Welcome to Chem 104A

Instructor: **Professor Peidong Yang**
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Office Hours: Tue 1:00 – 3:00 pm

TA:

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Dandan Zhang; zhangdandan@berkeley.edu, 4-5 Tuesday/Hild 320
Fan Cui; cuifan@berkeley.edu, 5-6 Friday/Hild. 320

Discussion Session: Location/Time: M 5:30-7:30 pm, 180 TAN

The discussion section should provide a valuable additional resource for this course. In the discussion section, the GSIs will reemphasize and expand on material covered during lecture. They will also entertain questions and work through "example" problems.

Course Website

http://nanowires.berkeley.edu/teaching/chem104a.html

Google " Chemistry 104A"

Chem 104A, UC, Berkeley

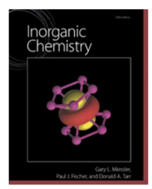
Chemistry 104A
Inorganic Chemistry

An introduction to inorganic chemistry
Topics covered will include:

Atomic structures, periodic trends,
Symmetry and group theory,
Molecular orbital theory, molecular structure,
Inorganic solids & band theory

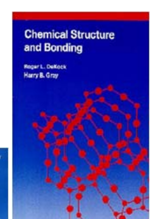
Completion of a general chemistry sequence (chemistry 1B, 3A or 4B) is prerequisite.

Chemistry 104A
Inorganic Chemistry: Textbook



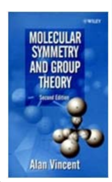
Miessler, G. L., Tarr, D. A. *Inorganic Chemistry*

DeKock and Gray, *Chemical Structure and Bonding, 2nd Ed.*, University Science Books, 1989

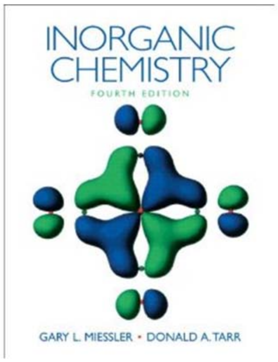


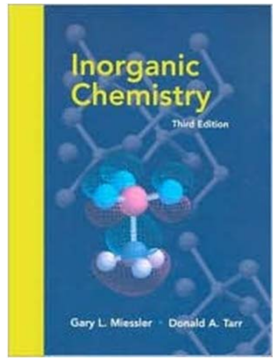
Optional (recommended)

Vincent, Molecular Symmetry and Group Theory, Wiley, 2001.



Important: The course material, and certainly what you will be responsible for on the exams, will be defined in lecture and based mainly on the class notes. *Therefore, attendance in class is a key to success*! The paperback book by Vincent is a valuable tool for learning about symmetry and group theory in chemistry. In addition, part of the course (in particular MO theory) will be based on material in the book by DeKock and Gray.





Chemistry 104A
Inorganic Chemistry: Reference Books

•Cotton, Wilkinson, and Gaus, *Basic Inorganic Chemistry*, Wiley, 1995

•Cotton, *Chemical Applications of Group Theory*, Wiley, 1990

•Douglas, McDaniel, and Alexander, *Concepts and Models of Inorganic Chemistry*, Wiley, 1994

•Huheey, Keiter, and Keiter, *Inorganic Chemistry, 4th Ed*. HaperCollins, 1993

•Shriver, Atkins, and Langford, *Inorganic Chemistry*, W. H. Freeman, 1990

•Porterfield, *Inorganic Chemistry*, Academic Press, 1993

•Cotton and Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed., Wiley, 1998

•Greenwood and Earnshaw, *Chemistry of the Elements*, Butterworth Heineman, 1997

Grading:

Problem sets (6)		10%
Exam 1	(Oct. 2nd , in class)	25%
Exam 2	(Oct 30th, in class)	25%
Final	(Dec 16th)	40%

Final Grades

Your grade for this class will be determined *exclusively* by the four criteria listed above (exams, problem sets, and final exam). Under no circumstances will alternative grading schemes be used to assign a final grade. Note that all grades are final, and not open to negotiation after they have been determined.

Examinations

Exams will cover material emphasized in the lectures, the required reading, and the problem sets. The midterms will be given in place of the regular lecture in class. No makeup exams will be given. Please mark these dates on your calendar immediately. If you have a legitimate reason (with documentation) to miss an exam, you may be excused from the exam and in this case your final grade will be based on your *prorated* other scores. If you know in advance of any reason that may cause you to miss any examination, you must see Prof. Yang immediately.

Note: Dishonesty and cheating will not be tolerated. Evidence of cheating on an exam will result in a grade of zero for that exam, and further disciplinary action by the University.

Regrade Policy

The GSI's will hand back midterm exams after lecture periods and also in their office hours. *Requests for regrades will only be considered if they are in the form of a written statement on a sheet of paper attached to the original, unaltered exam. No requests will be considered if they are handed in more than two weeks after the exam.*

Problem Sets

You are strongly encouraged to work through the problem sets, as this will test your understanding of the course material, and exam questions may be similar to the material covered in the problem sets. Problem sets will be assigned during lecture, and the GSI's will collect your answers at the end of the lecture the following week. They will grade two of the problems in each set, chosen randomly, and your cumulative score on these problems will determine 10% of your final grade. Also, if you are on a grade border, regularly completed problem sets will be taken into account in determining whether or not your grade should be higher.

Course Website

http://nanowires.berkeley.edu/teaching/chem104a.html

At this site, class notes and viewgraphs will also be posted. Please download the appropriate class notes and viewgraphs before coming to lecture.

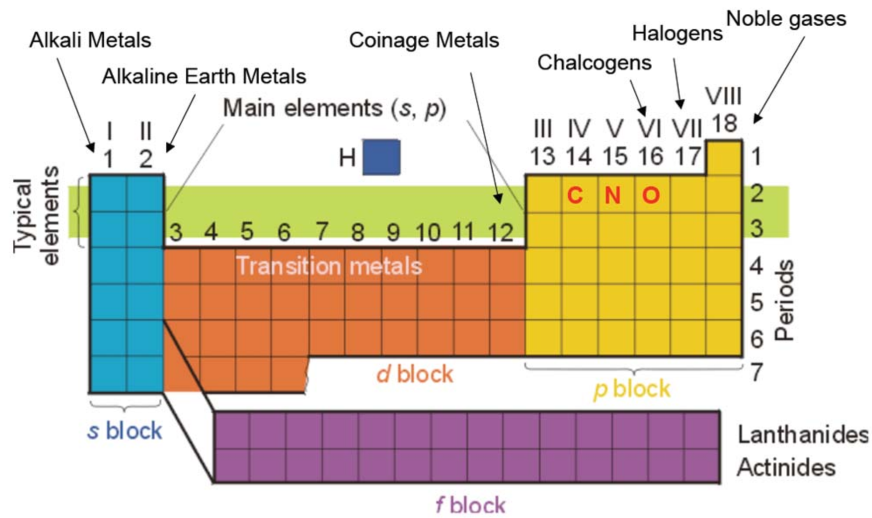
What is inorganic chemistry?

Organic Chemistry:

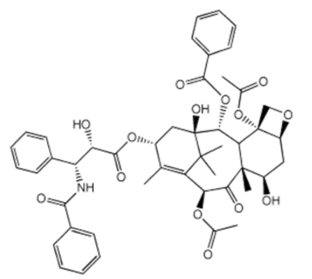
the chemistry of life
the chemistry of hydrocarbon compounds
C, H, N, O

Inorganic Chemistry:

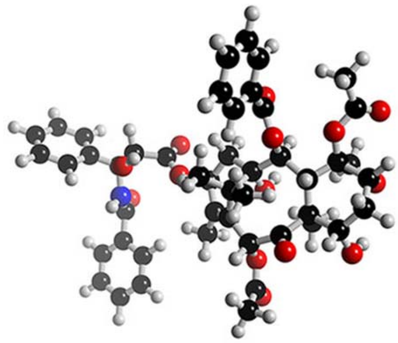
Non-living chemistry
Chemistry of "everything else"
Chemistry of the entire periodic table



Taxol the drug that now has the generic name "paclitaxel", and the registered tradename "Taxol ®" (Bristol-Myers Squibb Company)



The natural source, the Pacific yew tree, is an environmentally protected species, which is also one of the slowest growing trees in the world. Isolation of the compound, which is contained in the bark, involves killing the tree, and the quantities available by this method are pitifully small. It would take six 100-year old trees to provide enough taxol to treat just one patient.



Carbon: 4 bonds
Hydrogen: 1 bond
Nitrogen: 3 bonds
Oxygen: 2 bonds

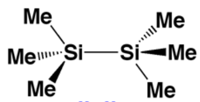
Constant "atomicity" (valence)

August Kekule (1829-1896, German)

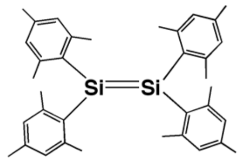
Organic molecules: successful
Inorganic molecules: ???

	Organic Compounds	Inorganic Compounds
Single Bond	✓	✓
Double Bond	✓	✓
Triple Bond	✓	✓
Quadruple bond	✕	✓
Coordination No.	Constant	Diverse
Geometry	Fixed	Diverse

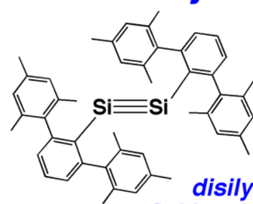
Multiple Bonds in Inorganic Chemistry



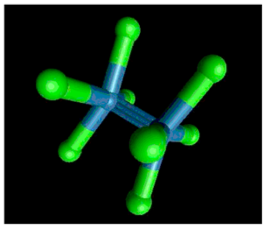
disilane

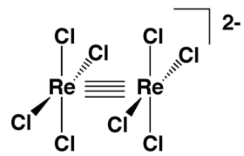


disilene
West, 1980

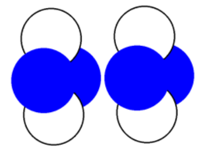


disilyne
Sekiguchi, 2005



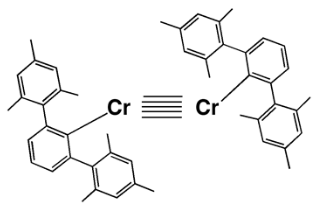


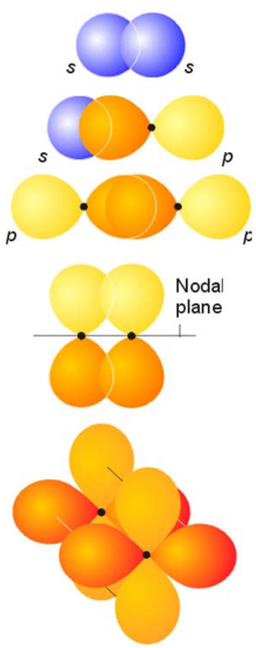
$\sigma + \pi + \pi + \delta$ *bonds*



δ *bond*

a pentuple bond
Power, 2005





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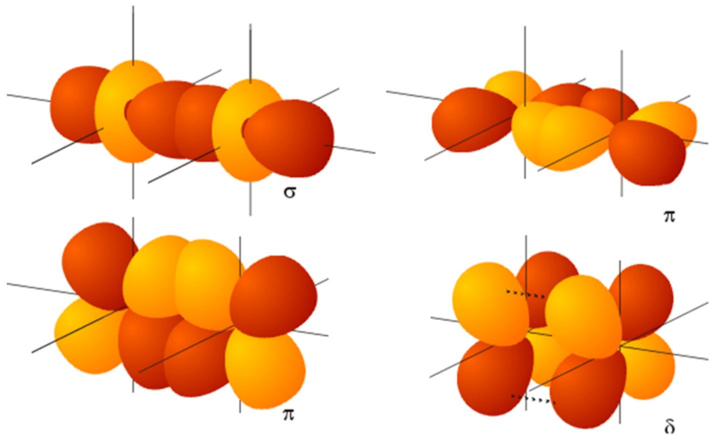
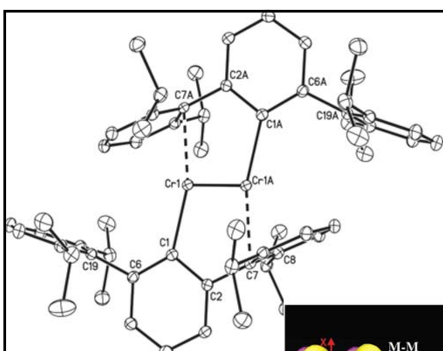
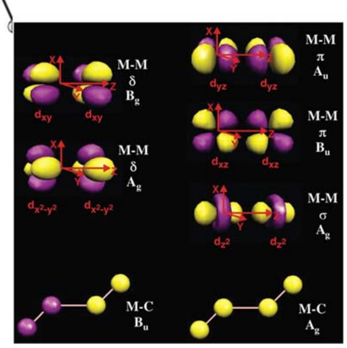
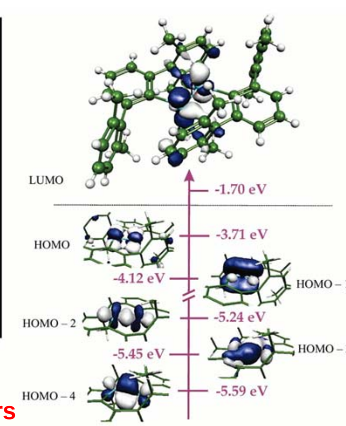


Chem 104A, UC, Berkeley



Science 4 November 2005:
Vol. 310. no. 5749, pp. 844 - 847





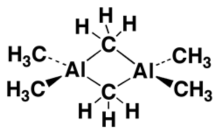
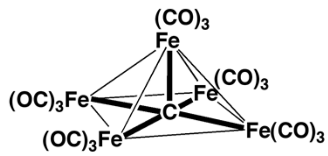
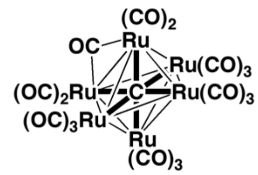
A Stable Compound with
Fivefold Bonding Between Two Chromium(I) Centers

Connectivity and Valence in Inorganic Chemistry

How many bonds can be formed to a single carbon atom?

organic chemistry: 2, 3 or 4 bonds

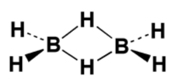
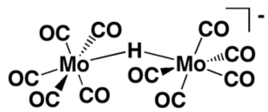
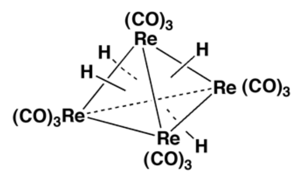
inorganic chemistry:

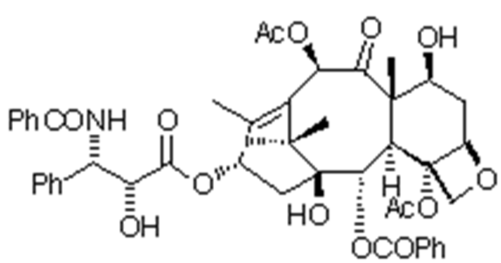
How many bonds can be formed to a single hydrogen atom?

organic chemistry: 1 bond

inorganic chemistry:

Total Synthesis of Taxol



Need catalysts!

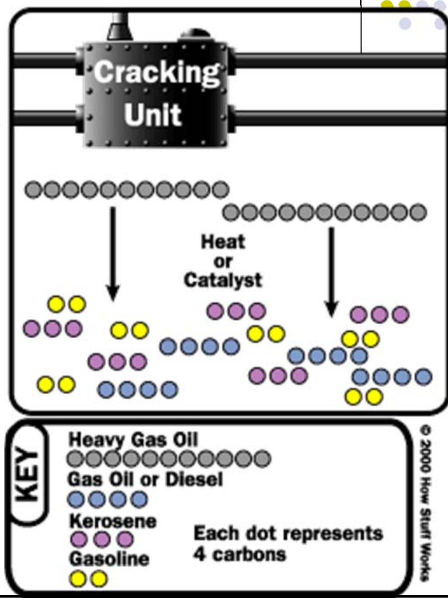
The Importance of Inorganic Chemistry

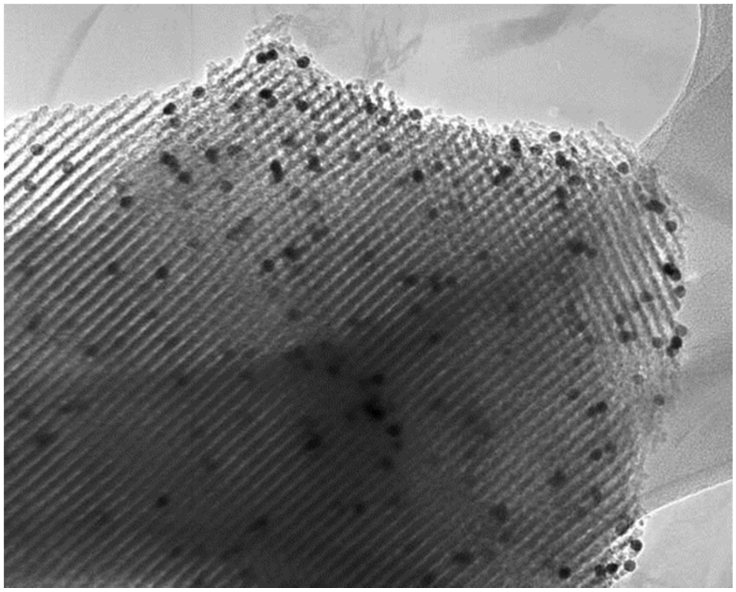
Oil Refining: Catalysts for converting crude oil to gasoline

Chevron Richmond Refinery

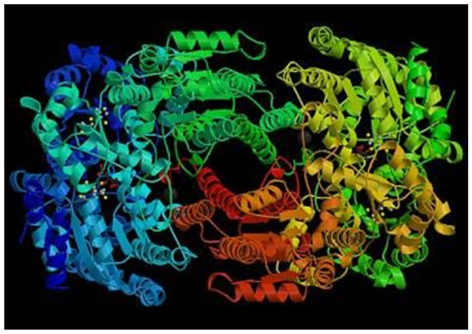
make transportation fuels, such as gasoline, jet fuel, and diesel fuel from crude oil

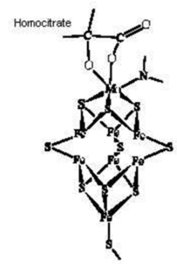
capacity of 245,000 barrels of crude oil per day.

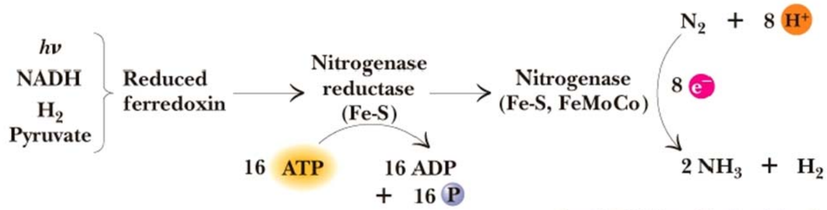




Bioinorganic Chemistry







Garrett & Grisham: Biochemistry, 2/e
Figure 26.6

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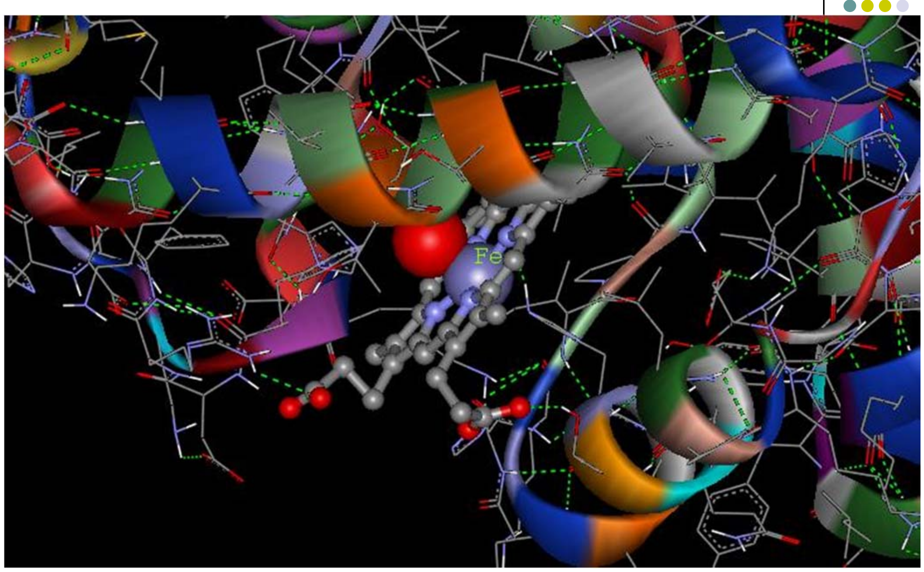
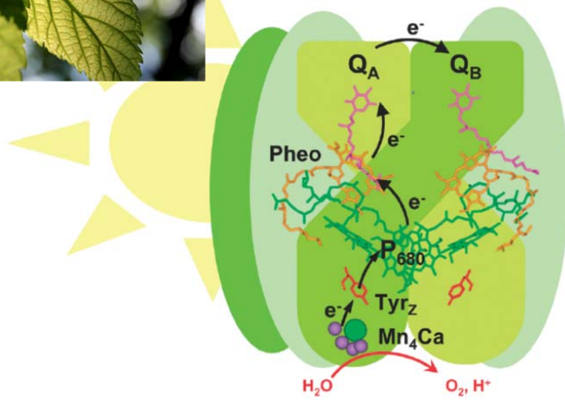
Hemoglobin



Photosynthesis



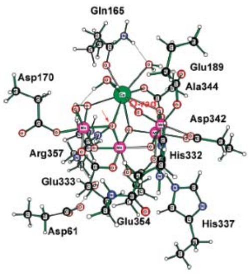


FIGURE 1. In PSII, excitation of the central chlorophylls P_{680} leads to charge separation in a series of electron-transfer reactions, generating reductive equivalents. New electrons are provided by oxidation of water at a catalytic Mn_4Ca complex, yielding molecular oxygen. This is the only known example of a rapid and efficient homogeneous water oxidation catalyst.

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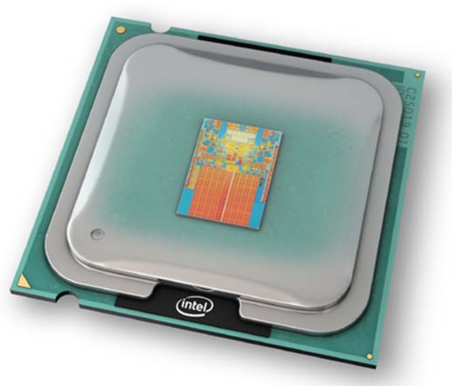
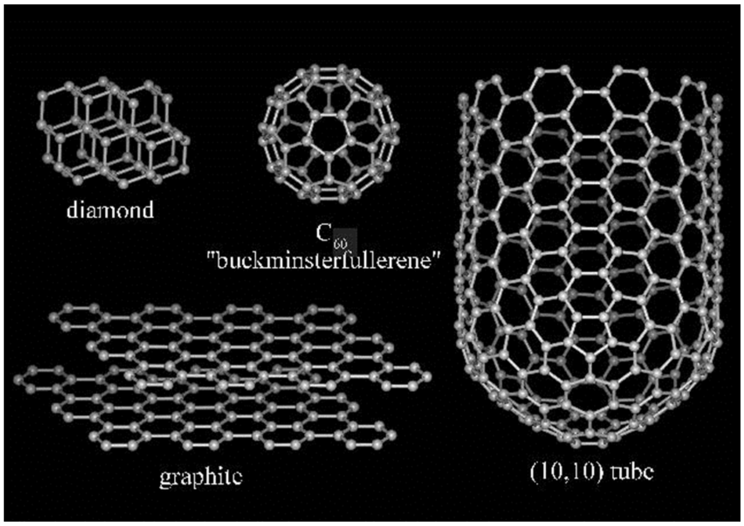
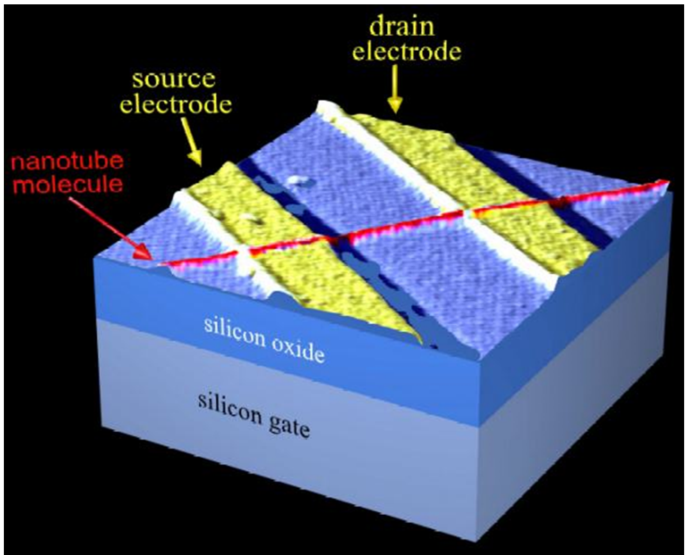
Semiconductor Industry



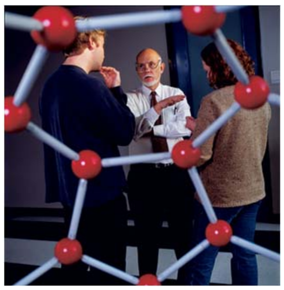
Nanoscience & Nanotechnology

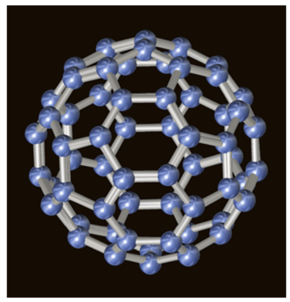




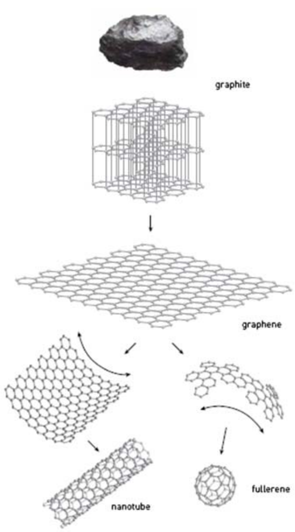
Buckyballs

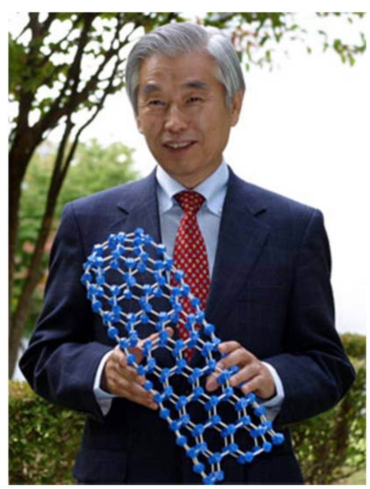
Harold Kroto from the University of Sussex, Robert Curl and Richard Smalley from Rice University—were awarded the Nobel Prize in Chemistry in 1996 for their discovery of a new composition of carbon, Carbon 60.





Carbon-60 buckyball is shaped like a soccer ball.





Carbon nanotube, 1991, NEC's Fundamental Research Laboratories

Discovery of Graphene

Andre Geim and Konstantin Novoselov
Nobel prize in Physics, 2010

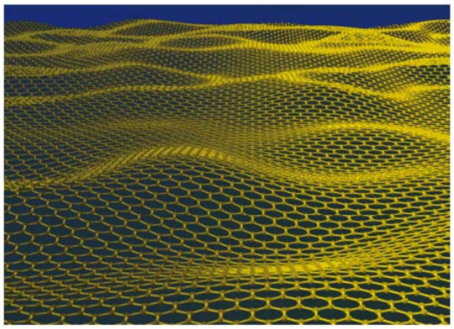
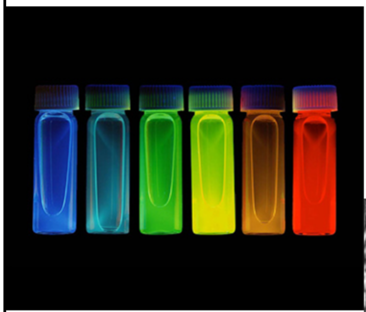
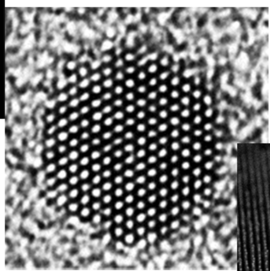
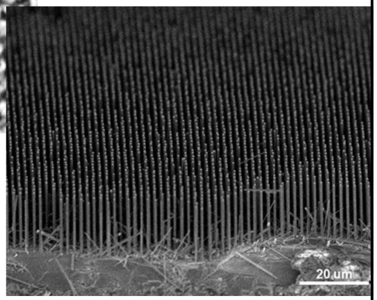


Figure 1. Graphene. The almost perfect web is only one atom thick. It consists of carbon atoms joined together in a hexagonal pattern similar to chicken wire.

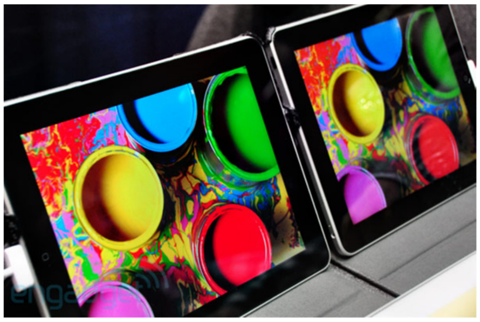






Quantum Dots, Nanowires

nanosys™

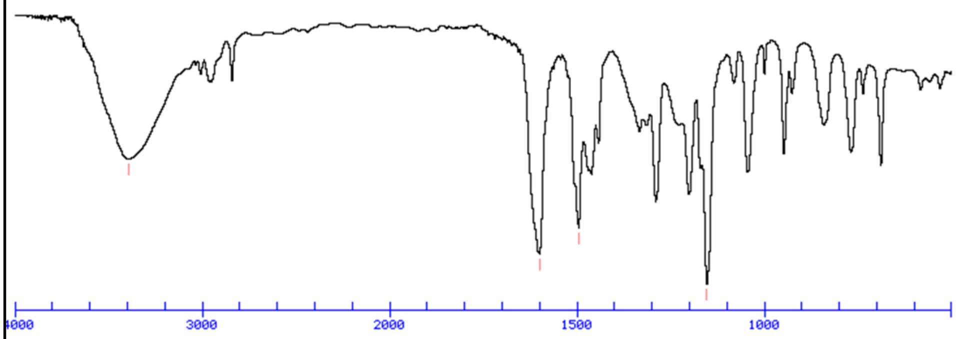


- Display technology
- Energy storage

Common applications of inorganic chemistry

- **Catalysts:** aluminum oxides, zeolites, transition metals
- **Semiconductors:** Si, Ge, GaAs, InP
- **Polymers:** silicones, $(SiR_2)_n$, polyphosphazenes
- **Superconductors:** NbN, $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2CaCu_2O_z$
- **Magnetic Materials:** Fe, $SmCo_5$, $Nd_2Fe_{14}B$
- **Lubricants:** graphite, MoS_2
- **Nanostructured materials:** nanoclusters, nanowires and nanotube
- **Fertilizers:** NH_4NO_3, $(NH_4)_2SO_4$
- **Paints:** TiO_2, $PbCrO_4$
- **Disinfectants/oxidants:** Cl_2, Br_2, I_2, MnO_4^-
- **Water treatment:** $Ca(OH)_2$, $Al_2(SO_4)_3$
- **Industrial processes:** H_2SO_4, NaOH, CO_2
- **Organic synthesis:** reaction catalysts
- **Biology:** Vitamin B_{12}, hemoglobin, Fe-S protein

What you will be able to do after taking this course?



Predicting IR spectra, chemical analysis

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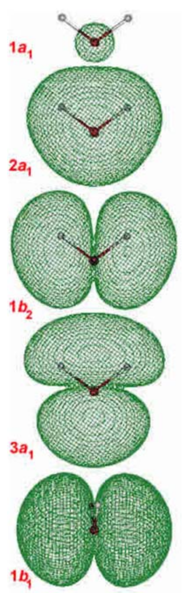
Understand Molecular Orbitals
Understand Chemical Reaction



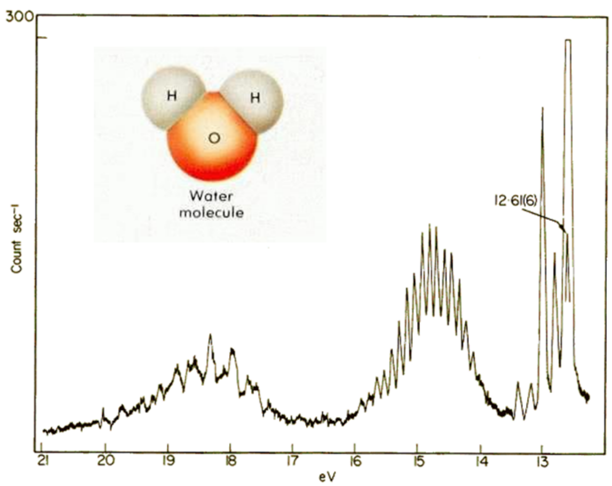
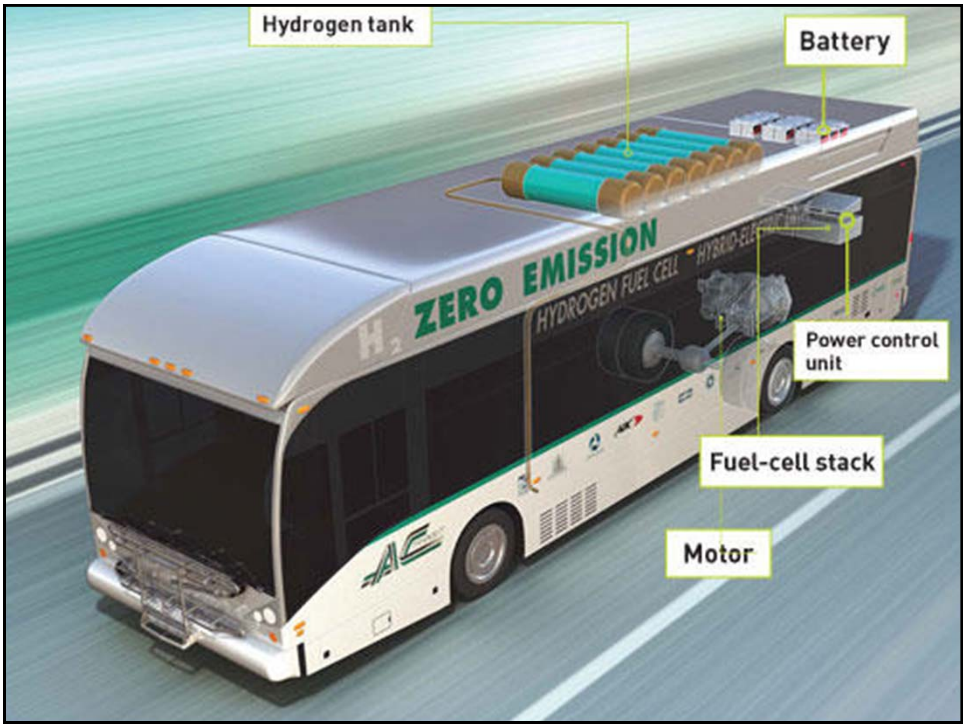


Figure 4.26 Water (full spectrum)



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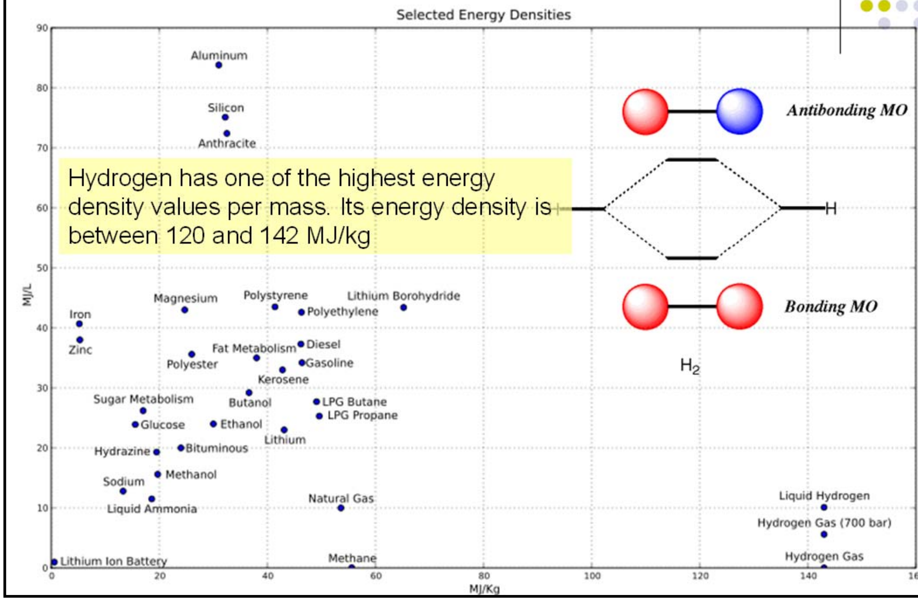
Hydrogen Car/Bus

A hydrogen bus system consists of non-renewable H_2 sources, hydrogen compressor, hydrogen tanks, and a bus propelled by electrical motors driven by a 60 kW hydrogen fuel cell stack and a 600V auxiliary battery.

Current source of hydrogen: reforming methane, a fossil fuel or electrolysis using grid-electricity

Hydrogen



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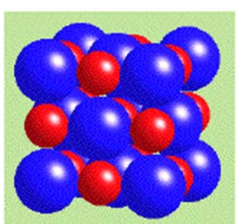
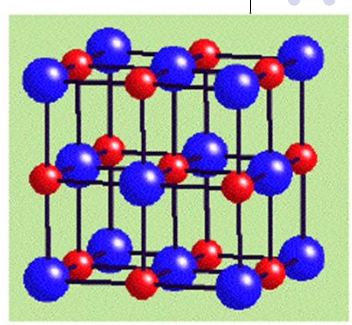
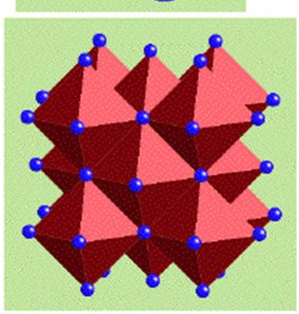
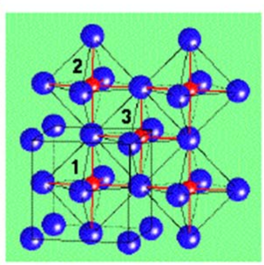
Common Crystal Structures and Electronic Structure

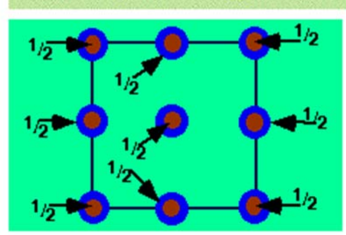


NaCl
Rock Salt
(Halite)









Atomic Structure

Reading: MT 1,2; DG 1

MT: Miessler, G. L., Tarr, D. A. *Inorganic Chemistry,*

DG: DeKock and Gray, *Chemical Structure and Bonding*, *2nd Ed*., University Science Books,

Rutherford Backscattering

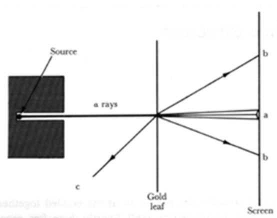


Figure 1-1 The experimental arrangement for Rutherford's measurement of the scattering of α particles by very thin gold foils. The source of the α particles was radioactive radium, which was encased in a lead block to protect the surroundings from radiation and to confine the α particles to a beam. The gold foil used was about 6×10^{-5} cm thick. Most of the α particles passed through the gold leaf with little or no deflection, at a. A few were deflected at wide angles, b, and occasionally a particle rebounded from the foil, c, and was detected by a screen or counter placed on the same side of the foil as the source.

Thomson Model   Rutherford Model

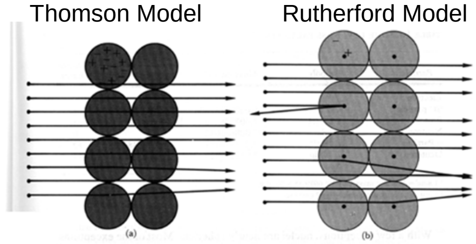
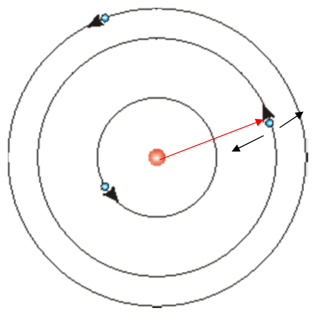
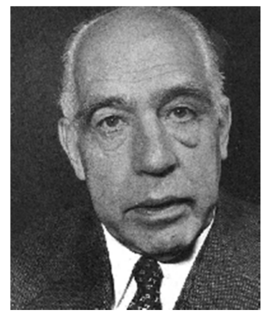


Figure 1-2 The expected outcome of the Rutherford scattering experiment, if one assumes (a) the Thomson model of the atom, and (b) the model deduced by Rutherford. In the Thomson model, mass is spread throughout the atom, and the negative electrons are embedded uniformly in the positive mass. There would be little deflection of the beam of positively charged α particles. In the Rutherford model all of the positive charge and virtually all of the mass is concentrated in a very small nucleus. Most α particles would pass through undeflected. But close approach to a nucleus would produce a strong swerve in the path of the α particle, and head-on collision would lead to its rebound in the direction from which it came.

1913, Danish Physicist, Niels Bohr





Electrostatic F_e = Outward F_o

$$\frac{m_e v^2}{r} = \frac{e^2}{r^2}$$

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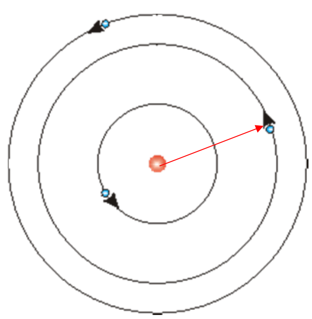
Total Energy:

E = KE + PE



$$\frac{m_e v^2}{r} = \frac{e^2}{r^2}$$

$$E = \frac{1}{2} m_e v^2 + \left(-\frac{e^2}{r}\right)$$

$$= \frac{1}{2}\left(\frac{e^2}{r}\right) - \frac{e^2}{r}$$

$$= -\frac{e^2}{2r}$$

E <0
What would be lowest energy state?

r → 0

Come to the rescue….

Energy Quantized (Planck Equation)

$$E = h\nu$$ → Frequency

Angular Momentum of electron is quantized.

$$m_e v.r = nh/2\pi$$ (v → velocity)

$$v = \frac{nh}{2\pi m_e r}$$

$$h = 6.62 \times 10^{-34} J.s$$

→ **Velocity of the electron quantized**

$$\frac{m_e v^2}{r} = \frac{e^2}{r^2}$$

$$v = \frac{nh}{2\pi m_e r}$$

→ $$r_n = \frac{n^2h^2}{4\pi^2 m_e e^2} = n^2 a_0$$

r_1=Bohr radius =a_0=0.529 Å

$$E = \frac{1}{2}m_e v^2 + (-\frac{e^2}{r})$$
$$= \frac{1}{2}(\frac{e^2}{r}) - \frac{e^2}{r}$$
$$= -\frac{e^2}{2r}$$

→ $$E_n = -\frac{e^2}{2r_n} = -\frac{2\pi^2 m_e e^4}{n^2h^2} = -\frac{k}{n^2}$$

k= 13.606 eV

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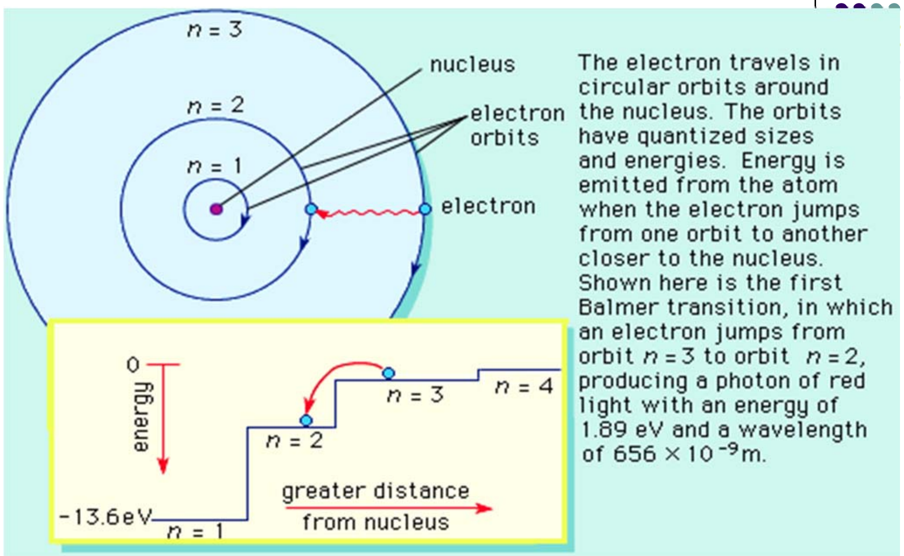

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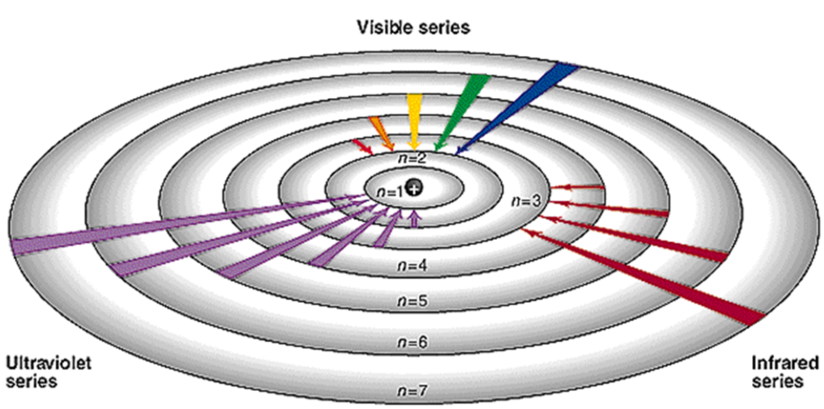

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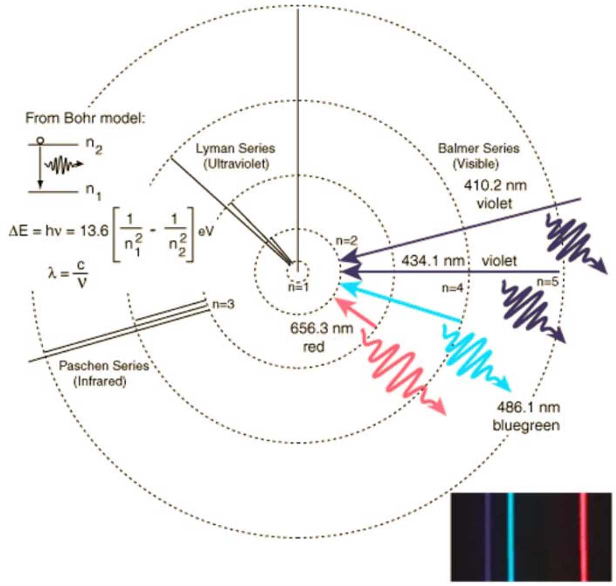

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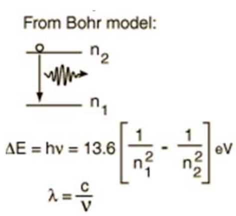


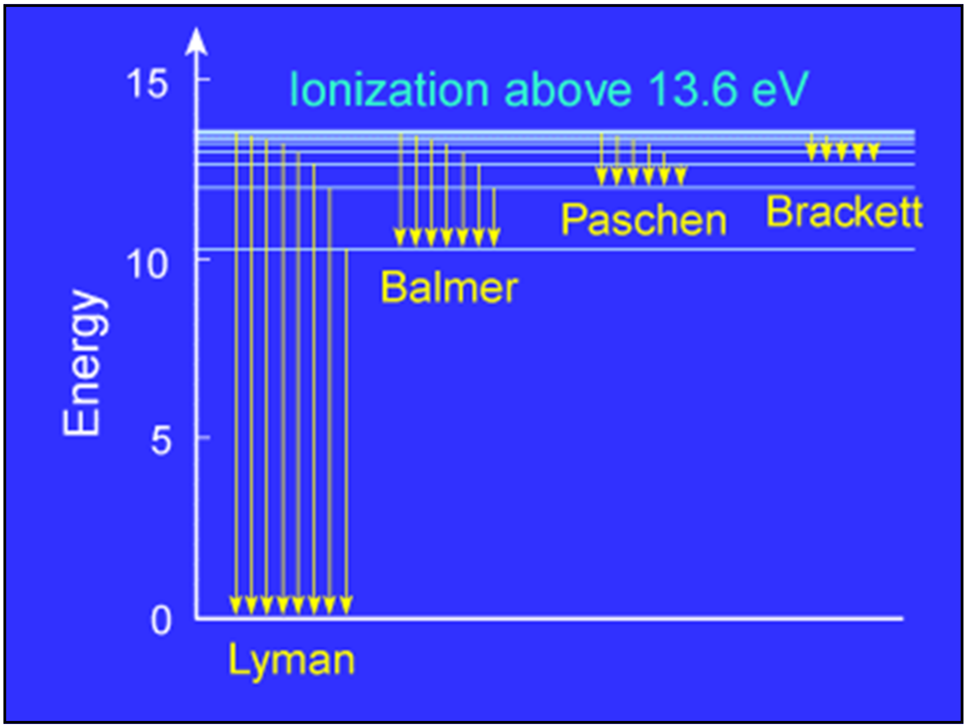
$$\bar{\nu} = R_H\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$wavenumber = 1/\lambda$$

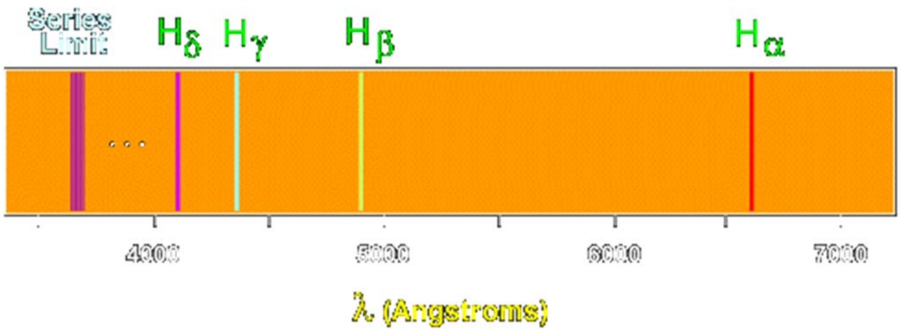
$$R_H = 109679 cm^{-1}$$ Rydberg constant

Lyman (n=1)

$$\bar{\nu}_H = 82259, 97492, 10824 cm^{-1}$$

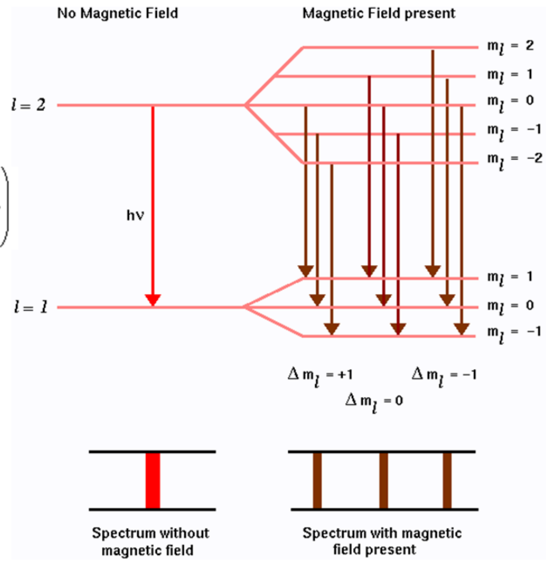


Balmer Series (n=2)



Bohr Model can NOT explain Zeeman effect.

$$\Delta E = h\nu = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$



Dual Nature of Matter

Reading: MT 2, DG 1

1924, French physicist Louis de Broglie:

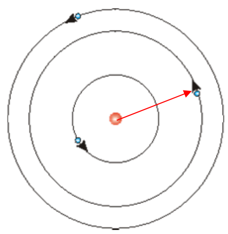
All matter possesses wave properties

$$\lambda = \frac{h}{m\text{v}} = \frac{h}{p}$$

$$h = 6.62 \times 10^{-34}\, J.s$$

Baseball: 200g
Speed: 3000cm/sec (67 miles/hour)

→ $\lambda = 10^{-32}\, cm$



Electron: $10^{-27}\, g$

Same velocity

→ $\lambda = 20\mu m$

Experimental evidence: electron diffraction

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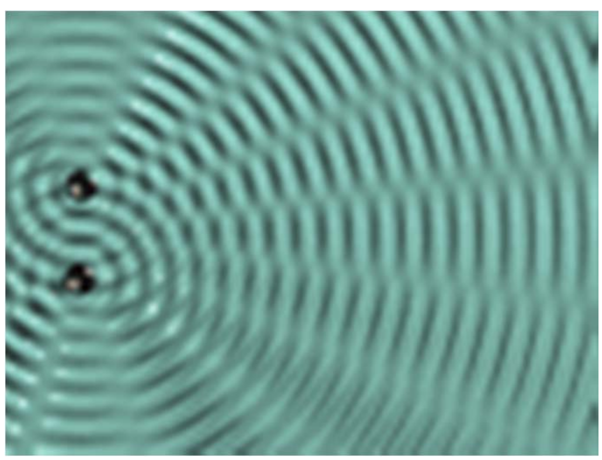
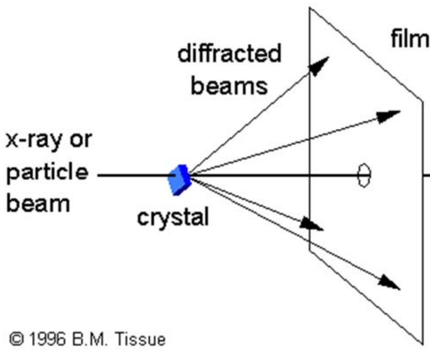
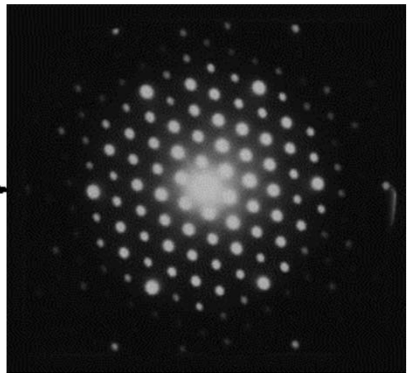
Interference between two point waves







The uncertainty principle

1927, Werner Heisenberg

It is impossible to know simultaneously both the momentum and the position of a particle with certainty.

$$(\Delta p_x)(\Delta x) \geq \frac{h}{4\pi}$$

$$h = 6.62 \times 10^{-34}\, J \bullet s$$

Accuracy: one part per trillion

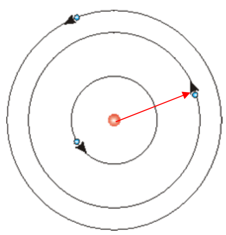
Baseball: 200g

Speed: 3000 cm/sec (67 miles/hour)

$$p = 6\times10^{5}\, g\cdot cm\cdot \sec^{-1}$$

$$\Delta p = 6\times10^{-7}\, g\cdot cm\cdot \sec^{-1}$$

$$\rightarrow \quad \Delta x = 10^{-21}\, cm$$



Electron: $10^{-27}\, g$

Same velocity

$$p = 3\times10^{-24}\, g\cdot cm\cdot \sec^{-1}$$

$$\Delta p = 3\times10^{-36}\, g\cdot cm\cdot \sec^{-1}$$

$$\rightarrow \quad \Delta x = 10^{9}\, cm$$

Electron motion: wavefunction ψ

Describes spatial properties of electron.

Must be: single valued, continuous, normalized

Schrodinger wave equation (1926):

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi = E\psi$$

$\psi : wavefunction / eigenfunction$

$x, y, z : coordinates$

$m : mass$

$h : Planck's$

$E : total-energy$

$V : potential-energy$

$$\rightarrow \quad \hat{H}\psi = E\psi$$

$\hat{H}$: Hamiltonian operator

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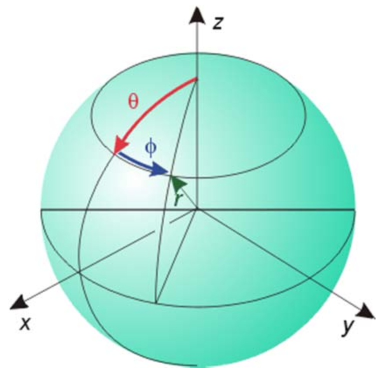
Converting to polar coordinates:

$$\psi_{n,l,m_l} = R_{n,l}(r) \cdot Y_{l,m_l}(\theta,\phi)$$

$R_{n,l}(r)$ **Radial part**

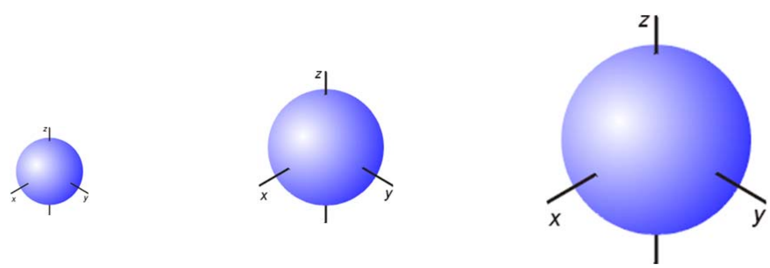
$Y_{l,m_l}(\theta,\phi)$ **Angular part**



n=1,2,3,4….= principle quantum number

(1): determine the energy of the electron
(2): indicate approximately the effective volume of the orbital.

$$E_n = -\frac{e^2}{2r_n} = -\frac{2\pi^2 m_e e^4}{n^2 h^2} = -\frac{k}{n^2}$$



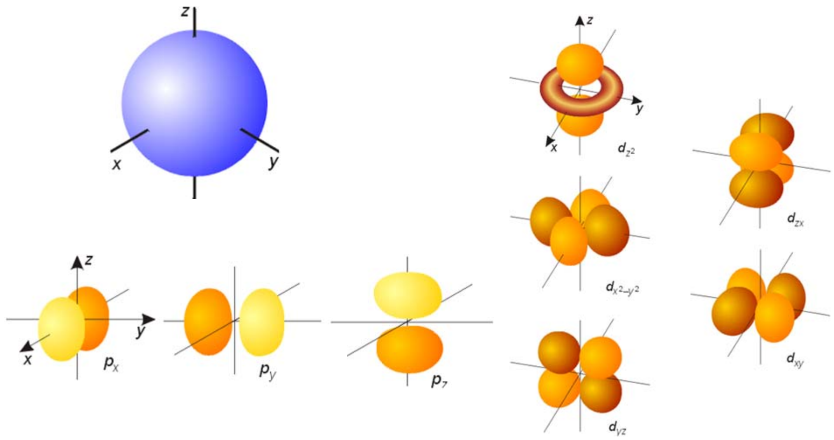
n=1 2 3

l **= angular momentum (or shape) quantum number**

0,1,2,3,4……

s, p, d, f…..

Determine general shape of the orbital

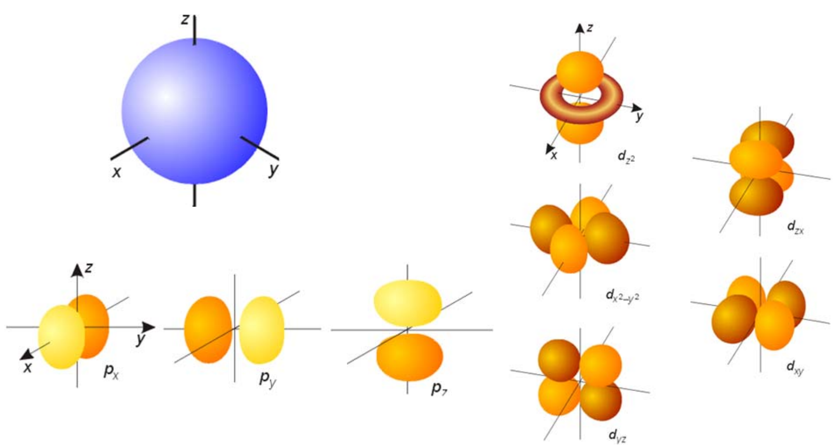


For each n, there are n possible angular momentum value

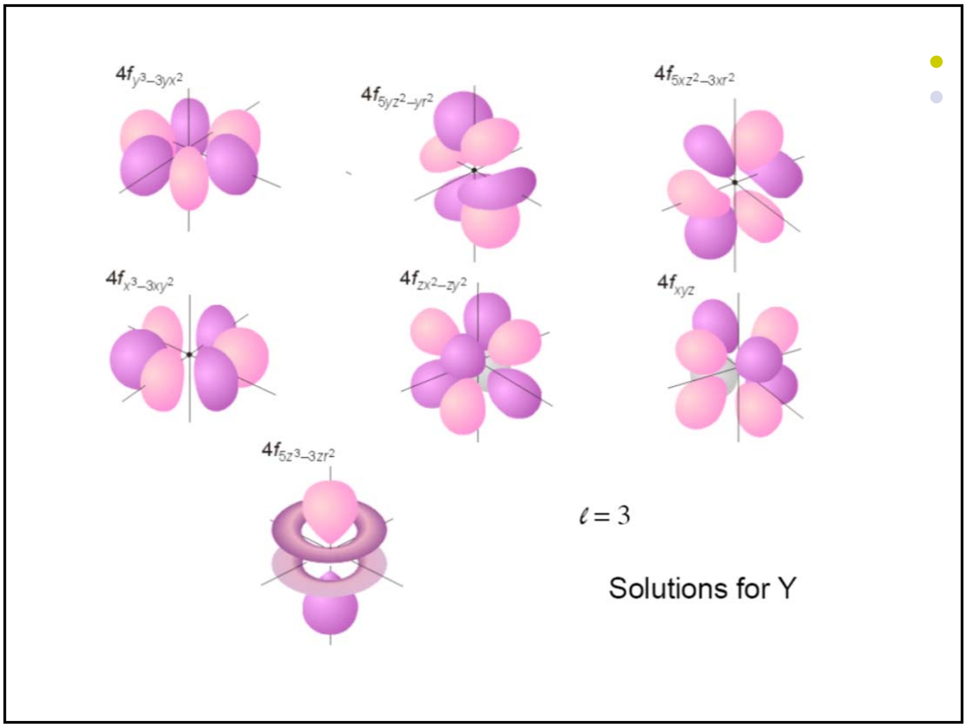
m_l **= magnetic/orbital orientation quantum number**

0,±1,±2,±3....

Determine orbital spatial orientation



For each l, there are 2l+1 possible m_l *value.*



$4f_{y^3-3yx^2}$
$4f_{5yz^2-yr^2}$
$4f_{5xz^2-3xr^2}$
$4f_{x^3-3xy^2}$
$4f_{zx^2-zy^2}$
$4f_{xyz}$
$4f_{5z^3-3zr^2}$
$\ell = 3$
Solutions for Y