies* or *eigenstate energies*. The lowest eigenstate energy is the *ground state energy*. All higher energies are called *excited state energies*.

The eigenstate energies E_n and eigenfunctions $\psi_n(\boldsymbol{x})$ of a physical system are of great importance, because the knowledge of $\psi_n(\boldsymbol{x})$ and E_n implies the knowledge of *all* relevant physical quantities.

Basics of quantum mechanics

Properties of the eigenfunctions ψ$_n$(x)

• Superposition principle

Any linear combination of solutions is also a solution of the **time-dependent** Schrödinger equation :

$$\Psi(\mathbf{x},t) = A_1\Psi_1(\mathbf{x},t) + A_2\Psi_2(\mathbf{x},t) + \ldots =$$

$$= A_1\psi_1(\mathbf{x})\mathrm{e}^{-i(E_1/\hbar)t} + A_2\psi_2(\mathbf{x})\mathrm{e}^{-i(E_2/\hbar)t} + \ldots$$

A condition on the A_n is that the new solution must be also normalized, i.e.,

$$\langle \Psi(\mathbf{x},t) | \Psi(\mathbf{x},t) \rangle = \int_{-\infty}^{\infty} \Psi^*(\mathbf{x},t)\Psi(\mathbf{x},t)\,dx = 1$$

which is equivalent to $\sum_n |A_n|^2 = 1$

Is $\psi(\mathbf{x}) = \sum_n A_n \psi_n(\mathbf{x})$ also a solution of the **time-independent** Schrödinger equation ?

Only if the solutions ψ$_1$($\boldsymbol{x}$)…ψ$_n$($\boldsymbol{x}$) correspond to states with the same energy.

• Ortogonality

Two eigenfunctions $\psi_n(\mathbf{x})$ and $\psi_m(\mathbf{x})$ solutions of the Schrödinger equation and having different energies $E_n \neq E_m$, are ***orthogonal***, i.e.,

$$\langle \psi_m(\mathbf{x}) | \psi_n(\mathbf{x}) \rangle = \int_{-\infty}^{\infty} \psi_m^*(\mathbf{x})\psi_n(\mathbf{x})\,dx = 0$$

Basics of quantum mechanics

Can we somehow “justify” the expression of the operator momentum p?

Let’s consider a plane wave

$$\psi\left(\mathbf{x},t\right)=\exp\left[i\left(\mathbf{k}\cdot\mathbf{x}-\omega t\right)\right]$$

if we assume that:

$$\mathbf{p}=-i\hbar\left(\frac{\partial}{\partial x},\frac{\partial}{\partial y},\frac{\partial}{\partial z}\right)$$

we have that

$$\left\langle\mathbf{p}\right\rangle=\left\langle\psi\left(\mathbf{x}\right)\middle|\mathbf{p}\middle|\psi\left(\mathbf{x}\right)\right\rangle=\hbar\mathbf{k}$$

With a «normalization» problem
if the plane wave extends
everywhere in the Universe.
A pure plane wave cannot be normalized.

Since for a generic wave

$$\mathbf{k}=\frac{2\pi}{\boldsymbol{\lambda}}$$

we obtain

$$\left\langle\mathbf{p}\right\rangle=\frac{h}{\boldsymbol{\lambda}}$$

which is the de Broglie relation.
(also called de Broglie momentum wavelength relation).

Basics of quantum mechanics

Can we somehow “justify” the expression of the operators energy *H*?

Let’s consider a plane wave

$$\psi(\mathbf{x},t) = \exp\left[i(\mathbf{k}\cdot\mathbf{x} - \omega t)\right]$$

if we assume that:

$$H = i\hbar\frac{\partial}{\partial t}$$

we have that

$$\langle H\rangle = \langle \psi(\mathbf{x})|E|\psi(\mathbf{x})\rangle = \hbar\omega$$

With a «normalization» problem
if the plane wave extends
everywhere in the Universe.
A pure plane wave cannot be normalized.

which is the Planck-Einstein relation expressing the energy of a photon
(also called Planck equation, Einstein relation, or Planck’s energy-frequency relation).

Note: These two “justifications” are not “demonstrations” that the *p* and *H* operators are “correctly defined”. They shows only that the axiomatic definition of the operators *p* and *H* are compatible with other quantum mechanical relationships such as the Planck-Einstein relation and the de Broglie relation.

Wavelength of an "object"

Wavelenght of an object (de Broglie wavelength):

$$\lambda = \frac{h}{p} = \frac{h}{\gamma m_0 v} = \frac{h}{m_0 v}\sqrt{1-\frac{v^2}{c^2}}$$

m_0 : mass of the object at rest $\qquad$ v : speed of the object

c : speed of the ligth in vacuum

(for a photon in vacuum $m_0 = 0$ and $v = c \Rightarrow \lambda = \frac{h}{p} = \frac{h}{E/c} = \frac{h}{hf/c} = \frac{c}{f}$)

When the «object» dimensions are **very large** with respect to its **wavelength** we do not see easily the «wave-like» behavior of the «object».

When the «object» dimensions are **comparable** or **smaller** with respect to its **wavelength** we can see its «wave-like» behavior.

(The «wave-like» behavior is more evident when the «object» has a wavelength similar to the size of the «obstacle» which interacts with it)

Wavelength of the particles: examples

PHOTONS: $m_0 = 0$ and $v = c$

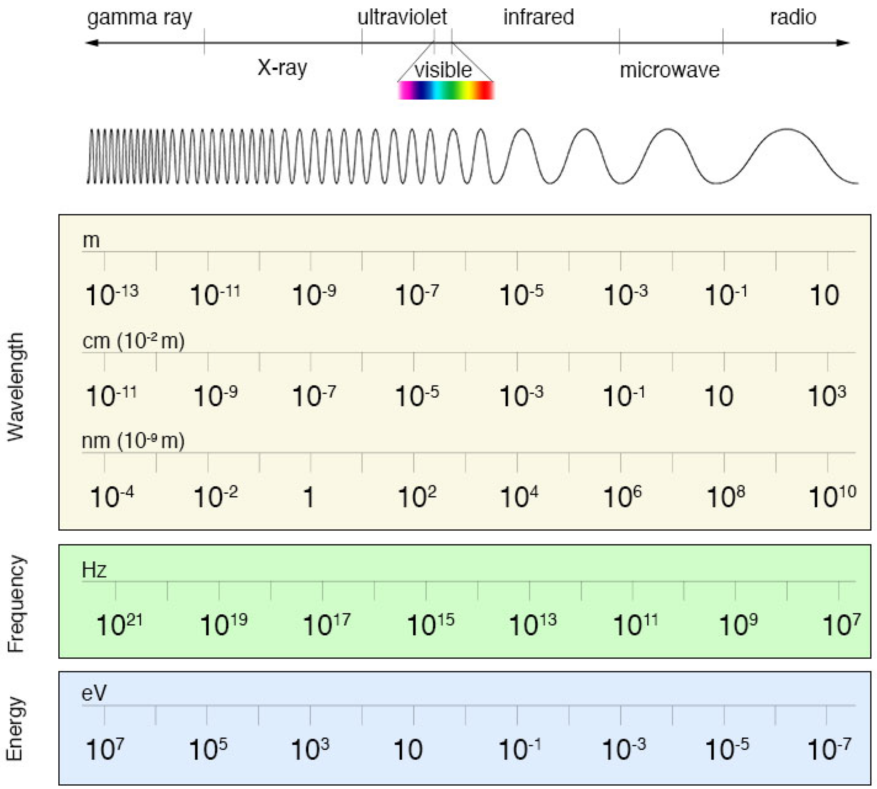
$$\lambda = \frac{h}{p} = \frac{h}{E/c} \Rightarrow$$

$E \cong 0.01$ eV (Infrared) → $\lambda \cong 100\ \mu$m

$E \cong 1$ eV (Visible) → $\lambda \cong 1\ \mu$m

$E \cong 10$ eV (UV) → $\lambda \cong 100$ nm

$E \cong 1000$ eV (X-ray) → $\lambda \cong 1$ nm



Wavelength of the particles: examples

ELECTRONS: $m_0 \cong 10^{-30}$ kg

$$\lambda = \frac{h}{m_0 v}\sqrt{1-\frac{v^2}{c^2}} \qquad E = \frac{1}{2}mv^2 \qquad v = \sqrt{\frac{2E}{m}} \qquad \Rightarrow$$

$E \cong 1$ eV → $v \cong 0.002c$ $\lambda \cong$ 1.2 nm

$E \cong 100$ keV → $v \cong 0.5c$ $\lambda \cong$ 0.004 nm

$E \cong 1$ MeV → $v \cong 0.94c$ $\lambda \cong$ 0.0009 nm

$\Rightarrow$ the size of an electron (zero because it is an elementary particle) is much smaller than its wavelength, diffraction from an array of atoms and interference pattern in double-slit experiments are observable (which demonstrates the "wave nature" of the electrons)

CRICKET BALL: $m_0 \cong 0.16$ kg

For $v << c$: $\lambda = \frac{h}{m_0 v}\sqrt{1-\frac{v^2}{c^2}} \cong \frac{h}{m_0 v} \Rightarrow$

$v \cong 160$ km/h=44 m/s (max speed in a game) $\Rightarrow \lambda \cong 10^{-34}$ m

$v \cong 0.04$ nm/s (extremely slow speed) $\Rightarrow \lambda \cong 10^{-22}$ m

$\Rightarrow$ the cricket ball size (0.07 m) is much larger than its wavelength, even at extremely slow speeds, its "wave nature" is hardly measurable.

Note on electron microscopes

The resolution limit (diffraction limited) of a "far field" microscope is:

$$d \cong \frac{0.6\lambda}{n\sin(\alpha)} \cong \frac{0.6\lambda}{NA} \qquad \text{(Abbe equation)}$$

n = refractive index of medium between point source and lens

α = half the angle of the cone from specimen plane to "objective", NA = numerical aperture

If aberrations and distortions are eliminated, this is the limit to lateral spatial resolution.

In the case of an electron microscope:

$$(1/2)mv^2 = eV, \text{ where } V \text{ is the accelerating voltage } \Rightarrow \lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

$$\begin{aligned} \Rightarrow 1 \text{ keV electron} &\rightarrow \quad v \cong 0.06c \qquad \lambda \cong 0.04 \text{ nm} \\ 10 \text{ keV electron} &\rightarrow \quad v \cong 0.19c \qquad \lambda \cong 0.01 \text{ nm} \\ 100 \text{ keV electron} &\rightarrow \quad v \cong 0.5c \qquad \lambda \cong 0.004 \text{ nm} \end{aligned}$$

In scannnig electron microscope (SEM) and transmission electron microscopes (TEM):

$$\alpha \cong 10^{-1} \div 10^{-2} \text{rad } (\Rightarrow \sin(\alpha) \cong \alpha), \quad n \cong 1 \text{ (vacuum)} \Rightarrow$$

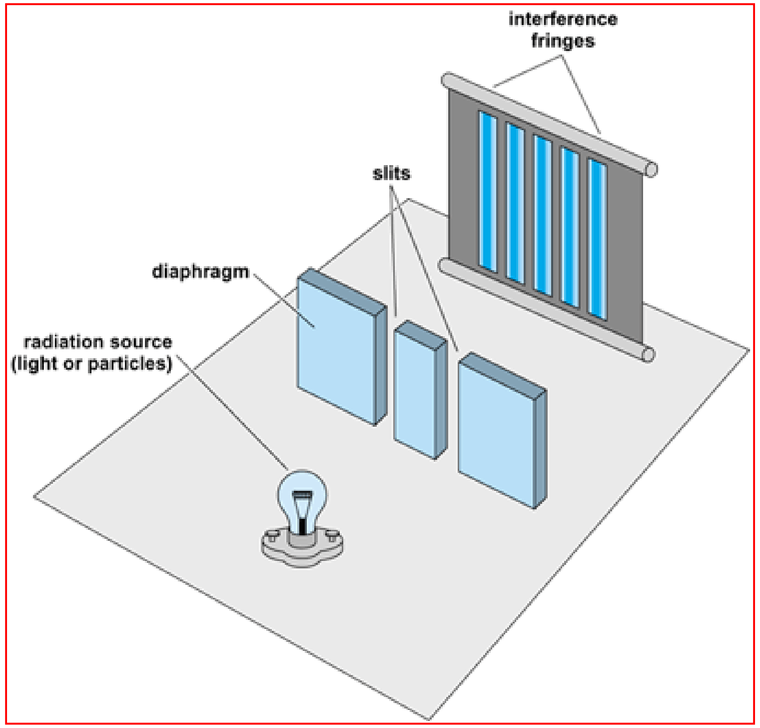
$$d \cong \frac{0.6\lambda}{n\sin(\alpha)} \cong 10\lambda \div 100\lambda$$

SEM: Energy: 1 keV to 30 keV, Max. Resolution: $\cong 0.5$ nm

TEM: Energy: 100 keV to 300 keV, Max. Resolution $\cong 0.05$ nm

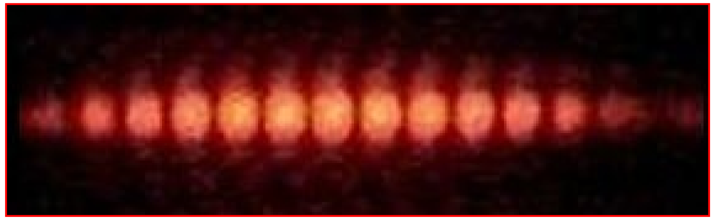
In practice:
SEM: The lateral resolution is 0.5 to 10 nm. The resolution is limited by factors such as the electron scattering.
TEM: The lateral resolution is 0.05 to 0.2 nm. The resolution is very close to the Abbe equation limit.

Wave behaviour of particles

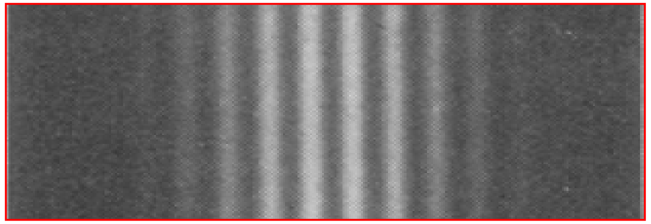


http://accessscience.com

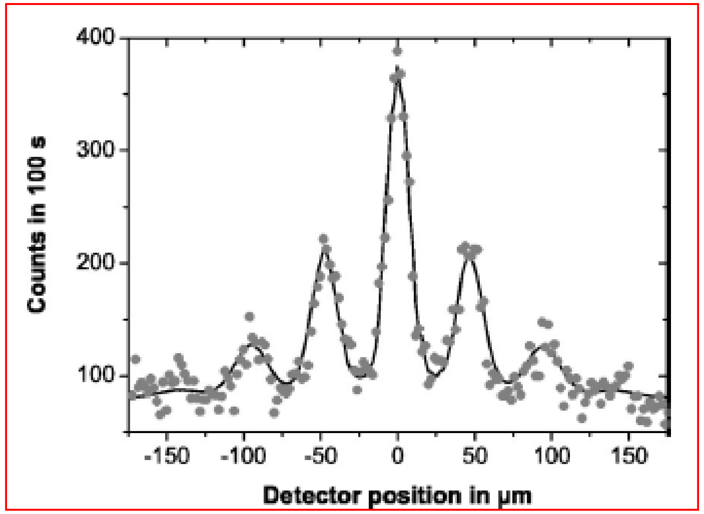
The interference pattern observed in an experiment with single particles suggests that each particle *interferes with itself*. In some sense, the particle must be passing through both slits simultaneously.

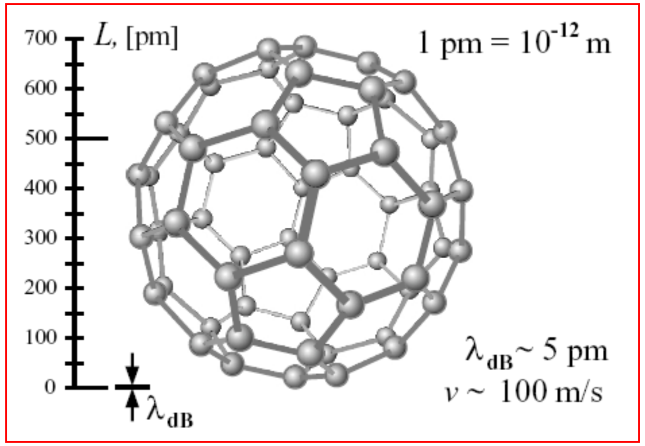


Visible light photons



Electrons





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C_{60} molecules

Nanotechnology

Nanoscale phenomena

Atomic structure

Interaction nucleus-electron

The electric field created by a nucleus of charge Ze at a distance r is

$$E = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{r^2}$$

The attrative force on an electron at distance r from the nucleus is

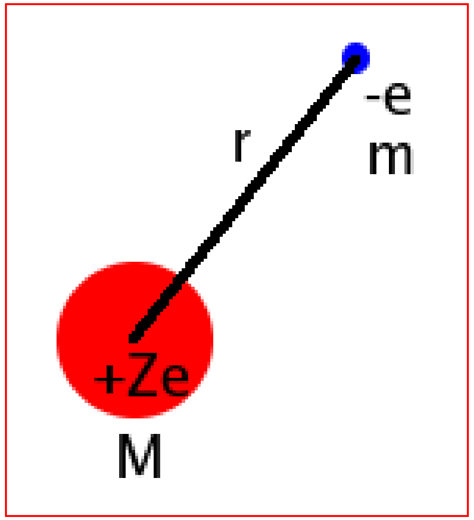
$$F = -eE = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r^2}$$

The potential energy of the electron is given by

$$U = -\int_{r_0}^{r} F dr + U(r_0)$$

Assuming $r_0 = \infty$ and $U(r_0 = \infty) = 0$ we have

$$U = -\int_{\infty}^{r} F dr = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$



http://users.aber.ac.uk

The atom

Time-independent Schrödinger equation of an atom (Z electrons + nucleus)

$$H_{atom}\psi_i = E_i\psi_i$$

H_{atom}: Hamiltonian operator (total energy)
ψ_i: Wavefunction of state i (possible state of the system)
E_i: Energy of state i (possible energy of the system)

Electron kinetic energy

Electron-Nucleus Coulomb interaction

Electron-Electron Coulomb interaction

Spin-Orbit Interaction

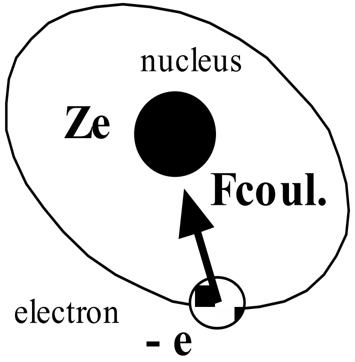
$$H_{atom} = \sum_{i=1}^{Z}\frac{p_i^2}{2m_e} - \sum_{i=1}^{Z}\frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i<j}^{Z}\frac{e^2}{4\pi\varepsilon_0\left|r_i - r_j\right|} + \sum_{i=1}^{Z}(\mathbf{l}_i\cdot\mathbf{s}_i)\xi(r_i)$$

Note: Here we do not consider the kinetic energy of the nucleus (Born-Oppenheimer approximation, see later in the course).

The hydrogen-like atom

- The “**hydrogen-like atom**” is an hypothetical atom with:
  - one electron of charge –e
  - one nucleus of charge Ze

with total energy that contains only:
- the kinetic energy of the electron
- the Coulomb interaction electron-nucleus

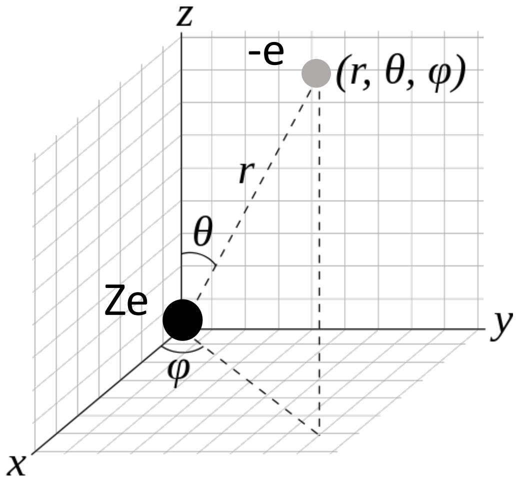


$$H_{atom} = \sum_{i=1}^{Z} \frac{p_{\xcancel{i}}^2}{2m_e} - \sum_{i=1}^{Z} \frac{Ze^2}{4\pi\varepsilon_0 r_{\xcancel{i}}} + \xcancel{\sum_{i<j}^{Z} \frac{e^2}{4\pi\varepsilon_0 \left| r_i - r_j \right|}} + \xcancel{\sum_{i=1}^{Z} (\mathbf{l}_i \cdot \mathbf{s}_i)\xi(r_i)} =$$

$$= \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

- The Hamiltonian operator is:

$$H = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r} \quad \rightarrow \quad H = -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



The hydrogen-like atom

- The time-independent Schrödinger equation for the hydrogen-like atom is

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad \text{where } H = -\frac{\hbar^2\nabla^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\Rightarrow$

The equation to be solved is the three-dimensional equation

$$\boxed{\frac{\hbar^2\nabla^2}{2m_e}\psi(x,y,z) + \left(E - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi(x,y,z) = 0}$$

Cartesian coodinates

Cartesian coordinates:

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$$

Spherical coordinates:

$$\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$$

or

$$\boxed{\frac{\hbar^2\nabla^2}{2m_e}\psi(r,\theta,\varphi) + \left(E - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi(r,\theta,\varphi) = 0}$$

Spherical coordinates

The hydrogen-like atom

- The **solutions** of the Schrödinger equation in spherical coordinates are:

$$\psi_{n,l,m}(r,\theta,\varphi)=\sqrt{\left(\frac{2Z}{na_0}\right)^3\frac{(n-l-1)!}{2n(n+l)!}}\,L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)\left(\frac{2Zr}{na_0}\right)^l e^{-\frac{Zr}{na_0}}\,Y_{l,m}(\theta,\varphi)$$

$$E_n=-\frac{m_e Z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}$$

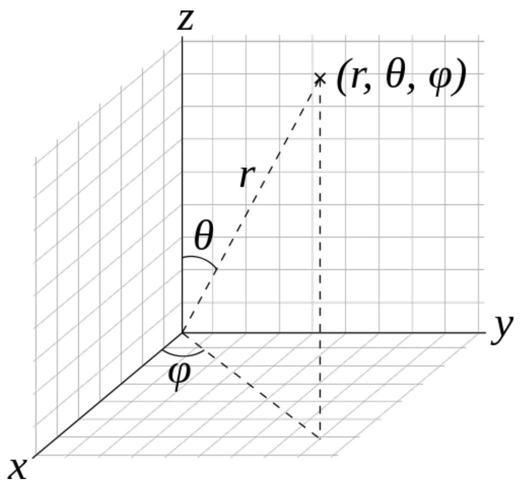
where:

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}\cong 0.5\times 10^{-10}\,\mathrm{m}\quad\text{(Bohr radius)}$$

$$L_{n-l-1}^{2l+1}\left(\frac{2r}{nr_0}\right):\text{generalized Laguerre polynomial}$$

$$Y_{l,m}(\theta,\varphi):\ \text{spherical armonic}$$

$$E_1=-\frac{m_e Z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2}:\text{Ionization energy}$$



Note: The simple Schrödinger equation for the hydrogen-like atom have quite complicated solutions (eigenfunctions), but simple eigenvalues.

The hydrogen-like atom

- The **solutions** of the Schrödinger equation of the hydrogen-like atom in spherical coordinates can be expressed in the form:

$$\boxed{\psi_{n,l,m}(r,\theta,\varphi) = R_{l,n}(r)\,Y_{l,m}(\theta,\varphi)}$$

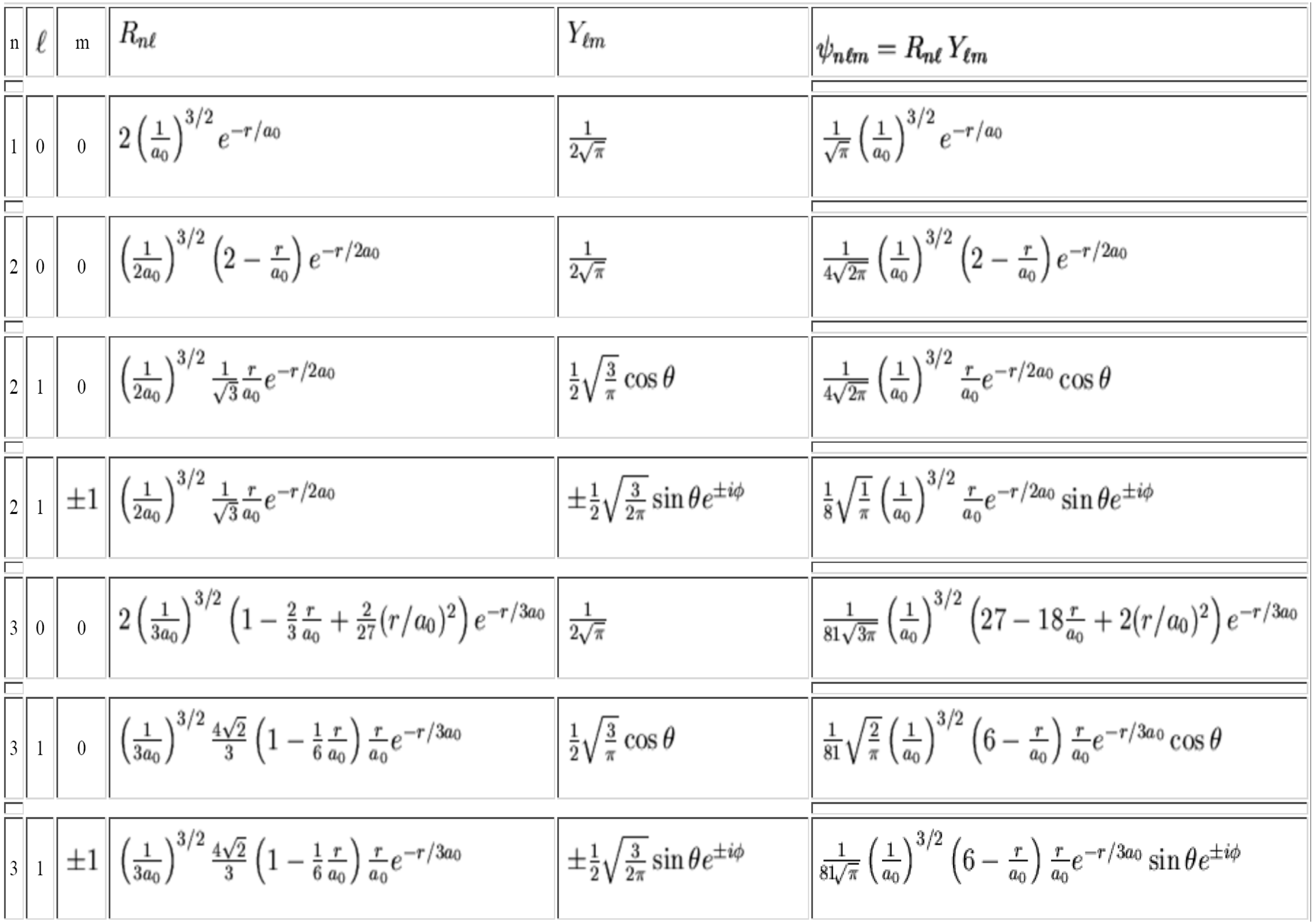
$$\boxed{R_{l,n}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}\,L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)\left(\frac{2Zr}{na_0}\right)^l e^{-\frac{Zr}{na_0}}}$$

$R_{n,l}(r)$: radial part of the solution

$Y_{l,m}(r)$: angular part of the solution

The hydrogen-like atom

Some solutions



n	ℓ	m	$R_{n\ell}$	$Y_{\ell m}$	$\psi_{n\ell m} = R_{n\ell} Y_{\ell m}$
1	0	0	$2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	0	$\left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$
2	1	0	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$
2	1	±1	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{8}\sqrt{\frac{1}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin\theta e^{\pm i\phi}$
3	0	0	$2\left(\frac{1}{3a_0}\right)^{3/2}\left(1-\frac{2}{3}\frac{r}{a_0}+\frac{2}{27}(r/a_0)^2\right)e^{-r/3a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(27-18\frac{r}{a_0}+2(r/a_0)^2\right)e^{-r/3a_0}$
3	1	0	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1-\frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\cos\theta$
3	1	±1	$\left(\frac{1}{3a_0}\right)^{3/2}\frac{4\sqrt{2}}{3}\left(1-\frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\pm\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi}$	$\frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\sin\theta e^{\pm i\phi}$

Energy (Hamiltonian) operator

The energy (hamiltonian) operator for the hydrogen-like atom expressed in spherical coordinates is

$$H = -\frac{\hbar^2\nabla^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \text{where:} \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Example: Average (expectation value) energy of the eigenfunctions of the hydrogen-like atom :

$$\langle H\rangle = \langle\psi_{n,l,m}|H|\psi_{n,l,m}\rangle = \int\psi_{n,l,m}H\psi_{n,l,m}dV = -\frac{m_eZ^2e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} = E_n$$

Specific example: Energy of the ground state (n=1, l=0, m=0) of the hydrogen atom

$$\langle\psi_{1,0.0}|H|\psi_{1,0,0}\rangle = \int\limits_{x=-\infty}^{+\infty}\int\limits_{y=-\infty}^{+\infty}\int\limits_{z=-\infty}^{-\infty}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}\left(-\frac{\hbar^2\nabla^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}dxdydz =$$

$$= \int\limits_{r=0}^{+\infty}\int\limits_{\theta=0}^{\pi}\int\limits_{\phi=0}^{2\pi}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}\left(-\frac{\hbar^2\nabla^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-r/a_0}r^2\sin\theta d\theta d\phi dr =$$

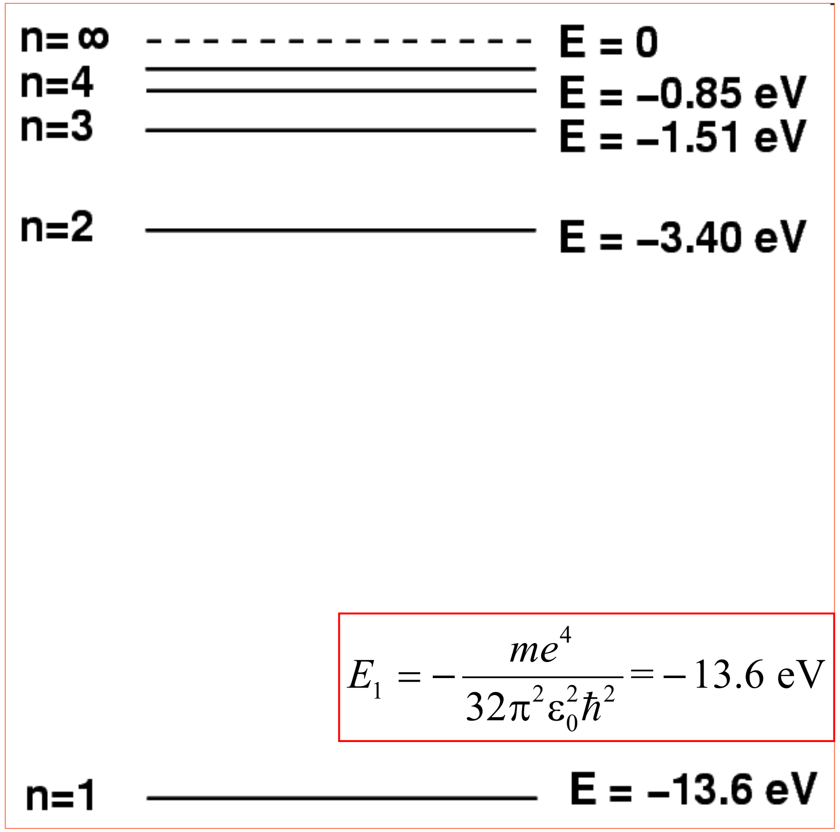
$$= \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots = -\frac{m_ee^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

The hydrogen-like atom

Energy levels for the hydrogen atom (Z=1)

$$Z=1 \Rightarrow \; E_n = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}$$

NOTE: The experimental values for the hydrogen atom energy differ from these theoretical values by less than 0.0001 eV!!



n= ∞ E = 0

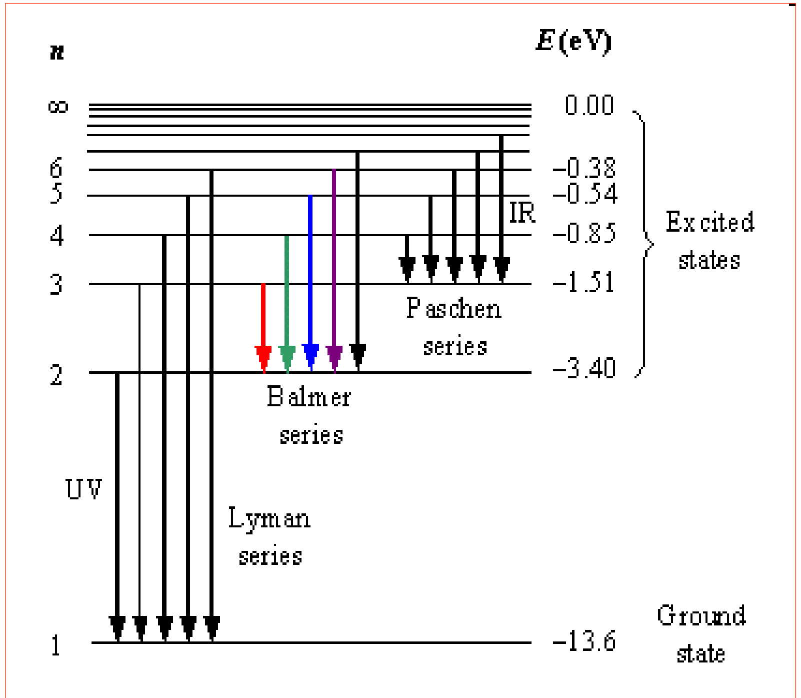
n=4 E = –0.85 eV

n=3 E = –1.51 eV

n=2 E = –3.40 eV

$$E_1 = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2} = -13.6\ \text{eV}$$

n=1 E = –13.6 eV



Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated.

Angular momentum operators

There are three **angular momentum** operators:
- Total angular momentum (usually denoted **J**)
- Orbital angular momentum (usually denoted **L**)
- Spin angular momentum (usually denoted **S**)

The total angular momentum **J** for a “effectively closed system” is conserved.

(“Effectively closed system”: no external forces or torques act on the system).

L and **S** are *not* generally conserved even in a “effectively closed system”.

(Spin–orbit interaction allows angular momentum to transfer back and forth between **L** and **S**, with the total **J** remaining constant).

Angular momentum operators

The orbital angular momentum operator $\mathbf{L}$ can be obtained as follow:

In classical mechanics

$\mathbf{L} = \mathbf{r} \times \mathbf{p}$ where $\mathbf{r}$ is the position and $\mathbf{p}$ is the momentum

Since, in quantum mechanics,

$\mathbf{p} = -i\hbar\nabla \qquad \Rightarrow$

$\mathbf{L} = -i\hbar\mathbf{r} \times \nabla$ where $\nabla = \dfrac{\partial}{\partial x}\hat{\mathbf{x}} + \dfrac{\partial}{\partial x}\hat{\mathbf{y}} + \dfrac{\partial}{\partial z}\hat{\mathbf{z}}$

The spin angular momentum operator $\mathbf{S}$ is an intrinsic property of many particles, with no classical equivalent.

The total angular momentum operator is $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

Angular momentum operators

The orbital angular momentum operators in spherical coordinates can be written as

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta}+\cot\theta\cos\phi\frac{\partial}{\partial\phi}\right),\quad L_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta}+\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right),\quad L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$L^2 = \hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

Example: Orbital angular momentum of the eigenfunctions of the hydrogen-like atom :

$$\left\langle\psi_{n,l,m}\middle|L^2\middle|\psi_{n,l,m}\right\rangle = \hbar^2 l(l+1) \qquad \left\langle\psi_{n,l,m}\middle|L_z\middle|\psi_{n,l,m}\right\rangle = \hbar m$$

This demonstrate that effectively that the quantum number l and m are associated with the orbital angular moment module and projection along the z-axis.

Specific example: Lets compute the expectation value of L^2 and L_z for state $\psi_{2,1,0} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$

$$\left\langle\psi_{2,1,0}\middle|L^2\middle|\psi_{2,1,0}\right\rangle = \int\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta r^2\sin\theta d\theta d\phi dr = 2\hbar^2$$

$$\left\langle\psi_{2,1,0}\middle|L_z\middle|\psi_{2,1,0}\right\rangle = \int\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta(-i\hbar\frac{\partial}{\partial\phi})\frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\cos\theta r^2\sin\theta d\theta d\phi dr = 0$$

Notes on orbital and spin angular momentum

1. An **electron** has an intrinsic angular momentum (called spin) given by $(1/2)\hbar$

2. An **electron** in a atom also an orbital angular momentum $\sqrt{\hbar^2 l(l+1)}$

3. The total angular momentum of an **atom** is the "vector combination"
of intrisic and orbital angular momentum of the electrons in the atoms.

4. A **photon** has an energy $\hbar\omega$, a linear momentum $\hbar\omega / c$, and an intrinsic angular momentum $\hbar$
(and eventually also an orbital angular momentum up to several times $\hbar$).

5. A **photon** can induce transitions between two atomic states with the condition that energy, linear momentum and total angular momentum are conserved.

The hydrogen-like atom

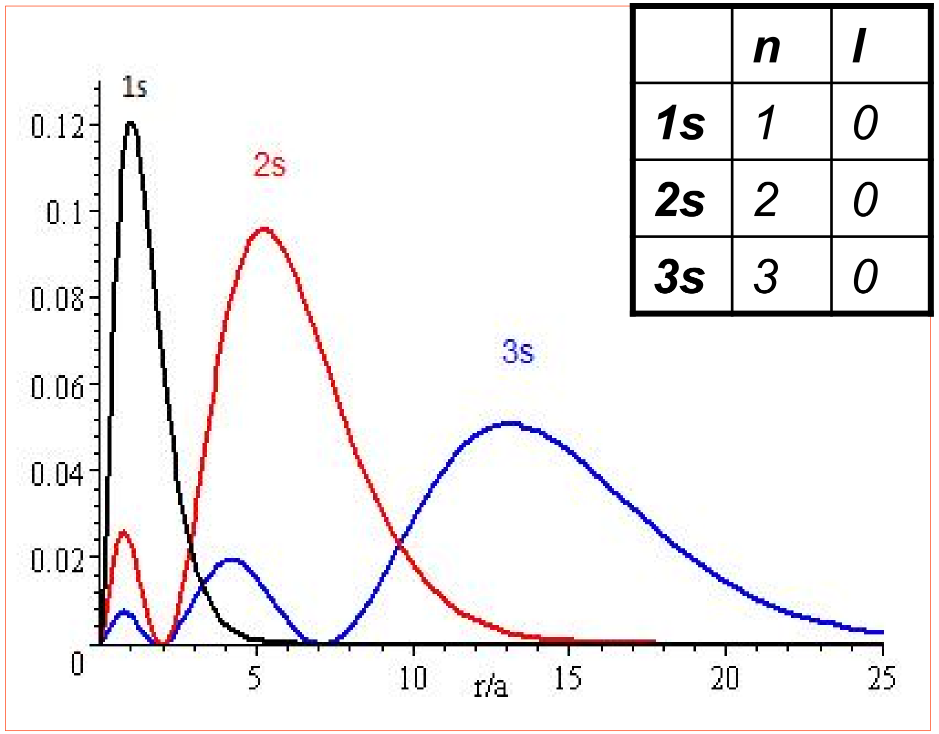
Quantum numbers

	Name	Values	Significance	
$\boldsymbol{n}$	Principal number	$n = 1, 2, 3, 4, \ldots$	Energy	$\langle H \rangle = E_n = -\frac{m_e Z^2 e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \frac{1}{n^2}$
$\boldsymbol{l}$	Orbital momentum number	$l = 0, 1, \ldots, n\text{-}1$	Orbital angular momentum (orbital shape)	$\langle L^2 \rangle = \hbar^2 l(l+1)$
$\boldsymbol{m}$	Magnetic quantum number	$m_l = -l, -l+1 \ldots, +l-1, +l$	Orbital angular momentum z-axis proj.	$\langle L_z \rangle = \hbar m$

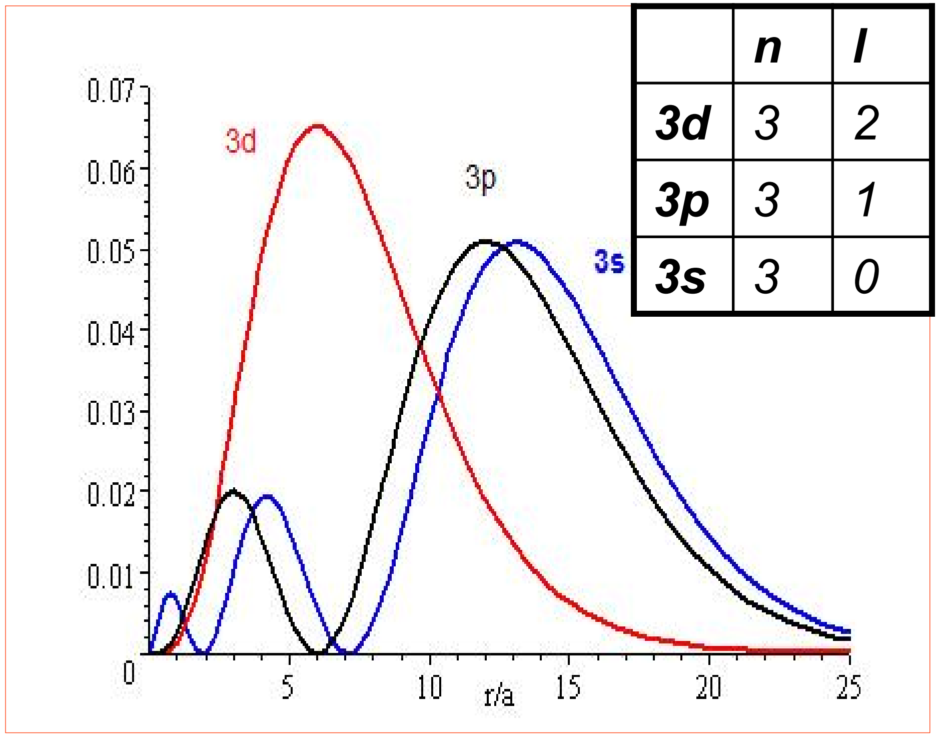
The hydrogen-like atom: orbitals representation

Radial distribution of probability of presence of an electron

$$D(r) = r^2 dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} \left|\psi\left(r,\theta,\varphi\right)\right| d\varphi$$



	n	***l***
1s	*1*	*0*
2s	*2*	*0*
3s	*3*	*0*



	n	***l***
3d	*3*	*2*
3p	*3*	*1*
3s	*3*	*0*

$$a = a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \cong 0.5\times10^{-10}\,\mathrm{m} \quad \text{(Bohr radius)}$$

Radial position operator

The radial position operator is r

Example: Average (expectation value) radial position of the eigenfunctions of the hydrogen-like atom :

$$\langle r \rangle = \langle \psi_{n,l,m} | r | \psi_{n,l,m} \rangle = \int \psi_{n,l,m} r \psi_{n,l,m} dV = \frac{n^2}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{l(l+1)}{n^2}\right)\right] a_0$$

Specific example: Energy of the ground state (n=1,l=0,m=0) of the hydrogen atom

$$\psi_{1,0.0} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\langle r \rangle = \langle \psi_{1,0.0} | r | \psi_{1,0,0} \rangle = \int_{x=-\infty}^{+\infty}\int_{y=-\infty}^{+\infty}\int_{z=-\infty}^{-\infty} \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} r \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} dxdydz =$$

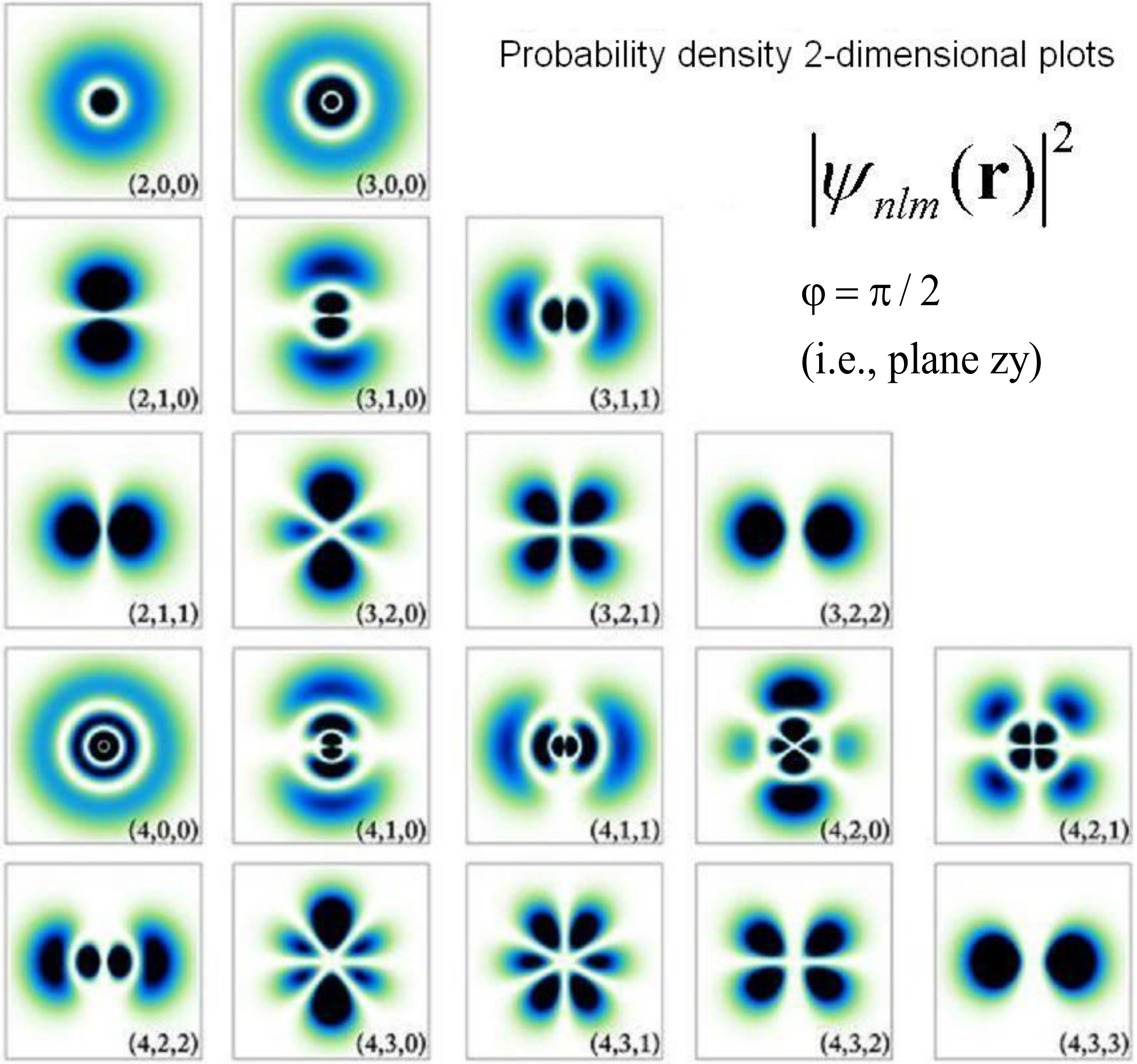
$$= \int_{r=0}^{+\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} r \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} r^2 \sin\theta d\theta d\phi dr = \ldots\ldots.. = (3/2)a_0$$

The expectation value $\langle r \rangle = (3/2)a_0$ is an estimation of the radius of an hydrogen atom in the ground state.

The Bohr radius a_0 corresponds to the maximum of $D(r)$ for an hydrogen atom in the ground state.

The hydrogen-like atom: orbitals representation

2D intensity map of the probability density


Probability density 2-dimensional plots

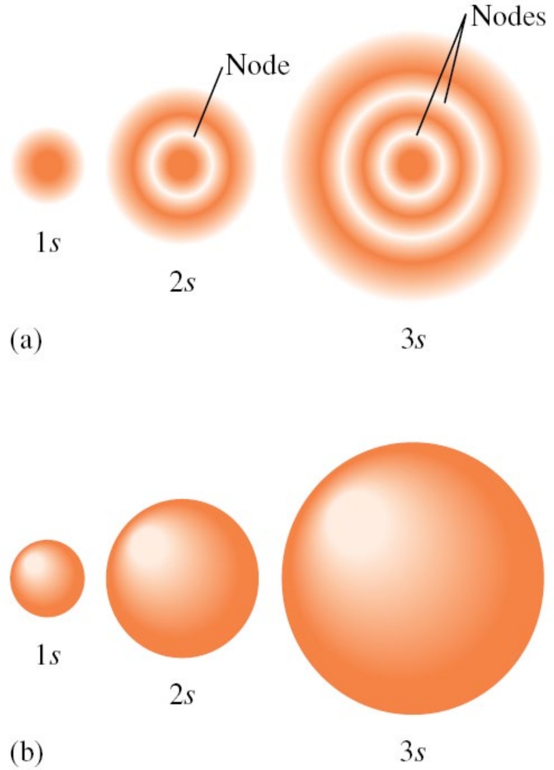
$$\left|\psi_{nlm}(\mathbf{r})\right|^2$$

$\varphi = \pi/2$

(i.e., plane zy)

http://vladimirkalitvianski.files.wordpress.com/2010/12/hydrogen_orbitals1.jpg

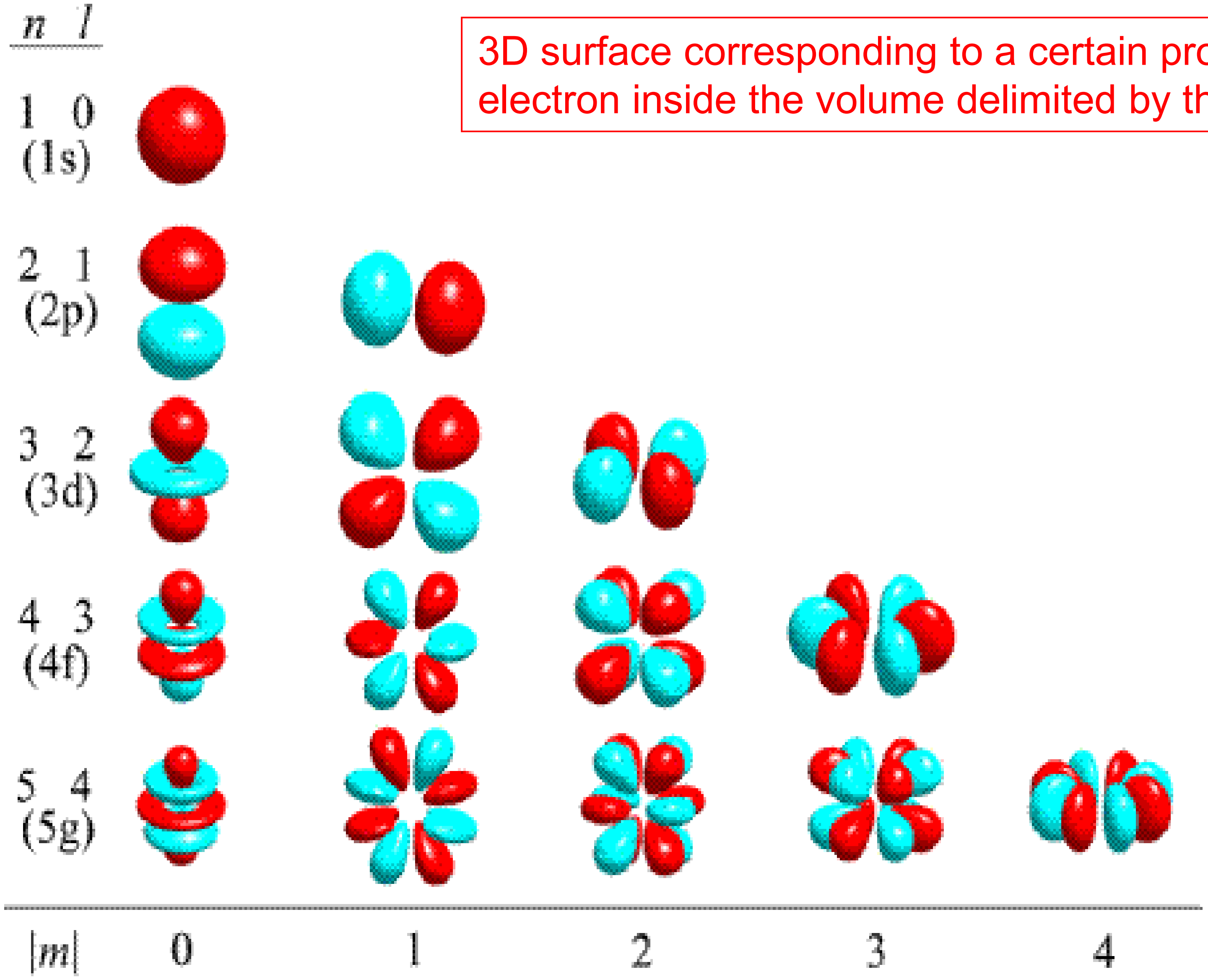
Two representations of the hydrogen 1*s*, 2*s*, and 3*s* orbitals. (a) The electron probability distribution. (b) The surface that contains 90% of the total electron probability (the size of the orbital, by definition).



The hydrogen-like atom: orbitals representation

-

3D surface corresponding to a certain probability (typically 90%) to find the electron inside the volume delimited by this surface

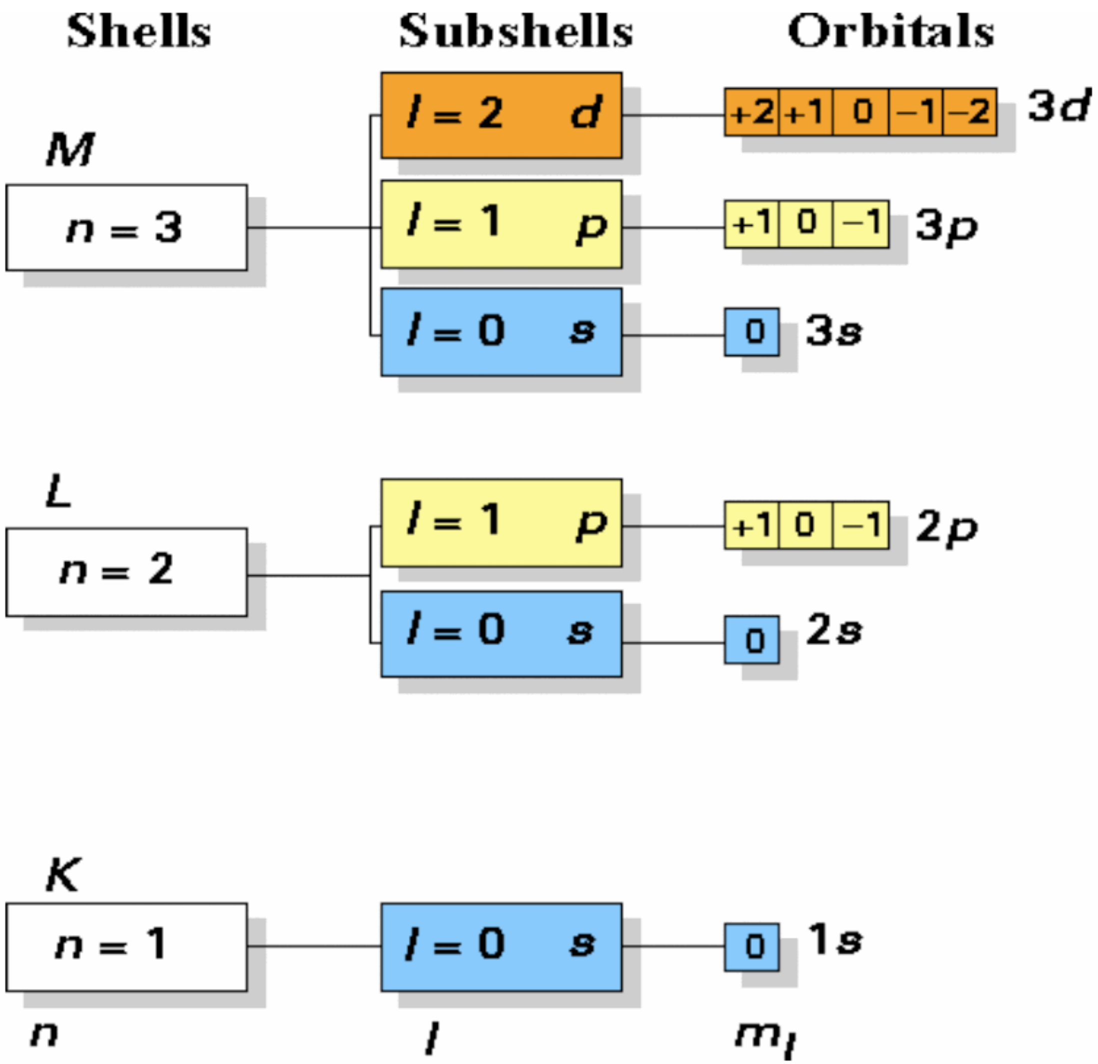


Note 1:
Red: positive sign of the wavefunction
Blu: negative sign of the wavefunction
The probability is, of course, always a positive number.

Note 2:
There are multiple valid surfaces enclosing 90% of the probability.
The selection of a single surface is often based on a surface where the probability density function is constant and enclose 90% of the total probability.

Hydrogen-like atom: shells, subshells,orbitals

Equivalent notations to indicate in a different way the states (n,l,m)



The real atom

The hydrogen-like atom:
- one electron with charge -e
- one nucleus with charge +Ze

$$H = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

The real atom:
- Z electrons, each with charge -e
- one nucleus with charge +Ze
- electrons are interacting with each other
- the orbital and the spin angular momentum of the electrons are interacting

$$H = \sum_{i=1}^{Z} \frac{p_i^2}{2m_e} - \sum_{i=1}^{Z} \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i<j}^{Z} \frac{e^2}{4\pi\varepsilon_0 \left|r_i - r_j\right|} + \sum_{i=1}^{Z} (\mathbf{l}_i \cdot \mathbf{s}_i)\xi(r_i)$$

Solving the Schrodinger equation for the real atom Hamiltonian is very difficult.

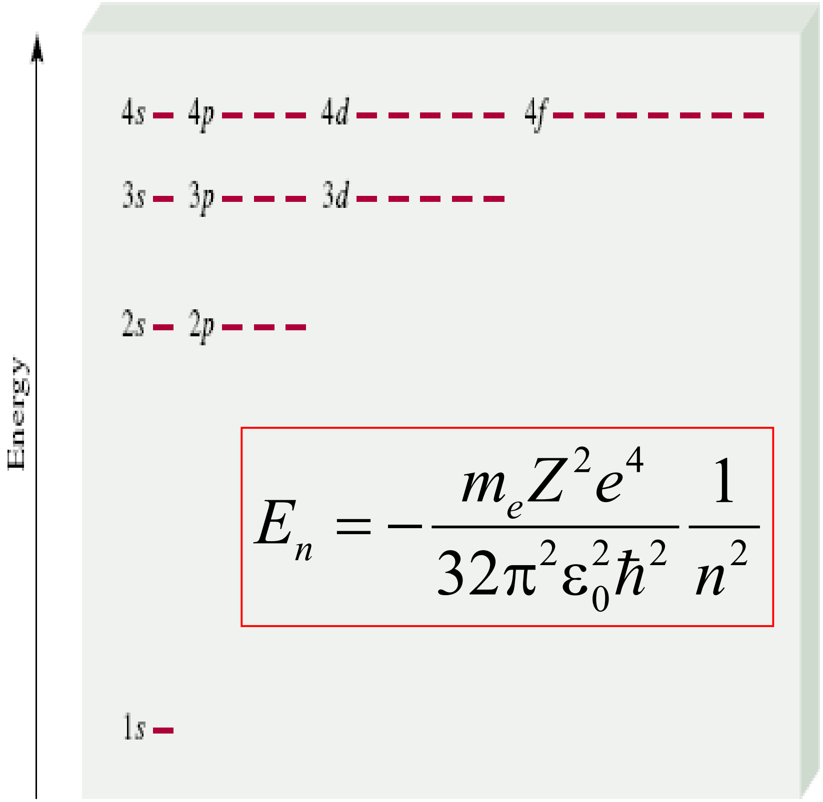
It is easier to:

1) Assume that the hydrogen-like atom gives the possible (states, wavefunctions, orbitals) also for the real atom.
2) Introduce some ad-hoc **rules** to describe the way the possible hydrogen-like orbitals are filled with the Z electrons of the real atom.

This approx. approach (i.e., **hydrogen-like atom orbitals + rules)** allows to explain most of the physical, chemical, optical, … properties of the real atoms without solving the complex Hamiltonian of the real atoms.

The hydrogen-like atom and the real atom

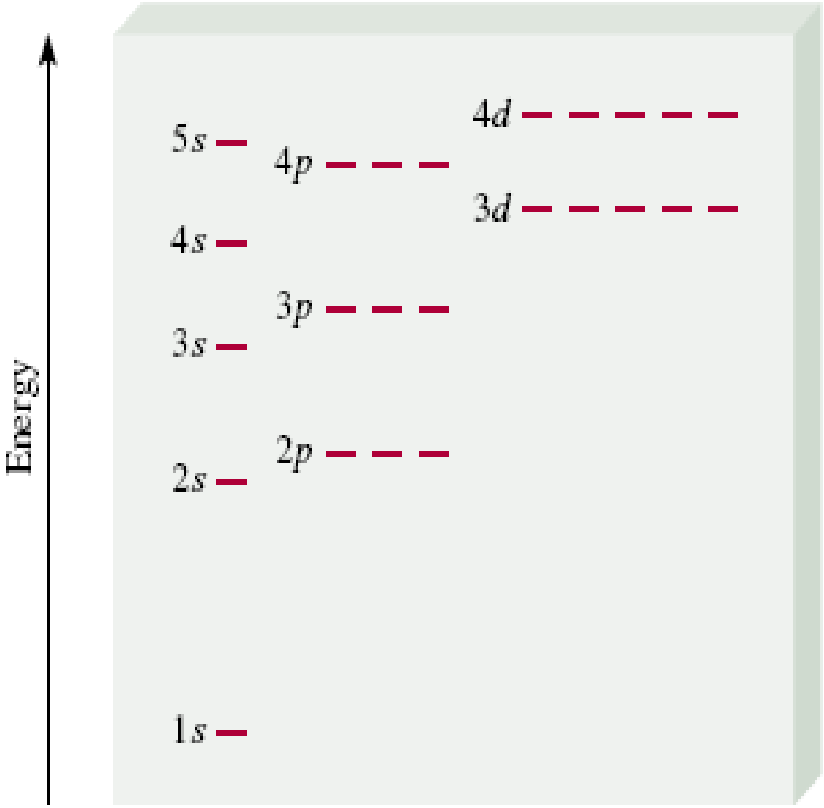
Hydrogen-like atom



$$E_n = -\frac{m_e Z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}$$

The energy of the possible states depends only on ***n** and **Z**.*

Real atom

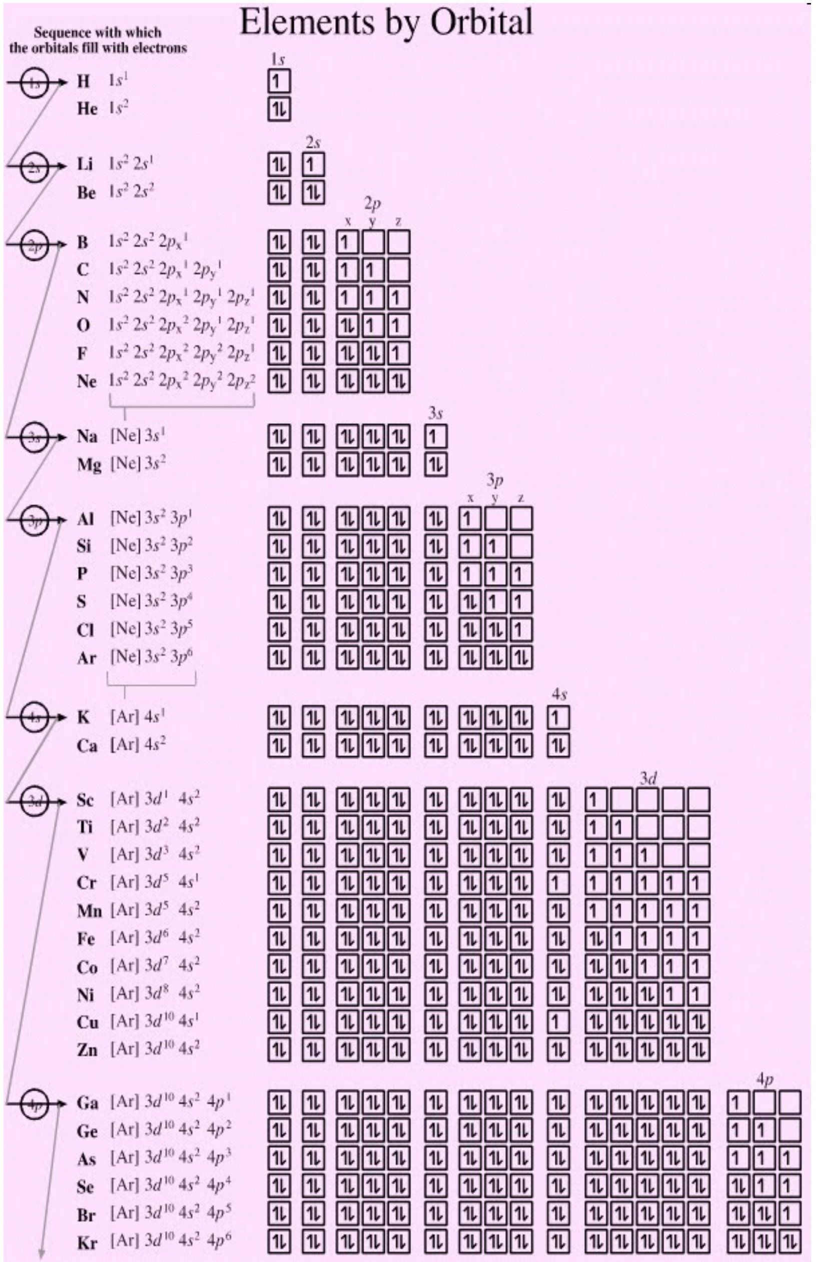


The energy of the possible states depends on ***n, Z***, and ***l*** (at least).

The real atom

The RULES

Pauli Exclusion Principle	Each orbital contains a **maximum of two electrons** which must be of opposite spin.
Build-up Principle	Electrons fill **lower energy orbitals first.**
Hund's Rule	**No pairing up.** Only when all the orbitals are half filled will pairing-up occur.
Madelung's Rule	Orbitals fill to **minimize *n* + *l*.** For identical *n*+*l*, **minimization** of *n*.

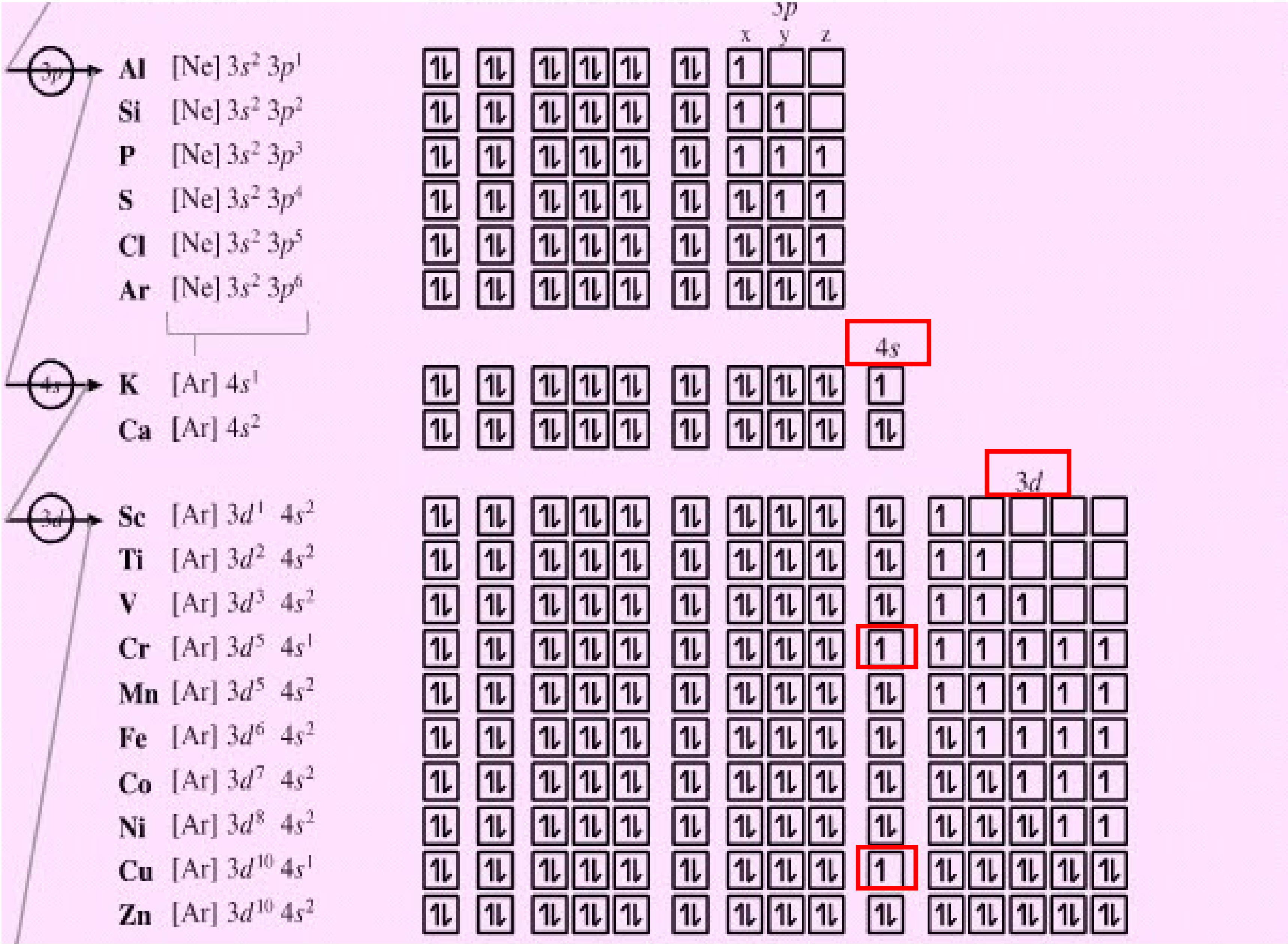


Elements by Orbital

Sequence with which the orbitals fill with electrons

H	$1s^1$
He	$1s^2$
Li	$1s^2\,2s^1$
Be	$1s^2\,2s^2$
B	$1s^2\,2s^2\,2p_x{}^1$
C	$1s^2\,2s^2\,2p_x{}^1\,2p_y{}^1$
N	$1s^2\,2s^2\,2p_x{}^1\,2p_y{}^1\,2p_z{}^1$
O	$1s^2\,2s^2\,2p_x{}^2\,2p_y{}^1\,2p_z{}^1$
F	$1s^2\,2s^2\,2p_x{}^2\,2p_y{}^2\,2p_z{}^1$
Ne	$1s^2\,2s^2\,2p_x{}^2\,2p_y{}^2\,2p_z{}^2$
Na	[Ne] $3s^1$
Mg	[Ne] $3s^2$
Al	[Ne] $3s^2\,3p^1$
Si	[Ne] $3s^2\,3p^2$
P	[Ne] $3s^2\,3p^3$
S	[Ne] $3s^2\,3p^4$
Cl	[Ne] $3s^2\,3p^5$
Ar	[Ne] $3s^2\,3p^6$
K	[Ar] $4s^1$
Ca	[Ar] $4s^2$
Sc	[Ar] $3d^1\,4s^2$
Ti	[Ar] $3d^2\,4s^2$
V	[Ar] $3d^3\,4s^2$
Cr	[Ar] $3d^5\,4s^1$
Mn	[Ar] $3d^5\,4s^2$
Fe	[Ar] $3d^6\,4s^2$
Co	[Ar] $3d^7\,4s^2$
Ni	[Ar] $3d^8\,4s^2$
Cu	[Ar] $3d^{10}\,4s^1$
Zn	[Ar] $3d^{10}\,4s^2$
Ga	[Ar] $3d^{10}\,4s^2\,4p^1$
Ge	[Ar] $3d^{10}\,4s^2\,4p^2$
As	[Ar] $3d^{10}\,4s^2\,4p^3$
Se	[Ar] $3d^{10}\,4s^2\,4p^4$
Br	[Ar] $3d^{10}\,4s^2\,4p^5$
Kr	[Ar] $3d^{10}\,4s^2\,4p^6$

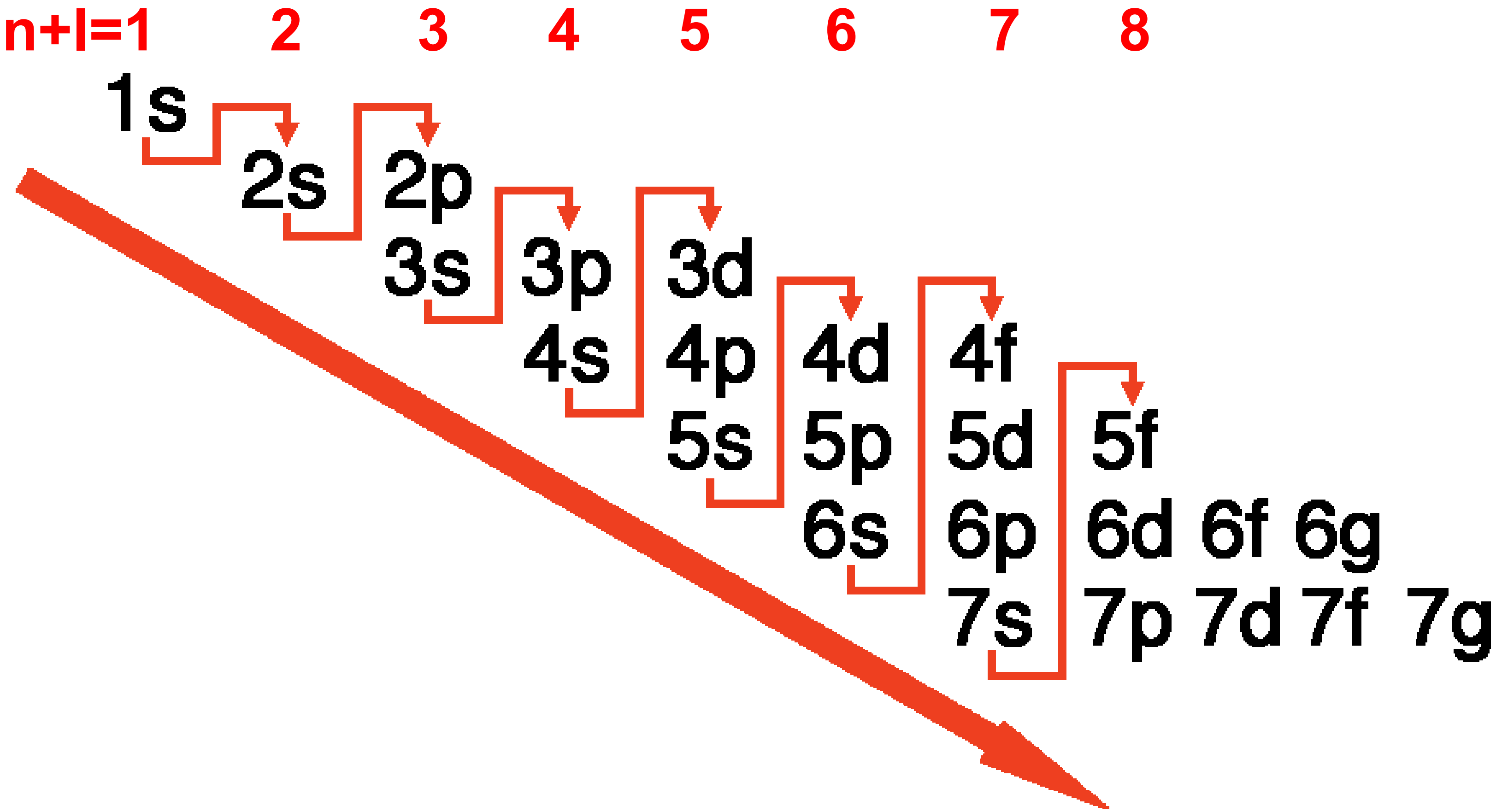
The real atom



The real atom

For a hydrogen like-atoms: minimize n (because E depends only on n)

For a real atoms: minimize *n+l*; for identical *n+l*, minimize *n* (Madelung's Rule)



Nanotechnology

Nanoscale phenomena

Molecular structure and band structure

Molecular structure and band structure: Outline

- Molecular structure
- Band structure

To understand the transition from **atoms** to **molecules** to **solids**
we will look mainly to:

- Electronic configuration of the atoms
- Electronegativity of the atoms

This will allow us to understand the basics of:

- Molecular structure
- Covalent, ionic, and hydrogen bonding
- Polarity of the molecules
- Band structure
- Intermolecular interactions
- …

Why and how atoms forms molecules ?

Why:

- To minimize the total energy (i.e., to achieve a more stable configuration).

Atoms are most stable if they have a completely filled or empty outer layer of electrons.

How:

- When atoms interact to form a chemical bond, only their outer regions are in contact.

For this reason, when we study chemical bonding, we are concerned primarily with the most external (valence) electrons of the atoms.

- Atoms will:

gain or lose electrons (ionic compounds)
share electrons (covalent compounds)

trying to make completely filled or empty "layers".

How we compute the molecular structure ?

- In general, no exact analytical solutions exists for the wavefunctions representing the structure of molecules.

- We can apply different methods to find approximate analytical solutions:

- Molecular orbitals with linear combination of atomic orbitals (MO-LCAO) methods
MO-LCAO methods are based on the assumption that the molecular wavefunctions are the sum of atomic-like wavefunctions.

- Valence band (VB) methods
VB methods are based on the assumption that the molecular wavefunctions are the product of atomic-like wavefunctions.

- To simplify the Hamiltonian of the molecule, all methods apply the Born-Oppenheimer (BO) approximation.

Born-Oppenheimer approximation

The Born-Oppenheimer (BO) approximation consists in assuming that the complete wavefunction decribing the molecule ψ_{total} is given by :

$$\Psi_{total} = \Psi_{electronic}\Psi_{nuclear}$$

$\psi_{electronic}$: Solution of the Schrödinger equation with H containing only the electronic variables

$\psi_{nuclear}$: Solution of the Schrödinger equation with H containing only the nuclear variables

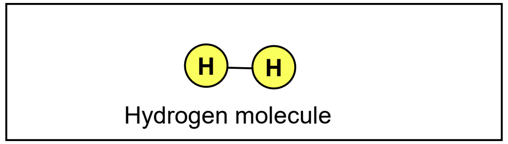
This means, in practice, that to find the "electronic" molecular wavefunction we consider only the "electronic" Hamiltonian (i.e., the nuclei are considered as fixed in space with zero kinetic energy).

The BO approximation success is due to the high ratio between nuclear and electronic masses. It simplify the computation because it simplify the Hamiltonian and reduce the number of spatial variables.

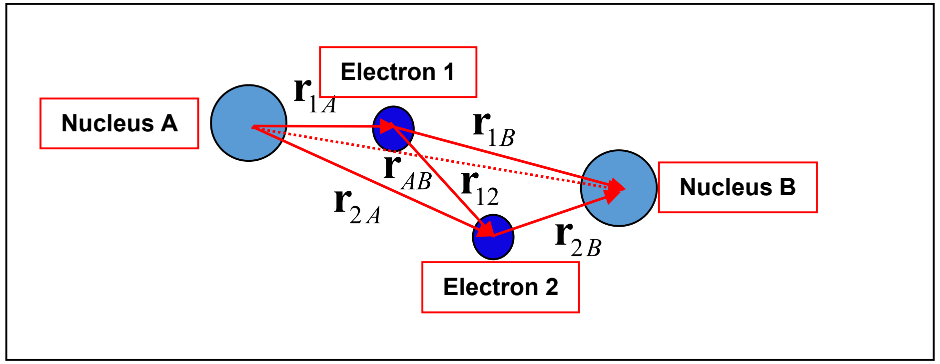
NOTE:To explain the "vibrational" energy levels of a molecule we have, of course, to consider the complete wavefunction ψ_{total} because the nuclei are actually changing their relative position in a molecular "vibration".

Born-Oppenheimer approximation

Example: The Hydrogen molecule H_2



Hydrogen molecule



The complete Hamiltonian for the hydrogen molecule H_2 is:

$$\hat{H} = -\frac{\hbar^2}{2m_A}\left(\nabla_A^2 + \nabla_B^2\right) - \frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}} - \frac{1}{r_{12}} - \frac{1}{r_{AB}}\right)$$

where $\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$

In the Born-Oppenheimer approximation the "electronic" Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}} - \frac{1}{r_{12}} - \frac{1}{r_{AB}}\right)$$

We solve the "electronic" Hamiltonian for a given distance between the nuclei r_{AB}.

The actual value of r_{AB} is the one which minimize the energy of the system.

Linear Combination of Atomic Orbitals (LCAO)

- First guess:

$$\Psi_{m,k} = \sum_{i=1}^{N} c_{i,k} \Psi_{a,i}$$

$$\Psi_{a,i} \text{ with } i = 1 \ldots n: \text{ Solutions of Schrodinger eq. with Hamiltonian of the single atom A}$$

$$\Psi_{a,i} \text{ with } i = (n+1) \ldots N: \text{ Solutions of Schrodinger eq. with Hamiltonian of the single atom B}$$

- Procedure:
  - Choose "trial" coefficients $c_{i,k}$
  - Introduce $\psi_{m,k}$ in Schrödinger eq. with the Hamiltonian of the 2 atoms system $\hat{H}$
  - Calculate energy E_k
  - Find $\{c_{i,k}\}$ that minimise E_k
  - Normalize wavefunctions $\psi_{m,k}$

$$E_k = \frac{\sum_{ij} c_{i,k} c_{j,k} H_{ij}}{\sum_{ij} c_{i,k} c_{j,k} S_{ij}}$$

$$H_{ij} = \int \Psi^*_{a,i} \hat{H} \Psi_{a,j} dV$$

$$S_{ij} = \int \Psi^*_{a,i} \Psi_{a,j} dV$$

H_{ii}: Coulomb integral

S_{ij}: Overlap integral (S_{ii} = 1, S_{ij} = 0 if i and j belongs to same atom)

$\hat{H}$: Total Hamiltonian of the 2 atoms system

Linear Combination of Atomic Orbitals (LCAO)

Some details about the LCAO method:

The molecular wavefunction has to be solution of the Schrodinger equation

$$\hat{H}\Psi_{m,k} = E_k \Psi_{m,k}$$

where $\hat{H}$ is the total Hamiltonian of the system of n atoms.

The expectation value for the energy is:

$$\int \Psi_{m,k}^{*} \hat{H} \Psi_{m,k} dV = E_k \int \Psi_{m,k}^{*} \Psi_{m,k} dV$$

Consequently, the energy is given by:

$$E_k = \frac{\int \Psi_{m,k}^{*} \hat{H} \Psi_{m,k} dV}{\int \Psi_{m,k}^{*} \Psi_{m,k} dV} = \frac{\sum_{ij} c_{i,k} c_{j,k} H_{ij}}{\sum_{ij} c_{i,k} c_{j,k} S_{ij}}$$

where we assumed

$$\Psi_{m,k} = \sum_{i=1}^{N} c_{i,k} \Psi_{a,i}$$

and defined

$$H_{ij} = \int \Psi_{a,i}^{*} \hat{H} \Psi_{a,j} dV$$

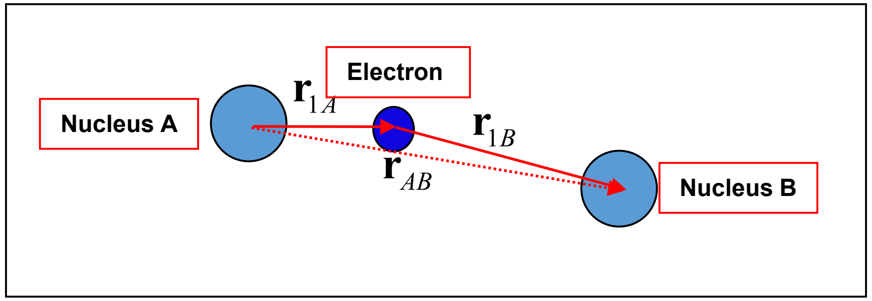
$$S_{ij} = \int \Psi_{a,i}^{*} \Psi_{a,j} dV$$

The coefficients $c_{i,k}$ and $c_{j,k}$ are obtained by:

1) Minimization of E_k

2) Normalization of $\Psi_{m,k}$ (i.e., $\int \Psi_{m,k}^{*} \Psi_{m,k} dV = 1$)

The hydrogen molecule ion H_2^+



The hydrogen molecule ion H_2^+ is the simplest molecule.

The complete Hamiltonian of the H_2^+ molecule is:

$$H = -\frac{\hbar^2}{2m_A}\left(\nabla_A^2 + \nabla_B^2\right) - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} - \frac{1}{r_{AB}}\right)$$

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

In the Born-Oppenheimer approximation we neglect the kinetic energy of the nuclei and we consider only the "electronic" Hamiltonian given by:

$$H_{el} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} - \frac{1}{r_{AB}}\right)$$

The hydrogen molecule ion H_2^+

If we apply the LCAO method to the H_2^+ we can assume that the molecular wavefunctions are given by

$\Psi_{m,k} = c_{1,k}\left|\psi_{1S,1}\right\rangle + c_{2,k}\left|\psi_{1S,2}\right\rangle$ (i.e., we consider only the ground state of the two atoms)

where:

$\left|\psi_{1S,1}\right\rangle = \left(1/\pi r_0^3\right)e^{-r_{1A}/r_0}, \left|\psi_{1S,2}\right\rangle = \left(1/\pi r_0^3\right)e^{-r_{1B}/r_0}$ (1s state of the hydrogen atom).

Appling the LCAO method we get two possible wavefunctions for the H_2^+ molecule:

$$\psi_{m,S} = \frac{1}{\sqrt{2(1+S_{12})}}\left(\left|\psi_{1S,1}\right\rangle + \left|\psi_{1S,2}\right\rangle\right) \qquad \psi_{m,A} = \frac{1}{\sqrt{2(1-S_{12})}}\left(\left|\psi_{1S,1}\right\rangle - \left|\psi_{1S,2}\right\rangle\right)$$

$$E_{m,S} = \frac{E+H_{12}}{1+S} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}} \qquad E_{m,A} = \frac{E-H_{12}}{1-S} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}}$$

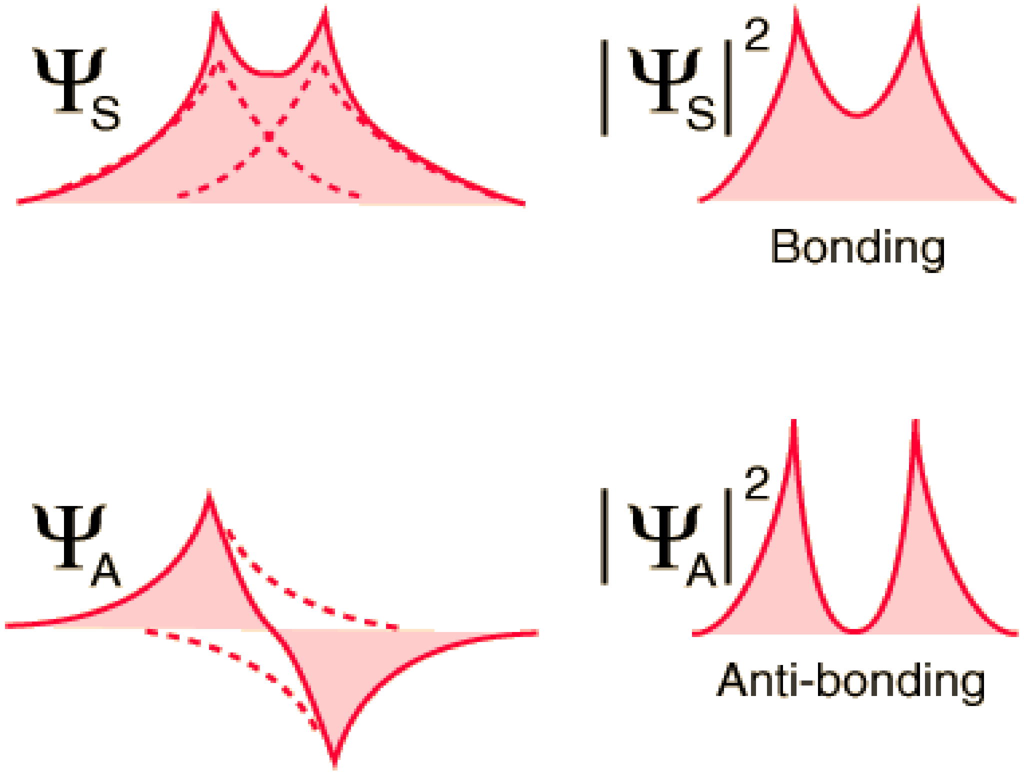
where:

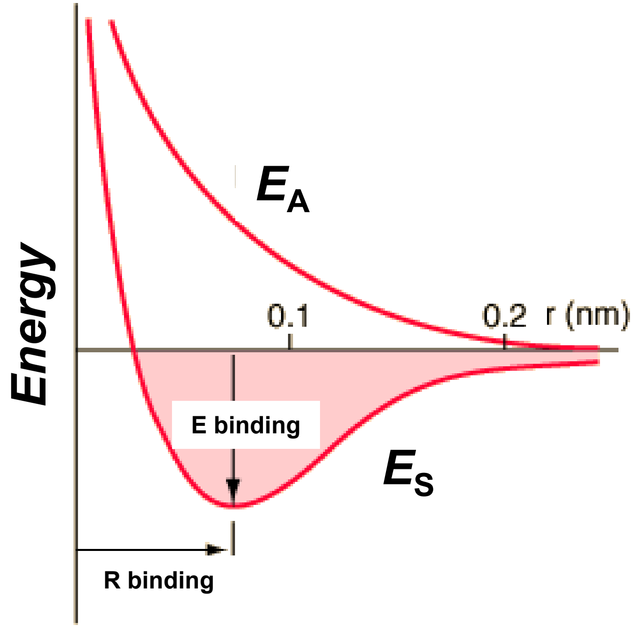
$E = H_{11} = H_{22} = \left\langle\psi_{1S,1}\middle|H_{el}\middle|\psi_{1S,1}\right\rangle = \left\langle\psi_{1S,2}\middle|H_{el}\middle|\psi_{1S,2}\right\rangle$ (Energy of the 1s state of the hydrogen atom)

$S = S_{12} = S_{21} = \left\langle\psi_{1S,1}\middle|\psi_{1S,2}\right\rangle$ (Overlap integral of the two atomic wavefunctions)

$H_{12} = H_{21} = \left\langle\psi_{1S,1}\middle|H_{el}\middle|\psi_{1S,2}\right\rangle = \left\langle\psi_{1S,2}\middle|H_{el}\middle|\psi_{1S,1}\right\rangle$

The hydrogen molecule ion H_2^+



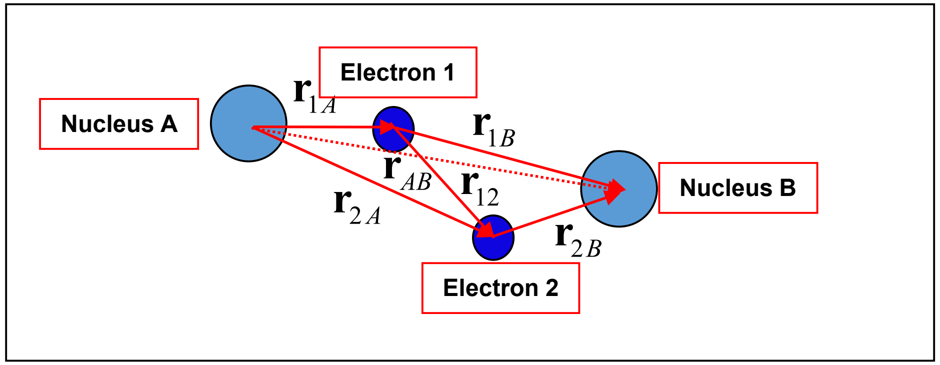


http://hyperphysics.phy-astr.gsu.edu

	MO	Exper.
Bond distance (Å)	1.33	1.06
Binding energy (eV)	-1.77	-2.8

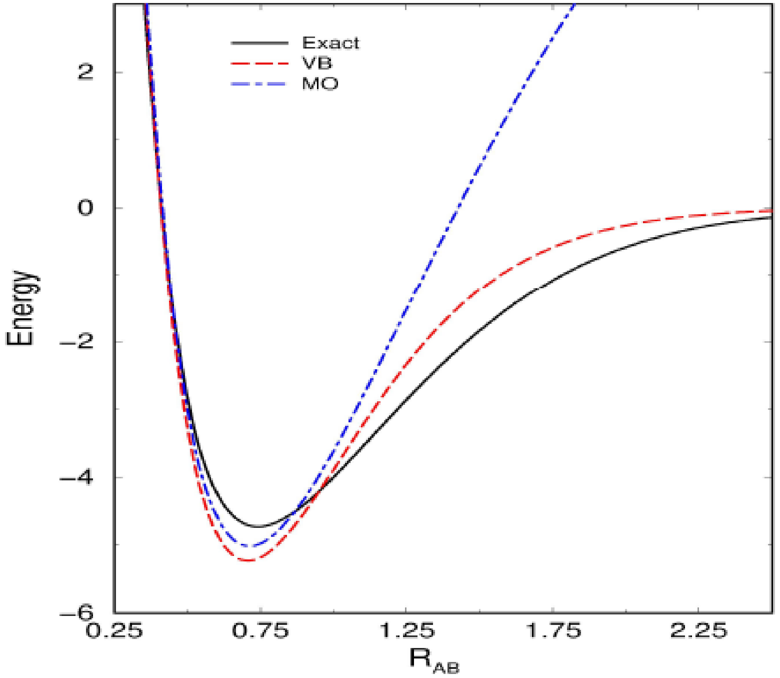
Exper.: From experimental results
MO: From molecular orbital theory calculation
(with LCAO with 1s wavefunctions as base).

The hydrogen molecule H_2



The "electronic" Hamiltonian of a system consisting of two hydrogen atoms is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}} - \frac{1}{r_{12}} - \frac{1}{r_{AB}}\right)$$

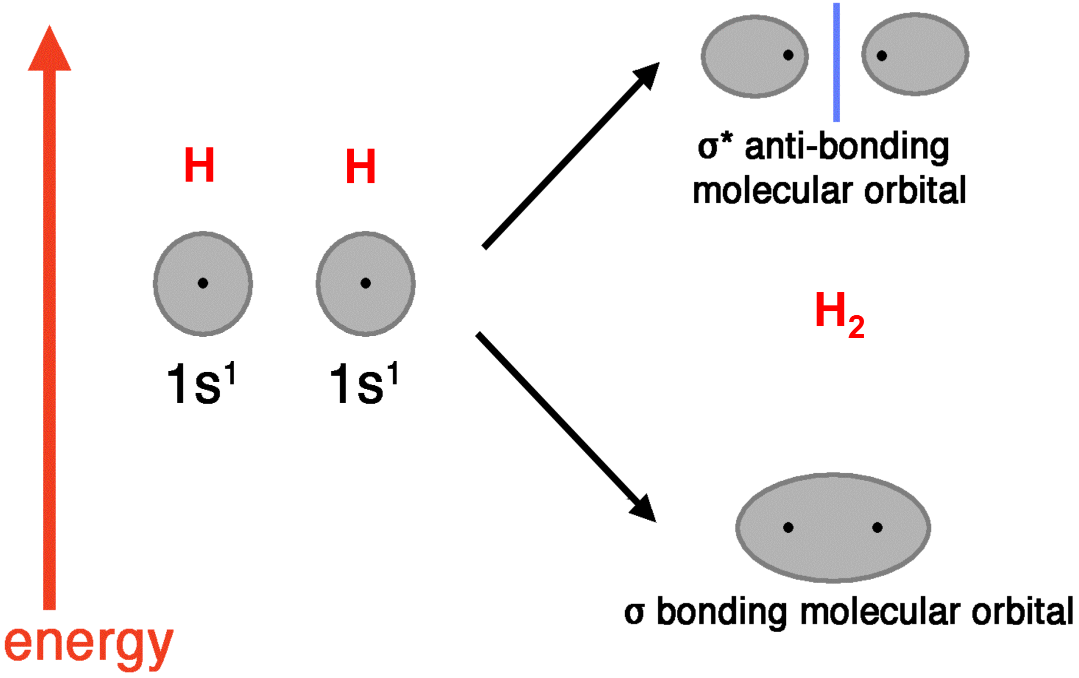


	MO	VB	Exper.
Bond distance (Å)	0.72	0.71	0.74
Binding energy (eV)	5.0	5.2	4.75

Exper./Exact: From experimental results
VB: From valence band theory calculations
MO: From molecular orbital theory calculation
(with LCAO with 1s wavefunctions as base).

The hydrogen molecule H_2

Redrawn from chemguide.co.uk, 2010

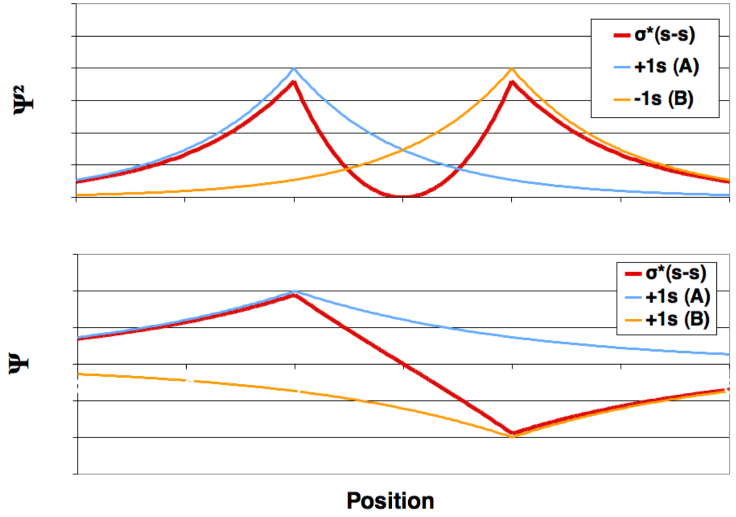


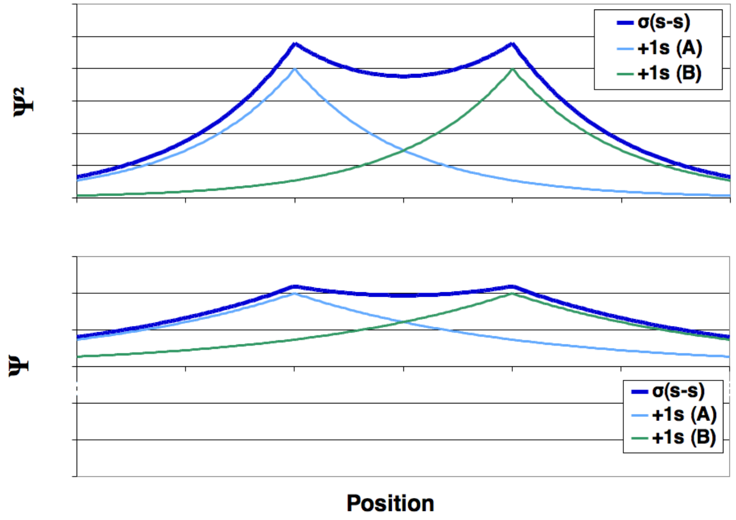
“node” where there is zero chance of finding the electrons

σ* anti-bonding molecular orbital

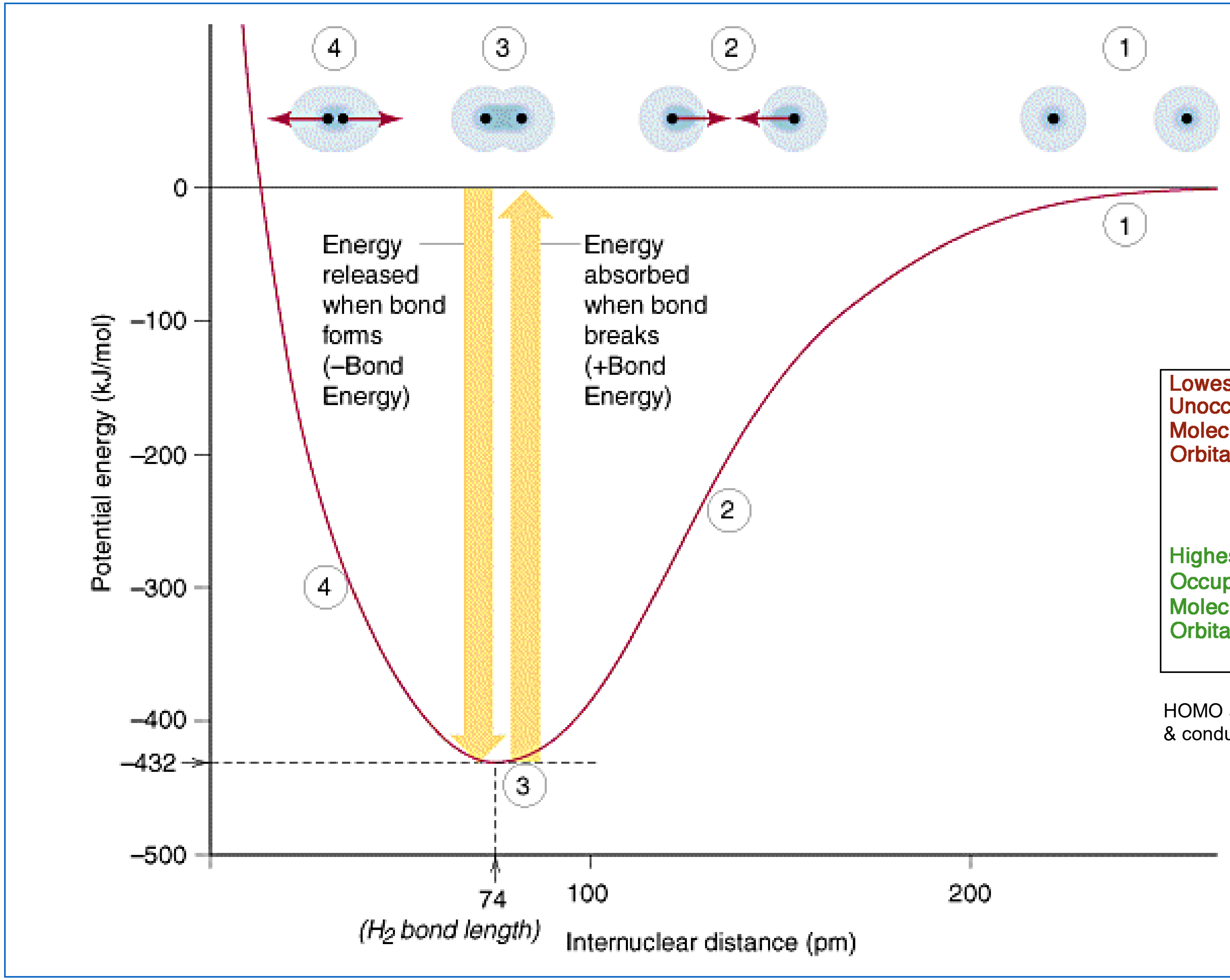
H_2

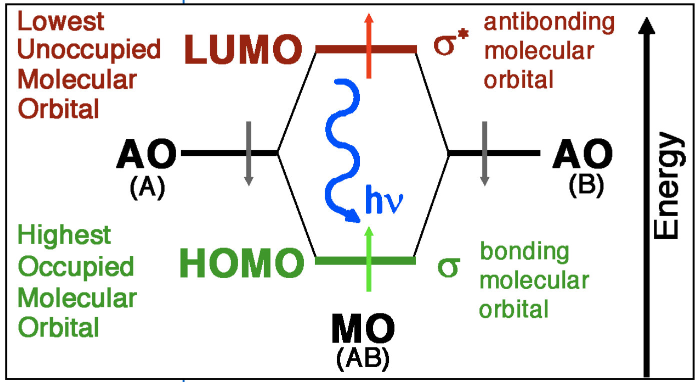
σ bonding molecular orbital





The hydrogen molecule H_2

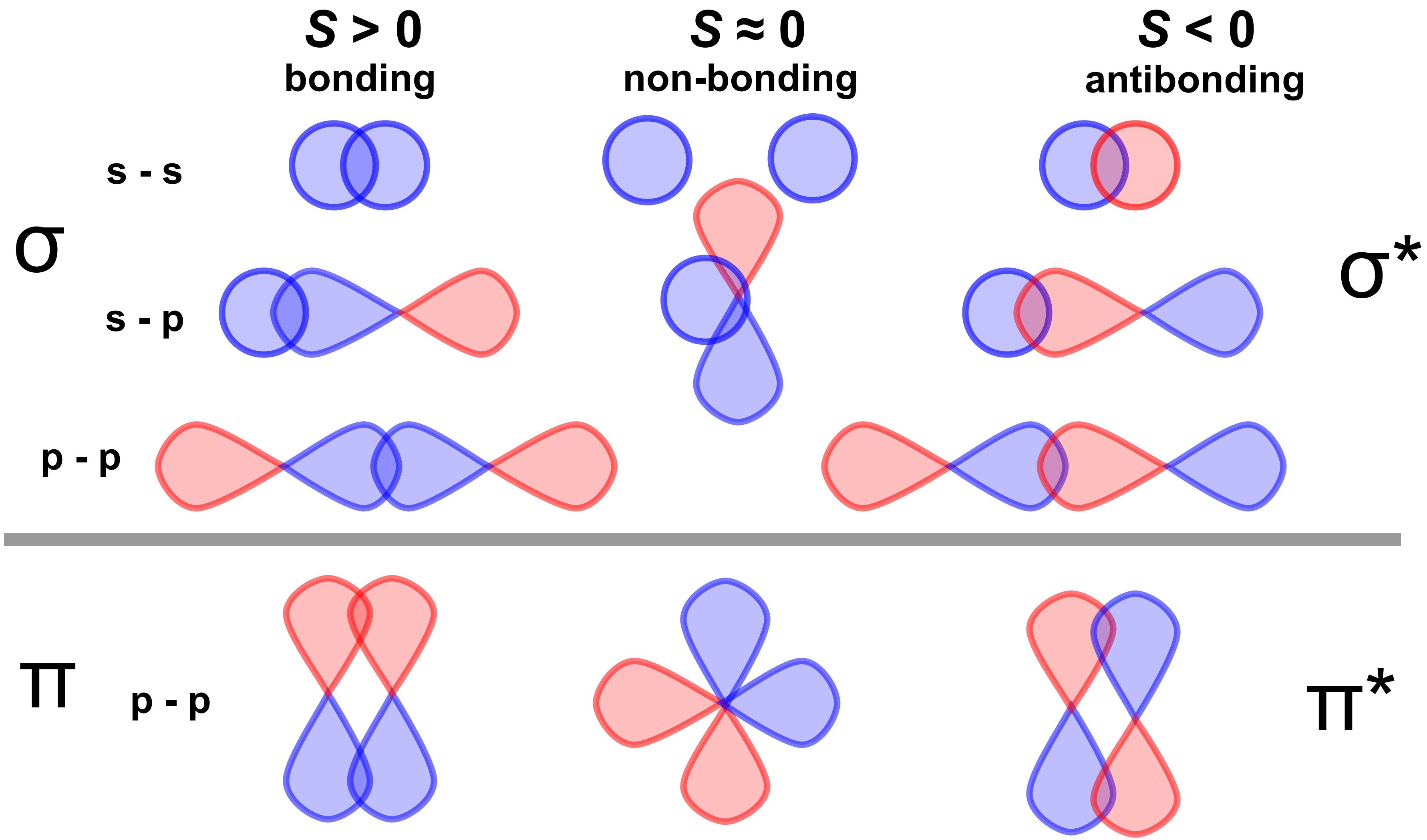




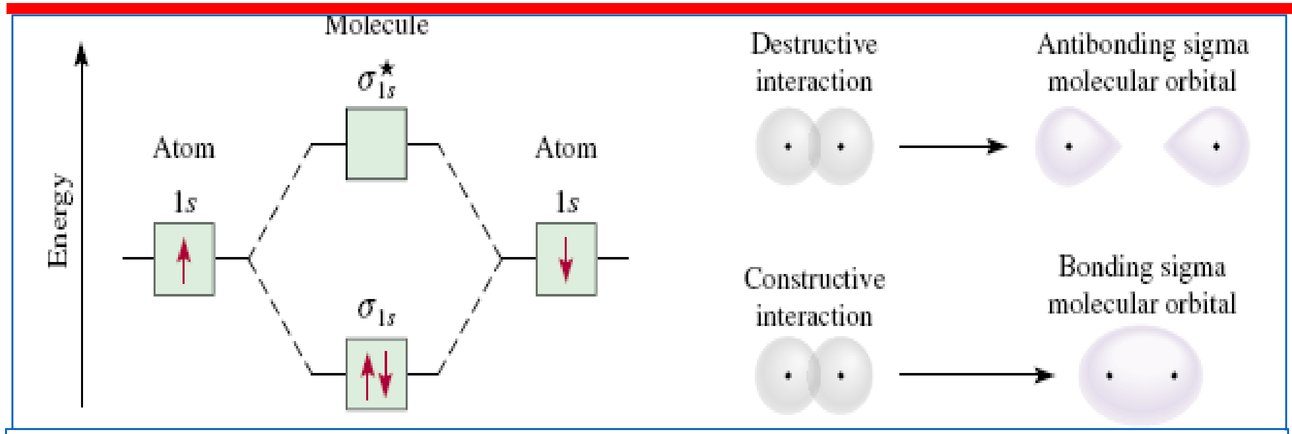
HOMO and LUMO are somehow the "precursors" of the valence & conduction band of an insulating / semiconducting crystals.

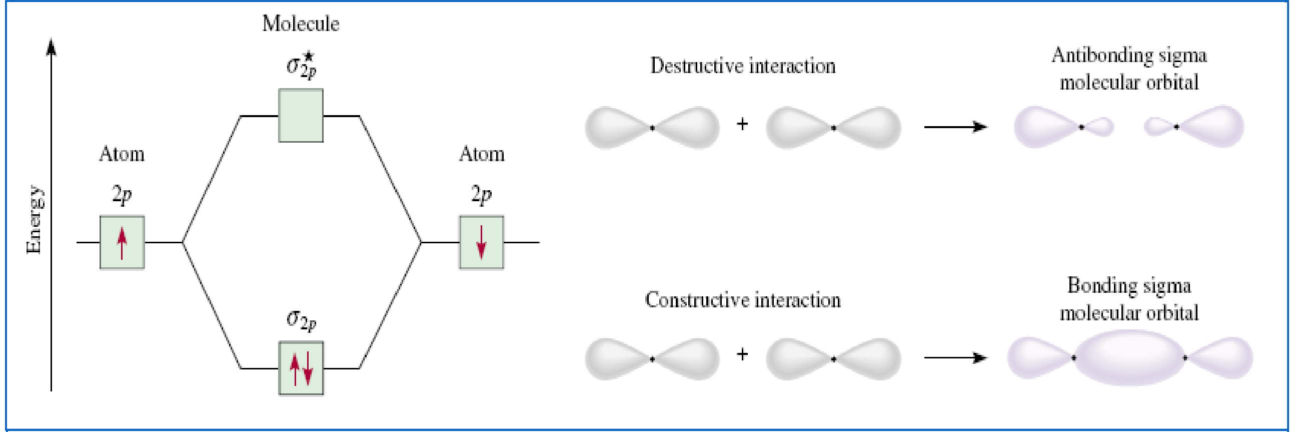
LCAO: Simple rules for strong bond

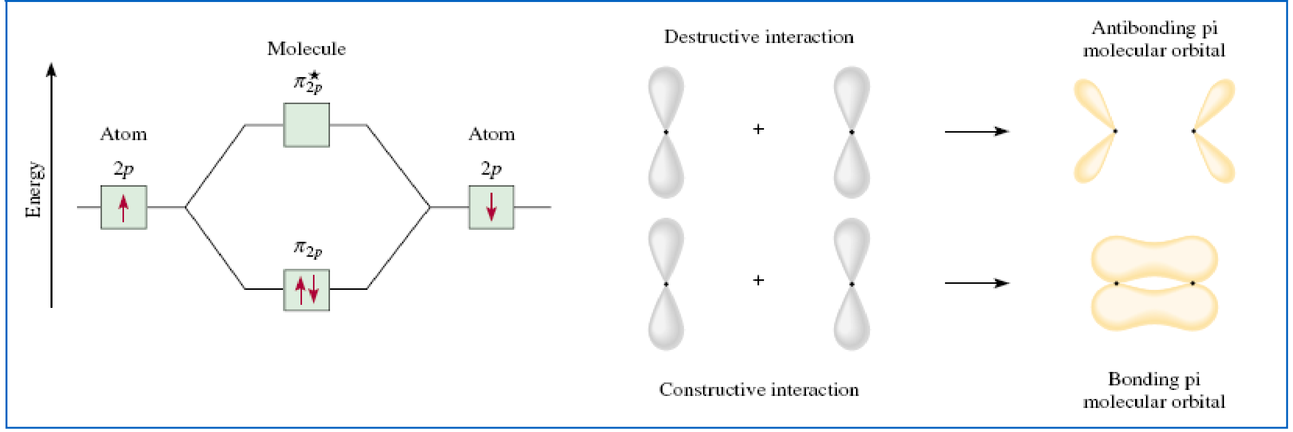
- Close values of corresponding energies of the atomic wave functions
- Large overlap integral S
- Ψ_A and Ψ_B must have identical symmetry along bond axis



Shape of some molecular orbitals







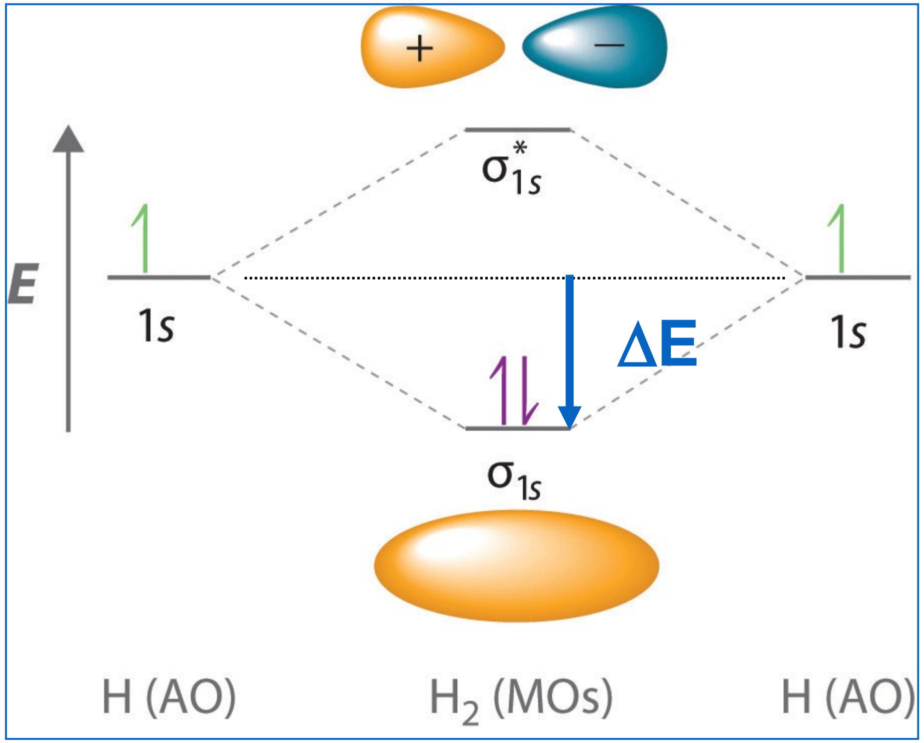
The shape of the molecular orbitals is obtained from the shape of the atomic orbitals which are combined.

Why hydrogen molecules H_2 exists ?

For H_2 we have to place 2 electrons.

The lower energy state is with 2 electrons
into the bonding molecular orbital.

The total energy of the H_2 molecule
is lower than the total energy of the H atoms separated
→
the H atoms prefers to form H_2 molecules
instead of remain separated.



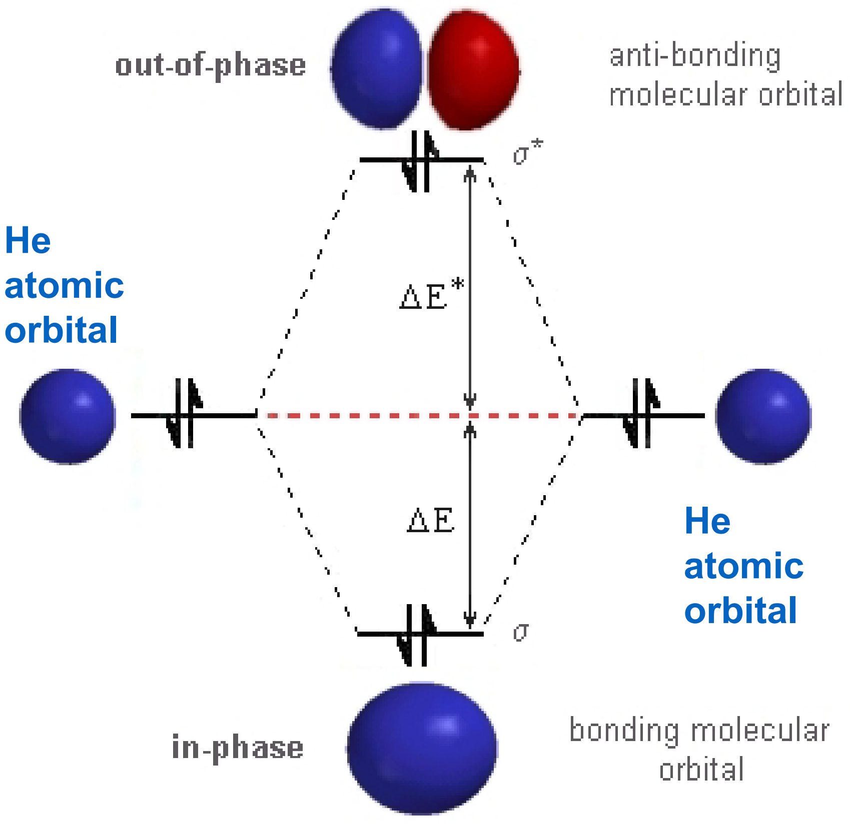
http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch02/heliummo01.jpg

Why helium molecules He_2 does not exist ?

Same diagram of hydrogen H_2 molecules.
(same atomic orbitals, the 1s orbitals).

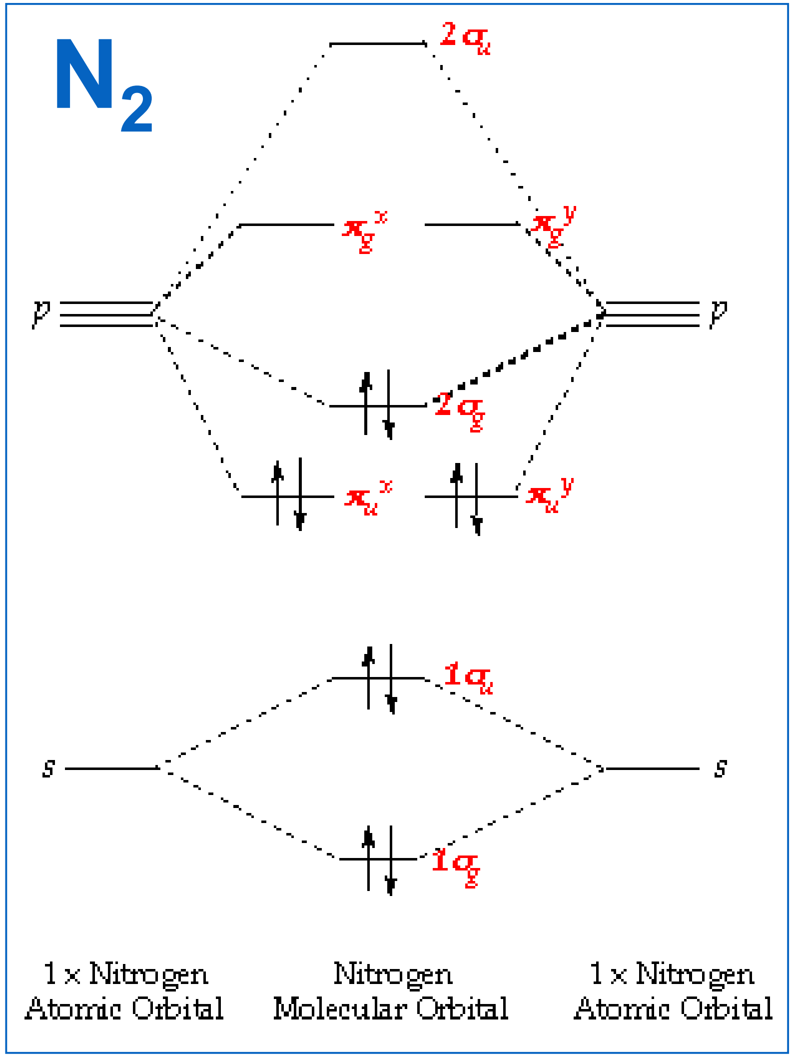
For He_2 we have to place 4 electrons.
2 electrons into the bonding molecular orbital.
2 electrons into the anti-bonding molecular orbital.

It can be computed that $\Delta E^* > \Delta E$.
→ the total energy of the two
He atom separated is lower than the
total energy of the He_2 molecule.
→ the He atoms prefers to stay separated !!

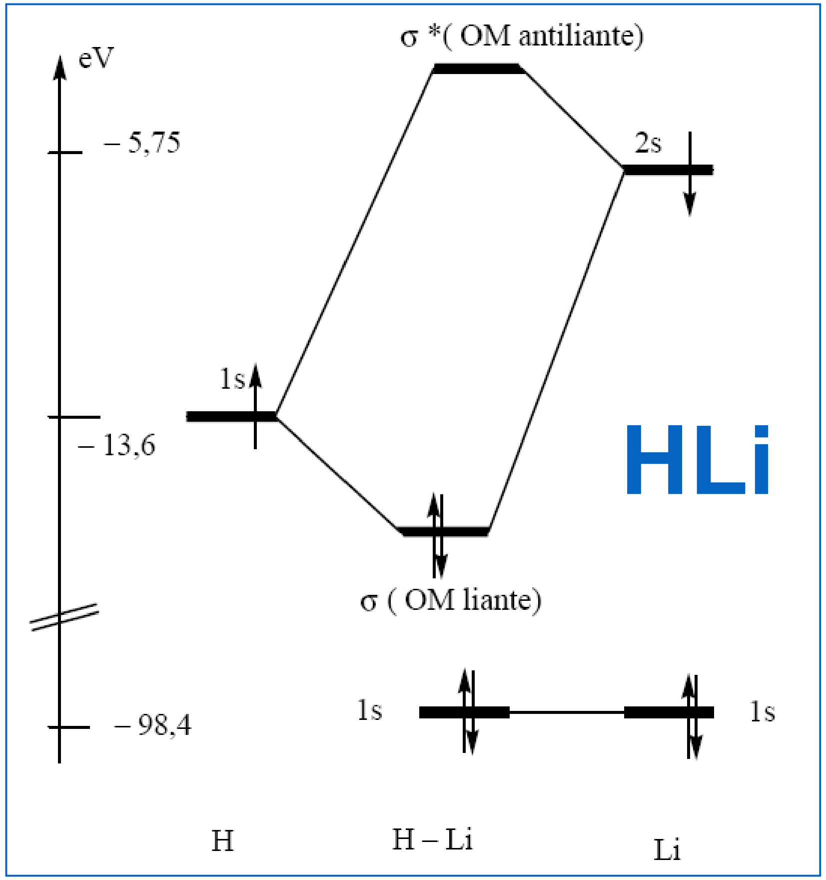


http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch02/heliummo01.jpg

Molecular orbitals of some molecules

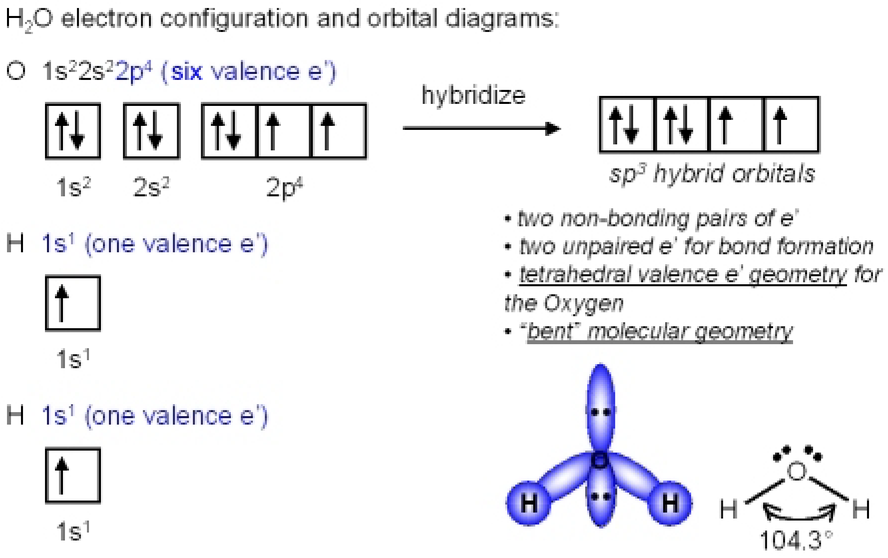


Two of the three Li electrons remains close to each of the Li atoms in a almost unperturbed 1s state of the Li atom.The third Li electron goes into a MO together with the H electron.



Molecular orbitals of some molecules

H_2O (water)



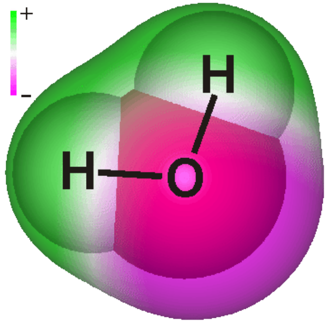
H_2O electron configuration and orbital diagrams:

O $1s^2 2s^2 2p^4$ (six valence e$^-$)

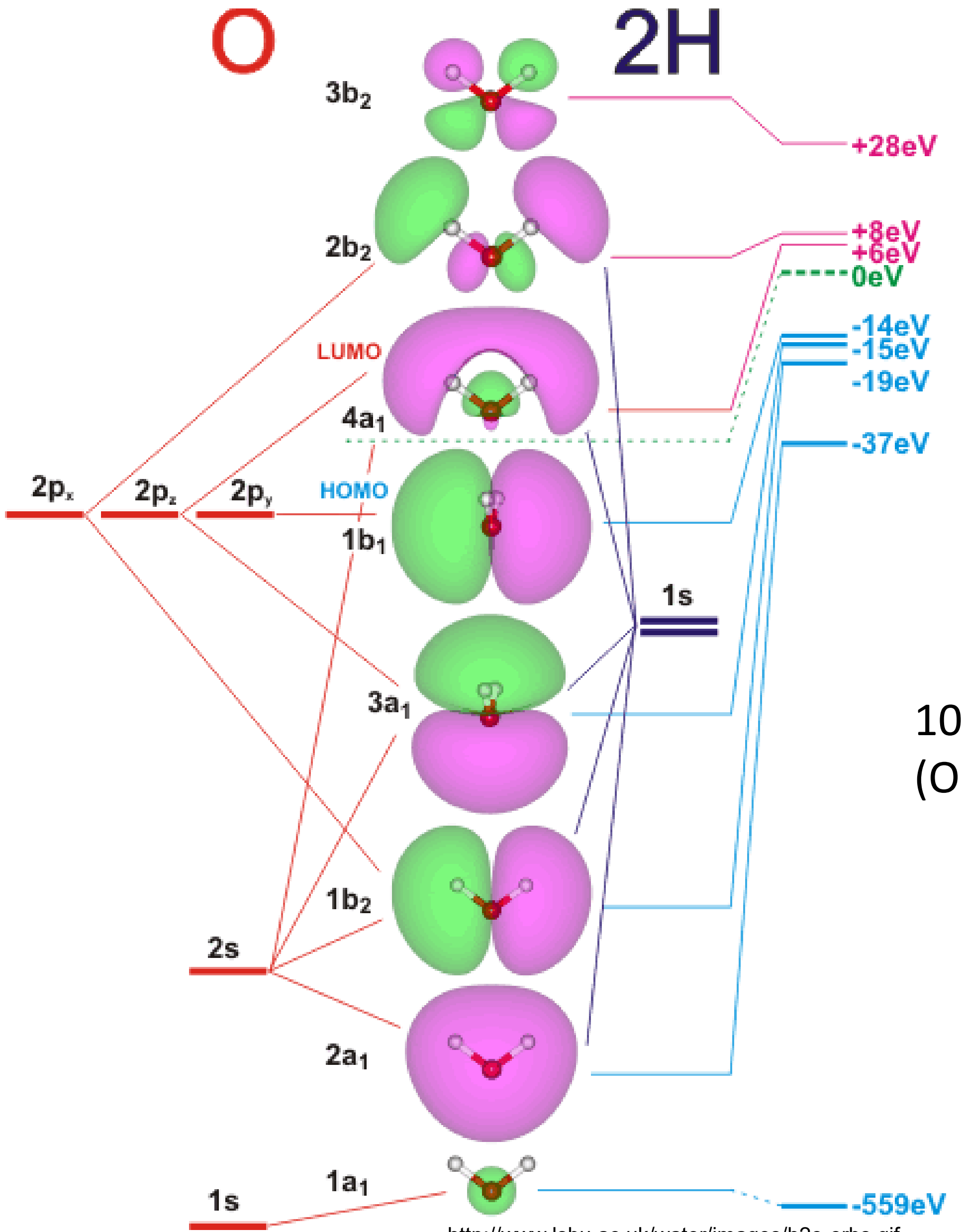
- two non-bonding pairs of e$^-$
- two unpaired e$^-$ for bond formation
- tetrahedral valence e$^-$ geometry for the Oxygen
- "bent" molecular geometry

H $1s^1$ (one valence e$^-$)

H $1s^1$ (one valence e$^-$)



http://www1.lsbu.ac.uk/water/h2o_orbitals.html



http://www.lsbu.ac.uk/water/images/h2o-orbs.gif

10 electrons
(O:8, 2H:2)

Interactions between atoms and molecules

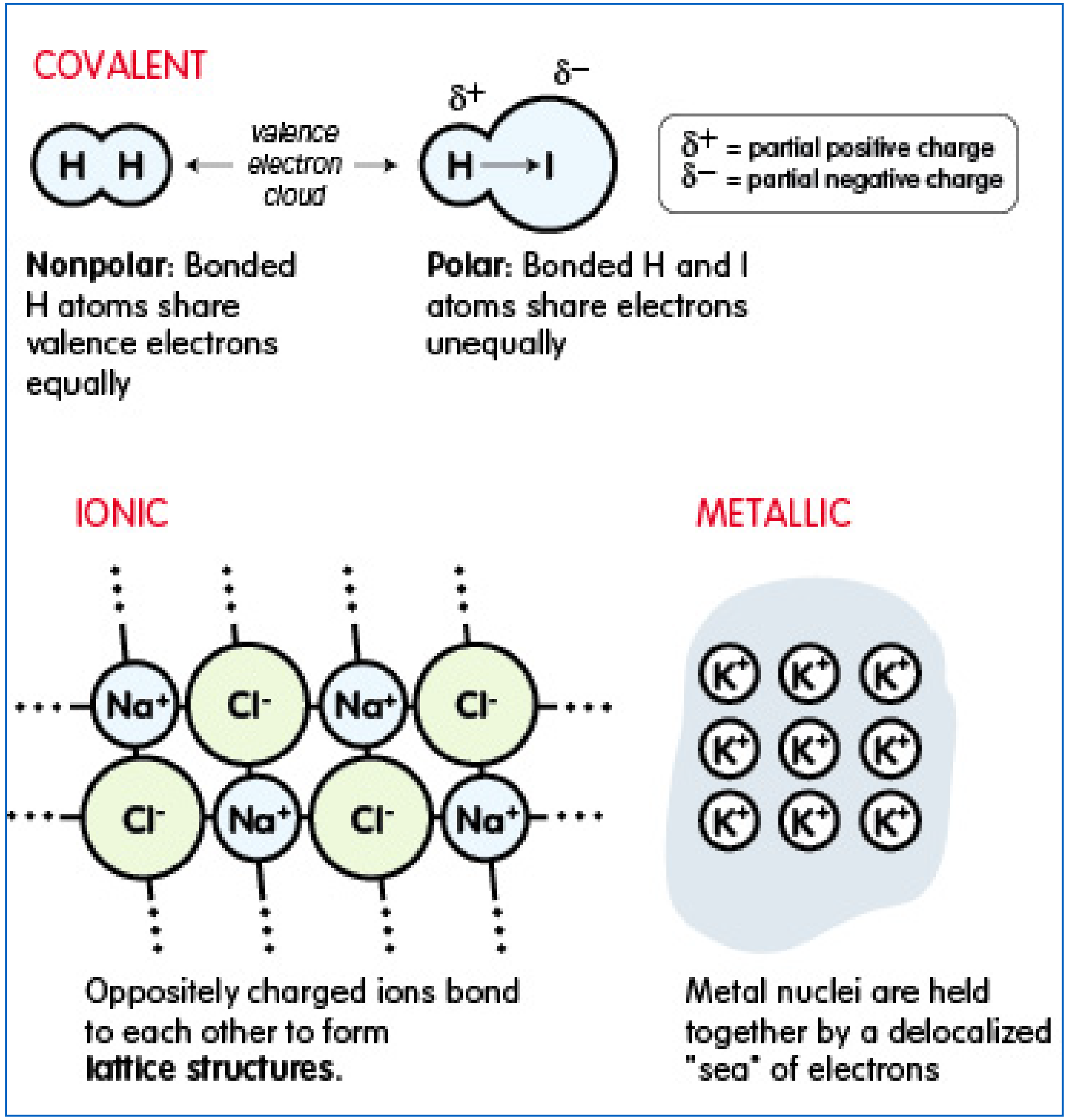
	Type	Strength (kJ/mol)	Example	Simplified description
Covalent bond	**Intra**molecular **Inter**atomic	Strong (100-1000)	H_2	Two atoms share valence electrons. The electrons of one atom are attracted by both nuclei.
Ionic bond	**Intra**molecular **Inter**atomic	Strong	Na^+Cl^-	The electrons are not shared. One atom accepts or donates one or more of its valence electrons to another atom. Electrostatic attractions between the ions.
Metallic bond	**Inter**atomic	Strong	Au	Metallic atoms that share valence electrons with many others. Each atom donates electrons to a "sea" of electrons.
Hydrogen-bond	**Inter**molecular **Intra**molecular	Weak (5-30)	Between H_2O molecules	Dipole-dipole interactions (between permanent dipoles). Forms between bonded hydrogen atoms and opposite charged molecules.
Van der Walls forces	**Inter**molecular **Inter**atomic	Weak	Between two graphite sheets	Dipole-dipole interactions.

$$\begin{aligned} 1000\ \text{kJ/mol} &\rightarrow 10\ \text{eV/molecule} \\ 100\ \text{kJ/mol} &\rightarrow 1\ \text{eV/molecule} \\ 10\ \text{kJ/mol} &\rightarrow 0.1\ \text{eV/molecule} \end{aligned}$$

Thermal energy:

$$k_B T \cong 0.026\ \text{eV} \quad @T = 300\ \text{K}$$

Interactions between atoms and molecules



Nonpolar: Bonded H atoms share valence electrons equally

Polar: Bonded H and I atoms share electrons unequally

Oppositely charged ions bond to each other to form **lattice structures.**

Metal nuclei are held together by a delocalized "sea" of electrons

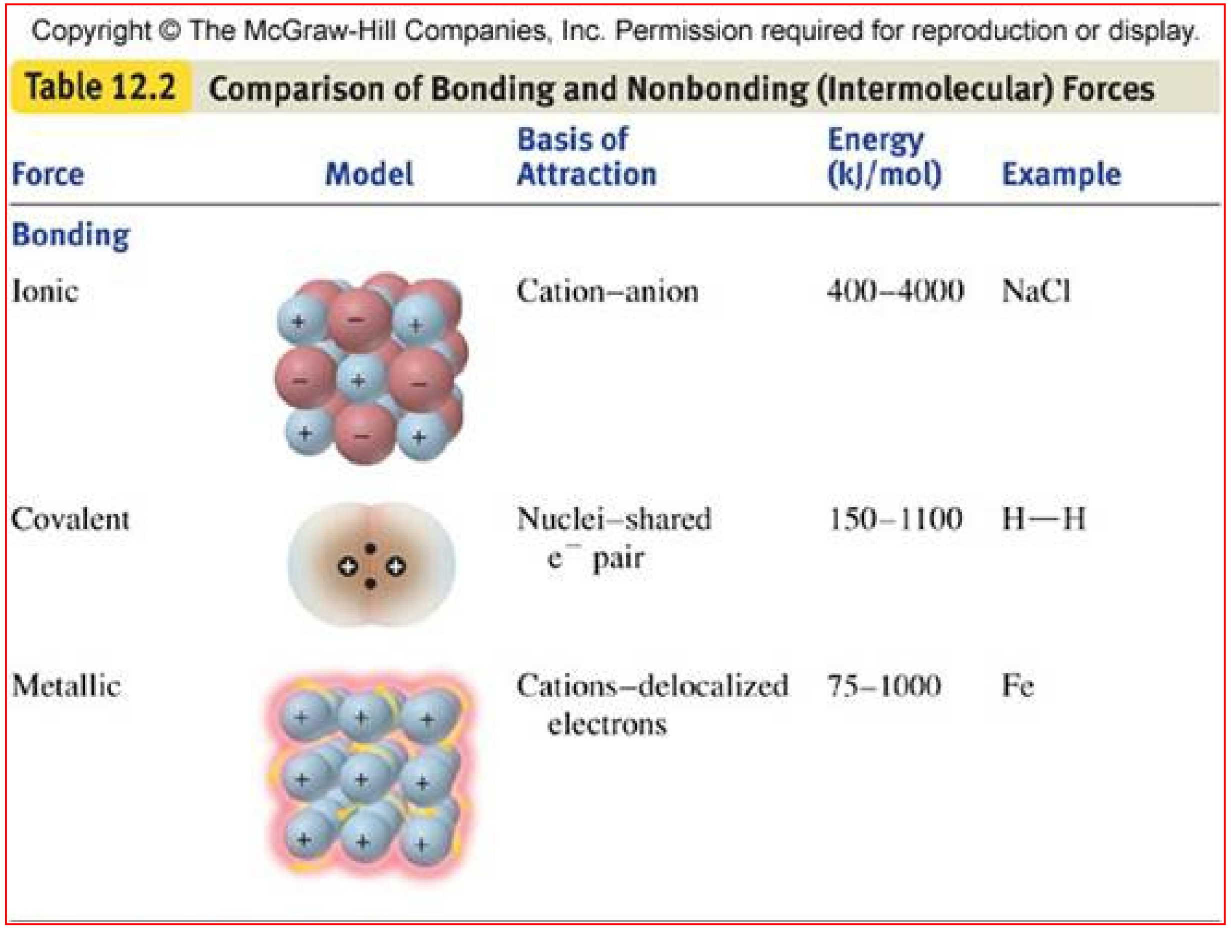


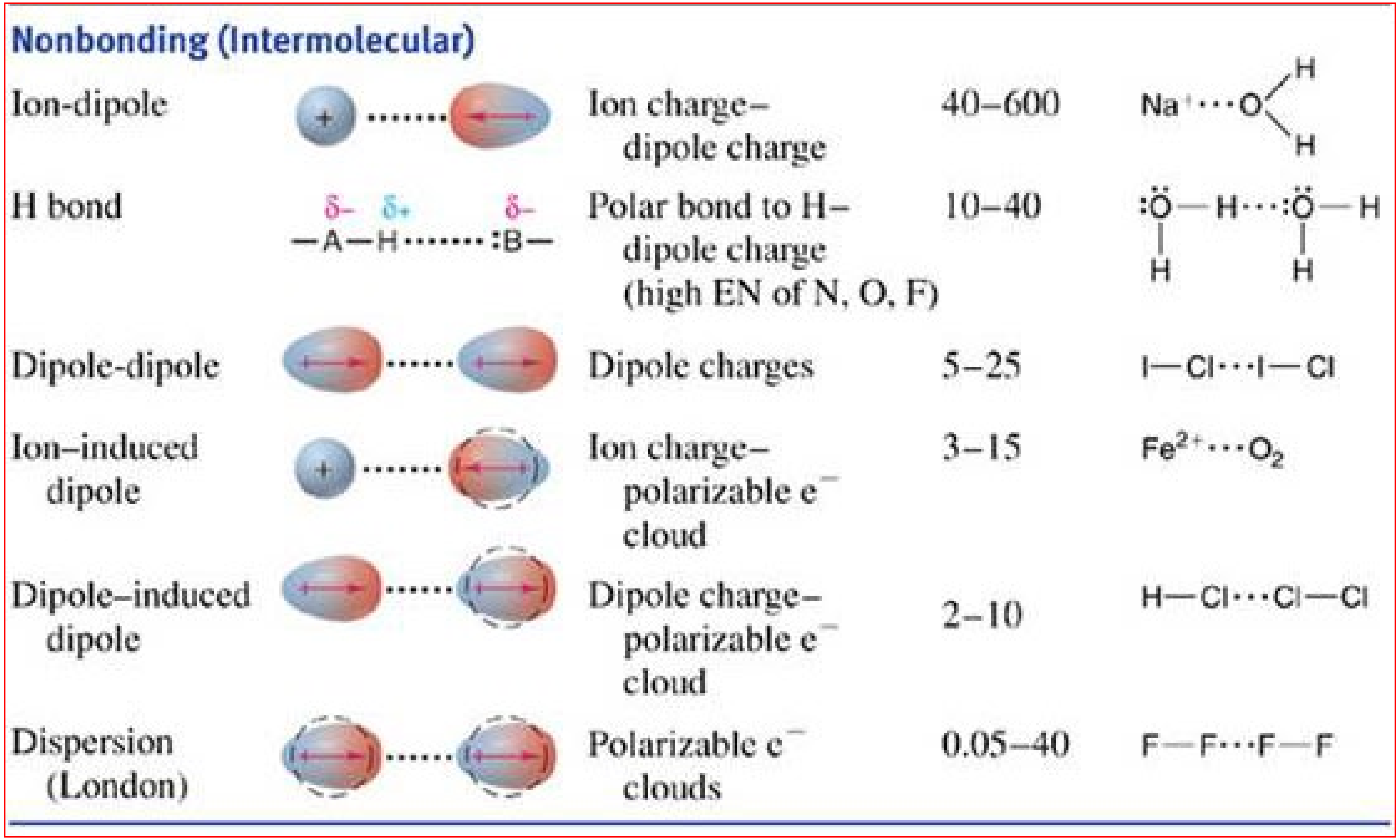
Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e⁻ pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

Interactions between atoms and molecules

Hydrogen-bond

Van der Walls forces



Nonbonding (Intermolecular)

Ion-dipole		Ion charge–dipole charge	40–600	$\mathrm{Na^+\cdots O(H)H}$
H bond	$\overset{\delta-}{-A}-\overset{\delta+}{H}\cdots\cdots\overset{\delta-}{:B}-$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$\underset{H}{:\ddot{O}}-H\cdots\underset{H}{:\ddot{O}}-H$
Dipole-dipole		Dipole charges	5–25	$\mathrm{I-Cl\cdots I-Cl}$
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$\mathrm{Fe^{2+}\cdots O_2}$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	$\mathrm{H-Cl\cdots Cl-Cl}$
Dispersion (London)		Polarizable e^- clouds	0.05–40	$\mathrm{F-F\cdots F-F}$

Ionic bond and covalent bond

Ionic bonds:
«Pure» (unrealistic) ionic bond: electrons are localized on one of the two atoms in the bond.

Pure ionic bonds can be understood by classical physics.

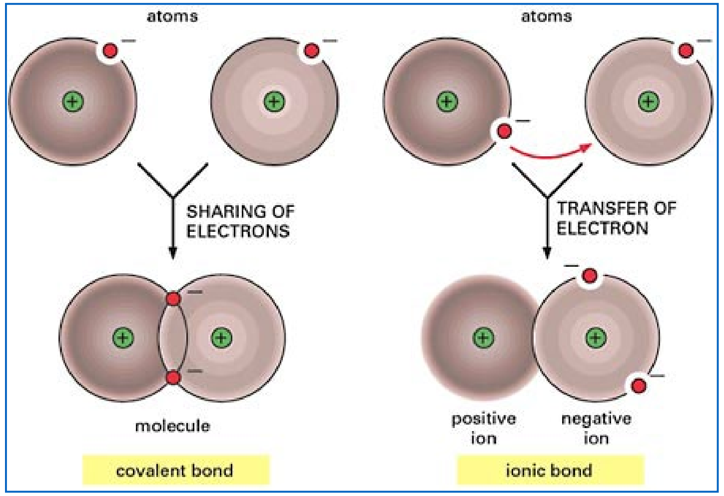
The forces between the atoms are characterized by isotropic continuum electrostatic potentials.
Their magnitude is proportional to the charge difference.

Covalent bonds:
The electron density within a bond is not assigned to individual atoms, but is instead delocalized between atoms.

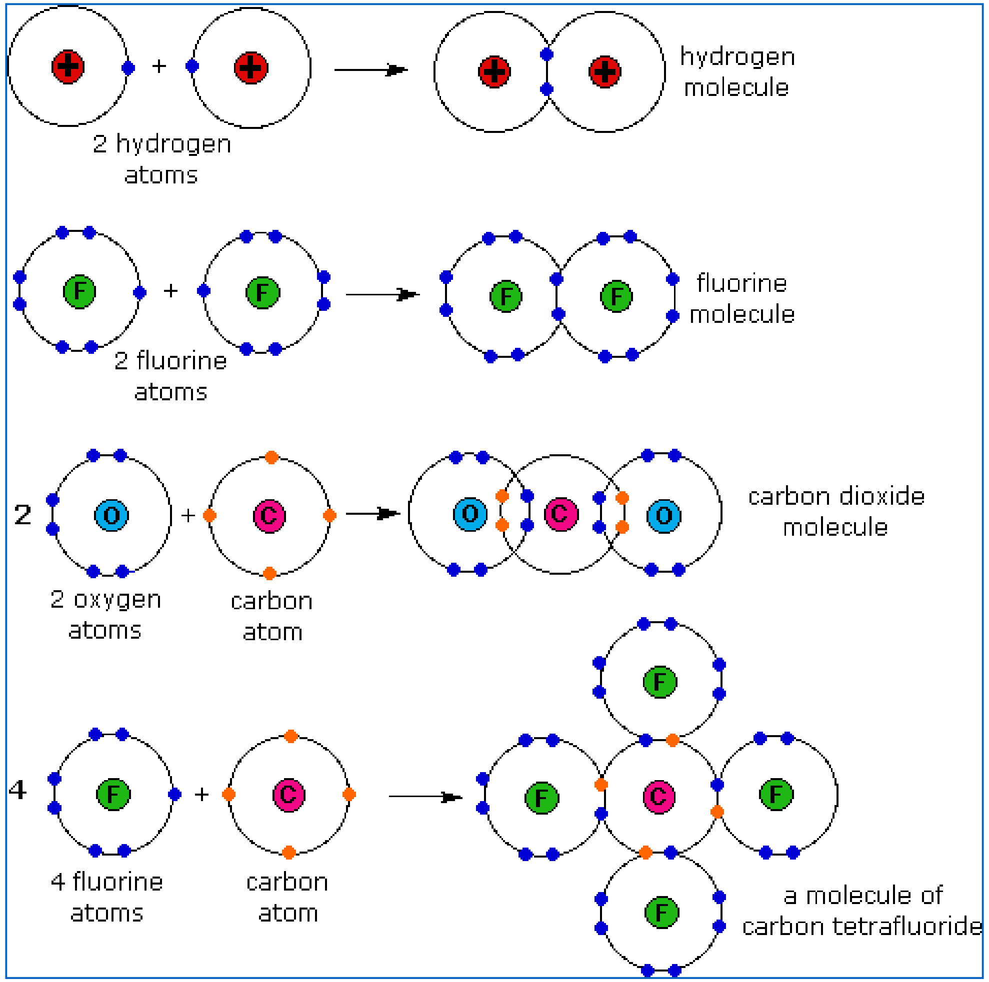
Covalent bonds are understood by quantum mechanics theories.
(valence bond (VB) or molecular orbital (MO) theory).

Covalent bonds may have directed anisotropic properties.
These may have their own names, such as sigma bond and pi bond.

Note:
In general, atoms form bonds that are intermediates between ionic and covalent, depending on the relative electronegativity of the atoms involved.



Covalent bond: Examples

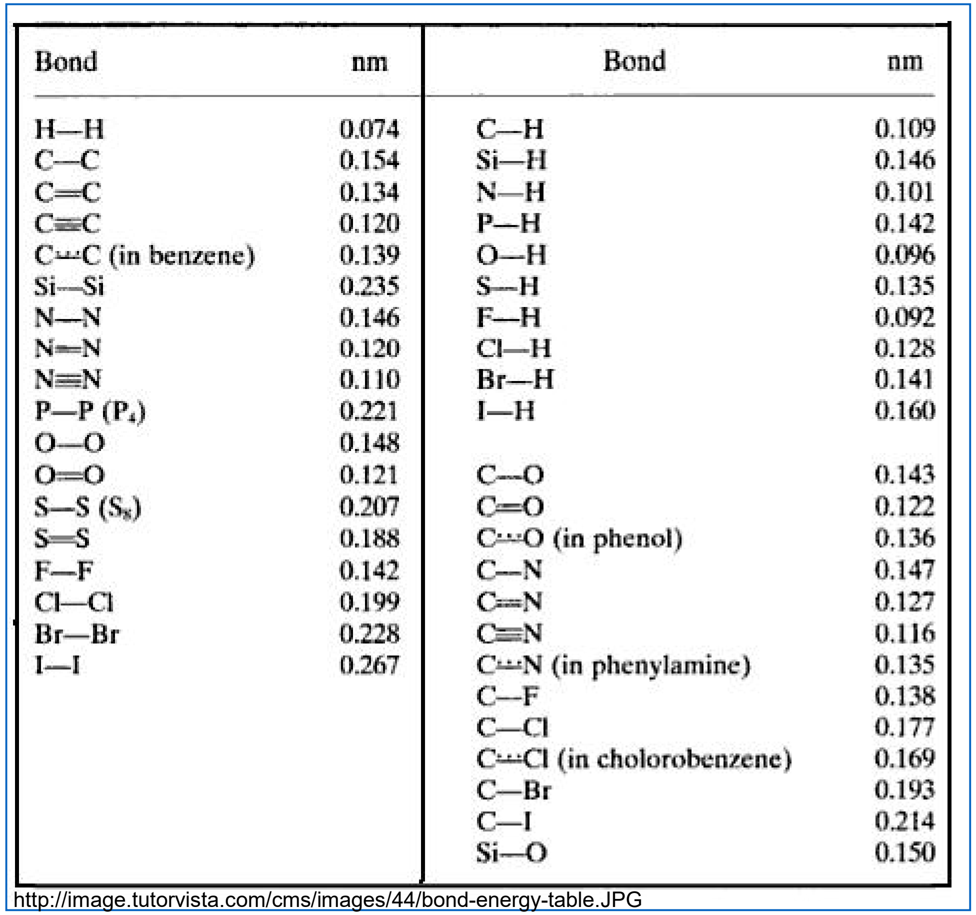


http://kgortney.pbworks.com/f/1288884584/lewisCovalentBonding.gif

- Covalent elements:
H_2, Li_2, B_2, C_2, N_2, O_2, F_2, Cl_2, S_8, P_4, I_2, diamond, graphite, silicon,….

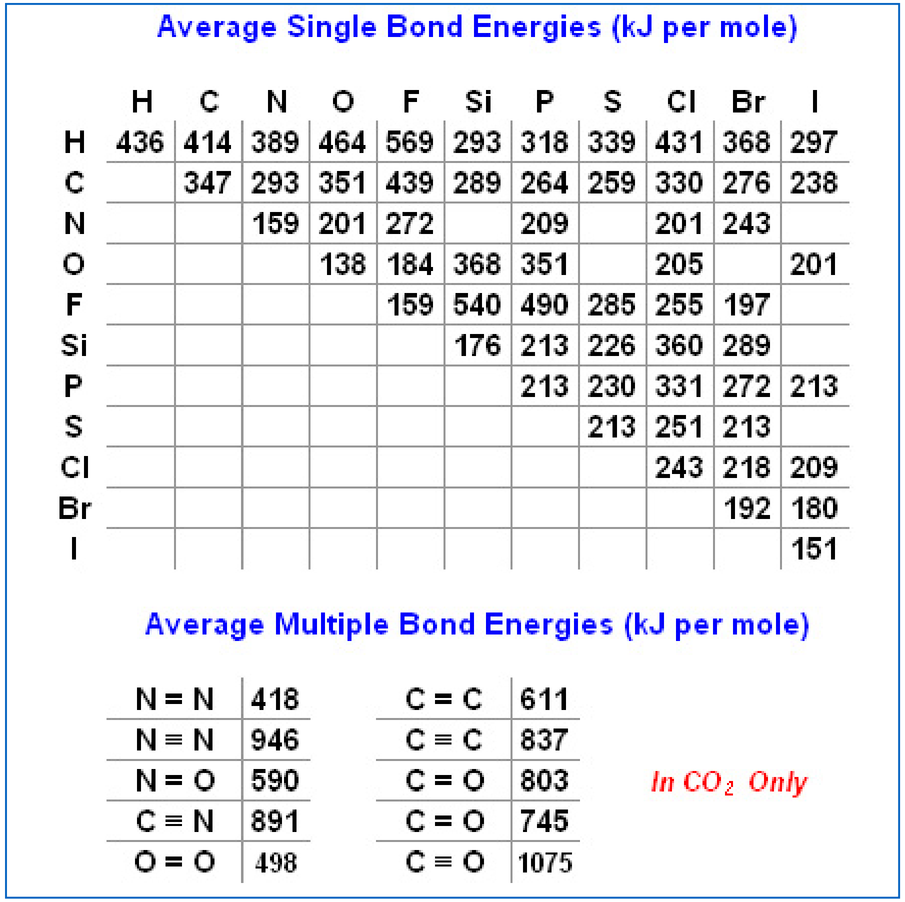
- Covalent compounds:
H_2O, NH_2, CH_4, $H_3C\text{-}CH_3$, $H_2C{=}CH_2$, SiO_2, CO_2, N_2O_4, NO_2, SO_2, SO_2,…

Covalent bond: Length and energy



Bond	nm	Bond	nm
H—H	0.074	C—H	0.109
C—C	0.154	Si—H	0.146
C=C	0.134	N—H	0.101
C≡C	0.120	P—H	0.142
C⋯C (in benzene)	0.139	O—H	0.096
Si—Si	0.235	S—H	0.135
N—N	0.146	F—H	0.092
N=N	0.120	Cl—H	0.128
N≡N	0.110	Br—H	0.141
P—P (P_4)	0.221	I—H	0.160
O—O	0.148		
O=O	0.121	C—O	0.143
S—S (S_8)	0.207	C=O	0.122
S=S	0.188	C⋯O (in phenol)	0.136
F—F	0.142	C—N	0.147
Cl—Cl	0.199	C=N	0.127
Br—Br	0.228	C≡N	0.116
I—I	0.267	C⋯N (in phenylamine)	0.135
		C—F	0.138
		C—Cl	0.177
		C⋯Cl (in cholorobenzene)	0.169
		C—Br	0.193
		C—I	0.214
		Si—O	0.150

http://image.tutorvista.com/cms/images/44/bond-energy-table.JPG



Average Single Bond Energies (kJ per mole)

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	414	389	464	569	293	318	339	431	368	297
C		347	293	351	439	289	264	259	330	276	238
N			159	201	272		209		201	243	
O				138	184	368	351		205		201
F					159	540	490	285	255	197	
Si						176	213	226	360	289	
P							213	230	331	272	213
S								213	251	213	
Cl									243	218	209
Br										192	180
I											151

Average Multiple Bond Energies (kJ per mole)

N = N	418	C = C	611	
N ≡ N	946	C ≡ C	837	
N = O	590	C = O	803	*In CO_2 Only*
C ≡ N	891	C = O	745	
O = O	498	C ≡ O	1075	

http://www.chem.umass.edu/genchem/whelan/class_images/111_Bond_Energies.jpg

1000 kJ/mol → 10 eV/molecule

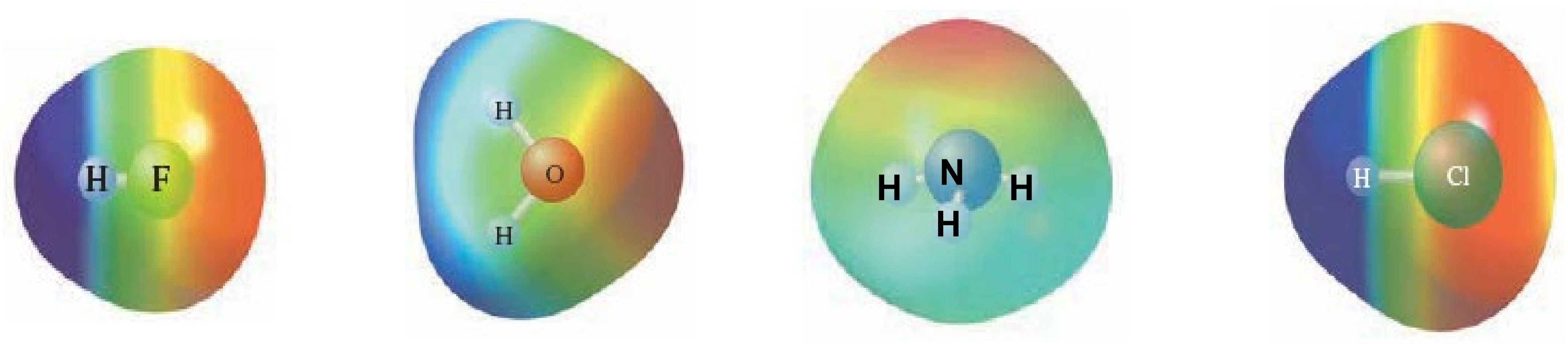
100 kJ/mol → 1 eV/molecule

Thermal energy:

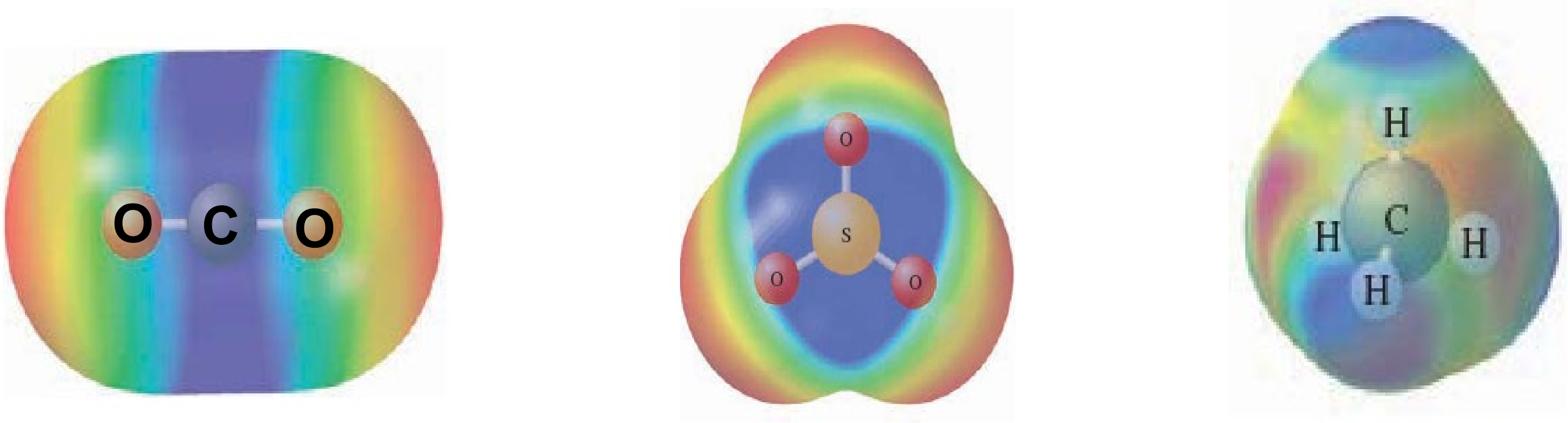
$$k_B T \cong 0.026 \text{ eV} \qquad @T = 300 \text{ K}$$

Covalent bond: Polar and non-polar molecules

POLAR (PERMANENT MOLECULAR ELECTRIC DIPOLE)



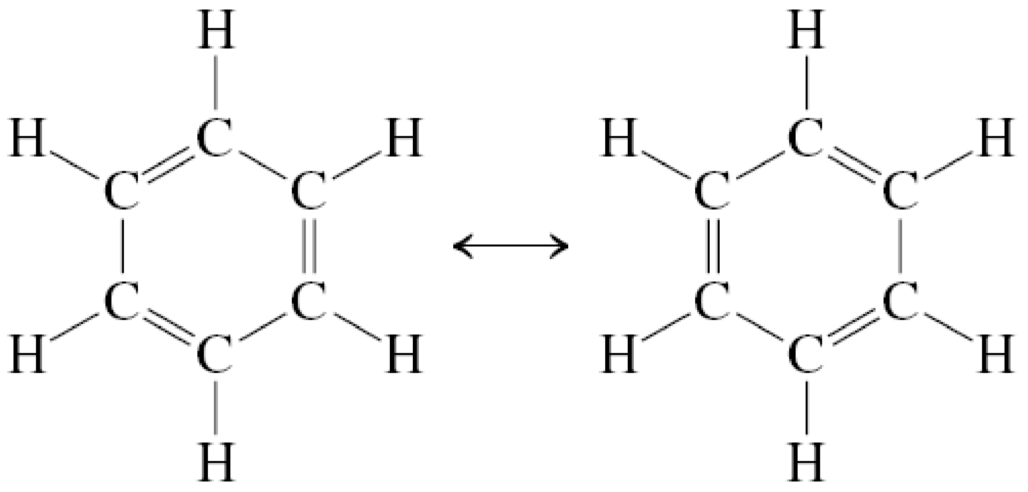
NON POLAR (NO MOLECULAR ELECTRIC DIPOLE)



RED: NEGATIVE CHARGE, BLUE: POSITIVE CHARGE

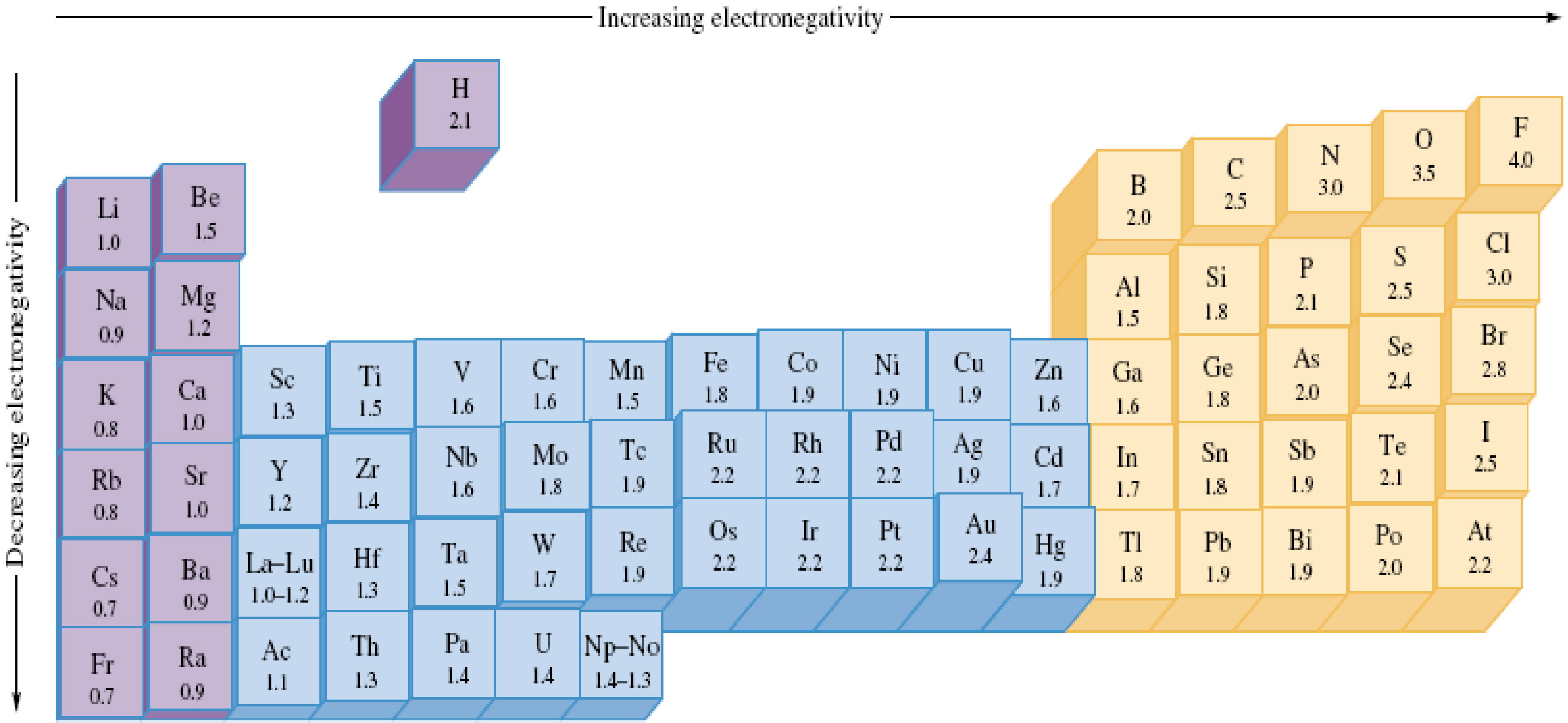
Covalent bond: Resonance moleculare structures

An example of resonance is the benzene molecule (C_6H_6):



If one of these resonance structures corresponded to the actual structure of benzene, there would be two different bond lengths between adjacent C atoms, one characteristic of the single bond and the other of the double bond. In fact, the distance between all adjacent C atoms in benzene is 140 pm, which is shorter than a C-C bond (154 pm) and longer than a C=C bond (133 pm). So it is neither a double bond nor a single bond.

Atomic electronegativity

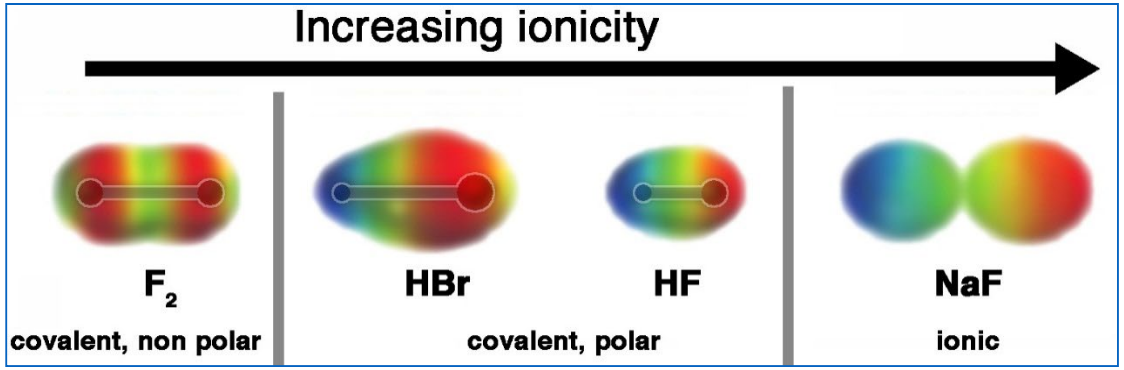


“Donors” side

“Acceptors” side

Atoms on the left tends to donate electrons to become more stable.
Atoms on the right tends to accept electrons to become more stable.

Electronegativity and bond type



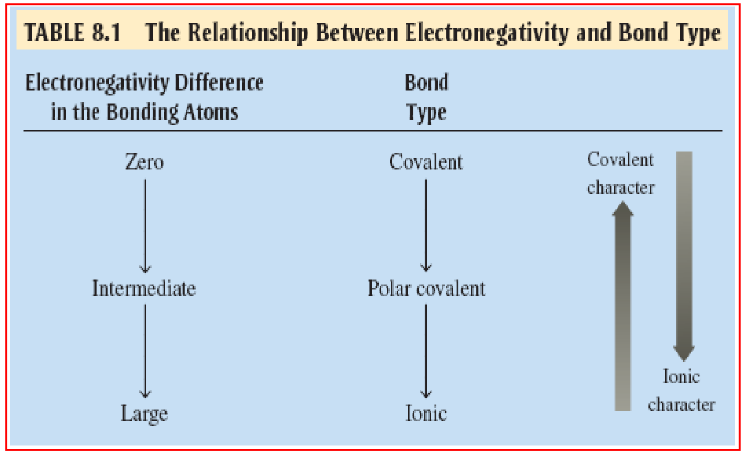
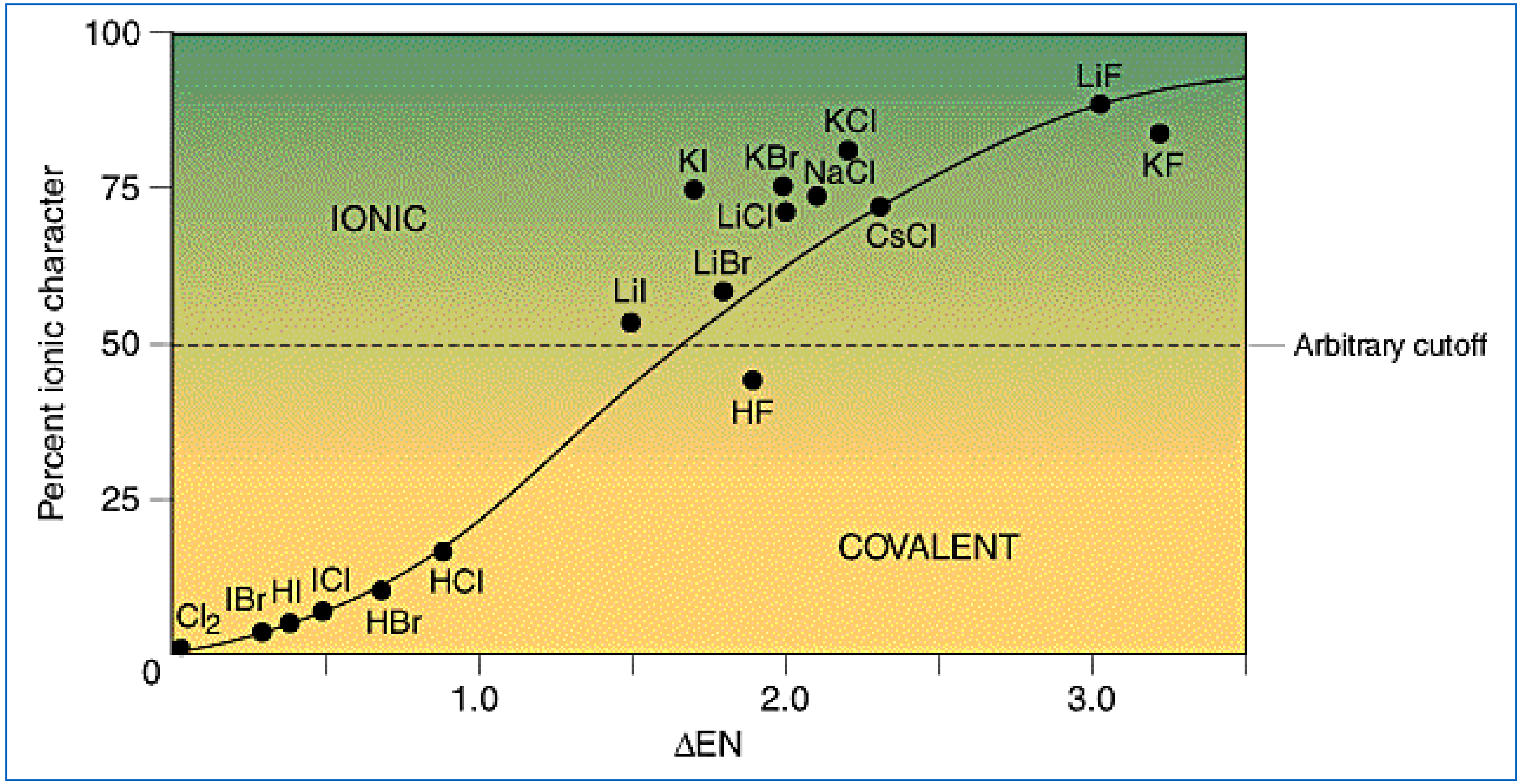


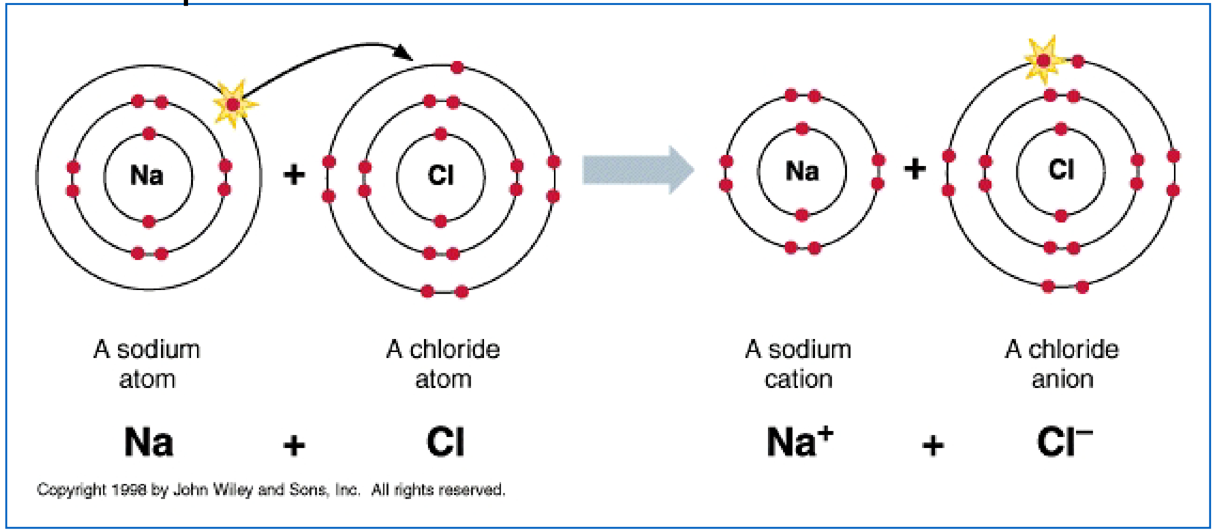
TABLE 8.1 The Relationship Between Electronegativity and Bond Type

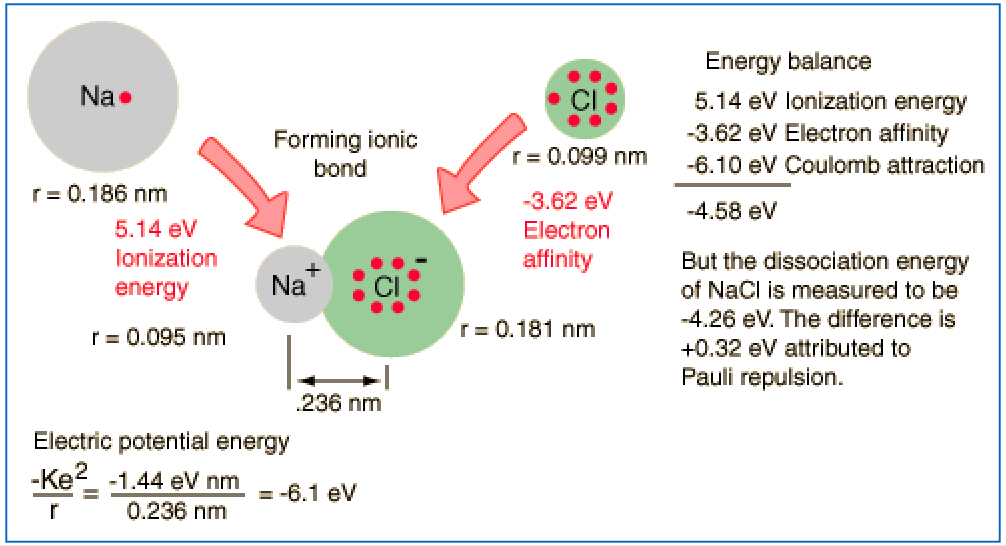
Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
Intermediate	Polar covalent
Large	Ionic



Ionic bond: Examples

- Ionic bonds commonly form between atoms of the 1st column and the 7th, and between the 2nd column and the 6th. (high difference in electronegativity).
- Example: NaCl





Energy balance

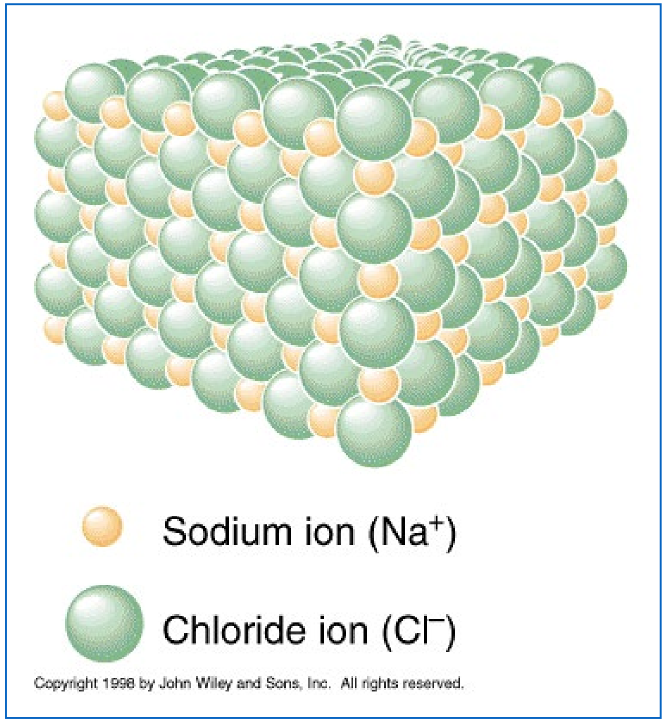
5.14 eV Ionization energy
-3.62 eV Electron affinity
-6.10 eV Coulomb attraction

-4.58 eV

But the dissociation energy of NaCl is measured to be -4.26 eV. The difference is +0.32 eV attributed to Pauli repulsion.

Electric potential energy

$$\frac{-Ke^2}{r} = \frac{-1.44 \text{ eV nm}}{0.236 \text{ nm}} = -6.1 \text{ eV}$$



http://hyperphysics.phy-astr.gsu.edu

Ionic bond: Examples

LiF

$$\begin{array}{ccccc} \cdot\mathrm{Li} \;+\; & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot & \longrightarrow & \mathrm{Li}^{+} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:^{-} \\ 1s^2 2s^1 & 1s^2 2s^2 2p^5 & & 1s^2 & 1s^2 2s^2 2p^6 \end{array}$$

CaO

$$\begin{array}{ccccc} \cdot\mathrm{Ca}\cdot \;+\; & \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\cdot & \longrightarrow & \mathrm{Ca}^{2+} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^{2-} \\ [\mathrm{Ar}]4s^2 & 1s^2 2s^2 2p^4 & & [\mathrm{Ar}] & [\mathrm{Ne}] \end{array}$$

Li_2O

$$\begin{array}{ccccc} 2\ \cdot\mathrm{Li} \;+\; & \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\cdot & \longrightarrow & 2\mathrm{Li}^{+} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^{2-} \\ 1s^2 2s^1 & 1s^2 2s^2 2p^4 & & [\mathrm{He}] & [\mathrm{Ne}] \end{array}$$

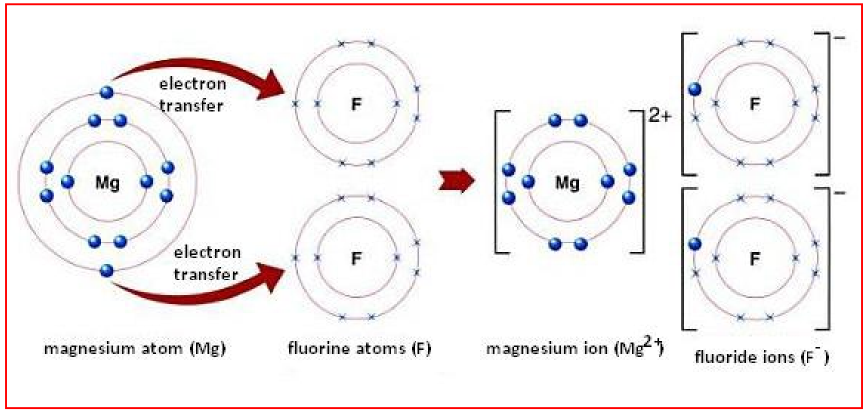
Mg_3N_2

$$\begin{array}{ccccc} 3\ \cdot\mathrm{Mg}\cdot \;+\; & 2\ \cdot\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{N}}}\cdot & \longrightarrow & 3\mathrm{Mg}^{2+} & 2\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:^{3-} \\ [\mathrm{Ne}]3s^2 & 1s^2 2s^2 2p^3 & & [\mathrm{Ne}] & [\mathrm{Ne}] \end{array}$$

Al_2O_3

$$\begin{array}{ccccc} 2\ \cdot\underset{\cdot}{\mathrm{Al}}\cdot \;+\; & 3\ \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\cdot & \longrightarrow & 2\mathrm{Al}^{3+} & 3\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^{2-} \\ [\mathrm{Ne}]3s^2 3p^1 & 1s^2 2s^2 2p^4 & & [\mathrm{Ne}] & [\mathrm{Ne}] \end{array}$$

Note: Ionic bonding is not only constrained to pairs of atoms.



Hydrogen bonding

- Definition of hydrogen bonding (IUPAC, 2011):
« The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation ».

- A **hydrogen bond** is the electromagnetic attractive interaction of a hydrogen atom and an electronegative atom, such as nitrogen, oxygen or fluorine, that comes from another molecule or chemical group. It is not a true chemical bond. The hydrogen has a polar bonding to another electronegative atom to create the bond.

- Hydrogen bonds occur between molecules (*intermolecularly*), or within different parts of a single molecule (*intramolecularly*).

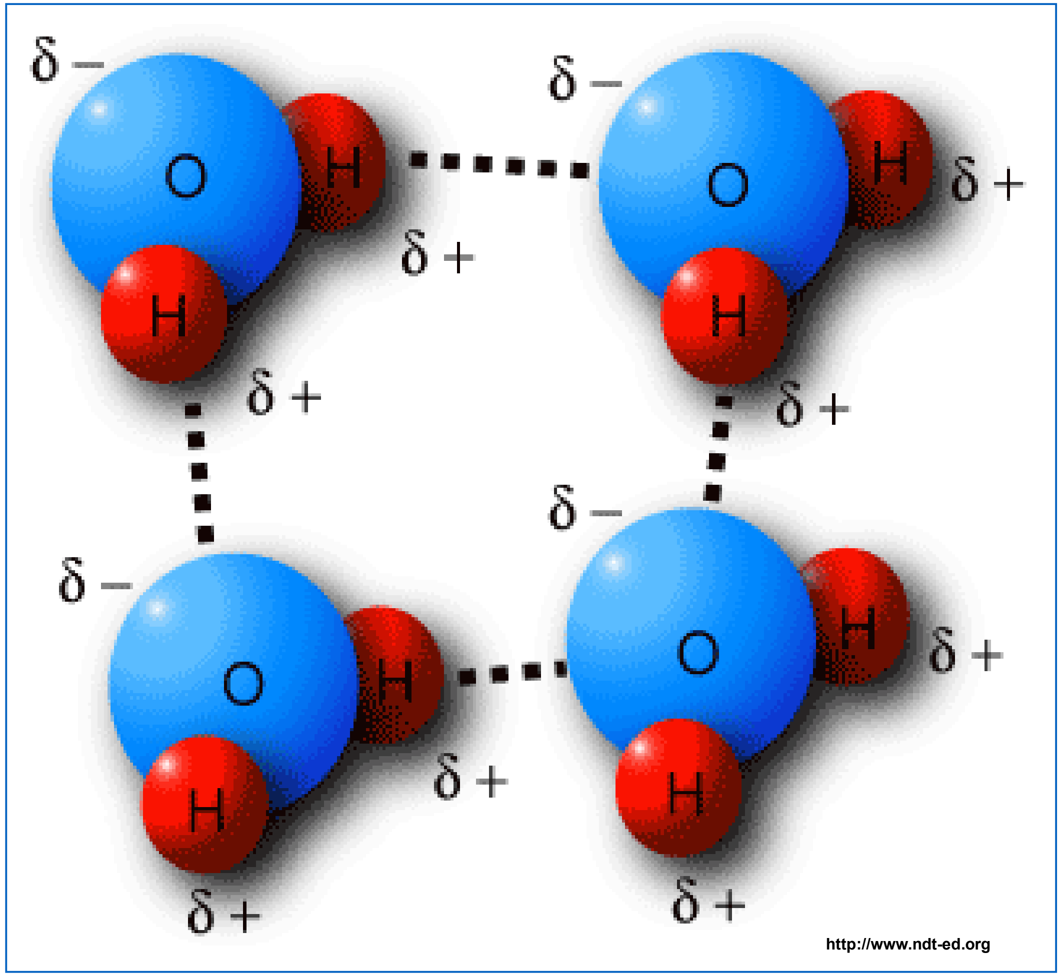
- The hydrogen bond (typically 5 to 30 kJ/mole, up to 160 kJ/mole) is stronger than a van der Waals interaction, but weaker than covalent and ionic bonds.

- It occurs in inorganic molecules (water,…), organic molecules (DNA, proteins,..).

- The length of hydrogen bonds depends on bond strength, temperature, and pressure.

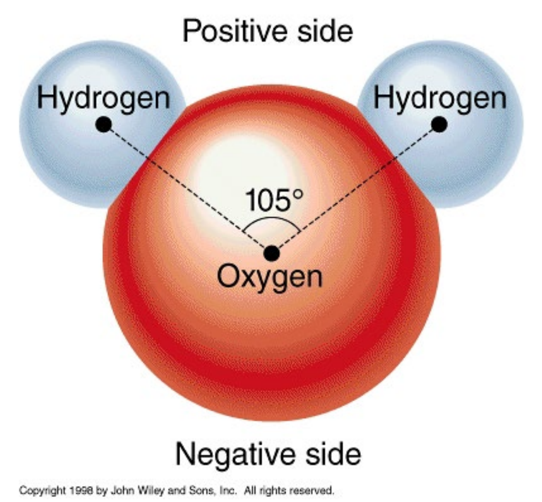
http://en.wikipedia.org/wiki/Hydrogen_bond

Hydrogen bonding



"To which molecule or atom does a hydrogen nucleus belong?"
Compare interatomic distances in the X−H (covalent) system and Y···H (hydrogen bond) systems:
X−H distance is typically ≈110 pm
Y···H distance is ≈160 to 200 pm.

Properties of the hydrogen bond in water
Bond strength: ≈23 kJ/mol
Partially covalent character
Distances: O···H: ≈ 200 pm, O-H : 95 pm



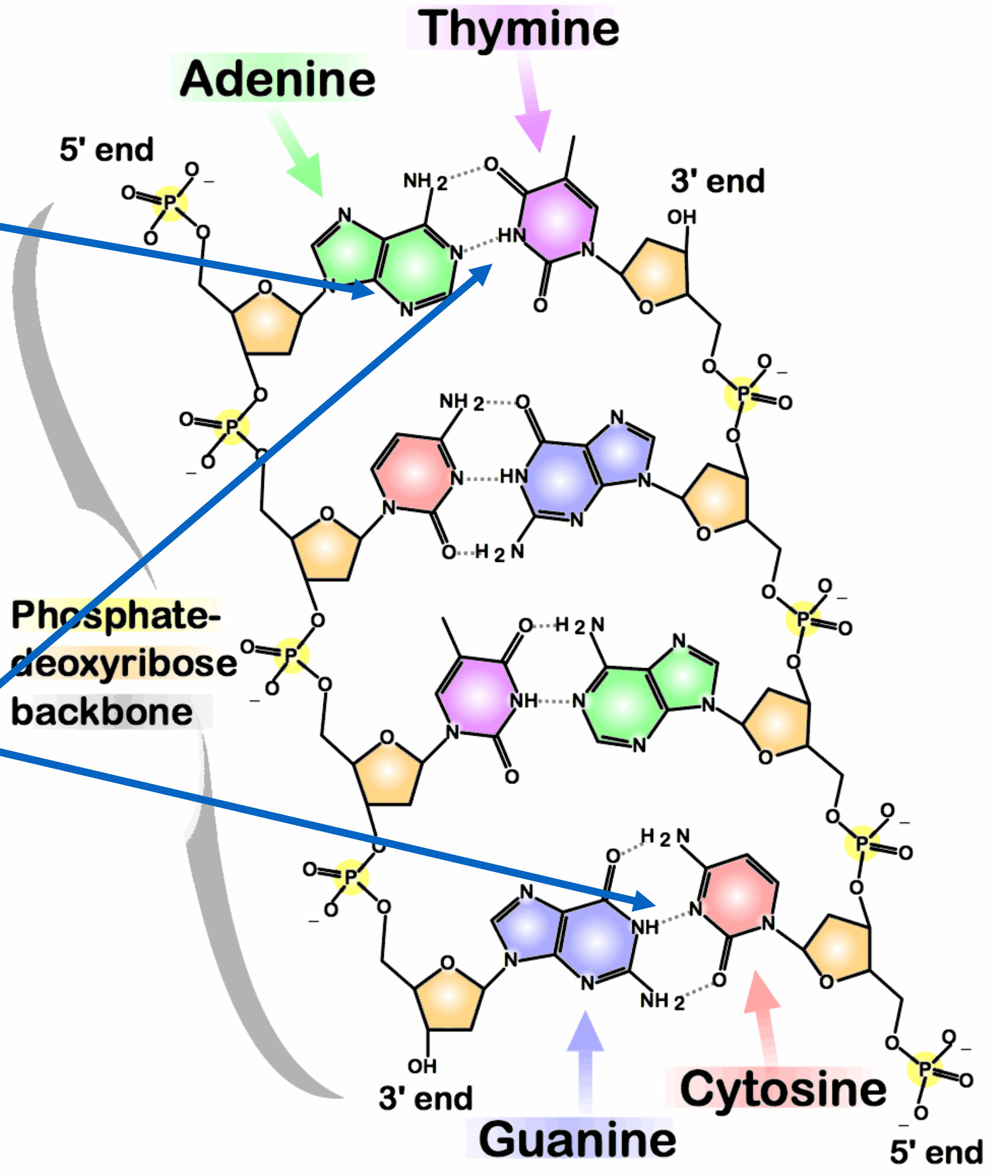
The Hydrogen bond in DNA

Backbone

Covalent-bonded: strong bond

Interbase pairing

Hydrogen bonds: weaker bond (easy cleaving / reassembly of both strands for transcription)



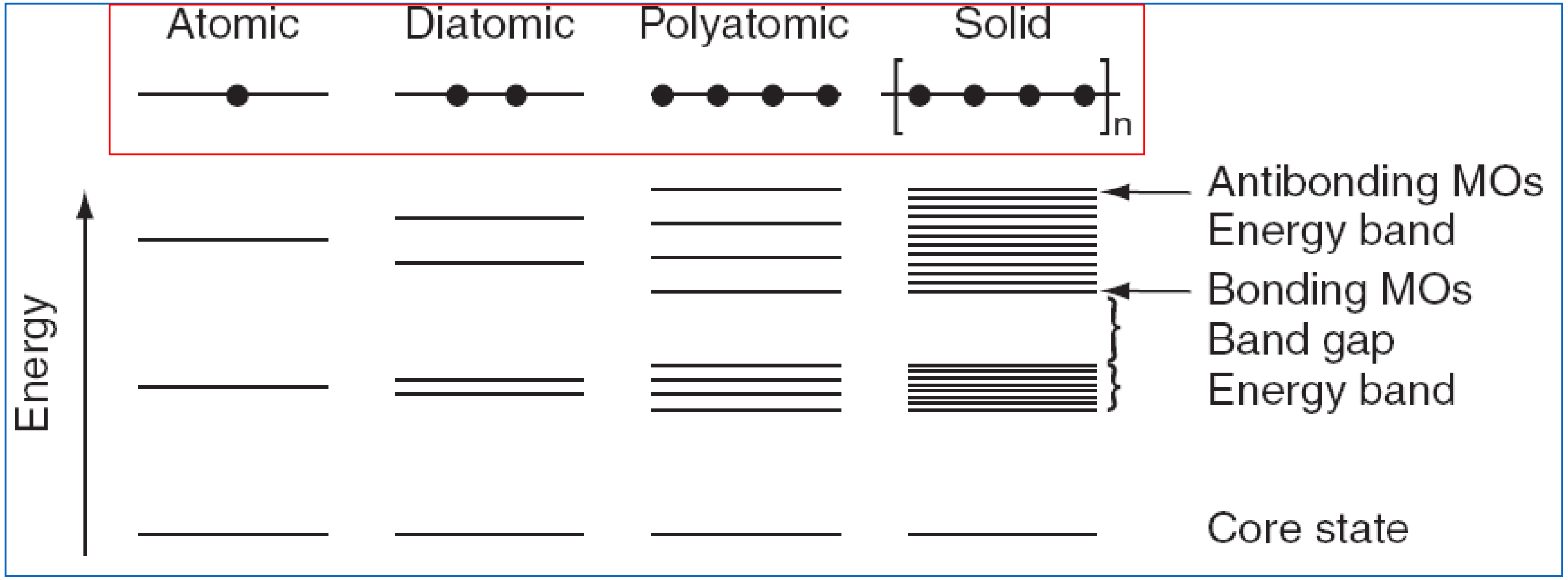
Adenine-Thymine: $\cong 20$ kJ/mol $\rightarrow$ 0.2 eV/bond

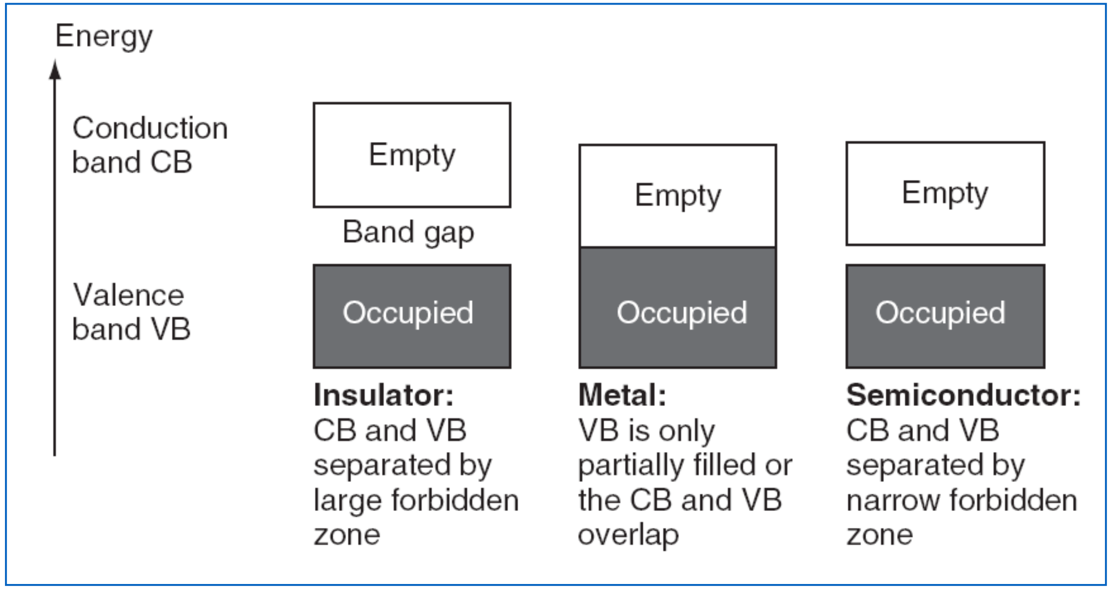
Guanine-Cytosine: $\cong 60$ kJ/mol $\rightarrow$ 0.6 eV/bond

Thermal energy: $k_B T \cong 0.026$ eV $\quad @T = 300$ K

Wikipedia

From molecular orbitals to band structure

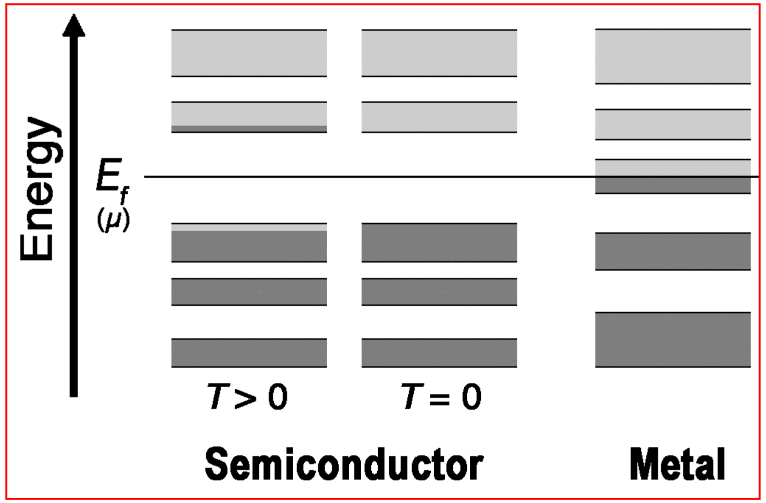




Insulator: CB and VB separated by large forbidden zone

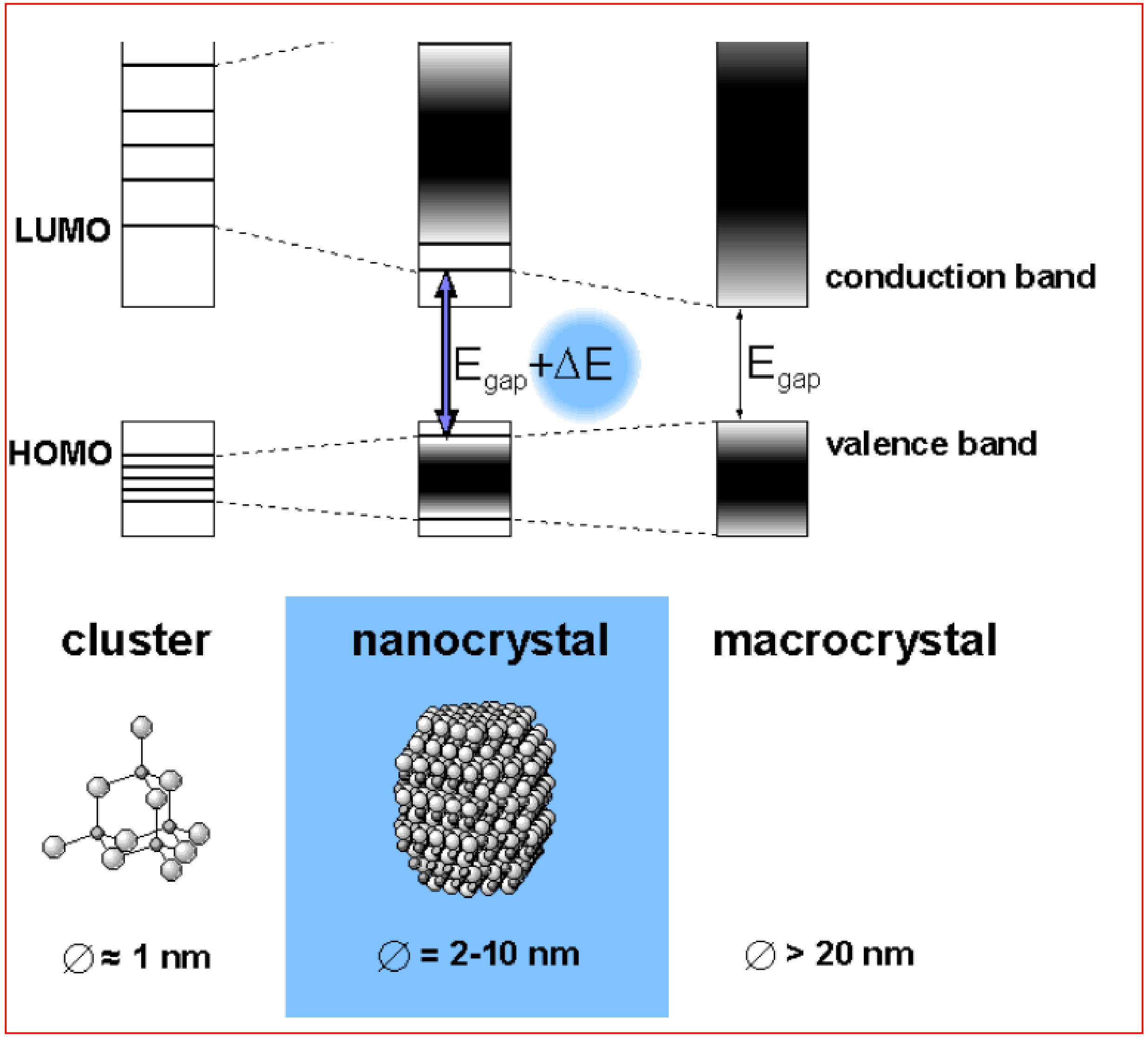
Metal: VB is only partially filled or the CB and VB overlap

Semiconductor: CB and VB separated by narrow forbidden zone

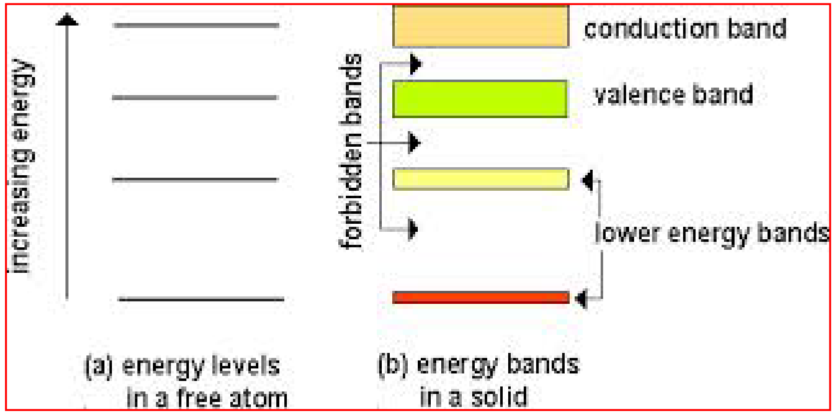


Kelsall_R.W.,_Hamley_I.W.,_Geaghegan_M._Nanoscale_Science_and_Technology__2005

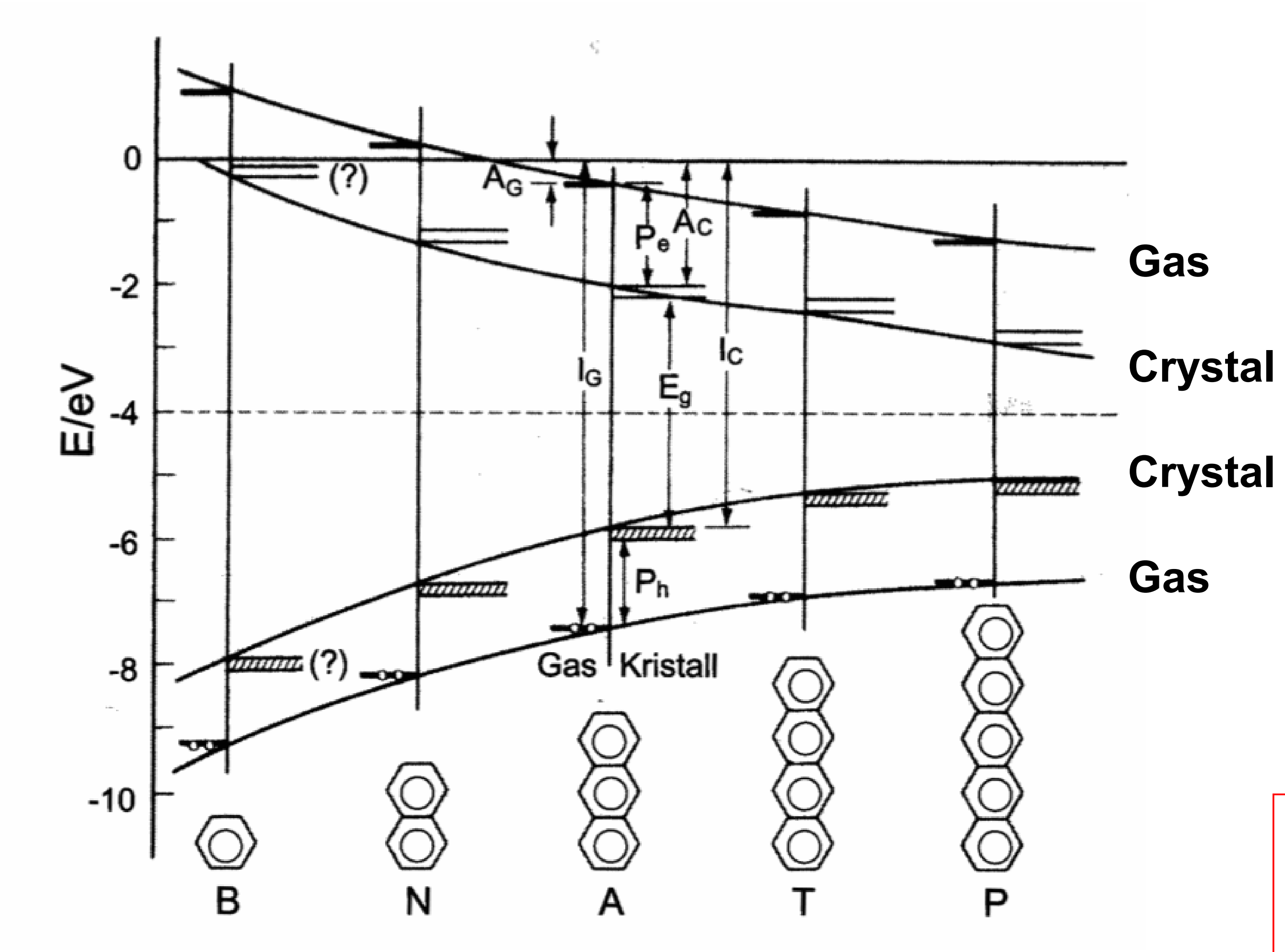
From molecular orbitals to band structure



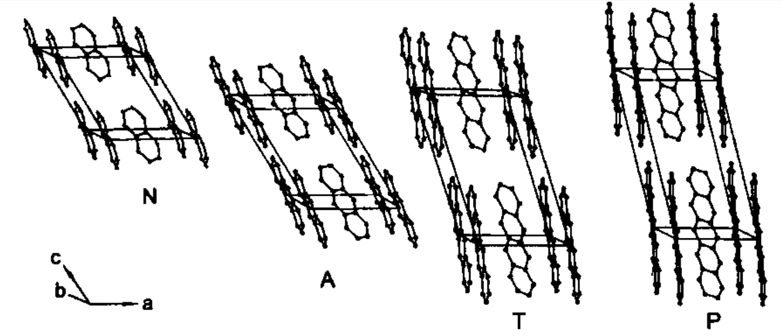
Usually moving from
single atom to clusters of atoms
to nanocrystals to macrocrystals
the bandgap becomes
smaller.



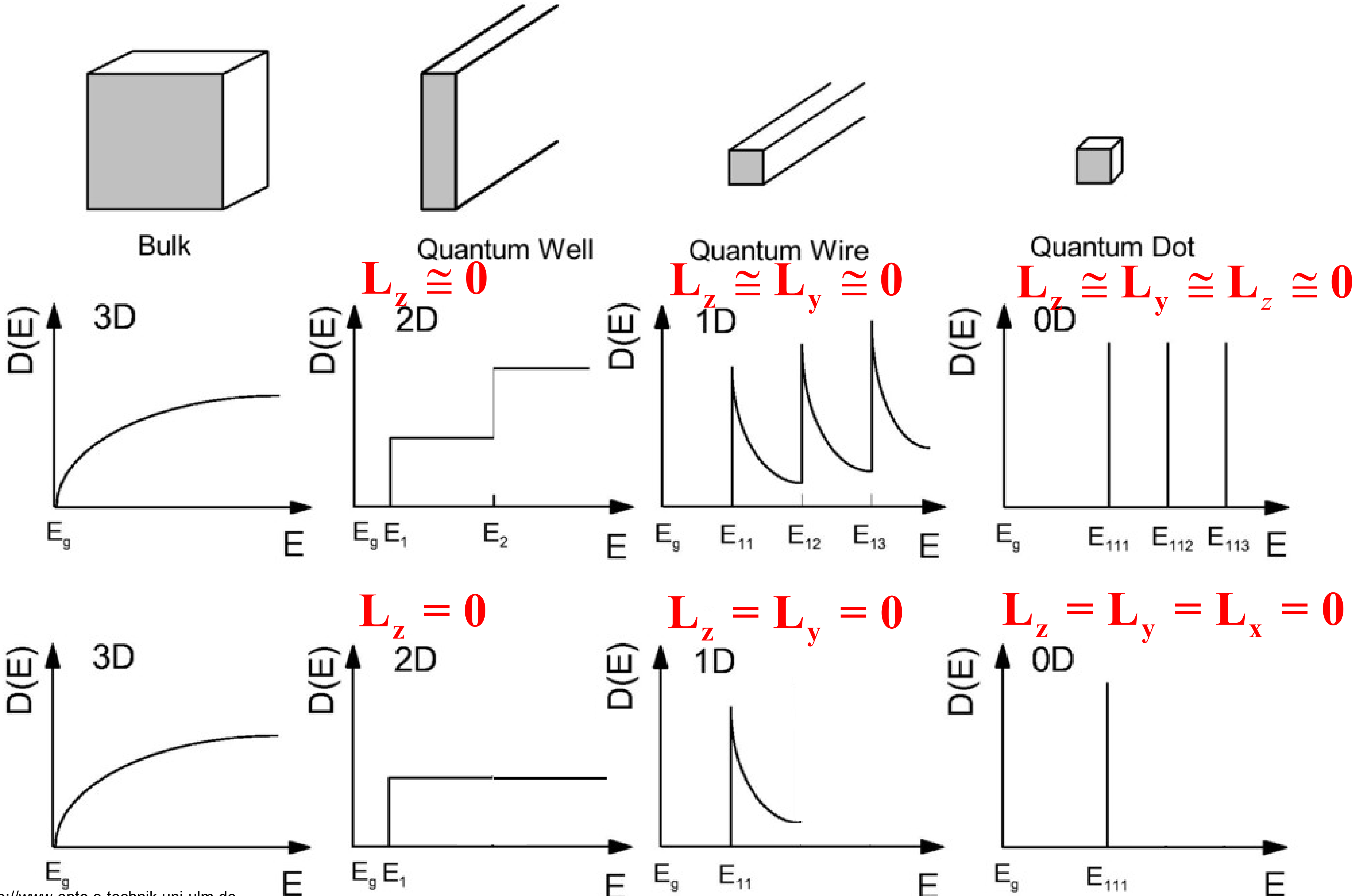
Band structure: Gas vs. Crystal



B = benzene
N = naphtalene
A = anthracene
T = tetracene
P = pentacene



Band structure in 3D, 2D, 1D, 0D objects



$L_z \cong 0$

$L_z \cong L_y \cong 0$

$L_z \cong L_y \cong L_z \cong 0$

$L_z = 0$

$L_z = L_y = 0$

$L_z = L_y = L_x = 0$

http://www-opto.e-technik.uni-ulm.de

Band structure in 3D, 2D, 1D, 0D objects

Simple assumptions:

- Electrons confined by an infinitely high potential walls in three dimensions.
- Constant potential within the walls.
- No interactions between the electrons.

Assuming
$$V(\mathbf{x}) = \begin{cases} V_0 & x \in (0, L)\ \&\ y \in (0, L)\ \&\ z \in (0, L) \\ \infty & \text{elsewhere} \end{cases}$$

the Schrödinger equation is:
$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{x}) + V_0\psi(\mathbf{x}) = E'\psi(\mathbf{x})$$

or, equivalently:
$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{x}) = E\psi(\mathbf{x})$$
$$E = E' - V_0$$

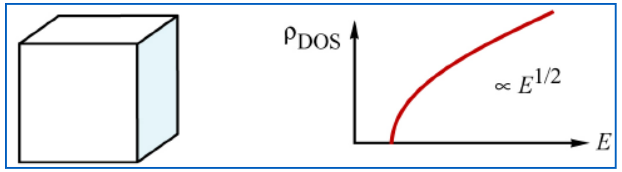
Due to the infinitely high wall of the potential, we have the following boundary conditions on the wavefunctions:
$$\psi(\mathbf{x}) = 0 \text{ for } \mathbf{x} \in ((-\infty, 0) \cup (L_x, \infty), (-\infty, 0) \cup (L_y, \infty), (-\infty, 0) \cup (L_z, \infty))$$

These boundary conditions impose that:
$$\psi(\mathbf{x}) = \left(\frac{2}{L_x}\right)^{1/2}\left(\frac{2}{L_y}\right)^{1/2}\left(\frac{2}{L_z}\right)^{1/2} \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

Substituting this function into the Schrödinger equation we get:
$$E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right) \qquad k_x = \pm\frac{2\pi}{L_x}n_x,\ k_y = \pm\frac{2\pi}{L_y}n_y,\ \ k_z = \pm\frac{2\pi}{L_z}n_z \qquad (n_x, n_y, n_z) \in \mathbb{N}$$

Band structure in 3D objects

3D OBJECT (Bulk, macroscopic object)



Assuming $$V(\mathbf{x}) = \begin{cases} V_0 & x \in (0,L) \,\&\, y \in (0,L) \,\&\, z \in (0,L) \\ \infty & \text{elsewhere} \end{cases}$$

we get: $$\psi(\mathbf{x}) = \left(\frac{2}{L}\right)^{3/2} \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

$$E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m_e}k^2 \qquad k_x = \pm\frac{2\pi}{L}n_x,\ k_y = \pm\frac{2\pi}{L}n_y,\quad k_z = \pm\frac{2\pi}{L}n_z \qquad (n_x, n_y, n_z) \in \mathbb{N}$$

Each state occupy a volume in the k-space: $v_k = (k_{x,n+1} - k_{x,n})(k_{y,n+1} - k_{y,n})(k_{z,n+1} - k_{z,n}) = \left(\frac{2\pi}{L}\right)^3$

The density of available states about the energy $g(E)$ is: $$g(E) \equiv \frac{dN_s}{dE}$$

The number of states in a k-space sphere of radius k and volume V_k is: $$N_s \equiv \frac{V_k}{v_k} = \frac{(4/3)\pi k^3}{(2\pi)^3 / L^3}$$

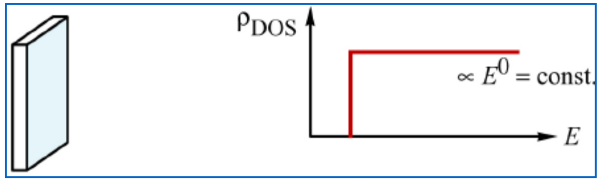
Since $$E = \frac{\hbar^2}{2m_e}k^2 \quad \rightarrow \quad k = \sqrt{\frac{2m_e}{\hbar^2}E} \quad \rightarrow g(E) = \frac{L^3}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{1/2}$$

The density of states $g(E)$ for electrons confined in a 3D object is proportional to $E^{1/2}$.

Band structure in 2D objects

2D OBJECT (Quantum well, thin film)

If we consider $L_z = 0 \Rightarrow$ the electrons are confined in two dimensions.



Assuming $$V(\mathbf{x}) = \begin{cases} V_0 & x \in (0,L)\ \&\ y \in (0,L)\ \&\ z = 0 \\ \infty & \text{elsewhere} \end{cases}$$

we get: $$\psi(\mathbf{x}) = \left(\frac{2}{L}\right)^2 \sin(k_x x)\sin(k_y y)$$

$$E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2\right) \qquad k_x = \pm\frac{2\pi}{L}n_x,\ k_y = \pm\frac{2\pi}{L}n_y, \qquad (n_x, n_y) \in \mathbb{N}$$

Each state occupy a surface in the k-space: $s_k = (k_{x,n+1} - k_{x,n})(k_{y,n+1} - k_{y,n}) = \left(\frac{2\pi}{L}\right)^2$

The density of available states about the energy $g(E)$ is: $g(E) \equiv \frac{dN_s}{dE}$

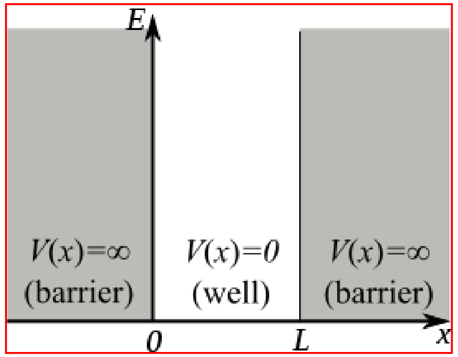
The number of states in a k-space circle of radius k and surface S_k is: $N_s \equiv \frac{S_k}{s_k} = \frac{\pi k^2}{(2\pi/L)^2}$

Since $E = \frac{\hbar^2}{2m_e}k^2 \quad \rightarrow \quad k = \sqrt{\frac{2m_e}{\hbar^2}E} \quad \rightarrow g(E) = \frac{L^2}{2\pi}\frac{m_e}{\hbar^2}$

The density of states $g(E)$ for electrons confined in a 2D object is constant.

Band structure in 1D objects

1D OBJECT (Quantum wire, nanowire)



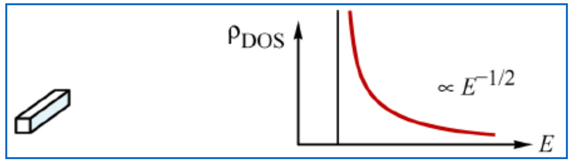
wikimedia.org

If we consider $L_z = L_y = 0 \Rightarrow$ the electrons are confined in one dimension.

Assuming $$V(\mathbf{x}) = \begin{cases} V_0 & x \in (0, L)\ \&\ y = z = 0 \\ \infty & \text{elsewhere} \end{cases}$$

we get: $$\psi(\mathbf{x}) = \left(\frac{2}{L}\right)^2 \sin(k_x x)$$

$$E = \frac{\hbar^2}{2m_e}\left(k_x^2\right) \qquad k_x = \pm\frac{2\pi}{L} n_x, \qquad n_x \in \mathbb{N}$$



Each state occupy a surface in the k-space: $s_k = (k_{x,n+1} - k_{x,n}) = \left(\frac{2\pi}{L}\right)$

The density of available states about the energy $g(E)$ is: $$g(E) = \frac{dN_s}{dE}$$

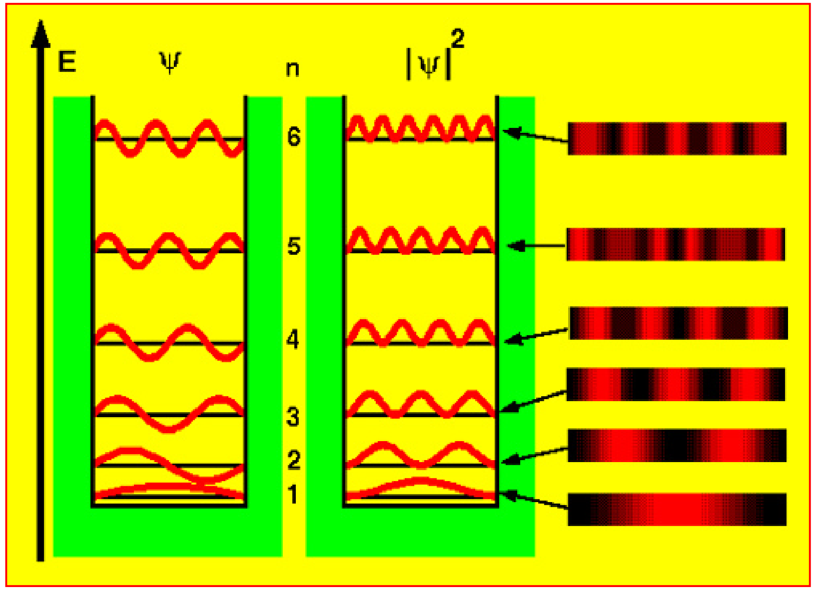
The number of states in a k-space line of length L_k is: $$N_s = \frac{L_k}{l_k} = \frac{k}{(2\pi / L)}$$

Since $E = \frac{\hbar^2}{2m_e} k^2 \quad \rightarrow \quad k = \sqrt{\frac{2m_e}{\hbar^2} E} \quad \rightarrow g(E) = \frac{L}{2\pi}\sqrt{\frac{2m_e}{\hbar^2}}\frac{1}{\sqrt{E}}$

The density of states $g(E)$ for electroncs confined in a 1D object is proportional to $1/\sqrt{E}$.

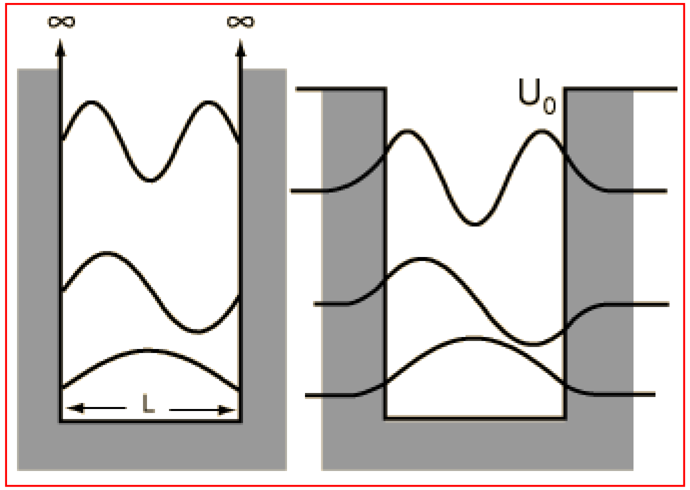
Band structure in 1D and 2D objects

1D

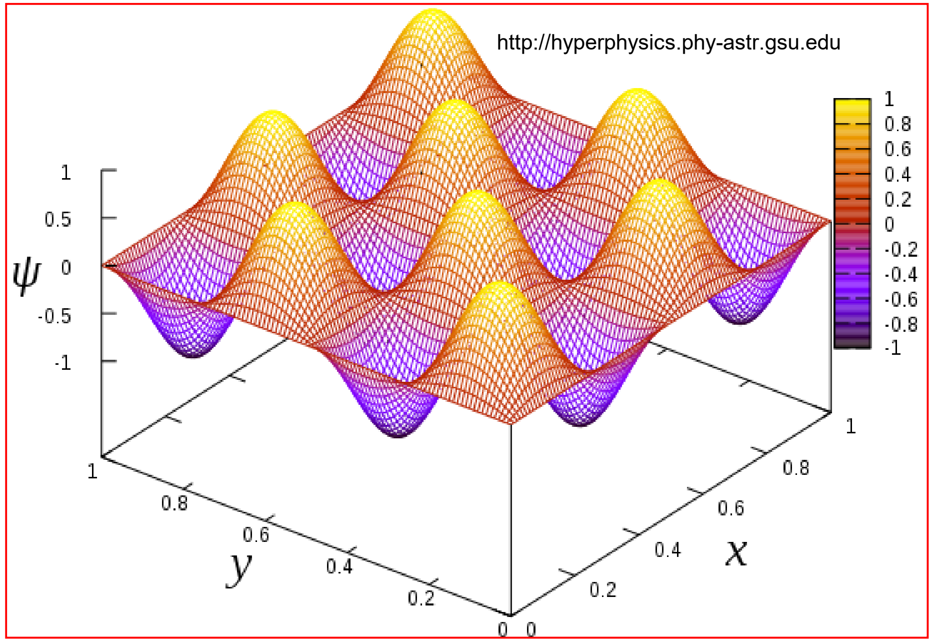


The density of states decreases when the energy increases.

Infinite barrier **Finite barrier**



2D



Wavefunction of a 2D well with n_x=4 and n_y=4

Band structure in 0D objects

0D OBJECT (Quantum dot, nanoparticle)

A "0D" object is a very small "3D" object.

Assuming $$V(\mathbf{x}) = \begin{cases} V_0 & \mathbf{x} \in ((0,L),(0,L),(0,L)) \\ \infty & \text{elsewhere} \end{cases}$$

we get: $$\psi(\mathbf{x}) = \left(\frac{2}{L}\right)^{3/2} \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

$$E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right) \qquad k_x = \pm\frac{2\pi}{L}n_x,\ k_y = \pm\frac{2\pi}{L}n_y,\quad k_z = \pm\frac{2\pi}{L}n_z \qquad (n_x, n_y, n_z) \in \mathbb{N}$$

Formally we get the same solution as in the 3D case.

However for a 0D object the energy separation between available states is much larger (see later).
The density of states curve g(E) is a series of delta function
(or, more realistically, narrow lines) well separeted one from the others.

Band structure: from 3D to 0D

$$E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right) \qquad k_x = \pm\frac{2\pi}{L_x}n_x,\ k_y = \pm\frac{2\pi}{L_y}n_y,\quad k_z = \pm\frac{2\pi}{L_z}n_z \qquad (n_x, n_y, n_z) \in \mathbb{N}$$

In a "macroscopic object" (3D): L_x, L_y, L_z are in the "micrometer and larger range".

ΔE for energy levels lebelled by n_x, n_y and n_z are small.

In a "quantum well" (2D): L_z is in the "nanometer range".

$L_x, L_y >> L_z$ are in the "micrometer and larger range".

ΔE for energy levels lebelled by n_z is large.

ΔE for energy levels lebelled by n_x and n_y is small.

In a "quantum wire" (1D): L_y and L_z are in the "nanometer range".

$L_x >> L_y, L_z$ is in the "micrometer and larger range".

ΔE for energy levels lebelled by n_y and n_z is large.

ΔE for energy levels lebelled by n_x is small.

In a "quantum dot" (0D): L_x, L_y, L_z are in the "nanometer range".

ΔE for energy levels lebelled by n_x, n_y and n_z are large.

Band structure: Fermi quantities in 3D objects

Lets assume that $L_x = L_y = L_z = L$. Since:

$$E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right) \qquad k_x = \pm\frac{2\pi}{L}n_x,\ k_y = \pm\frac{2\pi}{L}n_y,\quad k_z = \pm\frac{2\pi}{L}n_z \qquad (n_x, n_y, n_z) \in \mathbb{N}$$

Each state occupy a volume in the k-space: $v_k = (k_{x,n+1} - k_{x,n})(k_{y,n+1} - k_{y,n})(k_{z,n+1} - k_{z,n}) = \left(\frac{2\pi}{L}\right)^3 = \frac{(2\pi)^3}{V}$

Due to the Pauli exclusion principle, the N electrons contained in the real space volume $V = L^3$

occupy , at T=0 K, a sphere of volume V_F in the k-space of volume: $V_F = \left(\frac{2\pi}{L}\right)^3 \frac{N}{2}$

The radius of this sphere in the k-space k_F is: $k_F = \sqrt[3]{\frac{3}{4\pi}V_F} = \sqrt[3]{\frac{3\pi^2 N}{V}}$

The energy on the surface of this sphere in the k-space E_F is: $E_F = \frac{\hbar^2}{2m_e}k_F^2 = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$

V_F, k_F, E_F are called the Fermi volume, Fermi wavevector, and Fermi energy, respectively.

The k-space sphere is called the Fermi sphere.

T=0: Electrons occupy all states inside the Fermi sphere, leaving empty all those outside of it.

$T \neq 0$: Elettrons occupy also states outside the Fermi sphere, up to an energy of the order of $E_F + k_B T$

(leaving some energy states empty down to an energy of the order of $E_F - k_B T$).

Band structure: energy separation

3D OBJECT

The difference between two energy level energy on the Fermi surface is:

$$\Delta E(E_F) \cong \left(g(E_F)\right)^{-1} = \left(V\left(\frac{N}{V}\right)^{1/3}\frac{m_e\sqrt{3}}{\hbar^2\pi^{4/3}}\right)^{-1}$$

For a **micrometer** sized object with $L \cong 1\ \mu\text{m}$ and electron densitiy $(\text{N/V}) \cong 10^{29}\ \text{m}^{-3}$ (metal), we have:

$\Delta E(E_F) \cong 10^{-29}\,\text{J} \cong 10^{-10}\text{eV}$

The energy separation is much smaller than the termal energy k_BT

even at low temperatures (at 1 K, $k_BT \cong 9\times10^{-5}\ \text{eV}) \rightarrow$

$\rightarrow$ The quantization of the energy levels is not experimentally observable.

For a **nanometer** sized object with $L \cong 1\ \text{nm}$ and electron densitiy $(\text{N/V}) \cong 10^{29}\ \text{m}^{-3}$ (metal), we have:

$\Delta E(E_F) \cong 10^{-20}\,\text{J} \cong 10^{-1}\text{eV}$

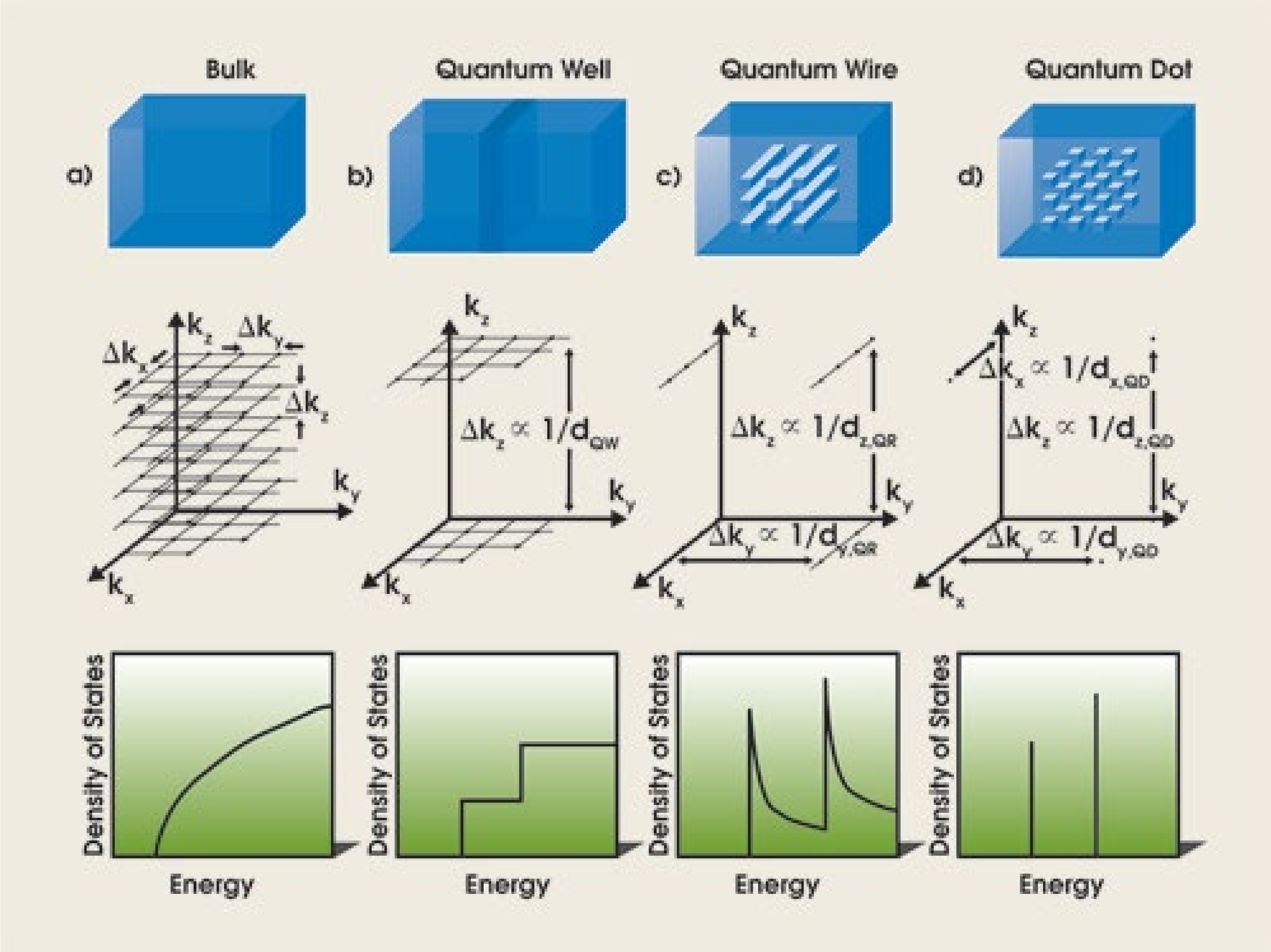
The energy separation is comparable to the termal energy k_BT at 300 K

and much larger at low temperatures (at 1 K, $k_BT \cong 9\times10^{-5}\ \text{eV}) \rightarrow$

$\rightarrow$ The quantization of the energy levels is experimentally observable.

(for semiconductors where N/V is smaller the energy separation is larger $(\Delta E(E_F) \propto 1/\sqrt[3]{N/V})$)

Band structure in 3D, 2D, 1D, 0D objects



http://www.photonics.com/images/spectra/features/2008/January/Invisage_Fig1.jpg

Band structure: a more general approach

Electrons in a periodic potential

The conduction electrons are not perfectly free even in metals, since they move through the regular crystalline array of ions.

In first approximation we can assume that the electrons feel only the spatially periodic potential produced by the ions $U(\mathbf{r})$, with

$$U(\mathbf{r}) = U(\mathbf{r}+\mathbf{R})$$

for all Bravais lattice vectors **R** (translational vectors of the crystal structure).

Consequently, the Hamiltonian is

$$H = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N_e}\nabla_i^2 + U(\mathbf{x})$$

This Hamiltonian is the sum of single particle Hamiltonian.

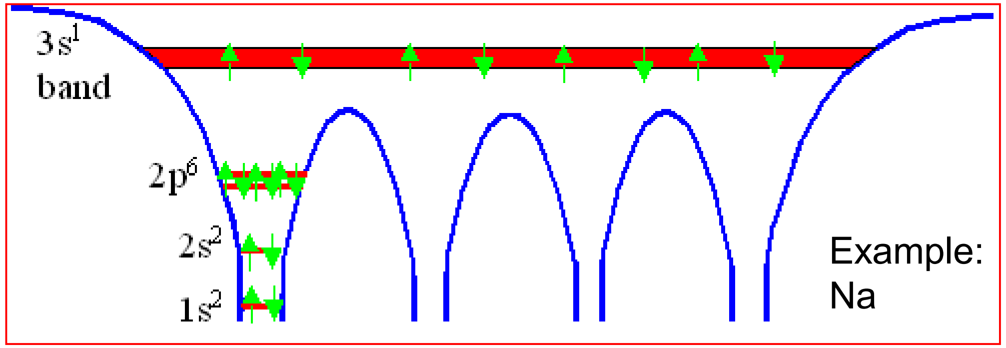
Consequently as starting point we can solve the one-particle Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + U(\mathbf{x})\right]\psi_i(\mathbf{x}) = E_i\psi_i(\mathbf{x})$$

Note that we are negletting:

- the interations between the electrons,
- the presence of impurities, vacancies, and misplaced ions
- the finite size of the crystal
- the "local nature" of some electron – ion interactions
- the thermal vibrations of the ions

……



Example: Na

Band structure: a more general approach

It can be shown (Bloch theorem) that the solutions of the Schrödinger equation for the one electron in a periodic potential can be chosen to have the form:

$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r})$ with: $u_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r}+\mathbf{R})$

$\mathbf{k}$ is any allowed vector obtained with a constant potential (see before)

Note 1: In absence of the periodic potential the wavefunction is the plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$

$\Rightarrow$ $u_{n,\mathbf{k}}(\mathbf{r})$ describes the deformation of the wavefunction due to the periodic potential.

Note 2: $\left\langle \psi_{n,\mathbf{k}}(\mathbf{x}) \middle| -\frac{\hbar}{i}\nabla \middle| \psi_{n,\mathbf{k}}(\mathbf{x}) \right\rangle \neq \hbar\mathbf{k}$ $\Rightarrow \hbar\mathbf{k}$ is not the momentum of an electron with wavefunction $\psi_{n,\mathbf{k}}(\mathbf{x})$

Note 3: $\psi_{n,\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{n,\mathbf{k}}(\mathbf{r})$

The Schrödinger equation becomes:

$$\left[-\frac{1}{2m_e}\left(\frac{\hbar}{i}\nabla + \hbar\mathbf{k}\right)^2 + U(\mathbf{x})\right] u_{n,\mathbf{k}}(r) = E_{n,\mathbf{k}} u_{n,\mathbf{k}}(r)$$

A complete knowledge of the band structure requires the solution of the eigenvalue problem for each vector **k** of the primitive cell of the reciprocal lattice (or the Brillouin zone). Calculations are usually performed only for some special, high-symmetry directions of the Brillouin zone, and the dispersion curves of Bloch electrons are also displayed only along these directions. These curves represent the "band structure" of the crystal under study.

Band structure: a more general approach

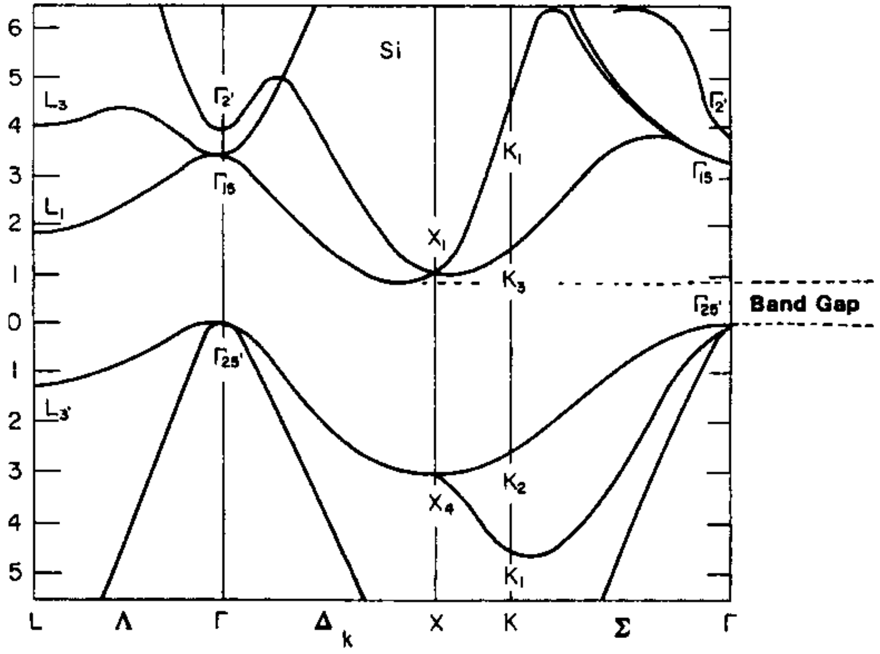
Rappresentation of Energy vs **k**
(energy values along some directions of the k-space**)**

[100] direction : $\dot{\Gamma}\overline{\quad\Delta\quad}\dot{X}$

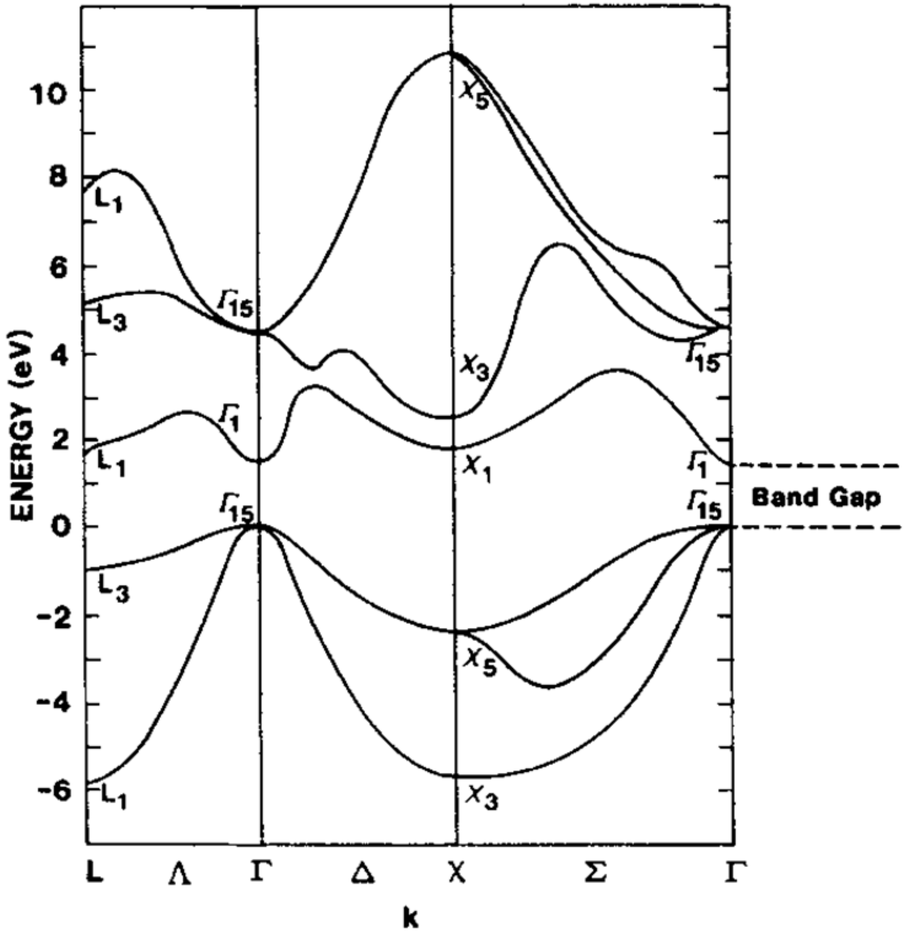
[111] direction : $\dot{\Gamma}\overline{\quad\Lambda\quad}\dot{L}$

[110] direction : $\dot{\Gamma}\overline{\quad\Sigma\quad}\dot{K}$

Si (semicond.)



GaAs (semicond.)



http://what-when-how.com/wp-content/uploads

Nanotechnology

Nanoscale phenomena

Intermolecular forces and surface phenomena

Interactions between atoms and molecules

	Type	Strength (kJ/mol)	Example	Simplified description
Covalent bond	**Intra**molecular **Inter**atomic	Strong (100-1000)	H_2	Two atoms share valence electrons. The electrons of one atom are attracted by both nuclei.
Ionic bond	**Intra**molecular **Inter**atomic	Strong	Na^+Cl^-	The electrons are not shared. One atom accepts or donates one or more of its valence electrons to another atom. Electrostatic attractions between the ions.
Metallic bond	**Inter**atomic	Strong	Au, Al, Cu, Fe, Mg, ..	Metallic atoms that share valence electrons with many others. Each atom donates electrons to a "sea" of electrons.
Hydrogen-bond	**Inter**molecular **Intra**molecular	Weak (5-30)	Between H_2O molecules	Dipole-dipole interactions (between permanent dipoles). Forms between bonded hydrogen atoms and opposite charged molecules.
Van der Walls forces	**Inter**molecular **Inter**atomic	Weak	Between two graphite sheets	Dipole-dipole interactions.

Van der Waals (VdW) forces

Keesom forces:
permanent electric dipole –
permanent electric dipole

Debye forces:
permanent electric dipole –
induced electric dipole

London forces:
induced electric dipole –
induced electric dipole

The charge distribution in the molecules changes with time, determining at certains instants a non zero electric dipole, which can induce a dielectric dipole in a another molecule.

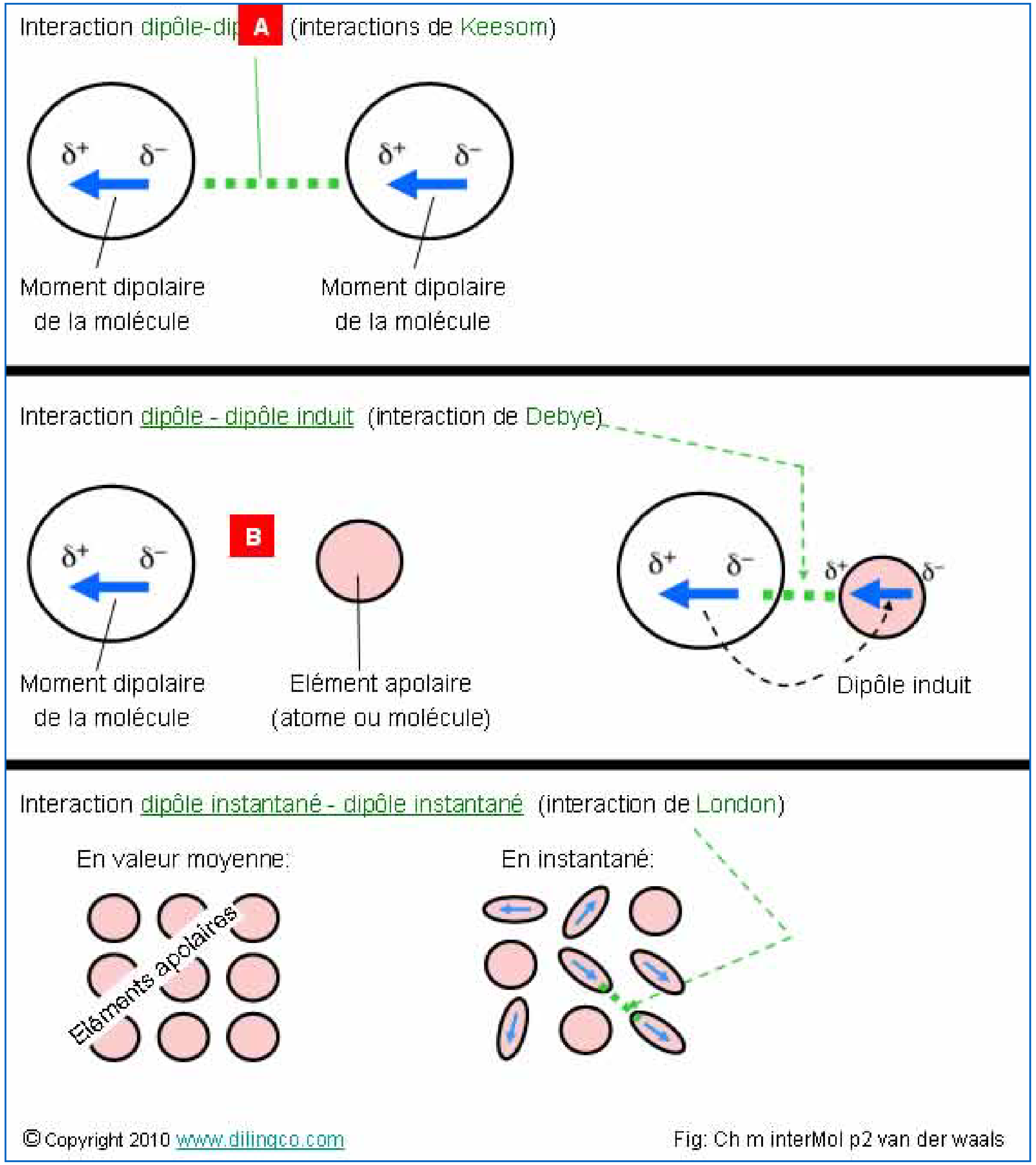


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Fig: Ch m interMol p2 van der waals

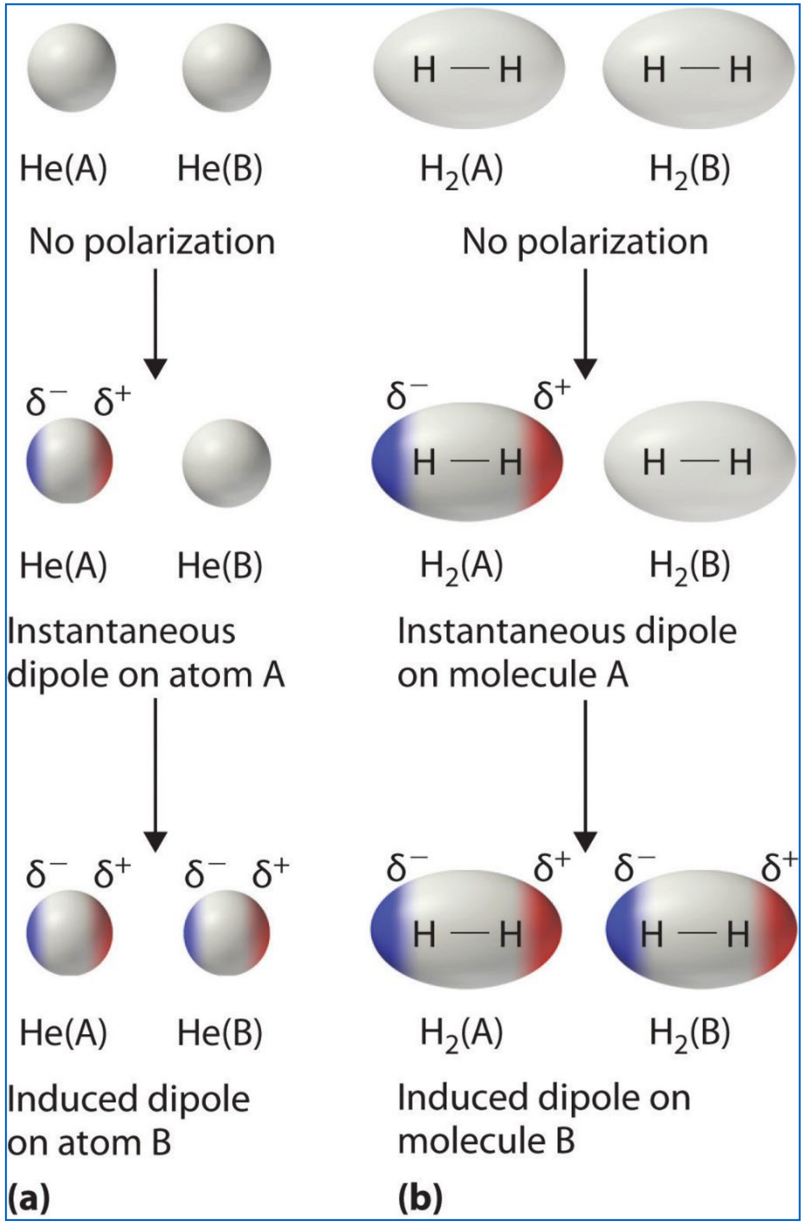
Van der Waals (VdW) forces: London dispersion

London dispersion forces is a weak intermolecular force arising from quantum induced instantaneous polarization multipoles in molecules (between molecules without permanent multipole moments).

London forces are exhibited because of the correlated movements of the electrons in interacting molecules. Because the electrons from different molecules tends to avoiding each other, electron density in a molecule becomes redistributed in proximity to another molecule.
This is frequently described as formation of "instantaneous dipoles" that attract each other.

London forces are the only attractive intermolecular force present between neutral atoms (e.g., a noble gas). Without London forces, there would be no attractive force between noble gas atoms, and they wouldn't exist in liquid form.

London forces become stronger as the atom or molecule are larger. This is due to the increased polarizability of molecules with larger, more dispersed electron clouds. This trend is exemplified by the halogens (from smallest to largest: F_2, Cl_2, Br_2, I_2). At room temperature: Fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid.



http://images.flatworldknowledge.com/averillfwk/averillfwk-fig11_005.jpg

Van der Waals (VdW) forces: key facts

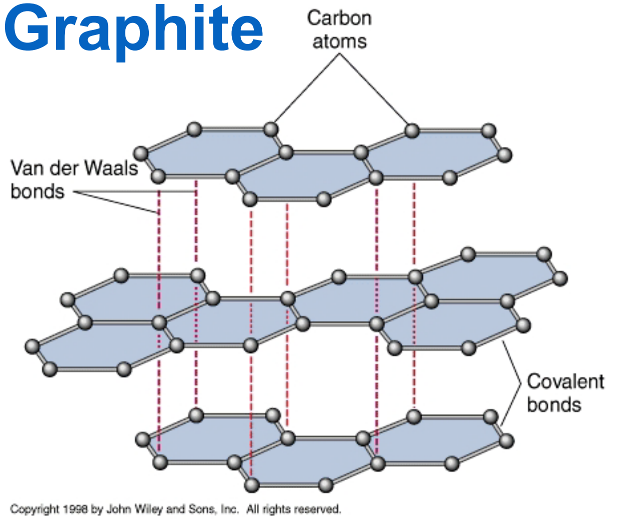
Van der Waals forces:

- sometimes used as a synonym for the totality of **inter**molecular forces.
- include attractions and repulsions between atoms, molecules,…,
- include the interactions between electric dipoles but also multipoles
- often described by the Lennard-Jones potential as approximate model for the isotropic part of a total repulsion plus attraction force as a function of distance.
- relatively weak compared to chemical bonds (covalent, ionic, metallic).
- play a fundamental role in structural biology, polymer science, nanotechnology, surface science, and condensed matter physics.
- responsible for physisorption, capillarity forces, forces between noble gases atoms, forces between nanoparticles, ….

http://en.wikipedia.org/wiki/Van_der_Waals_force

Local VdW forces: examples

Graphite



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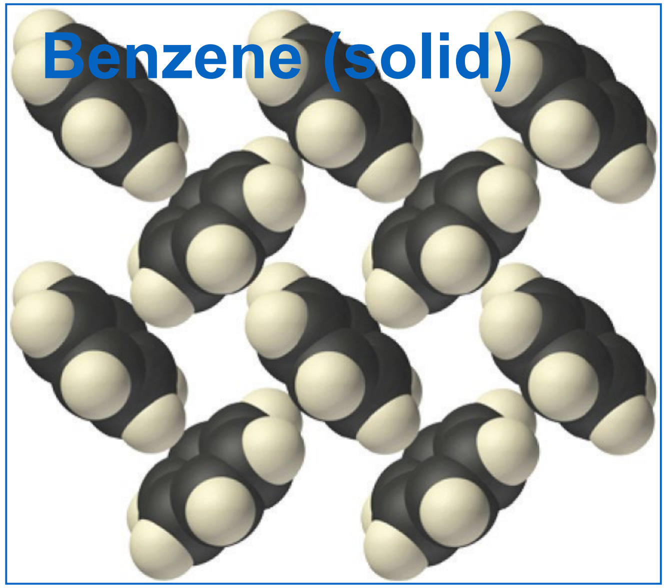
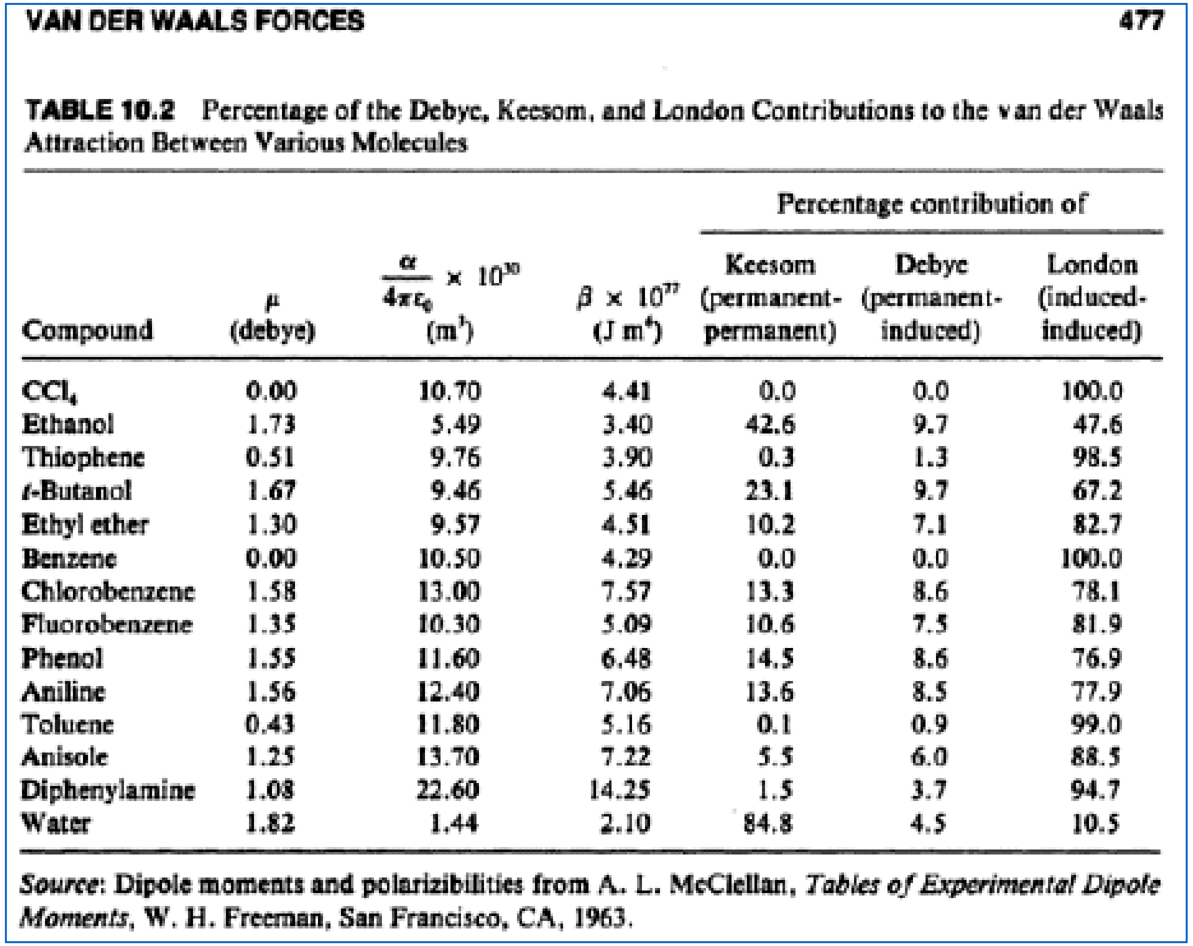
Benzene (solid)



Often different types of dipole-dipole interations are present at the same time



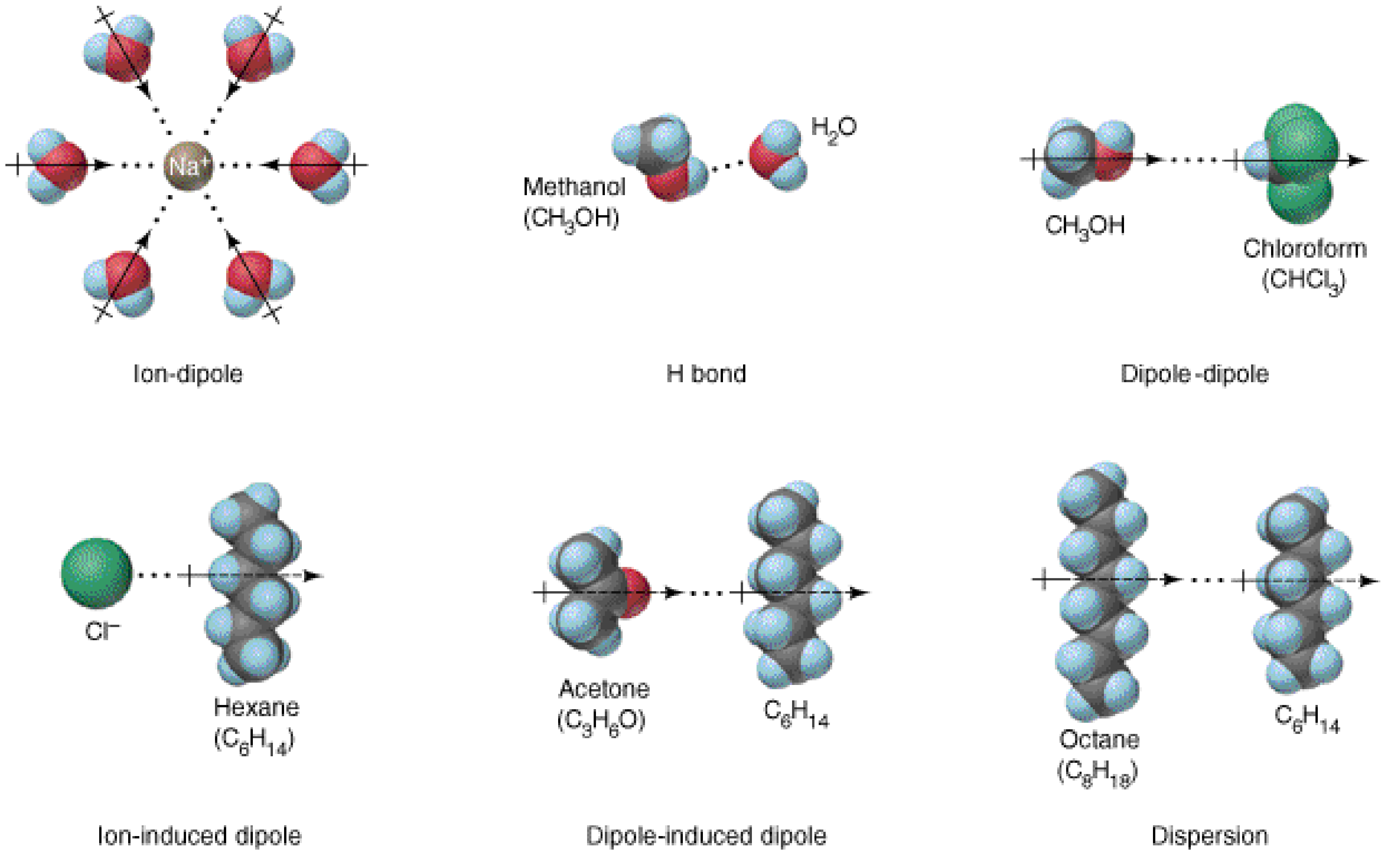
VAN DER WAALS FORCES 477

TABLE 10.2 Percentage of the Debye, Keesom, and London Contributions to the van der Waals Attraction Between Various Molecules

Compound	μ (debye)	$\frac{\alpha}{4\pi\varepsilon_0} \times 10^{30}$ (m^3)	$\beta \times 10^{77}$ ($J\ m^6$)	Percentage contribution of: Keesom (permanent-permanent)	Debye (permanent-induced)	London (induced-induced)
CCl_4	0.00	10.70	4.41	0.0	0.0	100.0
Ethanol	1.73	5.49	3.40	42.6	9.7	47.6
Thiophene	0.51	9.76	3.90	0.3	1.3	98.5
t-Butanol	1.67	9.46	5.46	23.1	9.7	67.2
Ethyl ether	1.30	9.57	4.51	10.2	7.1	82.7
Benzene	0.00	10.50	4.29	0.0	0.0	100.0
Chlorobenzene	1.58	13.00	7.57	13.3	8.6	78.1
Fluorobenzene	1.35	10.30	5.09	10.6	7.5	81.9
Phenol	1.55	11.60	6.48	14.5	8.6	76.9
Aniline	1.56	12.40	7.06	13.6	8.5	77.9
Toluene	0.43	11.80	5.16	0.1	0.9	99.0
Anisole	1.25	13.70	7.22	5.5	6.0	88.5
Diphenylamine	1.08	22.60	14.25	1.5	3.7	94.7
Water	1.82	1.44	2.10	84.8	4.5	10.5

Source: Dipole moments and polarizibilities from A. L. McClellan, *Tables of Experimental Dipole Moments*, W. H. Freeman, San Francisco, CA, 1963.

Local VdW forces: examples



http://www.science.uwaterloo.ca/~cchieh/cact/fig/interaction.gif

Lennard-Jones potential

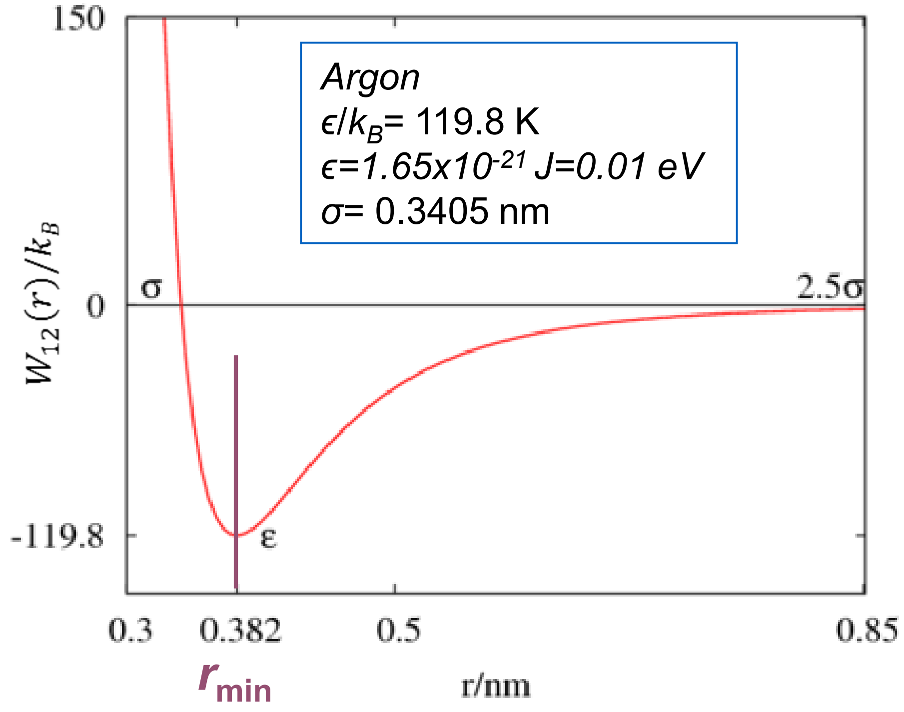
- The **Lennard-Jones potential** is an intermolecular pair potential between two neutral atoms or molecules:

$$W_{12}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] = \varepsilon\left[\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right]$$

  - $m = 6$ (attractive long-range term: **Van der Waals** forces)
  - $n = 12$ (repulsive short-range term: **Pauli repulsion** due to overlapping orbitals)
  - Typically: $r_{\min} \approx 0.5$ nm

$r = |\mathbf{r}_1 - \mathbf{r}_2|$
$W_{12}(r)$: intermolecular pair potential
σ: value of r at which $W_{12}(r)=0$
$r_{\min}$: value of r at which $W_{12}(r)$ is minimum
ϵ : well depth energy

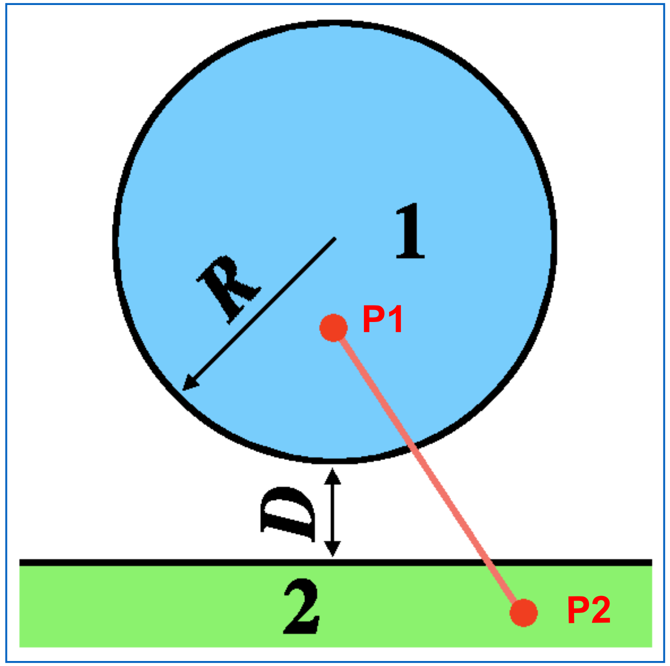
Lennard-Jones potential key-facts:
- Accurate model for noble gases
- Good approximation for neutral atoms and molecules
- Mathematically simple (fast calculations)
- Predicts a hexagonal close-packing of atoms



Macroscopic vdW: Hamaker constant

Potential: W

Force: $F = -\dfrac{\partial W}{\partial r}$



- **For two atoms or molecules**
  - (At long distance, $r \gg r_{\min}$):

$$W(r) = \varepsilon\left[\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right] \cong -2\varepsilon\left(\frac{r_{\min}}{r}\right)^{6} = -\frac{C}{r^6}$$

$$F(r) = -\frac{\partial W(r)}{\partial r} \propto \frac{1}{r^7}$$

- **For two solids**
  - VdW interactions are (double) summed over all atoms in both volumes:

$$W_{12}(D) = -\sum_{V1}\sum_{V2} \frac{C_{P_1,P_2}}{\left\|\vec{r}_{P_1,P_2}(D)\right\|^6}$$

Note: We assume that many-body interactions and retardation effects are negligible. (i.e., the forces are additive and non-retarded)

Israelachvili, Intermolecular and surface forces, 3rd ed. (2011), p. 253

Macroscopic vdW: Hamaker constant

- If both volumes are homogenous:

$$W_{12}(D) = -C_{12}\rho_1\rho_2 \int_{V1}\int_{V2} \frac{1}{\left\|\vec{r}_{12}(D)\right\|^6} dV_2 dV_1$$

ρ_1, ρ_2 : density of materials 1 and 2 (i.e., atoms or molucules per unit of volume)

C_{12} : interaction constant for an atom or molecule in material 1and an atom or molecule in material 2

$(C_{12} = 2\varepsilon_{12}(r_{\min 12})^6)$

- If we define the **Hamaker constant** A_{12}:

$$A_{12} \equiv -\pi^2\rho_1\rho_2 C_{12} \quad \Rightarrow \quad W_{12}(D) = -\frac{A_{12}}{\pi^2} \int_{V1}\int_{V2} \frac{1}{\left\|\vec{r}_{12}(D)\right\|^6} dV_2 dV_1$$

Unit: energy (in the order of 10^{-20} J)

Macroscopic VdW – many body and retardation effects

Hamaker extended the intermolecular VdW force to macroscopic bodies by:
- simple pairwise summation of vdW interactions between the molecules of the interacting bodies (neglecting **many-body interactions effects**).

- neglecting the finiteness of the speed of light **(**neglecting **retardation effects)**.
In some situations retardation effects are important also down to nanoscale distances.

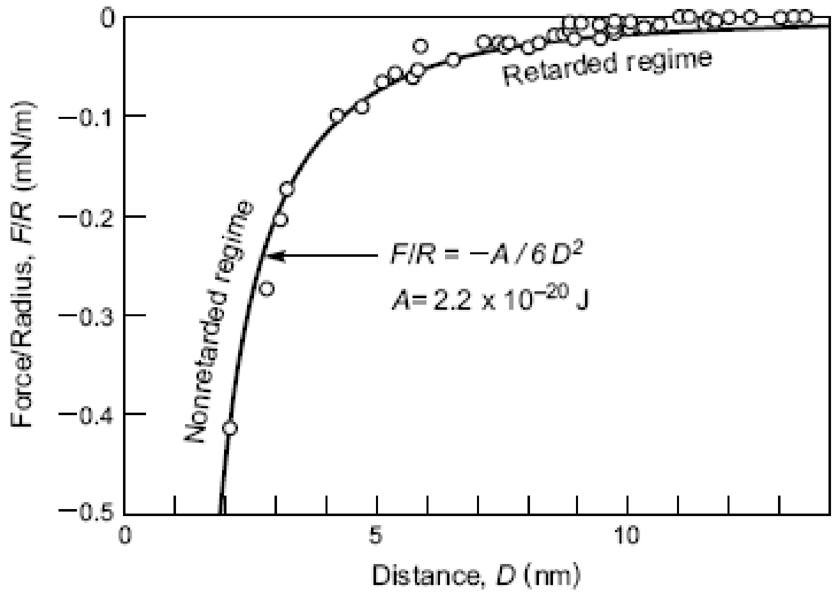


FIGURE 13.6 Attractive van der Waals force F between two curved mica surfaces of radius $R \approx 1$ cm measured in water and aqueous electrolyte solutions. The measured nonretarded Hamaker constant is $A = 2.2 \times 10^{-20}$ J. Retardation effects are apparent at distances above 5 nm where the measured forces are weaker than the extrapolated nonretarded force (solid line). *[Data from SFA experiments with surfaces in the crossed-cylinder geometry, equivalent to a sphere of radius R near a flat surface or two spheres of radius 2R, adapted from Israelachvili and Adams (1978) and Israelachvili and Pashley (unpublished).]*

Israelachvili, Intermolecular and surface forces, 3rd ed. (2011)

VdW forces: Hamaker constant of some materials

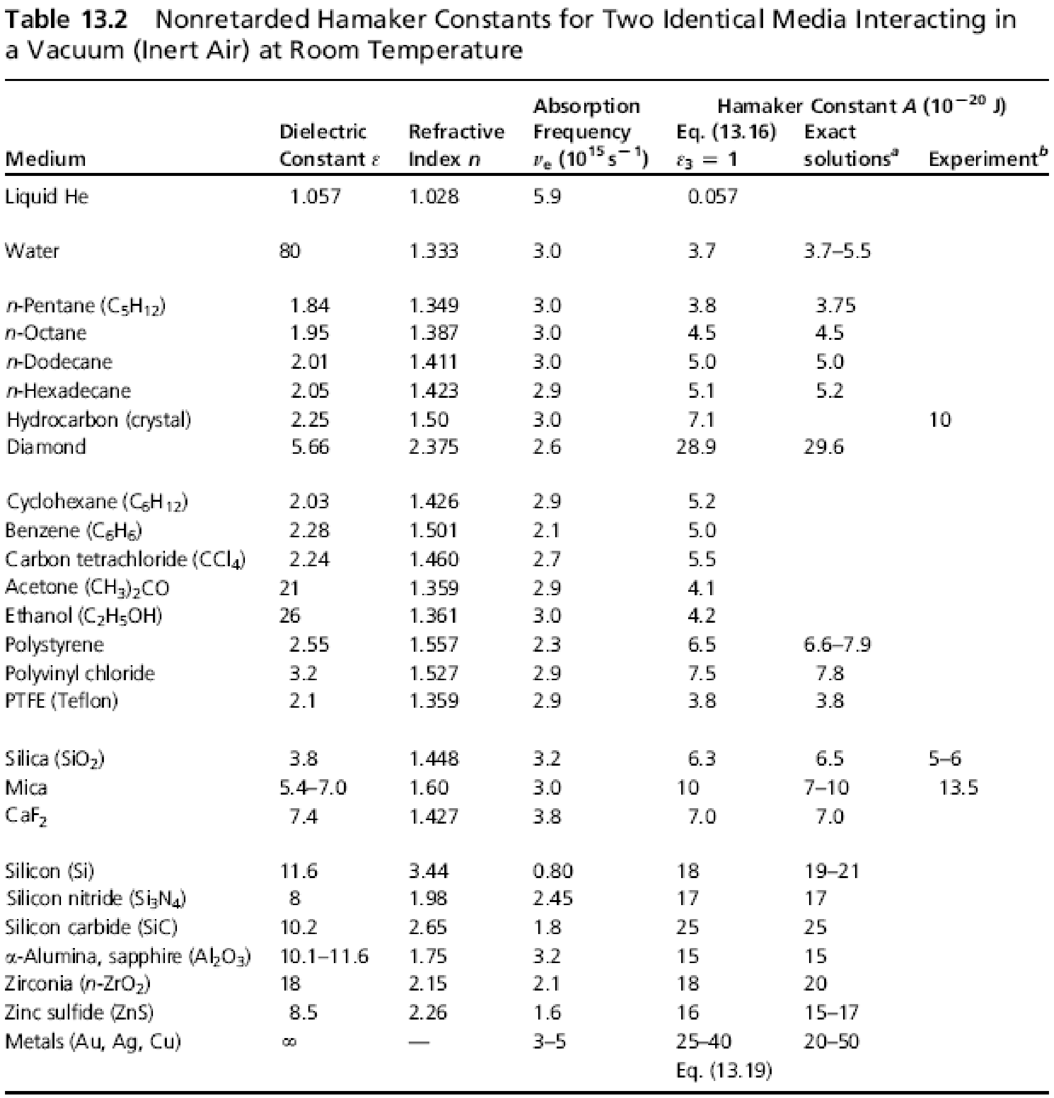


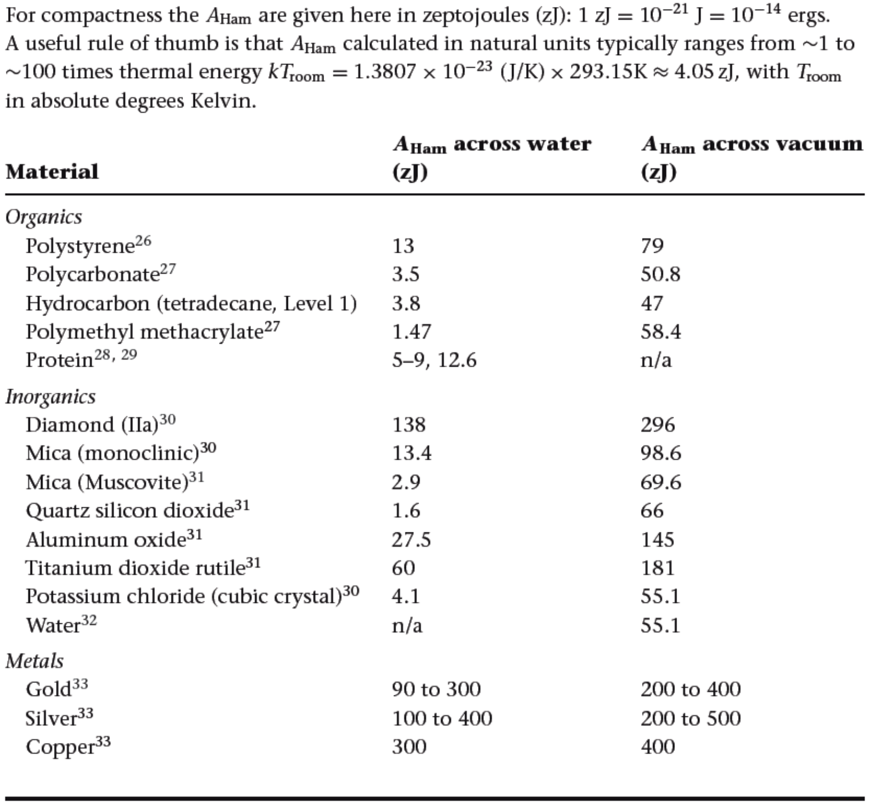
Table 13.2 Nonretarded Hamaker Constants for Two Identical Media Interacting in a Vacuum (Inert Air) at Room Temperature

Medium	Dielectric Constant ε	Refractive Index n	Absorption Frequency ν_e ($10^{15}\,s^{-1}$)	Hamaker Constant A (10^{-20} J) Eq. (13.16) $\varepsilon_3 = 1$	Exact solutions[a]	Experiment[b]
Liquid He	1.057	1.028	5.9	0.057		
Water	80	1.333	3.0	3.7	3.7–5.5	
n-Pentane (C_5H_{12})	1.84	1.349	3.0	3.8	3.75	
n-Octane	1.95	1.387	3.0	4.5	4.5	
n-Dodecane	2.01	1.411	3.0	5.0	5.0	
n-Hexadecane	2.05	1.423	2.9	5.1	5.2	
Hydrocarbon (crystal)	2.25	1.50	3.0	7.1		10
Diamond	5.66	2.375	2.6	28.9	29.6	
Cyclohexane (C_6H_{12})	2.03	1.426	2.9	5.2		
Benzene (C_6H_6)	2.28	1.501	2.1	5.0		
Carbon tetrachloride (CCl_4)	2.24	1.460	2.7	5.5		
Acetone ($(CH_3)_2CO$)	21	1.359	2.9	4.1		
Ethanol (C_2H_5OH)	26	1.361	3.0	4.2		
Polystyrene	2.55	1.557	2.3	6.5	6.6–7.9	
Polyvinyl chloride	3.2	1.527	2.9	7.5	7.8	
PTFE (Teflon)	2.1	1.359	2.9	3.8	3.8	
Silica (SiO_2)	3.8	1.448	3.2	6.3	6.5	5–6
Mica	5.4–7.0	1.60	3.0	10	7–10	13.5
CaF_2	7.4	1.427	3.8	7.0	7.0	
Silicon (Si)	11.6	3.44	0.80	18	19–21	
Silicon nitride (Si_3N_4)	8	1.98	2.45	17	17	
Silicon carbide (SiC)	10.2	2.65	1.8	25	25	
α-Alumina, sapphire (Al_2O_3)	10.1–11.6	1.75	3.2	15	15	
Zirconia (*n*-ZrO_2)	18	2.15	2.1	18	20	
Zinc sulfide (ZnS)	8.5	2.26	1.6	16	15–17	
Metals (Au, Ag, Cu)	∞	—	3–5	25–40 Eq. (13.19)	20–50	

Israelachvili, Intermolecular and surface forces, 3rd ed. (2011),p.263

Example: Water: $\rho_1 \cong \rho_2 \cong 3\times10^{28}\,\mathrm{m}^{-3},\ \varepsilon \cong 10^{-21}\,\mathrm{J},\ r_{\min} \sim 0.3\ \mathrm{nm}$

$C_{12} = 2\varepsilon\left(r_{\min}\right)^6 \sim 10^{-78}\,\mathrm{Jm}^6 \Rightarrow A_{12} = \pi^2\rho_1\rho_2C_{12} \sim 10^{-20}\,\mathrm{J}$



For compactness the A_{Ham} are given here in zeptojoules (zJ): 1 zJ = 10^{-21} J = 10^{-14} ergs. A useful rule of thumb is that A_{Ham} calculated in natural units typically ranges from ∼1 to ∼100 times thermal energy kT_{room} = 1.3807 × 10^{-23} (J/K) × 293.15K ≈ 4.05 zJ, with T_{room} in absolute degrees Kelvin.

Material	A_{Ham} across water (zJ)	A_{Ham} across vacuum (zJ)
Organics		
Polystyrene[26]	13	79
Polycarbonate[27]	3.5	50.8
Hydrocarbon (tetradecane, Level 1)	3.8	47
Polymethyl methacrylate[27]	1.47	58.4
Protein[28, 29]	5–9, 12.6	n/a
Inorganics		
Diamond (IIa)[30]	138	296
Mica (monoclinic)[30]	13.4	98.6
Mica (Muscovite)[31]	2.9	69.6
Quartz silicon dioxide[31]	1.6	66
Aluminum oxide[31]	27.5	145
Titanium dioxide rutile[31]	60	181
Potassium chloride (cubic crystal)[30]	4.1	55.1
Water[32]	n/a	55.1
Metals		
Gold[33]	90 to 300	200 to 400
Silver[33]	100 to 400	200 to 500
Copper[33]	300	400

Parsegian Van der Waals Forces, (2016),p.19

VdW forces: Hamaker constant of some materials

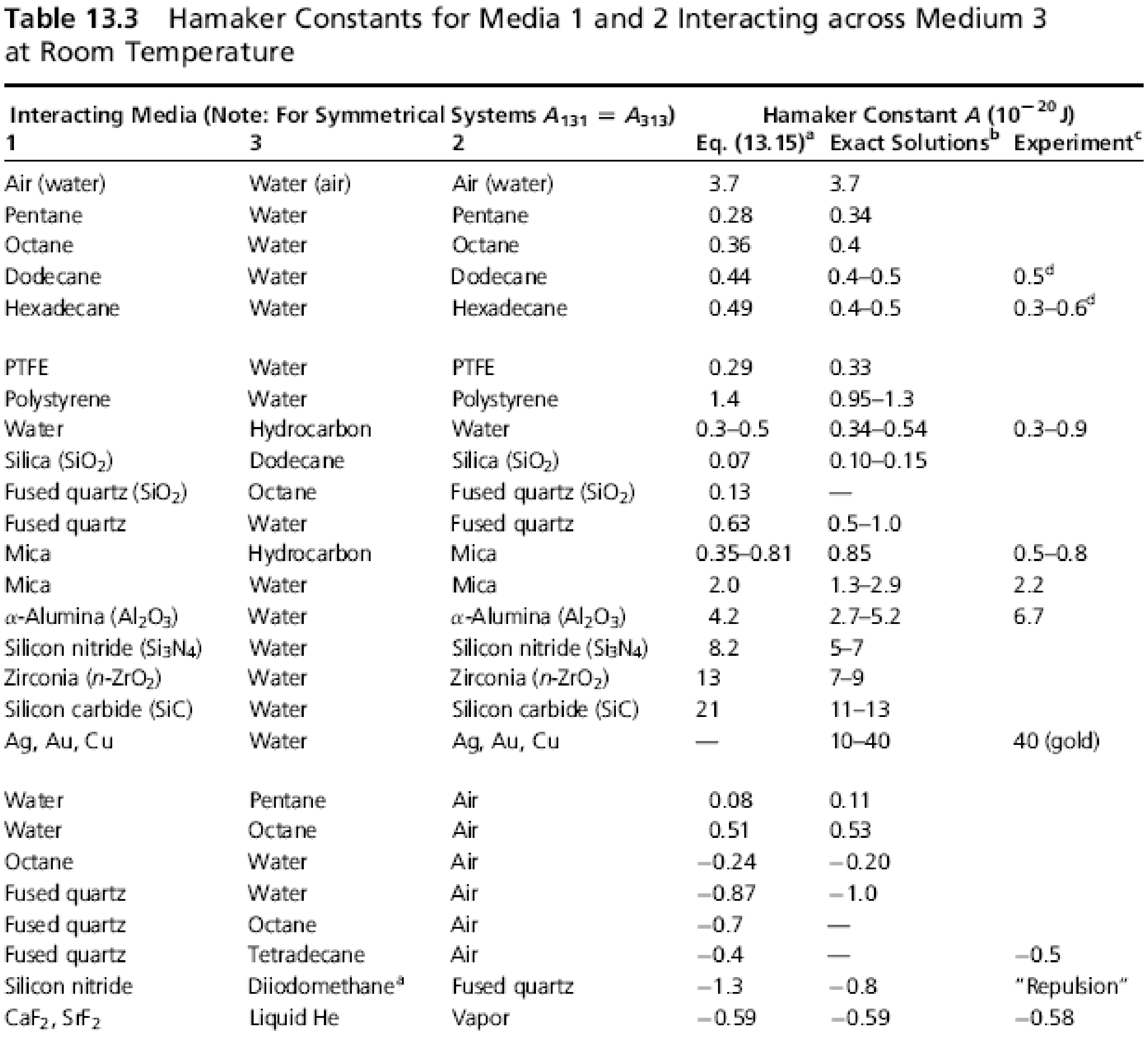


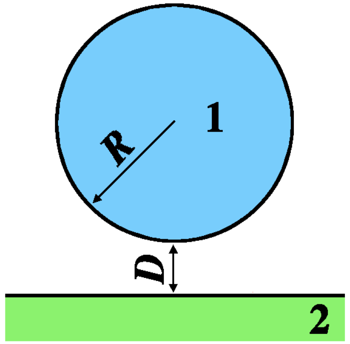
Table 13.3 Hamaker Constants for Media 1 and 2 Interacting across Medium 3 at Room Temperature

Interacting Media (Note: For Symmetrical Systems $A_{131} = A_{313}$)			Hamaker Constant A (10^{-20} J)		
1	3	2	Eq. (13.15)[a]	Exact Solutions[b]	Experiment[c]
Air (water)	Water (air)	Air (water)	3.7	3.7	
Pentane	Water	Pentane	0.28	0.34	
Octane	Water	Octane	0.36	0.4	
Dodecane	Water	Dodecane	0.44	0.4–0.5	0.5[d]
Hexadecane	Water	Hexadecane	0.49	0.4–0.5	0.3–0.6[d]
PTFE	Water	PTFE	0.29	0.33	
Polystyrene	Water	Polystyrene	1.4	0.95–1.3	
Water	Hydrocarbon	Water	0.3–0.5	0.34–0.54	0.3–0.9
Silica (SiO_2)	Dodecane	Silica (SiO_2)	0.07	0.10–0.15	
Fused quartz (SiO_2)	Octane	Fused quartz (SiO_2)	0.13	—	
Fused quartz	Water	Fused quartz	0.63	0.5–1.0	
Mica	Hydrocarbon	Mica	0.35–0.81	0.85	0.5–0.8
Mica	Water	Mica	2.0	1.3–2.9	2.2
α-Alumina (Al_2O_3)	Water	α-Alumina (Al_2O_3)	4.2	2.7–5.2	6.7
Silicon nitride (Si_3N_4)	Water	Silicon nitride (Si_3N_4)	8.2	5–7	
Zirconia (n-ZrO_2)	Water	Zirconia (n-ZrO_2)	13	7–9	
Silicon carbide (SiC)	Water	Silicon carbide (SiC)	21	11–13	
Ag, Au, Cu	Water	Ag, Au, Cu	—	10–40	40 (gold)
Water	Pentane	Air	0.08	0.11	
Water	Octane	Air	0.51	0.53	
Octane	Water	Air	−0.24	−0.20	
Fused quartz	Water	Air	−0.87	−1.0	
Fused quartz	Octane	Air	−0.7	—	
Fused quartz	Tetradecane	Air	−0.4	—	−0.5
Silicon nitride	Diiodomethane[a]	Fused quartz	−1.3	−0.8	"Repulsion"
CaF_2, SrF_2	Liquid He	Vapor	−0.59	−0.59	−0.58

Israelachvili, Intermolecular and surface forces, 3rd ed. (2011),p.263

Macroscopic VdW - spheres

- **Sphere – Surface:**



$$W_{12} \cong -\frac{A_{12}}{6}\frac{R}{D} \qquad \text{for } D \ll R$$

- **Example: Sphere Teflon (PTFE) (R=50 nm) – Surface Teflon (PTFE)**

$$F = -\frac{dW_{12}}{dD} = -\frac{A_{12}}{6}\frac{R}{D^2} \qquad A_{12} = 38\times10^{-21}\text{J}$$

Distance $D = 10$ nm: $W \cong 3\times10^{-20}$ J, $F \cong 3\times10^{-12}$ N

Distance $D = 5$ nm: $W \cong 6\times10^{-20}$ J, $F \cong 13\times10^{-12}$ N

Note: Gravitational force on a PTFE nanospheres:

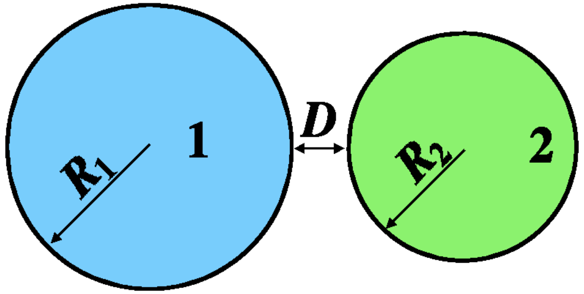
$r = 50$ nm $\Rightarrow$ $m \cong 10^{-18}$ kg, $F_{grav} \cong mg \cong 10^{-17}$ N

$r = 5$ µm $\Rightarrow$ $m \cong 10^{-12}$ kg, $F_{grav} \cong mg \cong 10^{-11}$ N

(at nanoscale the gravitational force is much weaker than the VdW force)

Macroscopic VdW - spheres

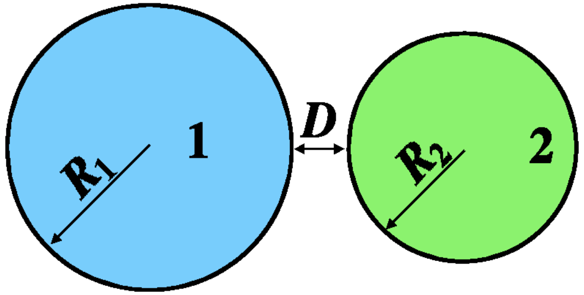
- **Sphere - Sphere**: general case (arbitrary *D/R* ratio)



This is interesting for nanoparticles VdW interactions

$$W(D) = -\frac{A}{6}\left\{\frac{2R_1R_2}{(2R_1+2R_2+D)D} + \frac{2R_1R_2}{(2R_1+D)(2R_2+D)} + \ln\frac{(2R_1+2R_2+D)D}{(2R_1+D)(2R_2+D)}\right\}.$$

- **Sphere - Sphere**: case D<<R_1,R_2



For $D \ll R_1, R_2$: $\quad W_{12} \cong -\frac{A_{12}}{6}\frac{R}{D}$

$$R = \frac{R_1 R_2}{R_1 + R_2}$$

Macroscopic VdW – summary of results

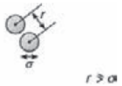
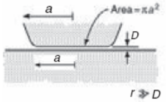
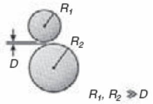
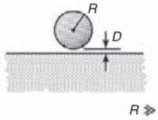
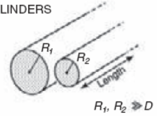
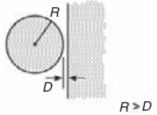
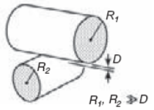
The Hamaker constant is defined as $A \equiv \pi^2 \rho_1 \rho_2 C_{12}$ where:

ρ_1, ρ_2 : number of atoms (molecules) per unit of volume in the two bodies

C_{12} : coefficient in the atom-atom (molecule-molecule) pair potential

Note 1:
Van der Waals interaction energy *W* and force *F* between macroscopic bodies:
A positive → *F* negative → attraction
A negative → *F* positive → repulsion

Note 2:
Van der Waals force decreases with decreasing particle size (*R*).
Inertial forces, such as gravity, decrease to a **greater** extent.
Hence, van der Waals forces become dominant for very small particles.
The van der Waals force of adhesion is also dependent on the surface topography. If there are surface asperities, that results in a greater total area of contact.

Geometry of bodies with surfaces *D* apart (*D*«*R*)		**Van der Waals Interaction***	
		Energy, *W*	**Force, *F* = −d*W*/d*D***
Two atoms or small molecules	TWO ATOMS or SMALL MOLECULES 	$-C/r^6$	$-6C/r^7$
Two flat surfaces (per unit area)	TWO FLAT SURFACES 	$W_{flat} = -A/12\pi D^2$	$-A/6\pi D^3$
Two spheres or macromolecules of radii R_1 and R_2	TWO SPHERES 	$\frac{-A}{6D}\left(\frac{R_1R_2}{R_1+R_2}\right)$	$\frac{-A}{6D^2}\left(\frac{R_1R_2}{R_1+R_2}\right)$ Also $F = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)W_{flat}$
Sphere or macro-molecule of radius *R* near a flat surface	SPHERE ON FLAT 	$-AR/6D$	$-AR/6D^2$ Also $F = 2\pi R W_{flat}$
Two parallel cylinders or rods of radii R_1 and R_2 (per unit length)	TWO PARALLEL CYLINDERS 	$\frac{-A}{12\sqrt{2}D^{3/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$	$\frac{-A}{8\sqrt{2}D^{5/2}}\left(\frac{R_1R_2}{R_1+R_2}\right)^{1/2}$
Cylinder of radius *R* near a flat surface (per unit length)	CYLINDER ON FLAT 	$\frac{-A\sqrt{R}}{12\sqrt{2}D^{3/2}}$	$\frac{-A\sqrt{R}}{8\sqrt{2}D^{5/2}}$
Two cylinders or filaments of radii R_1 and R_2 crossed at 90°	CROSSED CYLINDERS 	$\frac{-A\sqrt{R_1R_2}}{6D}$	$\frac{-A\sqrt{R_1R_2}}{6D^2}$ Also $F = 2\pi\sqrt{R_1R_2}W_{flat}$

Israelachvili, Intermolecular and surface forces, 3rd ed. (2011), p. 255

VdW - application to real gases

- **Ideal gas law**: $\boxed{PV = nRT}$

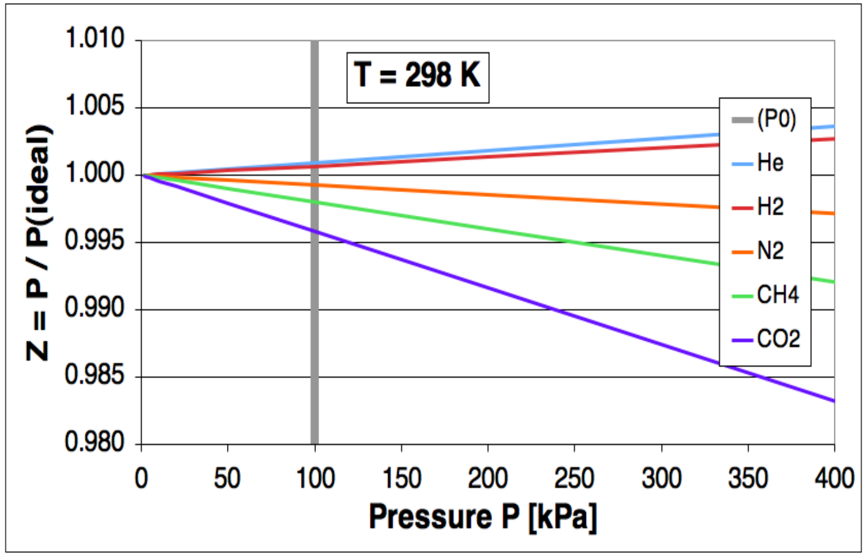
  R : ideal gas constant = 8.31 J/K mol ; T : temperature

  n : number of moles ; *P*: pressure; V : volume

- **Van der Waals correction to the ideal gas law:** $\boxed{\left[P + a\left(\frac{n}{V}\right)^2\right]\left(V - nb\right) = n\ R\ T}$

  a : intermolecular forces (**attractive only**)

  b : molecular volume of the gas



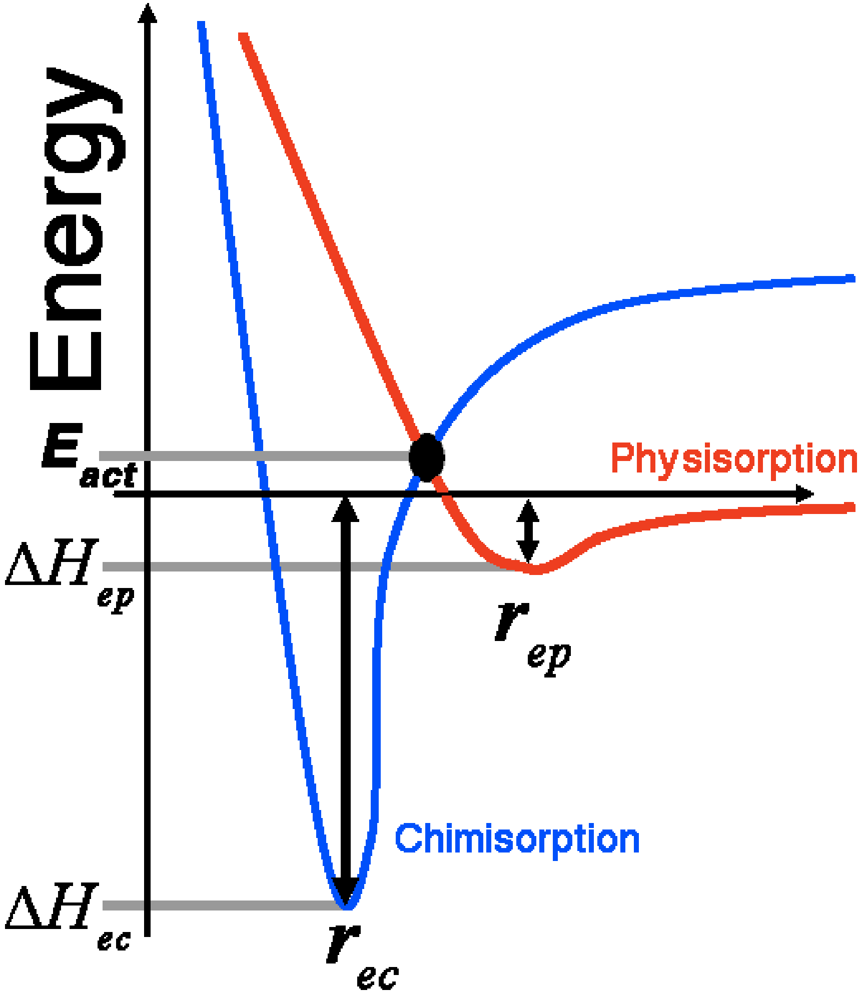
Gas	a [kPa/(mol/l)^2]	b [l/mol]
He	3.5	0.024
H_2	24.8	0.027
N_2	141	0.039
CH_4	228	0.043
CO_2	364	0.043

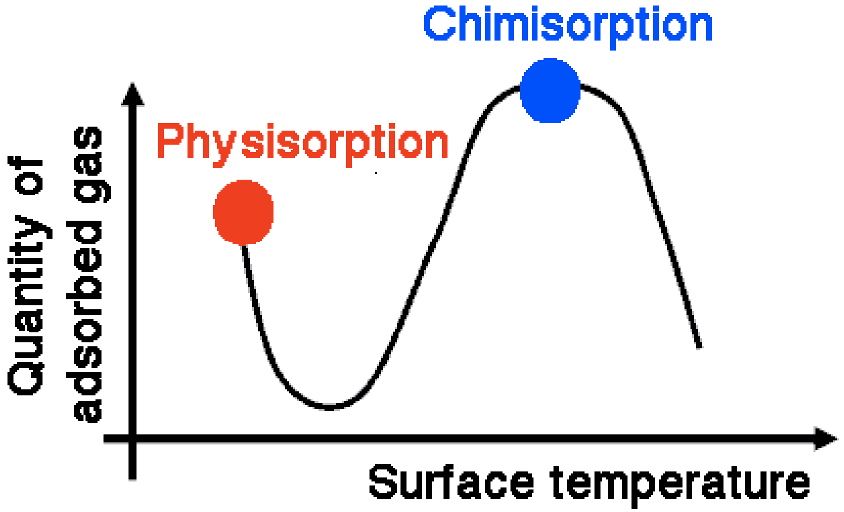
Physi- vs. Chemisorption: comparison

	Physisorption	Chemisorption
Origin of interaction	Van der Waals force (no common electronic orbitals)	Chemical bonds (common electronic orbitals)
Strength	Weak	Strong
Enthalpy	Exothermic (release of energy) $\lvert \Delta H_p \rvert < 20$ kJ/mol	Exothermic (release of energy) $\lvert \Delta H_p \rvert > 100$ kJ/mol
Equilibrium distance	0.4 to 0.6 nm (long-range interaction)	<0.3 nm (short-range interaction; formation of molecular bonds)
Specificity	Low	High
Temperature dependence	High close to boiling point	Formation depends on activation energy

Adsorption=retention of species (atoms, molecules, ions) on surface
Absorption=retention of species (atoms, molecules, ions) in volume

Physi- vs. Chemisorption: comparison





- Physical adsorption usually before chemical adsorption
- E_{act} = activation energy for chemical absorption
- Depending on the position of the 2 curves, chimisorption thermally activated or not

- Physisorption: no activation necessary
- Chimisorption: activation energy barrier must be overcome

Gas adsorption isotherms

Question

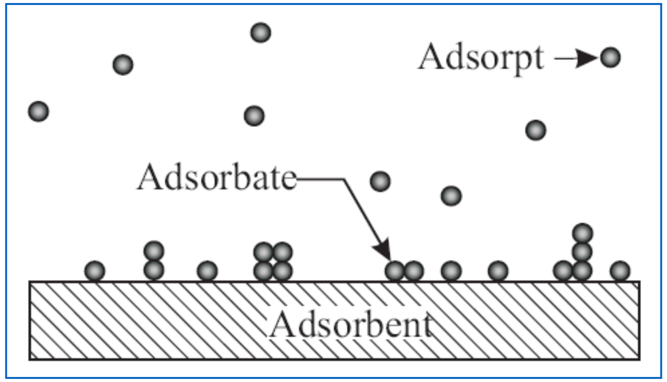
- Quantity of adsorbed gas vs *P* (at T=const.) ?

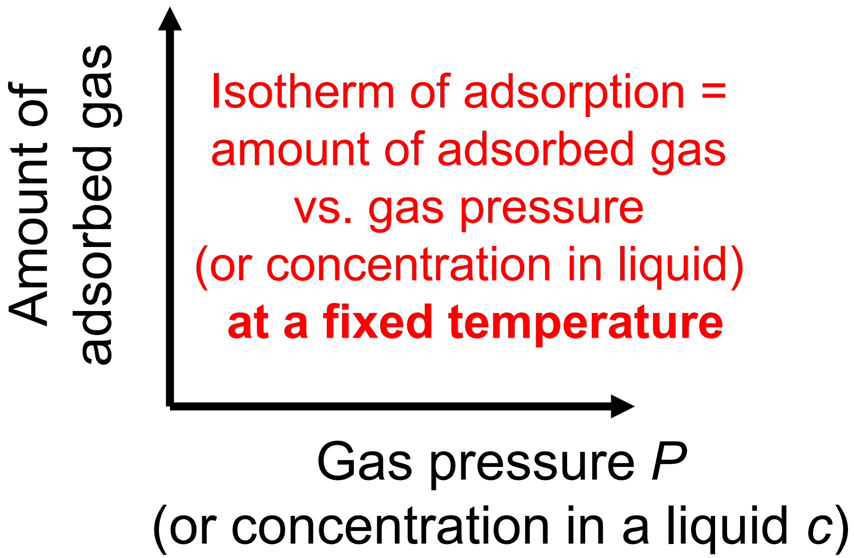
Important issues:

- Nature of adsorption (physical or chemical)

Models:

- Different models (Langmuir, Freundlich,…)





Amount of adsorbed gas

Isotherm of adsorption = amount of adsorbed gas vs. gas pressure (or concentration in liquid) **at a fixed temperature**

Gas pressure *P* (or concentration in a liquid *c*)

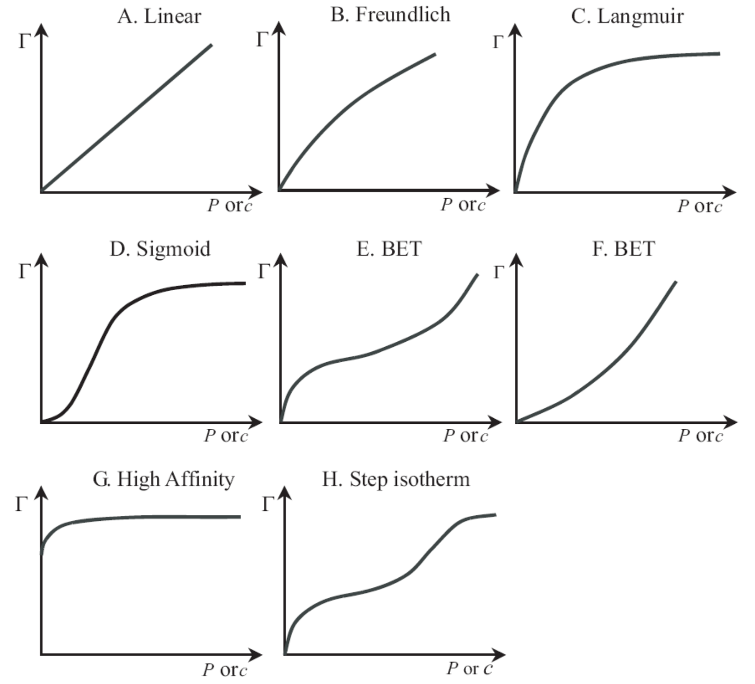
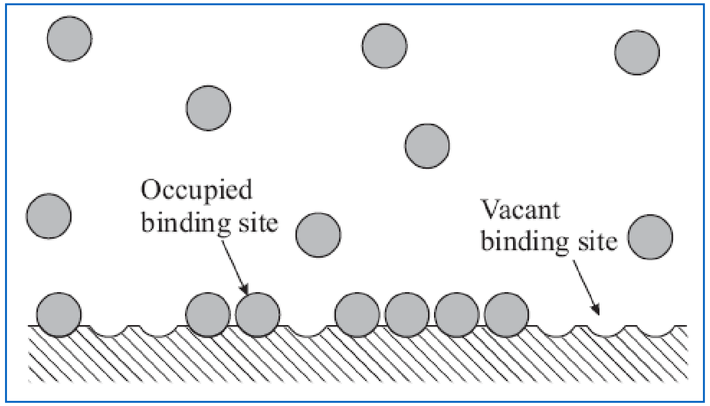


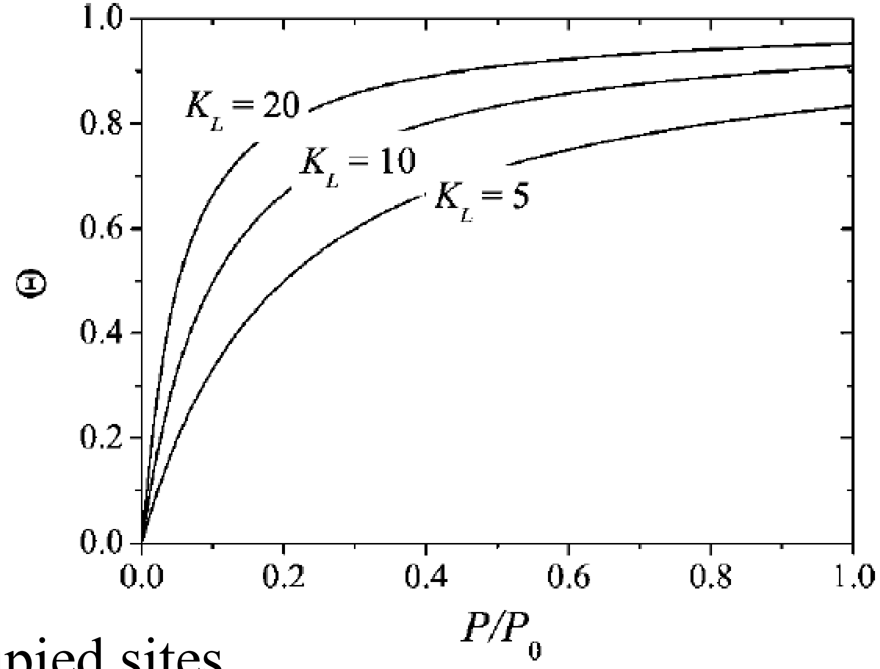
Figure 9.2: Schematic plot of eight types of adsorption isotherms commonly observed. If adsorption from the gas phase is studied, the abscissa is the partial pressure P. For adsorption from solution the concentration c is used.

Langmuir isotherm: simplified derivation of the equation

Assumptions of the Langmuir isotherm adsorption model:

1. Molecules adsorb on the surface (but not on each other, i.e. less than a monolayer)
2. Adsorbed molecules do not interact with each other
3. The surface is homogeneous: all locations adsorb molecules with the same probability.





Adsorption Rate

$$v_{ads} = k_{ads} P(1-\theta)$$

Desorption Rate

$$v_{des} = k_{des}\theta$$

Equilibrium Condition

$$v_{des} = v_{ads}$$

$$\Rightarrow$$

θ : Fraction of occupied sites

P : Pressure of the gas above the surface

$$\theta = \frac{k_{ads}P}{k_{des} + k_{ads}P} = \frac{K_L P}{1 + K_L P}$$

$$K_L = \frac{k_{ads}}{k_{des}}$$

Langmuir isotherm - temperature effect

From kinetic theory and thermodynamic consideration we get:

$$k_{des} = \frac{\exp\left(-Q/k_B T\right)}{\tau_0} \qquad k_{ad} = \frac{\sigma_A}{\sqrt{2\pi m k_B T}}$$

$$\Rightarrow K_L = \frac{k_{ad}}{k_{des}} = \frac{\sigma_A \tau_0 \exp\left(Q/k_B T\right)}{\sqrt{2\pi m k_B T}}$$

σ_A : molecular cross-section

Q: heat of adsoption

τ_0 : surface bond

vibration time $((10^{-12} \div 10^{-15})\mathrm{s})$

m : molecular mass

Consequences (quite intuitive):

- K_L increases for stronger bonding (larger Q).

→ Stronger bonding needs less pressure for same coverage.

- K_L decreases with increasing temperature (thermal activation profile)

→ Increasing temperature needs more pressure for same coverage.

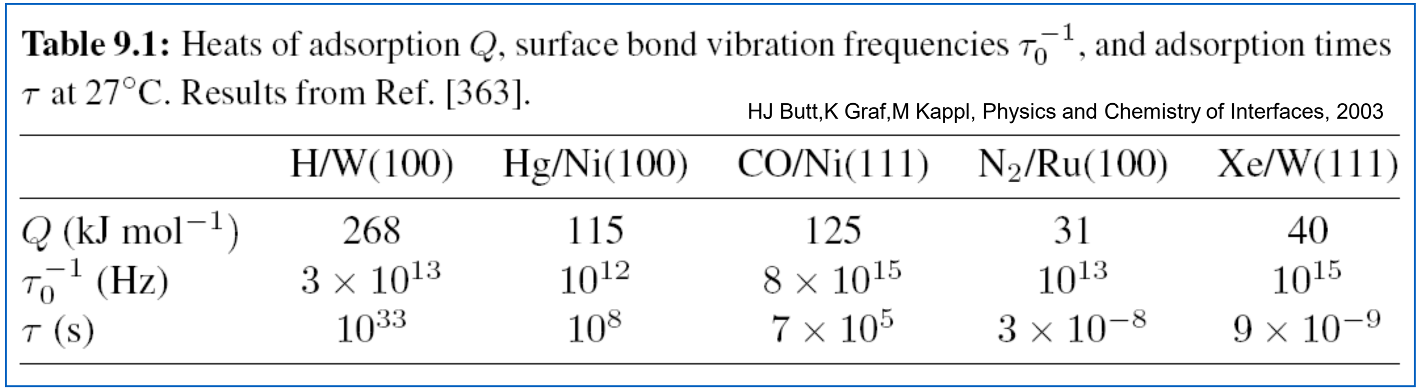


Table 9.1: Heats of adsorption Q, surface bond vibration frequencies τ_0^{-1}, and adsorption times τ at 27°C. Results from Ref. [363].

HJ Butt,K Graf,M Kappl, Physics and Chemistry of Interfaces, 2003

	H/W(100)	Hg/Ni(100)	CO/Ni(111)	N_2/Ru(100)	Xe/W(111)
Q (kJ mol^{-1})	268	115	125	31	40
τ_0^{-1} (Hz)	3×10^{13}	10^{12}	8×10^{15}	10^{13}	10^{15}
τ (s)	10^{33}	10^{8}	7×10^{5}	3×10^{-8}	9×10^{-9}

Pure chemisorption and intermediate case

Pure chemisorption

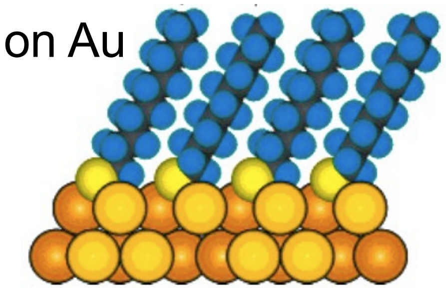
- Negative enthalpy, $\Delta H_c < -100$ kJ/mol
- Covalent / ionic / metallic
- Distance < 3Å

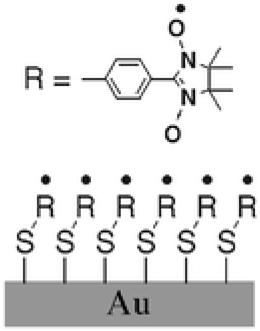
Examples:

O$_2$ on metals

Thiols on Au

Thiols on Au





Weak chemisorption + hydrogen bond

- $\Delta H_{2\ldots n} \approx 44$ kJ/mol
- $\Delta H1 \approx 25$ kJ/mol

$$\mathrm{SiO_2} \underset{\mathrm{HT}}{\overset{\mathrm{H_2O}}{\rightleftarrows}} \mathrm{SiO{-}H} \underset{\mathrm{HT}}{\overset{\mathrm{H_2O}}{\rightleftarrows}} \mathrm{SiO{-}H{\cdots}H_2O}$$

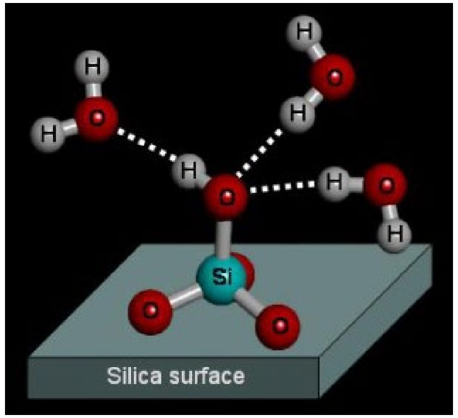
Example:

H_2O on SiO$_2$ surface

(creation of silanol sites on SiO$_2$,

physical absorption of more H_2O layers)

H_2O on SiO$_2$ surface



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Surface tension (or energy)

The concept of “surface tension” is important to understand adhesion and wetting phenomena.

Surface tension (or energy) definition:

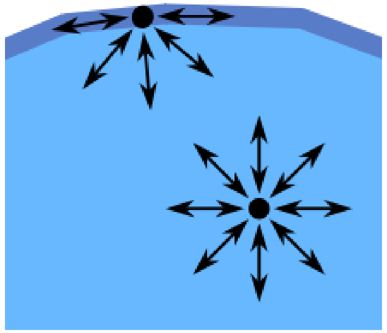
$$\gamma \equiv \left(\frac{\partial G}{\partial A}\right)_{T,P,\mu}$$

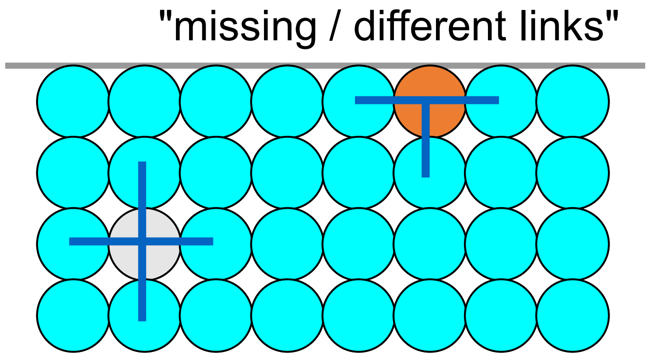
Energy to create a unitary surface *A* at constant temperature *T*, pressure *P*, and chemical potential μ. *G* is the Gibbs free energy ($G=U+PV-TS$). *S* is the entropy, *U* is the internal energy.
The work required to increase a surface by dA is $dW=\gamma dA$.

Units of the surface tension γ: N/m
(force per unit of length [N/m] or energy per unit surface [$J/m^2=Nm/m^2=N/m$])

Note 1:
The internal energy *U* of a system is the total energy contained within it, including:
1.Kinetic energy of molecules (due to translation, rotation, and vibration).
2.Potential energy from intermolecular and atomic forces (chemical bonds, electrostatic interactions)

Note 2:
$\Delta G<0$: Spontaneous process (reaction occurs naturally)
$\Delta G>0$: Non-spontaneous process (requires energy input)
$\Delta G=0$: System is at equilibrium





Surface tension: usually refers to liquid. Surface energy: refers also to solids.

Surface tension: Adhesion & cohesion work

Work of **adhesion** and **cohesion** in vacuum are the reversible work done to separate two surfaces or media from contact to infinity in vacuum.

- The work (per unit of area) to separate two materials 1 and 2 is the **adhesion work** and it is given by:

$$W_{AD}(1,2) = W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$$

γ_1 : surface tension of material 1

γ_2 : surface tension of material 2

γ_{12} : interfacial tension between material 1 and material 2 (i.e., energy per unit of surface required to separate material 1 from material 1 into a medium of material 2).

- The work (per unit of area) to separate into two parts a material (to create a surface of double area) is the **cohesion work** and it is given by

$$\boxed{W_C(1,1) = W_{11} = 2\gamma_1}$$

Note: since all media attract each other in vacuum W_{11} and W_{12} are always positive.

Surface tension: Adhesion & cohesion work

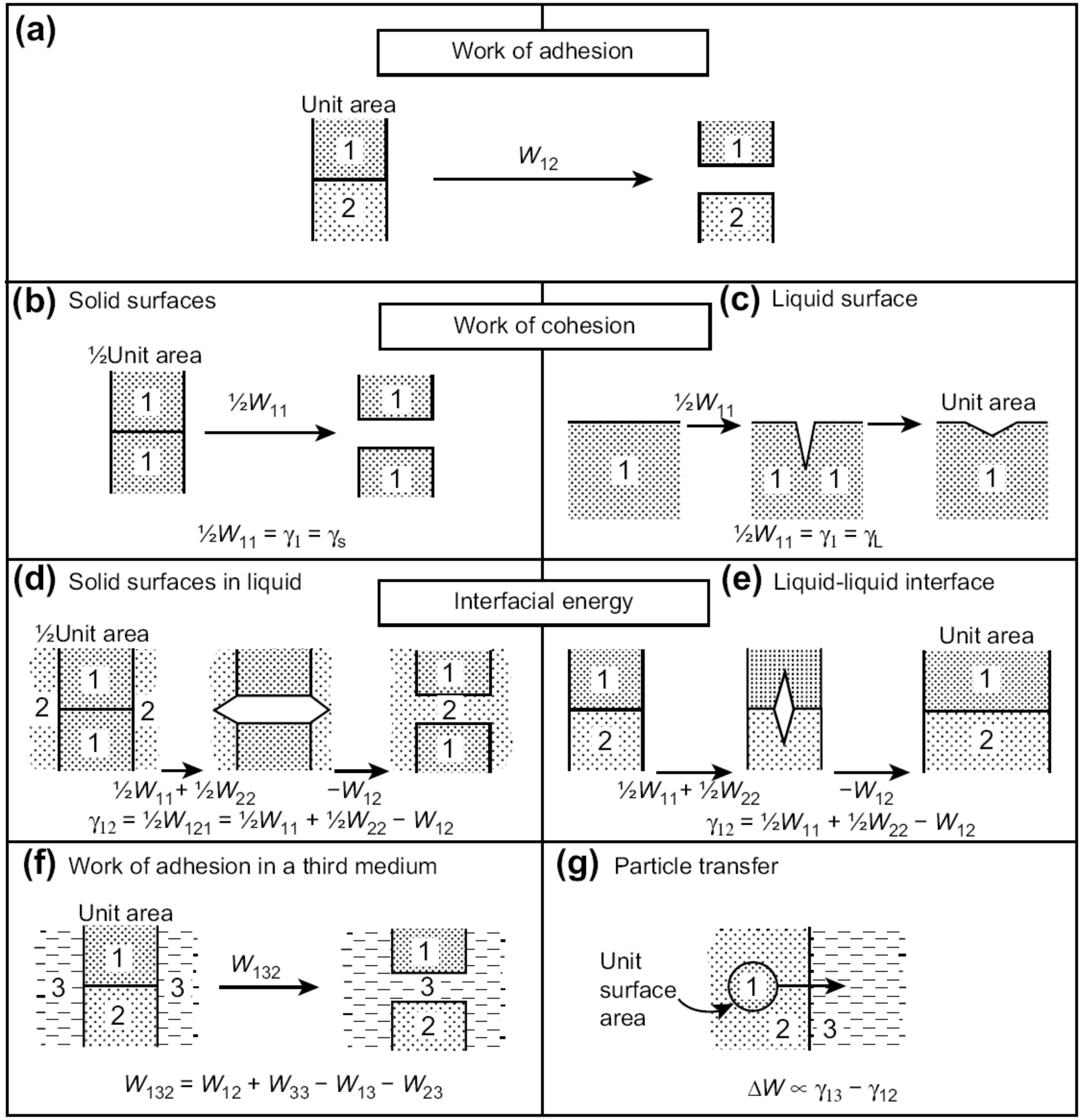
Definition of various energy terms associated with the adhesion of solid surfaces and the surface change in liquids.

Note that *W* and γ are idealized thermodynamic quantities,
assuming reversibility and smooth surfaces.

In practice only with liquids can the area be changed gradually and reversibly.

For solids, the adhesion and cohesion and debonding processes involve plastic deformation with the dissipation of irreversible energy as heat.

Note the positive sign of *W* (i.e., $W>0$) for the work of adhesion/cohesion.
The reference state of zero energy
is the contact state.



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Surface and intefacial energies

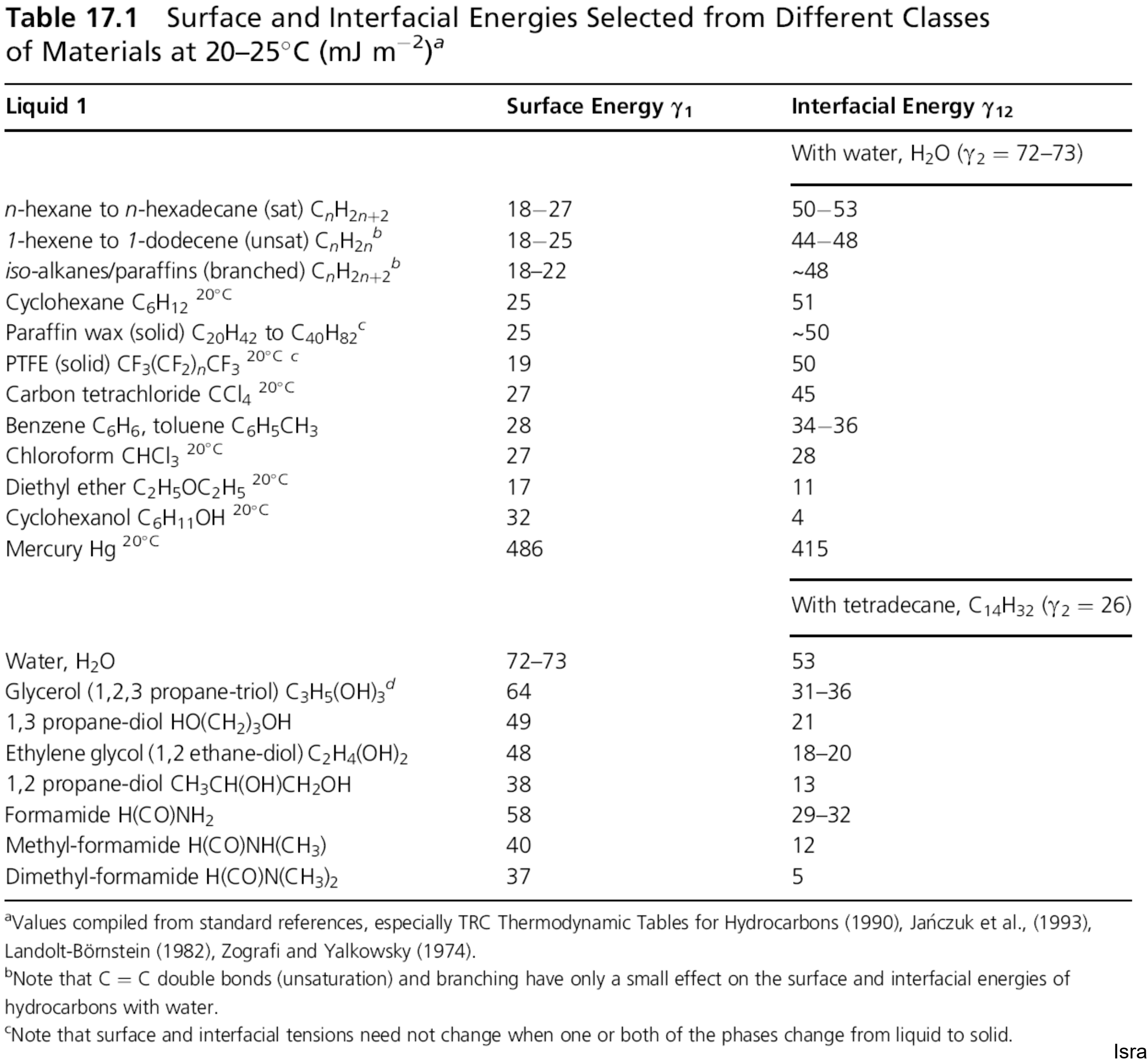

Table 17.1 Surface and Interfacial Energies Selected from Different Classes of Materials at 20–25°C (mJ m^{-2})[a]

Liquid 1	Surface Energy γ_1	Interfacial Energy γ_{12}
		With water, H_2O ($\gamma_2 = 72–73$)
n-hexane to *n*-hexadecane (sat) C_nH_{2n+2}	18–27	50–53
1-hexene to *1*-dodecene (unsat) C_nH_{2n}[b]	18–25	44–48
iso-alkanes/paraffins (branched) C_nH_{2n+2}[b]	18–22	~48
Cyclohexane C_6H_{12} $^{20°C}$	25	51
Paraffin wax (solid) $C_{20}H_{42}$ to $C_{40}H_{82}$[c]	25	~50
PTFE (solid) $CF_3(CF_2)_nCF_3$ $^{20°C}$ [c]	19	50
Carbon tetrachloride CCl_4 $^{20°C}$	27	45
Benzene C_6H_6, toluene $C_6H_5CH_3$	28	34–36
Chloroform $CHCl_3$ $^{20°C}$	27	28
Diethyl ether $C_2H_5OC_2H_5$ $^{20°C}$	17	11
Cyclohexanol $C_6H_{11}OH$ $^{20°C}$	32	4
Mercury Hg $^{20°C}$	486	415
		With tetradecane, $C_{14}H_{32}$ ($\gamma_2 = 26$)
Water, H_2O	72–73	53
Glycerol (1,2,3 propane-triol) $C_3H_5(OH)_3$[d]	64	31–36
1,3 propane-diol $HO(CH_2)_3OH$	49	21
Ethylene glycol (1,2 ethane-diol) $C_2H_4(OH)_2$	48	18–20
1,2 propane-diol $CH_3CH(OH)CH_2OH$	38	13
Formamide $H(CO)NH_2$	58	29–32
Methyl-formamide $H(CO)NH(CH_3)$	40	12
Dimethyl-formamide $H(CO)N(CH_3)_2$	37	5

[a] Values compiled from standard references, especially TRC Thermodynamic Tables for Hydrocarbons (1990), Jańczuk et al., (1993), Landolt-Börnstein (1982), Zografi and Yalkowsky (1974).

[b] Note that C = C double bonds (unsaturation) and branching have only a small effect on the surface and interfacial energies of hydrocarbons with water.

[c] Note that surface and interfacial tensions need not change when one or both of the phases change from liquid to solid.

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Surface tension: values

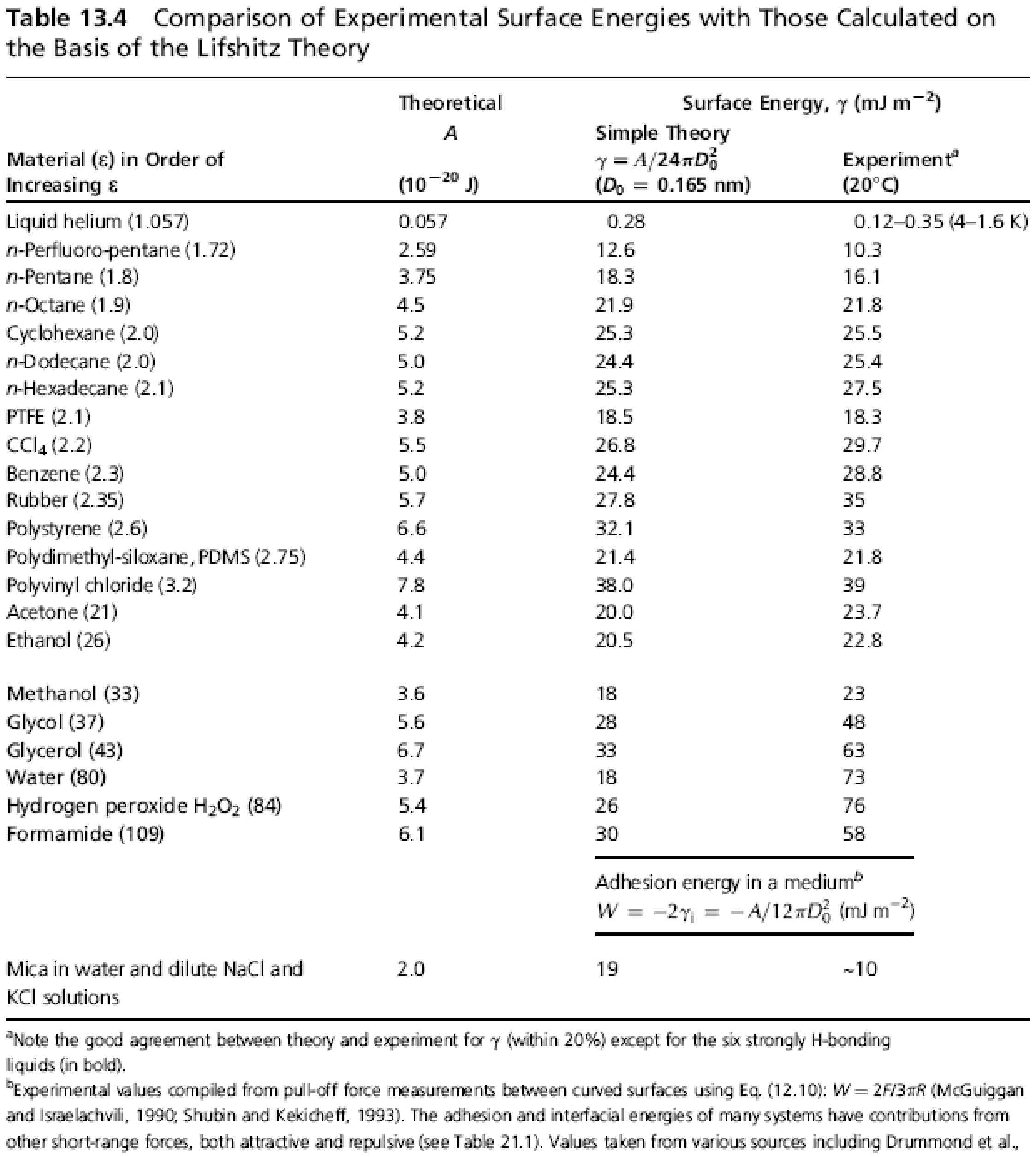

Table 13.4 Comparison of Experimental Surface Energies with Those Calculated on the Basis of the Lifshitz Theory

Material (ε) in Order of Increasing ε	**Theoretical A (10^{-20} J)**	**Surface Energy, γ (mJ m^{-2})** Simple Theory $\gamma = A/24\pi D_0^2$ (D_0 = 0.165 nm)	Experiment[a] (20°C)
Liquid helium (1.057)	0.057	0.28	0.12–0.35 (4–1.6 K)
n-Perfluoro-pentane (1.72)	2.59	12.6	10.3
n-Pentane (1.8)	3.75	18.3	16.1
n-Octane (1.9)	4.5	21.9	21.8
Cyclohexane (2.0)	5.2	25.3	25.5
n-Dodecane (2.0)	5.0	24.4	25.4
n-Hexadecane (2.1)	5.2	25.3	27.5
PTFE (2.1)	3.8	18.5	18.3
CCl_4 (2.2)	5.5	26.8	29.7
Benzene (2.3)	5.0	24.4	28.8
Rubber (2.35)	5.7	27.8	35
Polystyrene (2.6)	6.6	32.1	33
Polydimethyl-siloxane, PDMS (2.75)	4.4	21.4	21.8
Polyvinyl chloride (3.2)	7.8	38.0	39
Acetone (21)	4.1	20.0	23.7
Ethanol (26)	4.2	20.5	22.8
Methanol (33)	3.6	18	23
Glycol (37)	5.6	28	48
Glycerol (43)	6.7	33	63
Water (80)	3.7	18	73
Hydrogen peroxide H_2O_2 (84)	5.4	26	76
Formamide (109)	6.1	30	58
		Adhesion energy in a medium[b] $W = -2\gamma_i = -A/12\pi D_0^2$ (mJ m^{-2})	
Mica in water and dilute NaCl and KCl solutions	2.0	19	~10

[a] Note the good agreement between theory and experiment for γ (within 20%) except for the six strongly H-bonding liquids (in bold).

[b] Experimental values compiled from pull-off force measurements between curved surfaces using Eq. (12.10): $W = 2F/3\pi R$ (McGuiggan and Israelachvili, 1990; Shubin and Kekicheff, 1993). The adhesion and interfacial energies of many systems have contributions from other short-range forces, both attractive and repulsive (see Table 21.1). Values taken from various sources including Drummond et al.,

Water	72.2 mN/m
Ethylene glycol	48.4 mN/m
Xylene	32.0 mN/m
Butyl acetate	27.6 mN/m
White Spirit	26.0 mN/m
Melamine resin (HMMM)	58.0 mN/m
Epoxy	47.0 mN/m
Polyester	41.3 mN/m
Polyacrylate	35.0 mN/m
Long oil alkyd	26.0 mN/m
Glass	70.0 mN/m
Steel, pre-treated	45.0 mN/m
Polystyrol	42.0 mN/m
PVC	39.5 mN/m
Polyethylene	33.2 mN/m
Polypropylene	28.0 mN/m
PTFE	19.0 mN/m

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Surface tension: some notes

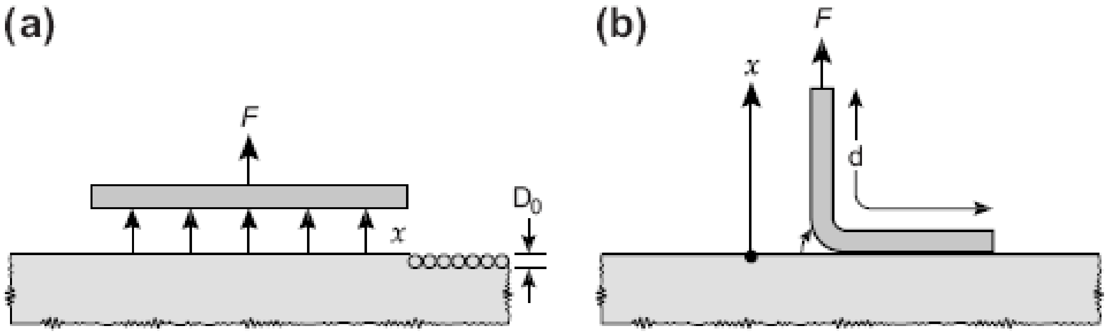
1. When the process of increasing the surface area of a medium takes place in a foreign vapor, such as laboratory air, some adsorption of vapor molecules (e.g., water, hydrocarbons) may take place on the newly created surface. This lowers γ_S and γ_L from their values in vacuum, and the surface energies in vapor are denoted by γ_{SV} and γ_{LV}.

Examples:
mica cleaved in high a vacuum: γ_S=4500 mJ/m^2
mica cleaved in humid laboratory air: γ_{SV} =300 mJ/m^2

2. The intermolecular forces that determine the surface energy of a substance are the same as those that determine its latent heat and boiling point. Substances such as metals with high boiling points (T_B >2000 C) usually have high surface energies (γ > 1000 mJ/m^2), while lower boiling point substances have lower surface energies.

Examples:
Mercury: γ=485 mJ/m^2, T_B=357 C; Water: γ=73 mJ/m^2, T_B = 100 C;
Argon: γ=13.2mJ/m^2, T_B=-186 C; and Hydrogen: γ=2.3 mJ/m^2, T_B=-253 C.

3. Surfaces separation: two different path with same net change in energy but different adhesion forces.



Surface tension: some notes

Different ways of looking at the origin of surface tension.

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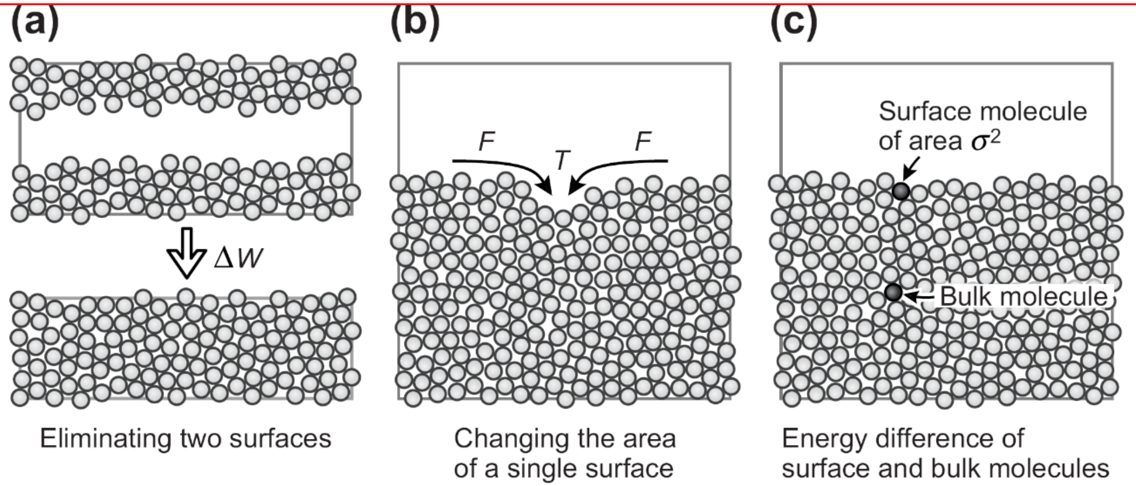
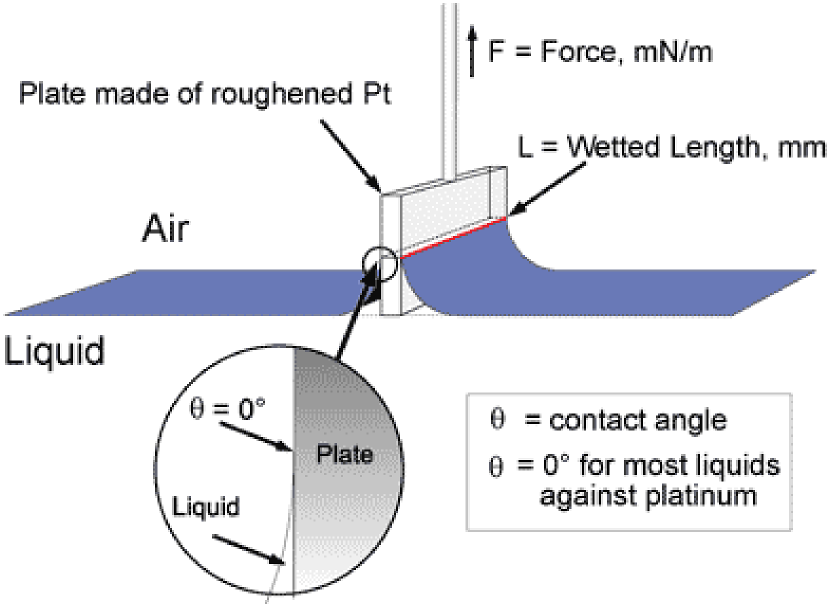


FIGURE 17.3 Different ways of looking at the origin of surface energies and surface tension forces of pure (single-component) systems. The situation can be very different when a liquid surface contains a monolayer or sub-monolayer of adsorbed molecules that are "insoluble" in the bulk liquid (see insoluble monolayers in Chapter 19).

Simple experimental set-up to measure surface tension (for liquids)



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Surface tension: examples

Beading of rain water on a waxy surface, such as a leaf. Water adheres weakly to wax and strongly to itself, so water clusters into drops.
Surface tension gives them their near-spherical shape, because a sphere has the smallest possible surface area to volume ratio (energy minumum)

Flotation of objects **denser** than water occurs when the object is nonwettable and its weight is small enough to be borne by the forces arising from
surface tension. The gravity force per unit of surface is weaker than the surface tension.

https://en.m.wikipedia.org

Surface tension and contact angle: simple theory

Let's assume that we slightly increase the contact angle by δθ. This perturbation induces a variation of the liquid-vapor surface δA_{LV}, the liquid-solid surface δA_{SL}, and the solid-vapour surface A_{SV} related by:

$\delta A_{LV} = \cos\theta\ \delta A_{SL}$ and $\delta A_{SL} = -\delta A_{SV}$

The energy increments related to surfaces is:

$$\delta W = \gamma_{LV}\delta A_{LV} + \gamma_{SL}\delta A_{SL} + \gamma_{SV}\delta A_{SV} = \gamma_{LV}\delta A_{LV} + \gamma_{SL}\delta A_{SL} - \gamma_{SV}\delta A_{SL} =$$

$$=(\gamma_{LV}\cos\theta + (\gamma_{SL} - \gamma_{SV}))\delta A_{SL}$$

Without other contributions (e.g., gravity) to the energy variation, the equilibrium condition

$$\delta W = 0$$

determines

$$(\gamma_{LV}\cos\theta + (\gamma_{SL} - \gamma_{SV}))\delta A_{SL} = 0$$

and, hence,

$$\gamma_{LV}\cos\theta + \gamma_{SL} = \gamma_{SV}$$

which is the Young equation.

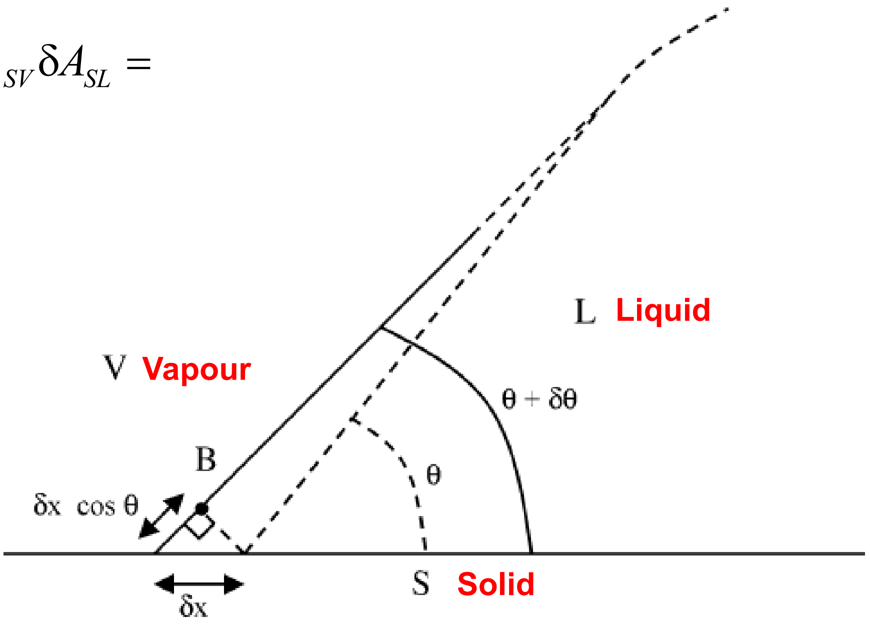


Fig. 1. When the liquid advances, the area of the LV surface will increase by a value proportional to cos θ, provided that the new surface meets the initial one asymptotically. This geometrical construction is the basis of the most popular "derivation" of Young's equation.

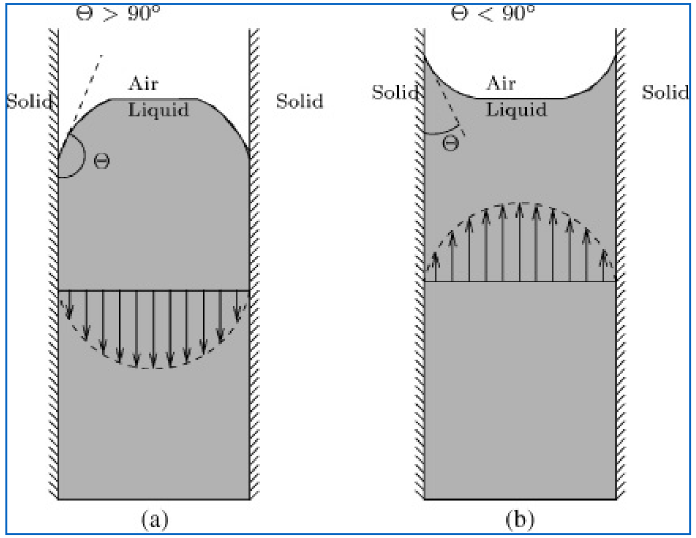
Young equation

$$\gamma_{LV}\cos\theta + \gamma_{SL} = \gamma_{SV}$$

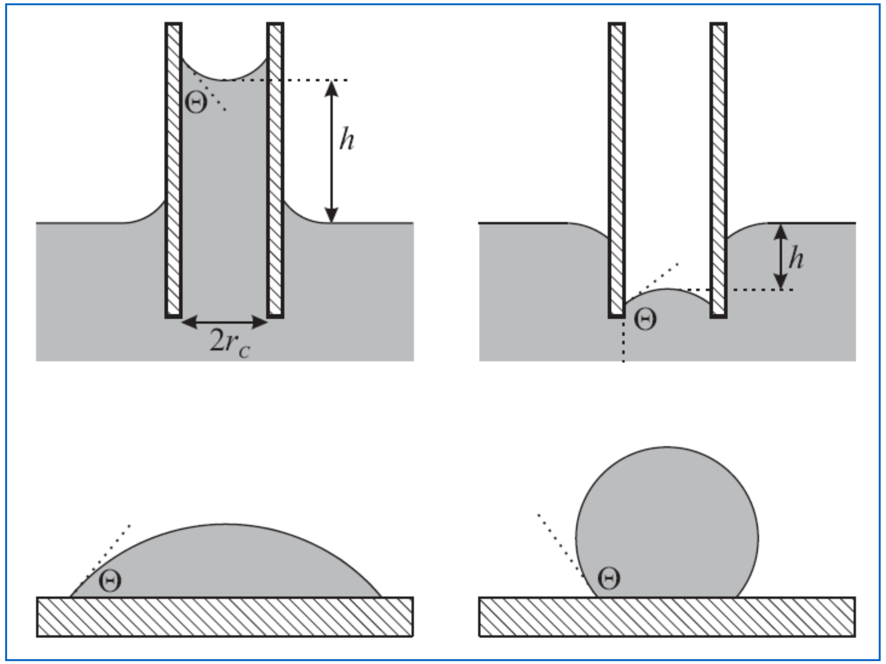
NOTES:
- The Young equation is strictly valid only in thermodynamic equilibrium (i.e., in presence of a saturated vapor of the liquid).
- The Young equation is also valid if we replace the gas with a second immiscible liquid (e.g., contact angle of a drop of water on a solid surface in oil).

Surface tension and contact angle: notes

- The contact angle is the same on **all surfaces** (including, for example, the curved surface inside a capillary).



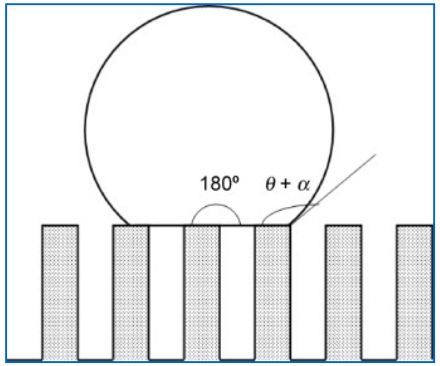
http://ej.iop.org/images/1464-4258/7/8/L02/Full/9737801.jpg



H.J. Butt,K. Graf, M.Kappl,_Physics_and_Chemistry_of_Interfaces__2003

- The contact angle can drastically modified by:

- chemical or topographical modification of the solid surface
- solutes into the liquid



Contact angle: “reciprocity” and molecularly thin films

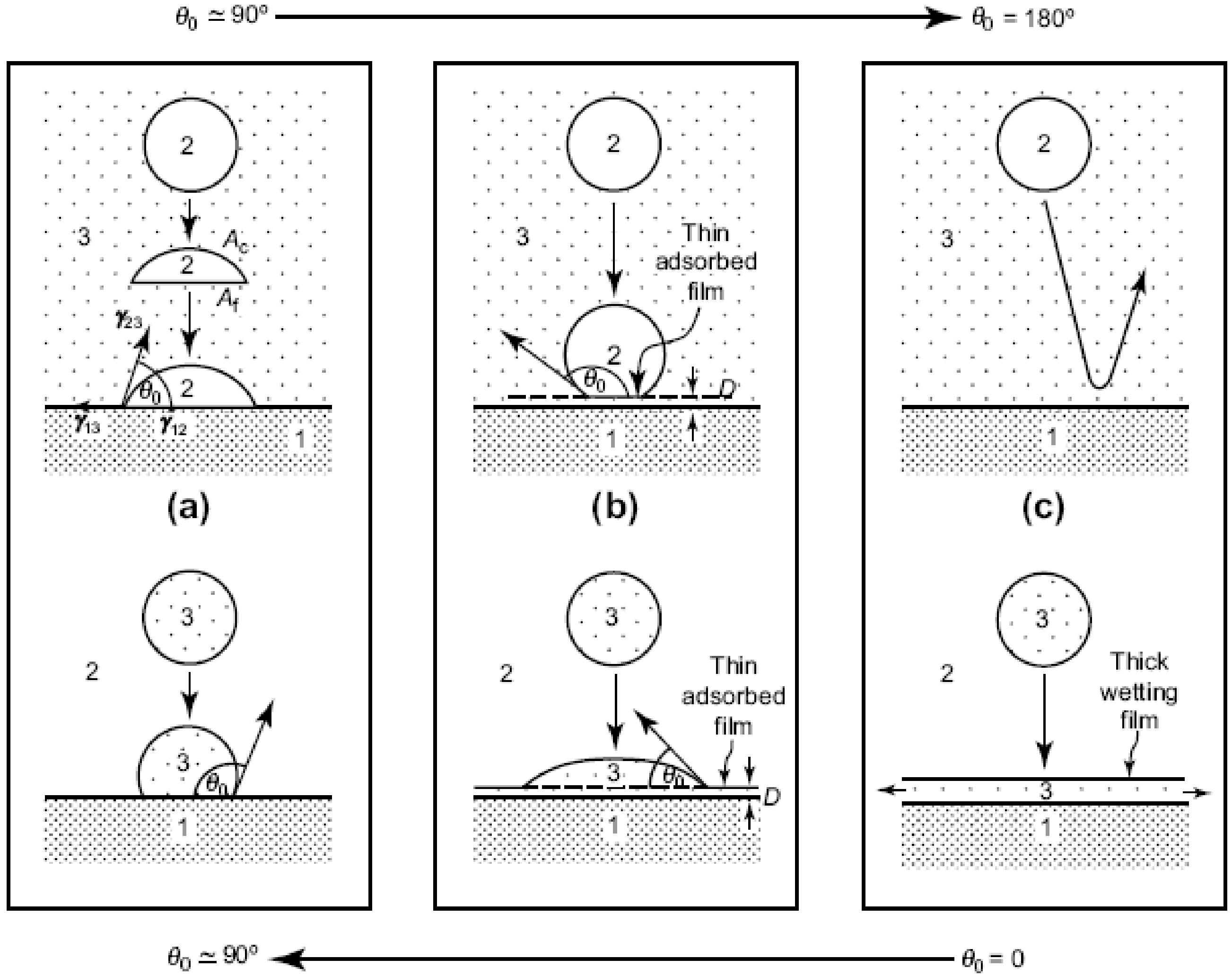


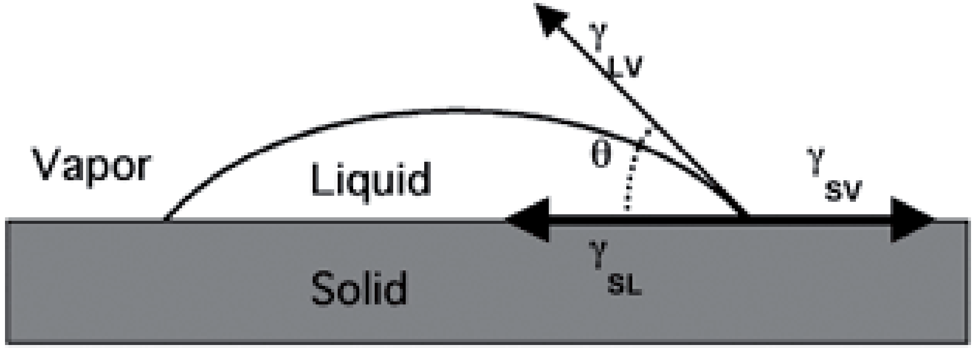
FIGURE 17.6 Contact angles and their manifestation from $\theta = 0$ to $\theta = 180°$. Note that the upper and lower drawings in each box are formally equivalent on interchanging media 2 and 3 and replacing θ_0 by $(180° - \theta_0)$. The thin adsorbed films in the middle panel are an example of “autophobicity”—the nonwetting of a liquid on a layer of itself. Such films can be molecularly thin with “quantized” thicknesses. For a spreading droplet on a surface they are referred to as precursor films.

Surface tension and contact angle

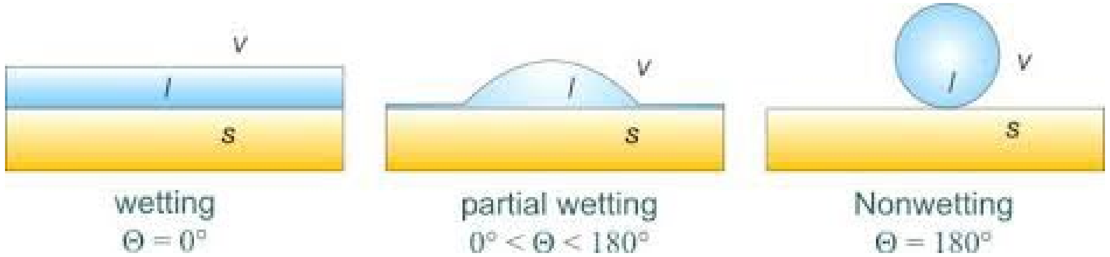
Young Equation

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

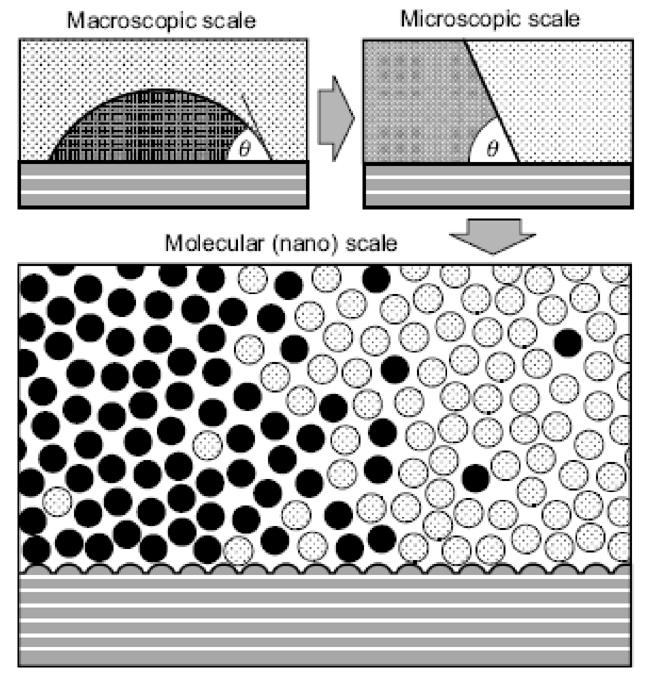
$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$



The Young equation is intuitively given by the balance of forces at the contact line between liquid, solid, and vapour



$\gamma_{SV} >> \gamma_{SL}$ $\gamma_{SV} \sim \gamma_{SL}$ $\gamma_{SV} << \gamma_{SL}$



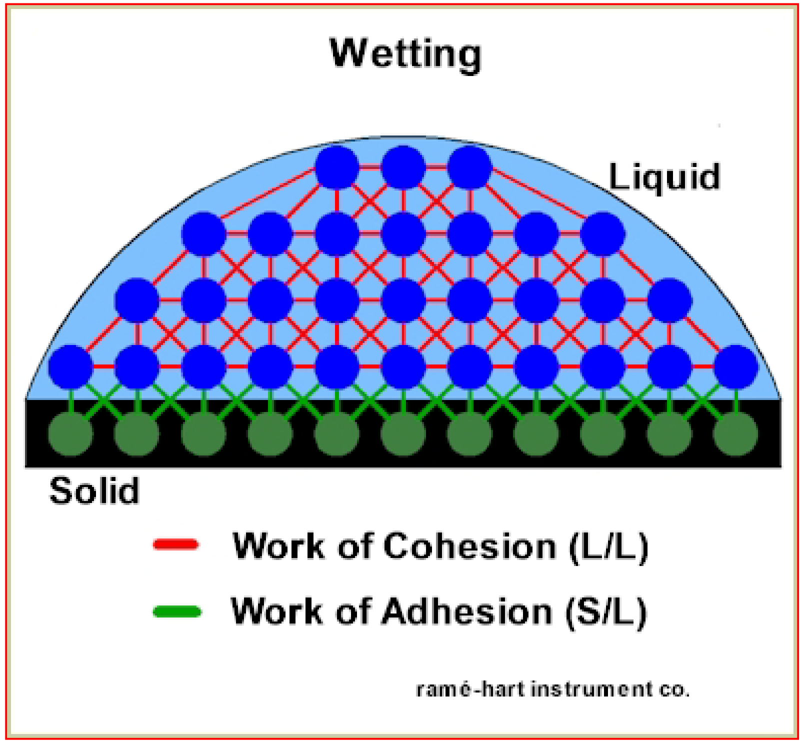
Note:

If $\gamma_{SV} - \gamma_{SL} > \gamma_{LV}$ we would have cosθ>1 !!.

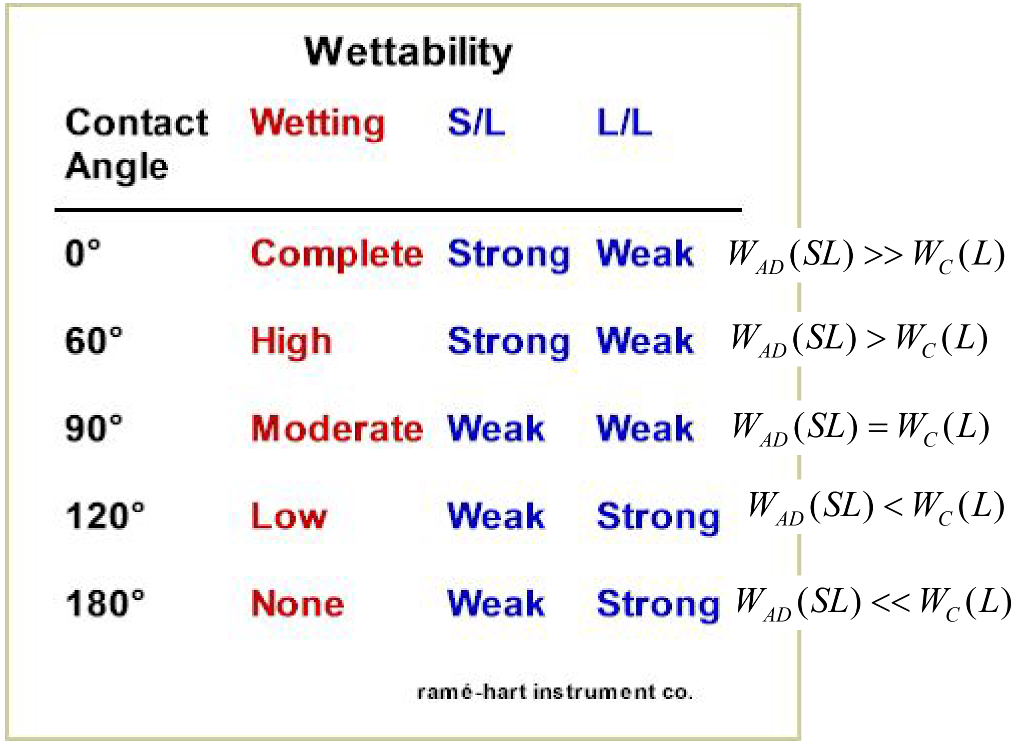
Is $\gamma_{SV} - \gamma_{SL} > \gamma_{LV}$ physically possible ? No.

Israelachvili, Intermolecular and surface forces, 3rd ed. (2011)

Contact Angle vs Adhesion and cohesion



ramé-hart instrument co.



Wettability

Contact Angle	Wetting	S/L	L/L	
0°	Complete	Strong	Weak	$W_{AD}(SL) >> W_C(L)$
60°	High	Strong	Weak	$W_{AD}(SL) > W_C(L)$
90°	Moderate	Weak	Weak	$W_{AD}(SL) = W_C(L)$
120°	Low	Weak	Strong	$W_{AD}(SL) < W_C(L)$
180°	None	Weak	Strong	$W_{AD}(SL) << W_C(L)$

ramé-hart instrument co.

Surface tension in nanoparticles

For small clusters how close are the values of γ to those of bulk surfaces ?

The magnitude of the effective surface energy for a very small cluster is within 15% of that of the planar macroscopic surface of closed-packed molecules !

Planar surface: $\gamma \cong \sqrt{3}w/4a^2 \cong 0.43w/a^2 \text{ J/m}^2$

Single atom: $\gamma \cong 12w/2(4\pi a^2) \cong 0.48w/a^2 \text{ J/m}^2$

13-atoms cluster: $\gamma \cong 7\times 12w/2(4\pi(3a)^2) \cong 0.37w/a^2 \text{ J/m}^2$

w : pair energy molecular interaction

a : molecular radius

Israelachvili,Intermolecular and Surface Forces, 3rd, 2011, page 423

Surface tension in nanoparticles

Notes:
The previous calculations assumed that atoms and molecules interacts via additive pair potentials (no retardation, no many-body interactions). This is correct for **molecular solids and liquids** (i.e., composed of molecules held together by the van der Waals forces) but generally wrong for metallic, semiconducting, covalent, ionic, and hydrogen-bonding compounds.

However, several metals and semiconductors nanoparticles behaves like van der Waal substances.

Examples:
-Gold droplets melting point is 1336 K for large particles, 1000 K for 4 nm diameter particles, 500 K for 2.5 nm particles. Very small Au clusters behaves like van der Waals solids (the metallic bond is no more the most significant).

- Water droplets with less than 20 molecules are probably in the liquid state already at 200 K, due to the inability of a H-bonding network to develop in these clusters. A related phenomena is also present in thin water films: between 0 and -20 °C the surface of ice has a thin layer of water on it (responsible for the low friction of ice).

Israelachvili,Intermolecular and Surface Forces, 3rd, 2011, page 423)

Melting of nanoparticles

At a given temperature T the Gibbs free energy G for a nanoparticle is given by:

$$NG = NG_\infty + fN^{2/3}\gamma$$

f : Geometrical factor (it depends on the nanoparticle shape)

γ : surface tension per atom

G : volume energy per atom for the nanoparticle in a given phase

G_∞ : volume energy per atom for the bulk material in a given phase

N : number of atoms in the nanoparticle

$fN^{2/3}$: number of atoms on the surface of the nanoparticle

The surface tension γ is usually weakly dependent on temperature (in a given phase)

The equilibrium between the phase 1 and the phase 2 is governed by the equation

$$N(G_1 - G_2) = N(G_{1\infty} - G_{2\infty}) + fN^{2/3}(\gamma_1 - \gamma_2)$$

$G_1 = G_2$: Equilibrium between the two phases (phase transition)

$G_1 > G_2$: Phase 2 is favored

$G_1 < G_2$: Phase 1 is favored

Melting of nanoparticles

For **inorganic solids :**

$G_{L\infty} - G_{S\infty} = a - bT$ $\quad$ a, b are positive costant

γ is temperature independent

Consequently, at the phase transition, we have:

$0 = N(a - bT_m) + fN^{2/3}(\gamma_L - \gamma_S)$ (for the nanoparticle)

$0 = N_\infty(a - bT_{m\infty}) + fN_\infty^{2/3}(\gamma_L - \gamma_S)$ (for the bulk material)

Hence:

$$T_m - T_{m\infty} = \frac{f}{b}(\gamma_L - \gamma_S)\left(\frac{1}{N^{1/3}} - \frac{1}{N_\infty^{1/3}}\right) \cong \frac{f}{b}(\gamma_L - \gamma_S)\frac{1}{N^{1/3}} \quad \text{(because } N_\infty \gg N\text{)}$$

The melting point depends on the difference $\gamma_L - \gamma_S$ and the size of the particle.

Since usually $\gamma_L < \gamma_S \Rightarrow T_m < T_{m\infty} \Rightarrow$

$\Rightarrow$ The melting temperature of a nanoparticle is lower than the one of a bulk material

Since $T_m - T_{m\infty} \propto 1/N^{1/3} \Rightarrow T_m(N-1) < T_m(N) \Rightarrow$

$\Rightarrow$ The melting temperature decreases if the particle size decreases.

Melting of nanoparticles

Comparison with experimental results:

$$T_m = T_{m\infty} + \left(f / bN^{1/3} \right)(\gamma_L - \gamma_S) \;= T_{m\infty}\left[1 - \alpha / 2R\right]$$

R : nanoparticle radius

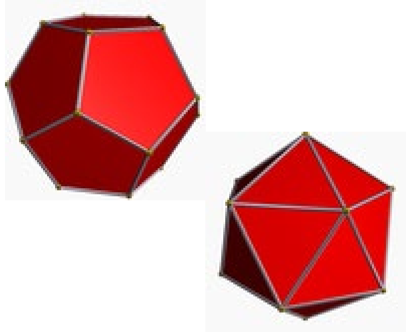
$$\alpha = \frac{f}{bT_{m\infty}}(\gamma_S - \gamma_L)\frac{2}{\left((4/3)\pi\rho\right)^{1/3}}$$

$\alpha > 0$ for inorganic materials (value from 0.4 nm to 3.3 nm) $\Rightarrow T_m < T_{m\infty}$

	$T_{m\infty}$ (K)	α (nm) (theory)	α (nm) (exper.)
Al	933	1.14	0.6
Au	1336	0.92	0.96
In	429.4	1.95	0.974
Sn	505.1	1.57	1.476

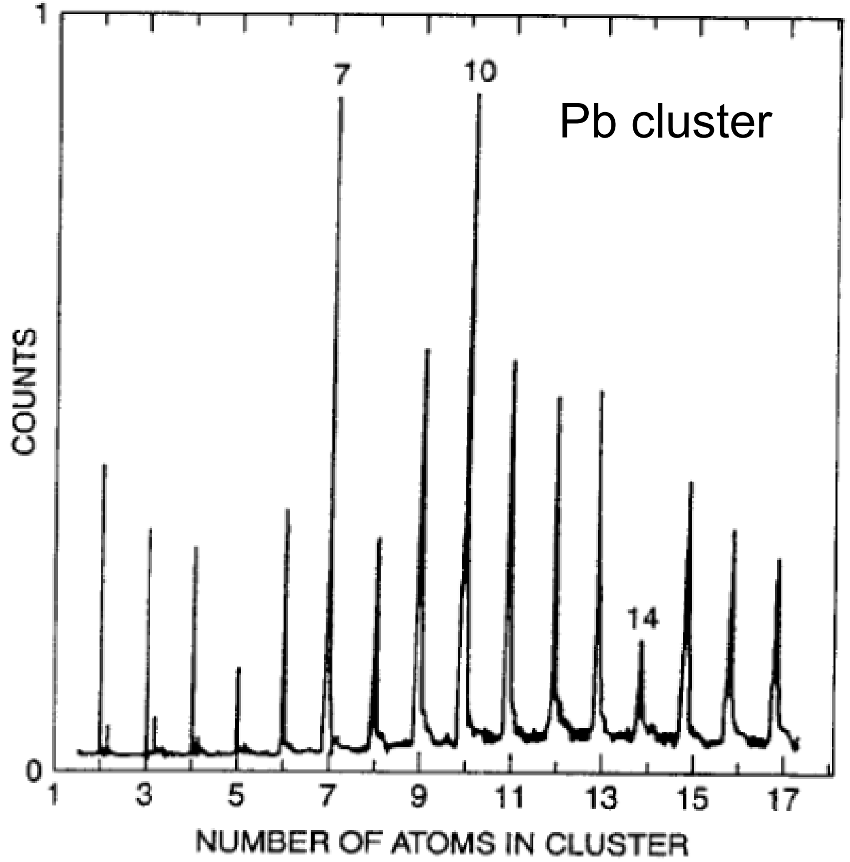
Note 1:
By coating the nanoparticle or introducing the nanoparticle in a matrix we change the surface tension and, consequently, the melting point.

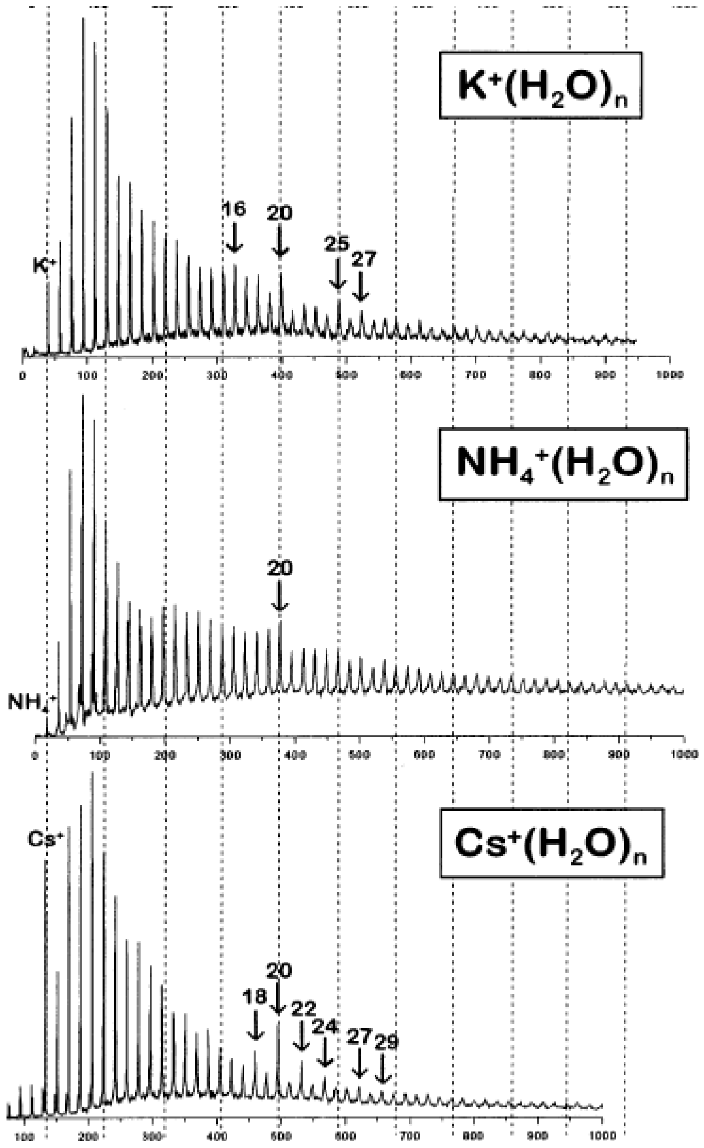
Note 2:
Nanoparticles of very small size (2 nm and below) are usually not spherical (they form regular polyedra such as dodecahedron, icosadreon,…)
For non-spherical nanoparticles the ratio surface/volume is larger and the variation of melting temperature with the size is larger and dependent on the shape of the nanoparticle.



Nanoparticles: magic numbers

Magic numbers: small nanoparticles can be more stable (or less stable)
if composed by a specific number of atoms.



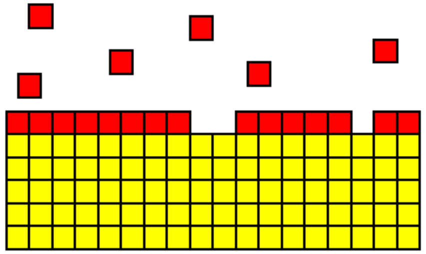
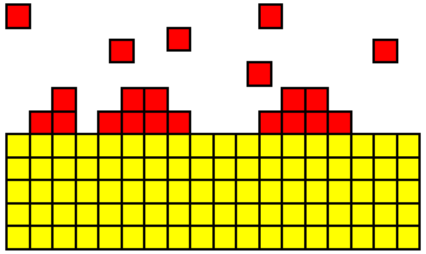
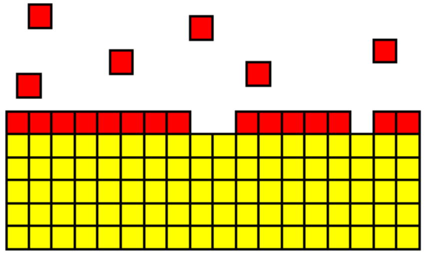


F. Sobott et al./International Journal of Mass Spectrometry 185/186/187 (1999) 271–279

Growth of thin films on a substrate

$$\Delta\gamma = \gamma_F + \gamma_{S/F} - \gamma_S$$

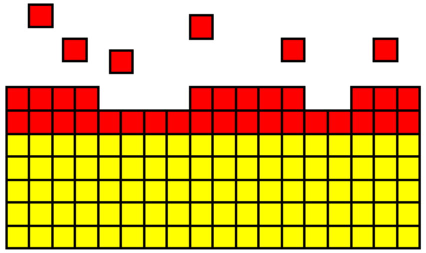
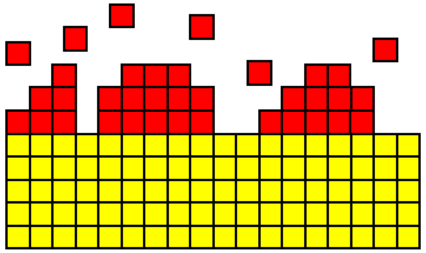
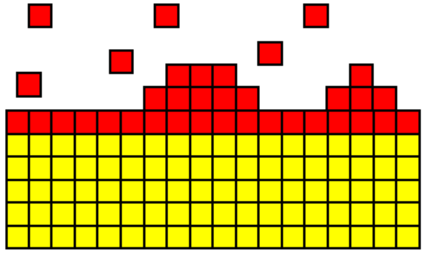
S: Substrate
F: Film
S/F: Substrate/Film interface

$\Delta\gamma < 0$

$\Delta\gamma > 0$

$1: \Delta\gamma < 0, \; 2: \Delta\gamma > 0$

layer - by - layer growth
(Frank - van der Merve)

adatom cohesive force **weaker** than surface adhesive force.

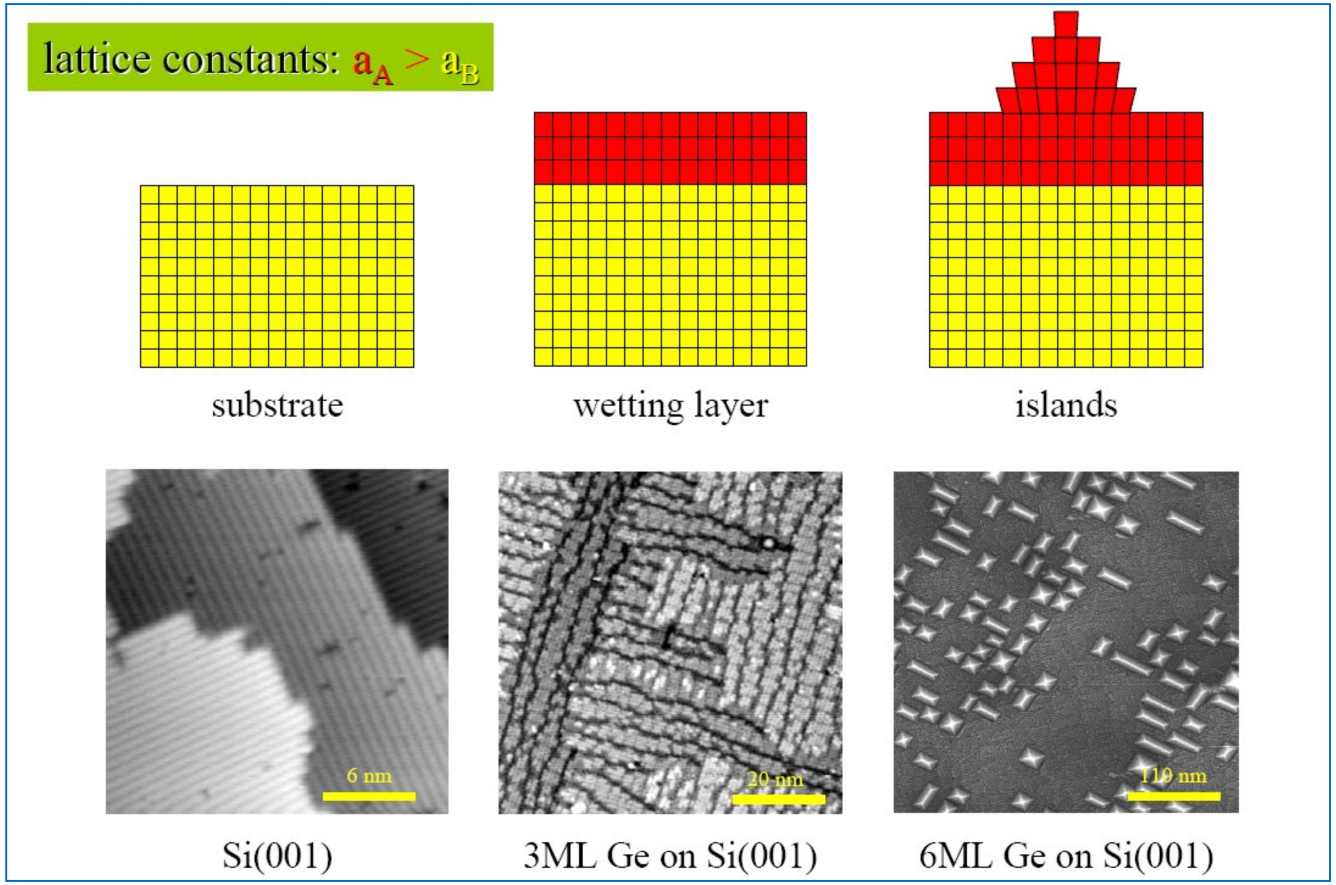
island growth
(Volmer - Weber)

adatom cohesive force **stronger** than surface adhesive force.

layer - by - layer
+ island growth
(Stranski - Krastanov)

Two steps process.

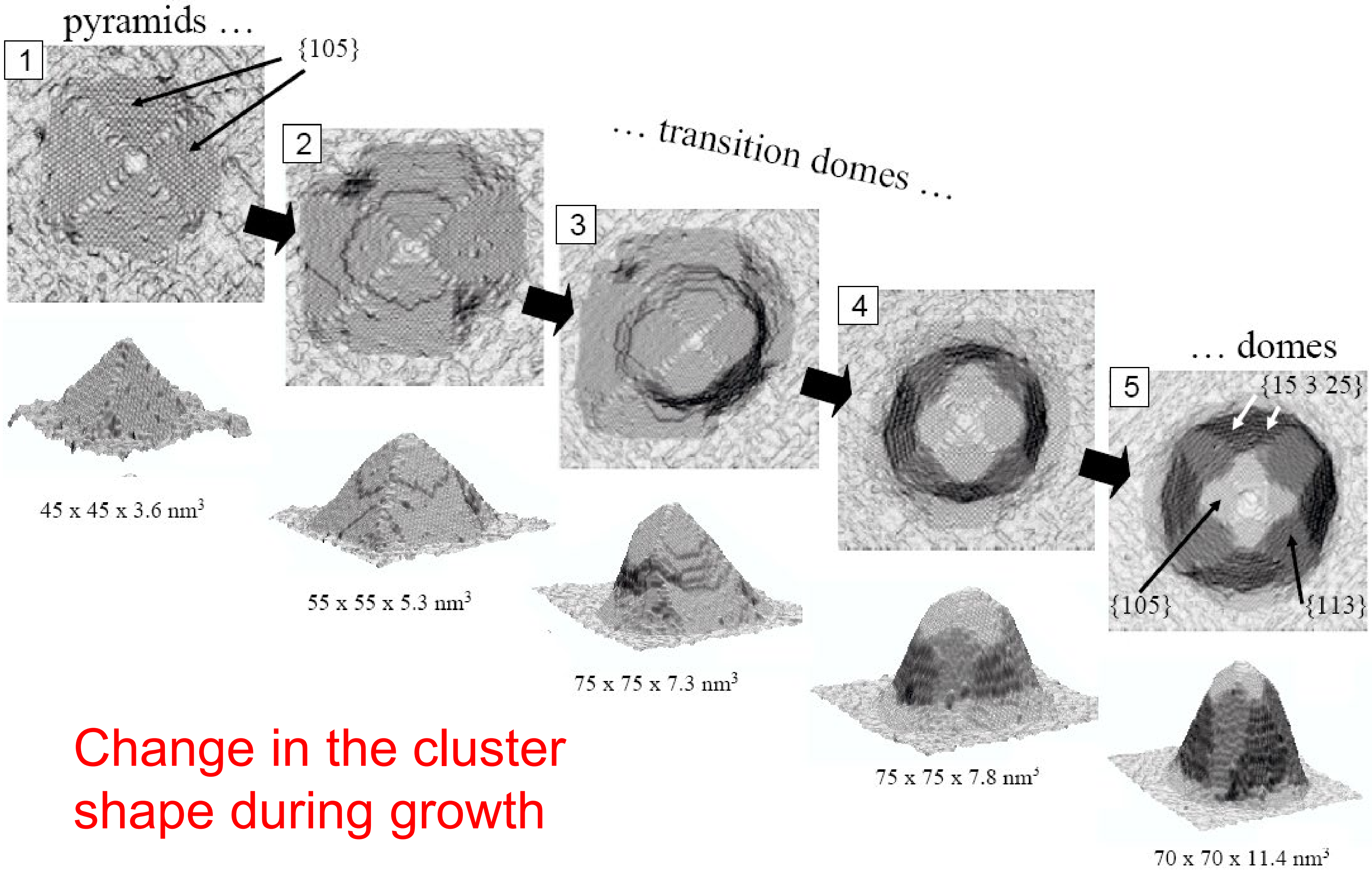
Growth of thin films on a substrate



Stranski–Krastanov growth (SK) follows a two step process: initially, complete films of adsorbates, up to several monolayers thick, grow in a layer-by-layer fashion on a crystal substrate. Beyond a critical layer thickness growth continues through the nucleation and coalescence of adsorbate islands. While initial film growth follows a Frank-van der Merve (FM) mechanism, non-trivial amounts of strain energy accumulate in the deposited layers. At a critical thickness, it is energetically favorable to nucleate islands and further growth occurs by a Volmer-Weber (VW) type mechanism.

Growth of thin films on a substrate

Pyramid-to-Dome transformation : Ge/Si(001)



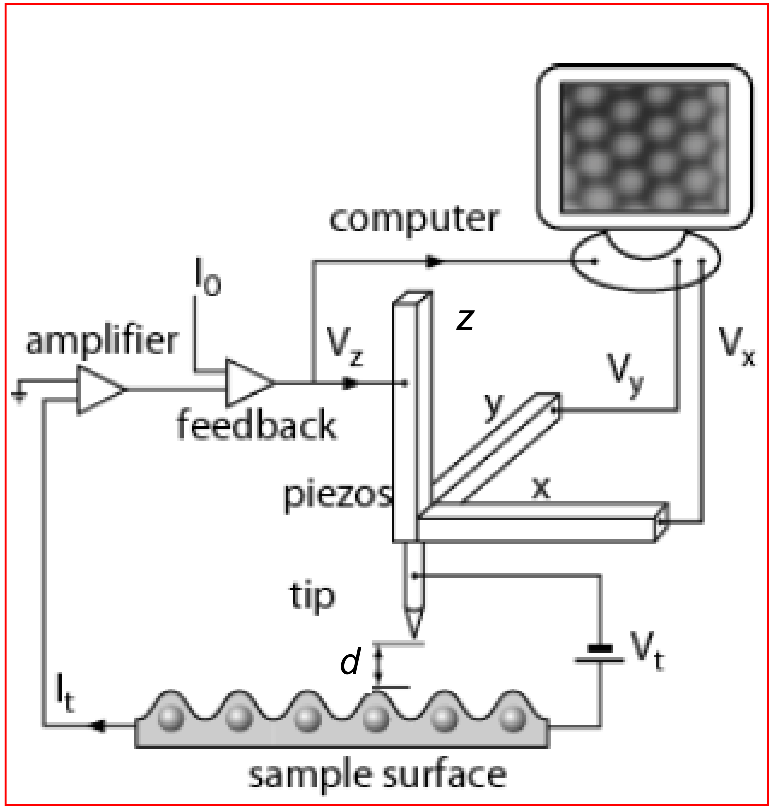
Change in the cluster shape during growth

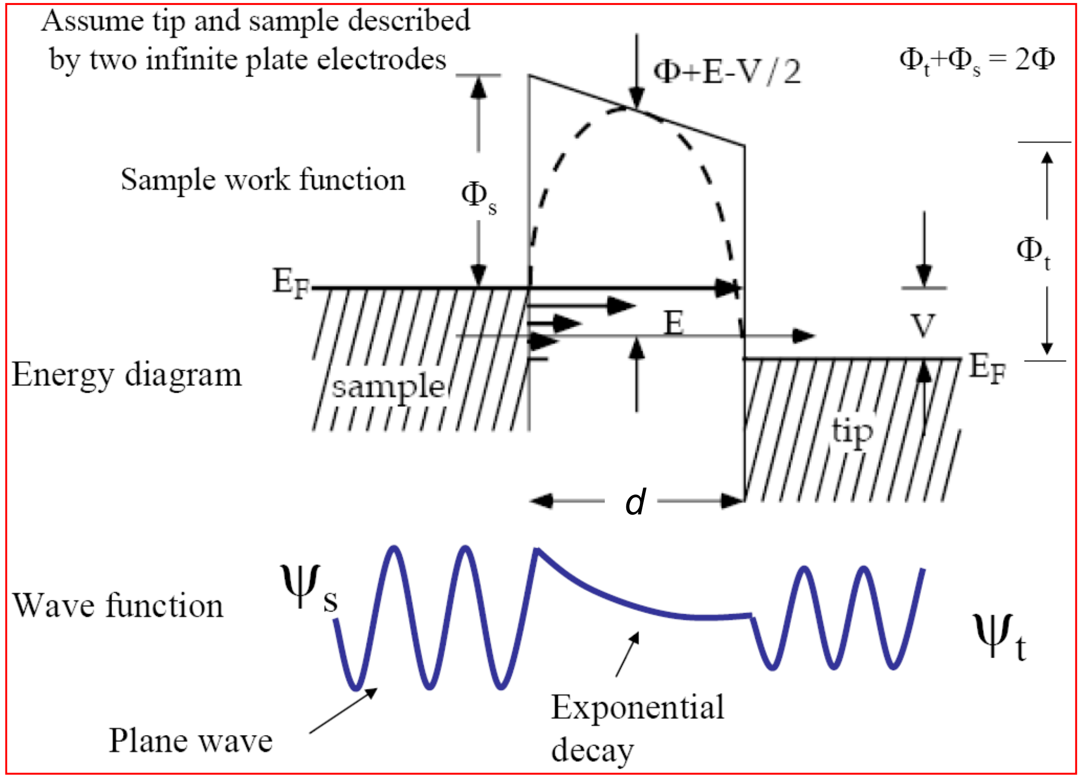
Nanotechnology

Nanoscale phenomena

Examples of Nanoscale Phenomena

Tunneling current: quick overview

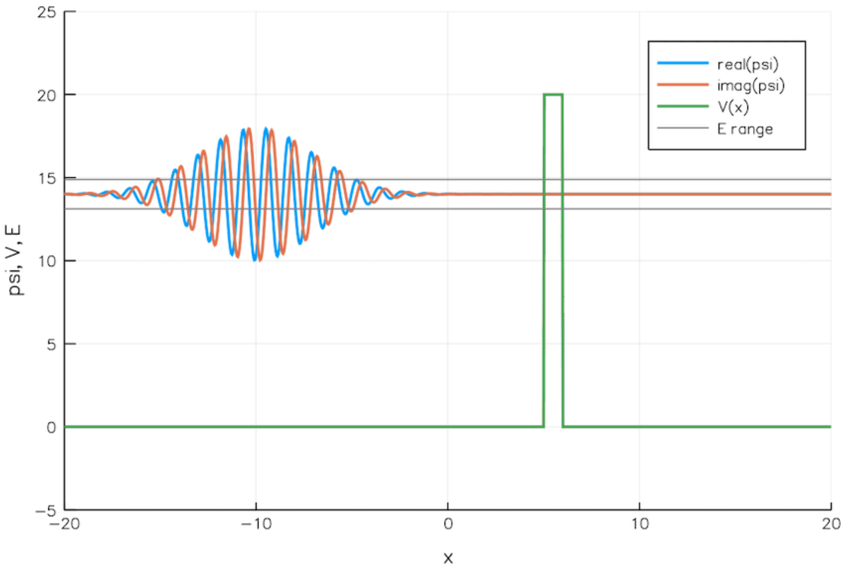




Key-facts:

- Tunneling of electrons, or any particle, across a classically forbidden region of space (a barrier higher than their kinetic energy) is possible in quantum mechanics and is a direct consequence of the wave nature of the particle.
- The electrons of a metallic tip can cross the vacuum barrier to the adjacent surface if the distance between them is sufficiently small and the barrier height is not infinitely large. To establish a net current in one direction, for example from tip to sample, a bias voltage must be applied between the electrodes.

Tunneling current: elementary qualitative model



One-dimensional Schrodinger equation for an electron of mass m incident upon a barrier $U(x)$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x)+U(x)\Psi(x)=E_0\Psi(x)$$

The solutions for this electron approaching the barrier from the left are

$\Psi_1(x)=A\exp\left(ikx\right)+\mathrm{B}\exp\left(-ikx\right)$ where $k=\sqrt{2mE_0}\,/\,\hbar$ (before the barrier)

$\Psi_2(x)=C\exp\left(\kappa x\right)+\mathrm{D}\exp\left(-\kappa x\right)$ where $\kappa=\sqrt{2m(U-E_0)}\,/\,\hbar$ (in the barrier)

$\Psi_3(x)=F\exp\left(ikx\right)$ where $k=\sqrt{2mE_0}\,/\,\hbar$ (after the barrier)

A: Amplitude incoming wave, B: Amplitude reflected wave, F: Amplitude transmitted wave

Tunneling current: elementary qualitative model

The transmission of the wavefunction through the barrier is: $T = \dfrac{|F|^2}{|A|^2}$

Imposing the following continuity conditions: $A = C$ and $F = C\exp(-\kappa d)$

$$\Rightarrow \qquad T = \frac{|F|^2}{|A|^2} = \exp(-2\kappa d) = \exp\left(-2\frac{\sqrt{2m(U-E_0)}}{\hbar}d\right)$$

The trasmission probability depends on the electron energy, barrier height, and barrier widht.

Let's consider the specific case of an STM, with tip and sample made of the same metallic material.

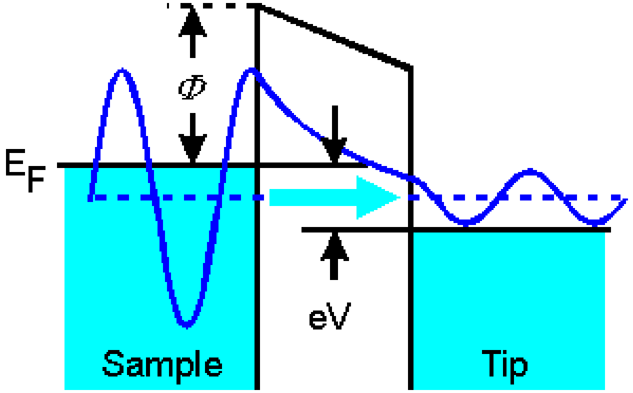
If the applied voltage V is small compared to the workfunction $(eV \ll \Phi) \Rightarrow \kappa \cong \dfrac{\sqrt{2m\Phi}}{\hbar}$

The tunneling current is due to electrons going from the filled state on one side to to the empty states at the same energy on the other side (elastic tunneling).

The total number of filled states available on one side having energy above those empty on the other side is approx. given by $\rho(E_F)V$

Consequently, the tunneling current is :

$$I \propto T\rho(E_F)V = \rho(E_F)V\exp\left(-2\frac{\sqrt{2m\Phi}}{\hbar}d\right)$$



Tunneling current: elementary qualitative model

More in general, if the tip and the sample are not made with the same material,

$I \propto V \rho_s(E_F) \rho_t(E_F) e^{-2\kappa d}$

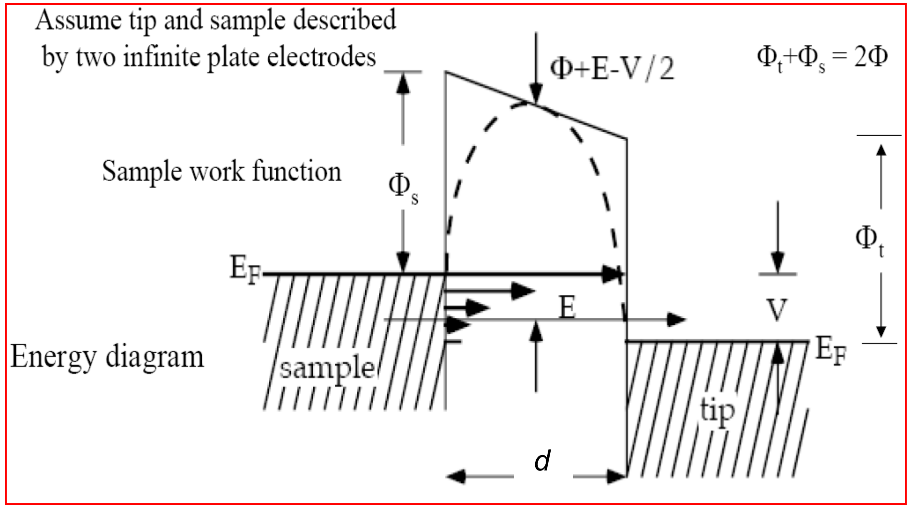
d : distance tip-sample

$\rho_s(E_F)$: density of states at the Fermi energy in the sample material

$\rho_t(E_F)$: density of states at the Fermi energy in the tip material

$\kappa = \sqrt{2m\left(\Phi - eV\right)} / \hbar \cong \sqrt{2m\Phi} / \hbar$ for $\Phi \gg eV$

$\Phi = (\Phi_s + \Phi_t)/2$ (average work-function)



Notes:

$I \propto e^{-ad}$ $\Rightarrow$ a small variation of distance generate a large variation of I !

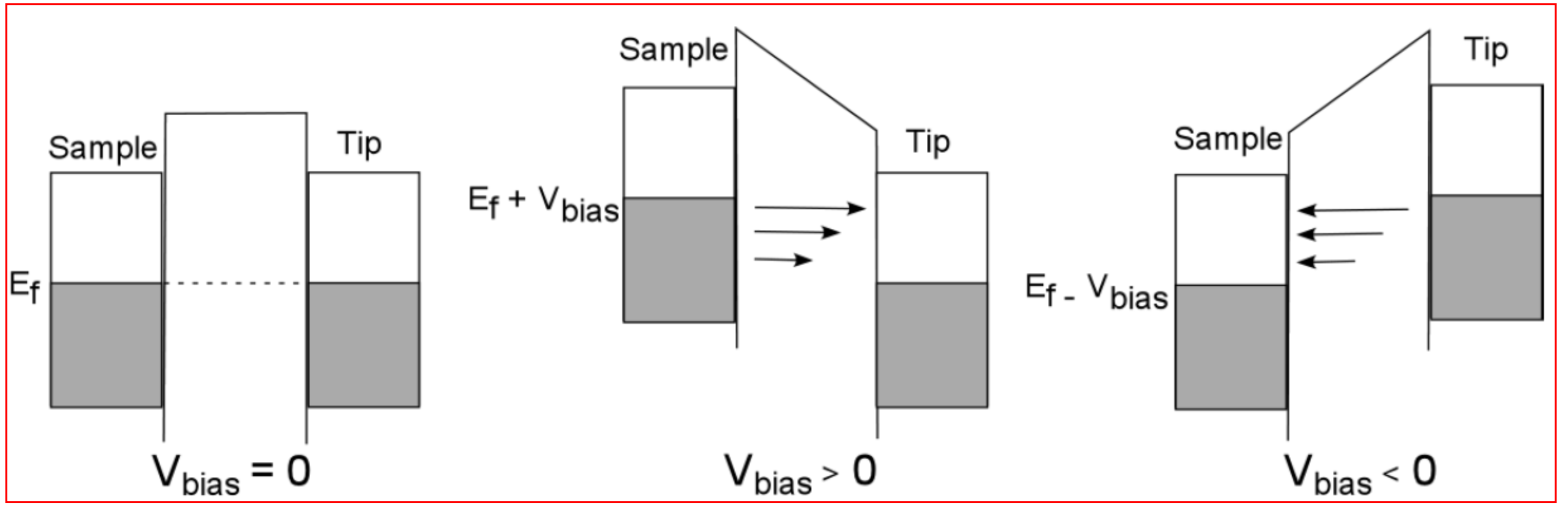
$\sqrt{2m} / \hbar \cong 2.5 \times 10^{19}\,\mathrm{m}^{-1}\mathrm{J}^{-1/2} \cong 1\ \text{Å}^{-1}\mathrm{eV}^{-1/2}$

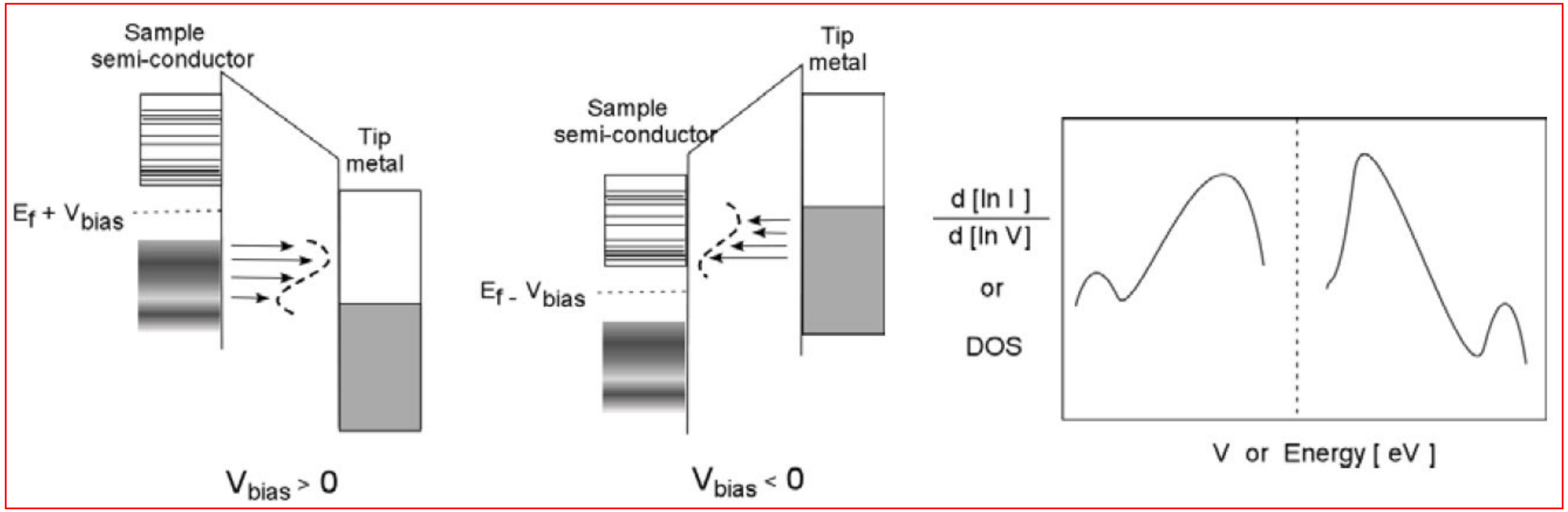
Scanning tunneling microscope: Vertical resolution: better than 0.01 Å

Lateral resolution: atomic resolution

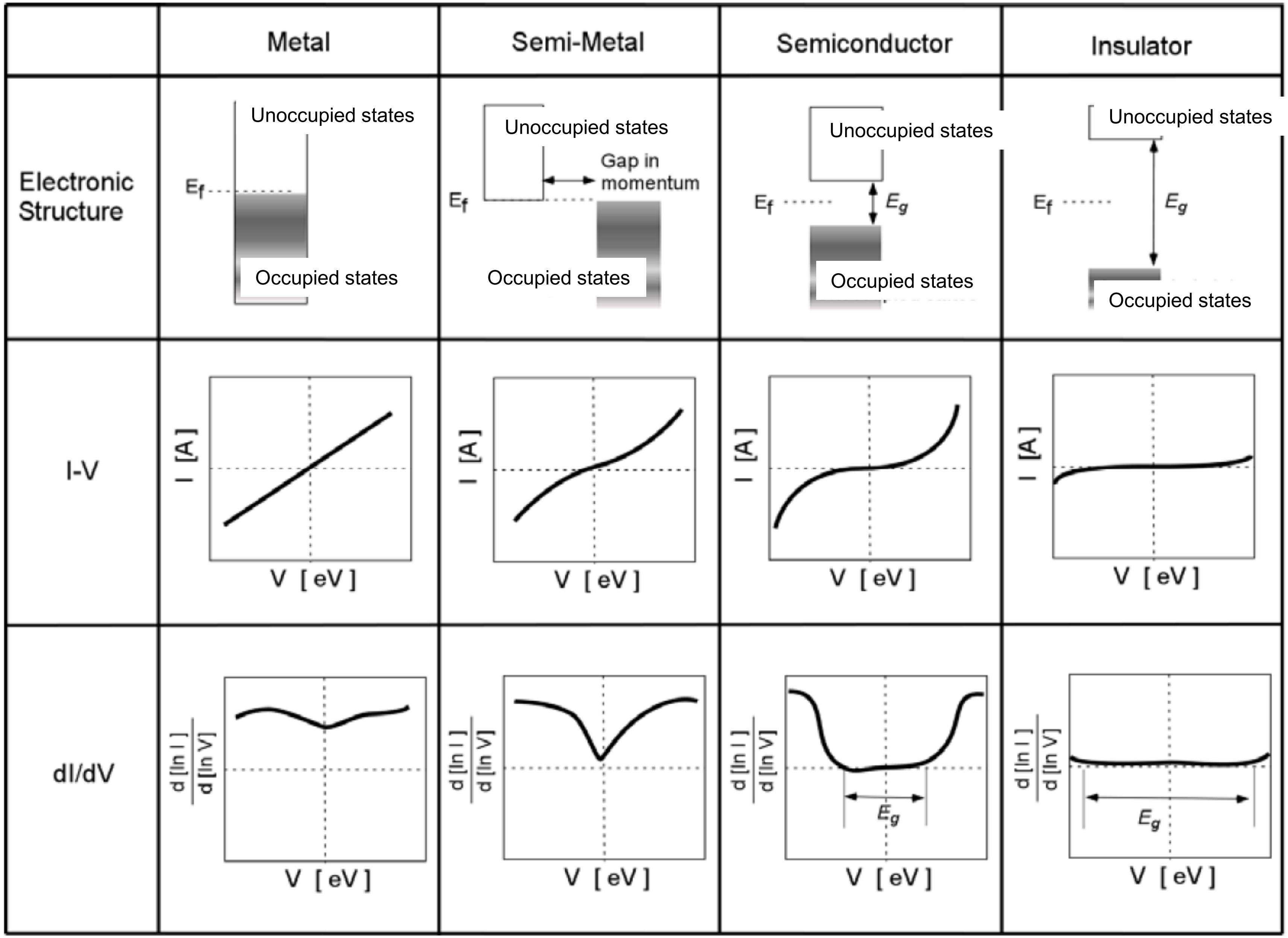
Tunneling current: spectroscopy of density of states

$$I \propto \int_{0}^{eV} \rho_s\left(E_F + eV + \varepsilon\right)\rho_t\left(E_F + \varepsilon\right)d\varepsilon$$



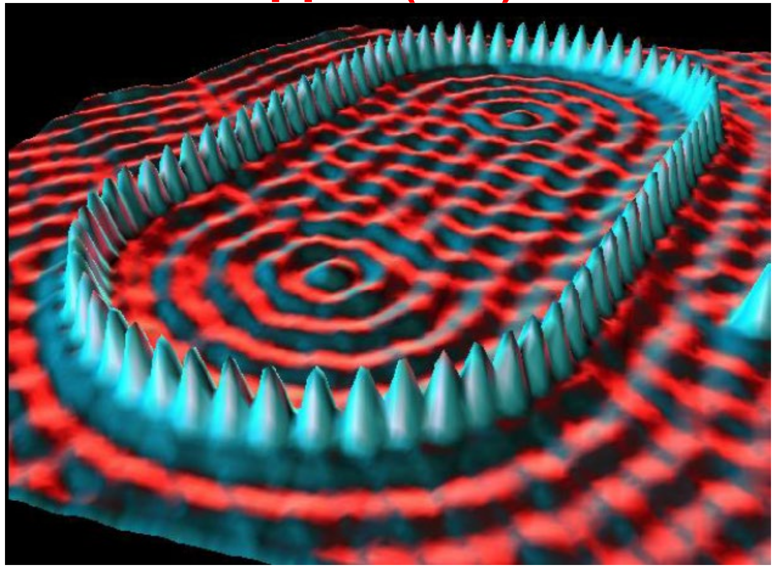


Tunneling current: spectroscopy of density of states



Tunneling current: manipulation and imaging

Iron on Copper (111)



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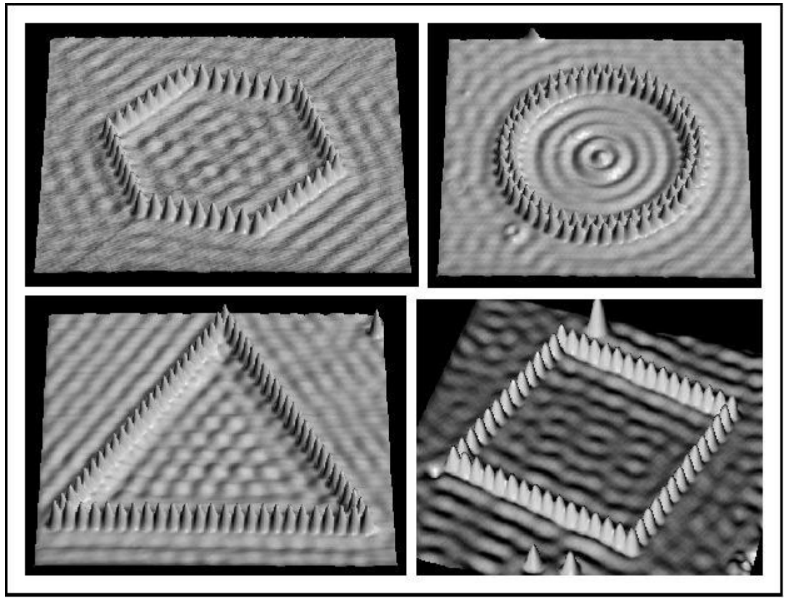
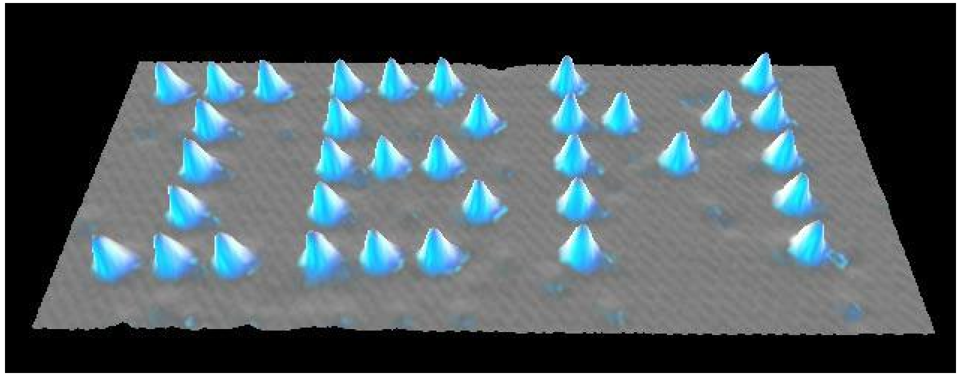
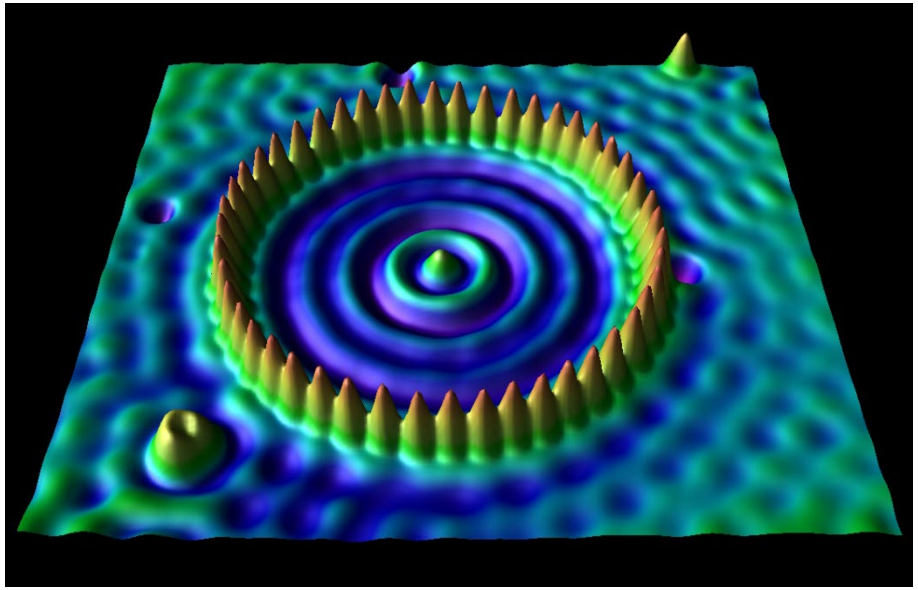


Xenon on Nickel (110)

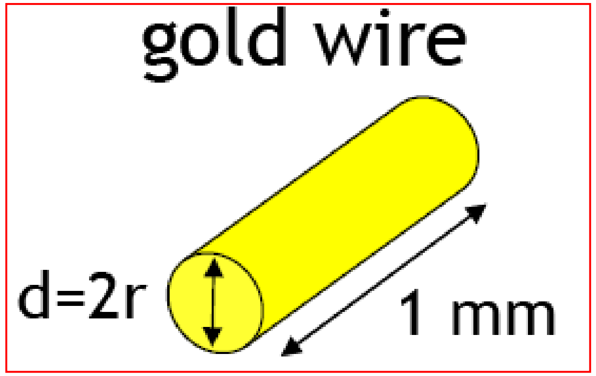


http://www.almaden.ibm.com/vis/stm/images/stm10.jpg

Manipulation and imaging of single atoms (and of electron density interferences)



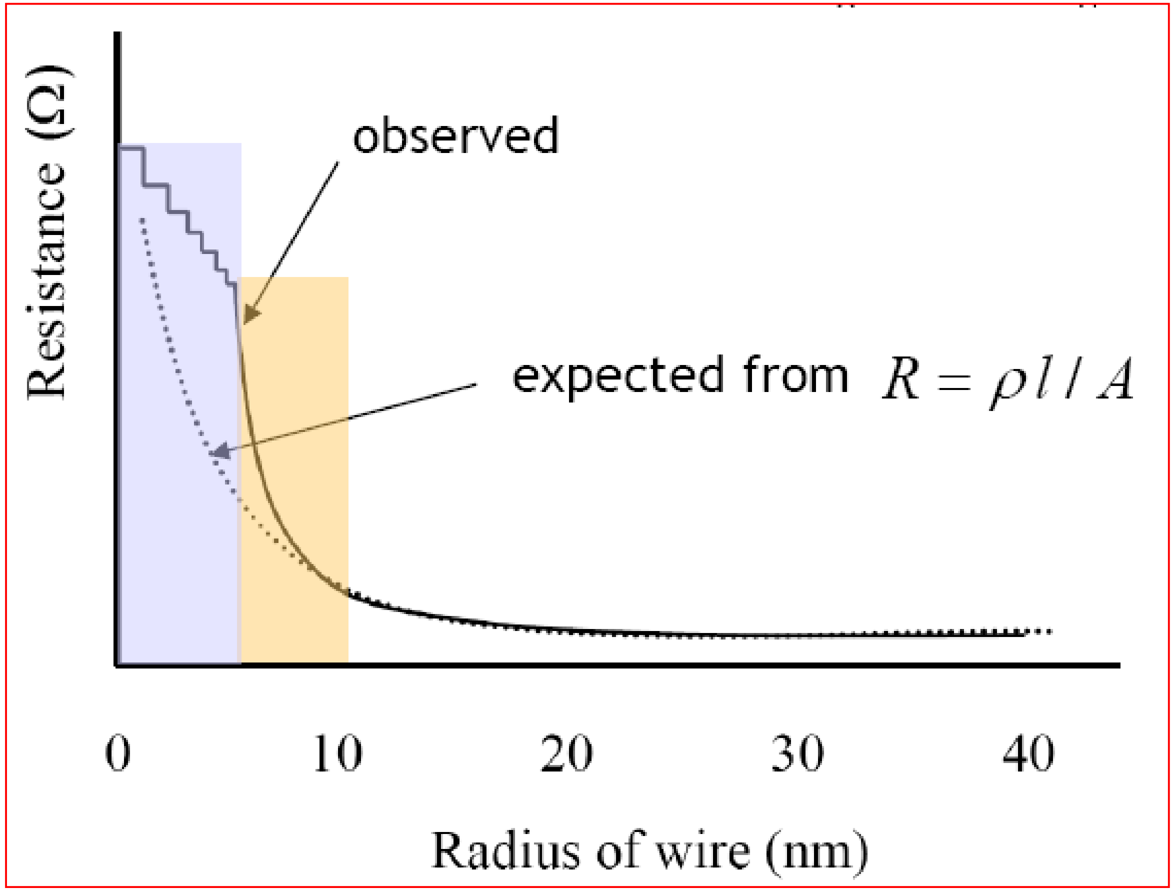
Conductance quantization: experimental evidence



Conductance quantization: first observed in 1988.
1. B. J. van Wees et al."Quantized Conductance of Point Contacts in a Two-Dimensional Electron Gas" *Physical Review Letters* 60, 848-850, 1988.
D. A. Wharam et. Al. "One-dimensional transport and the quantisation of the ballistic resistance," *Journal of Physics C: Solid State Physics* 21, L209-L214, 1988.

mesoscopic effects
- surface scattering

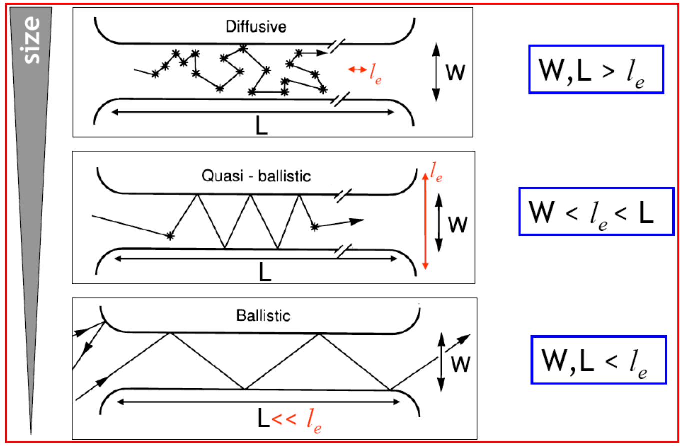
quantum effects



Conductance quantization: conditions

Conditions to observe conductance quantization:

- Low temperature ($k_B T$ small with respect to energy separation of the possible states)
- Ballistic transport
- 1D electron system (nanowire)



l_e … mean free path (between elastic or inelastic scattering events)

Conductance quantization can be observed by:

- changing the voltage applied across the nanowire
- changing the nanowire lateral dimensions (e.g., by a gate voltage acting on a channel)

In both cases the conductance changes by steps having the following amplitude:

$$\Delta G = G_0 = \frac{2e^2}{h}$$

In Quantum Point Contacts (constrictions between two electrically conducting regions with a width comparable with the electron wavelength) the conductance changes by steps of amplitude G_0 and have absolute values given by:

$$G = N\frac{2e^2}{h} \qquad N \cong \frac{2W}{\lambda}, \quad \lambda = \frac{h}{p}$$

Conductance quantization: simplified theory

The current in 3D wire of section S is given by: $I = JS = nevS = n_L ev$

($n_L \equiv nS$: number of electrons per unit of length of the wire partecipating to the current)

We can tentatively write the current an a 1D wire as: $I \approx e \int_{E_F}^{E_F+eU} \frac{g_{1D}(E)}{L} v(E)\, dE$

$\left(g_{1D}(E)/L : \text{ the density of states per unit of length for a 1D wire} \right)$

The density of states of a 1D system is: $g_{1D}(E) = \frac{L}{2\pi\hbar}\sqrt{\frac{2m_e}{E}}$

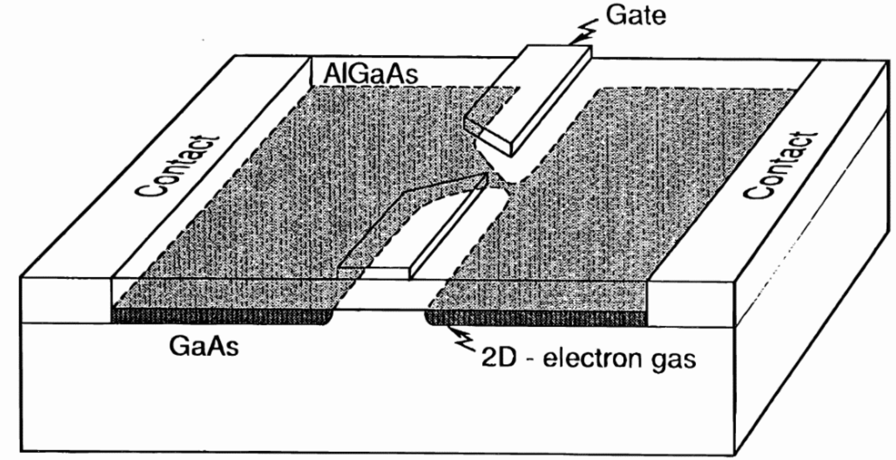
The group velocity is, by definition, given by: $v(E) = \sqrt{\frac{2E}{m_e}}$

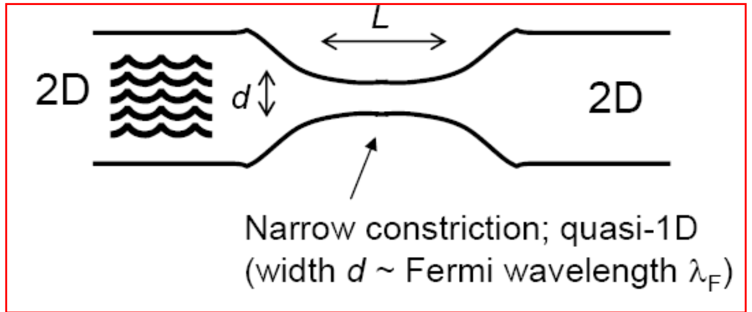
Consequently: $g_{1D}(E)\, v(E) = \frac{L}{\pi\hbar}$

and $I \approx e\frac{1}{\pi\hbar}\int_{E_F}^{E_F+eU} dE = \frac{e^2 U}{\pi\hbar}$

Finally $G = \frac{I}{U} \approx \frac{e^2}{\pi\hbar} = \frac{2e^2}{h}$

Conductance quantization: experimental evidence

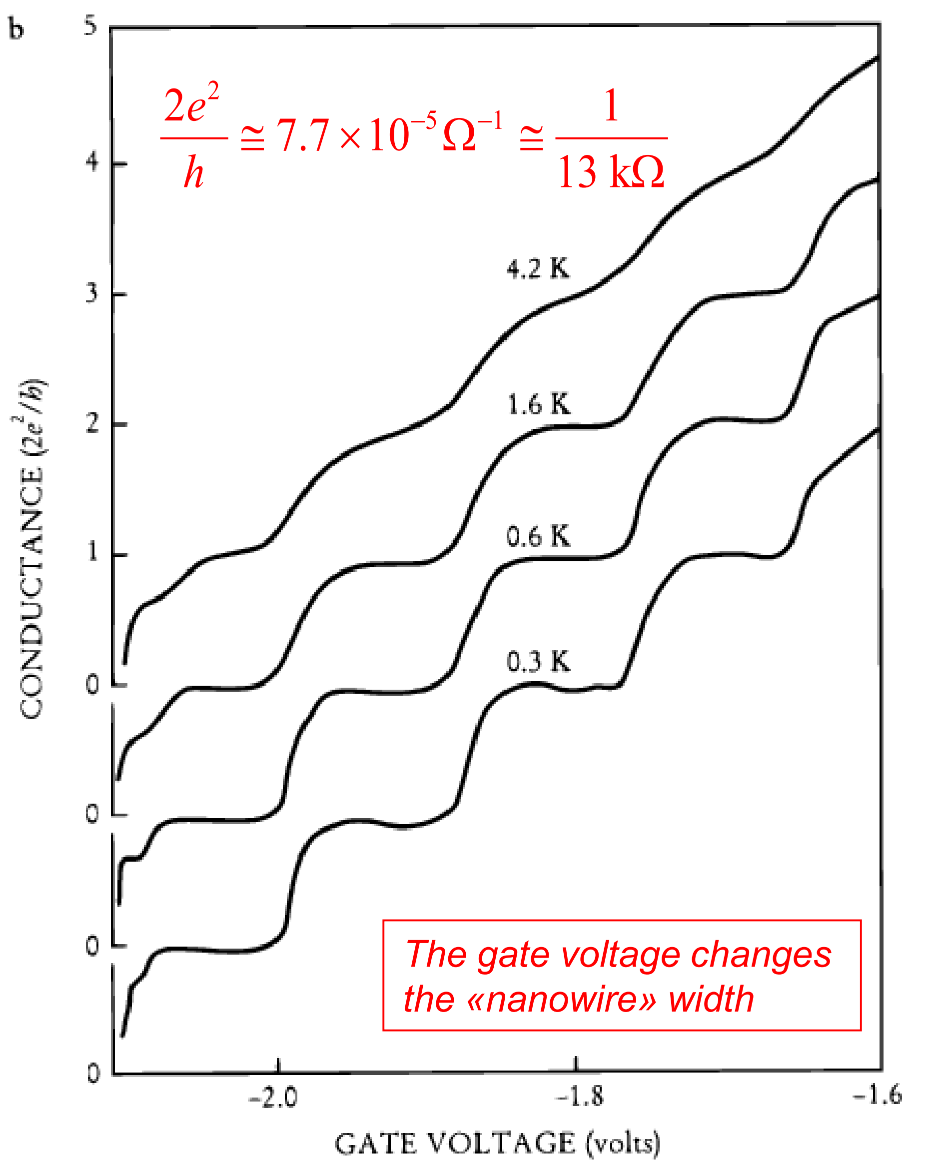




Narrow constriction; quasi-1D (width d ~ Fermi wavelength λ_F)

Conductance quantization: As the gate voltage defining the constriction is made less negative, the width of the point contact increases continuously, but the number of propagating modes at the Fermi level increases stepwise.

- The conductance steps are smeared out when the thermal energy becomes comparable to the energy separation of the modes.



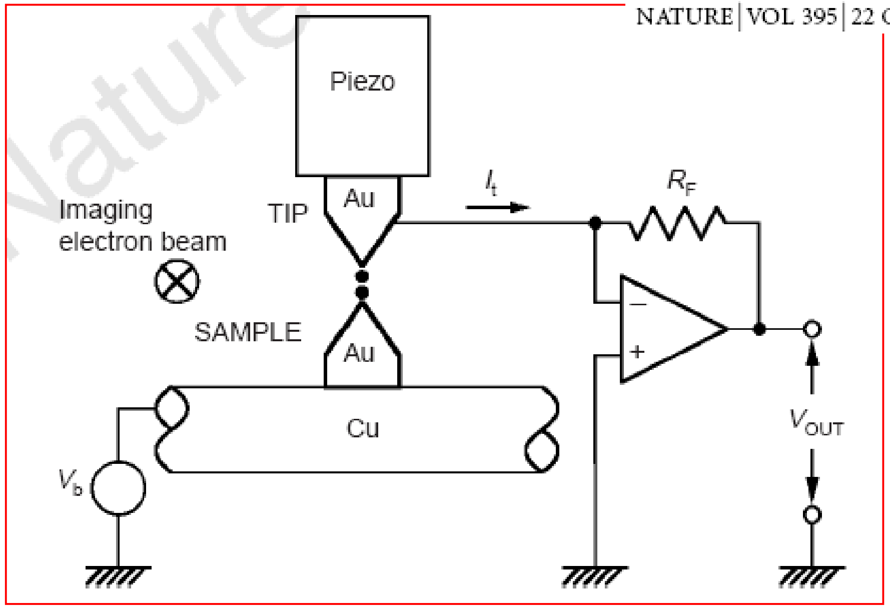
$$\frac{2e^2}{h} \cong 7.7\times10^{-5}\,\Omega^{-1} \cong \frac{1}{13\ \text{k}\Omega}$$

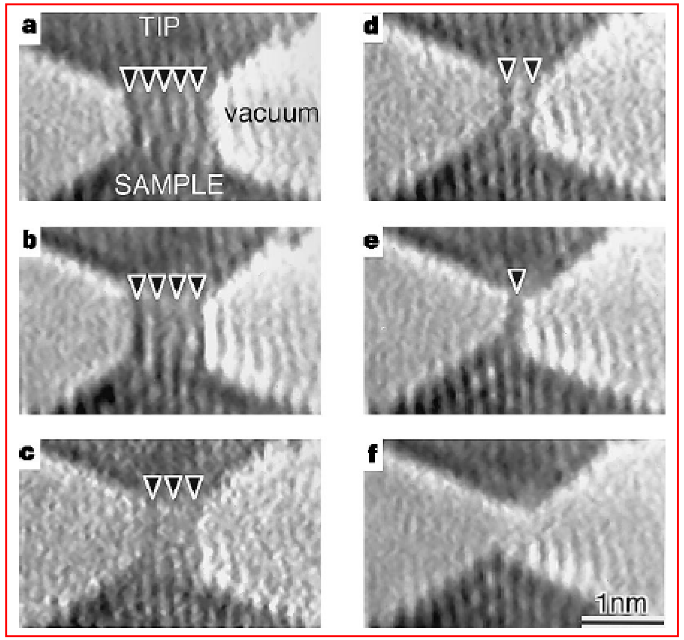
The gate voltage changes the «nanowire» width

http://sciencewise.info/definitions/Quantum_point_contact_by_Carlo_Beenakker

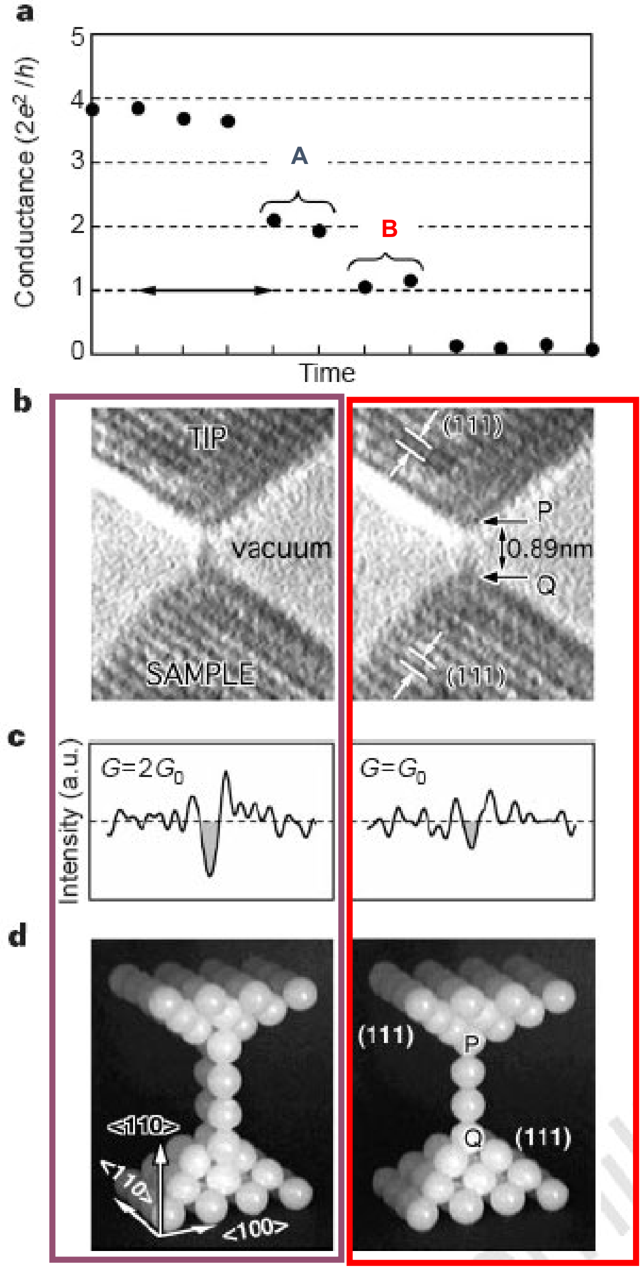
Conductance quantization: experimental evidence

NATURE | VOL 395 | 22 OCTOBER 1998 | www.nature.com





Different «nanowire» widths



Coulomb blockade (CB)

•**Coulomb blockade (CB)** is the increased resistance at small bias voltages of an electronic device comprising at least one low-capacitance tunnel junction. Because of the CB, the resistances of devices are not constant at low bias voltages, but increase to infinity at the limit of zero bias voltage.

•An arrangement of two conductors with an insulating layer in between not only has a resistance, but also a finite capacitance. The tunnel junction behaves as a capacitor.

• Current through a tunnel junction is a series of events in which exactly one electron passes (*tunnels*) through the tunnel barrier. The tunnel junction capacitor is charged with one charge e by the tunnelling electron, causing a voltage buildup $U=e/C$, where C the capacitance of the junction.

•If the capacitance is very small, the voltage buildup can be large enough to prevent another electron from tunnelling. The electrical current is then suppressed at low bias voltages and the resistance of the device is no longer constant.

•The increase of the differential resistance around zero bias is called the Coulomb blockade.

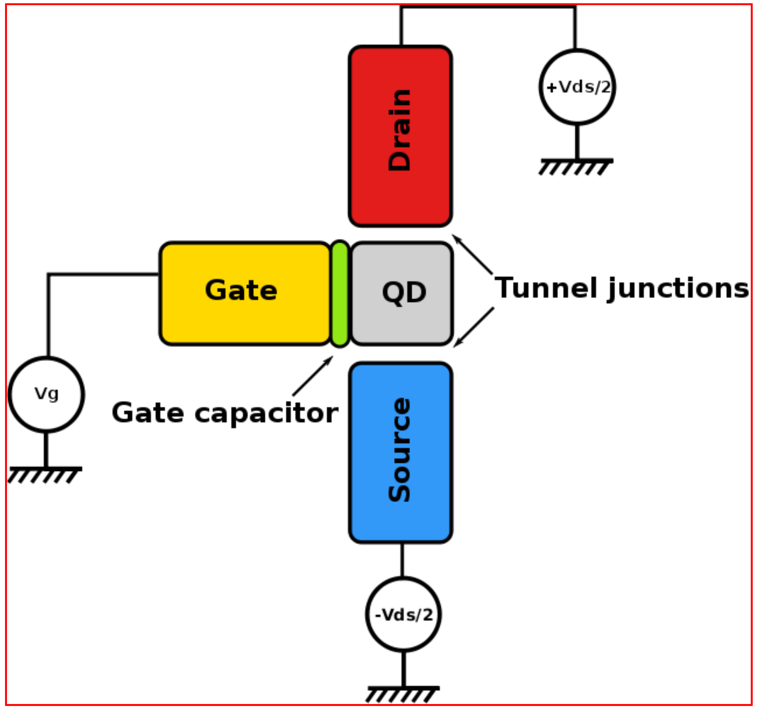
Single electron transistor (SET)

- A simple device in which the Coulomb blockade can be observed is the so-called **single electron transistor (SET).**

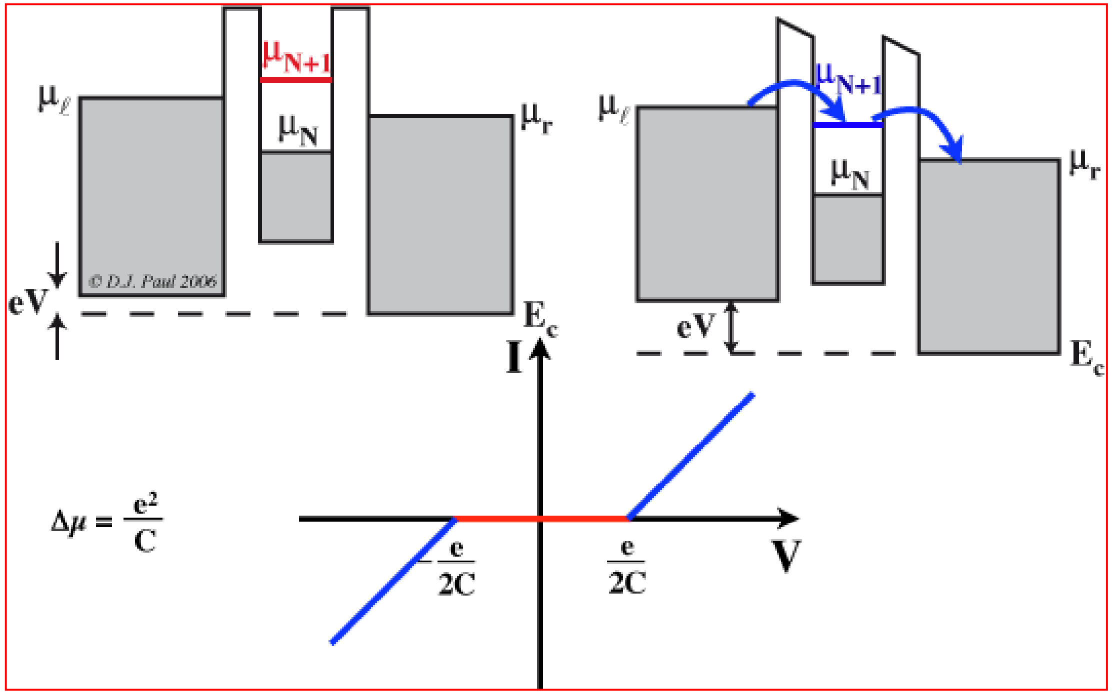
- SET: two electrodes (*drain* and *source*), connected through tunnel junctions to one common electrode with a low self-capacitance, known as the *island*. The electrical potential of the island can be tuned by a third electrode (*gate*), capacitively coupled to the island with a relatively thick insulating layer (to prevent tunneling from the gate to the island).

- In the blocking state no accessible energy levels are within tunneling range of the electron on the source contact. All energy levels on the island electrode with lower energies are occupied.

When a positive voltage is applied to the gate electrode the energy levels of the island electrode are lowered. The electron can tunnel onto the island, occupying a previously vacant energy level. From there it can tunnel onto the drain electrode where it inelastically scatters and reaches the drain electrode Fermi level.



http://upload.wikimedia.org



http://www.sp.phy.cam.ac.uk

SET: general approx. features

To observe Coulomb blockade three criteria have to be met:

1. $V < e/2C$

(otherwise electrons have enough energy to overcome Coulomb energy barrier)

2. $k_BT < e^2/2C$

(otherwise electrons cross the island via thermal exictation)

3. $R_T > h/e^2 \cong 26\ \mathrm{k}\Omega$

(R_T : tunneling resistance. This condition is obtained from the uncertainty principle and correspond to a situation where simultaneous tunneling events are negligible)

Example: $k_BT < e^2/C$

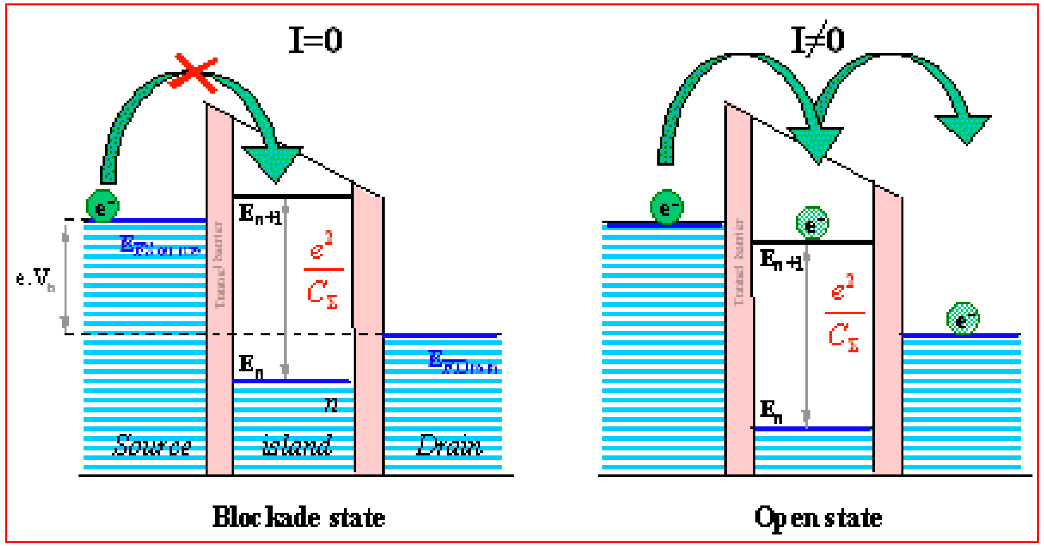
requires, at T=1 K, a capacitance

$C < e^2/k_BT \cong 10^{-15}$ F=1 fF.

Capacitance of a metallic sphere

in a dielectric medium ε_r: C=$4\pi\varepsilon_0\varepsilon_r R$

For $R = 100$ nm, $\varepsilon_r = 4 \Rightarrow C \cong 0.1$ fF



http://www.lne.eu/en/r_and_d/images_r_and_d/electrical_metrology/etm_fig3.gif

Single electron transistor (SET): a simple theory

The energy that determines the transport of electrons through single electron devices is the Helmoltz's free energy $F = E_a - W$

$E_a = E_C + E_K$ (Total energy stored in the device)

W (Work done by the power sources)

$E_C = e^2 / 2C$ (Energy required to charge an island with one electron)

$E_K = 1 / g(E_F)$ (Quantum kinetic energy of the added electron, $g(E_F) \propto V^{2/3}$)

Usually we have $E_C \gg E_K$ (i.e., the quantization due the small size of the island is negligible)

The only transitions possible (at $T = 0$) are those where $\Delta F < 0$.

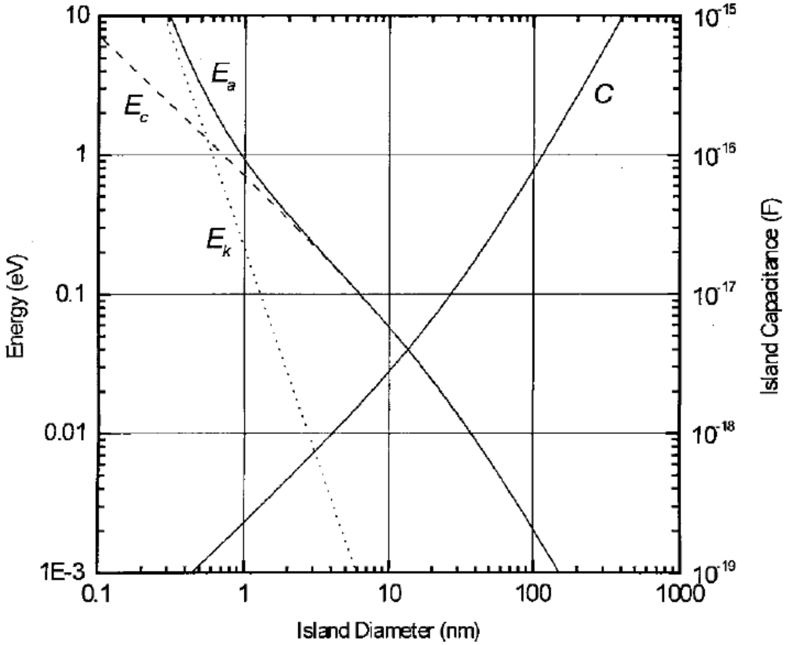


Fig. 2. Single-electron addition energy E_a (solid line), and its components: charging energy E_c (dashed line) and electron kinetic energy E_k (dotted line), as calculated using (1) and (2) for a simple model of a conducting island. In this model, the island is a round three-dimensional (3-D) ball with a free, degenerate electron gas (electron density $n = 10^{22}$ cm^{-3}, effective electron mass $m = m_0$), embedded into a dielectric matrix (dielectric constant $\varepsilon = 4$), with 10% of its surface area occupied by tunnel junctions with a barrier thickness of 2 nm.

Single electron transistor (SET): a simple theory

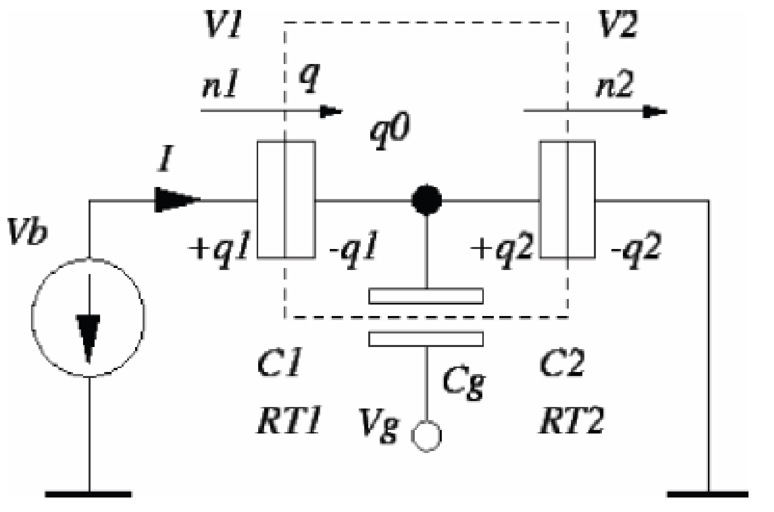
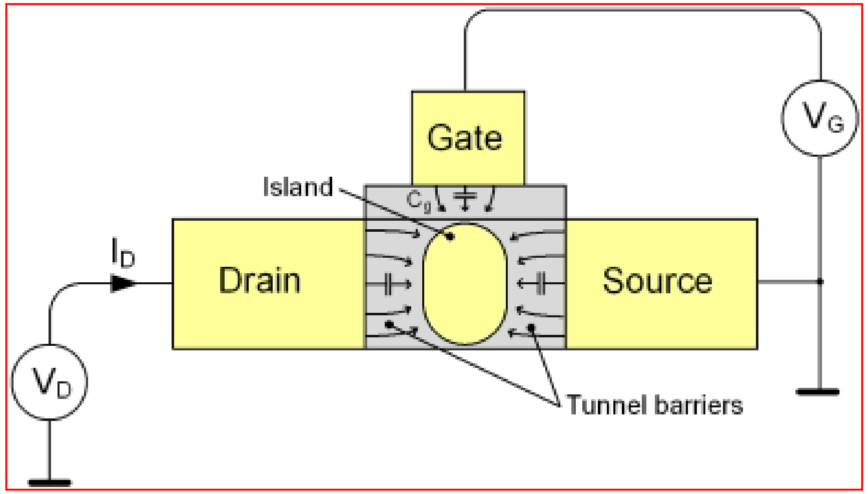


Figure 5: equivalent circuit for single electron transistor



The Gate-Island oxide is much thicker than the Drain-Island and Source-Island oxide (negligile tunneling from Gate to Island)

q_0 is induced by stray capacitances and impurities (background charge)

Total charge on the island: $q = q_2 - q_1 + q_0 + C_g(V_g - V_2) = -ne + q_0 + C_g(V_g - V_2)$

where $n \equiv n_1 - n_2$

$V_1 = q_1 / C_1 \quad , \quad V_2 = q_2 / C_2 \quad , \quad V_b = V_1 + V_2$

From these equations we get:

$$V_1 = \frac{(C_2 + C_g)V_b - C_g V_g + ne - q_0}{C_\Sigma}, \qquad V_2 = \frac{C_1 V_b + C_g V_g - ne + q_0}{C_\Sigma}, \quad C_\Sigma = C_1 + C_2 + C_g$$

Single electron transistor (SET): a simple theory

$$F(n_1,n_2)=E_C-W$$

$$E_C=\frac{q_1^2}{2C_1}+\frac{q_2^2}{2C_2}+\frac{q_g^2}{2C_g}=\frac{V_1^2}{2}+\frac{V_2^2}{2}+\frac{V_g^2}{2}$$

$$W=-\left(n_1eV_bC_1/C_\Sigma\right)-\left(n_2eV_bC_2/C_\Sigma\right)$$

$$\Delta F_1^{\pm}=F(n_1\pm1,n_2)-F(n_1,n_2)$$

$$\Delta F_2^{\pm}=F(n_1,n_2\pm1)-F(n_1,n_2)$$

The change in the free energy after a tunnel event in junction 1 and junction 2 are:

$$\Delta F_1^{\pm}=\frac{e}{C_\Sigma}\left(\frac{e}{2}\pm\left(\left(C_2+C_g\right)V_b-C_gV_g+ne-q_0\right)\right)$$

$$\Delta F_2^{\pm}=\frac{e}{C_\Sigma}\left(\frac{e}{2}\pm\left(C_1V_b+C_gV_g-ne+q_0\right)\right)$$

At T=0, the possible (energetically favorable) transitions are those with $\Delta F_1^{\pm}<0$ or $\Delta F_2^{\pm}<0$.

These conditions generates the V_bV_g *plots* (also called *Coulomb diamonds*)

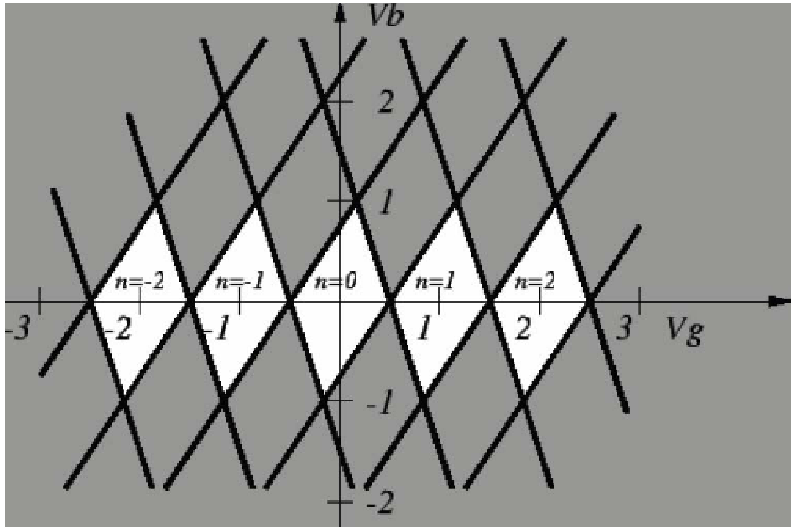
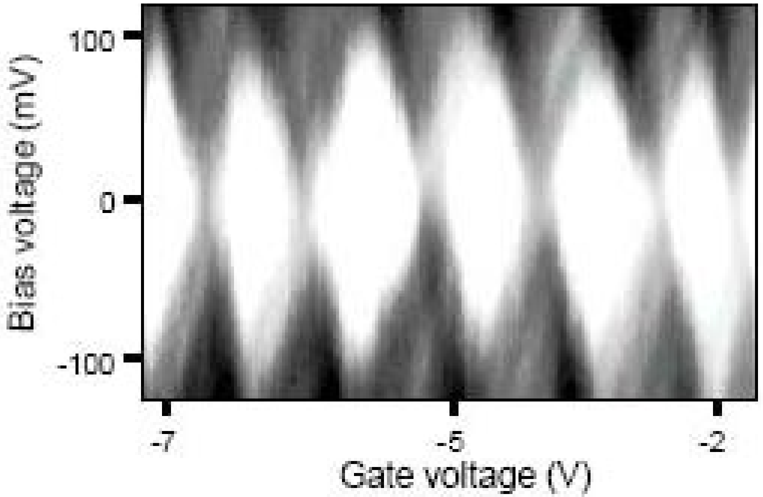
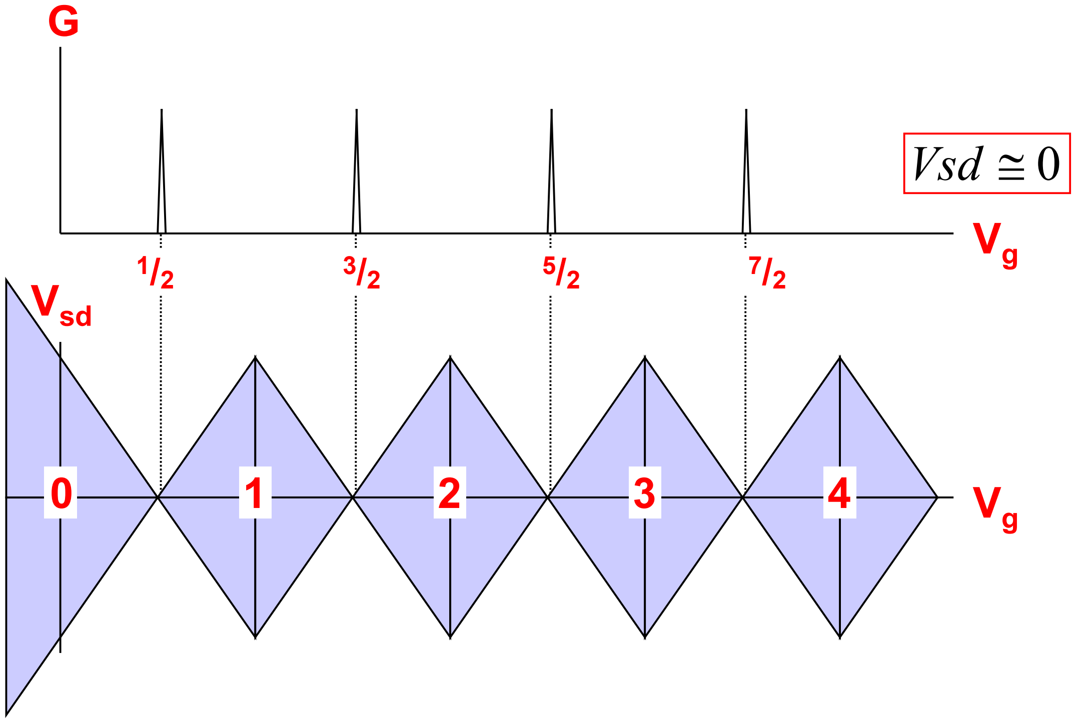


Figure 6: "Coulomb diamonds"



Single electron transistor (SET): a simple theory



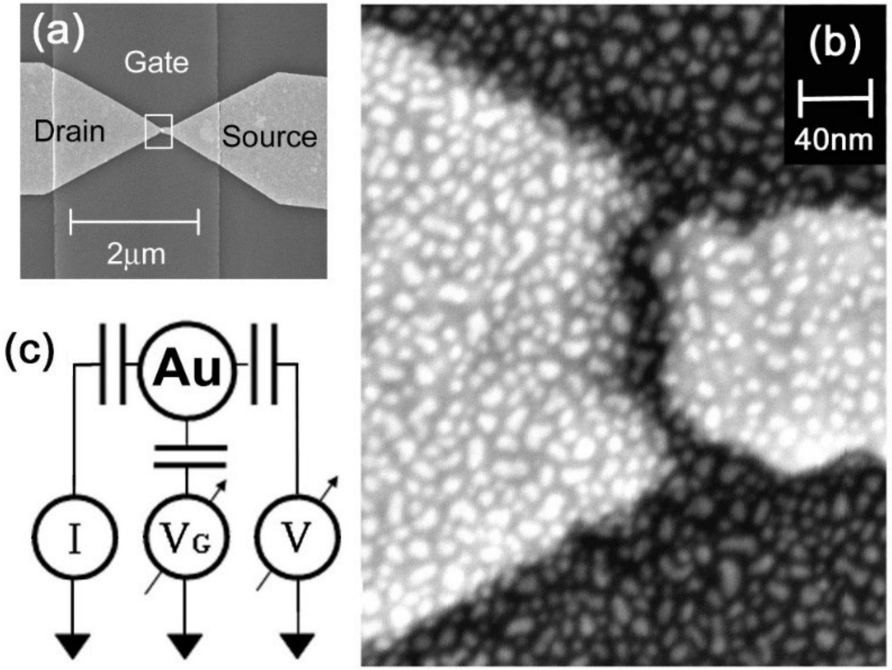
- In the region 0, tunneling is forbidden by the Coulomb blockade and the only stable charge state is the one with **zero** electrons on the island.

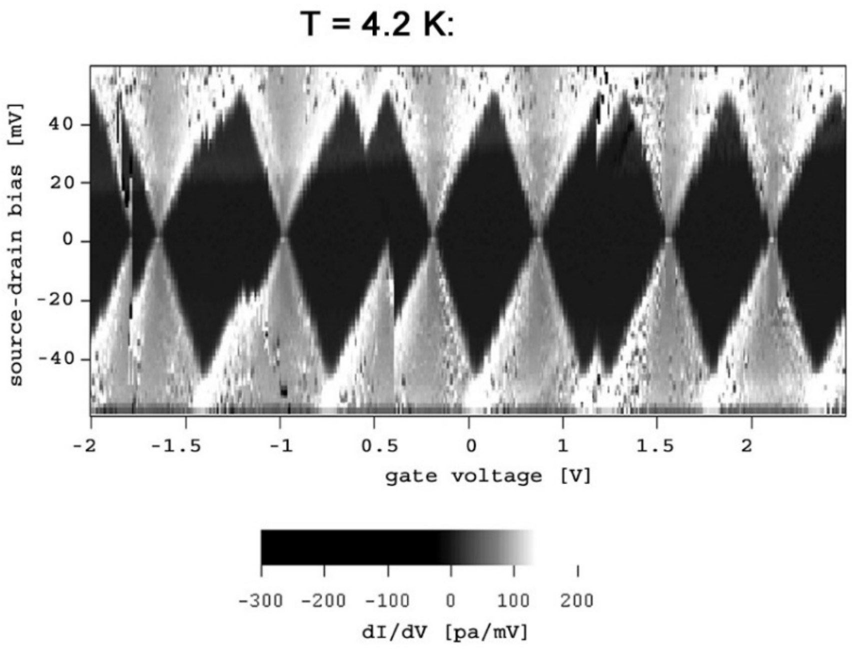
- The regions 1,2,3.. are also a region of Coulomb blockade where the only stable charge state is **one, two, three,…** electrons on the island.

- Within the regions 1,2,3,.. the conductance G is zero (no current flows from source to drain). At the interesection of these regions the G is not zero. Outside of these regions G is not zero.

- When a bias voltage is applied that is large enough to overcome the Coulomb blockade, current flows as electrons tunnel from the source onto the island and then from the island to the drain.

SET: experiments





(a) Top-view SEM image of the device geometry, with gold source and drain electrodes on top of an oxidized aluminum gate.
(b) Expanded view of the region outlined with a white rectangle in (a). A 10 nm gap made by electromigration is visible, along with deposited gold nanoparticles.
(c) Circuit schematic for the Au-nanoparticle SET

http://people.ccmr.cornell.edu

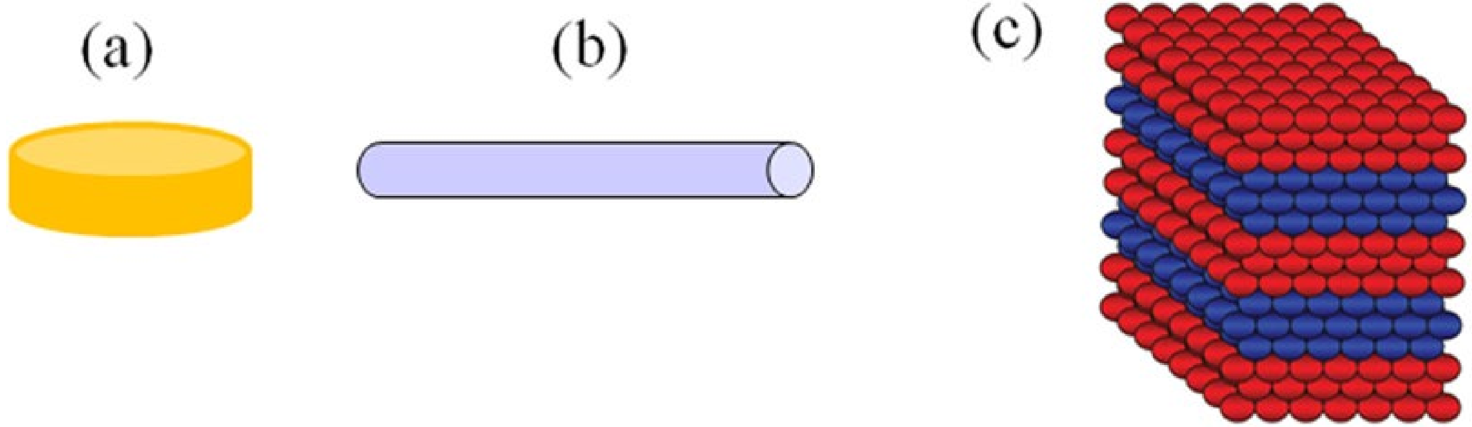
http://www.rikenresearch.riken.jp/images/figures/hi_3678.jpg

Nanomagnetism: Nanoscaled magnetic "objects"

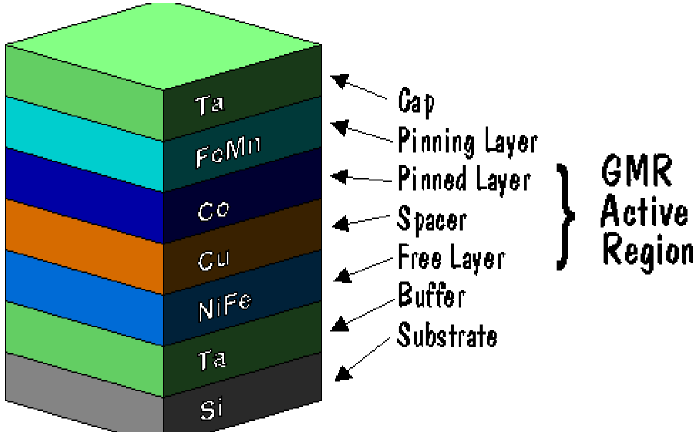
Nanodots
Nanoparticles

Nanowires

Ultrathin films and multilayers



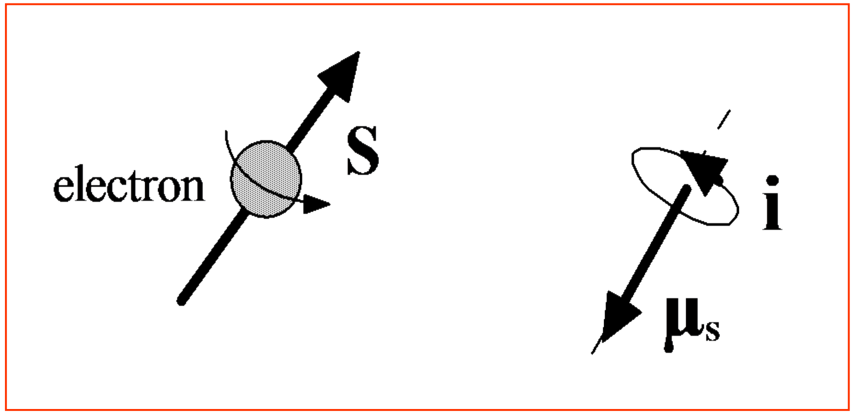
Ultrathin complex multilayers



Nanomagnetism: Microscopic sources of magnetic field

Intrinsic magnetic moment of an electron

$$\mu_S = 2\mu_B\sqrt{s(s+1)} = \mu_B\sqrt{3} \approx \mu_B$$



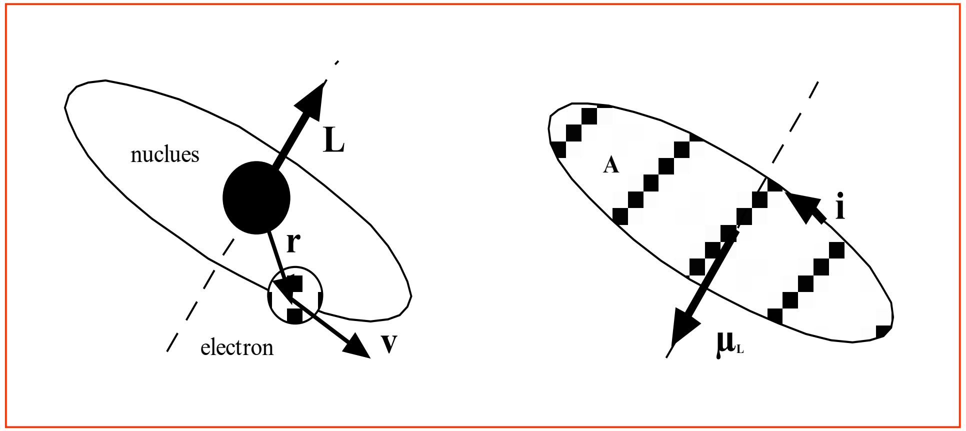
(classical picture: the electron rotates about itself (!?!))

$$\mu_B \equiv \frac{e\hbar}{2m_e} \cong 9.3\times10^{-24} \ \ \mathrm{Am}^2$$

is called *Bohr magneton*.

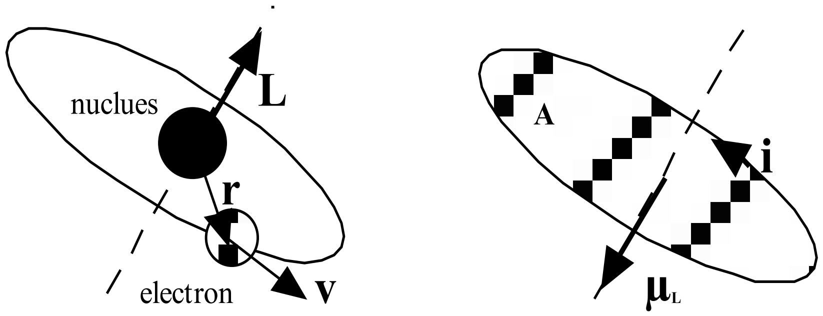
Orbital magnetic moment of an electron

$$\mu_L = -\frac{e}{2m_e}L \approx \mu_B$$



Nanomagnetism: Microscopic sources of magnetic field

Orbital magnetic moment of an electron



- Equilibrium between **Coulomb force** and **centrifugal force:**

$$\frac{e}{4\pi\varepsilon_0 r^2} = m_e\frac{v^2}{r} \quad\Rightarrow\quad v = e\sqrt{\frac{1}{4\pi\varepsilon_0 r}\frac{1}{m_e}}$$

- **Orbital angular momentum:**

$$L = r m_e v \qquad \Rightarrow (\text{for} \quad r \sim 10^{-10}\,\text{m}) \qquad L = e\sqrt{\frac{m_e r}{4\pi\varepsilon_0}} \cong 10^{-34}\,\text{Js} \cong \hbar$$

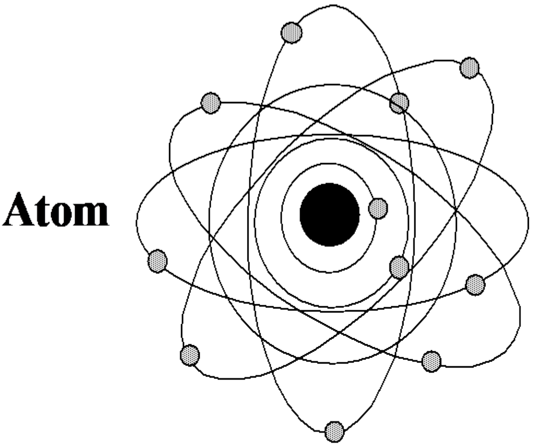
- The **orbital magnetic moment** is then**:**

$$\mu_L = iA = -\left(\frac{ev}{2\pi r}\right)(\pi r^2) = -\frac{ev}{2}r = -\frac{e}{2m_e}L \approx \mu_B$$

Note:

$$i \sim \frac{\mu_B}{A} \sim \frac{\mu_B}{\pi r^2} \sim 0.3\text{ mA}$$

Magnetic moment of an atom



Questions:

- The **magnetic moment of an atom** with **Z electrons** is the **"sum"** of the magnetic moment of each electron ?
- Yes. We will see how the **"sum"** must be done.

- For an atom with many electrons, the magnetic moment **is much larger** than the Bohr magneton ?
- No. The biggest is only **a few times the Bohr magneton (**because filled shells have zero angular momentum).

- The **magnetic moment of the nucleus** is negligible with respect to that of the electron ?
- Yes. It is at least **1000 times smaller** (because $\mu \propto 1/m$) **.**

How to compute the total magnetic moment of an atom ?

1. Solve the **Schrödinger equation** for the atomic system (electrons + nucleus)

$$H_{atom}\psi_i = E_i\psi_i$$

H_{atom}: Hamiltonian operator (total energy)

ψ_i: Wavefunction of state i (possible state of the system)

E_i: Energy of state i (possible energy of the system)

Electron kinetic energy

Electron-Nucleus Coulomb interaction

Electron-Electron Coulomb interaction (Exchange)

Spin-Orbit Interaction (Anisotropy)

$$H_{atom} = \sum_{i=1}^{Z}\frac{p_i^2}{2m} - \sum_{i=1}^{Z}\frac{Ze^2}{r_i^2} + \sum_{i<j}^{Z}\frac{e^2}{\left|r_i - r_j\right|^2} + \sum_{i=1}^{Z}(\mathbf{l}_i\cdot\mathbf{s}_i)\xi(r_i)$$

2. Compute the value of the **magnetic moment** for each state of the system

$$\mu_i = \left|\langle\psi_i|\mu|\psi_i\rangle\right|$$

μ: Magnetic moment operator

Magnetic moment of an atom or ion

Russel-Saunders Rule

The total angular momentum of the atom or ion is given by
(valid more accurately for light atoms where the spin-orbit coupling is weaker than spin-spin and orbit-orbit couplings):

$$\boxed{\mathbf{J} = \mathbf{L} + \mathbf{S} = \sum_{i=1}^{Z} \mathbf{L}_i + \sum_{i=1}^{Z} \mathbf{S}_i}$$

Hund Rules

1) The spin vectors **S**$_i$ are arranged to maximize total spin **S**
Physical interpretation: minimization of the exchange energy

$$\boxed{E_{exc} = -J\mathbf{S}_i \cdot \mathbf{S}_j}$$

2) The orbital vectors **L**$_i$ are arranged to maximize total momentum **L**
Physical interpretation: electrons with the same sign of angular momentum can more easily «avoid» each other because they precess in the same direction.

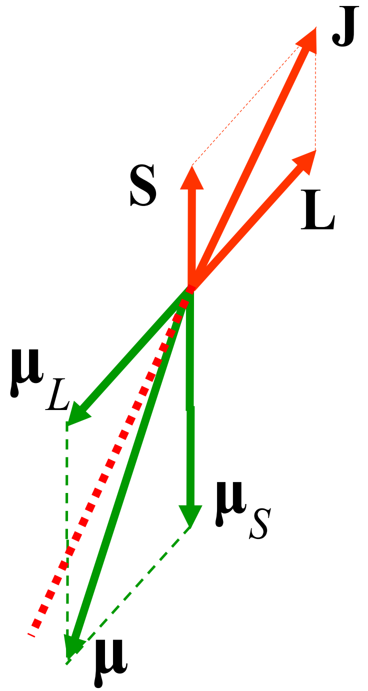
3) If a «shell», specified by (*n*,*l*), is:

$$\boxed{\text{Less than half filled: } \mathrm{J} = |\mathrm{L} - \mathrm{S}| \qquad \text{More than half filled: } \mathrm{J} = |\mathrm{L} + \mathrm{S}|}$$

Physical interpretation: minimization of the spin-orbit coupling. This rule is often not valid (ok pour rare-earths but not for transition metals)

Magnetic moment of an atom or ion

In general: $\boldsymbol{\mu} \neq -\mu_B \mathbf{J}$ (with $\mathbf{J} = \mathbf{L} + \mathbf{S}$)



Total orbital magnetic moment: $\boldsymbol{\mu}_L \equiv \mu_B g_L \mathbf{L} = -\mu_B \mathbf{L}$

Total spin magnetic moment: $\boldsymbol{\mu}_S \equiv \mu_B g_S \mathbf{S} \cong -\mu_B 2\mathbf{S}$

Total magnetic moment: $\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\mu_B(\mathbf{L} + 2\mathbf{S})$

Case 1: J=0 and **zero** partially filled shells $\Rightarrow$ $\boldsymbol{\mu} = 0$

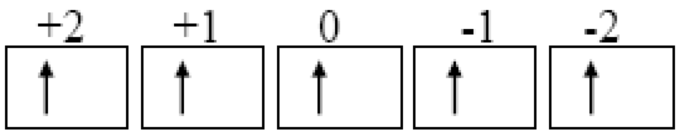
Case 2: $\mathrm{J} \neq 0$ and **one** partially filled shells $\Rightarrow$ $\boldsymbol{\mu} \neq 0$

$$\mu = \mu_B g_J \sqrt{J(J+1)} \qquad g_J \cong \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Case 3: J=0 and **one** partially filled shells $\Rightarrow$ $\boldsymbol{\mu} \neq 0$ (complex case)

Magnetic moment of an atom or ion

Ground state of a 3d^5 ion (Mn^{2+})



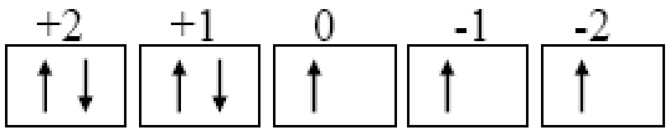
$L = 0,\ S = 5/2,\ J = 5/2$

$m_L = L\ \mu_B = 0\ \mu_B\ ,$

$m_S = g_e\ S\ \mu_B = 5\ \mu_B\ ,$

$m_{at} = g\ J\ \mu_B = 5\ \mu_B$

Ground state of a 3d^7 ion (Co^{2+})

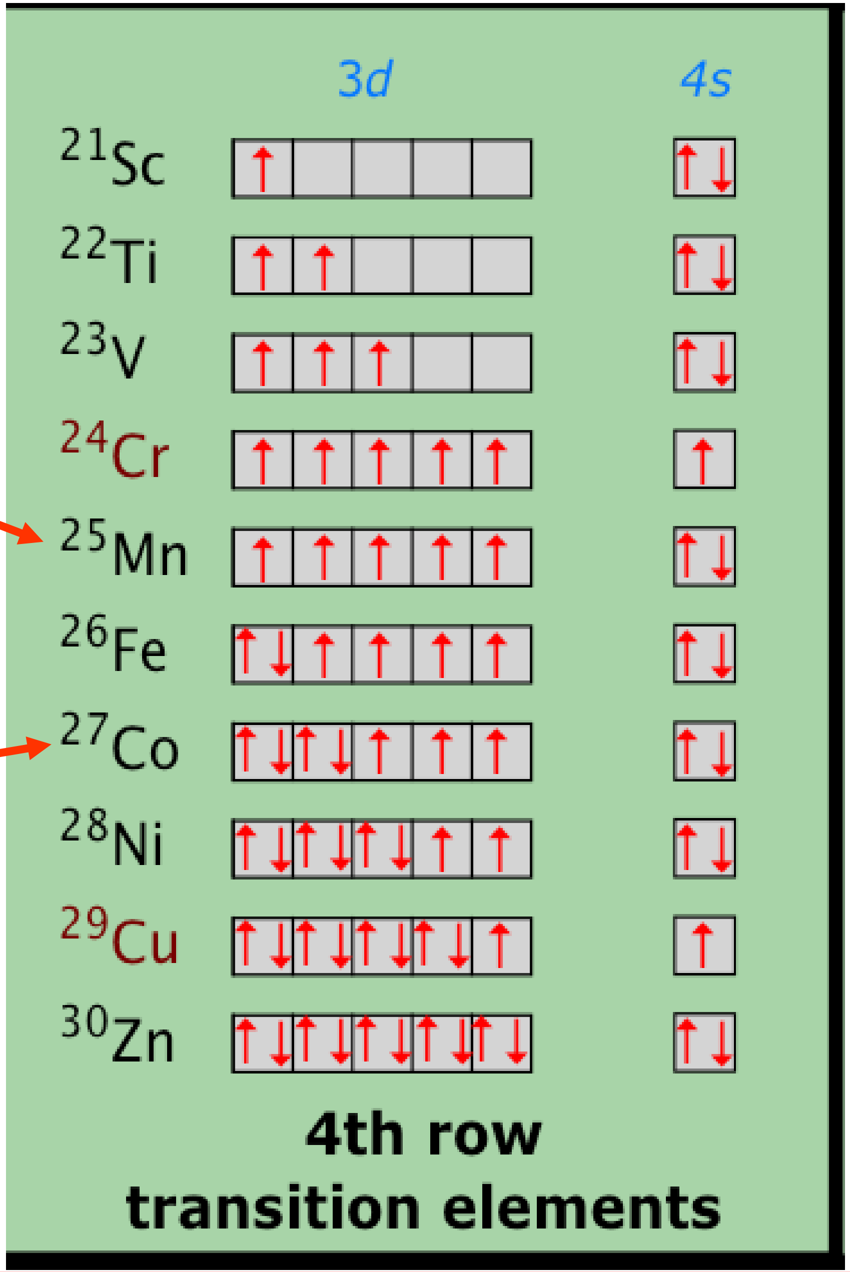


$L = 3,\ S = 3/2,\ J = 9/2$

$m_L = L\ \mu_B = 3\ \mu_B\ ,$

$m_S = g_e\ S\ \mu_B = 3\ \mu_B\ ,$

$m_{at} = g\ J\ \mu_B = 6\ \mu_B$



	3d					4s
^{21}Sc	↑					↑↓
^{22}Ti	↑	↑				↑↓
^{23}V	↑	↑	↑			↑↓
^{24}Cr	↑	↑	↑	↑	↑	↑
^{25}Mn	↑	↑	↑	↑	↑	↑↓
^{26}Fe	↑↓	↑	↑	↑	↑	↑↓
^{27}Co	↑↓	↑↓	↑	↑	↑	↑↓
^{28}Ni	↑↓	↑↓	↑↓	↑	↑	↑↓
^{29}Cu	↑↓	↑↓	↑↓	↑↓	↑	↑
^{30}Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

4th row transition elements

Magnetic moment of an atom or ion

Rare earths ions

ion	shell	m_l							S	L	J	term
		+3	+2	+1	0	-1	-2	-3				
La^{3+}	$4f^0$								0	0	0	${}^1S_0$
Ce^{3+}	$4f^1$	↓							$\frac{1}{2}$	3	$\frac{5}{2}$	${}^2F_{5/2}$
Pr^{3+}	$4f^2$	↓	↓						1	5	4	${}^3H_4$
Nd^{3+}	$4f^3$	↓	↓	↓					$\frac{3}{2}$	6	$\frac{9}{2}$	${}^4I_{9/2}$
Pm^{3+}	$4f^4$	↓	↓	↓	↓				2	6	4	${}^5I_4$
Sm^{3+}	$4f^5$	↓	↓	↓	↓	↓			$\frac{5}{2}$	5	$\frac{5}{2}$	${}^6I_{5/2}$
Eu^{3+}	$4f^6$	↓	↓	↓	↓	↓	↓		3	3	0	${}^7F_0$
Gd^{3+}	$4f^7$	↓	↓	↓	↓	↓	↓	↓	$\frac{7}{2}$	0	$\frac{7}{2}$	${}^8S_{7/2}$
Tb^{3+}	$4f^8$	↓↑	↑	↑	↑	↑	↑	↑	3	3	6	${}^7F_6$
Dy^{3+}	$4f^9$	↓↑	↓↑	↑	↑	↑	↑	↑	$\frac{5}{2}$	5	$\frac{15}{2}$	${}^6H_{15/2}$
Ho^{3+}	$4f^{10}$	↓↑	↓↑	↓↑	↑	↑	↑	↑	2	6	8	${}^5I_8$
Er^{3+}	$4f^{11}$	↓↑	↓↑	↓↑	↓↑	↑	↑	↑	$\frac{3}{2}$	6	$\frac{15}{2}$	${}^4I_{15/2}$
Tm^{3+}	$4f^{12}$	↓↑	↓↑	↓↑	↓↑	↓↑	↑	↑	1	5	6	${}^3H_6$
Yb^{3+}	$4f^{13}$	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↑	$\frac{1}{2}$	3	$\frac{7}{2}$	${}^2F_{7/2}$
Lu^{3+}	$4f^{14}$	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	0	0	0	${}^1S_0$

		J	Exp.		$g_J\sqrt{J(J+1)}$	g_J	$g_J J$
Ce^{3+}	4f × 1	5/2	2.4		2.54	6/7	$\simeq 2.0\,\mu_B$
Pr^{3+}	4f × 2	4	3.5		3.58	4/5	$\simeq 3.0\,\mu_B$
Nd^{3+}	4f × 3	9/2	3.5		3.62	8/11	$\simeq 3.0\,\mu_B$
Pm^{3+}	4f × 4	4	-	≠	2.68		$\simeq 0\,\mu_B$
Sm^{3+}	4f × 5	5/2 → 1	1.5	≠	0.845	~ 1	$\simeq 1.0\,\mu_B$
Eu^{3+}	4f × 6	0 → 3	3.4	≠	0	~ 1	$\simeq 3.0\,\mu_B$
Gd^{3+}	4f × 7	7/2	8.0		7.94	2	$= 7.0\,\mu_B$
Tb^{3+}	4f × 8	6	9.5		9.72	3/2	$= 9.0\,\mu_B$
Dy^{3+}	4f × 9	15/2	10.6		10.63	4/3	$= 10.0\,\mu_B$
Ho^{3+}	4f × 10	8	10.4		10.60	5/4	$= 10.0\,\mu_B$
Er^{3+}	4f × 11	15/2	9.5		9.59	6/5	$= 9.0\,\mu_B$
Tm^{3+}	4f × 12	6	7.3		7.55	7/6	$= 7.0\,\mu_B$
Yb^{3+}	4f × 13	7/2	4.5		4.54	8/7	$= 4.0\,\mu_B$

Transition metal ions

		J	Exp.		$g_J\sqrt{J(J+1)}$		$2\sqrt{S(S+1)}$
Ti^{3+}	3d × 1	3/2	1.80	≠	1.55		1.73
V^{3+}	3d × 2	2	2.80	≠	1.63		2.83
Cr^{3+}	3d × 3	3/2	3.84	≠	0.77		3.87
Cr^{2+} Mn^{3+}	3d × 4	0	4.82	≠	0	→	4.90
Mn^{2+} Fe^{3+}	3d × 5	5/2	5.88		5.92	**L = 0**	5.92
Fe^{2+} Co^{3+}	3d × 6	4	5.53	≠	6.70		4.90
Co^{2+}	3d × 7	9/2	4.96	≠	6.54		3.87
Ni^{2+}	3d × 8	4	2.82	≠	5.59		2.83
Cu^{2+}	3d × 9	5/2	1.95	≠	3.55		1.73

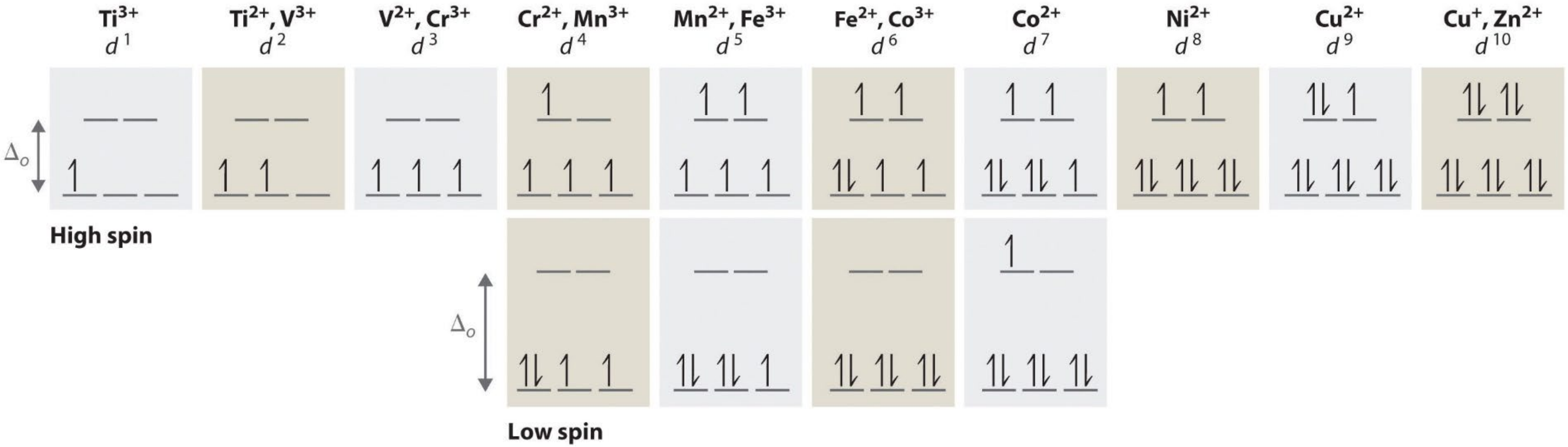
??

The magnetic moment of an ion or atom predicted by the **hydrogen-like atom model plus simple rules** is often not very accurate
(especially for transition metal ions)

http://www7b.biglobe.ne.jp/~kcy05t/rare.html

From atoms to solids

If the ions are not isolated, the 3d levels are often no more isoenergetic due to the interaction with the **ligand** atoms. If the energy required to pair up an electron in the lower energy state is smaller than the splitting than the low spin configuration is favored (and the ion has a smaller magnetic moment with respect to the isolated condition).



From atoms to solids

$$H_{total} = H_{Zeeman} + H_{Exchange} + H_{Anisotropy} + H_{Dipolar}$$

$$H_{total} = \mu_0 \mathbf{H} \sum_i \mathbf{m}_i - \sum_{i<j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j - \sum_i k_i (\mathbf{m}_i \cdot \mathbf{e}_i)^2 - \frac{\mu_0}{8\pi} \sum_{i,j\neq i} \left[\frac{3(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} - \frac{(\mathbf{m}_i \cdot \mathbf{m}_j)}{r_{ij}^3} \right]$$

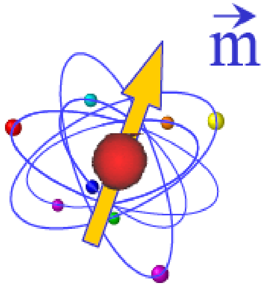
$\mathbf{H}$: applied magnetic field

$\mathbf{m}_i$: magnetic moment of atom i

From atoms to solids

Intra-atomic exchange, electron correlation effects:

LOCAL (ATOMIC) MAGNETIC MOMENTS



d or *f* electrons

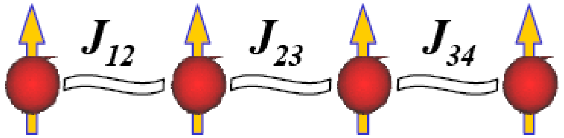
↑↓ ↑↓ ↑ ↑ ↑

Hund's rules

Inter-atomic exchange:

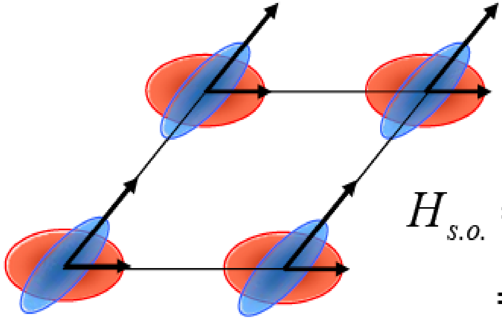
MAGNETIC ORDER

$$H_{exc} = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$



Spin-Orbit Coupling:

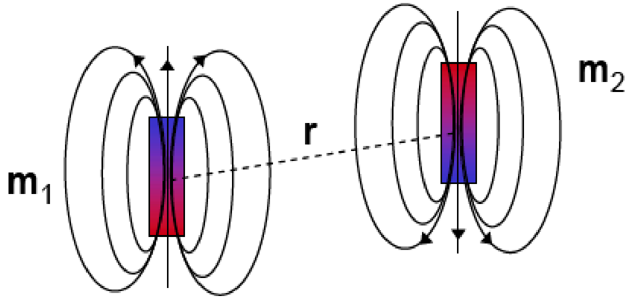
MAGNETOCRYSTALLINE ANISOTROPY: K



$$H_{s.o.} = \lambda \mathrm{L} \cdot \mathbf{S}$$
$$= \sum \xi \mathbf{s}_i \cdot \mathbf{l}_i$$

Dipolar Interaction:

SHAPE ANISOTROPY



$$H_{dip} = \frac{\mathbf{m}_1 \cdot \mathbf{m}_2}{r^3} - 3\frac{(\mathbf{m}_1 \cdot \mathbf{r})(\mathbf{m}_2 \cdot \mathbf{r})}{r^5}$$

Types of magnetism

Diamagnetism: Atoms or ions with **zero** magnetic moment:

Ex: water, diamond, graphite, copper, silver, bismuth, most organic compounds, solid noble gases (He, Ne, Ar, Kr, Xe), ionic crystals (NaCl, LiF, ……), …

Paramagnetism: Atoms or ions with **non-zero** magnetic moment but weak interactions between them:

Ex: Solids with transition metal ions: $CuSO_4$*$5H_20$, $FeCl_3$* $6H_20$,….

Pauli paramagnetism: Paramagnetism due to the spin of the conduction electrons.

Ex: Solid metals: Al, W, Li, Na, K, ….

Ferromagnetism, Antiferromagnetism, …: Atoms or ions with **non-zero** magnetic moment with strong magnetic interactions between them.

Ex: Solid metals: Fe, Co, Ni, …..
Insulators: $Y_3Fe_5O_{12}$, Fe_3O_4, Fe_2O_3…

Types of magnetism

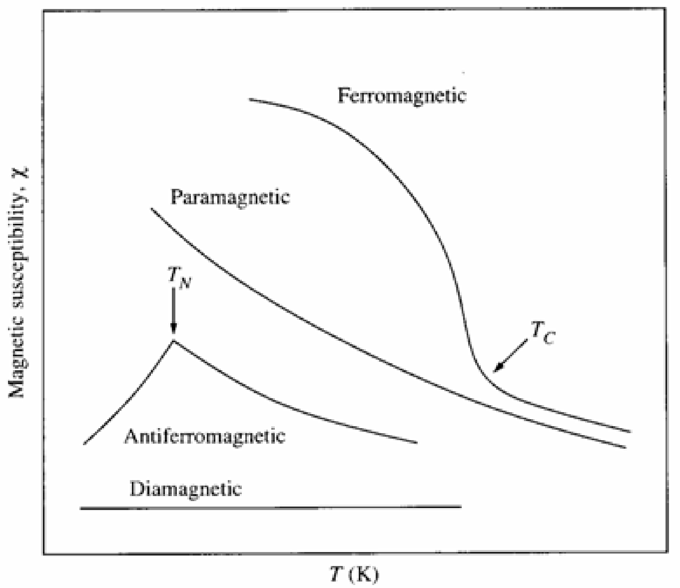


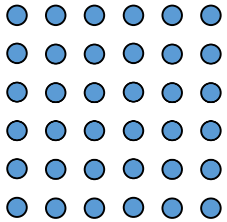
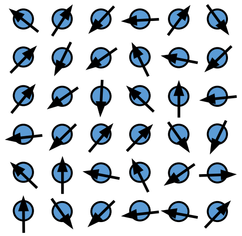
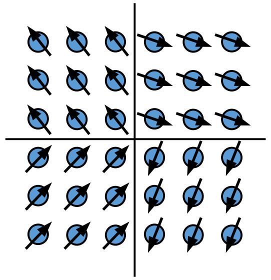
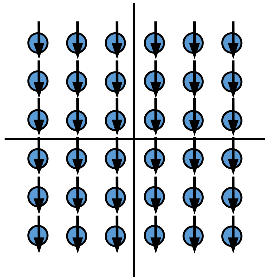
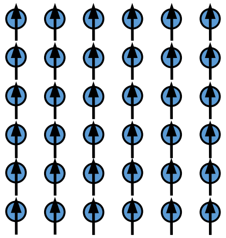
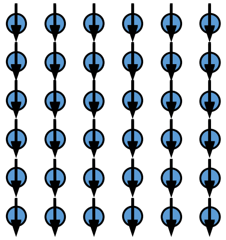
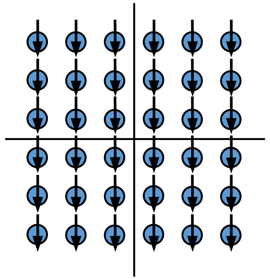
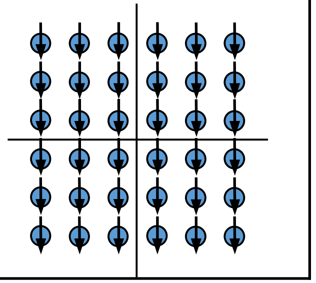
Fig. 11.59 Variation of magnetic susceptibility with temperature for diamagnetic, paramagnetic, ferromagnetic, and antiferromagnetic substances. Transitions to paramagnetic behavior for ferromagnetic and antiferromagnetic substances occur at the Curie (T_C) and Neel (T_N) temperatures, respectively.

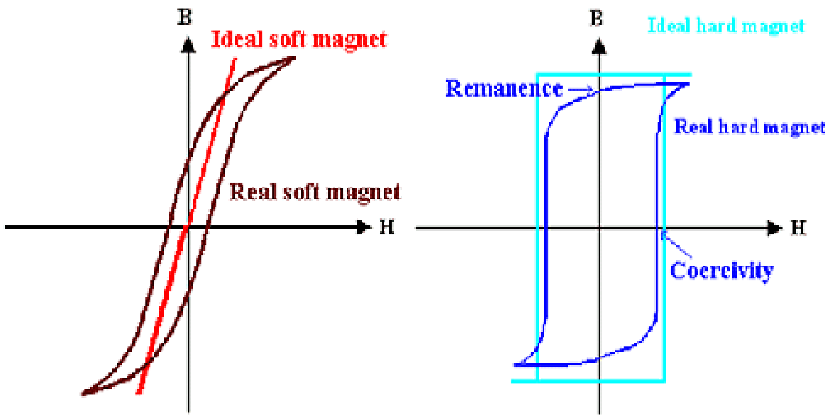
Several materials have different behavior depending on temperature. (e.g., ferromagnetic below the Curie temperature, paramagnetic above the Curie temperature)

$$\boxed{\mathbf{M} = \chi \mathbf{H}}$$

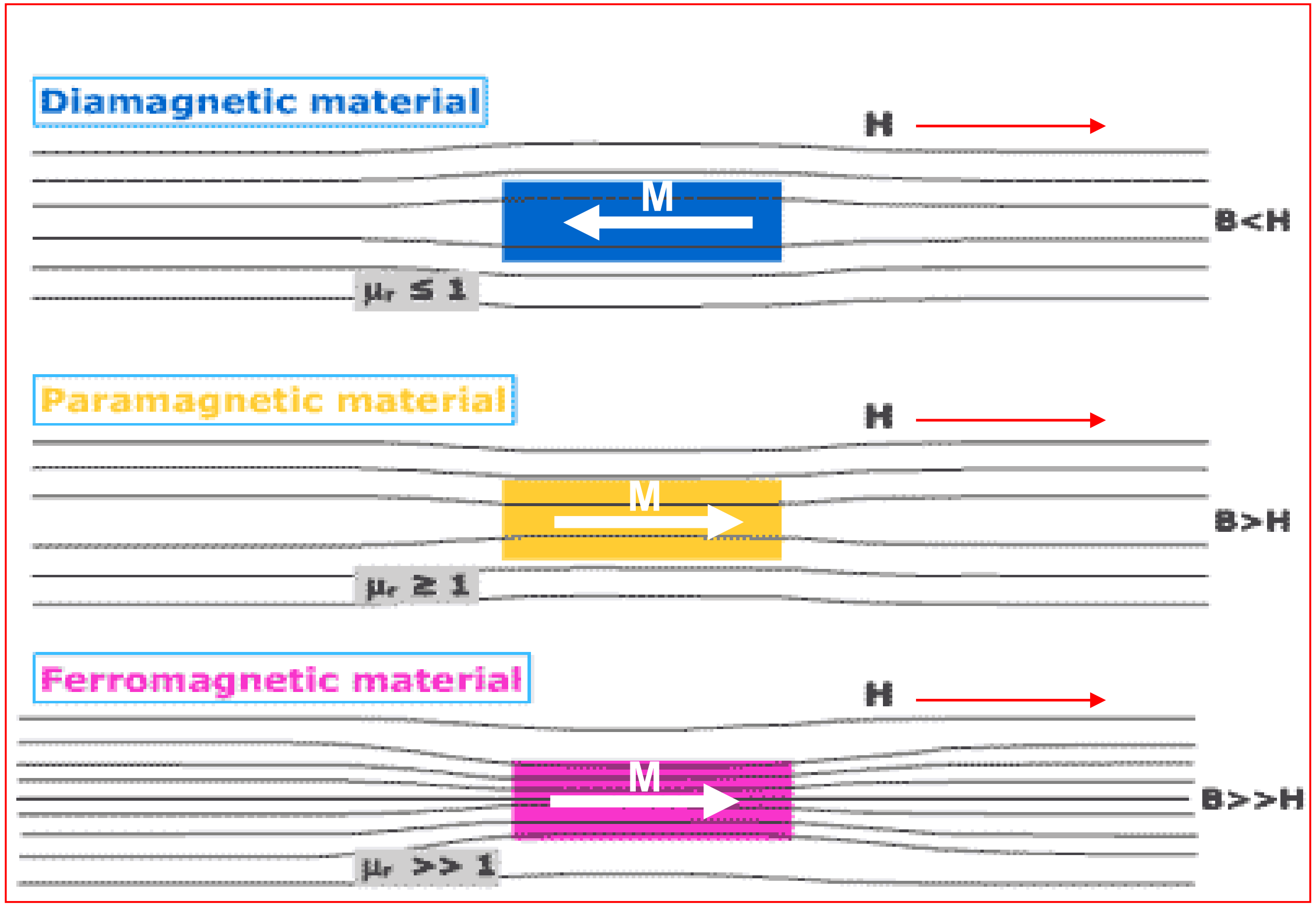
Type	Typical values	Physical Origin
Diamagnetism	$\chi \approx -10^{-6}$	Non-interacting «induced» atomic magnetic dipoles
Paramagnetism	$\chi \approx +(10^{-5} \div 10^{-3})$	Orientation of non-interacting «permanent» atomic magnetic dipoles
Super-paramagnetism	$\chi \approx +10^{-2}$	Orientation of non-interacting «permanent» large (many atoms) magnetic dipoles
Ferromagnetism	$\chi = +\left(0 \div 10^{6}\right)$	Orientation + coupling + anisotropy of «permanent» atomic magnetic dipoles

Types of magnetism

	DIAMAGNETIC	PARAMAGNETIC	FERROMAGNETIC SOFT (IDEAL)	FERROMAGNETIC HARD (IDEAL)
$B = 0$				
$\mathbf{B} \quad \downarrow$ $mB >> kT$				



Types of magnetism



$\mathbf{B} < \mu_0 \mathbf{H}$ (inside the material)

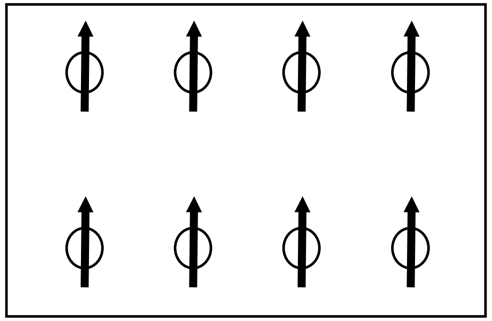
$\mathbf{B} > \mu_0 \mathbf{H}$ (inside the material)

$\mathbf{B} \gg \mu_0 \mathbf{H}$ (inside the material)

$$\boxed{\mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M} \text{ (everywhere)}}$$

Types of «Ferromagnetism»

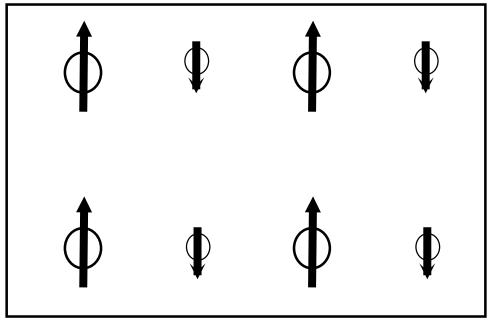
Ferromagnetism



Same atoms with parallel dipole orientation

$$\boxed{\mathbf{M}_{total} \neq 0}$$

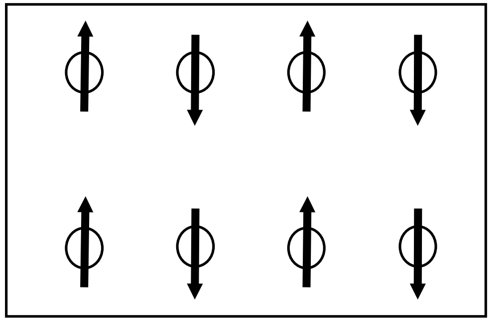
Ferrimagnetism



Two kinds of atoms with antiparallel dipole orientation

$$\boxed{\mathbf{M}_{total} \neq 0}$$

Antiferromagnetism



Two kind of atoms with antiparallel dipole orientation and exactly inverse values.

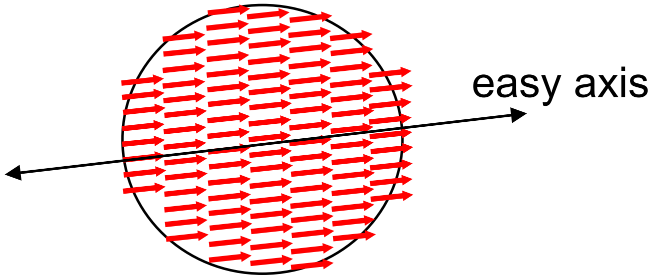
$$\boxed{\mathbf{M}_{total} = 0}$$

Superparamagnetism

Superparamagnetism appears in ferromagnetic or ferrimagnetic single magnetic domain nanoparticles, having a diameter below 3 to 50 nm, depending on the materials.

In a single nanoparticle:

1) The atomic magnetic moment are alligned in the same direction due to the exchange interaction.
2) Usually there are two stable orientations, antiparallel to each other and separated by an energy barrier, along the so called easy axis of the nanoparticle. This energy barrier is called magnetic anisotropy energy.



At finite temperature, there is a finite probability for the magnetization to flip and reverse its direction. The mean time between two flips, called the Néel relaxation time, is:

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right)$$

τ_N : average time that it takes for the nanoparticle's magnetization to randomly flip due to thermal fluctuations.

τ_0 : is a characteristic time of the material, called the *attempt time* (typically: 10^{-9} to 10^{-10} s).

K: nanoparticle's magnetic anisotropy energy density

V : particle volume

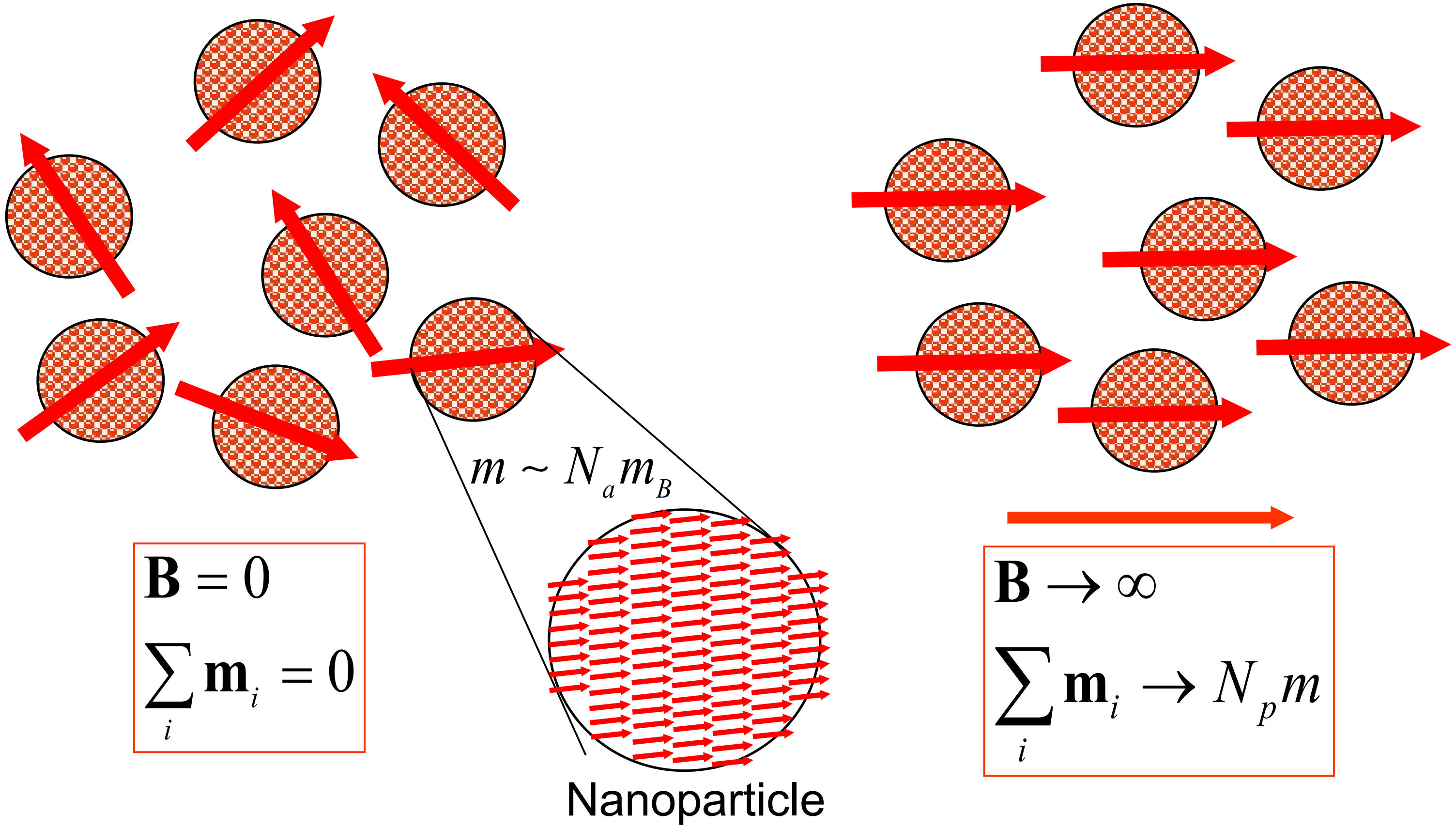
τ_N is the range from **nanoseconds** to **millions of years**, depending on V, T, and K

Superparamagnetism

Behaviour of N_p ferromagnetic nanoparticules each with N_a atoms inside:

Ensemble of nanoparticles in B=0

Ensemble of nanoparticles in large B



$$m \sim N_a m_B$$

$$\mathbf{B} = 0$$

$$\sum_i \mathbf{m}_i = 0$$

$$\mathbf{B} \to \infty$$

$$\sum_i \mathbf{m}_i \to N_p m$$

Inside each nanoparticle the N_a atoms have their magnetic moments all alligned in the same direction due to the exchange interaction. Each nanoparticle has a magnetic moment **m** of about $N_a\mu_B$

Superparamagnetism

An external magnetic field tends to “orient” the magnetic moment of the nanoparticle in the direction of the magnetic field.

In an **ensemble of paramagnetic atoms**: each atom is interacting with the external magnetic field but the interaction with the other atoms is negligible. The effective magnetic moment is the one of a single atom (about 1 μ_B).

In an **ensemble of superparamagnetic nanoparticles:** inside each nanoparticle the atoms are strongly coupled by the exchange interaction and, hence, interact globally with the external magnetic field. The effective magnetic moment is about $N_a\mu_B$, where N_a is the number of atoms in the nanoparticle.

The "volume averaged" magnetization of an **ensemble of superparamagnetic nanoparticles** is

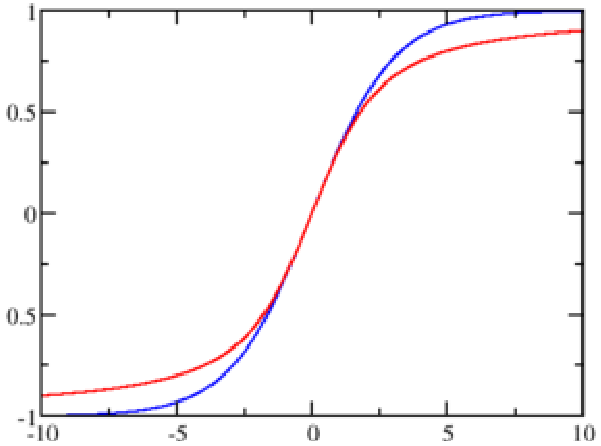
$$M = \frac{N_p}{V} m L\left(\frac{mB}{kT}\right) = \frac{N_p}{V} m \left(\frac{1}{\tanh\left(\frac{mB}{kT}\right)} - \frac{kT}{mB} \right)$$

m: is the magnetic moment of a single nanoparticle ($m \cong N_a \mu_B$)

N_p: Number of nanoparticles in the ensemble

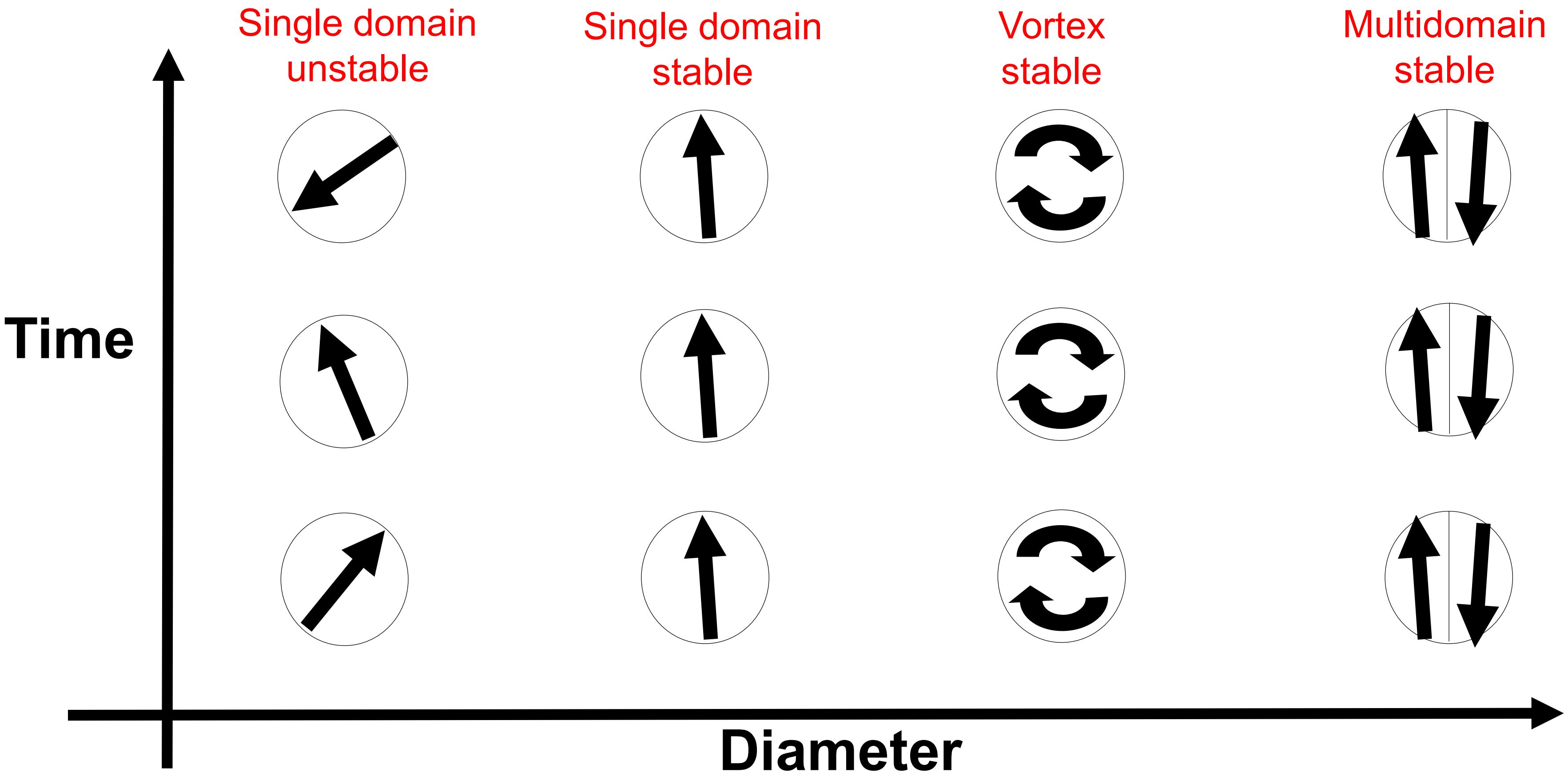
V: Volume of the ensemble

$L(x) = \frac{1}{\tanh(x)} - \frac{1}{x}$: Langevin function



Langevin function (red line), compared with tanh(x/3)(blue line).

Nano and microdots magnetism



Single domain unstable

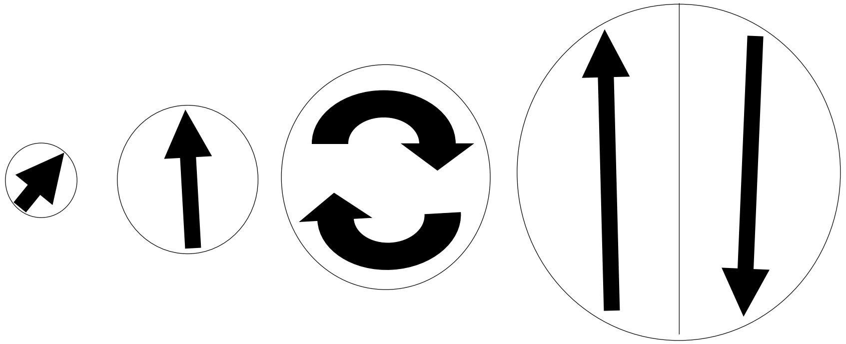
Single domain stable

Vortex stable

Multidomain stable

Time

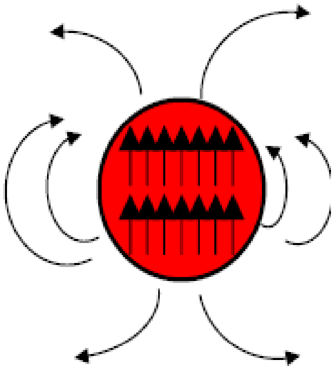
Diameter



Nano and microdots magnetism

exchange energy J coupling spins

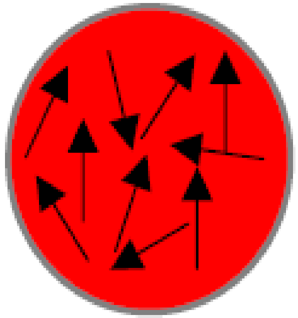
$$H_{exc} = -\sum J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$$



Temperature increase

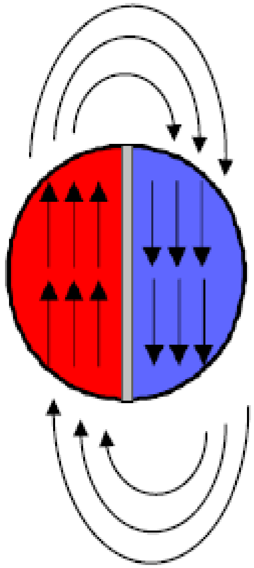
Size increase

$H_{exc} << kT$



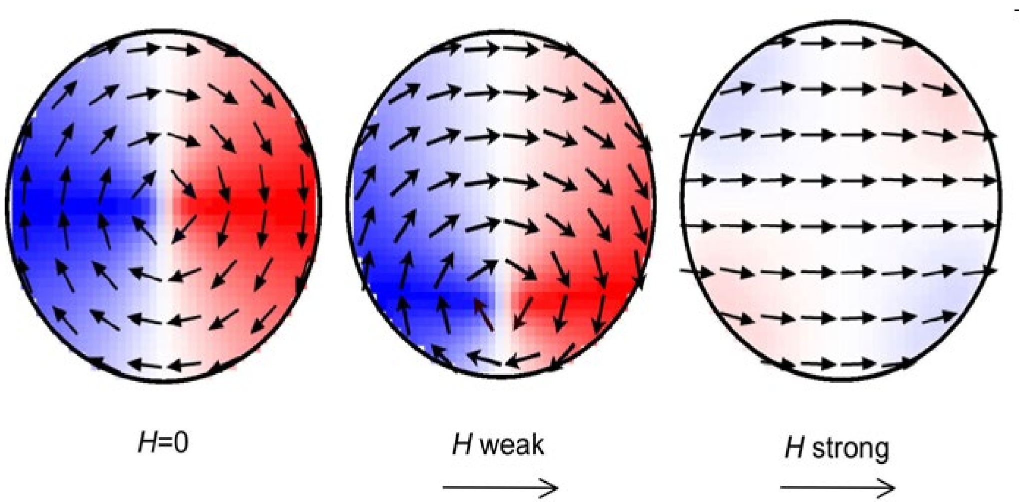
Coupling is destroyed and the net magnetic moment is zero

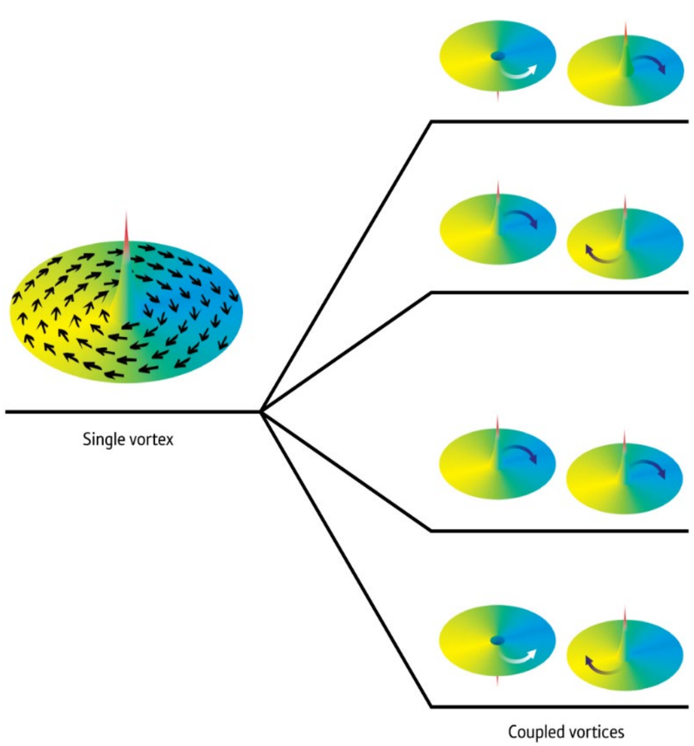
Domain formation -> magnetic moment is strongly reduced

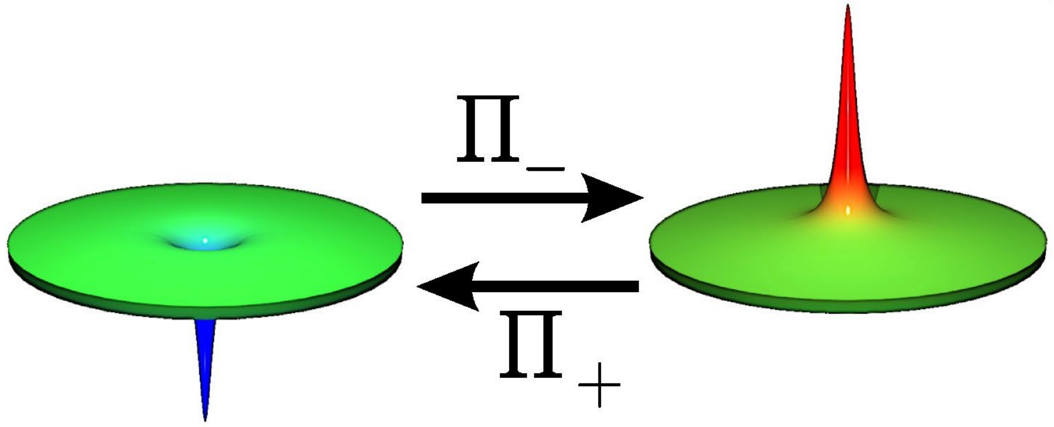


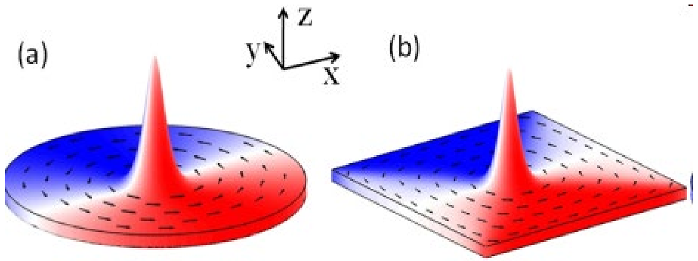
Gain in the magnetostatic energy at the expenses of the exchange energy

Magnetic domains in nanodots

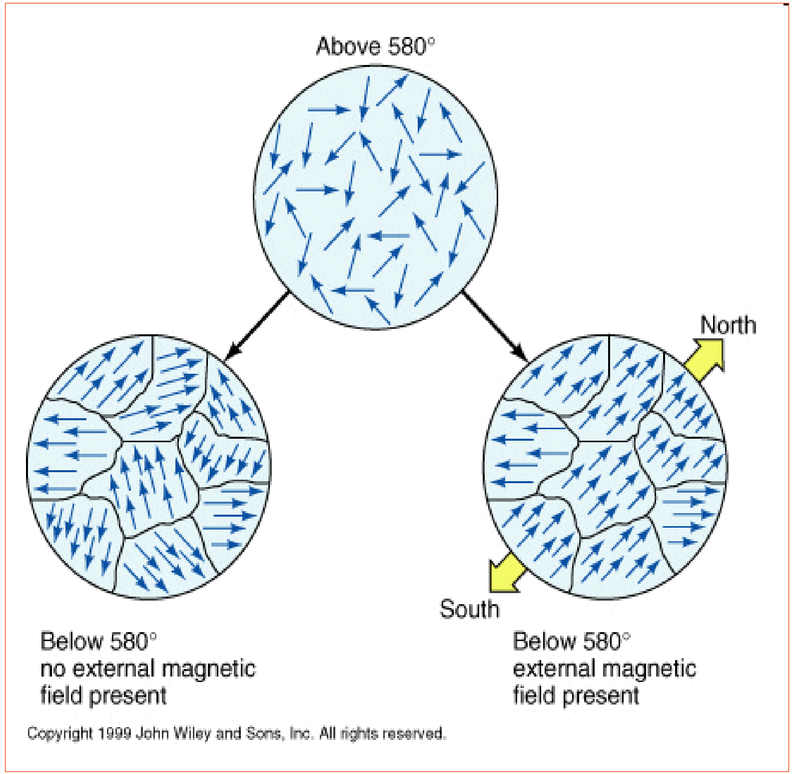








Magnetic domains in large particles



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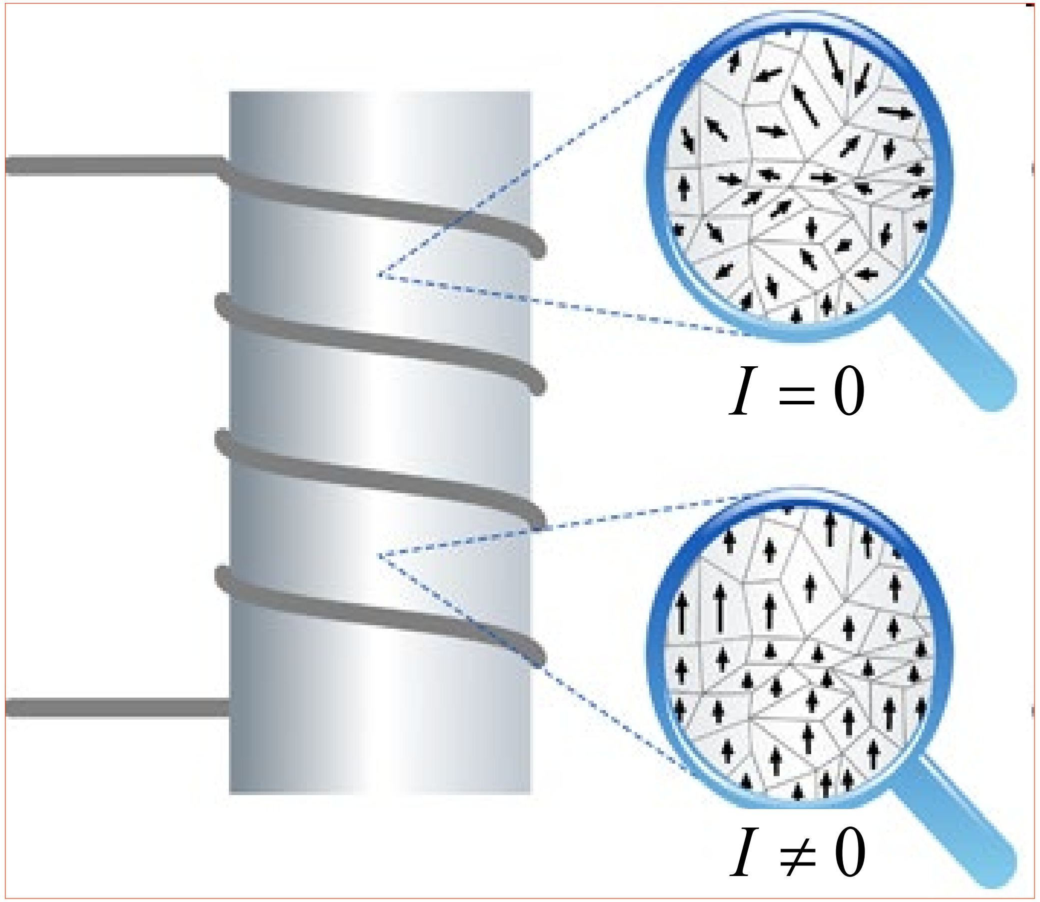
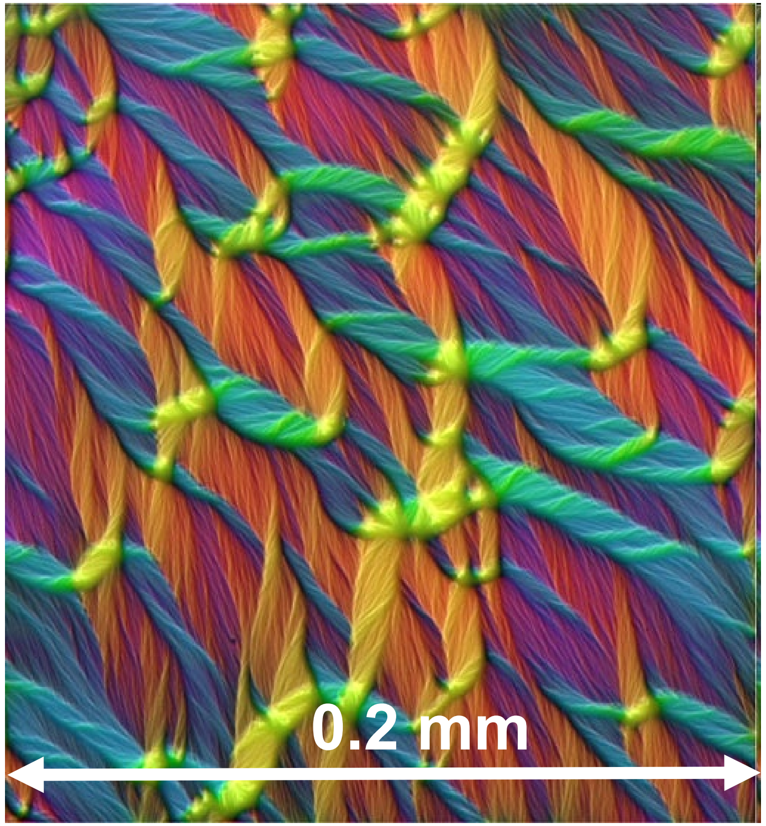
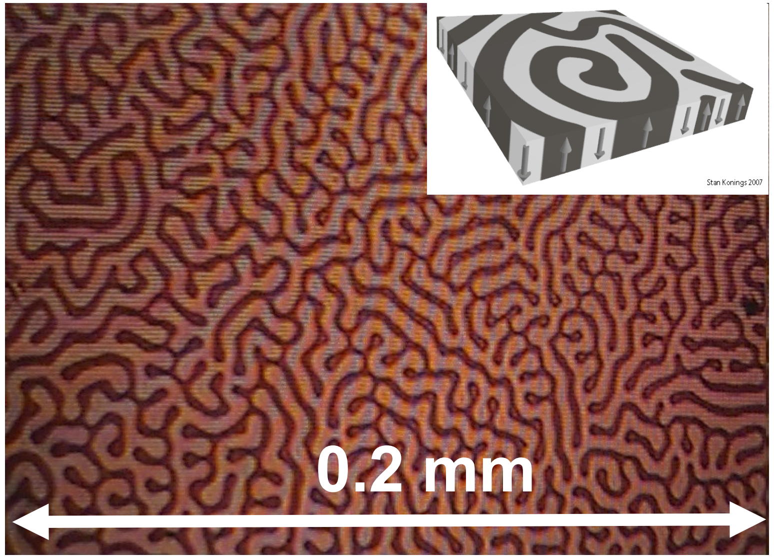


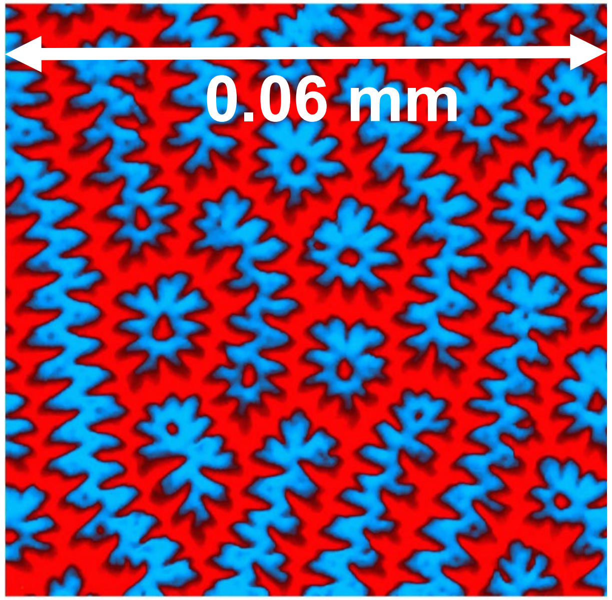
Magnetic domains in thin films



Co thin film (20 nm)
(color scale=magnetization direction)

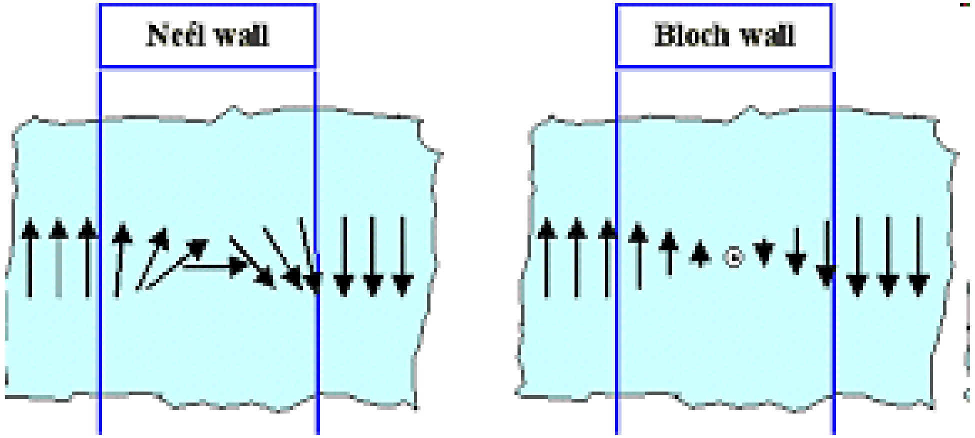


$Bi_{0.6}Tm_{2.4}Ga_{1.15}Fe_{3.85}O_{12}$ (8 μm)

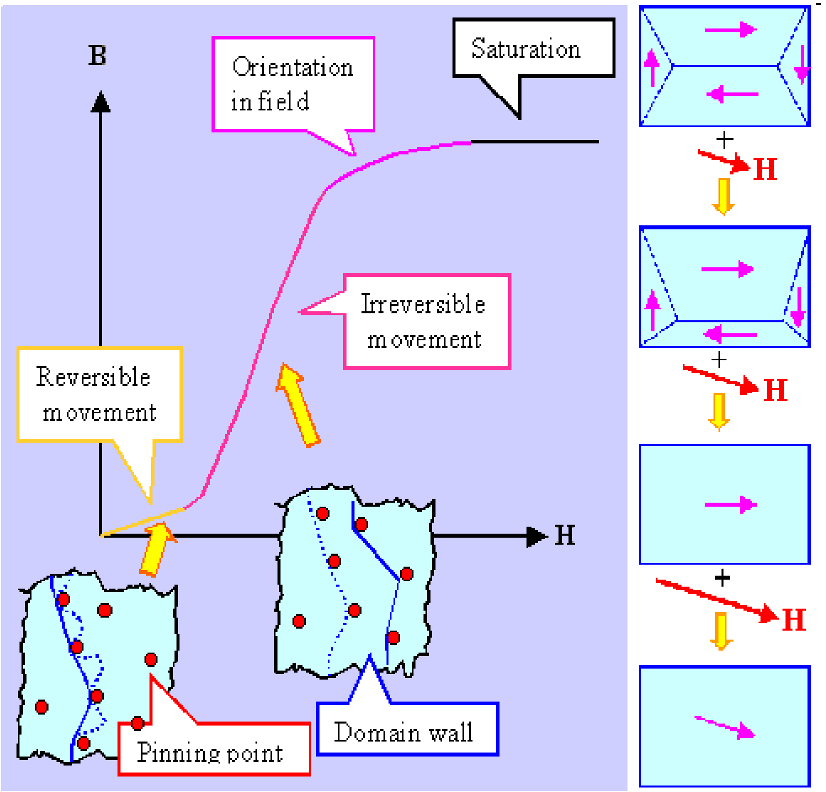


$Y_3Fe_5O_{12}$ (8 μm)

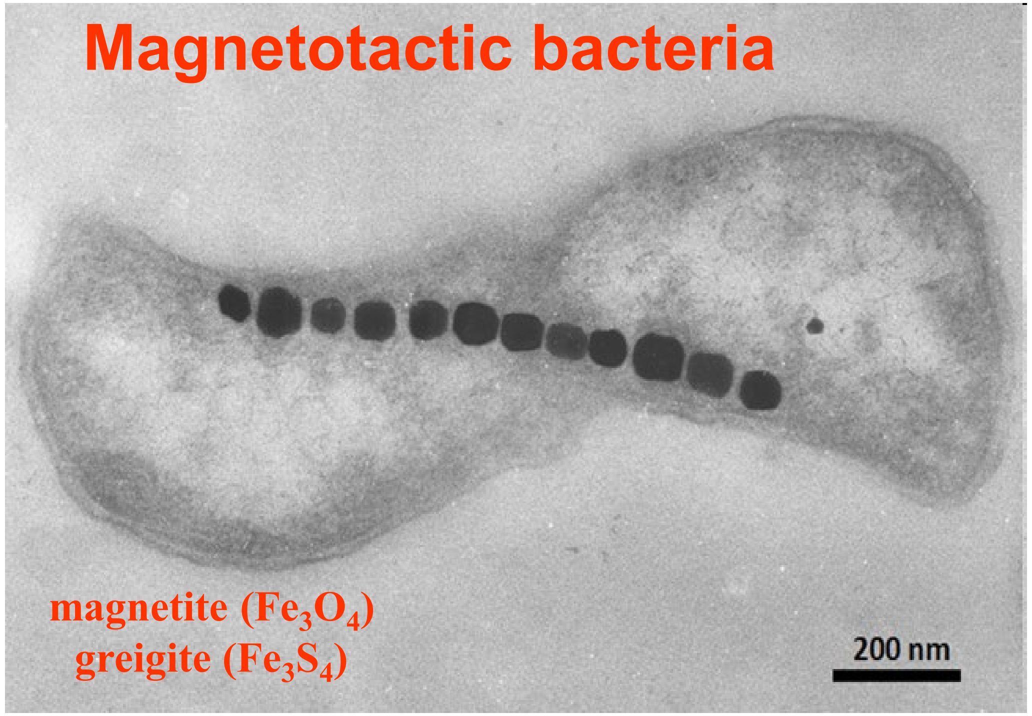
Magnetic domains, domains wall, typical lenghts



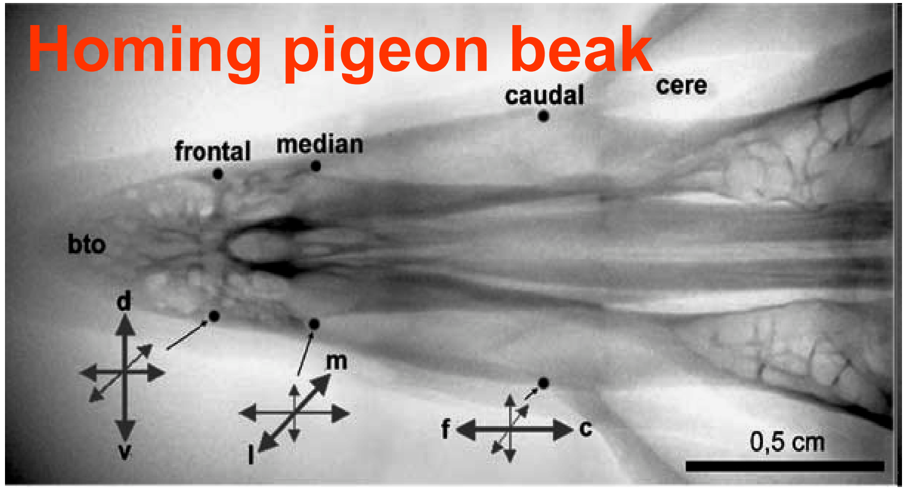
Length	**Typ. Value (nm)**
Interatomic distance	0.2
Domain size	~ 10- 10^4
Domain wall width	~ 1- ~ 10^2
Critical superparamagnetic diameter	~ 1- ~ 10^2

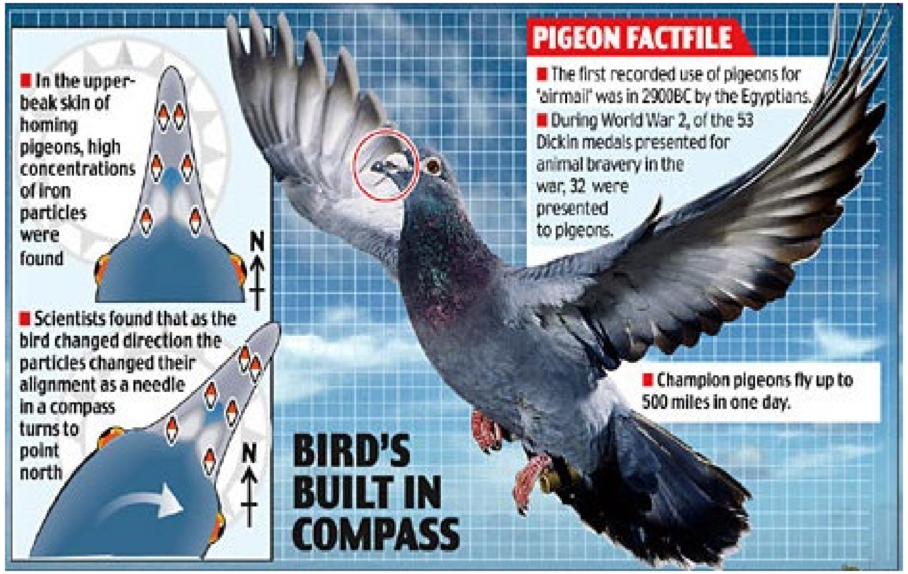


Nanomagnetism: in animals


Magnetotactic bacteria

magnetite (Fe_3O_4)
greigite (Fe_3S_4)


Homing pigeon beak

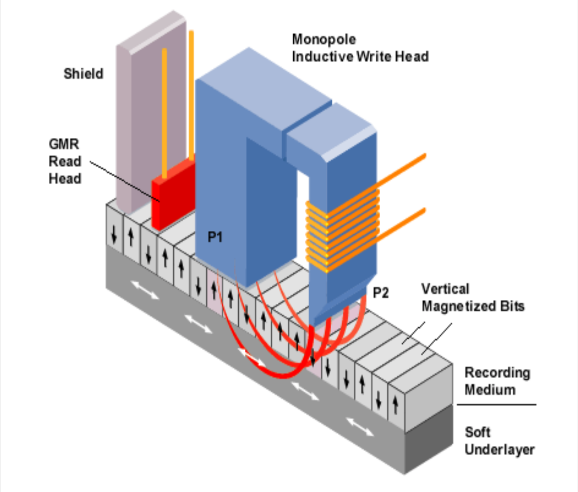

PIGEON FACTFILE

- The first recorded use of pigeons for 'airmail' was in 2900BC by the Egyptians.
- During World War 2, of the 53 Dickin medals presented for animal bravery in the war, 32 were presented to pigeons.
- Champion pigeons fly up to 500 miles in one day.

- In the upper-beak skin of homing pigeons, high concentrations of iron particles were found
- Scientists found that as the bird changed direction the particles changed their alignment as a needle in a compass turns to point north

BIRD'S BUILT IN COMPASS

Applications of Nanomagnetism: Magnetic data storage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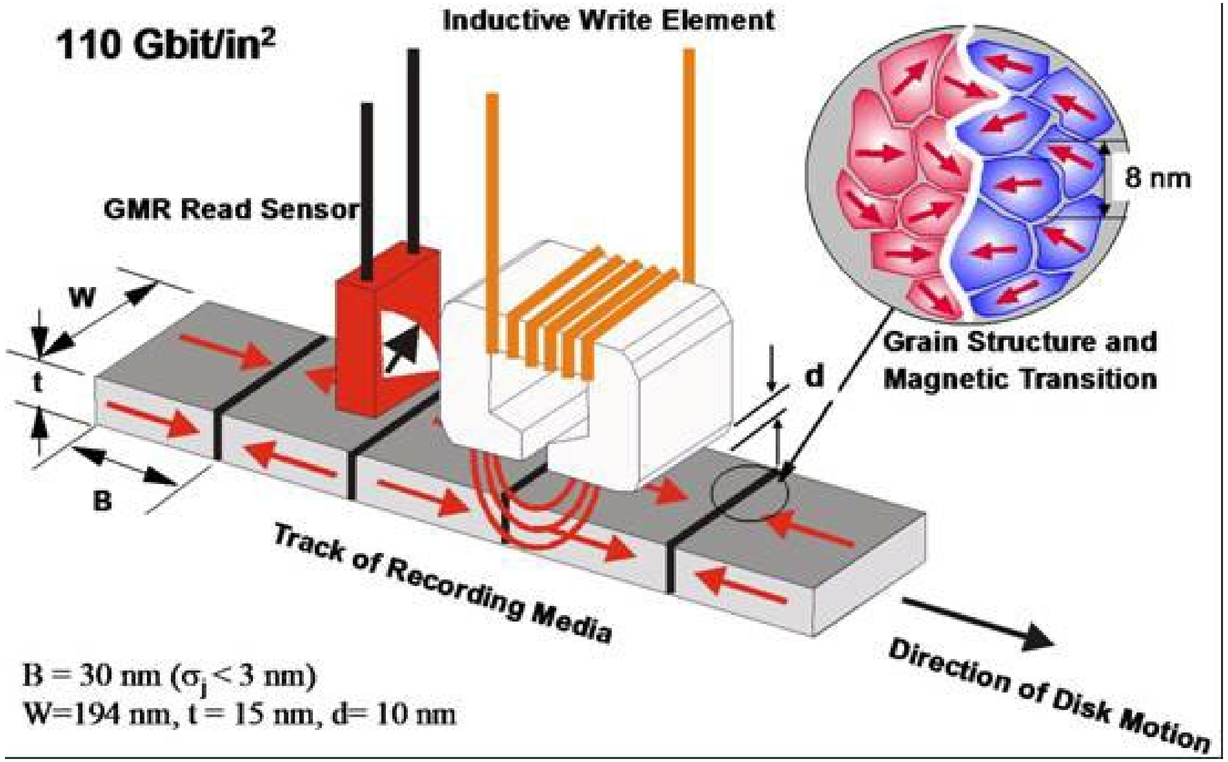
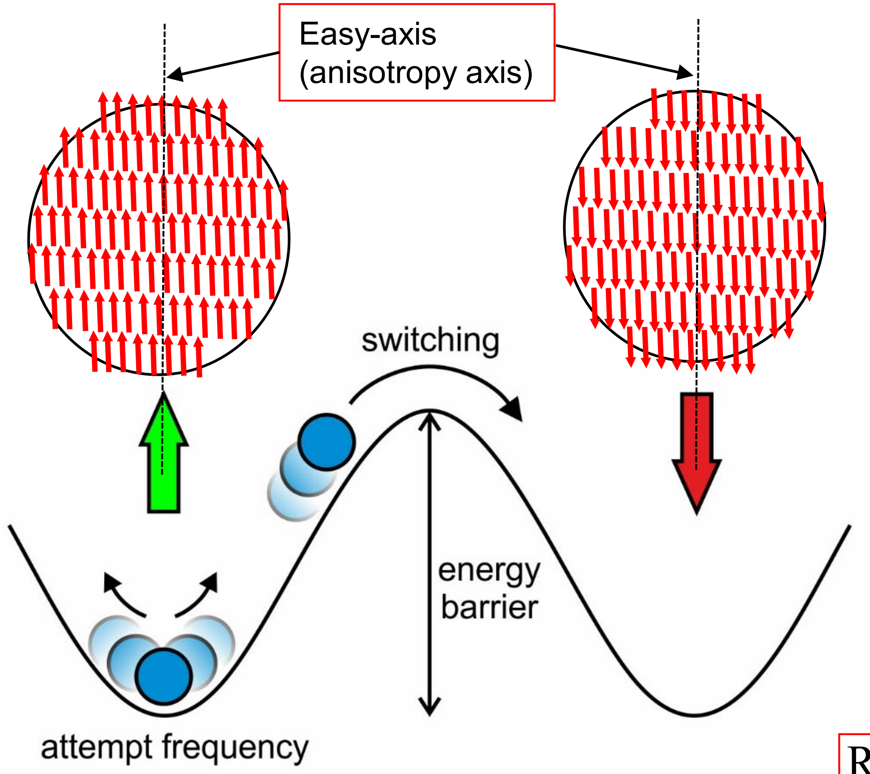


Present: several particles (grains) per bit
Future: single particle per bit ?

Anisotropy Energy



$KV << kT \Rightarrow$

Magnetization flips direction often ($\tau_N \cong \tau_0$) $\Rightarrow$

Information cannot be stored

$KV >> kT \Rightarrow$

Magnetization flips direction rarely ($\tau_N \rightarrow \infty$) $\Rightarrow$

Information can be stored

Relaxation time (average time to jump from one minumum to the other):

$$\tau_N = \tau_0 \exp(\frac{KV}{kT})$$

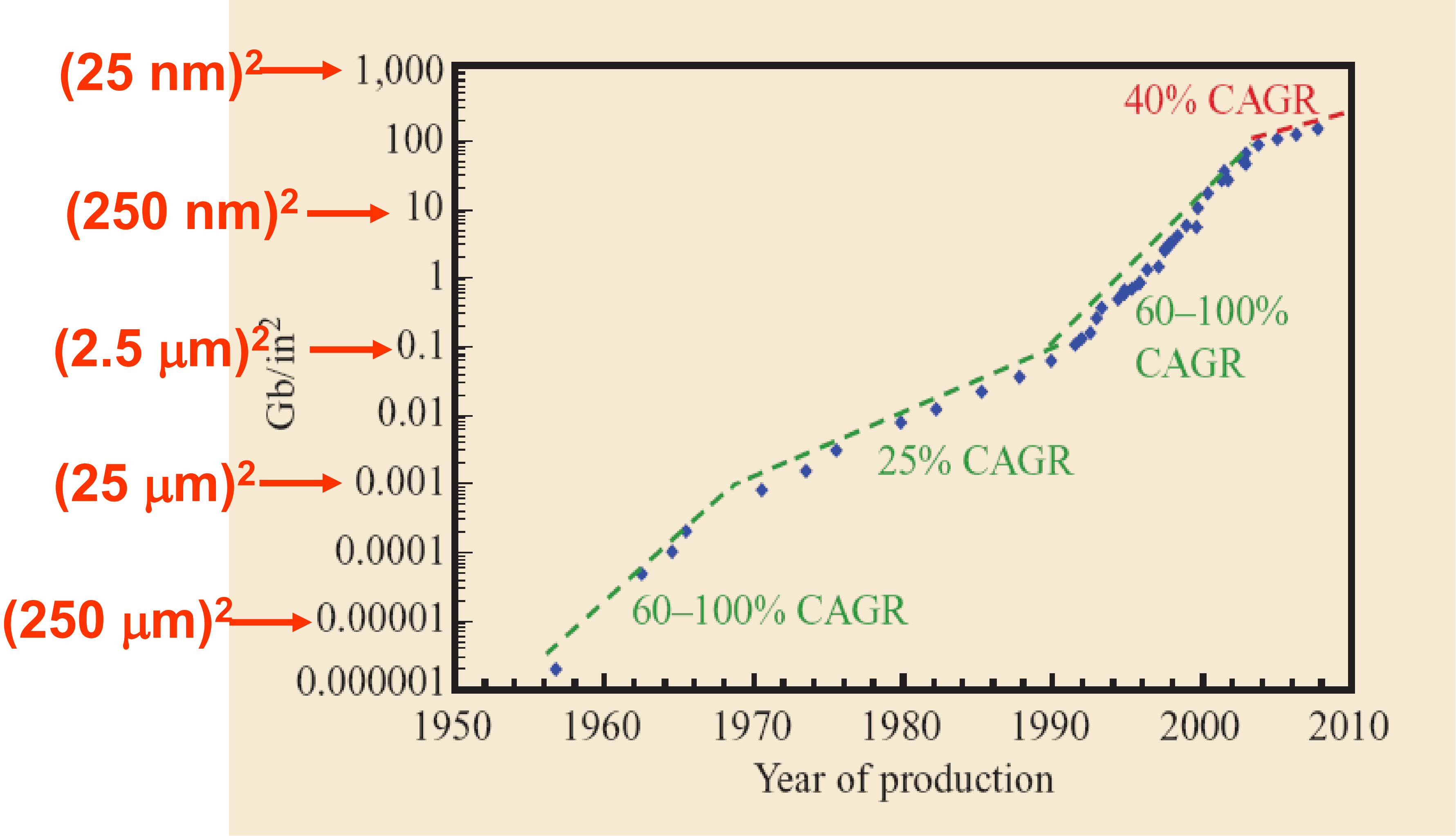
Assuming $\tau_0 \cong 0.1$ ns we have that:

$KV = 43\ kT \Rightarrow\ \tau \cong 15$ years

$KV = 40\ kT \Rightarrow\ \tau \cong 9$ months

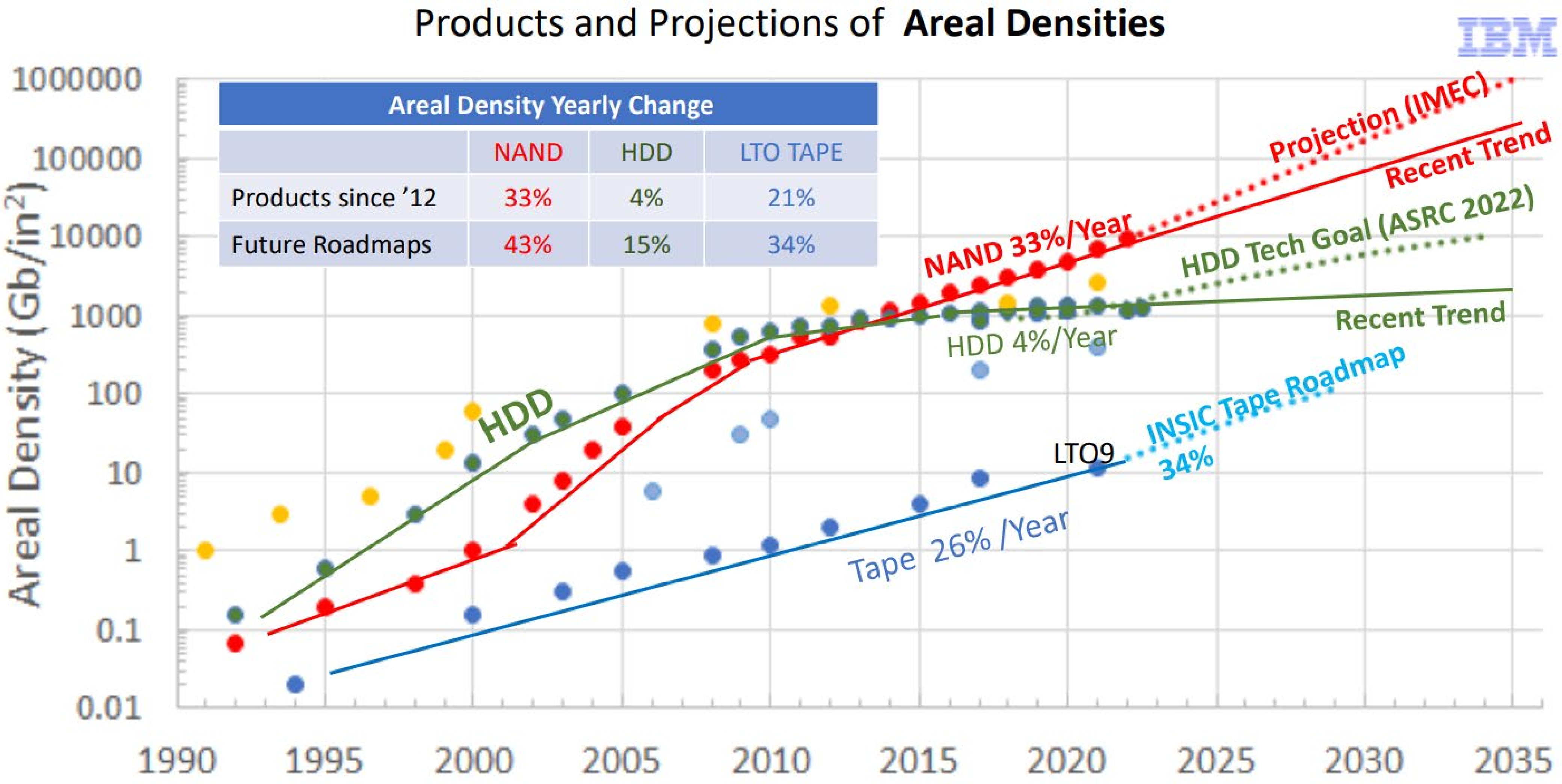
$KV = 23\ kT \Rightarrow\ \tau \cong 1$ s

Nanomagnetism: Magnetic data storage



2012: 1 Tbit/inch^2, i.e., 1 bit on (25 nm)^2
2024: 1.5 Tbit/inch^2

Data storage: overview



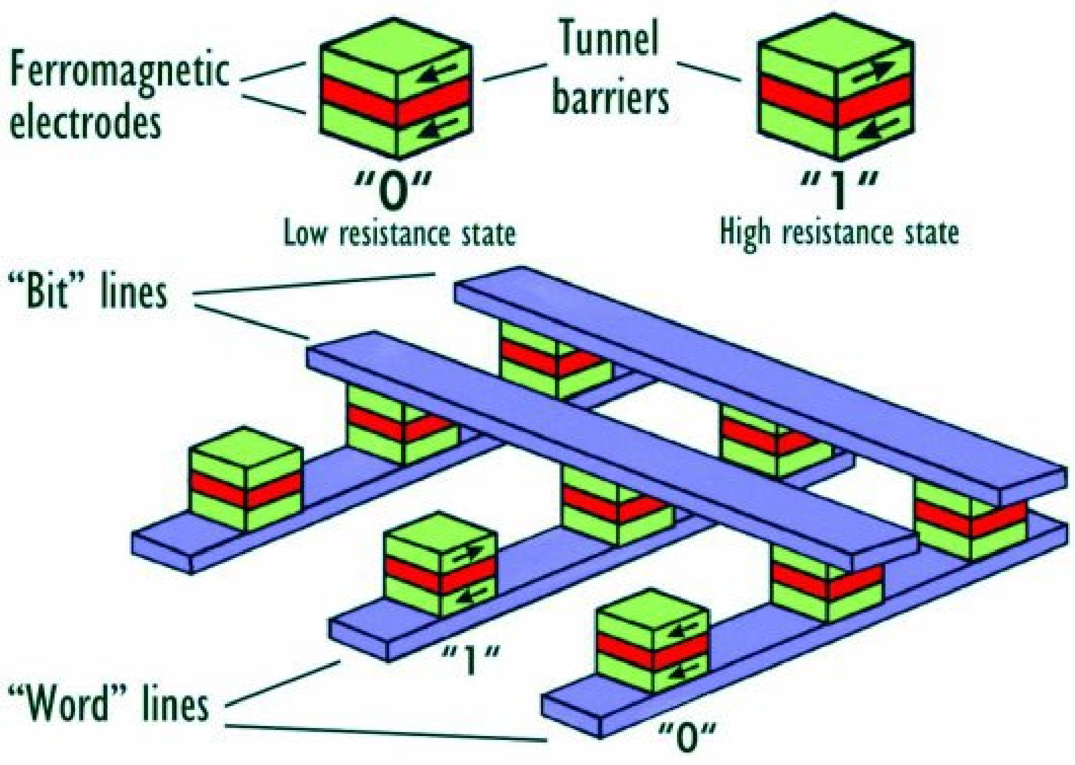
Products and Projections of **Areal Densities**

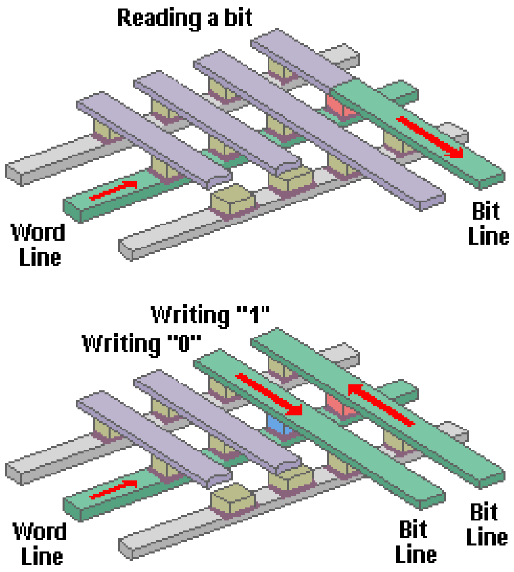
Areal Density Yearly Change			
	NAND	HDD	LTO TAPE
Products since ’12	33%	4%	21%
Future Roadmaps	43%	15%	34%

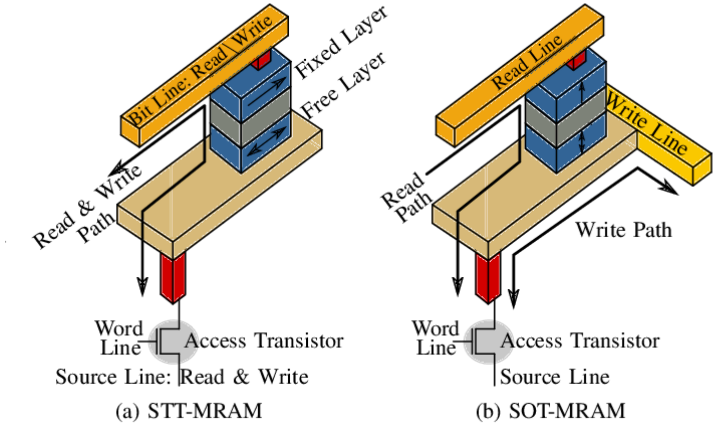
HDD (Hard disk drive): magnetic storage device with spinning disks coated with a magnetic materials.
NAND (Flash memory): trapped electrons inside an insulated gate within a MOSFET transistor. Used in SSD, USB flash drives,….
LTO (Linear tape-open): magnetic tape storage technology. Used for data backup and archiving.

Nanomagnetism: Magnetic data storage

MRAM (magnetoresistive RAM):
A new approach to magnetic data storage



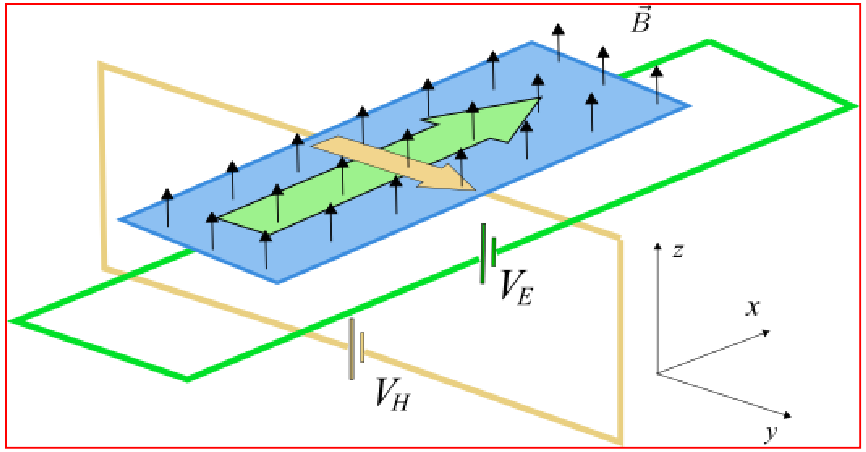




(a) STT-MRAM

(b) SOT-MRAM

Quantum Hall effect in a 2D electron gas



$$\rho_{xy} = \frac{V_H}{I}\frac{1}{N_y} \qquad \rho_{xx} = \frac{V_E}{I}\frac{1}{N_x}$$

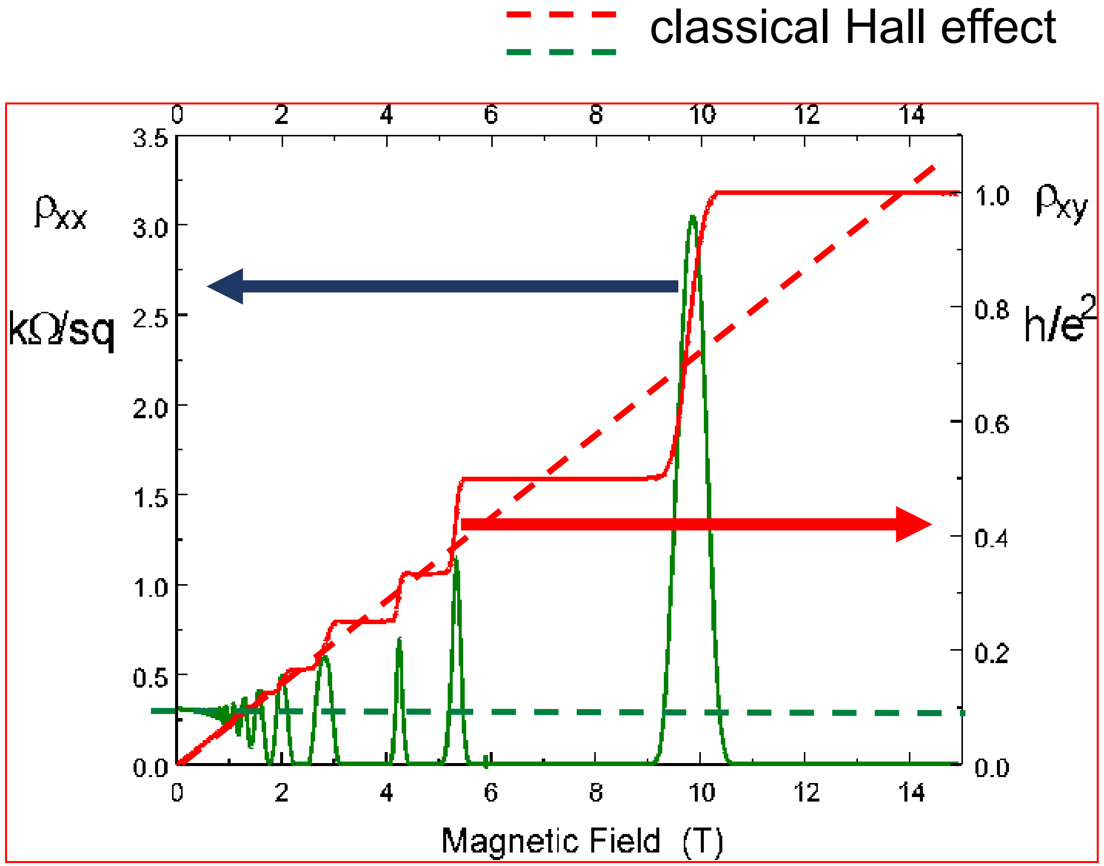
N_i : No. of squares in i-direction

$$\rho_{xy} = \frac{1}{\nu}\frac{h}{e^2}$$

$$\frac{h}{e^2} = 25812.807557(18)\,\Omega$$

(Resistance standard !!)

ν=1,2,3,4,5,....1/3, 2/5, 3/7, ...



http://www.warwick.ac.uk/~phsbm/iqhe.gif

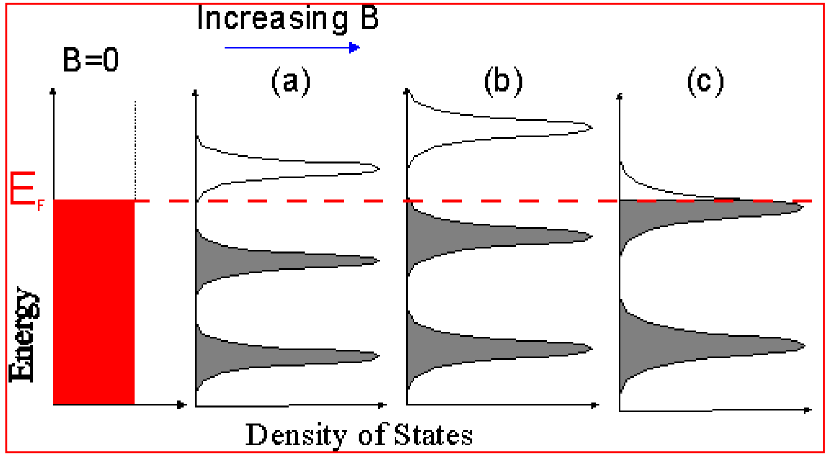
Quantum Hall effect in a 2D electron gas

In **two dimensions**, electrons in a magnetic field follow circular cyclotron orbits.

These orbits are quantized. The energy levels (called Landau levels) of these orbits are:

$$E_n = \hbar\omega_c\left(n+1/2\right) = \hbar\frac{eB}{m}\left(n+1/2\right)$$

$\omega_c = \dfrac{eB}{m}$ is the "classical" cyclotron frequency.



For strong magnetic fields, many single particle states have the same energy E_n.

For a sample of area A, in magnetic field B, the degeneracy of each Landau level is:

$N = 2BA/\Phi_0$ Φ_0: is the quantum of flux.

For sufficiently strong B, each Landau level may have so many statesthat all of the free electrons in the system, at low T, sit in only a few Landau levels it is in this regime where one observes the quantum Hall effect.

Note: As for the Coulomb blockade in a 0D object, also for the quantum Hall effect in 2D object the energy levels discretization due to the "nanoscale size" is not the dominant phenomenon.

Casimir effect and force

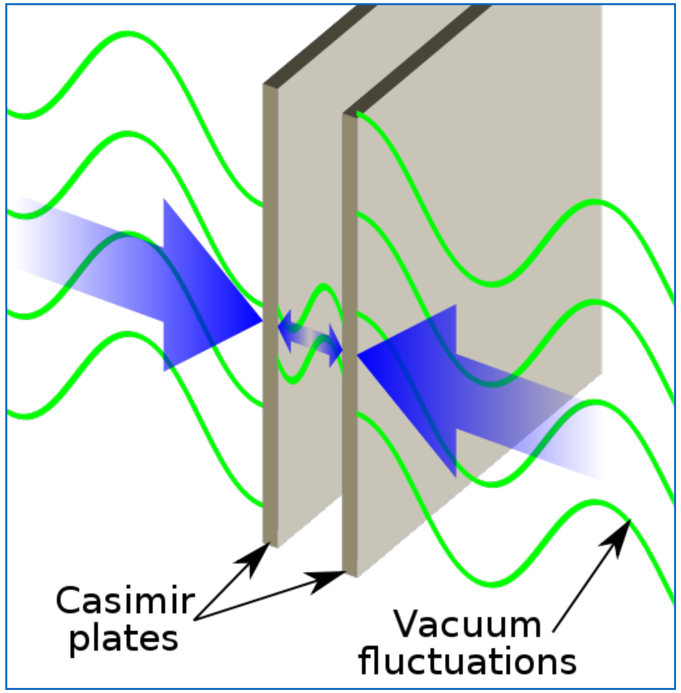
The Casimir effect and force are considered, by most of the people, a purely quantum phenomena related to zero-point quantum fluctuations of the electromagnetic field.
(some people consider the Casimir force as a result of quantum relativistic retarded van der Waals (London) forces).

The Casimir effect is present even in absence of a net charge, electric dipole or multipole (permanent or induced), magnetic dipole, external fields, etc. etc.

Example: Two uncharged metallic plates in a vacuum without any external electromagnetic field.

Classical description: since there are no charges and no external fields, there is no field nor forces between the plates.

Quantum electrodynamic description (QED): there are virtual photons between the plates which generate a net force (either attraction or repulsion depending on the arrangement of the plates and the materials between them).



The Casimir effect is present between infinite conductivity metallic plates but also for finite-conductivity metals and dielectrics of different geometries.

In the nanoscale: The actractive force produces stiction (but could be used for actuation). In presence of fluids, it can be also repulsive and, hence, could avoid stiction.

Casimir effect and force

1. Casimir force between **two parallel "ideal" plates**

(T=0, perfect reflection, perfectly parallel, perfectly flat surfaces, $A >> d^2$)

$$F_c = \frac{\hbar c \pi^2}{240}\frac{A}{D^4} \qquad \left(\frac{\hbar c \pi^2}{240} = 1.3\times 10^{-27}\ \mathrm{Nm}^2\right)$$

D: Distance between the two plates, A: surface of the plates

For $A=(1\ \mu\mathrm{m})^2, D = 10\ \mathrm{nm} \ \Rightarrow\ F_c = 0.13\ \mu\mathrm{N}$

(which is, in principle, an easily measurable force but other forces or surface imperfection make these measurements challenging)

Note: the Casimir equivalent pressure is $P = F_c / A = 130\ \mathrm{kPa} \cong 1\ \mathrm{atm}$!!

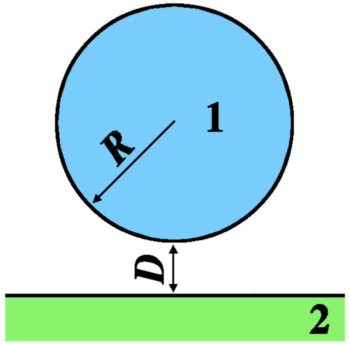
2. Casimir force between an **"ideal" plate and an "ideal" sphere**

$$F_c = 2\pi R \frac{\hbar c \pi^2}{720}\frac{1}{D^3} \qquad (\text{for } R >> D \text{ and } A=\infty)$$

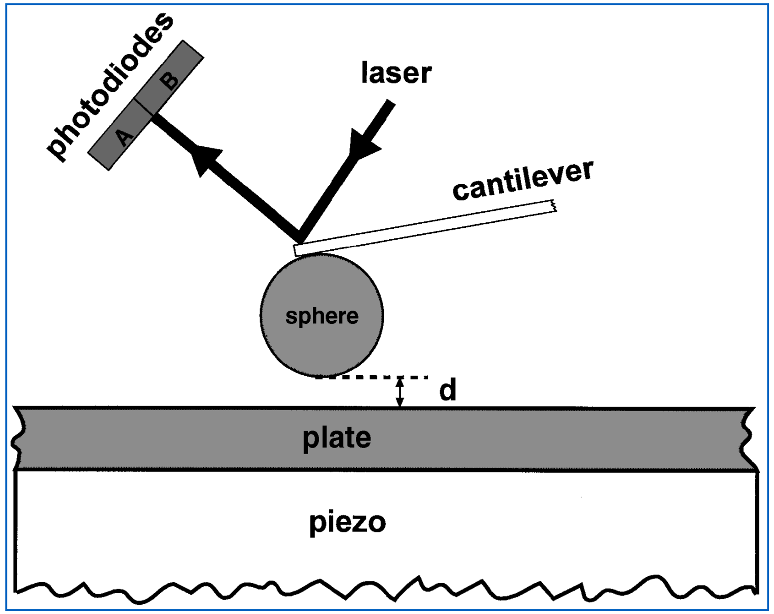
D: Distance between the sphere and the plane,

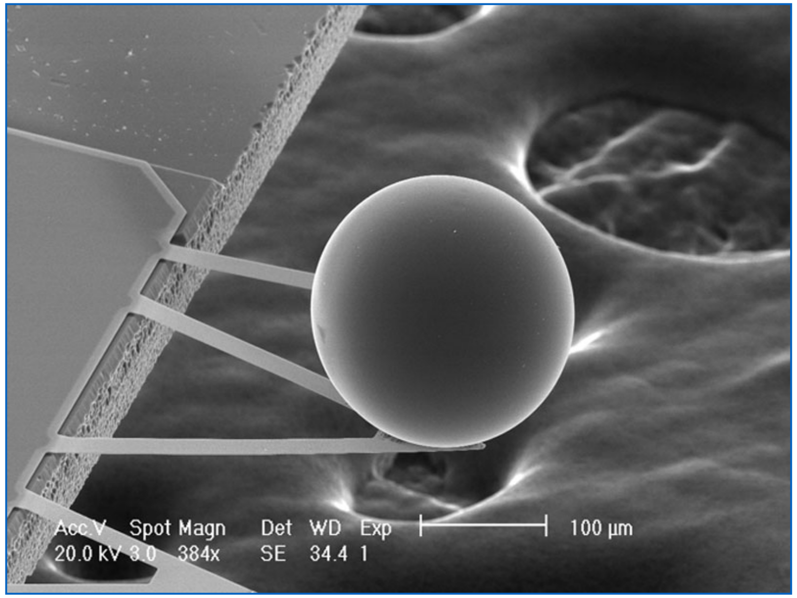
A: Surface of the plate

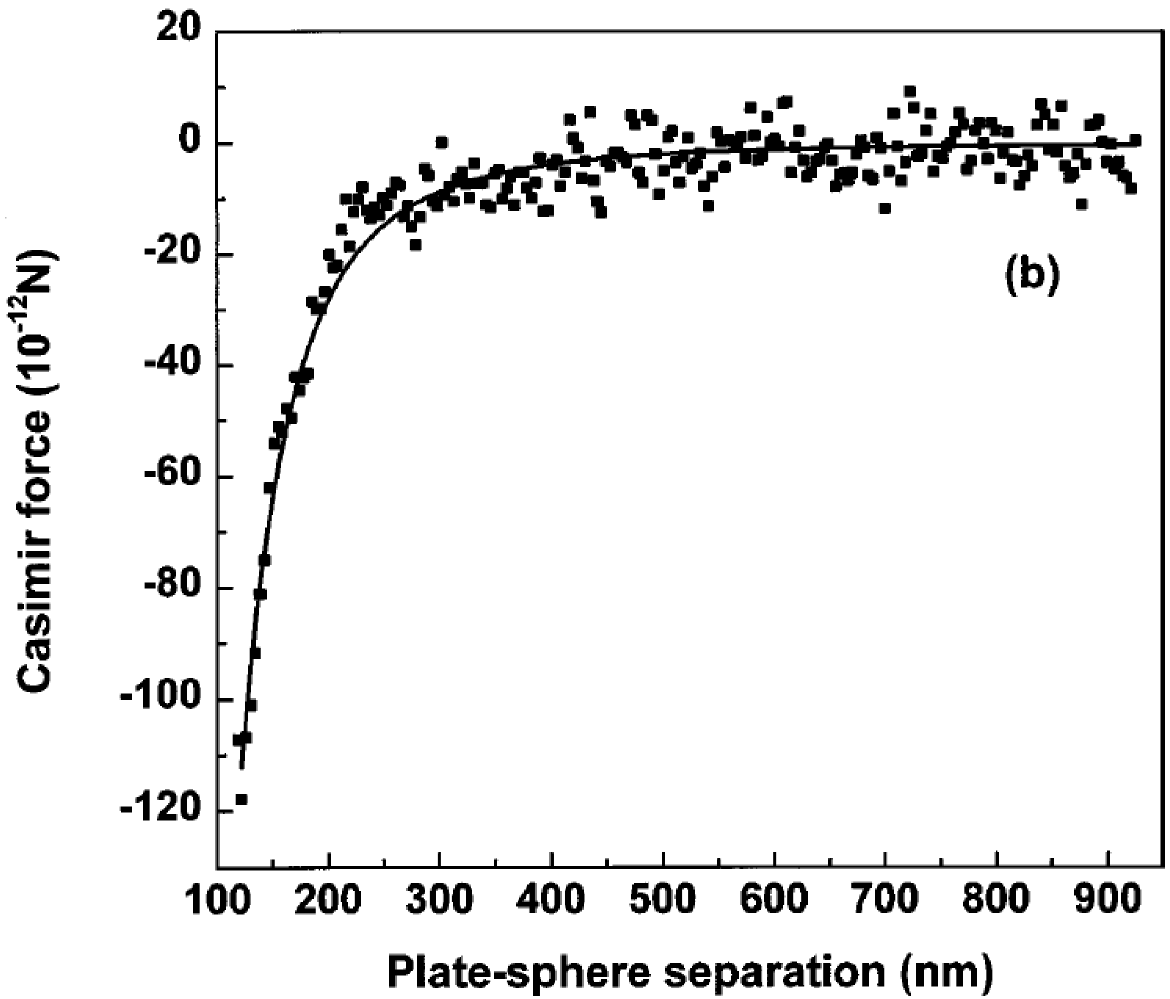
R: radius of the sphere



Casimir effect and force







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G. L. Klimchitskaya et al., Rev. Mod. Phys. 81, 1827 (2009)