INDEX

CHAPTER NO.	CHAPTER NAME	PAGE NO.
1	QUANTUM CHEMISTRY	1
1.1	Introduction:	1
1.2	Postulates of Quantum Mechanics:	9
1.3	Detailed Explanation of The Parameters Involved In The Postulates:	10
1.4	The Time Independent Schrödinger Wave Equation:	24
1.5	The Schrodinger Equation And De Broglie Waves	51
1.6	Tunnelling	52
1.7	Valence Bond Theory	54
1.8	Variation Principle	60
1.9	Perturbation	63
1.10	Molecular Orbital Theory	67
1.11	Symmetric and Antisymmetric Wave – Functions of Hydrogen Molecules:	75
1.12	Huckel Molecular Orbital Theory	79
1.13	Atomic Structure	92
1.14	Identical Particles:	98
1.15	Zeeman Effect	101
2	SPECTROSCOPY	105
2.1	Microwave Spectroscopy	105
2.2	Infra-Red Spectroscopy	121
2.3	Electronic Spectroscopy	146
2.4	Raman Spectroscopy	151
3	SYMMETRY & GROUP THEORY	173
3.1	Introduction	173
3.2	Symmetry Element And Symmetry Operations:	173
3.3	Symmetry Elements	173
3.4	Symmetry Operations/Elements:	174
3.5	Point Group	182
3.6	Groups Representations:	187
3.7	Character Table & Its Derivation	196
3.8	Problems For Better Understanding	206
3.9	Formation of Hybrid Orbitals	209
3.10	I.R. And Raman Spectroscopy Explain By Group Theory:	216
3.11	Solved Problems:	222
3.12	Salcs And The Projection Operator Technique	227
4	STATISTICAL THERMODYNAMICS	232
4.1	Introduction:	232

4.2	Significance of Statistical Thermodynamics In The Physical Chemistry:	232
4.3	Ergodic Hypothesis:	232
4.4	Ensembles And Type of Ensembles:	233
4.5	Types of Statistics:	234
4.6	Sterling's Theorem or Approximation:	237
4.7	Partition Function:	237
4.8	Residual Entropy	243
5	SOLID STATE CHEMISTRY	251
5.1	Crystal Lattice:	251
5.2	Classification of Crystalline Solid:	252
5.3	Unit Cell:	252
5.4	Basic Shapes of Unit Cell:	254
5.5	Symmetry In Crystal Lattice:	254
5.6	Locating Atom In The Unit Cell:	257
5.7	Lattice Plane:	258
5.8	Interplanar Distance	259
5.9	X-Ray Diffraction and Bragg's Equations	263
5.10	Crystal Structure Determination From X-Ray Data:	264
5.11	Densities of The Crystal:	269
5.12	Scattering Factor (*F*) And Structure Factor (F)	274
5.13	Packing In Solids	280
5.14	Ionic Crystals:	286
5.15	Defects In Solids	290
5.16	Electrical Properties of Solids.	296
5.17	Magnetic Properties:	299
5.18	Energetics of Crystal:	301
6	SOLUTION STATE AND GASEOUS STATE	303
6.1	Solution & Colligative Properties	303
6.2	Kinetic Theory of Gases:	313
6.3	Deduction of Various Gas Laws from Kinetic Gas Equation:	315
6.4	Maxwell's Distribution of Molecular Velocities:	316
6.5	Principle of Equipartition of Energy:	320
6.6	Real gases: Van der Waals Equation:	321

Chapter 1

Quantum Chemistry

1.1 Introduction:

Classical mechanics was invented by **Sir Isaac Newton** to describe and predict the motions of objects such as the planets as they move about the sun. Although classical mechanics was a great success when applied to objects much larger than atoms, it was a complete failure when applied to atoms and molecules.

It was superseded by quantum mechanics, which has enjoyed great success in explaining and predicting atomic and molecular properties. However, quantum mechanics was built upon classical mechanics, and someone has said that if classical mechanics had not been discovered prior to quantum mechanics, it would have had to be invented in order to construct quantum mechanics.

1.1.1 The Old Quantum Theory

1. The Atomic Nature of Matter:

All of ordinary matter is made up of atoms. Although the idea of atoms was introduced by the Greek philosopher Democritus, it became part of chemistry only after 1803, when Dalton proposed his atomic theory.

This theory asserts that each element has its own characteristic type of atoms, and that atoms combine as units to produce compounds. Dalton's theory did not include any information about the structure of atoms and how they could bind to other atoms to make molecules. Dalton even proposed that atoms might have little hooks that could snag similar hooks on other molecules. In the 1870s Thomson showed that the "cathode rays" emitted by negatively charged metals in a vacuum consisted of negatively charged particles, now known as electrons.

Thomson pictured an atom as containing stationary electrons imbedded in a positive matrix, like raisins in an English plum pudding. However, Rutherford discovered in 1911 that an atom contains a very small positive nucleus, so that the electrons must orbit the nucleus. The charge on the electron was measured by Mulliken in a series of experiments carried out between 1908 and 1917.

Moseley, in 1913, discovered the concept of atomic number in 1913, showing that each element was characterized by the charge on its nucleus.The atomic nucleus can be regarded as being made up of protons and neutrons. Protons and neutrons now appear to be made up of quarks, and the "superstring" theory proposes that quarks, electrons, and other fundamental particles consist of vibrations of tiny strings. For most chemical purposes, it is sufficient to regard an atom as consisting of a positive nucleus and a number of negative electrons.

2. Newtons Corpuscular Theory:

Newton's corpuscular theory was based on postulates as follows:

a. Newton proposed that a source of light emits many minute, elastic, rigid and massless particles called corpuscles.
b. These particles travel through a transparent medium at very high speed in all direction along a straight line.
c. These corpuscles enter our eyes and produce the sensation of vision.
d. Due to different sizes of the corpuscles, they produce different colours.
e. These light particles are repelled by a reflecting surface and attracted by transparent materials.

Merits:

1. It explains the rectilinear propagation of light.
2. It could explain the reflection and refraction of light separately.

Drawbacks:

1. Newton's corpuscular theory fails to explain simultaneous phenomenon of partial reflection and refraction on the surface of transparent medium such as glass or water.
2. The corpuscular theory fails to explain optical phenomena such as interference, diffraction, polarization etc.
3. According to this theory, velocity of light is larger in the denser medium than in the rarer medium, experimentally it is proved wrong (v_a<v_d).
4. As the particles are emitted from the source, mass of the source of light should decrease but experiment proved that mass of the source of light is constant

3. Youngs Double Slit Experiment:

The **double-slit experiment** is a demonstration that light and matter can display characteristics of both classically defined waves and particles; moreover, it displays the fundamentally probabilistic nature of quantum mechanical phenomena. This type of experiment was first performed, using light, by Thomas Young in 1801, as a demonstration of the wave behavior of light. At that time it was thought that light consisted of either waves or particles. With the beginning of modern physics, about a hundred years later, it was realized that light could in fact show behavior characteristic of waves and particles.

The experiment belongs to a general class of "double path" experiments, in which a wave is split into two separate waves that later combine into a single wave.

In the basic version of this experiment, a coherent light source, such as a laser beam, illuminates a plate pierced by two parallel slits, and the light passing through the slits is observed on a screen behind the plate. The wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on the screen – a result that would not be expected if light consisted of classical particles. However, the light is always found to be absorbed at the screen at discrete points, as individual particles (not waves); the interference pattern appears via the varying density of these particle hits on the screen. Furthermore, versions of the experiment that include detectors at the slits find that each detected photon passes through one slit (as would a classical particle), and not through both slits (as would a wave). However, such experiments demonstrate that particles do not form the interference pattern if one detects which slit they pass through. These results demonstrate the principle of wave–particle duality.

4. Huygens Principle:

In 1678, Dutch physicist, Christiaan Huygens, believed that light was made up of waves vibrating up and down perpendicular to the direction of the light travels, and therefore formulated a way of visualising wave propagation. This became known as 'Huygens' Principle'.

Huygens' Wave Theory: Postulates on which Huygens' wave theory are given as follows:

1. The source of light emits light in the form of waves.
2. Light waves are like sound wave, which are longitudinal in nature.
3. Light waves move with constant speed in a homogeneous medium.
4. Different colours of light are due to different wavelengths of light waves.
5. When light waves enter in our eyes we feel the sensation of vision.
6. Light waves travel through vacuum due to presence of a hypothetical medium called as luminiferous ether.

Merits:

1. Wave theory of light is helpful to explain phenomena such as reflection, refraction, interference and diffraction.
2. The phenomenon of Partial reflection and refraction of light can be satisfactorily explained using the wave theory of light.
3. As per the wave theory of light, velocity of light in optically denser medium is less than the velocity of light in a rarer medium, which is correct (va>vd).

Demerits:

1. Wave theory of light assumed the presence of hypothetical ether medium but experiment proved that there is no ether or drag.
2. Rectilinear propagation of light is not explained by this wave theory.
3. Wave theory of light could not explain phenomena such as Compton effect and polarization of light.
4. Wave theory of light could not explain bending of wave through an obstacle.
5. Wave theory of light assumed that light waves are longitudinal in nature but experiment proved that they are electromagnetic transverse waves.

5. Blackbody Radiation: The Failure of Classical Theory:

Any object will radiate energy in the form of electromagnetic radiation purely as a consequence of its temperature. The red glow of an electric heater and the bright white light of the tungsten filament in an incandescent light bulb are familiar examples. This radiation is referred to as **blackbody radiation.**

The physical properties of blackbody radiation depend only on the temperature of the object, not on its composition. If we measured the intensity of blackbody radiation versus the wavelength emitted at different temperatures, we would obtain a series of curves similar to the ones shown in Figure

1. Experiments at the end of the nineteenth century by Josef Stefan and Wilhelm Wien led to two important empirical laws of blackbody radiation, now named the Stefan-Boltzmann law and Wien's law. (An empirical law is one that is formulated purely on the basis of experimental data.)

- Stefan-Boltzmann law: The total intensity of blackbody radiation emitted by an object (obtained by integrating the curves in Figure 1 over all wavelengths) is proportional to the fourth power of the absolute temperature (that is, the temperature in kelvins)

  (total radiant emittance) = $\boldsymbol{\sigma T^4}$

  Where the Stefan–Boltzmann constant σ has the experimental value:

  $$\sigma = 5.67051 \times 10^{-8}\, Jm^{-2}\, s^{-1}\, K^{-4}$$
  $$= 5.67051 \times 10^{-8}\, Wm^{-2}\, K^{-4}$$

  where the joule (J) is the unit of energy and the watt
  (W, equal to joules per second) is the unit of power and T is the absolute temperature.

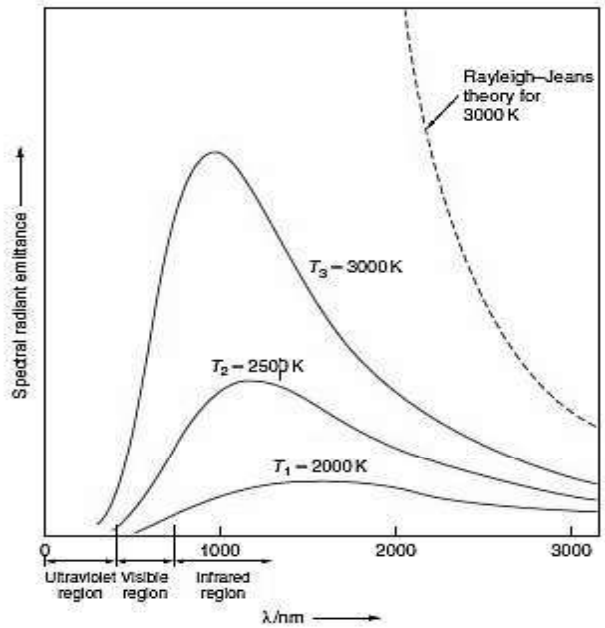


Figure 1. The Quantized Energies of an Oscillator as Postulated by Planck.

The horizontal line segments are plotted at the heights of the assumed energy values, 0, hν, 2hν, 3hν, 4hν, 5hν, 6hν, 7hν, etc.

- Wien's Law: The wavelength of maximum intensity (λ_{max}) is inversely proportional to the absolute temperature:

$$\lambda_{max} T = 2.90\ x\ 10^{-3} m.K$$

Since, $\lambda_{max} = \frac{h \times c}{4.965 \times T \times k_B}$ where h, c and k_B is plank constant velocity of light and Boltzmann constant respectively.

6. Einstein's Theory of the Photoelectric Effect:

In 1905, only five years after Planck presented his quantum theory, Albert Einstein used the theory to explain the **photoelectric effect**—a phenomenon in which electronsare ejected from the surface of certain metals exposed to electromagnetic radiation.

Experimentally, the photoelectric effect is characterized by three primary observations:

- The number of electrons ejected is proportional to the intensity of the light.
- No electrons can be ejected if the frequency of the light is lower than a certain threshold frequency, which depends upon the identity of the metal.
- The kinetic energy of the ejected electrons is proportional to the difference between the frequency of the incident light and the threshold frequency.

The photoelectric effect could not be explained by the wave theory of light. In the wave theory the energy of a light wave is proportional to the square of the amplitude (intensity) of the light wave, not its frequency. This contradicts the second observation of the photoelectric effect. Building on Planck's hypothesis, Einstein was able to explain the photoelectric effect by assuming that light consisted of particles (light quanta) of energy hν, where ν is the frequency of the light. These particles of light are called **photons.**

Electrons are held in a metal by attractive forces, and so removing them from the metal requires light of a sufficiently high frequency (which corresponds to a sufficiently high energy) to break them free. We can think of electromagnetic radiation (light) striking the metal as a collision between photons and electrons. According to the law of conservation of energy, we have energy input equal to energy output.

If ν exceeds the threshold frequency, Einstein's theory predicts:

$$\frac{1}{2}mv^2 = h\nu - \varphi \qquad \text{------- (1)}$$

Where, φ, called work function of the metal, is similar to ionization energy and $\frac{1}{2}mv^2$ is kinetic energy of emitted electron.

The work function measures how strongly the electrons are held in the metal. The threshold frequency is the smallest frequency for which Equation 1 has a solution.

This occurs when the kinetic energy of the electron is zero, in which case equation 1 gives:

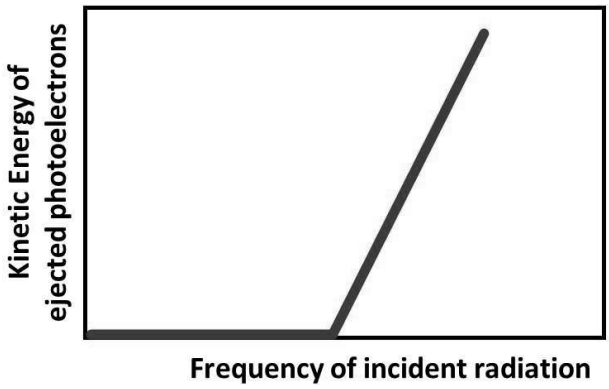
$$h\nu_{threshold} = \varphi$$

Therefore,

Kinetic energy = $\frac{1}{2}mv^2 = h\nu - h\nu_{threshold} = h(\nu - \nu_{threshold})$

The kinetic energy of electron is also equal to = -e x V_s, Where V_s is the stopping potential.

Consequently, Einstein's theory predicts that the kinetic energy of the ejected electron is proportional to the difference between the incident and threshold frequencies, as required.



Kinetic energy of ejected electrons versus the frequency of applied electromagnetic radiation.

7. The Wave–Particle Duality of Light:

Since light exhibits a particle-like nature in some experiments and wave-like properties in other experiments, we say that it exhibits a wave–particle duality. We cannot give a simple answer to the question: "What is light really like?" We use the wave description when it explains a particular experiment, and use the particle description when it explains another experiments like interference, diffraction, etc.

8. The Bohr Model Was an Early Attempt to Formulate a Quantum Theory of Matter:

The work of Planck and Einstein showed that the energy of electromagnetic radiation at a given frequency (ν) is quantized in units of h ν. The extension of this quantum hypothesis to matter paved the way for the solution of yet another nineteenth-century mystery in physics: the emission spectra of atoms.

Emission Spectra of Atoms: Evidence of the Energy Quantization of Matter

Ever since the seventeenth century, chemists and physicists have studied the characteristics of **emission spectra,** which are either continuous or line spectra of the radiation emitted by substances. The emission spectrum of a substance can be seen by energizing a sample of material either with thermal energy (heating) or with some other form of energy (such as a high-voltage electrical discharge). A "red-hot" or "white-hot" iron bar freshly removed from a high-temperature source produces a characteristic glow. This visible glow is the portion of its emission spectrum that is sensed by eye. The warmth of the same iron bar represents the infrared region of its emission spectrum. The emission spectra of the sun and of a heated solid are both continuous; that is, all wavelengths of visible light are represented in the spectra.

The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelengths from red to violet; rather, the atoms produce bright lines in different parts of the visible spectrum.
These **line spectra** are light emissions at specific wavelengths.

The Emission Spectrum of Hydrogen:

At the end of the nineteenth century, physicists began exploring the emission spectra of atoms in quantitative detail. Of particular interest, because of the simplicity and importance of the first element, was the emission spectrum of hydrogen.

The Swedish physicist Johannes Rydberg analyzed the existing experimental data and formulated the following equation for the frequencies of the lines in the hydrogen emission spectrum:

$$\bar{\nu} or \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 109680\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^{-1} \quad and\ (n_2 > n_1)$$

where n_1 and n_2 are two positive integers and R_H is a constant known as Rydberg's constant, equal to 109677.581 cm^{-1} if the wavelengths are measured in a vacuum. Classical physics was unable to explain this relationship.

The First Five Spectral Series in the Emission Spectrum of Hydrogen

Series	n_1	n_2	Spectral Region
Lyman	1	2, 3, 4, ...	Ultraviolet
Balmer	2	3, 4, 5, ...	Visible
Paschen	3	4, 5, 6 ,.....	Near Infrared
Bracket	4	5, 6, 7,.....	Infrared
Pfund	5	6, 7, 8 ,.....	Far infrared

9. The Wave-Particle Duality of Matter—The de Broglie Hypothesis:

Niels Bohr received the 1922 Nobel Prize in physics for his hydrogen atom theory, based on an assumption of quantization of angular momentum. In 1923 a graduate student at the University of Paris named Prince Louis de Broglie was trying to find a physical justification for Bohr's hypothesis of quantization.

In classical physics, one thing that is quantized is the wavelength of a standing wave. De Broglie sought a way to relate this to Bohr's theory and came up with the idea that a moving particle such as an electron is accompanied by a "fictitious wave." According to Einstein's theory of relativity, a particle of energy E has a mass m such that

$$E = mc^2 \qquad \ldots\ldots \quad (1)$$

where c is the speed of light. If we apply this to a photon and use the Planck–Einstein relation, for the energy and if we replace mc by the momentum p, The Eq. 1 becomes

$$E = \frac{hc}{\lambda} = pc \; or \; \lambda = \frac{h}{p} \qquad \ldots\ldots \quad (2)$$

Where λ is the wavelength of the photon and h is Planck's constant. De Broglie deduced that the velocity of the wave accompanying a particle was the same as the velocity of the particle.

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad ---------- \quad (3)$$

We omit de Broglie's argument, which is more complicated. The quantization assumption of Bohr's theory arises naturally from Eq. 3 if one assumes that the circumference of a circular electron orbit in a hydrogen atom is equal to an integral number of wavelengths. This assumption means that the wave repeats itself with the same phase (with crests in the same positions) on each trip around the orbit. For a circular orbit

$2\pi r = n\lambda = \frac{nh}{mv}$ Therefore, $mvr = \frac{nh}{2\pi}$

In terms of kinetic energy

$$p = \sqrt{2mE_k}$$

Where E_k is kinetic energy

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_k}}$$

If a charged particle carrying charge q is associated through a potential difference V volts, then kinetic energy $E_k = Qv$.

Therefore, de-Broglie wave length for charged particle of charge q and accelerated through a potential difference of V volt is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mqV}}$$

When a material particle like neutron is in thermal equilibrium at temperature T, then they possess Maxwell distribution of velocities and so the kinetic energy of most of material is given by

$$E_k = kT$$

Where k is Boltzmann's constant $k=1.38\times10^{-23}$

10. The Heisenberg Uncertainty Principle:

One of the assumptions of classical physics is that the dynamical variables (positions and moment) of a particle in motion have well-defined, precise values.

However, the concept of a precise position becomes ill-defined when we try to describe a particle as a wavelike object.

A wave is an object that is extended over some region of space. To describe the problem of trying to locate a subatomic particle that behaves like a wave, Werner Heisenberg formulated what is now known as the

Heisenberg Uncertainty Principle:

It is impossible to know simultaneously both the momentum p (defined as mass time's velocity) and the position of a particle with certainty.

Stated mathematically we have:

$$\Delta x\, \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2}$$

where Δx and $\Delta p$are the uncertainties in measuring the position and momentum, respectively.

Thus, if we measure the momentum of a particle more precisely (that is, if we make Δpa small quantity), our knowledge of the position will become correspondingly less precise (that is, Δxwill become larger).

Similarly, if the position of the particle is known more precisely, then its momentum must be known less precisely.

This inverse relationship arises because the position of a wavelike particle is determined by the region of space occupied by the wave, but the momentum, through the de Broglie relationship, is related to the wavelength of the wave.

1.1.2 Solved Problems:

1. Newton's corpuscular theory could explain correctly the phenomenon of:
   a. interference of light
   b. diffraction of light
   c. rectilinear propagation of light
   d. simultaneous reflection and refraction of light.

   Answer: d: simultaneous reflection and refraction of light.

2. Huygens' wave theory of light could not explain:
   a. reflection
   b. refraction
   c. interference
   d. photoelectric effect

   Answer: d. photoelectric effect

3. Huygens' original theory of light assumed that light propagates in the form of:
   a. transverse mechanical waves.
   b. longitudinal mechanical waves.
   c. transverse electromagnetic waves.
   d. minute elastic particles.

   Answer: b. longitudinal mechanical waves

4. The phenomenon of diffraction and refraction indicates that light is having:
   a. particle nature
   b. wave nature
   c. both particle and wave nature
   d. neither particle nor wave nature

   Answer: b. wave nature

5. Two points, equidistant from a point source of light, are situated at diametrically opposite positions in an isotropic medium. The phase difference between the light waves passing through the two points is :
   a. zero
   b. π rad
   c. π/2 rad
   d. 2 π rad

   Answer: a. 0 rad

6. Given that the work function of Na is 1.82 eV. What is the threshold energy?

   Explanation:

$$h\vartheta_0 = 1.82\ \text{eV}$$
$$h\vartheta_0 = 1.82\ \times 1.6\ \times 10^{-19}$$
$$\vartheta_0 = \frac{1.82\ \times 1.6\ \times 10^{-19}}{6.6\ \times 10^{-34}}$$
$$\vartheta_0 = 0.40\ \times 10^{15}\text{s}^{-1}$$

7. If light of wavelength 4000 A strikes a metal surface with work function 2.13 eV, calculate the energy of the photons and the kinetics energy of the emitted electron. Also calculate the enrgy of the emitted electron?

   Explanation:

$$E = \frac{hc}{\lambda}$$
$$E = \frac{6.6\ \times 10^{-34} \times 3 \times 10^{8}}{4000 \times 10^{-10}}$$
$$E = 4.98\ \times 10^{-20}$$

Kinetic energy = $\frac{1}{2}mv^2 = h\nu - h\nu_{\text{threshold}}$

$$KE = (5 \times 10^{-20} - 2.13 \times 1.6 \times 10^{-19})$$
$$KE = 1.8\ \times 10^{-19}\ \text{J}$$
$$KE = \frac{1}{2}mv^2$$
$$v = \left(\frac{2E}{m}\right)^{\frac{1}{2}} = \sqrt{\frac{2 \times 1.8\ \times 10^{-19}}{9.1\ \times 10^{-31}}} = = \sqrt{4\ \times 10^{11}} = 6.3\ \times 10^{5}\text{s}^{-1}$$

8. Which of the following is NOT a correct consequence of the Heisenberg uncertainty principle:
   a. The shorter the lifetime of an excited state of an atom, the less accurately can its energy be measured.
   b. An electron in an atom cannot be described by a well-defined orbit.
   c. The momentum of an electron cannot be measured exactly.
   d. Measurement of one variable in an atomic system can affect subsequent measurements of other variables.
   e. A harmonic oscillator possesses a zero-point energy.

   Answer: (C) Yes it CAN be measured exactly, but then uncertainty in position is infinite

9. The ionization energy for hydrogen atom is 13.6 eV. The ionization energy for the ground state of Li^{++} is approximately
   a. 13.6
   b. 27.2
   c. 40.8
   d. 54.4
   e. 122.4 eV

   Answer: (E) $Z^2\ \times\ 13.6\ =\ 122.4\ eV$