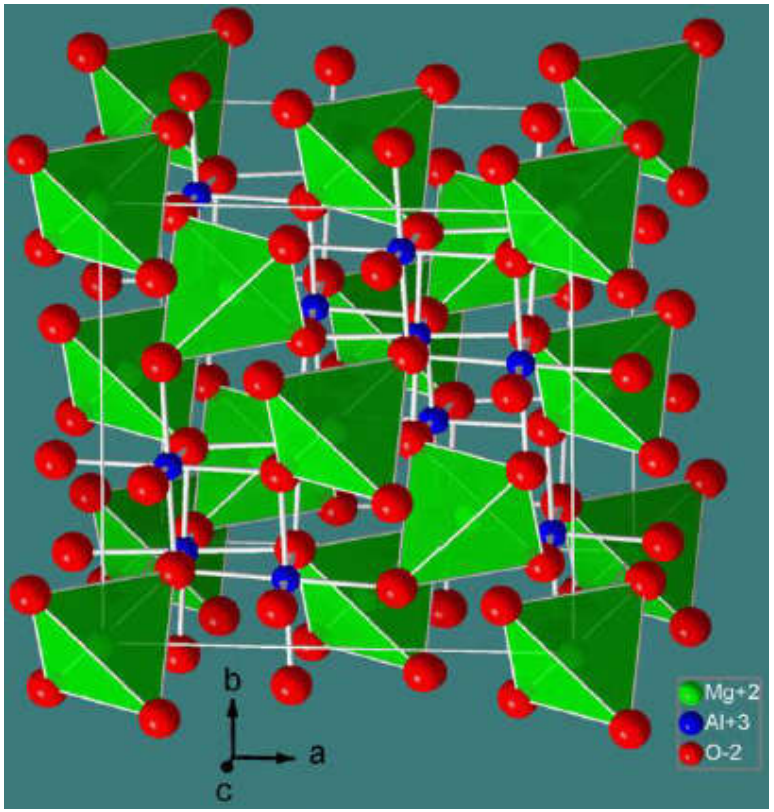
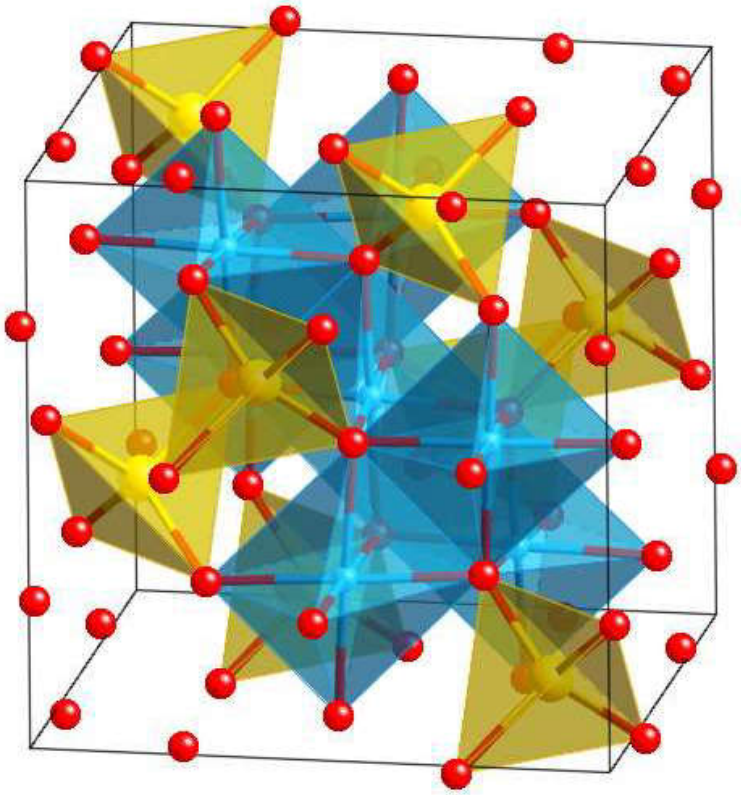
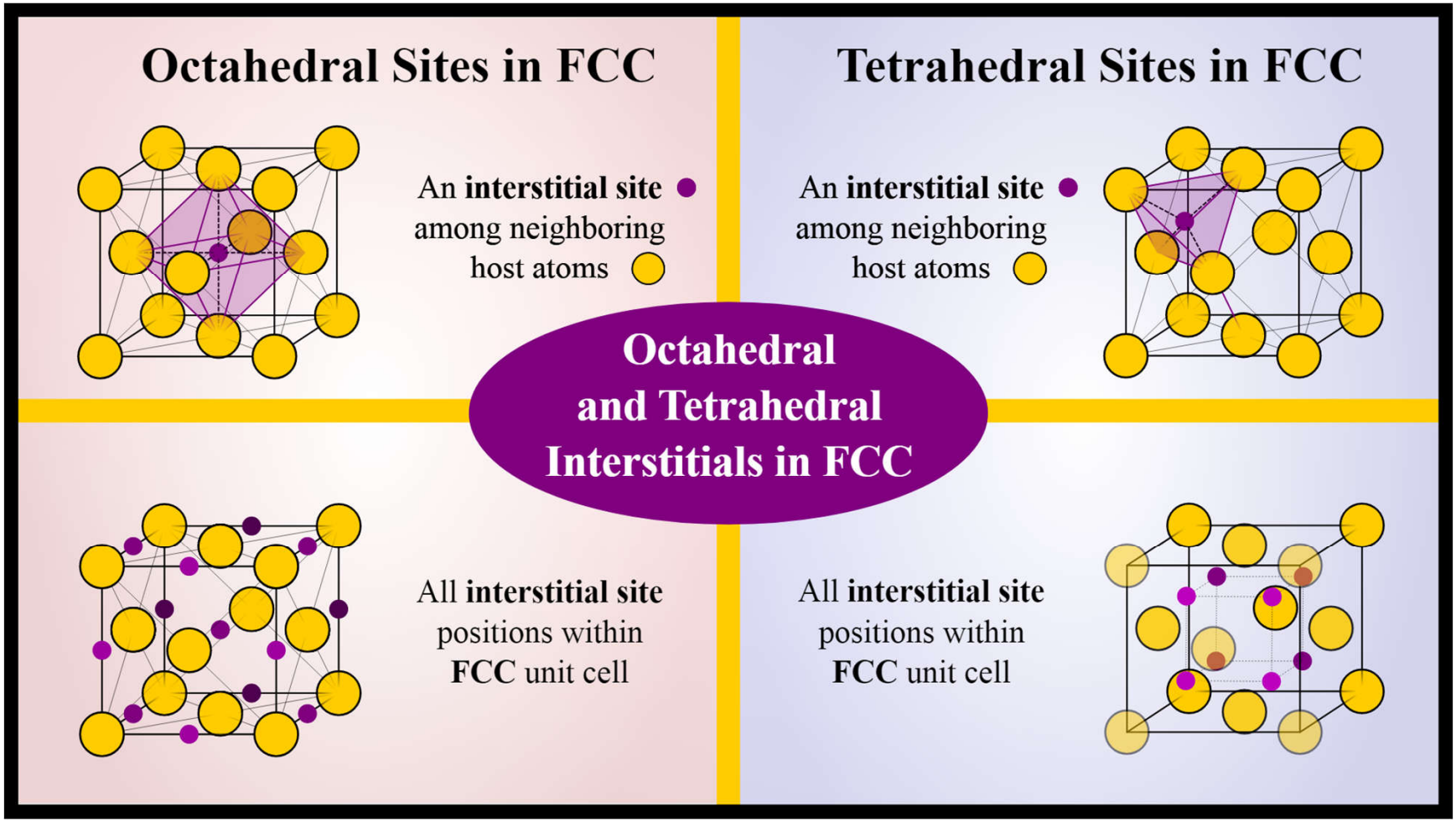
Normal spinel structures are usually cubic close-packed oxides with one octahedral and two tetrahedral sites per formula unit.

B^{3+} ions occupy half the octahedral holes, while A^{2+} ions occupy one-eighth of the tetrahedral holes.






Octahedral Sites in FCC
An interstitial site among neighboring host atoms
Tetrahedral Sites in FCC
An interstitial site among neighboring host atoms
Octahedral and Tetrahedral Interstitials in FCC
All interstitial site positions within FCC unit cell
All interstitial site positions within FCC unit cell

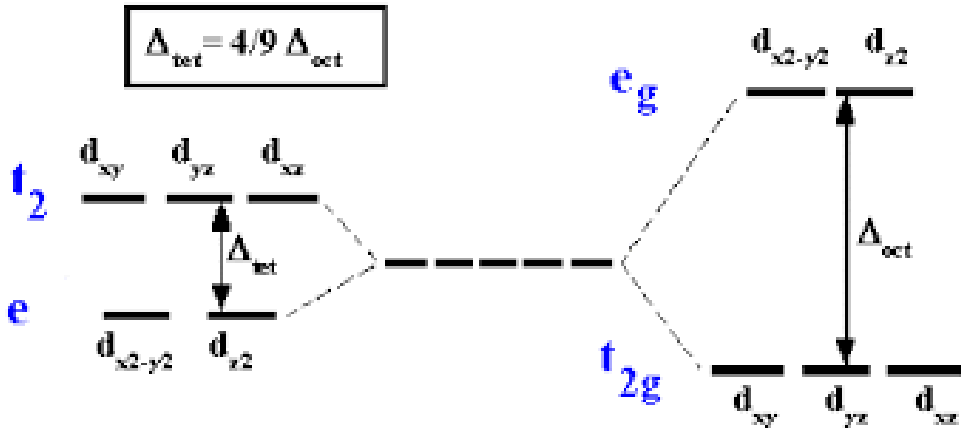
Crystal Structure	Face-centered Cubic (FCC)
Unit Cell Type	Cubic
Relationship Between Cube Edge Length *a* and the Atomic Radius *R*	$a = 2R\sqrt{2}$
Close-Packed Structure	Yes
Atomic Packing Factor (APF)	74%
Coordination Number	12
Number of Atoms per Unit Cell	4
Number of Octahedral Interstitial Sites	4
Number of Tetrahedral Interstitial Sites	8
Size of Octahedral Voids	$r = 0.414\ R$
Size of Tetrahedral Voids	$r = 0.225\ R$

Inverse Spinels usually have alternate arrangement.

The $\mathbf{A^{II}}$ ions occupy the **octahedral** voids, whereas half of $\mathbf{B^{III}}$ ions occupy the **tetrahedral** voids

It can be represented as: $\mathbf{(B^{III})^{tet}(A^{II}B^{III})^{oct}O_4}$

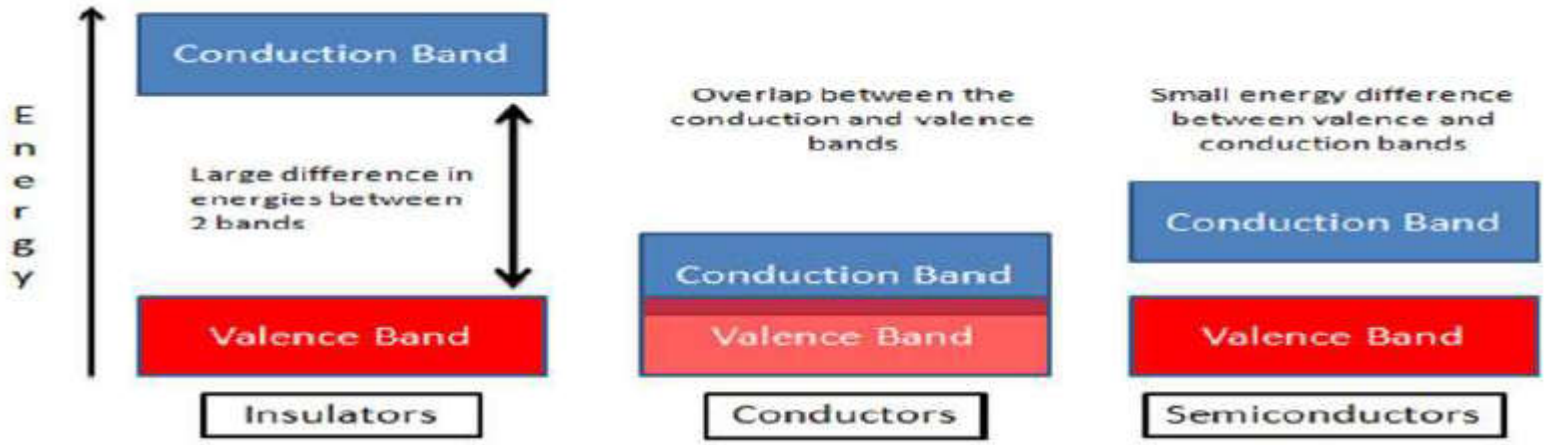
Energy levels of the d-orbitals in common stereochemistries



Tetrahedral field | free-ion | Octahedral field

Semiconductors:

A Semiconductor is a material which has Electrical Conductivity between that of conductor and that of an insulator.

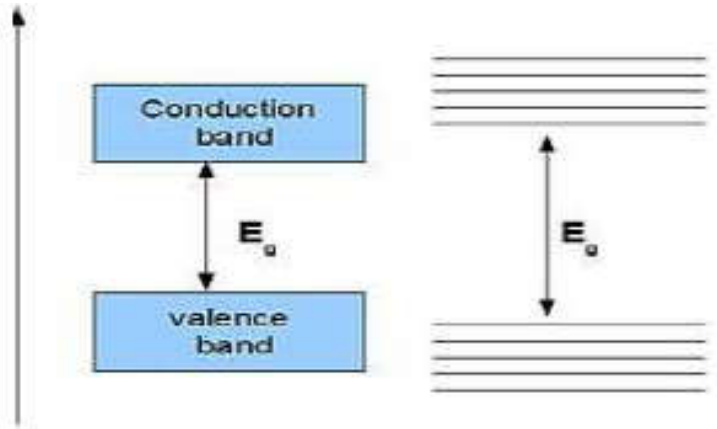


Quantum confinement is the spatial confinement of electron hole pairs in one or more dimensions within a material.

-1D confinement-quantum wells

-2D confinement- quantum wires

-3D confinement-quantum dot



• Electron hole pairs become spatially confined when the diameter of a particle approaches the de Broglie wavelength of electrons in the conduction band.

• As a result the energy difference between energy bands is increased with particle size decreasing.

Relativity

$$E = mc^2$$

Photoelectric effect $E = hf = \frac{hc}{\lambda}$

The de Broglie Hypothesis

$$\lambda \overset{?}{=} \frac{h}{p} = \frac{h}{mv}$$

$9.1093837 \times 10^{-31}$ kilograms

Planck's constant = $6.62607015 \times 10^{-34}$ m^2 kg / s

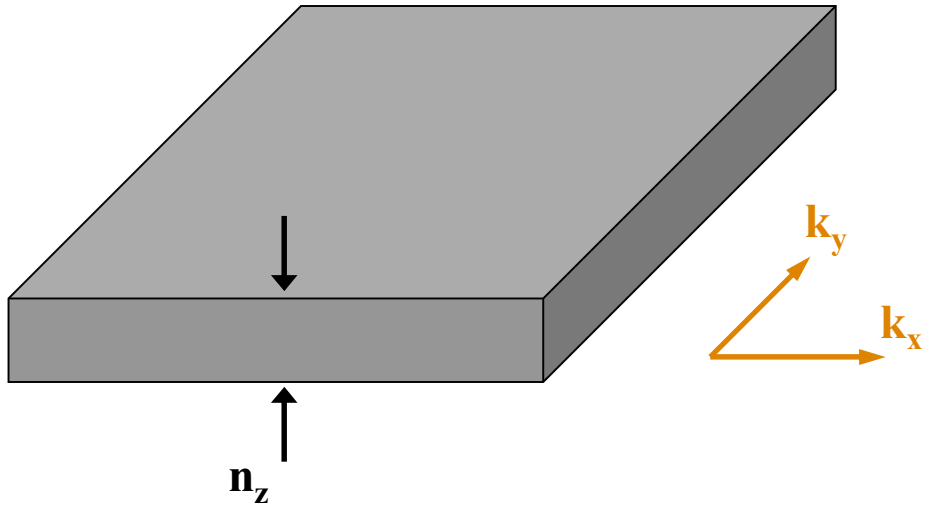
1. Thin Films & Quantum Wells

Electrons are **Confined in 1 Direction:**

⇒ They can easily have

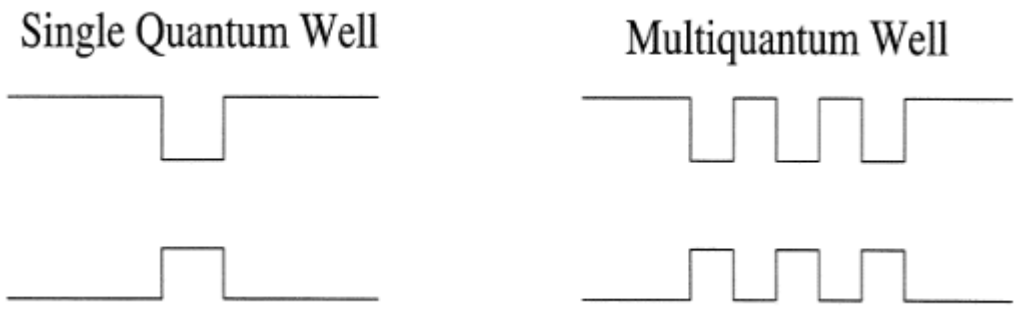
Motion in 2 Dimensions!

⇒ There is 1 Dimensional Quantization!



The quantum well in nanotechnology is formed by **sandwiching a material (fore example GaAs) between the two layers of another material having broader gap** (For example aluminium arsenide). The layers are prepared by the chemical vapor deposition or epitaxy.

Quantum well lasers with one active are called single-quantum-well (SQW) lasers and lasers with multiple quantum well active region



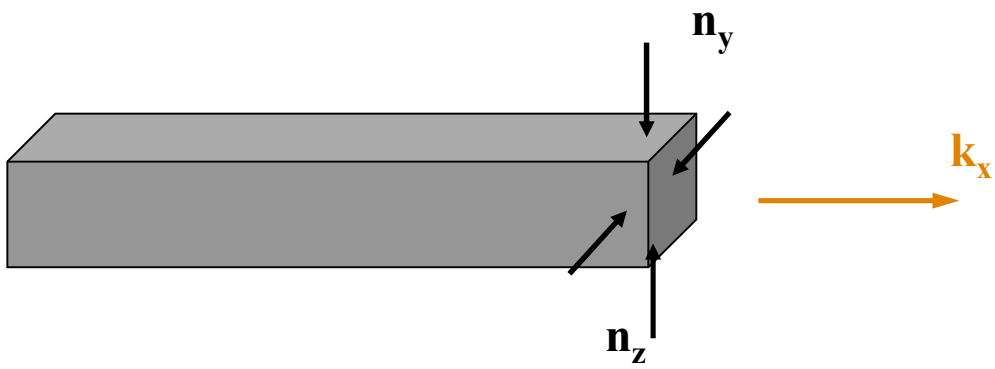
2. Quantum Wires

Electrons are ***Confined in 2 Directions*:**

⇒ They can easily have

***Motion in 1 Dimension*!**

⇒ ***There is 2 Dimensional* Quantization!**



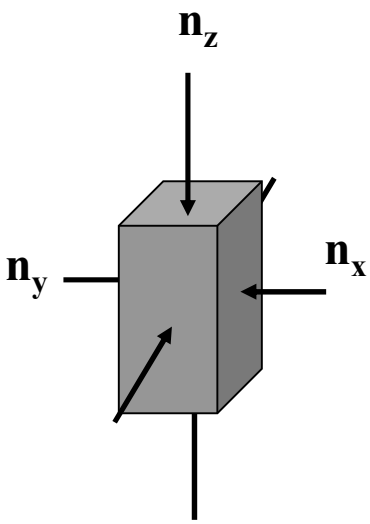
3. Quantum Dots

Electrons are ***Confined in 3 Directions*:**

⇒ They can easily have

***Motion in 0 Dimensions*!**

⇒ ***There is 3 Dimensional* Quantization!**



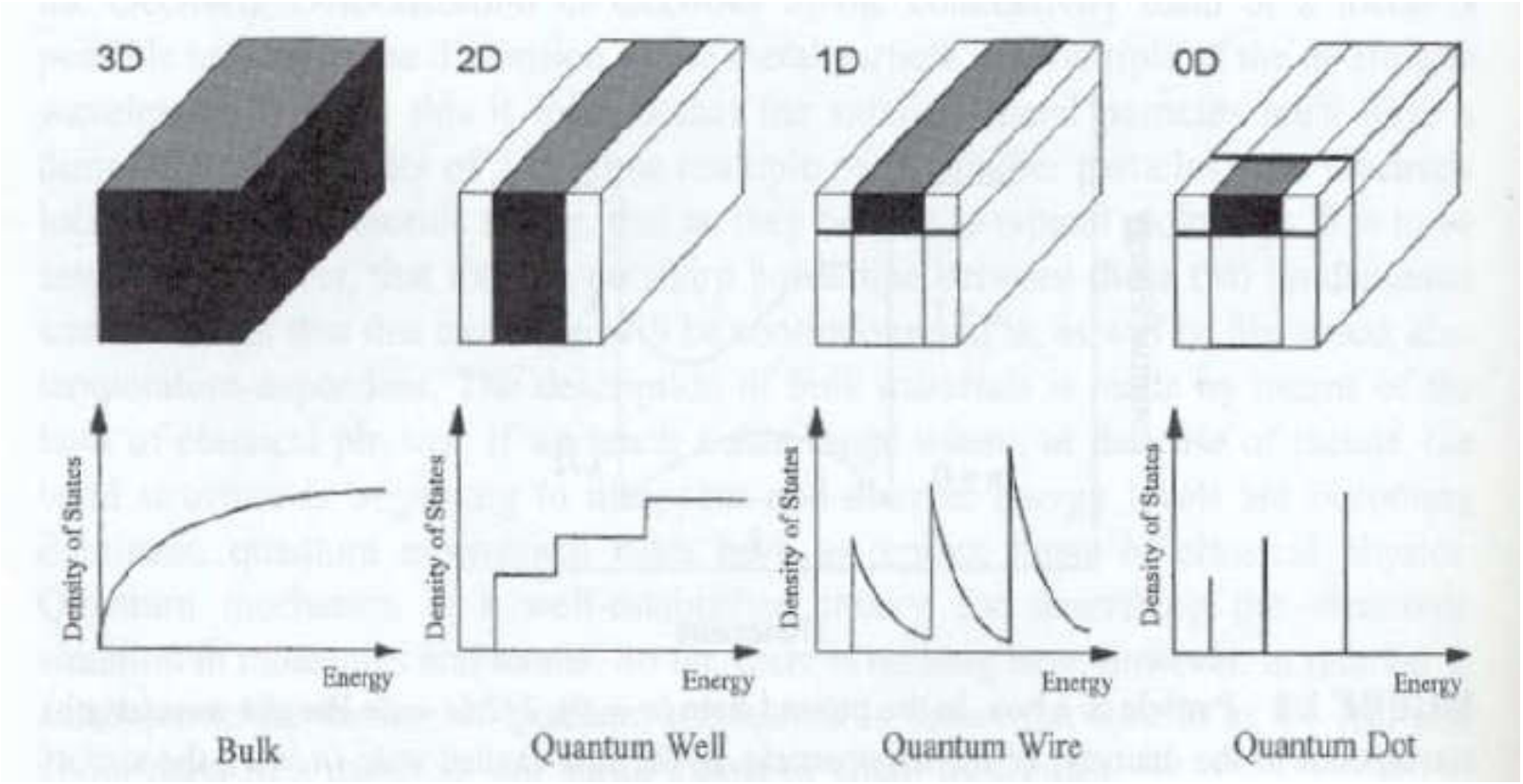
Each further confinement direction

changes a continuous component

to a discrete component

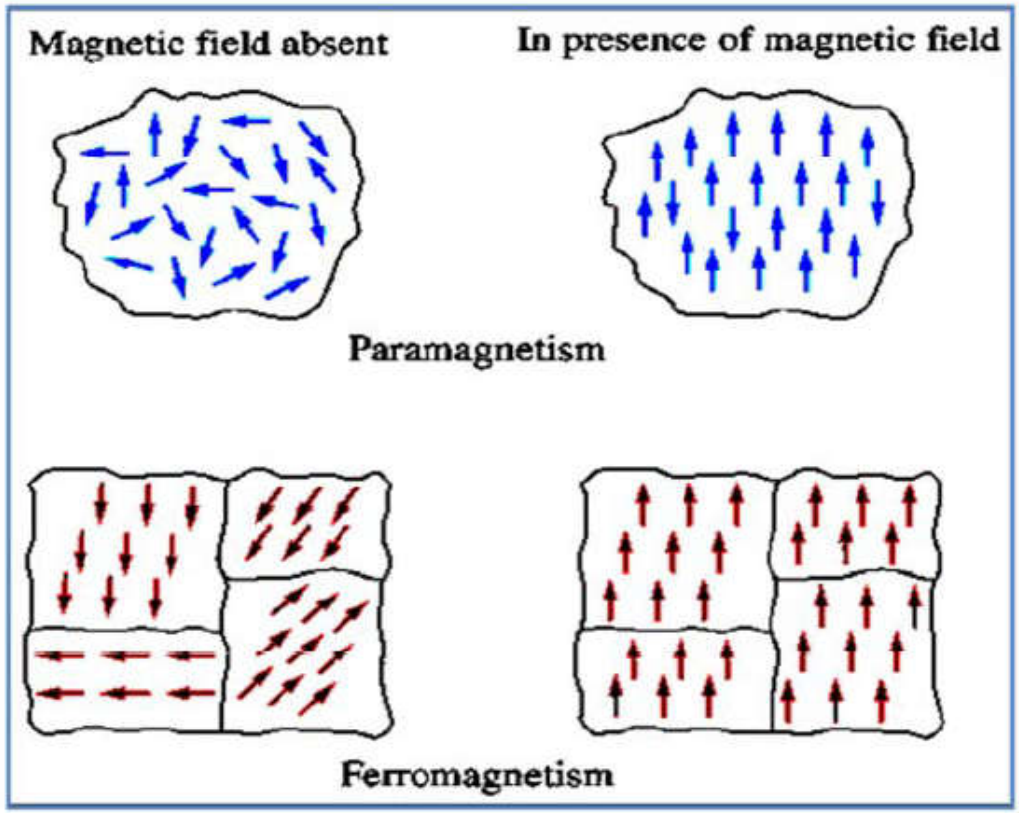
characterized by

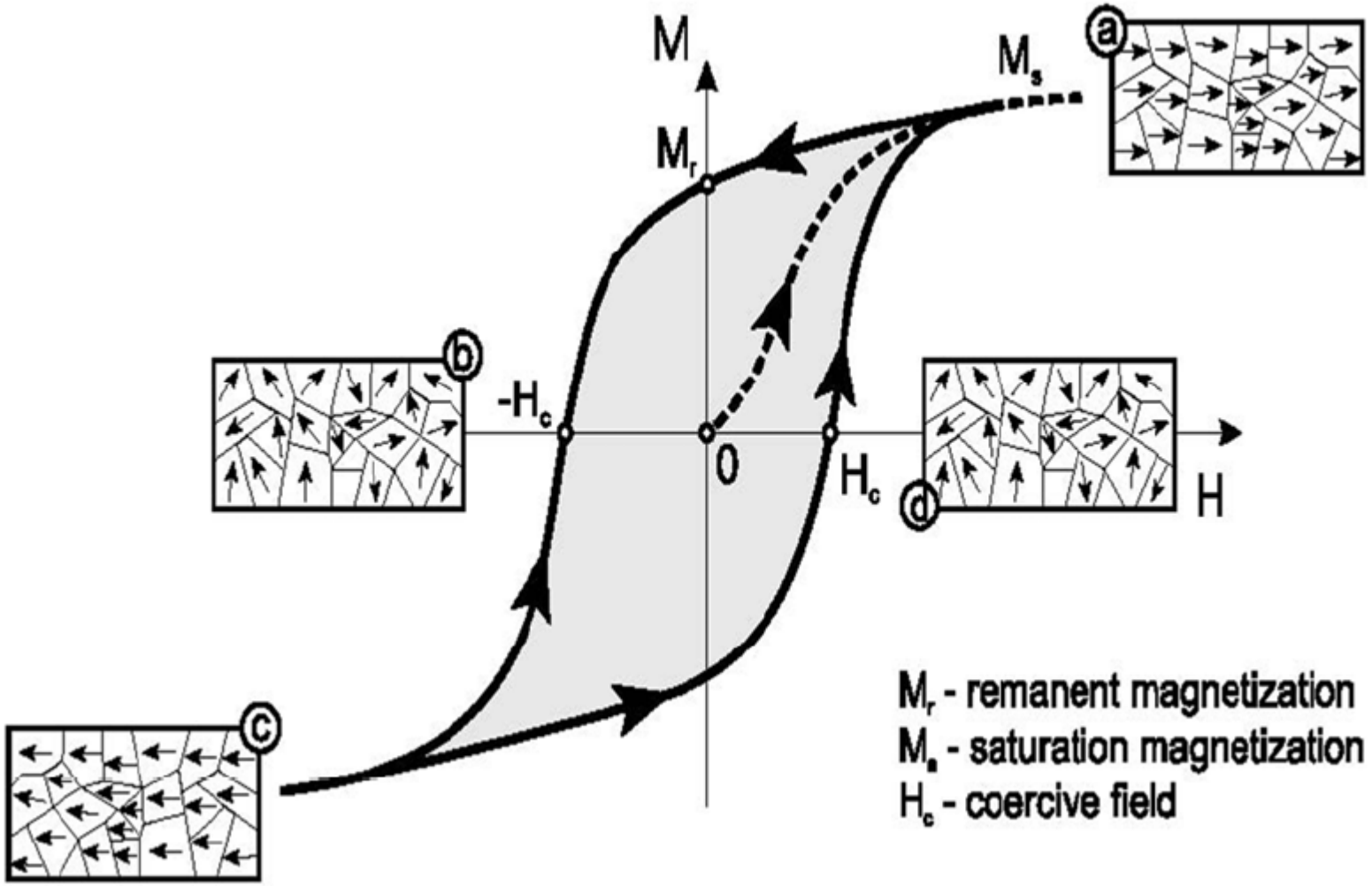
a quantum number n.


3D
2D
1D
0D
Density of States
Energy
Density of States
Energy
Density of States
Energy
Density of States
Energy
Bulk
Quantum Well
Quantum Wire
Quantum Dot

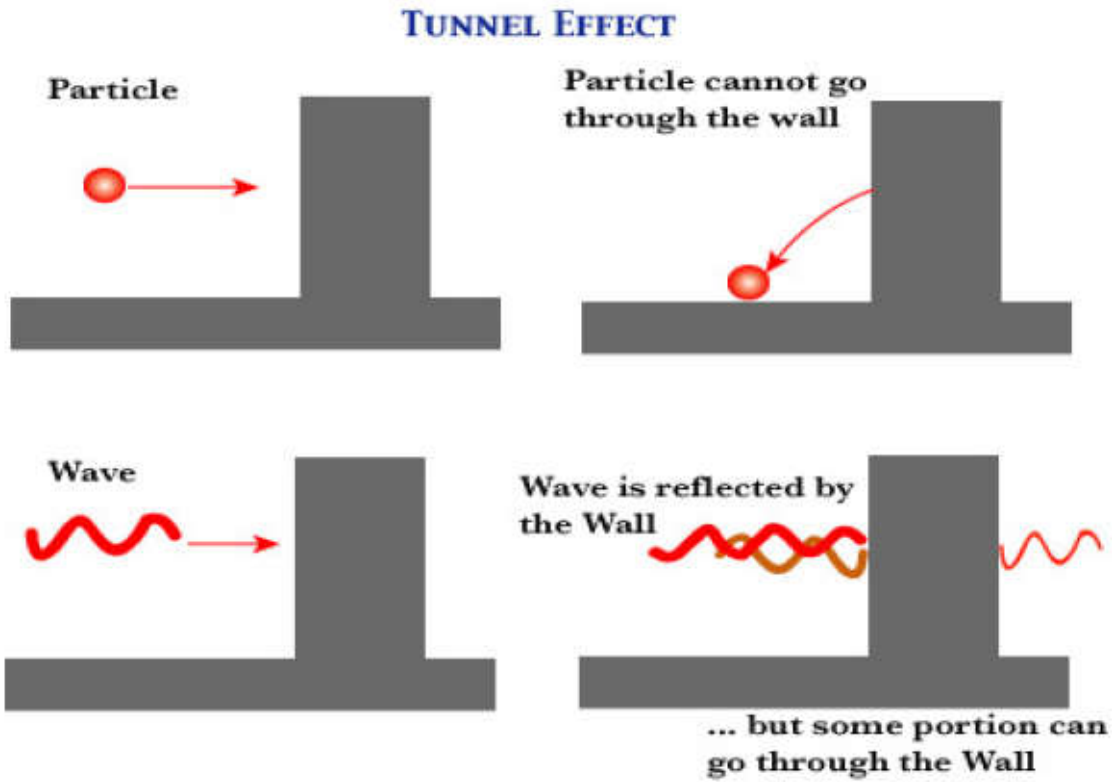
Magnetic Properties:

- The Magnetic Moment of Nano particles is found to be very less when compared them with its bulk size.

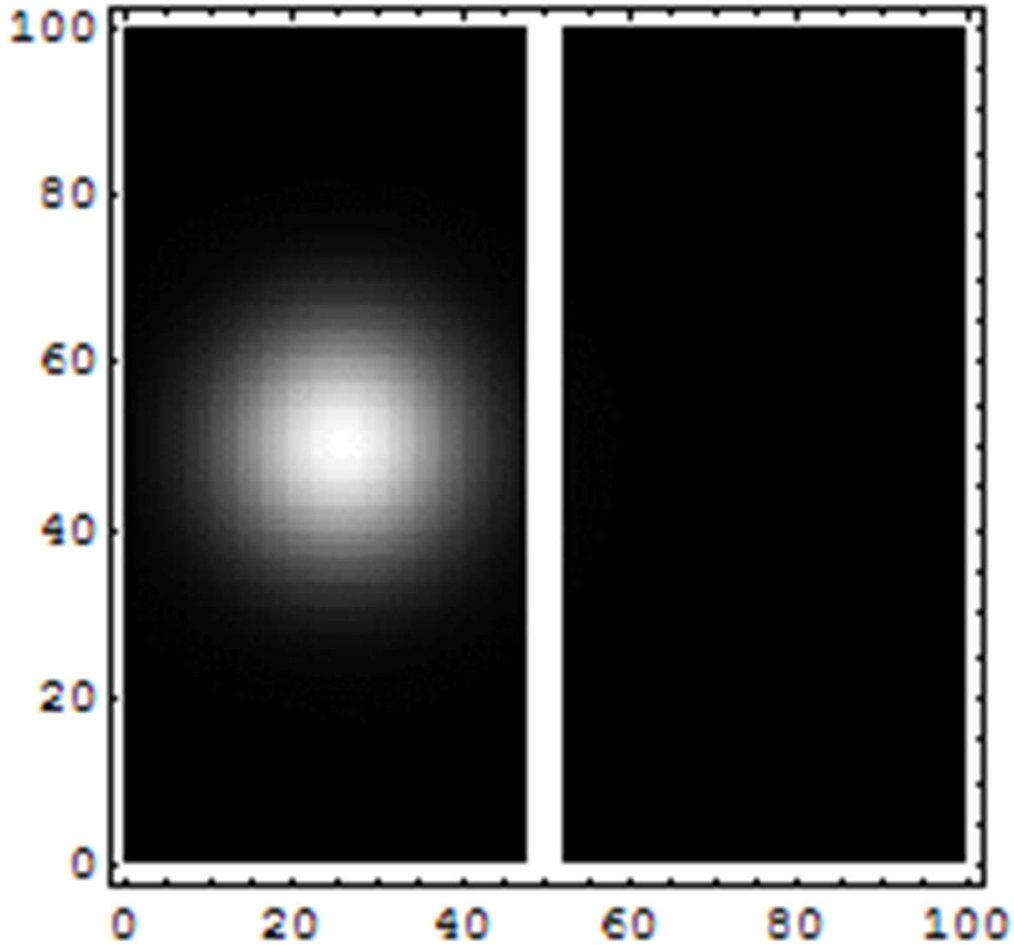



M
M_s
M_r
a
b
c
d
$-H_c$
0
H_c
H
M_r - remanent magnetization
M_s - saturation magnetization
H_c - coercive field

Consider a ball trying to roll over a hill. The following table gives a picture how the perception differs from classical mechanics to that of quantum mechanics:

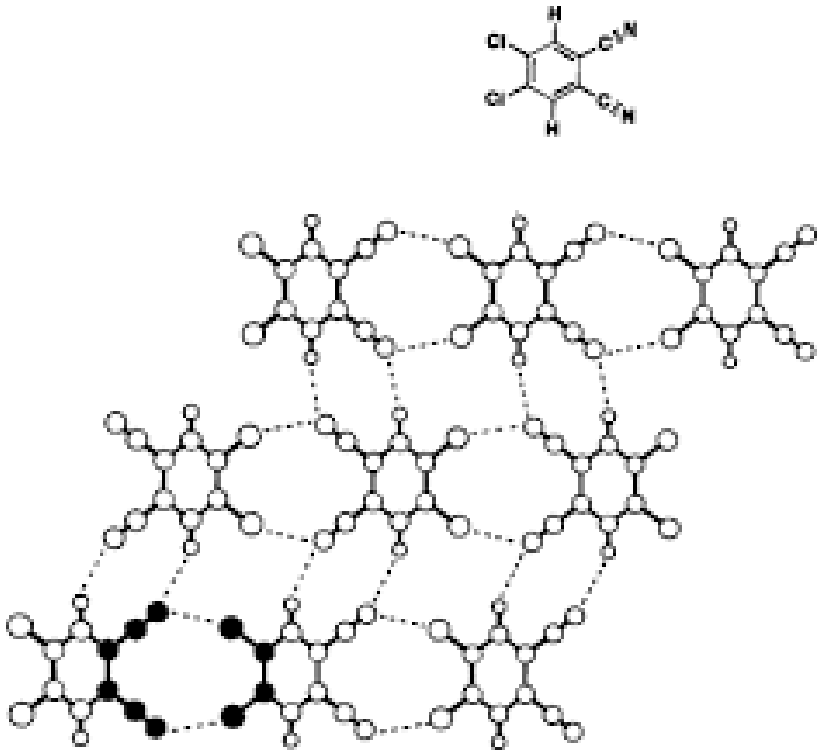


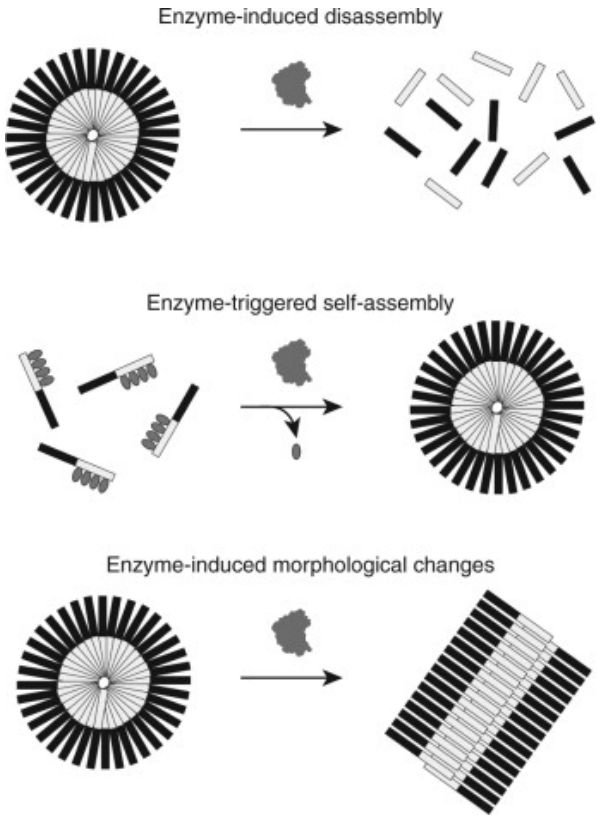
Classical Mechanics	Quantum Mechanics
• The ball does not have enough energy to classically surmount a barrier and thus will not be able to reach the other side. Thus, a ball without sufficient energy to surmount the hill would roll back down • Lacking the energy to penetrate a wall, it would bounce back (reflection) • In the extreme case, the ball may bury itself inside the wall (absorption).	• The ball can, with a very small probability, tunnel to the other side, thus crossing the barrier. • Here, the ball could, in a sense, borrow energy from its surroundings to tunnel through the wall or roll over the hill, paying it back by making the reflected electrons more energetic than they otherwise would have been


100
80
60
40
20
0
0
20
40
60
80
100

Supramolecular Structures:

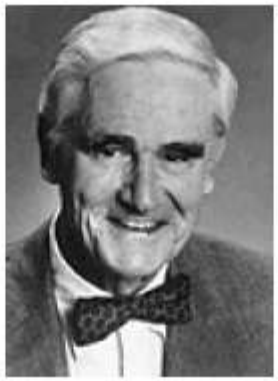
More complex than a molecule, also: composed of many molecules




Enzyme-induced disassembly
Enzyme-triggered self-assembly
Enzyme-induced morphological changes

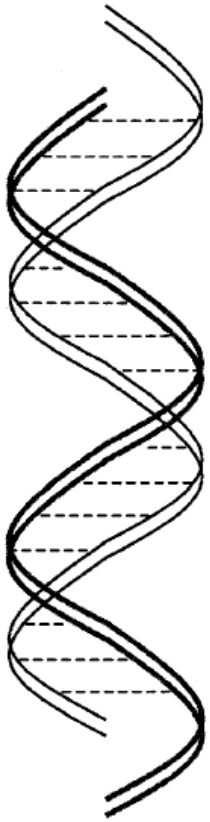
Supramolecular Chemistry:

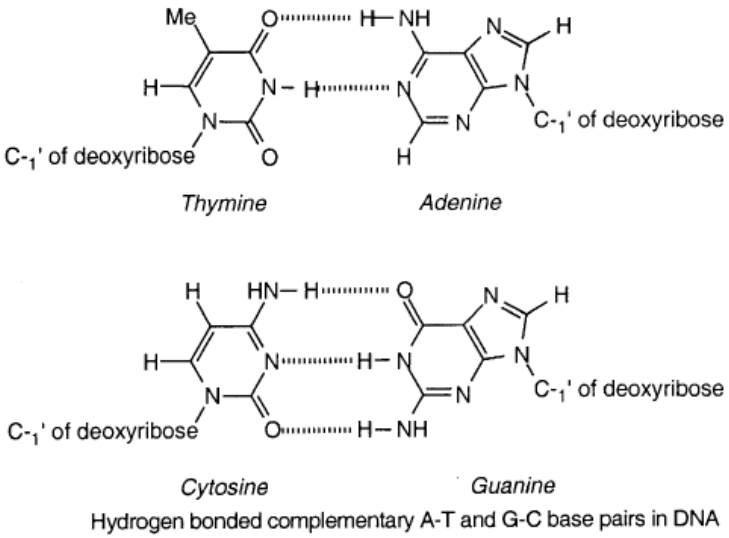
A term introduced by Jean-Marie Lehn, is "chemistry beyond the molecule", i.e. the chemistry of molecular assemblies using noncovalent bonds.


Nobel Prize in 1987: Pederson C , Cram D J, Lehn J M

Two DNA strands form a helical supramolecular assembly **through hydrogen bonding interactions that form between the bases**. Thymine can hydrogen bond preferentially with adenine. Cytosine hydrogen bonds preferentially with guanine.

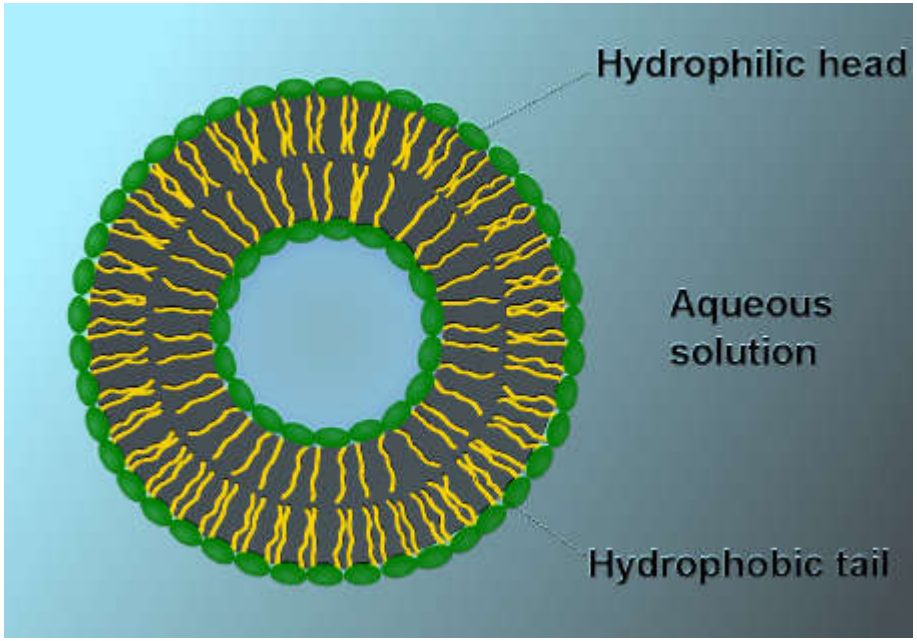


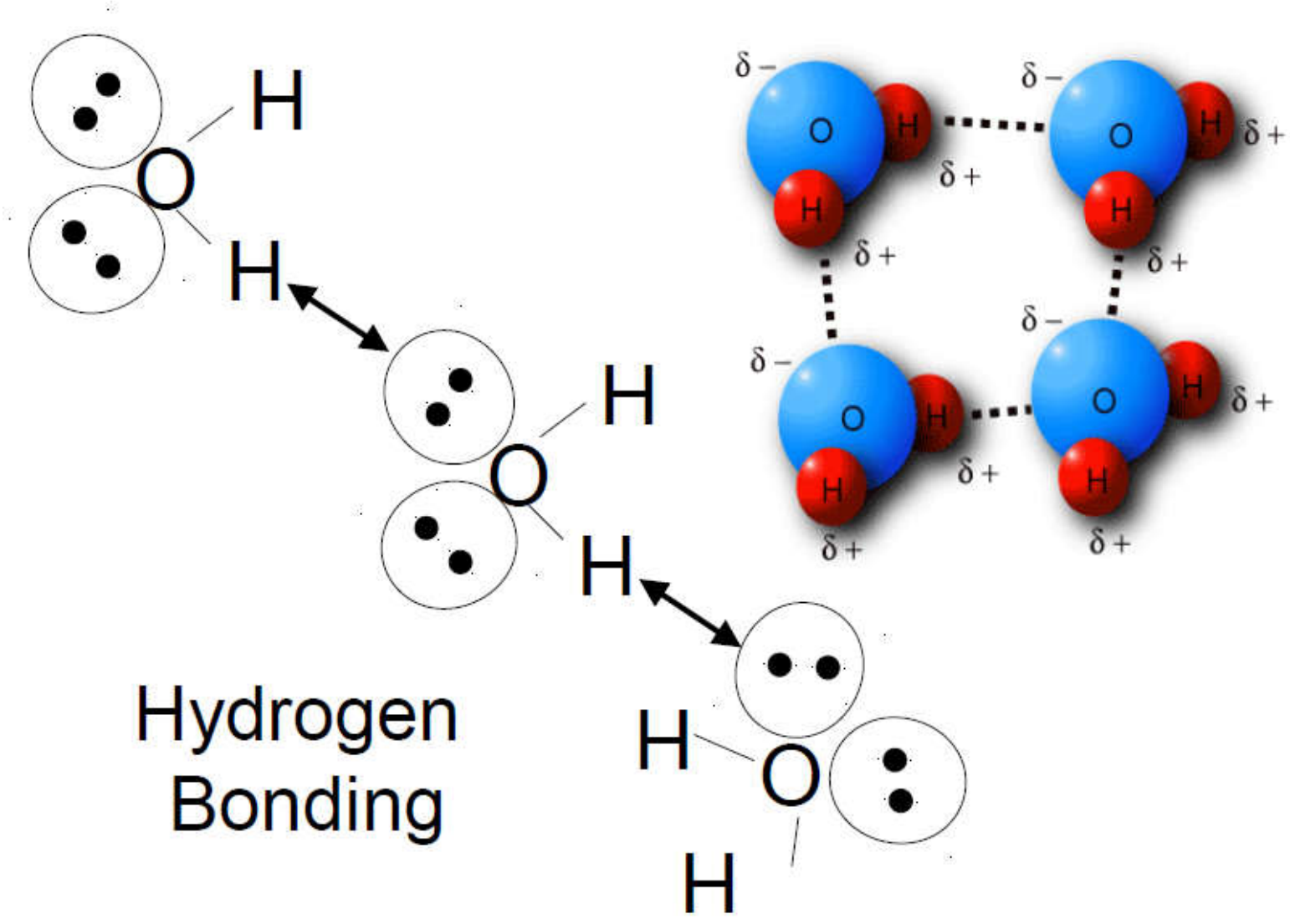


Hydrogen bonded complementary A-T and G-C base pairs in DNA

Self Assembly:

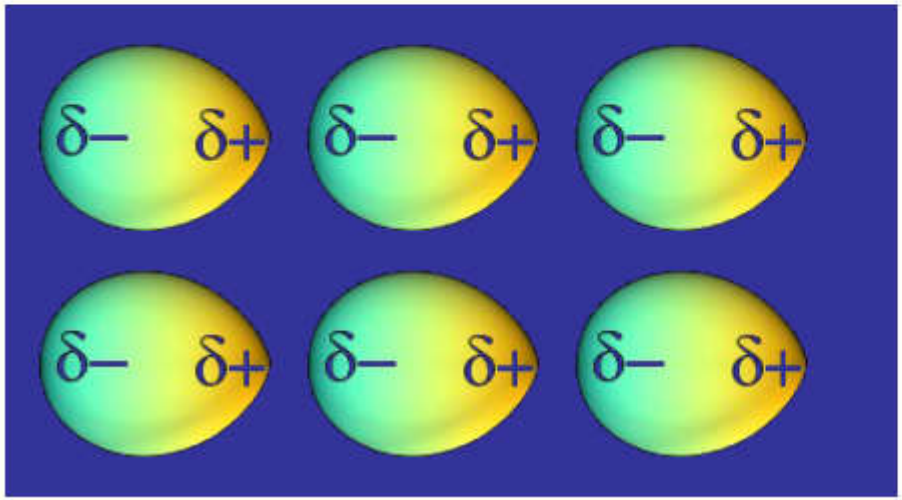
Self Assembly is defined as the spontaneous association of numerous individual units of material into well organized, well defined structures without external instruction.

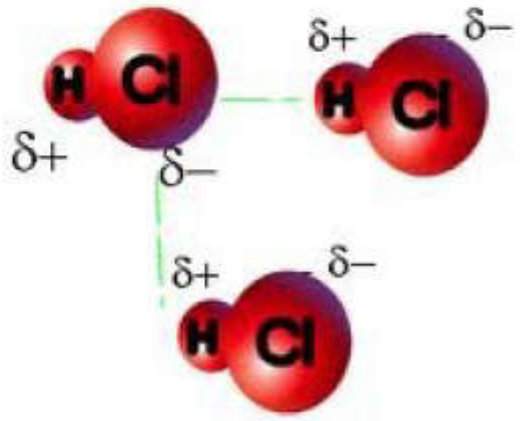



H
O
H
H
O
H
H
O
H
δ –
δ +
O
H
H
Hydrogen
Bonding

Dipole Interaction

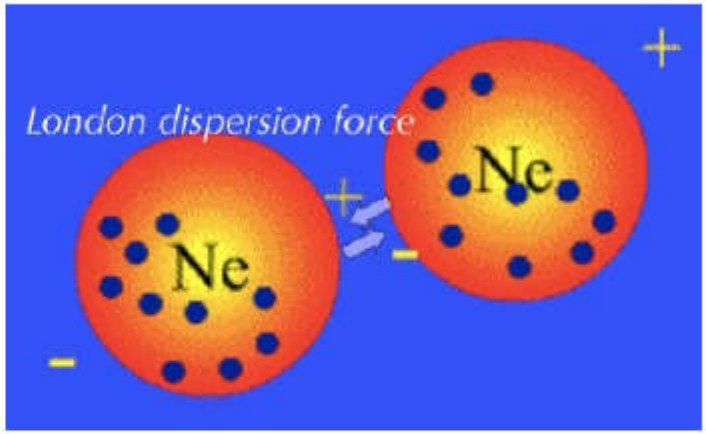
- The partial positive and negative ends of the molecules hold the molecules together.

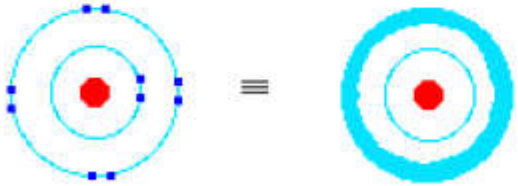




London Dispersion Forces (LDF)

instantaneous dipole–induced dipole forces,
London forces are induced dipoles caused by temporary rearrangement of the electron cloud.



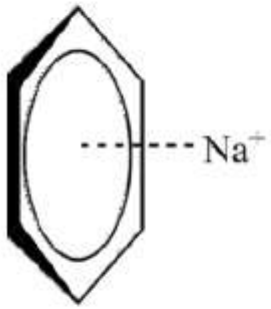


Neon

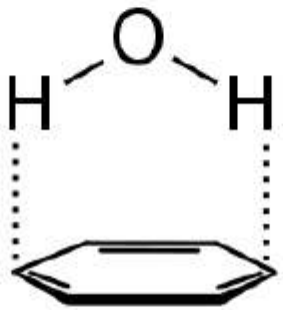
no permanent dipole

Assembled by π-π interaction

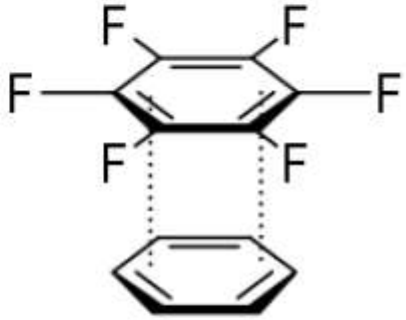
Some simple models:



Cation–π interaction bn benzene and a Na cation.

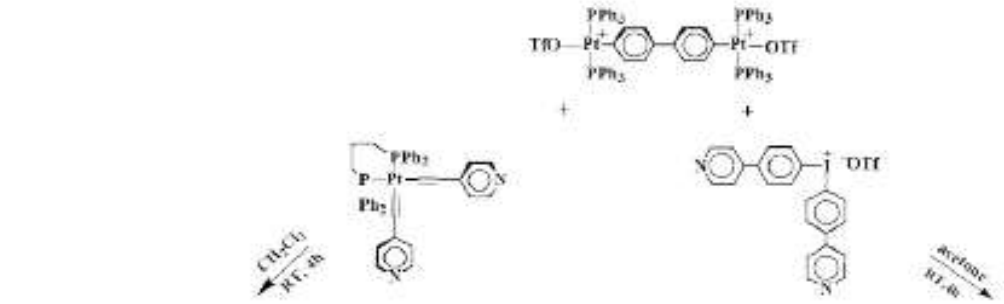


Polar π interaction bn water molecule and benzene

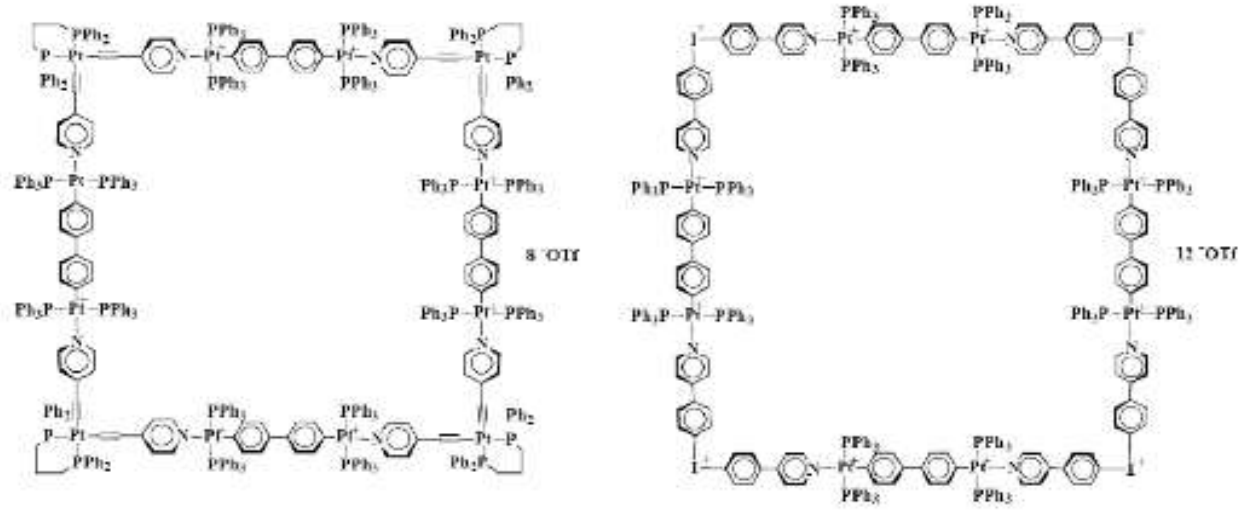


Π - π interaction bn e rich benzene & e poor hexafluorobenzene

Assembled by metal-ligand



Nanosized cavities



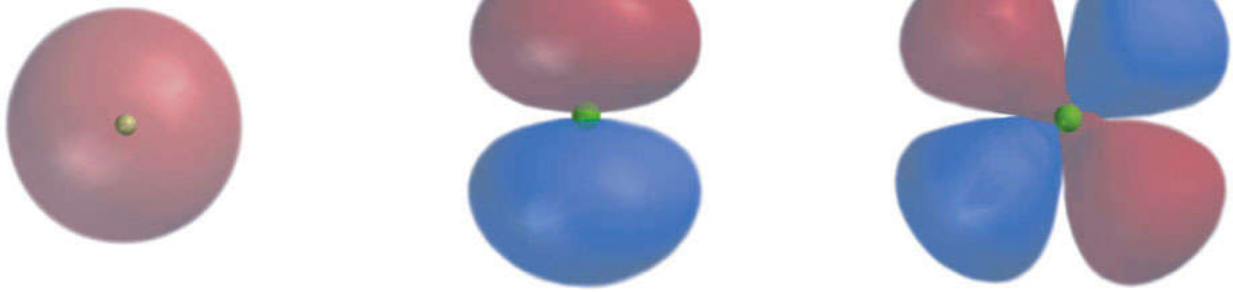
Valence Bond Theory and Molecular Orbital Theory:

s and *p* orbitals most important in organic and biological chemistry

s orbitals: spherical, nucleus at center

p orbitals: dumbbell-shaped, nucleus at middle

d orbitals: elongated dumbbell-shaped, nucleus at center

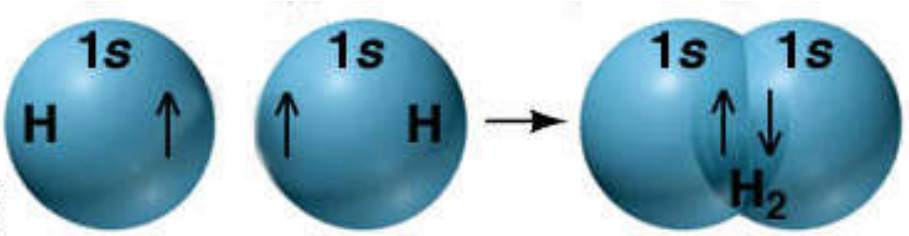


An *s* orbital

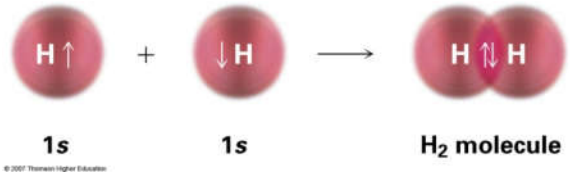
A *p* orbital

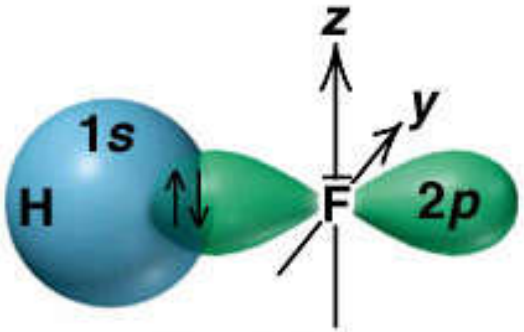
A *d* orbital

Orbital Overlap and Spin Pairing in Three Diatomic Molecules

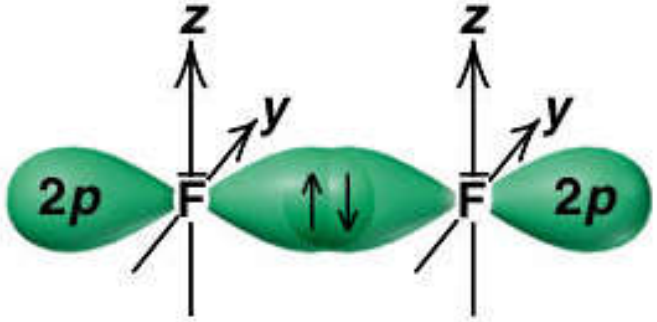


A Hydrogen, H_2





B Hydrogen fluoride, HF



C Fluorine, F_2

1. sp^3 Orbitals and the Structure of Methane

Carbon has 4 valence electrons ($2s^2\ 2p^2$)

In CH_4, all C–H bonds are identical (tetrahedral)

***sp*³ hybrid orbitals**: *s* orbital and three *p* orbitals combine to form four equivalent, unsymmetrical, tetrahedral orbitals (sppp = sp^3)