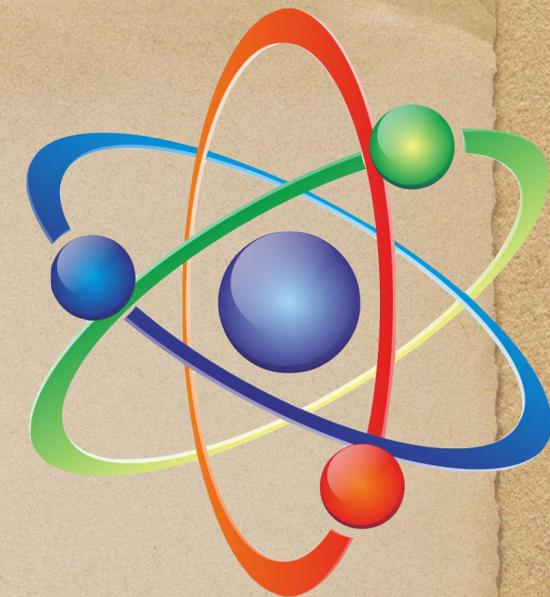


# Atomic and molecular physics



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# Who I am? My journey ...



Univ. of Nigeria, Nsukka  
BSc, MSc (solid state physics)



2020 -

UK



2017 - 2020



The Abdus Salam

**International Centre  
for Theoretical Physics**

Condensed matter & statistical physics,  
Diploma, 2008



Delft University of Technology



**CHALMERS**  
UNIVERSITY OF TECHNOLOGY

Nanoscience & Nanotechnology  
Double MSc, 2010

PhD, 2015  
Germany

**Friedrich-Alexander-Universität  
Erlangen-Nürnberg**



# Synopsis

- To provide a general atomic and molecular physics overview to the undergraduate and graduate students in physics.
- Great emphasis will be placed on familiarity with quantum mechanical description of the simplest atom (hydrogen) and its alike.
- Attempt will be made to briefly highlight different current researches in the area of atomic and molecular physics, if time permits.



# Outline

- History and basic backgrounds
  - Overview of different area of basic research in this field
  - Discuss methodology/concept for understanding the subject
- Atomic physics and atomic structure
- Molecular physics and molecular structure
- Modern research in the field of atom and molecules physics

Nuclear Physics lecture, Mark Dalton  
Material physics lecture, ...

## References:

Physics of Atoms and Molecules — B H Bransden & C J Joachain, Pearson International (2011),  
The Physics of Atoms & Quanta: Intro. to experiment and theory — Hakan & Wolf

# History and basic backgrounds

## History

Atom — Greek word “a-tomio” which means “uncuttable”

The physics of atoms and molecules rely on a long history of discoveries, both experimental and theoretical. We shall briefly recognise the key steps which are at the root of modern atomic and molecular physics.

## Greek philosophers:

Anaxagoras (500 - 428 BC), Emedocles (484 - 424 BC)... Democritus (460 -370 BC)

- argued that the atoms are invisible particles which differ from each other in form, position and arrangement.

Aristotle (384 - 322 BC) and almost everybody else

- rejected the atomic hypothesis and supported the concept of the continuity of matter.

**Problem:** Neither had any experimental or theoretical evidence.



# History and basic backgrounds contd...

## Modern times

Experimental discovery of the gas laws

1662: Robert Boyle (1627 - 1691) — extended mathematics to chemistry

Empirical law:  $PV = RT$

Understanding of the rainbow — birth of spectroscopy

1666 - 72: Issac Newton — by refracting white light with a prism, he resolved it into its component colours (red, orange, yellow, green, blue and violet)

Other notable works:

Thomas Melvill(e) (1749) — flame emission spectroscopy

He used a prism to observe a flame coloured by various salts.

...



# History contd...

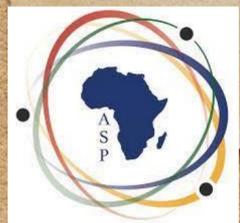
## Laws of chemical combinations

1801: J.L. Proust — law of definite proportions which states that when chemical elements combine to form a given compound, the proportion by weight of each element is always the same

1807: J. Dalton — law of multiple proportions which state that when two elements combine in different ways, to form different compounds, then for a fixed weight of one element, the weights of the other element are in the ratio of small integers.

1808: Dalton hypothesis — the elements are composed of discrete atoms. Compounds are formed when atoms of different elements combine in a simple ratio. Atoms can neither be created nor destroyed

1811: Avogadro — the first to distinguish between atoms (the discrete particles of the elements) and molecules (the discrete particles of compounds). At fixed pressure and temperature, equal volumes of different gases contain equal numbers of molecules.



**Question:** How to determine the Avogadro's number,  $N_A$ ?

# History contds...

## Kinetic theory of gases

1738: D. Bernoulli – interpretation of the empirical gas laws as kinetic model

### Nineteenth century

R. Clausius, J.C. Maxwell and L. Boltzmann – explain the physical properties of gases

### Assumptions:

1. A gas consists of a large number of particles called molecules which make elastic collisions with each other and with the walls of the container
2. The molecules of a particular substance are all identical and are small compared with the distances that separate them.
3. The temperature of a gas is proportional to the average kinetic energy of the molecules.

Despite none fully acceptance of the chemistry explanation until late nineteenth century due to chemists ignored the kinetic theory, many experimental advancement were made in the field.

# History contds...

Other notable works of

William Herschel — discovery of the infrared light

Thomas Young (1801) — the wave theory of light

Joseph von Fraunhofer (1814) — invented spectroscope

...

Sir David Brewster (1827) — produces absorption spectra in a laboratory.

1885: J. Balmer — Experimental observed discrete lines in the visible spectrum of hydrogen.

He showed that the wavelength could be fit by  $\lambda = B \left( \frac{n^2}{n^2 - 4} \right)$ , where an integer  $n \geq 3$  &  $B = 4/R_H$  (Rydberg const)

## Electron

1833: M. Faraday — laws of electrolysis

1897: J.J. Thompson — studies with cathode rays led to electron discovery

1897: J.S. Townsend — direct measurements of the smallest possible charge,  $e$

Late nineteenth century — Newton's law of motion and Maxwell's electromagnetic equations is inadequate to describe atomic phenomena.

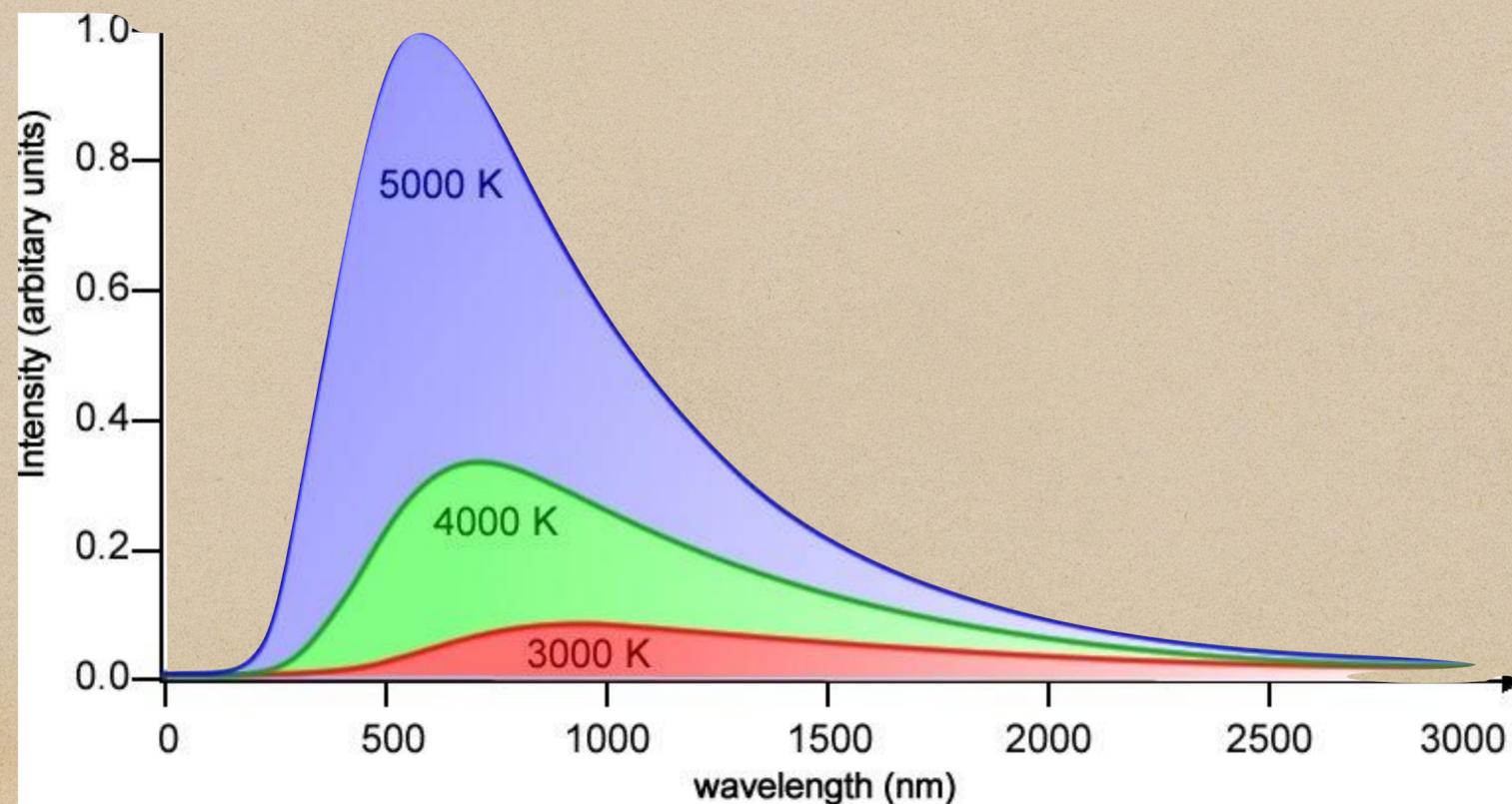


## What way forward?

**Black body radiation** — a study of the properties of radiation from hot bodies provide the first evidence of the quantisation of energy.

1879: J. Stefan empirical law — the power emitted per unit area,  $R$ , from a body at the absolute temperature  $T$  (K), could be represented by:  $R = e\sigma T^4$

where  $e$  is the emissivity which varies with the nature of the surface and  $\sigma$  is the Stefan's constant.



# Blackbody radiation...

1893: W. Wien — based on general thermodynamics arguments, show that the spectral distribution function for energy density a cavity is  $\rho(\lambda) = \lambda^{-5} f(\lambda T)$ ,  
 $\lambda$  is wavelength of the radiation and  $f(\lambda T)$  is a function to be determined beyond thermodynamical reasoning.  
**Wien's displacement law:** the wavelength of the peak of each curves corresponds to a different temperature.

For a number of standing electromagnetic waves (modes) per unit volume within a cavity, the energy density reads

$$\rho(\lambda) = \frac{8\pi}{\lambda^4} \bar{\epsilon}, \quad \bar{\epsilon} - \text{the avg. energy in the mode with wavelength } \lambda$$

Lord Rayleigh and J. Jeans approach:  $f(\lambda T) = 8\pi k(\lambda T)^3$ ;  $\bar{\epsilon} = kT$  — **Ultra-violet catastrophe!**

$$\text{Rayleigh-Jeans distribution law: } \rho(\lambda) = \frac{8\pi}{\lambda^4} (kT)$$

1899: O. Lummer & E. Pringsheim — experimentally measured the spectral distribution as a function of temperature



# 1900: Planck's quantum theory

## Postulate:

The energy of an oscillator of a given frequency  $\nu$  cannot take arbitrary values between zero and infinity, but can only take on the discrete values  $n\varepsilon_0$ , where  $n$  is a positive integer or zero, and  $\varepsilon_0$  is a finite "quantum" of energy, which may depend on the frequency.

Average energy of an ensemble of oscillators, each of frequency  $\nu$ , in thermal equilibrium is;

$$\bar{\varepsilon} = \frac{\varepsilon_0}{e^{\beta\varepsilon_0} - 1}$$

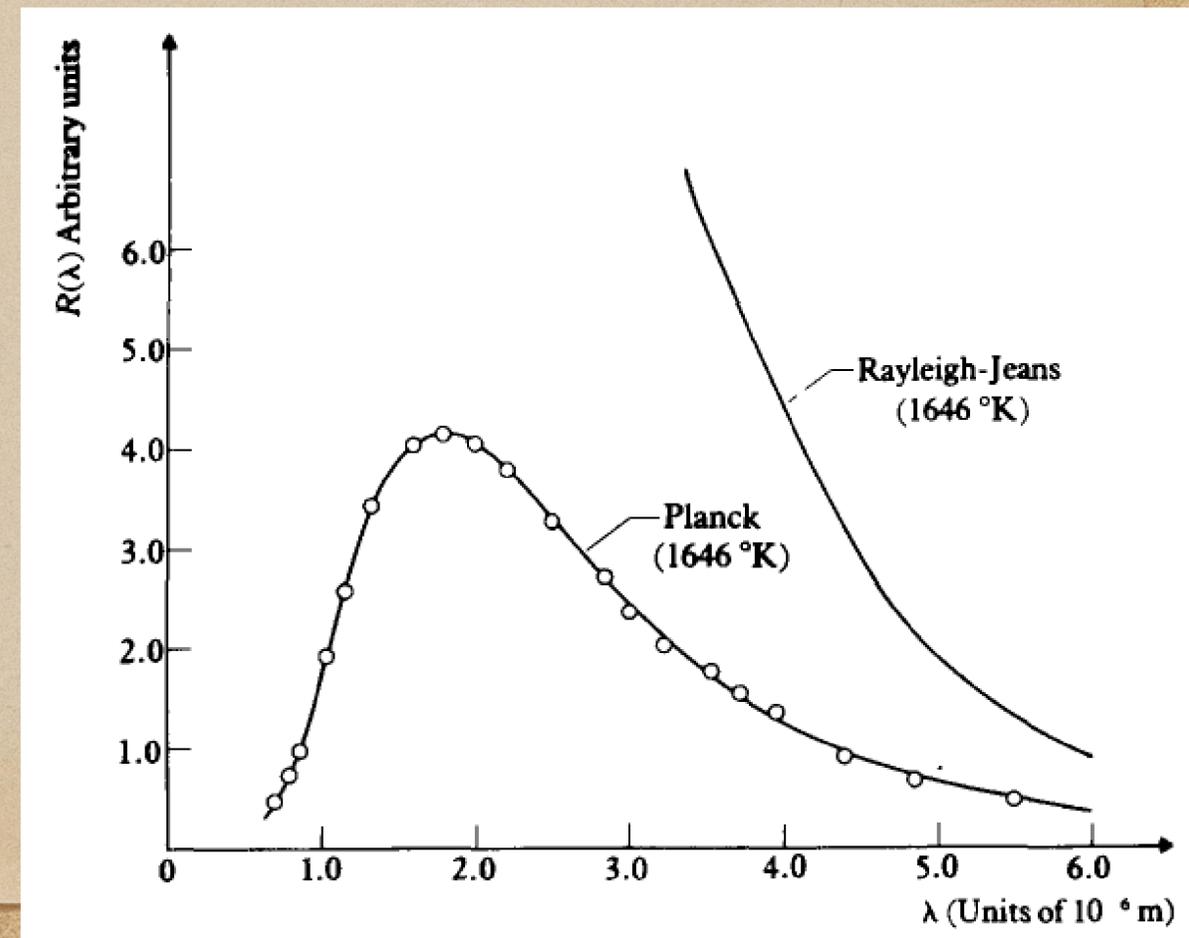
Then,

$$\rho(\lambda) = \frac{8\pi}{\lambda^4} \frac{\varepsilon_0}{e^{\varepsilon_0/kT} - 1}$$

To satisfy Wein's law:  $\varepsilon_0 = h\nu$

$h$  is Planck's constant ( $h = 6.6262 \times 10^{-34}$  Joule - sec).

$$\text{Planck's distribution law: } \rho(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$



## Is Planck's quantum theory acceptable?

Planck's theory was not accepted readily. However it was not long before the quantum concept was used to explain other phenomena.

In 1905, A. Einstein was able to interpret the **photoelectric effect** by introducing the idea of photons, or light quanta, and in 1907 he used the Planck formula for the average energy of an oscillator to derive the law of Dulong and Petit concerning the specific heat of solids.

Subsequently N. Bohr, in 1913, was able to invoke the idea of quantisation of atomic energy levels to explain the existence of line spectra.

Geiger, Marsden and Rutherford (1906 - 1913): Based on the scattering of  $\alpha$  particles by metallic foils of various thickness, Rutherford found that  $\alpha$  particles had charge to mass ratio  $q/M$  equals the doubly ionised helium atom.

Atom is mostly empty space with a small positively charged nucleus (protons) containing most of the mass and low mass negatively charged particles (Thompson's electrons) orbiting this nucleus.

# Early quantum formulation and Bohr's idea - I

1913: Neils Bohr's — based on Rutherford's  $\alpha$ -scattering experiment and the observation of discrete spectra, Bohr introduced the energy level quantisation of atom

The **postulates** were:

1. Electron moves in circular orbit about proton under Coulomb attraction.

$$\text{Electrostatic attractive force} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \quad \text{Centrifugal force} = \frac{mv^2}{r}$$

$Ze$  - Charge of nucleus,  $v$  - velocity of electron,  $r$  - radius

2. Electron can revolve only in those orbits whose angular momentum is an integral multiple of  $\hbar = h/2\pi$ . That is;  $L = mvr = n\hbar \quad n = 1, 2, 3, \dots$

$$\text{Radius of the orbit, } r = 4\pi\epsilon_0 \frac{n^2\hbar^2}{mZe^2} \text{ and velocity, } v = \frac{n\hbar}{mr}$$

3. Total energy of the electron in orbit remains constant.  $E = E_{kin} + E_{pot}$

$$E_n = -\frac{mZ^2e^4}{(4\pi\epsilon_0)^2 2\hbar^2} \frac{1}{n^2}$$

4. Radiation is emitted only when the electron jumps from one discrete orbit to another orbit of a lower energy. When electrons absorb radiation, the reverse transition occurs.  $\Delta E = E_f - E_i = h\nu = hc/\lambda$

## Early quantum formulation and Bohr's idea - II

$$\text{Electron energy, } E_n = \frac{-13.6Z^2}{n^2} \text{ eV}$$

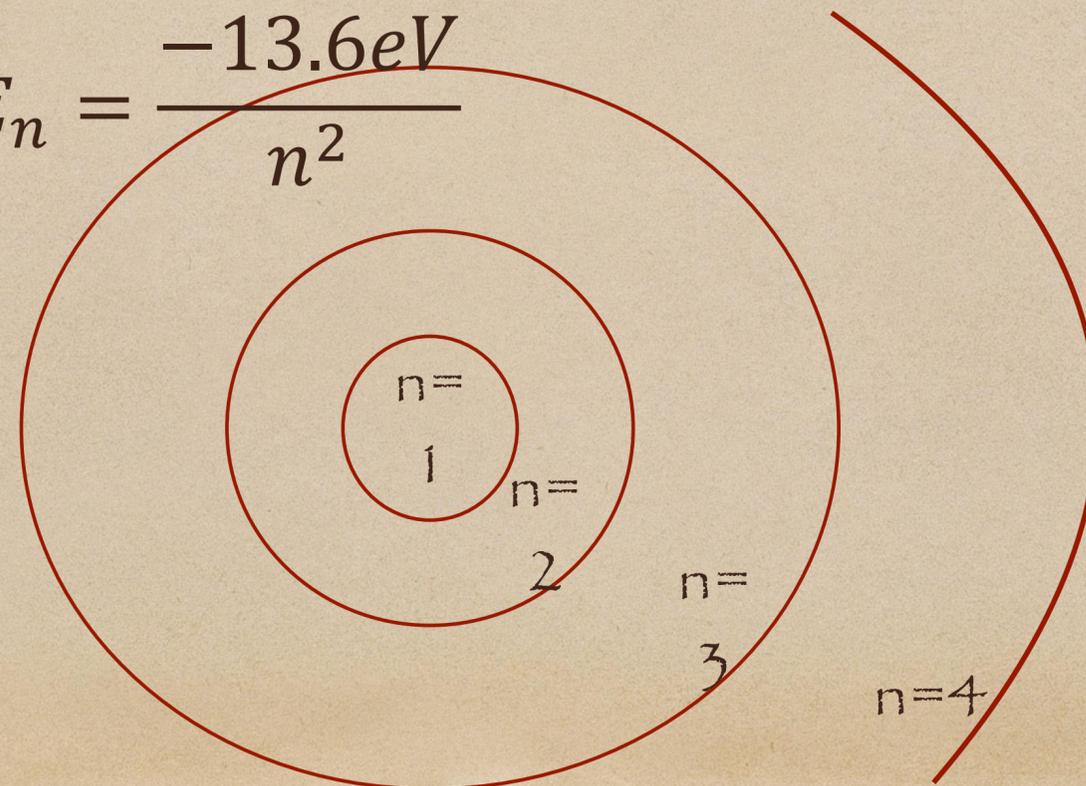
$$\text{Orbit radius, } r = \frac{n^2 a_0}{Z}$$

$Z$  — atomic number and  $a_0$  — Bohr radius

Niels Bohr, 1922 Nobel prize in physics — investigation of atomic structure and radiation

For  $Z = 1$  (Hydrogen)

$$E_n = \frac{-13.6 \text{ eV}}{n^2}$$



n=4	—
n=3	— -1.5 eV
n=2	— -3.4 eV
n=1	— -13.6 eV

### Questions:

- How does the velocity of ground state hydrogen electron compare to velocity of light?
- Is the non-relativistic model justified?

Hint:  $r_1 = 5.29 \times 10^{-11} \text{ meter}$



## Failures of Bohr model

Bohr model is not in fact a correct description of the nature of electron orbits.

Some of the shortcomings of the model are:

1. Fails to describe why certain spectral lines are brighter than others. That is, no mechanism for calculating transition probabilities.
2. It violates the uncertainty principle which states that position and momentum cannot be simultaneously measured.

From Bohr model, the linear momentum  $p = mv = n\hbar/r$

From Heisenberg uncertainty principle,  $\Delta p \sim \hbar/\Delta x \sim \hbar/r$

Bohr's model only valid at the classical limit, i.e. large  $n$  limit

Thus, full quantum mechanical treatment is needed to model electron in hydrogen atom

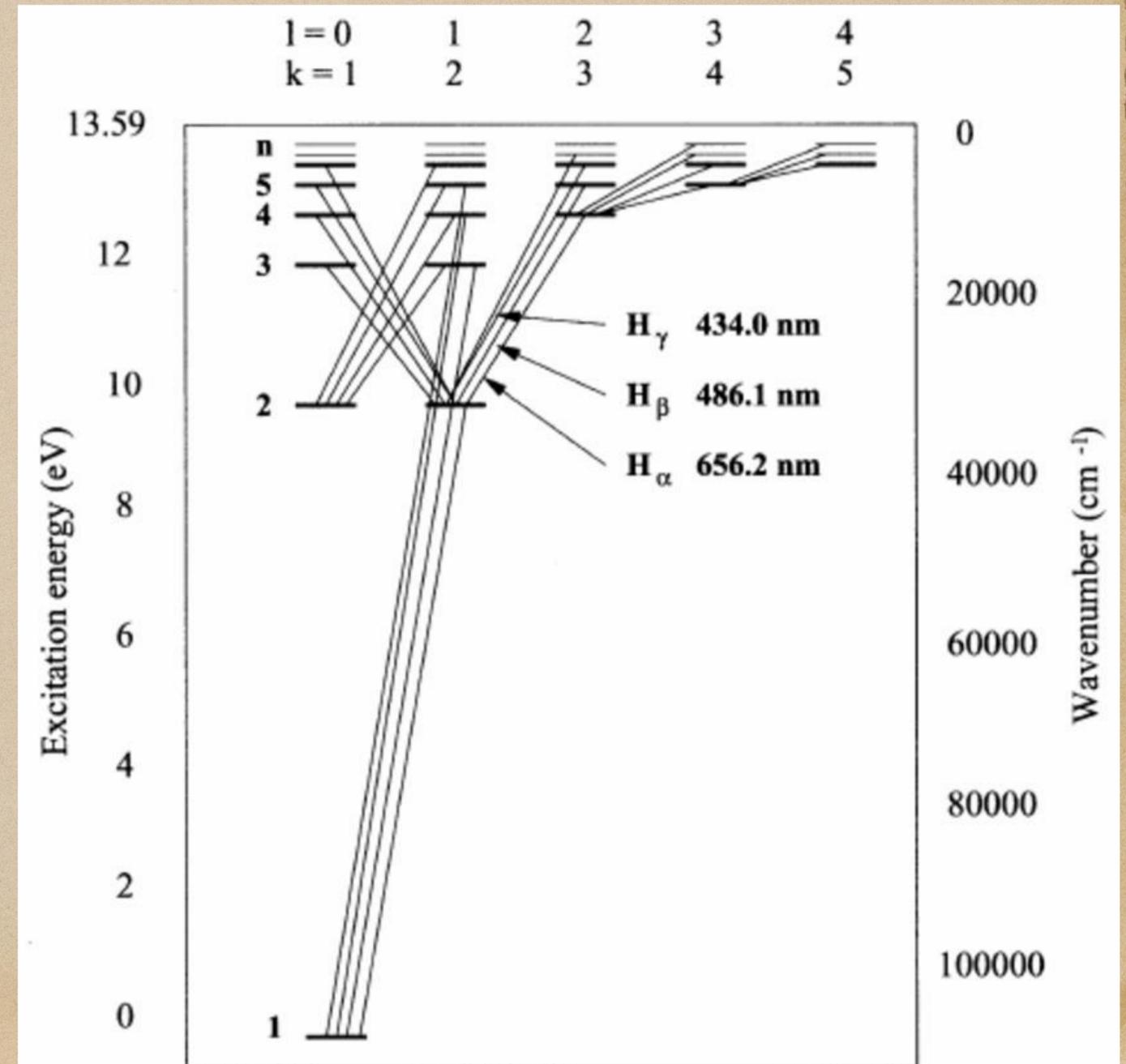
# Hydrogen spectrum

A single quantum number  $n$  cannot actually explain the transitions in an atom.

Quantum mechanically, we have four quantum numbers:

- Principal quantum number -  $n$
- Azimuthal quantum number -  $l$
- Magnetic quantum number -  $m_l$
- Spin quantum number -  $s$

Selection rule must be modified



# Schrödinger equation for the Atom - I

Hydrogen is one electron atom and perhaps the simplest system in nature,  $Z = 1$ .  
The potential associated with the attractive Coloumbic force between the positive charge proton and the

$$\text{negative charge electron is } V(\vec{r}) = -\frac{ze^2}{4\pi\epsilon_0 r}.$$

Since it is a two body problem, we introduced a reduced mass (to treat it as one body problem)  $\mu = \frac{mM}{m+M}$ ,  
where  $m$  and  $M$  are the masses of the electron and proton respectively.

kinetic energy + potential energy = Total energy

$$\frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z) = E$$

For quantum mechanical treatment, the classical dynamical quantities would be replaced with their corresponding quantum mechanical operators.

$$p_x \rightarrow -i\hbar\partial/\partial x, p_y \rightarrow -i\hbar\partial/\partial y, p_z \rightarrow -i\hbar\partial/\partial z, E \rightarrow -i\hbar\partial/\partial t,$$

Let introduce a wave function describing the electron as;  $\psi = \psi(x, y, z, t)$



# Schrödinger equation for the Atom - II

Then,

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V(r)\right) \psi = -i\hbar \frac{\partial \psi}{\partial t}, \text{ where } \psi \equiv \psi(\vec{r}, t) \text{ and } V(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$\nabla$  is Laplacian operator

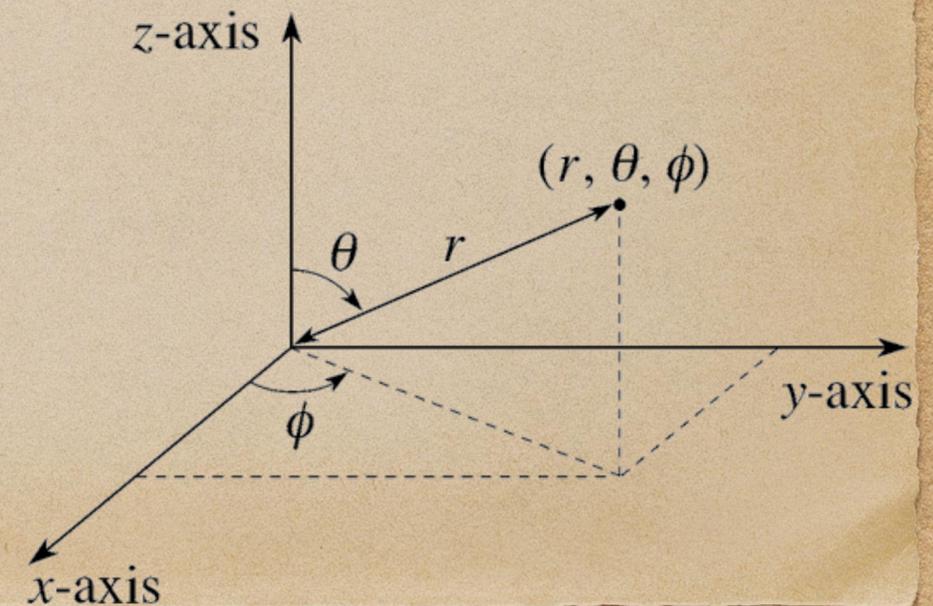
## Time-dependent SE equation

Since the potential  $V$  is independent of the time and angle, we simplify the equation in two ways. First, the time dependent part (RHS) of the equation is replaced by the energy eigenvalue. Secondly, writing the Hamiltonian in spherical coordinates, we can separate the wave function  $\psi(\vec{r})$  into a product of radial-only and angular-only parts.

In spherical polar coordinates, 
$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi(r, \theta, \phi) + V(r)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

where

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



# Schrödinger equation for the Atom - III: Separation of variables

Assuming the eigenfunction is separable:  $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$

Substituting  $\psi(r, \theta, \phi)$  into the SE, carrying out the differentiations and rearranging

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -\frac{\sin^2 \theta}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) - \frac{2\mu}{\hbar^2} r^2 \sin^2 \theta [E - V(r)]$$

We can separate the resulting partial differential eqn. into a set of three ordinary differential eqns.:

$$\frac{d^2 \Phi}{d\phi^2} = -m_l^2 \Phi$$

$$-\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{m_l^2 \Theta}{\sin^2 \theta} = l(l+1)\Theta$$

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} [E - V(r)]R = l(l+1) \frac{R}{r^2}$$

Schrödinger equation produces three quantum numbers



# Schrödinger equation for the Atom - IV: Solutions

## Azimuthal part

A particular solution of the first ODE is  $\Phi(\phi) = e^{im_l\phi}$ .

The eigenfunctions must be single valued, i.e.,  $\Phi(0) = \Phi(2\pi)$  and using Euler's formula,  $1 = \cos m_l 2\pi + i \sin m_l 2\pi$ .

This is satisfied if and only if;  $m_l = 0, \pm 1, \pm 2, \dots$

Thus, solutions only exist when  $m_l$  have a certain integer values. It is called a quantum number. It plays role when atom interacts with magnetic fields, known as the magnetic quantum number in spectroscopy.

## Polar part, $\Theta(\theta)$

Making change of variable,  $z = r \cos \theta$ , the 2nd ODE is transformed into an associated Legendre equation:

$$\frac{d}{dz} \left[ (1 - z^2) \frac{d\Theta}{dz} \right] + \left[ l(l + 1) - \frac{m_l^2}{1 - z^2} \right] \Theta = 0.$$

**Solutions:**  $\Theta_{lm_l}(\theta) = \sin^{|m_l|} \theta F_{l|m-l|}(\cos \theta)$ , where  $F_{l|m-l|}(\cos \theta)$  are associated Legendre polynomial functions.

For finite  $\Theta$ ;  $l = 0, 1, 2, 3, 4, \dots$ ;  $m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l$



# Schrödinger equation for the Atom - IV: Solutions representation

Spherical harmonic solutions:  $Y_l^{m_l}(\theta, \phi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$   
 It is product of trigonometric and polynomial functions

Few spherical harmonics are:

$$Y_0^0 = 1$$

$$Y_1^0 = \cos\theta Y_1^{\pm 1} = (1 - \cos^2\theta)^{1/2} e^{\pm i\phi}$$

...

.....

$$|Y_0^0(\theta, \phi)|^2$$



$$|Y_1^0(\theta, \phi)|^2$$



$$|Y_1^{\pm 1}(\theta, \phi)|^2$$



$$|Y_2^0(\theta, \phi)|^2$$



$$|Y_2^{\pm 1}(\theta, \phi)|^2$$



$$|Y_2^{\pm 2}(\theta, \phi)|^2$$



$$|Y_3^0(\theta, \phi)|^2$$



$$|Y_3^{\pm 1}(\theta, \phi)|^2$$



$$|Y_3^{\pm 2}(\theta, \phi)|^2$$



$$|Y_3^{\pm 3}(\theta, \phi)|^2$$



Taken from: Wolfram MathWorks



## Schrödinger equation for the Atom - V: Radial part

For hydrogen atom,  $Z = 1$ . Assuming the ground state  $n = 1, l = 0$ ; the third ODE can be written as

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[ E + \frac{e^2}{4\pi\epsilon_0 r} \right] R = 0$$

Taking the derivative and assume solution  $R = Ae^{-r/a_0}$ , where  $A$  and  $a_0$  are constants. The eq. becomes;

$$\left( \frac{1}{a_0^2} + \frac{2\mu}{\hbar^2} E \right) + \left( \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2} - \frac{2}{a_0} \right) \frac{1}{r} = 0.$$

To satisfy this equation for any value of  $r$ , both expressions in brackets must equal zero. We have

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}; \quad E = -\frac{\hbar^2}{2\mu a_0^2}$$

What are their values numerically?

For each positive integer of  $n$ , the radial wave equation has many solutions. Bound-state solutions are only possible if,  $E_n = -\frac{Z^2 \mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -13.6 \frac{Z^2}{n^2} \text{ eV}$ . The principal q. no.  $n = l + 1, l + 2, \dots$

# Molecules

## What is a molecule?

A molecule is an electrically neutral group of two or more atoms held together by chemical bonds. — Wikipedia

Many atoms can combine to form a particular molecules, E.g. hydrogen (H) and Oxygen (O) atoms form water ( $H_2O$ ); Chlorine (Cl) and Sodium (Na) atoms form NaCl molecules. Bonding between oppositely charged bodies could be understood in the light of Coulomb interaction (attraction) but atoms of the same type can still form bonds, a typical example is hydrogen molecule  $H_2$ .

In contrast to atoms, molecules have two more degrees of freedom: rotational and vibrational

### Our goal

To understand the formation of molecule from atom in the quantum mechanical framework.

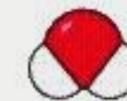


14  Nitrogen (N)

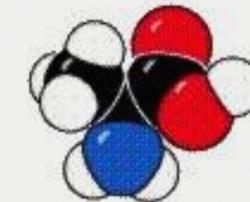
16  Oxygen (O)

12  Carbon (C)

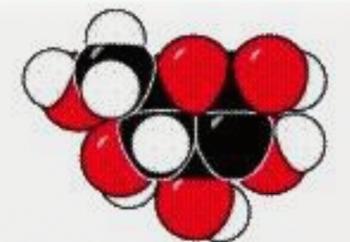
1  Hydrogen (H)



Water  
(molecular weight = 18)



Alanine  
(molecular weight = 89)



Glucose  
(molecular weight = 180)

## Molecules contd...

In molecules, the potential seen by the electrons lacks a central character. For the simplest of molecules, the homonuclear diatomic molecule, the potential is two-centred. The increase in the number of nuclei, increases the complexity nature of the attractive potential.

How can the problem be simplified?

Take into account the large difference in the masses of the nuclei and the electrons.

This is important in the analysis of molecular structure and spectra

First, let us compare the energies and masses of the electrons and the nuclei in a molecule

$$m_e = 9.1095 \times 10^{-31} \text{kg}$$

$$m_N = 1.6750 \times 10^{-27} \text{kg}$$

Let us consider electrons in a potential well of size  $R$  (bond-length or molecule size), the electrons energy

$$\text{estimate, } E_e \approx \frac{p^2}{2m} \approx \frac{\hbar^2}{2mR^2}$$

## Molecules contd...

Now consider a diatomic molecule, the energy of the nucleus can be estimated by treating the molecule (specifically a diatomic molecule) as a linear harmonic oscillator. That is, the molecule is bound due to the electronic attraction but would fall apart due to nuclear repulsion in the absence of electrons. The oscillator energy would be  $E_{vib} = M\omega_{vib}^2\delta^2/2$  where  $\omega$   $\delta$  are the frequency of oscillation and the displacement respectively.

Analysing the amount of energy that will result in dissociation show that the energy of nuclear oscillations (vibrational energy) is considerably smaller than the electronic energy.

$$\text{Bound state estimate: } \hbar\omega_{vib} \sim (m/M)^{1/2}E_e$$

can be approximated as a rigid rotator with the quantised energy levels given by  $l(l+1)\hbar^2/2I$ , where the moment of

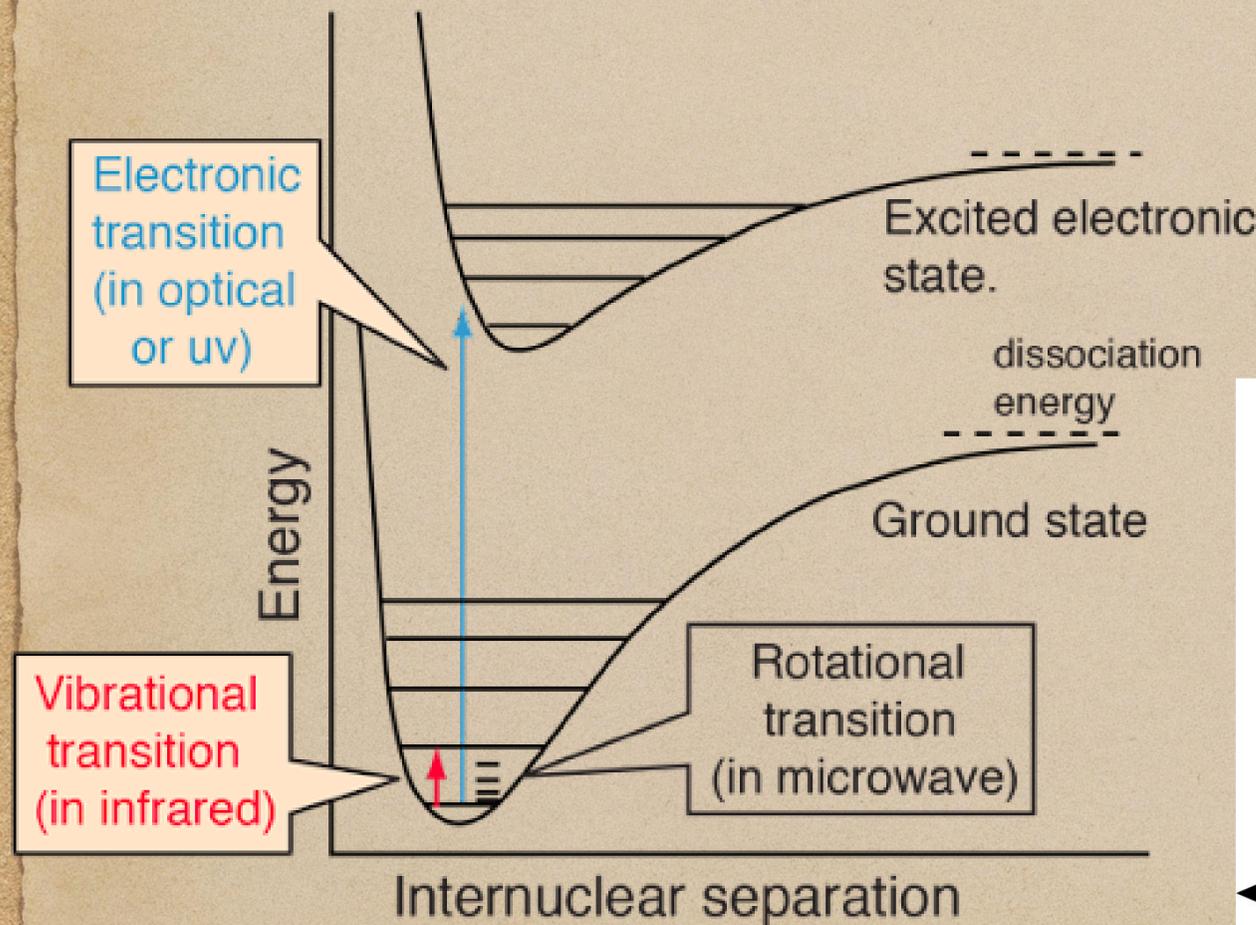
$$\text{Thus, rotational energy } E_{rot} \approx \frac{\hbar^2}{I} \approx \frac{m}{M}E_e$$

# Molecules: Energy scales

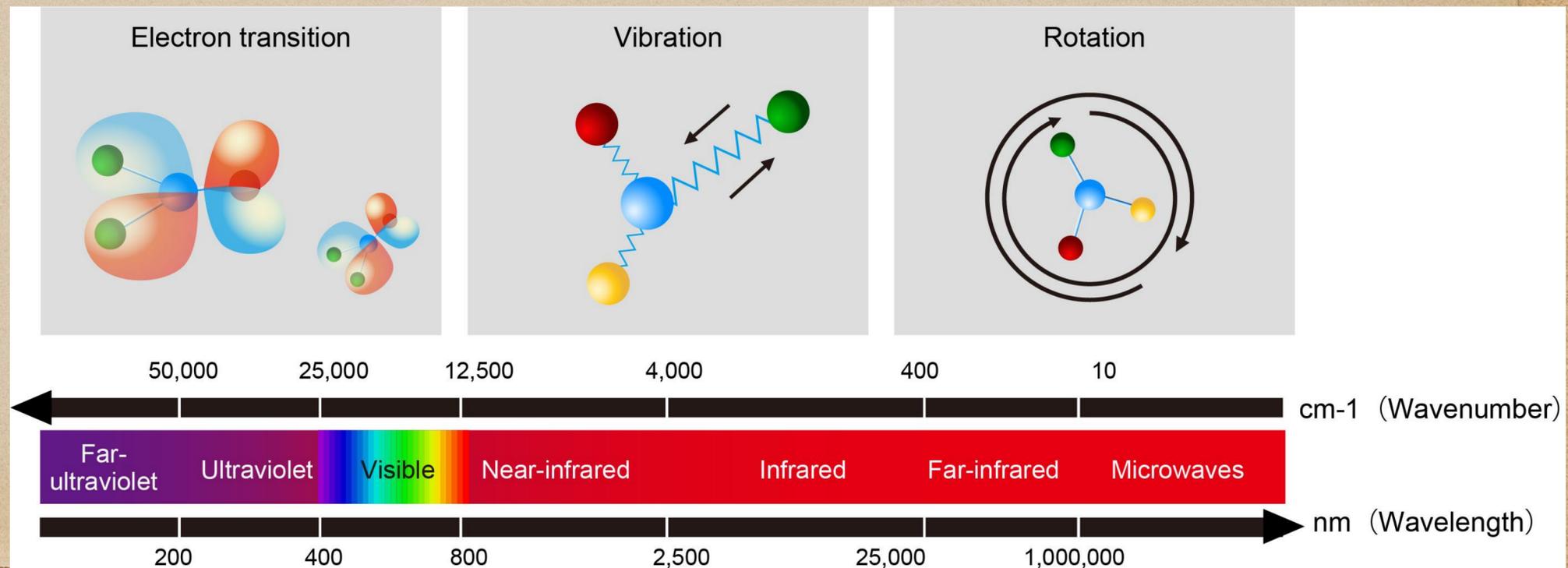
Thus;

$$E_{rot} < E_{vib} < E_{elec}$$

The difference in the energies allows us to separate the three kinds of motion and corresponds to a difference



From: [www.yokogawa.com](http://www.yokogawa.com)



## Molecules: Born-Oppenheimer approximation

This is finding the solution of the Schrodinger equation of a molecule by the assumption that the electronic motion and the nuclear motion can be well separated. That is, based on the energy and time scale difference that we discussed in previous slide.

Then, molecular wave functions

$$\psi_{molecule}(\vec{r}_i, \vec{R}_j) = \psi_{electrons}(\vec{r}_i, \vec{R}_j) \psi_{nuclei}(\vec{R}_j)$$

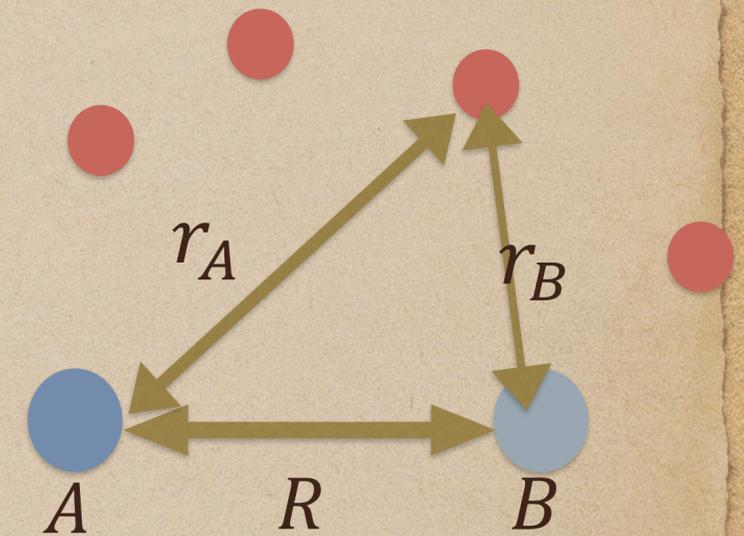
- Electronic wave function depends on nuclear positions but not their velocities. That is, nuclear motion is much slower than the electron motion that they can be seen to be fixed.
- Nuclear motion (rotation, vibration) sees a smeared out potential from the fast moving electrons.



# Schrodinger equation of diatomic molecules: Born-oppenheimer approx.

Consider a diatomic molecule with nuclei located at  $R_A$  and  $R_B$  having masses  $M_A$  and  $M_B$ , charges  $Z_A$  and  $Z_B$ . Assuming that the molecules have  $n$  electrons, the Schrodinger equation can be written as

$$\left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 + V \right) \Psi = E\Psi$$



Where,  $\Psi$  is the total electronic and nuclear wave function;  $E$  is the total energy  
 1st term: Kinetic energy of the nuclei with reduced mass  $\mu = m_A m_B / (m_A + m_B)$

2nd term: KE of the electrons

$$\text{The potential, } V = \sum_{i>j=1}^n \frac{e^2}{r_{ij}} - \sum_{i=1}^n \frac{Z_A e^2}{r_{iA}} - \sum_{i=1}^n \frac{Z_B e^2}{r_{iB}} + \frac{Z_A Z_B e^2}{R}$$



## Schrodinger equation of diatomic molecules: Born-Oppenheimer approx.

- Now introduce the Born-Oppenheimer or the adiabatic approximation; the nuclear motion is slow compared to the electronic motion. This will eliminate the nuclear kinetic energy term.
- The total molecular wave function can be written as combination of the electron wave function and the nuclear wave function.
- After substituting into the Schrodinger equation ( $SE$ ) and separation of variables
- ...
- .....
- We have  $SE$  of nuclear motion of diatomic molecule and another  $SE$  of electrons motion



# Schrodinger equation of diatomic molecules: Born-Oppenheimer approx.

Solve the resulting SE of nuclear motion (spherical coordinate) in analogue to the hydrogen atom

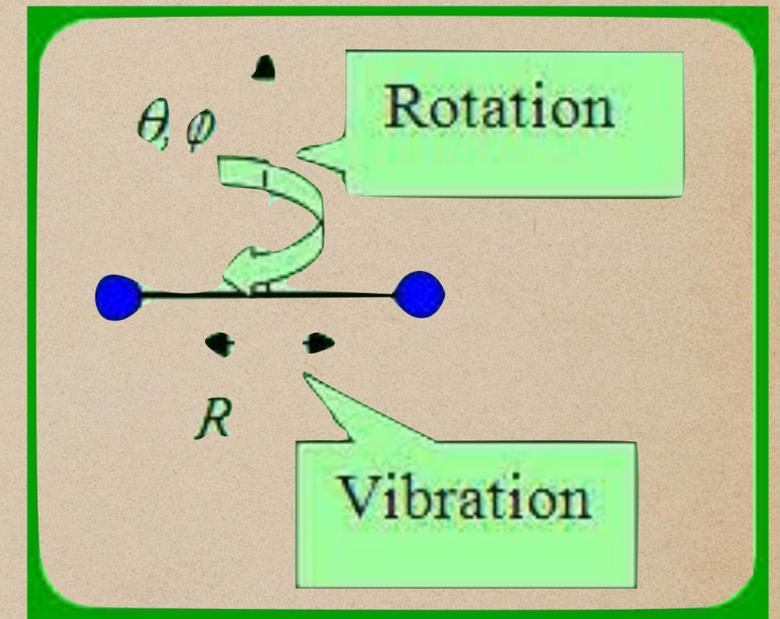
$$\text{Rotational energy, } E_J = \frac{\hbar^2}{2\mu R^2} J(J+1)$$

$J$  – rotational quantum number (angular momentum) of the molecule

In classical mechanics, energy of a rotating body  $E_a = 1/2 I_a \omega_a^2$

$\omega_a$  – the angular velocity (rad/sec)

The magnitude of the angular momentum  $|J| = I_a \omega_a$



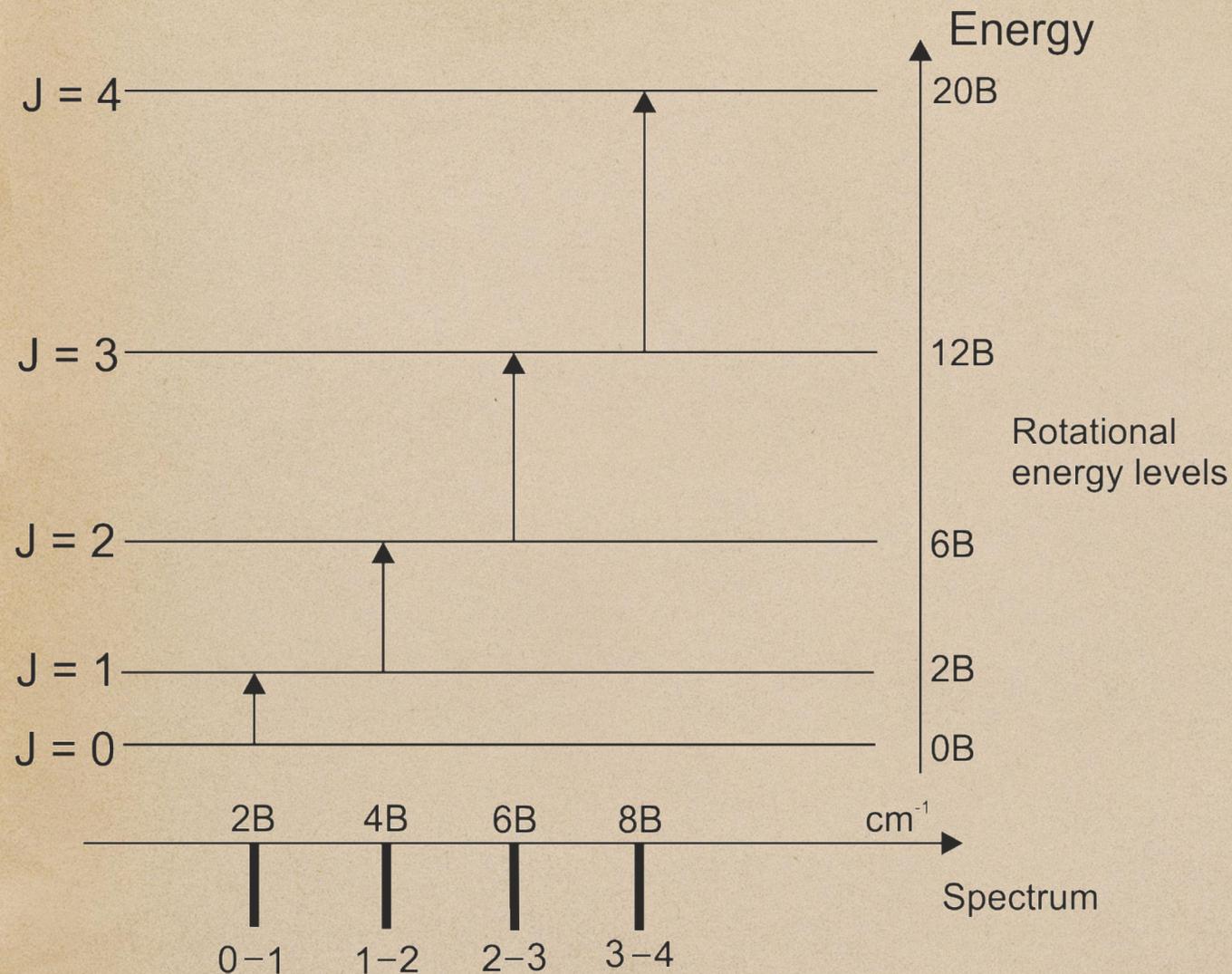
$$\text{Therefore, } E_J = \frac{J(J+1)\hbar^2}{2I}, J = 0, 1, 2, \dots$$

In terms of a rotational term,  $F(J) = E_J/hc = BJ(J+1)cm^{-1}$ , where the rotational constant  $B = \frac{\hbar^2}{4\pi cI}$

It means large molecules have closely spaced energy levels.



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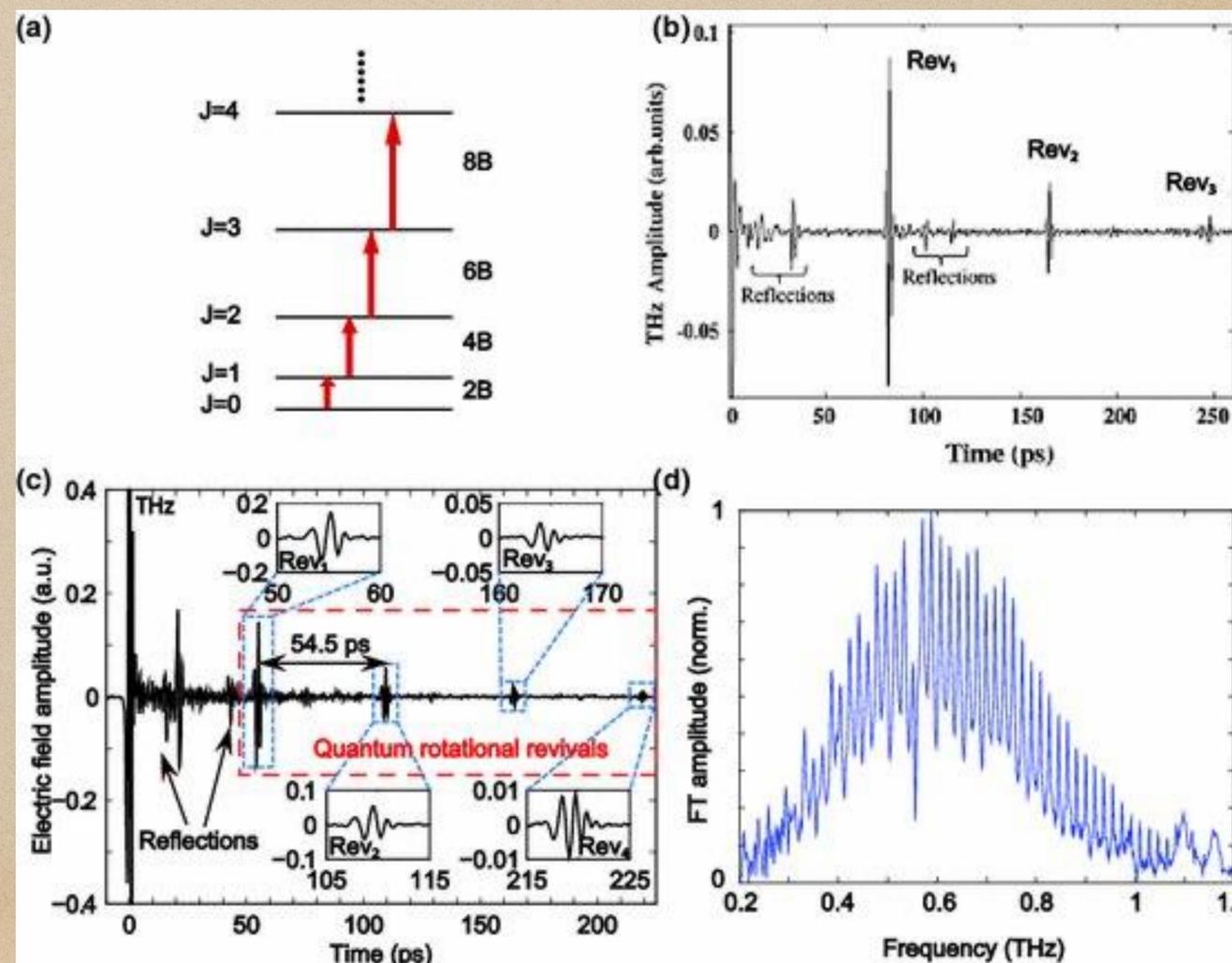


Rotational spectra selection rules  
 Transitions are only allowed according to selection rule for angular momentum;

$$\Delta J = \pm 1$$

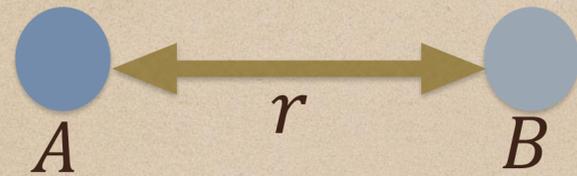
$$F(J) - F(J - 1) = 2BJ$$

Schematic energy level diagram of molecular rotations (see figures)  
 From: Lu et al, Two-Dimensional Spectroscopy at Terahertz Frequencies,  
 Topic in current chem 376 (2018)



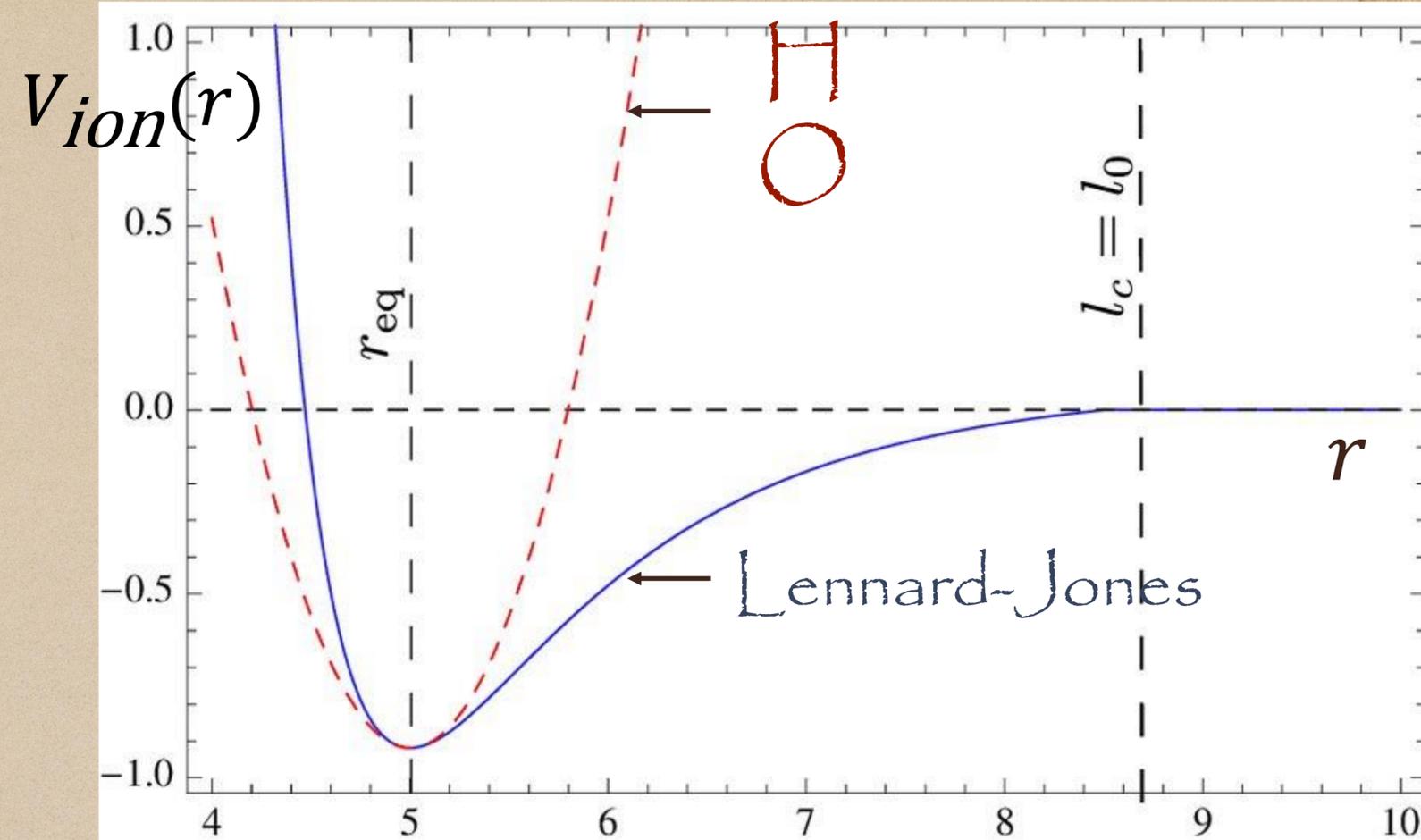
# Schrodinger equation of diatomic molecules: Born-Oppenheimer approx.

## Molecular vibrational motion



Lennard-Jones potential

$$V_{LJ}(r) = \varepsilon \left[ \left( \frac{R_e}{r} \right)^{12} - 2 \left( \frac{R_e}{r} \right)^6 \right]$$



Then, expanding  $V_{ion}(r)$  around the equilibrium molecular separation  $R_e$ ;

$$V_{ion}(r) = V_{ion}(R_e) + \frac{dV_{ion}}{dr} \Big|_{R_e} (r - R_e) + \frac{1}{2} \frac{d^2V_{ion}}{dr^2} \Big|_{R_e} (r - R_e)^2 + \dots$$

Equilibrium  
= No force

Harmonic

Anharmonicity



# Schrodinger equation of diatomic molecules: Born-Oppenheimer approx.

## Harmonic approximation

Expanding the ionic potential between the diatomic molecule up to second order

$$V_{ion} = \frac{1}{2} \frac{d^2V}{dx^2} x^2 = \frac{1}{2} kx^2$$

Large (small)  $k$  means stiff (weak) bond between the atom A & B.

The Schrodinger equation for relative motion of diatomic molecule A-B with a quadratic potential energy (harmonic oscillator) reads:

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_n}{dx^2} + \frac{1}{2} kx^2 \psi_n = E_n \psi$$

**Solutions:** Hermite polynomial + Gaussian wave function .

The vibrational energy levels;  $E_n = \left(n + \frac{1}{2}\right) \hbar\omega$ ,  $\omega = \sqrt{k/\mu}$ , and  $n = 0, 1, 2, \dots$  is vibrational quanta

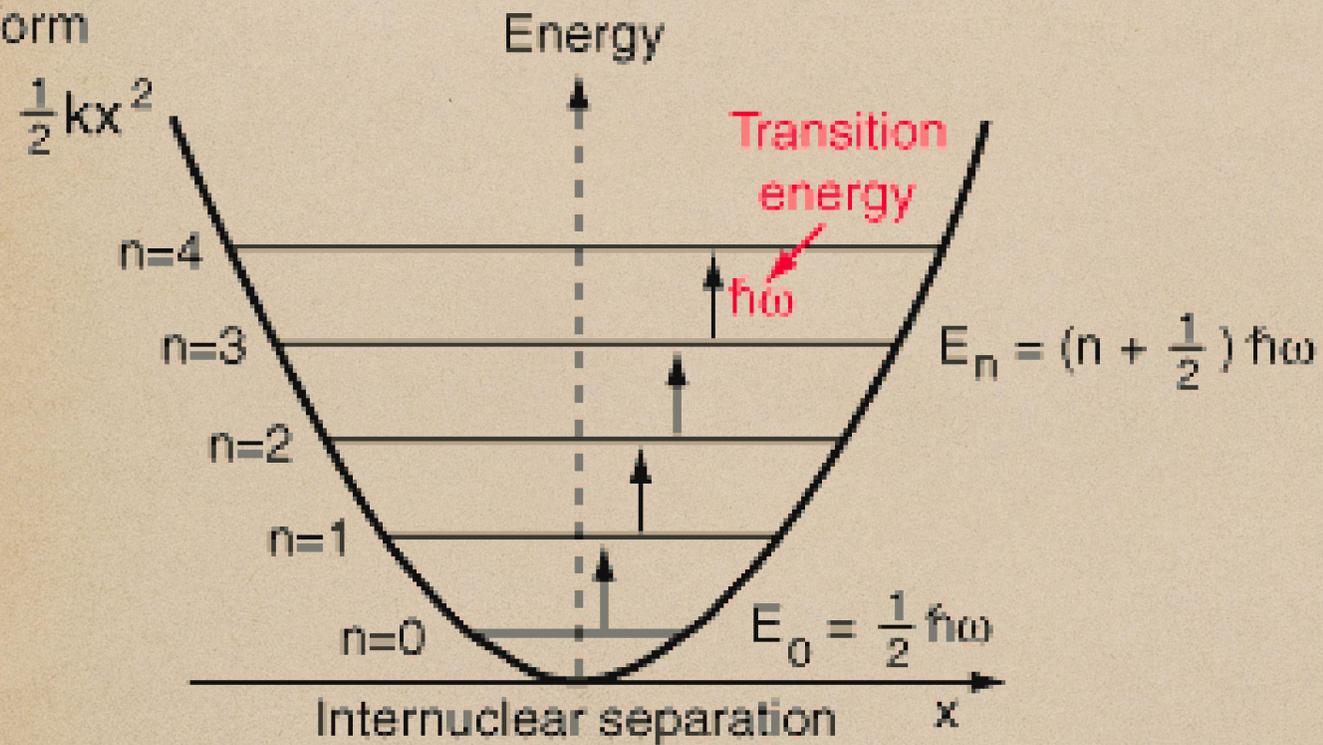
# Schrodinger equation of diatomic molecules: Born-Oppenheimer approx.

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega, n = 0, 1, 2, \dots$$

Vibrational terms of molecule in terms of wavenumber

$$G(n) = \left( n + \frac{1}{2} \right) \tilde{n}$$

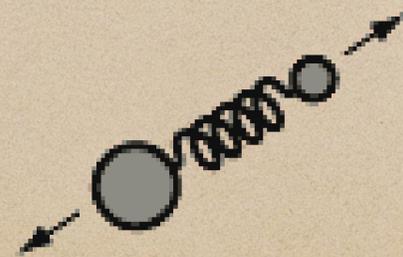
Potential energy of form



$$\tilde{n} \equiv \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

## Downsides

- The harmonic/parabolic potential approx. is poor at high excitation energies
- Harmonic potential does not describe molecular dissociation



$x=0$  represents the equilibrium separation between the nuclei.



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## Anharmonicity

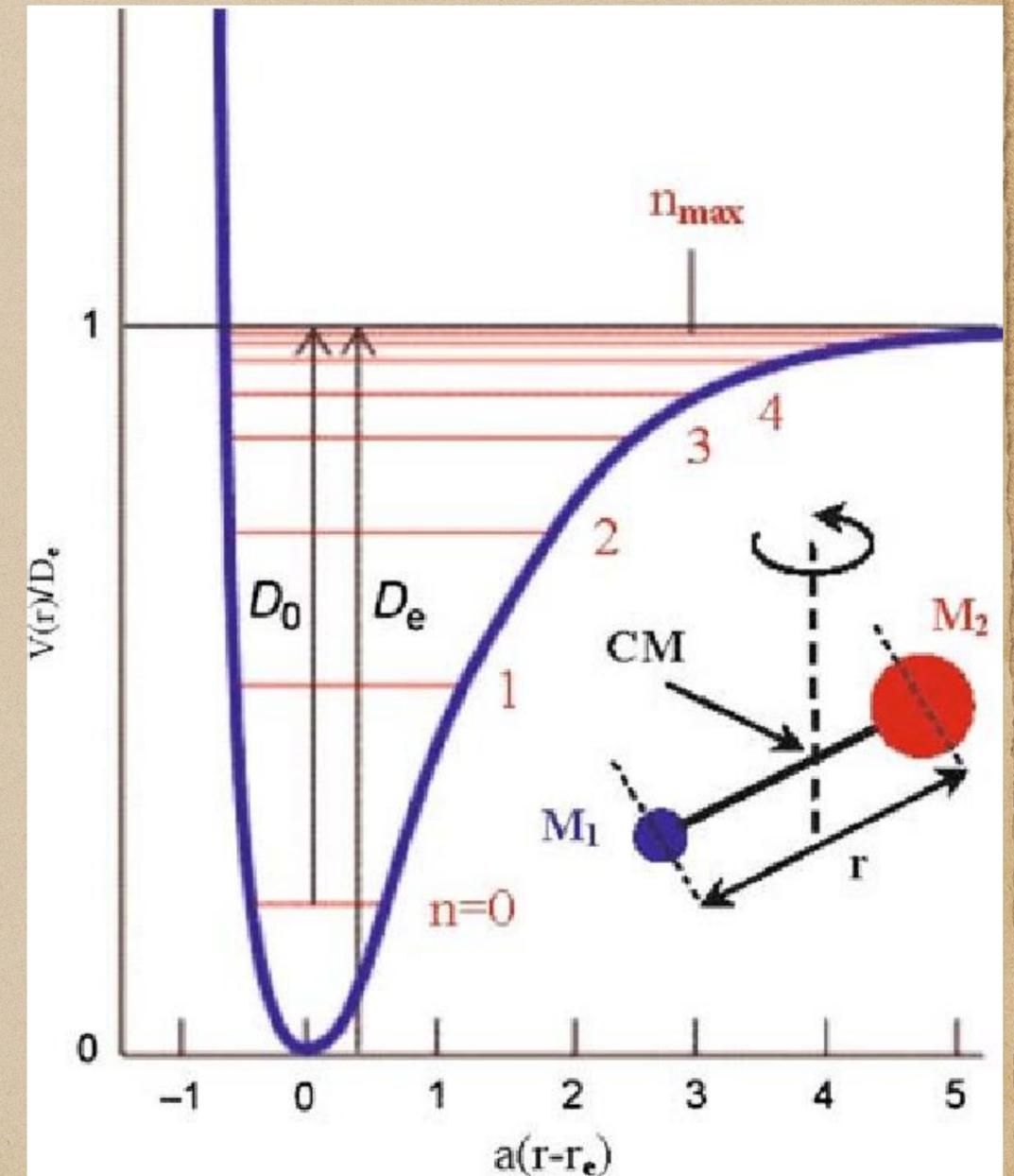
In reality, the failure of the interatomic potential from a parabola (harmonic oscillations) results into effects like second order nonlinear oscillations, thermal expansion, finite phonon lifetime among others. Thus, the use of a asymmetric potential is required, e.g Morse potential.

### Morse potential

A closed-form solution and resembles the true potentials.

$$V_M(r) = hcD_e \left[ 1 - e^{-a(r-R_0)} \right]^2$$

$$\text{Where, } a = \sqrt{\frac{\mu\omega^2}{2hcD_e}}$$



# Schrodinger equation of diatomic molecules: Born-Oppenheimer approx.

The Schrodinger equation can be solved for the Morse potential, resulting permitted energy levels reads;

$$G(v) = \left(v + \frac{1}{2}\right) \tilde{\nu} - \left(v + \frac{1}{2}\right)^2 \tilde{x}_e \tilde{\nu}, \text{ where } \tilde{x}_e = \frac{\nu}{4D_e}.$$

The number of vibrational levels for a Morse oscillator is finite:  $v = 0, 1, 2, 3, \dots, v_{max}$

## Coupling of rotational and vibrational motion

Neglecting constants;

$$\text{Rotational motion: } E(R) = \frac{J(J+1)\hbar^2}{2\mu R_0^2}$$

$$\text{Vibrational motion: } E(R) = \left(n + \frac{1}{2}\right) \hbar\omega_0, \text{ where } \omega_0^2 = \frac{1}{\mu} \left[\partial^2 E_a / \partial R^2\right]_{R=R_0}$$

The two are not strictly independent. For instance, the torque  $I = \mu R_0$  should be replaced by  $I = \mu R^2$ , where  $R$  is now given by the instantaneous value owing to vibrational motion.



# Schrodinger equation of diatomic molecules

The energy should take the form

$$E(R) = E_{ele}(R_0) + \left(n + \frac{1}{2}\right) \hbar \omega_0 + \frac{1}{2\mu R^2} J(J+1) \hbar^2$$

↓  
Electronic energy

↘  
Vibrational

↘  
Centrifugal distortion,  $R \rightarrow R_0$

$$F_{centri} = \mu \omega^2 R_0 = J / \mu R_0^3 \equiv J / \mu R^3$$

$$F_{harmonic} = -\mu \omega^2 (R - R_0)$$

$$dE = -\int F_{centri} dR$$

$$E_{rot} = \frac{J^2}{2\mu R_0^2} - \frac{J^4}{2\mu^3 R_0 \omega^2}$$

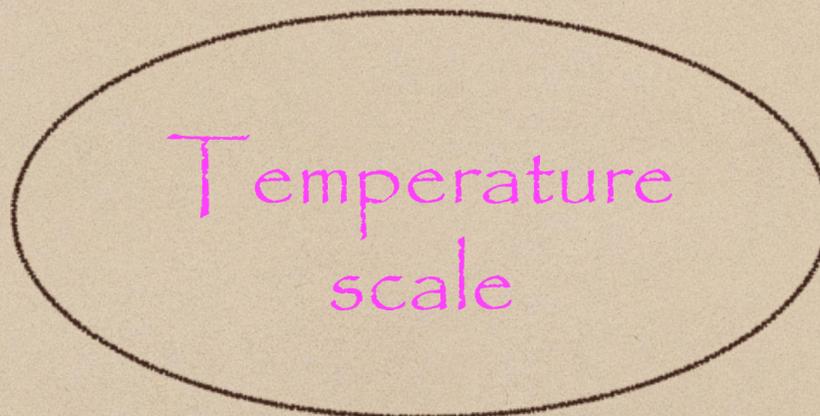
# Atomic & molecular physics at diff. Temperature

$\sim 10^4 - 10 \text{ K}$

Fusion Plasma and stellar environment, Understanding the Molecular interactions in astrophysics, Formation of complex molecules in interstellar environment

$\sim 10^{-1} \text{ K}$

Atomic and Molecular beams, Clusters



$\sim 10^{-6} \text{ K}$

Laser cooled atoms, Atomic clocks, Nanotechnology using cold atoms

$\sim 10^{-9} \text{ K}$

Bose-Einstein Condensation, Fermi Sea, Quantum many body physics, Matter wave optics, Atom interferometry,

— Atomic Physics is bedrock of condensed matter physics

# Some current researches

## Computational physics

COMMENT

What's next for atomic and molecular physics software?

Andrew Brown

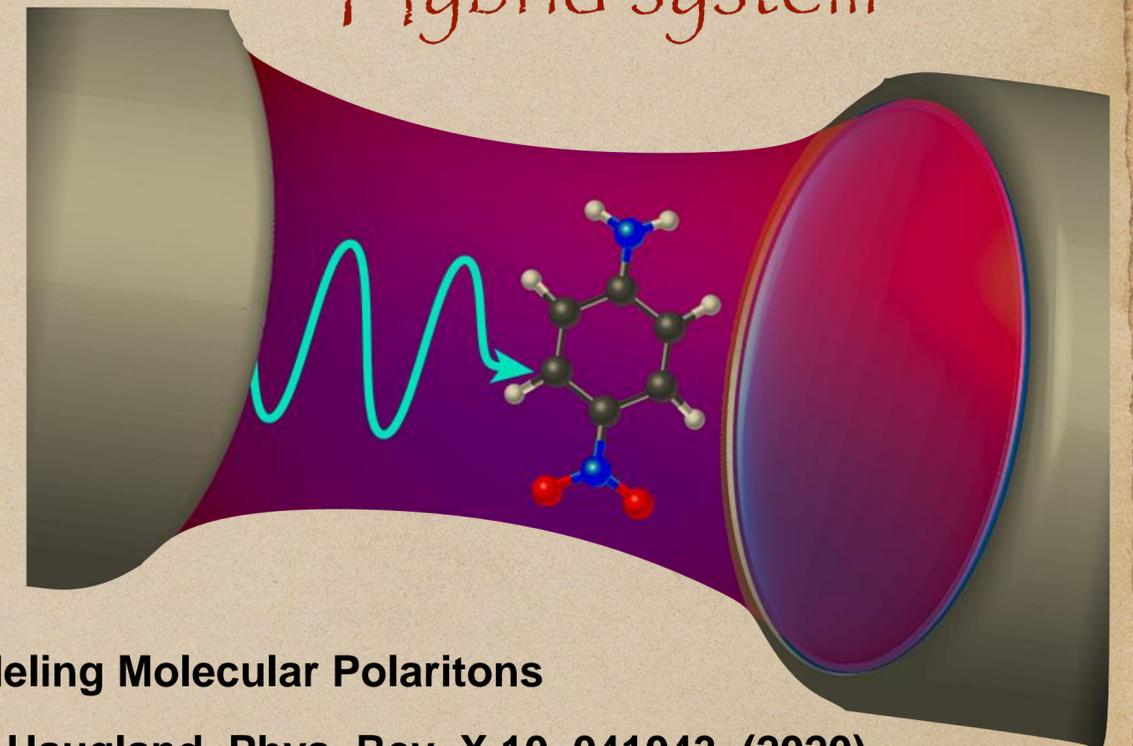
Centre for Theoretical Atomic, Molecular and Optical Physics (CTAMOP), Queen's University Belfast, UK

If you are interested in atomic molecular and optical physics, your first step should be to give yourself a solid grounding in the history of the numerical methods that are still used after nearly 100 years of development [1]. Then, for some simple problems, you might be able to engineer a pen-and-paper solution or even a short piece of computer code. However, for real, heavyweight atomic molecular and optical

# Thanks to ASP



## Hybrid system



Modeling Molecular Polaritons

T.S. Haugland, Phys. Rev. X 10, 041043 (2020)

On personal note:

Can we study/infer atoms and molecular behaviour from thermodynamics?

