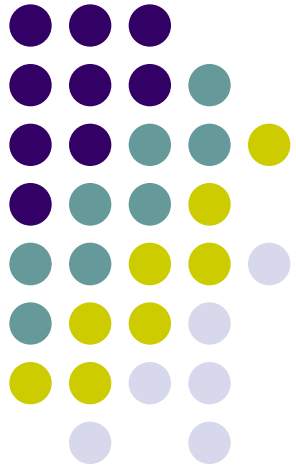
Structure of matter



ATOM

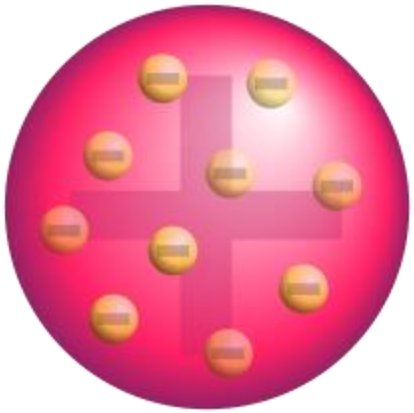
ατομος – indivisible

- Greek atomists - **Democrite and Leukip** 300 b.c.
- **R. Bošković** - accepts the concept of atom and defines the force
- **J. Dalton** - accepts the concept of atom and defines the chemical element 1800.g
- **R. Brown** - experimental proof of atom existence 1827 g.
- **D. Mendeleev** - periodic table of elements 1866 g.

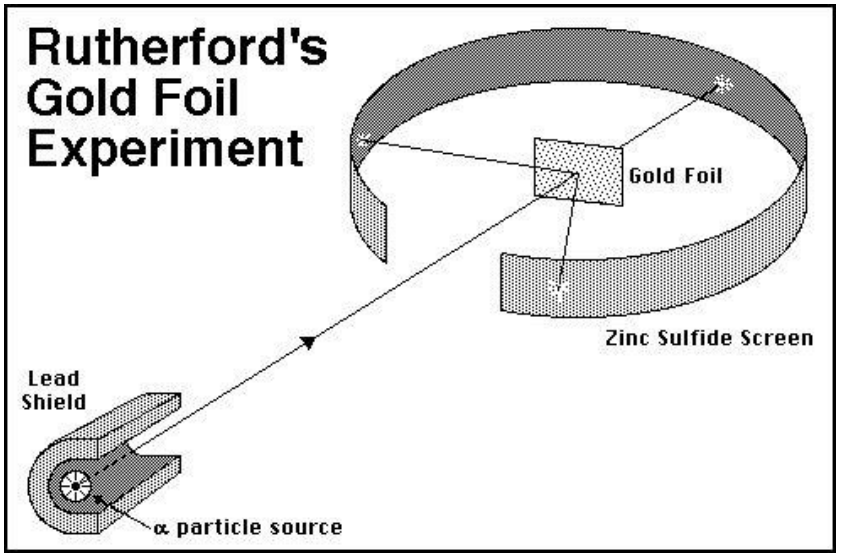
Atomic structure

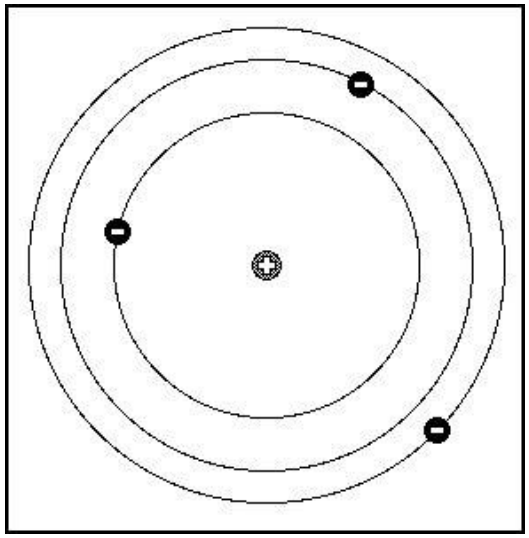
- **J.J.Thomson** - discovery of electron 1897, first atomic model
- **E. Rutherford** - discovery of nuclear atom (planetary model)
- **N. Bohr** - model of hydrogen atom - postulates
- **A.Sommerfeld** - additional quantum states (ℓ, m)

Thomson's model of atom



planetary model of atom





Balmer's formula and Bohr's postulates for hydrogen atom

$$\frac{1}{\lambda} = \frac{b k^2}{k^2 - n^2} \qquad \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3,4,..$$

principal quantum number

- I. when electron moves on equipotential surface, in the electric field of nucleus, there is no absorption or emission of energy - **stationary** state

- II. energy emission - by transition of electron from orbit of higher energy to orbit of lower energy: $\Delta E = E_n - E_m$

- III. radius of spherical orbit and energy of equipotential surface have only discrete values:

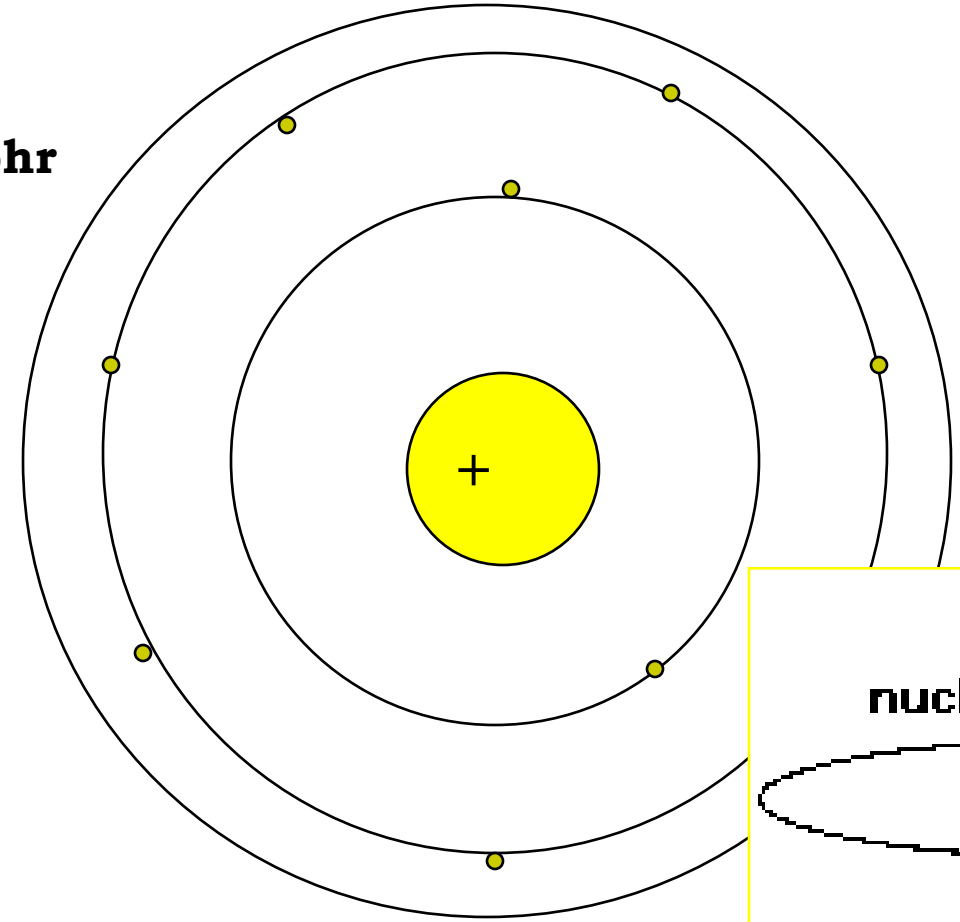
$r_n \sim n^2$ $\qquad$ $E_n \sim 1/n^2$

Extension of model – new quantum numbers

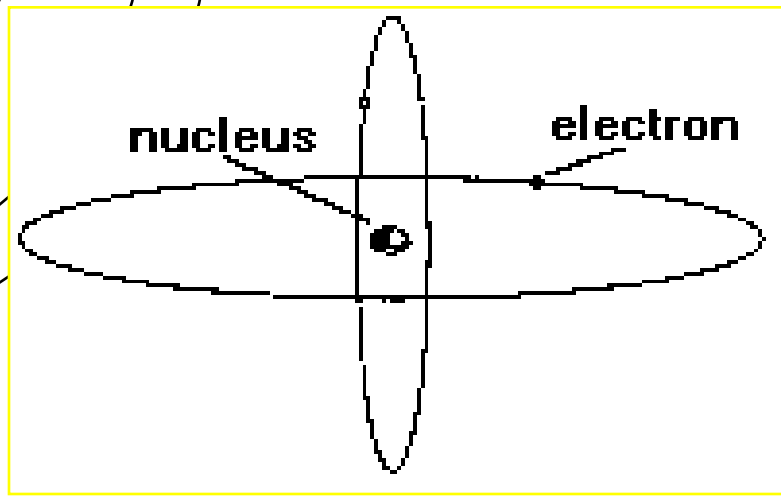
- Bohr's model – in accordance with emission spectrum of hydrogen atom
- atoms with more electrons produced spectra with more lines, not predicted by Bohr's theory
- Sommerfeld added two more quantum numbers for the characterization of electrons in the same shell - ℓ and m_ℓ
- this could be possible if orbits are not circular but elliptic
- Uhlenbeck and Goudsmit introduced spin (S) as intrinsic angular moment of electron in order to explain the behavior of atom in magnetic field - new quantum number m_S

Early models of atom

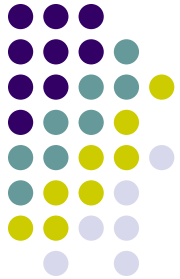
Bohr



Sommerfeld



The wave nature of particles
L. de Broglie



- the quantization of orbits is required to get the circumference for the constructive interference of particle waves:

$$2\, r_n \pi = k\, \lambda$$

- the wavelength of particle is determined by its momentum:

$$\lambda = \frac{h}{mv}$$

- observed diffraction of electron on crystal was the direct proof of its wave nature

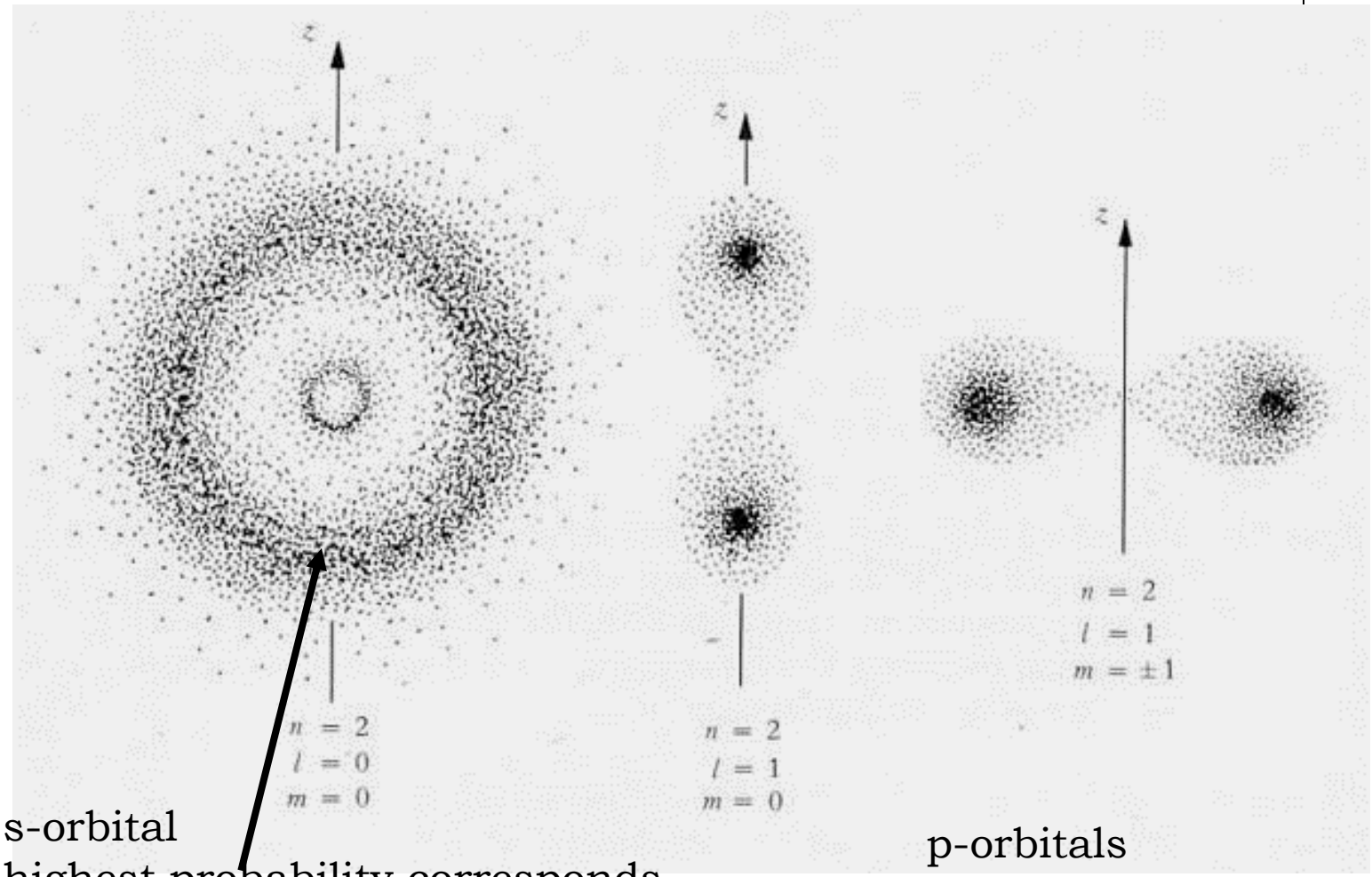
Quantum mechanics

- **E. Schrödinger** - **wave mechanics**
- electron motion in atom is described by wave function $\Psi(r)$
- he postulated the time independent equation of motion for the hydrogen atom

$$\nabla^2\Psi + \frac{8\pi^2 m}{h}\left(E + \frac{ke^2}{r}\right)\Psi = 0$$

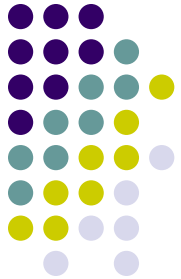
- the solutions are wave functions and energies for stationary states which depend on 3 quantum numbers: n, ℓ, m_ℓ
  in each state there are n^2 functions of same energy
- $\Psi^2(r)$ represents the distribution of probability density of electronic cloud around the nucleus

distribution of probability density - electronic cloud



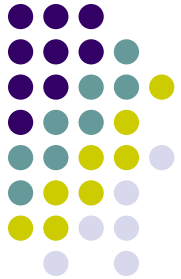
s-orbital
highest probability corresponds to Bohr's radius

p-orbitals



- **W. Heisenberg** - **matrix mechanics**
- the only reliable parameters are those which could be measured – observables like density, intensity, energy
- all possible events are considered but with different probabilities
- the physical quantities are expressed as matrices, and their relations are presented by matrix equations

$$\begin{bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{bmatrix}$$



Completion and expansion of theory

- **M. Born and N. Bohr**: both theoretical approaches are included in unique theory of quantum mechanics
- **W. Pauli**: introduced the concept of spin into theory
- **P. Dirac**: expanded the theory by introduction of relativistic effects - **field quantization**

Heisenberg's uncertainty principle

the philosophical background of quantum mechanics

- it is not possible to determine simultaneously and with arbitrarily high precision the values of particular pairs of observables

$$\Delta x \cdot \Delta p \phi \frac{h}{4\pi}; \qquad \Delta E \cdot \Delta t \phi \frac{h}{4\pi}$$

- some observations are mutually incompatible; some pairs of properties are not just simultaneously unknown, they are unknowable≥
- subatomic particles do not have predicted trajectory
- if something is happening now, there is only a probability that certain event will happen in future
- the cause and consequence are not unambiguously connected

- **orbital** - region of highest probability to find electron
- **electronic cloud** - regions of probability to find electron

Quantum numbers

- ***n* - principal quantum number**: introduces quantization of electron energy in electric field of nucleus; energy shells: K,L,M,N..; the number of electrons in one shell is $2n^2$

$$E \propto \frac{1}{n^2}$$

- ℓ **- orbital quantum number**: introduces quantization of orbital momentum, *L*; orbitals s,p,d..; values: 0, 1, ... *n*-1

$$L \propto \sqrt{\lambda(\lambda+1)}$$

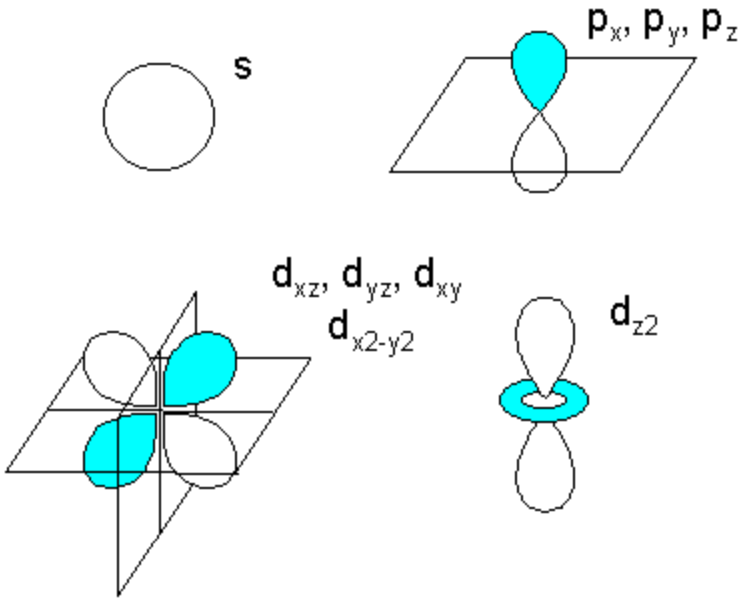
- m_ℓ **- magnetic quantum number**: discrete orientations of orbital momentum vector in the external magnetic field;
- values: from $-\ell$ to $+\ell$

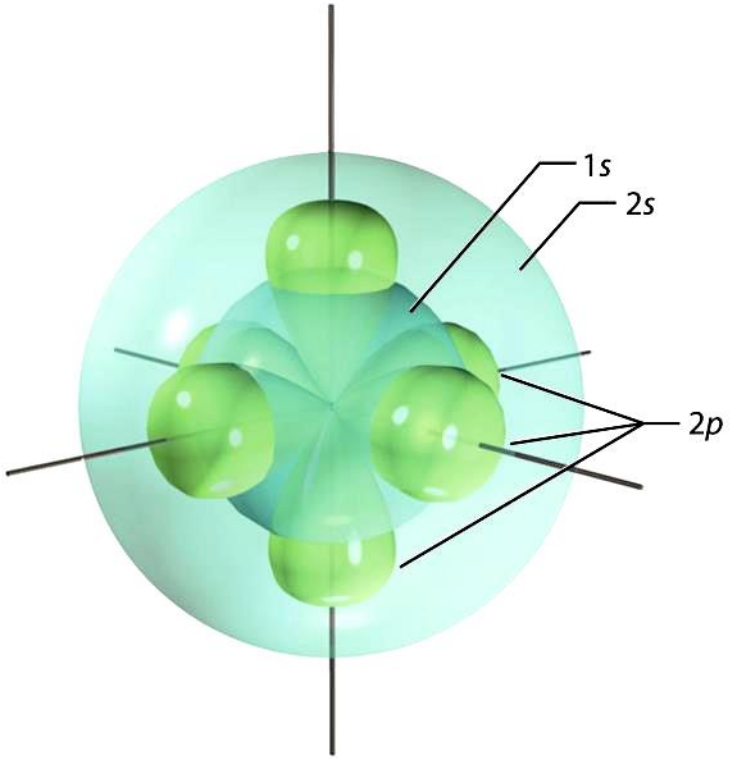
$$L_z \propto m_\lambda$$

- m_s **- spin magnetic quantum number**: discrete orientation of spin vector in the external magnetic field; two values +½ and -½

$$S_z \propto m_S$$

Atomic orbitals



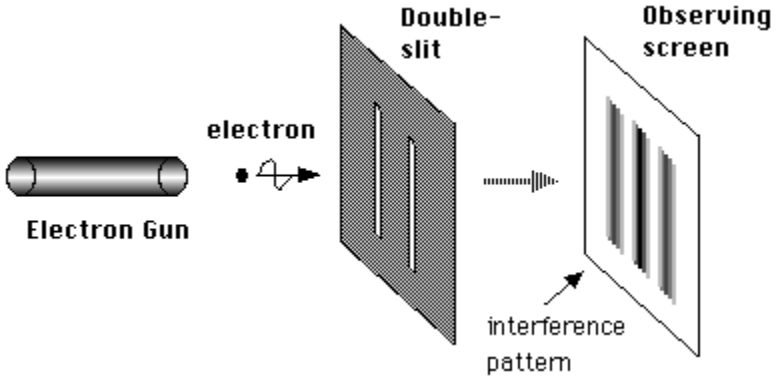


Pauli's exclusion principle

- the wave functions for two electrons in the shell cannot be the same – $2n^2$ electrons in one shell
- that principle determines the atomic volume - the dimensions of molecules and bodies
- the lowest energy levels are most populated

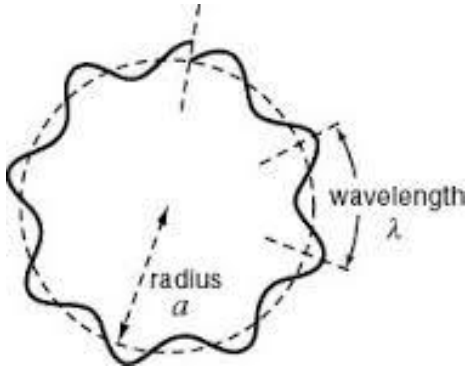
- **L. de Broglie**

electron: particle or wave?

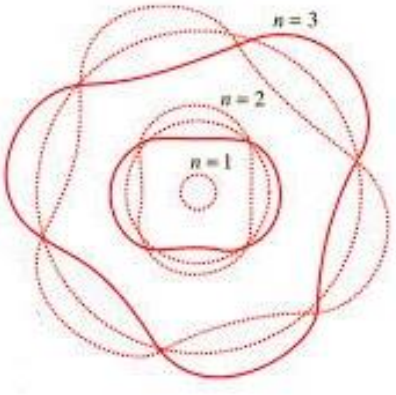


$$\lambda = h/mv$$

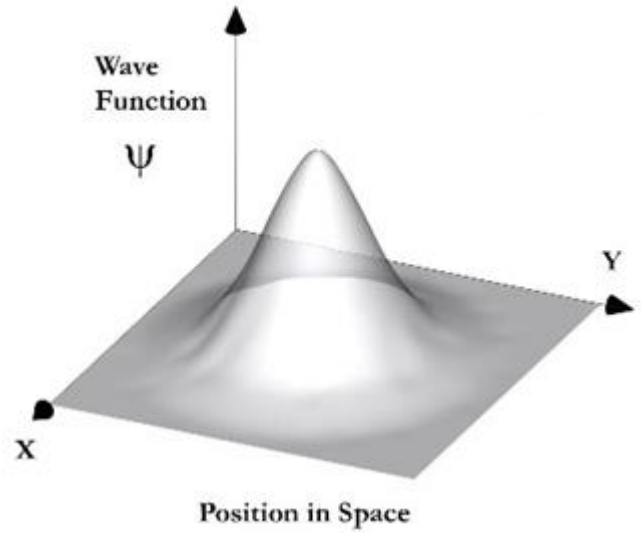
Constructive interference of electron



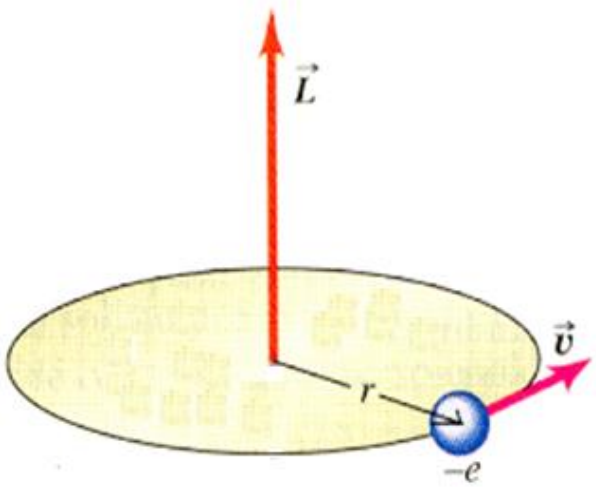
$$2r_n\pi = k\lambda$$



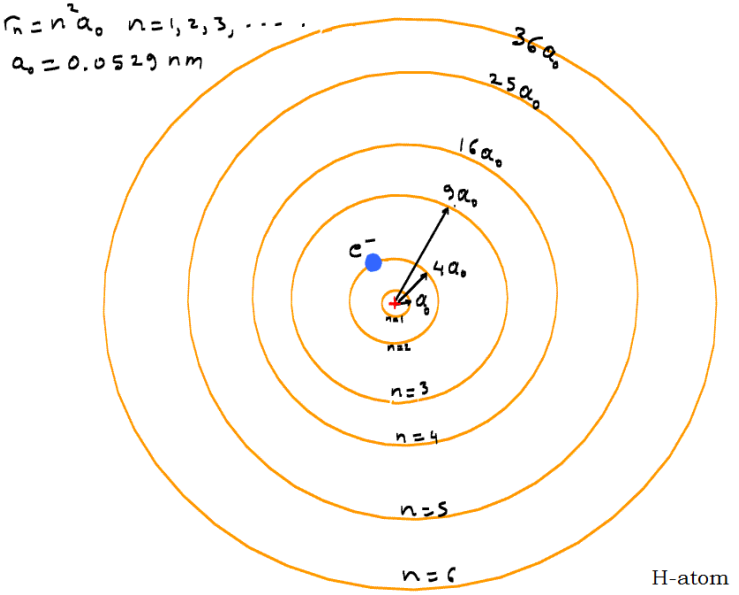
- **E. Schrodinger**
- The most general form is the time-dependent Schrödinger equation, which gives a description of a system evolving with time; equation that describes the changes over time of a physical system in which quantum effects, such as wave–particle duality, are significant.



Orbital (angular) momentum of electron



$$\vec{L} = m\vec{r} \times \vec{v}$$

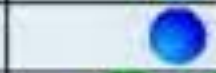
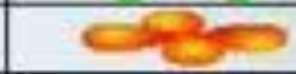
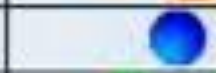
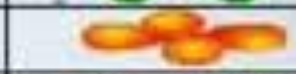


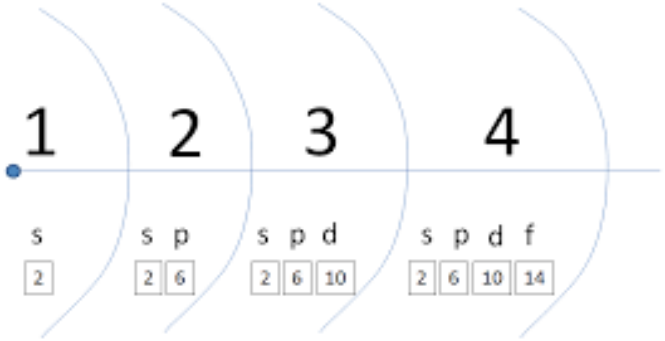
H-atom

angularni moment elektrona

Quantized magnitude of orbital momentum!!! → orbitals

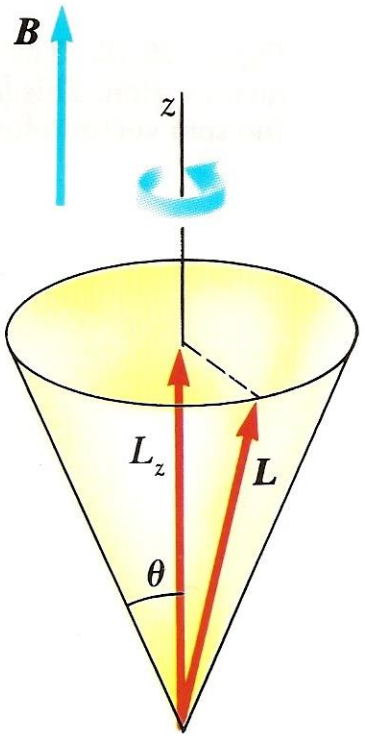
l	$0,1,2,3,..(n-1)$

n = 1	l = 0		s orbital
n = 2	l = 0		s orbital
	l = 1		p orbital
n = 3	l = 0		s orbital
	l = 1		p orbital
	l = 2		d orbital
n = 4	l = 0		s orbital
	l = 1		p orbital
	l = 2		d orbital
	l = 3	complex shape	f orbital

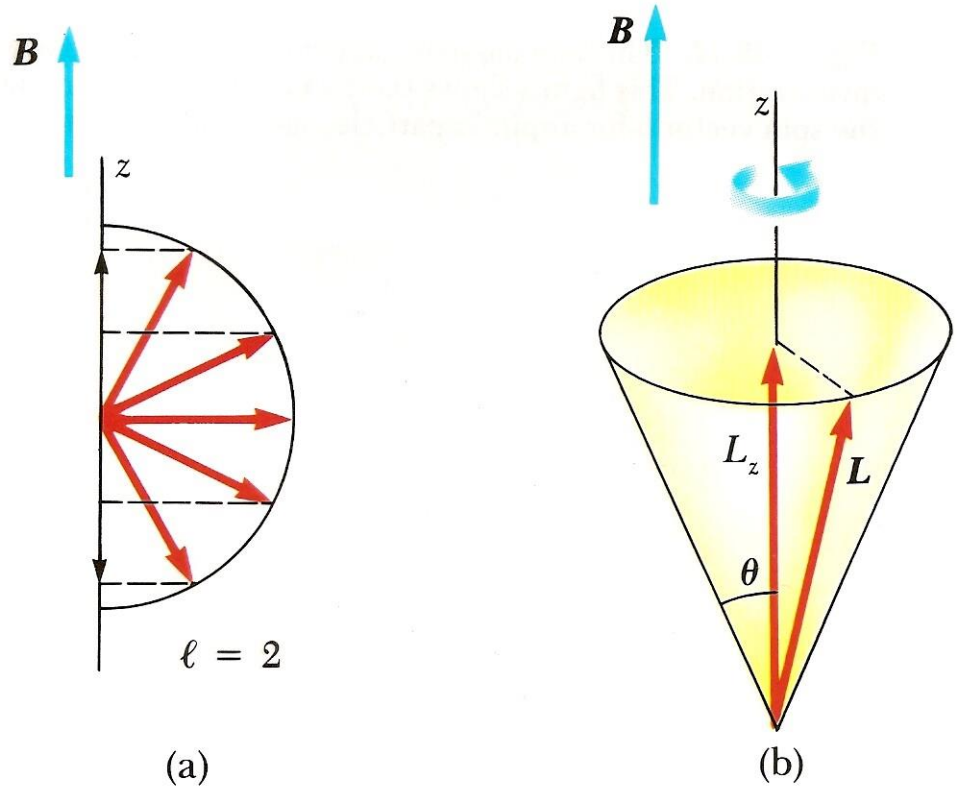


Electron has an orbital momentum.

In external magnetic field → orbital magnetic momentum has precession

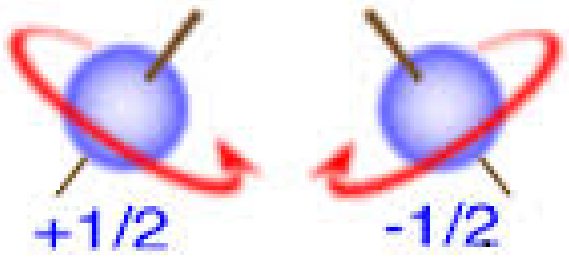


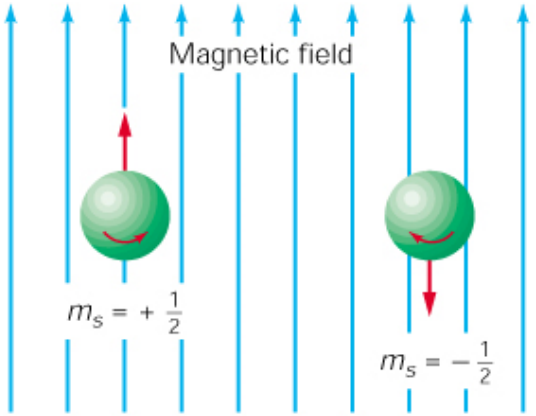
The direction of orbital momentum is quantized – discrete orientation.



m_l	$-l, (-l+1), .., -1, 0, 1, .. (l-1), l$

In external magnetic field → discrete orientation of spin

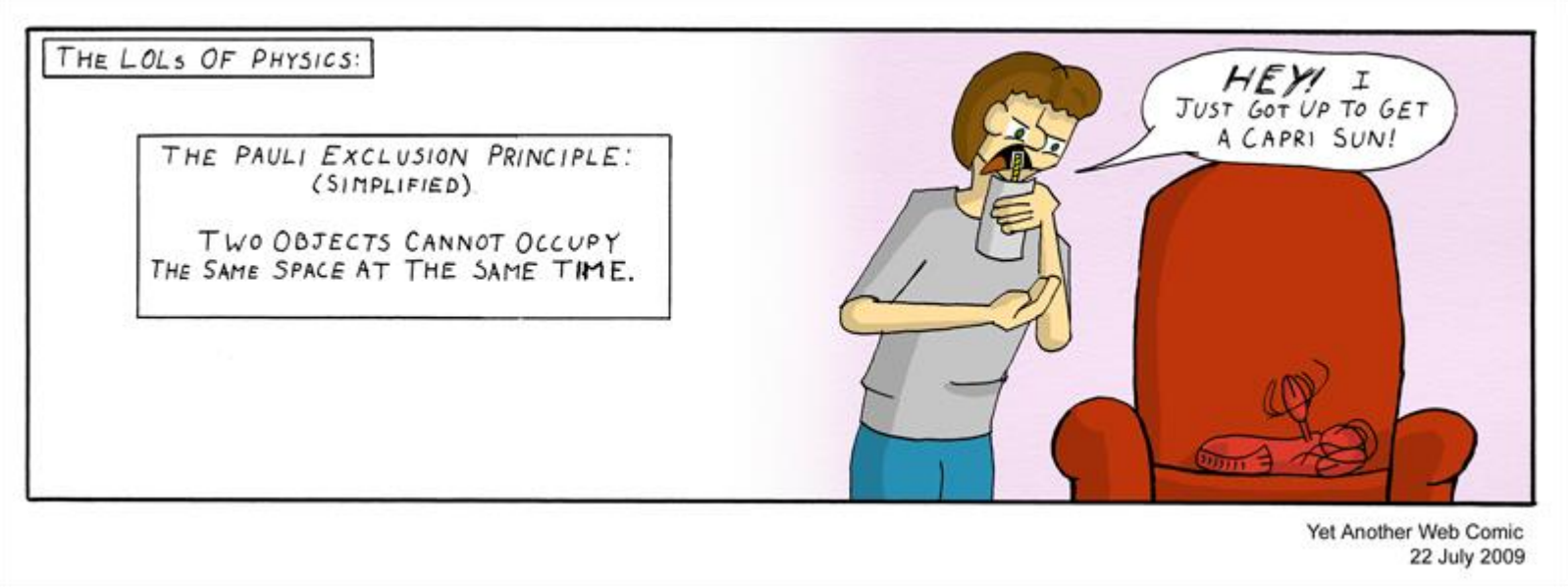




The presentation of spin is not real!

m_s	$-\frac{1}{2}, +\frac{1}{2}$

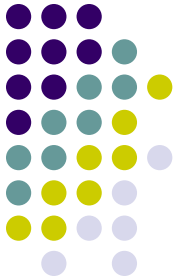
PRINCIPAL	$\boldsymbol{n}$	$1,2,3,..\infty$
ORBITAL	$\boldsymbol{l}$	$0,1,2,3,..(n-1)$
MAGNETIC ORBITAL	m_l	$-l,(-l+1),..,-1,0,1,..(l-1),l$
MAGNETIC SPIN	m_s	$-\frac{1}{2},+\frac{1}{2}$



MOLECULE

- molecule is a stable association of atoms
- its structure is determined by requirement for the minimal potential energy of the system
- the solution of Schrödinger's equation gives molecular orbitals for the electrons in chemical bonds
- inner orbitals are atomic orbitals
- energy of bonding (full) orbital and antibonding (*) (usually empty) orbital
- the antibonding orbital can be populated when the molecule is in excited state - higher energy

Types of molecular bonds

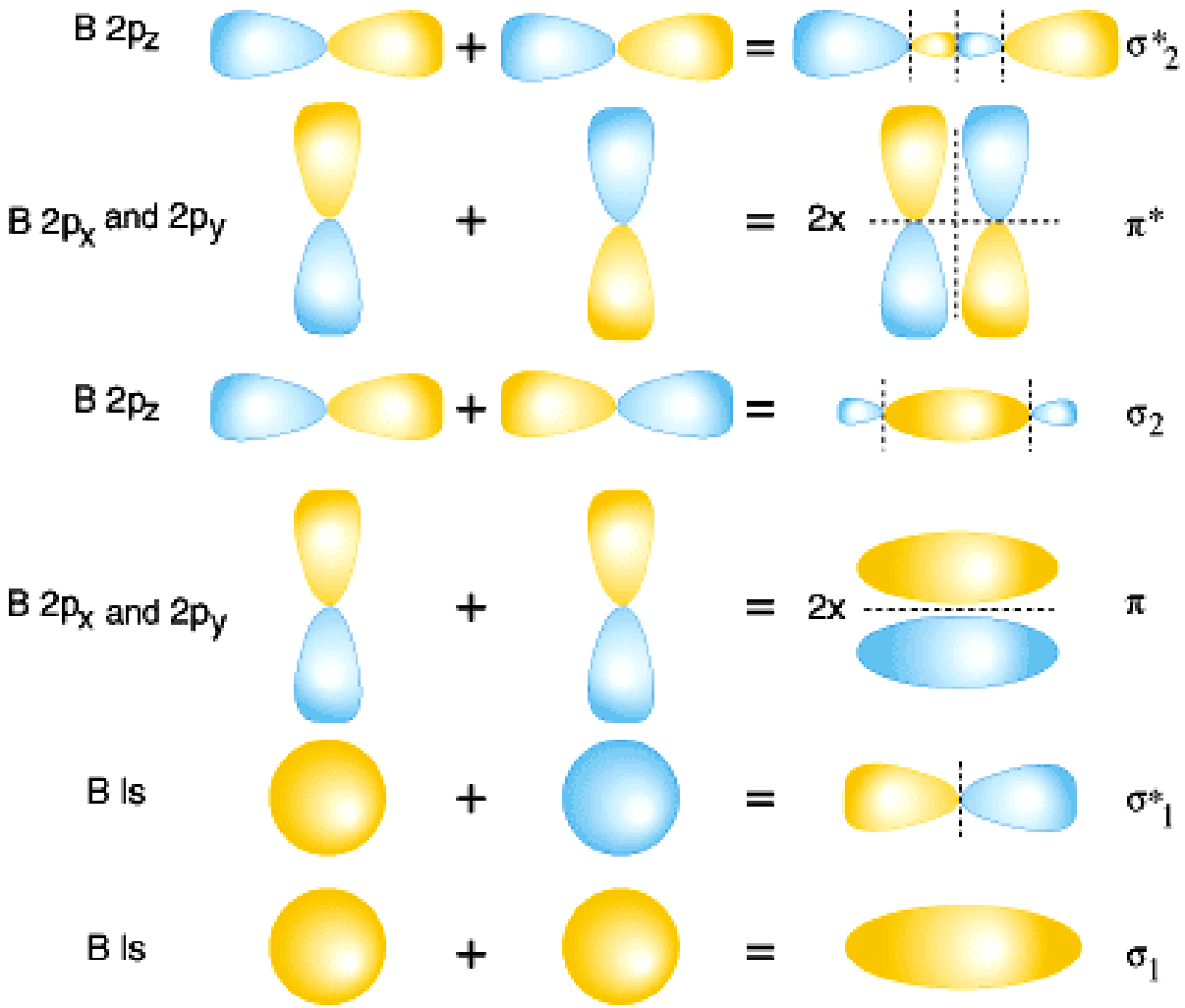


- **Covalent bond**
- formed from the atomic orbitals of electrons in outer shell - electron pair in molecular orbital
- atomic orbitals molecular orbital

  s σ or σ^*

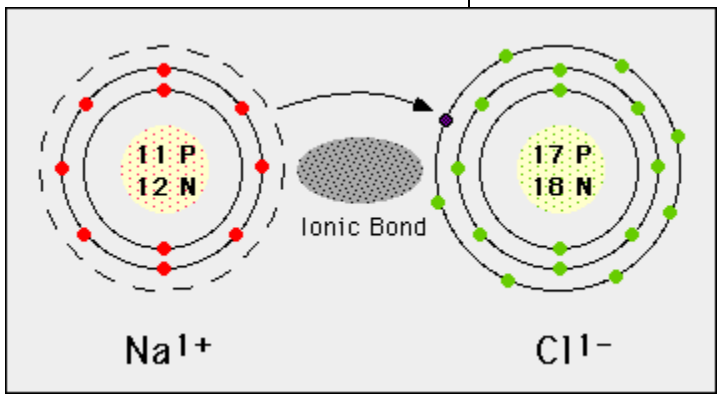
  p π or π^*
- hybrid molecular orbitals; sp, sp^2, sp^3 ...
- the direction of chemical bonds are determined by maximal overlapping of atomic orbitals - molecules have determined volume structure and shape

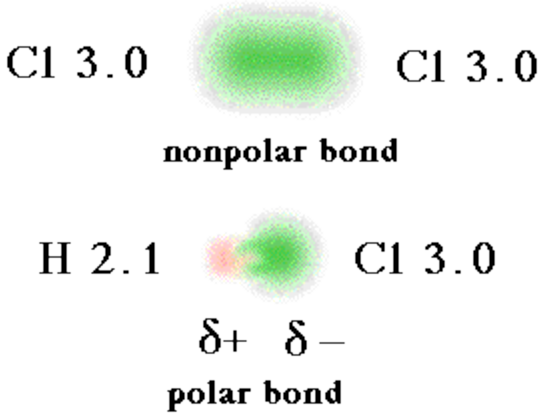
Some types of covalent bonds



- **Ionic bond** – the electron affinity of one atom is much higher than of the other
- electron density is transferred to one atom: in the process of dissociation we get two counter ions
- - there is additional electrostatic interaction between two ions which lowers the energy of the bond
- **Polar bond** – part of molecule is more electronegative and the electron cloud is located mostly over that part
- the centers of positive and negative charge in the molecule are separated; polar molecule is acting as electric dipole with moment

$$\vec{p} = q\vec{l}$$





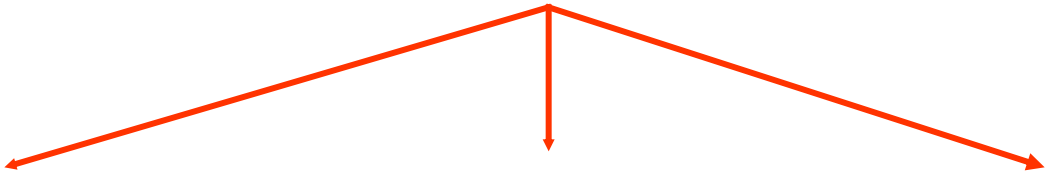
Intermolecular bonds

- **Electrostatic and van der Waals's bonds**
  - between two close smaller molecules
  - between individual sections of large molecules
  - between molecules in water
- **Hydrogen bonding – H bridge**
  - hydrogen atom bound to oxygen, nitrogen, or halogen element forms the bond with other such atom at different part of macromolecule
  - hydrogen bond has electrostatic character
- **Hydrophobic interaction**
- - is the result of specific properties of water as solvent; non polar molecules disturb the hydrogen bonding network in water; disturbance is minimized when these molecules form clusters which are stabilized by hydrophobic interactions

Energy of the molecule

- energy of molecule is always lower than the total energy of its free atoms
- energy of molecular bond is the amount of energy needed for the separation of atoms

energetic states

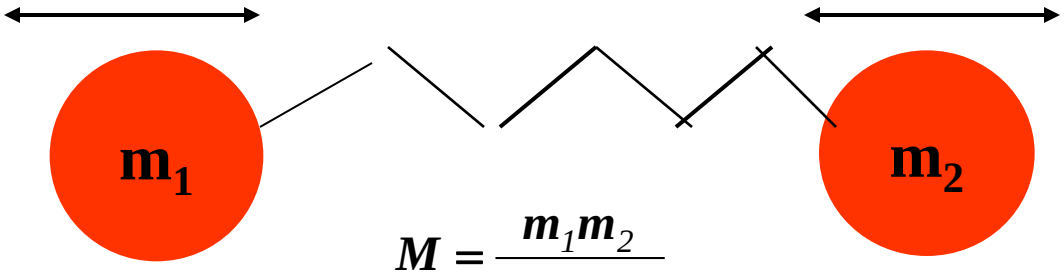


electronic	vibration	rotational
transitions between molecular orbitals	transitions between vibration states	transitions between rotational states

Vibrations of atoms in two atom molecule

- quantum mechanics
- vibration quantum number ν

$$E = \frac{h}{2\pi\sqrt{\frac{k}{M}}}\left(\nu + \frac{1}{2}\right) = \frac{h}{2\pi}\omega\left(\nu + \frac{1}{2}\right)$$



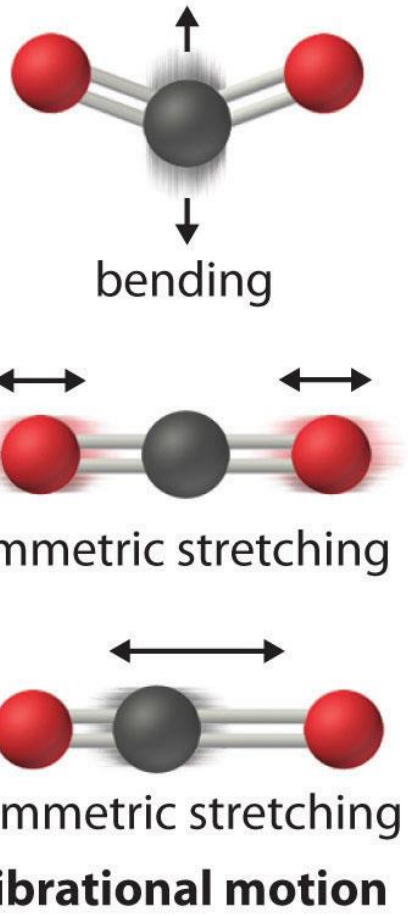
$$M = \frac{m_1 m_2}{m_1 + m_2}$$

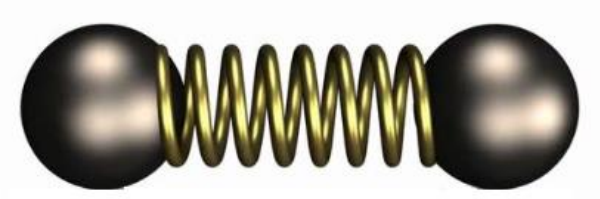
reduced mass of the molecule

$$\Delta E = E(\nu+1) - E(\nu) = \frac{h}{2\pi}\omega\left[\nu + 1 + \frac{1}{2} - \nu - \frac{1}{2}\right] = \frac{h\omega}{2\pi}$$

~ 0.1 eV

energy of transition between adjacent states is constant





http://physics.mef.hr/Predavanja/Predavanje%20spektroskopija/index.html

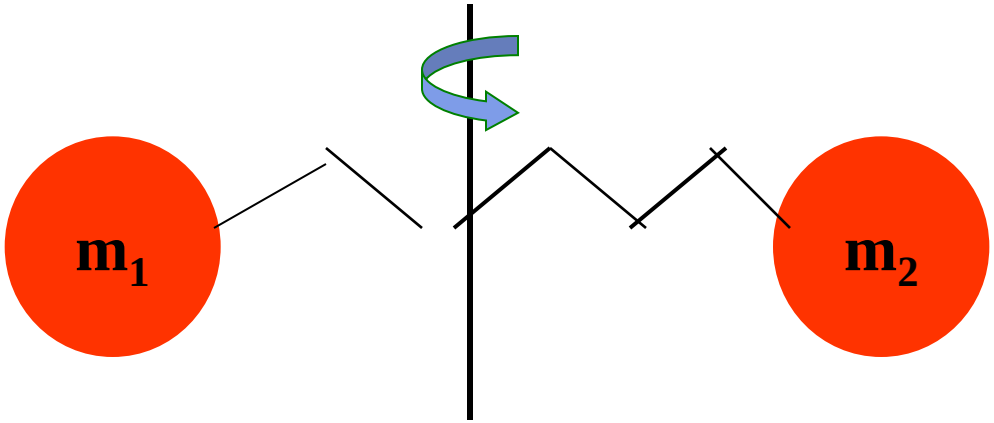
Rotation of two atom molecule

quantum mechanics rotational quantum number j

$$E = \frac{h^2}{8\pi^2}\frac{j(j+1)}{I}$$

momentum of inertia

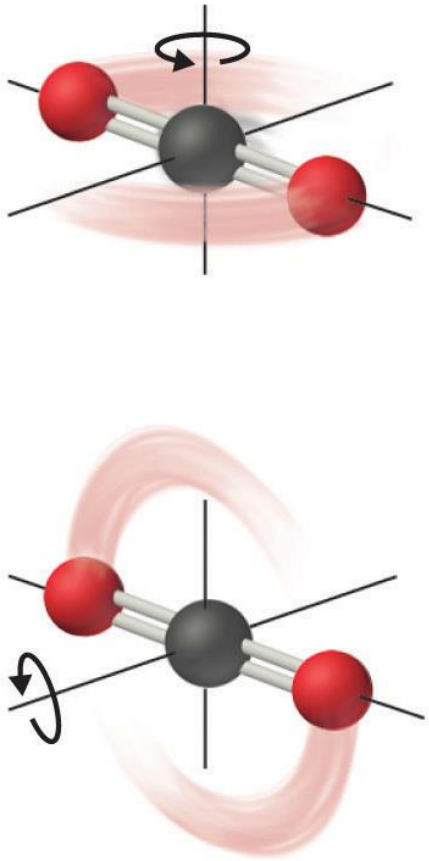
$$I = Mr^2$$



$$\Delta E = \frac{h^2}{8\pi^2 I}\left[(j+1)(j+2) - j(j+1)\right] = \frac{h^2}{4\pi^2 I}(j+1)$$

~ 0.005 eV

energy of transition between adjacent states depends on j



rotational motion

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