

# Quantum Chemistry and Spectroscopy

Sem-IV (general course)

Physical Chemistry

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## *Particle in One Dimensional Box*

### Quantisation of motion

If a stretched string is rigidly clamped at both ends then it will have fixed length. We can only set up standing wave on it. This standing wave can only have definite and discrete frequencies (fundamental mode and overtones). So quantisation of motion arises due to confining of the wave at definite region of space. This concept is applied to all kind of waves including matter wave. For matter wave, dealing with energy (E) is easier than frequency because of Schrodinger equation.

### Confinement Principle

An electron of an atom held within the atom by coulombic interaction between electron and nucleus and it can exist only in a set of discrete energy states. This electron is not a free electron. On the other hand an electron moving in positive x direction and subject to no net force is a free particle that can have any reasonable value. According to confinement principle, Confinement of a wave leads to quantisation – that is, to the existence of discrete states and discrete energies. (Halliday, Resnick and Walker – Fundamentals of Physics, 6<sup>th</sup> edition . (page 980).

### Particle in one dimensional box

A particle of mass m is confined in region along x direction between  $x = 0$  and  $x = a$ . suppose, the particle experience no potential energy,  $V(x) = 0$  inside this region,  $\psi(x)$  is the wave function associate with it . This is called the problem of a free particle in one dimensional box. This simple model has a crude application to the  $\pi$  electron in linear conjugated hydrocarbon. Schrodinger equation for this problem is

$$(d^2/dx^2)\psi(x) + (2mE/\hbar^2) \psi(x) = 0 \quad 0 \leq x \leq a$$

So it is a free particle , particle is not subject to any kind of force other than a uniform potential field which is taken as zero. There is no potential barrier to restrict the motion of the particle.

$$(d^2/dx^2)\psi(x) + (2mE/\hbar^2) \psi(x) = 0$$

equation of this type canbe generally written as

$$(d^2y/dx^2) + \omega^2 y = 0$$

General solution of this equation is  $y(x) = c_1 e^{i\omega x} + c_2 e^{-i\omega x}$

Or  $y(x) = A \cos \omega x + B \sin \omega x$

The probability of finding the particle outside the region is zero.  $\Psi(x)$  is continuous inside this box of length a. Therefore  $\psi(0) = \psi(a) = 0$  is the boundary for this problem.

*Now the discrete wave patterns (in which the string can oscillate) are those for which the length a of the string is equal to integral multiple of half wave length. Where n indicates state of the oscillating string.*

*For particle wave n is called quantum number.*

$$a = (n \lambda / 2)$$

The general solution of Schrodinger equation for this problem is

$$\psi(x) = A \cos kx + B \sin kx$$

where  $k = (2mE)^{1/2} / \hbar$

Applying boundary condition

$\psi(0) = 0$  implies  $A = 0$ .

The second boundary condition gives

$\psi(a) = B \sin ka = 0$

So  $ka = n\pi$  where  $n = 1, 2, 3, \dots$

Now  $\psi(x) = A \sin kx = A \sin(n\pi x/a)$

Putting  $k = n\pi/a$  we find that  $E_n = (\hbar^2/8ma) n^2$   $n = 1, 2, 3, \dots$

So energy of the particle is quantised. (So the introduction of integral arises in the same natural way as in vibrating string for which the number of nodes is integral). The quantum state for lower possible energy state  $E_1$  is called ground state. It can be changed to an excited state only if an external source provides the energy that is required for this transition. If confined electron is to absorb a photon, the energy  $h\nu$  of the photon must be equal to the energy difference  $\Delta E$  between initial energy level to next higher energy level.

$\Delta E = h\nu = E_{n+1} - E_n$

*(Though absorption and emission can be applied to the electron traps. But in reality it cannot be applied to one dimensional case because photo absorption and emission require conservation of angular momentum.)*

### Zero point energy

$E_1$  is the ground energy state for particle in one dimensional box. Electron will occupy this state unless no energy is supplied to excite the electron in its next higher energy state. If ground state energy was zero it would have  $|\Psi|^2 = 0$ . So there cannot be any electron inside the one dimensional box. So it is an important conclusion that any confined system cannot exist in state with zero energy. They always have a certain minimum energy ( $E = \hbar^2/8ma$  here) called *zero point energy*.

### Normalisation of the Wave function

According to the Born approximation

$p(x) = \Psi_n^*(x) \Psi_n(x) dx$

is the probability that a particle is located between  $x$  and  $x + dx$ . Particle is confined in space between  $x=0$  and  $x=a$  so the probability of the particle lies between  $x=0$  and  $x=a$  must be unity.

$\int_0^a \Psi_n^*(x) \Psi_n(x) dx = \int_0^a A^2 \sin^2(n\pi x/a) dx = 1$

The wave function that satisfy this equation is said to be normalised.

$\Psi_n(x) = \sqrt{\frac{2}{a}} \sin(n\pi x/a)$

$A = \sqrt{\frac{2}{a}}$  is called normalisation constant.

## Postulate of quantum Mechanics

**Postulate 1** *A state of a system is defined by a mathematical function  $\psi$ , called the state function or the wave function which determines all measurable quantities of the system at that state.  $\Psi$  is a function of coordinates of all the particles and also time. Wave function  $\Psi$  is interpreted physically as  $|\Psi|^2$  being the probability density for finding the particles at given locations in space. For one particle system  $|\Psi|^2$  is probability of finding the particle at time  $t$*

with coordinates  $x_1$  to  $x_1+dx$ ,  $y_1$  to  $y_1+dy$ , and  $z_1$  to  $z_1+dz$  in a tiny volume of dimension  $dx dy dz$ .

$$\Pr(x_1 < x < x_1+dx, y_1 < y < y_1+dy, z_1 < z < z_1+dz)$$

$$= |\Psi(x_1, y_1, z_1, t)|^2 dx dy dz$$

$\Psi$  is a complex quantity so value of  $|\Psi|^2 = \Psi^* \Psi$  where  $\Psi^*$  is complex conjugate of  $\Psi$ . For one particle one dimensional (say in x direction) system, the probability of finding the particle somewhere in x direction must be 1. So  $\int_{-\infty}^{+\infty} |\Psi|^2 dx = 1$ .

**Postulate 2** to every physically measurable or observable quantity like position, momentum, energy etc of a system there corresponding a linear operator in quantum mechanics.

An operator is a rule for transforming a given function into another function. Suppose  $\hat{A}$  symbolise an operator that transforms a function  $f(x)$  into  $g(x)$  then  $\hat{A} f(x) = g(x)$ .

**(operator) (function) = (new function)**

In quantum mechanics, each physical property of a system has a corresponding operator. (list of quantum mechanical operator see McQuarrie, sec 4.2). When an operator is applied to a function gives the function back but multiplied by the constant  $c$ ,  $\hat{A} f = c f$  then  $f$  is called an eigen function of  $\hat{A}$  with eigen value  $c$ .

The operators that corresponds to physical entities in quantum mechanics are linear.

$$\hat{A}(f + g) = \hat{A} f + \hat{A} g \quad \text{and} \quad \hat{A}(cf) = c \hat{A} f$$

If the system's state function  $\psi$  happens to be an eigen function of  $\hat{A}$  correspond to the property  $A$  with eigen value  $c$ , then a measurement of  $A$  is certain to give the value  $c$  as the result.

The average value of any physical property  $A$  in a system whose state function is  $\psi$  is given by  $\langle A \rangle = \int \psi^* \hat{A} \psi dt$

Where  $\hat{A}$  is the operator for property  $A$  and integral is done over whole space.

## Commutation relation

The product of two operators is define by operating them on a function. Suppose  $a$  and  $b$  are two operators and  $f(x)$  is a function.  $ab f(x)$  indicates that  $b$  is operating upon  $f(x)$ , producing new function and then  $a$  is operating on that new function. Consider two fundamental operators  $x$  and  $p$ ,  $xpf(x) = x(-i\hbar) \frac{d}{dx} f(x)$  and  $pxf(x) = (-i\hbar) \frac{d}{dx} xf(x) = (-i\hbar)f(x) - x(-i\hbar) \frac{d}{dx} f(x)$  and  $(xp - px)f(x) = i\hbar f(x)$  if  $f(x)$  is differentiable. So  $x$  and  $p$  non commutating. It is customary to use  $[Ab] = ab - ba$  and this is called commutator of  $a$  and  $b$ . if  $[Ab] = 0$  then  $a$  and  $b$  commute with each other. commutator operator have simultaneous eigenstates. These cannot be measured simultaneously.

**Postulate 3:** The only possible value that can be observed of a physical properties like energy, angular momentum etc. of a system in a stationary state are the eigenvalues of the operator of the type

$$\hat{A} \psi = c\psi$$

then  $\psi$  is wave behaved function called an eigen function of operator  $\hat{A}$  of the observable obtained by Schrodinger prescription with eigen value  $c$ .

Postulate 3. In any measurement of the observable associated with

**Postulate 4:** If a system is in a state described by a normalized wave function  $\Psi$ , then the average value of the observable corresponding to  $\hat{A}$  is given by

$$\langle A \rangle = \int \psi^* \hat{A} \psi \, d\tau / \int \psi^* \psi \, d\tau$$

When the wave function is normalised  $\int \psi^* \psi \, d\tau = 1$

( integrations are done over all space of wave function)

**Postulate 5** The wave function or state function of a system evolves in time according to the time-dependent Schrodinger equation  $\hat{H} \psi = (ih/2\pi) \frac{\partial}{\partial t} \psi$

## Spectroscopy

In 1900 Max Planck explained the phenomenon “Black Body Radiation” by concluding that light must be quantised.

When light enters the cavity with a small opening, it is reflected throughout the internal surface. The light that escapes is representative of the internal temperature of the cavity. Classical theory predicts that the intensity of the light that escapes increases with the frequency of the light. Classically, the intensity of the light increases to infinity as the temperature increases. Experimentally, the maximum intensity shifts to the blue as temperature increases.

$$\rho(\nu) d\nu = [ (8 \pi h) / c^3 ] \nu^3 [ 1 / (e^{(h\nu/kT)} - 1) ]$$

Planck’s equation corrected for classical failure by stating that energy can only be transferred in a finite minimum quantity.

In 1905 Albert Einstein used Planck’s Law to explain the Photoelectric Effect.

When light strikes the surface of certain metals, electrons are ejected. The ejected electrons produce a current that proportional to their number.

It is found that the current produced follows the light intensity. And there is a frequency dependence, below which, no electrons are ejected.

1905 –Einstein: oscillators in light source can only have quantized energies

$$E = nh\nu \quad (n = 0, 1, 2, 3, \dots)$$

As oscillators change their energy from  $nh\nu$  to  $(n-1)h\nu$ , emit radiation of frequency  $\nu$  and energy  $h\nu$  (photon). If the photons energy is more than  $\Phi$  then an electron is ejected:

$$KE(\text{electron}) = E(\text{photon}) - \Phi = \frac{1}{2} m_e v^2$$

### The Wave-like Nature of a Particle

Louis de Broglie in response to Planck & Einstein’s assertion that light was “particle-like” (photon) stated that small particles moving fast could exhibit a characteristic wavelength.

$$E = mc^2 \quad \text{so, } E = h\nu = mc^2 \text{ (it can be concluded that particles have a wave length)}$$

$h(\nu/c) = mc = p$  momentum, (it can be concluded that light have a mass)

Again  $(v/c) = (1/\lambda)$

$$p = (h/\lambda)$$

(Example 1: What is the de Broglie wavelength of an electron traveling at 0.1 c (c= speed of light)?  $c = 3.00 \times 10^8$  m/s  $m_e = 9.1 \times 10^{-31}$  kg,  $h = 6.63 \times 10^{-34}$  J s

$$\lambda = (h/p) = (h/mc) = (6.63 \times 10^{-34}) / [(3.00 \times 10^8)(0.1)(9.1 \times 10^{-31})]$$
$$= 2.4 \times 10^{-11} \text{ m} = 0.24 \text{ \AA} \text{ (on the order of atomic dimensions)}$$

Example 2: What is the de Broglie wavelength of a 1 gram marble traveling at 10 cm/s (given,  $h = 6.63 \times 10^{-34}$  J s)

$$\lambda = (h/p) = (h/mc) = (6.63 \times 10^{-34}) / [(0.1)(10^{-3})]$$
$$= 6.6 \times 10^{-30} \text{ m} = 6.6 \times 10^{-20} \text{ \AA} \text{ (insignificant)}$$

So, from the above discussion it can be concluded that the wave looks like superimpose on a particle or the electron appears as a build up of amplitude in the wave.

De Broglie showed that Bohr's arbitrary quantum rule was natural corollary of de Broglie's hypothesis if one assumed that an electron in a stable Bohr orbit may be regarded as a standing wave and thus must consist of an integral number of wave length.

Therefore

$$n\lambda = 2\pi r \quad n = 1, 2, 3, \dots$$

putting the value of  $\lambda$  from above to de Broglie equation

$$\lambda = (2\pi r/n) = (h/p) \text{ or } pr = (nh/2\lambda) \text{ or } mvr = (nh/2\pi)$$

that is Bohr quantum condition. So quantisation comes naturally if we consider the waves associated with particles in their bound state.

### ***Spectroscopy and its importance in chemistry***

Spectroscopy measure the interaction of matter with radiation. It deals with the observation of the ways atoms or molecules exchange energy with the outer world. According to Bohr's resonance condition spectra arises from absorption and emission of definite quanta of radiation when transitions occur between two energy levels ( $E_1$  and  $E_2$ ).

$$|E_2 - E_1| = hv = (hc/\lambda) = hc\bar{\nu}$$

Where  $h$  = Planck constant,  $\nu$ ,  $\lambda$ ,  $\bar{\nu}$  are frequency, wave length, and wave number of the emitted and absorbed radiation. By means of this interpretation of the energy level based on quantum mechanics details information can be derived concerning structure of atoms and molecules or crystal, arrangement of ions in molecules or crystals, shape of the molecules, dissociation energies etc. analysis of kinetics of photochemical reactions requires understanding of photochemical process that can occur when light is absorbed by chemical reactants.

## **Interaction of electromagnetic radiation with matter**

An atom can interact with electromagnetic radiation and its electronic state may change thereby giving spectra. This type of spectroscopy is known as electronic spectra owing to the

fact that outer most orbital electron transits from one energy level to another energy level. A molecule also can absorb or emit energy during its transition between two different electronic levels. A molecule can change its energy in two other possible ways, which do not occur in atoms. The vibration of atoms within the molecules and rotational states of the molecules. When electron is expelled from inner most energy level of the atom X rays generate.

Vibrational and rotational levels are also quantised so certain distinct of vibrational and rotational levels are permissible. The wavelength of the absorption and emission radiation is described by the difference between the energy levels. Generally rotational spectra are found in the microwave and far infra-red region, for this a molecule must have permanent dipole moment. Vibrational – rotational spectra are found in mid and near infra – red region and electronic spectra in visible and ultraviolet region.

### Type of spectra

A spectrum (sequence of ordered things, here light) which consists of bright lines produced by the emission of electromagnetic radiation called *emission* spectra, and the dark lines produced by absorption of incident light is known as *absorption* spectrum. The spectra generally consist of closely spaced lines packed into groups are called *bands*.

Radiation Region	Frequency range(Hz)	Wave number ( cm <sup>-1</sup> )	Molecular energy levels involved	Information obtained
Radio frequency	10 <sup>6</sup> to 10 <sup>9</sup>	3x10 <sup>-1</sup> to 3x10 <sup>-4</sup>	Reversal of spin of nuclear or electrons	Structural information of molecules
Microwave	10 <sup>9</sup> to 10 <sup>11</sup>	0.3 to 3	Rotation of heavy molecules	Inter molecular distance and dipole moment
Far Infra-red	10 <sup>11</sup> to 10 <sup>13</sup>	3 to 300	Rotation of light and vibration of heavy molecules	Inter molecular distance and bond force constant
Mid and near infra-red	10 <sup>13</sup> to 10 <sup>14</sup>	300 to 3000	Vibration-rotation of light molecules	Inter molecular distance and bond force constant
Visible and Ultra violet	10 <sup>14</sup> to 10 <sup>16</sup>	3000 to 30000	Electronic transition	Bond dissociation energy
X – rays	10 <sup>16</sup> to 10 <sup>18</sup>	3x10 <sup>5</sup> to 3x10 <sup>7</sup>	Energy change of inner electron	Structure of crystal
Γ - rays	10 <sup>18</sup> to 10 <sup>20</sup>	3x10 <sup>7</sup> to 3x10 <sup>9</sup>	Rearrangement of nucleus	-

When the excitation energy is small, transition between rotational levels are possible and spectral lines are appeared in microwave and far infra – red region. Rotational spectra provide information about the moment of inertia (distribution of mass around an axis), interatomic distances, bond angle and dipole moment. If excitation is sufficient, transition occur between vibrational levels ( vibrational transition is associate with number of rotational transition) which gives information about vibrational frequency and force constant of the bond.