Chapter 7: Atomic Structure
The Dual Nature of the Electron

In our discussions, we will consider the electron in two different ways:
  (1) as a particle, with characteristic mass and charge
  (2) as a wave, with characteristic frequency which can undergo diffraction, like light.

This interrelationship between particle and wave behavior was shown first for light and other electromagnetic radiation. E.g. light can be described as a wave with characteristic wavelength (λ), frequency (ν) :

$$c = \lambda \nu$$

where c = speed of light = 3.00×10^8 m/s
λ = wavelength (m)
ν = frequency (s^{-1} or cycles/s or Hz)

However, in some experiments such as the photoelectric effect (Section 5-10) light behaves like it was composed of particles, called photons, having certain amount of energy.

$$E = h\nu = \frac{hc}{\lambda}$$

where E = energy of a photon (J/photon)
h = Planck's constant, 6.63×10^{-34} J·s

Note: De Broglie in 1925 thought that other particles like electrons might also exhibit wave properties under the right conditions and gave us this relationship :

$$\lambda = \frac{h}{m_v v}$$

wave-like   particle-like

where λ = wavelength (m)
m_v = mass at velocity, v (kg)
v = velocity (m/s)
h = Planck's constant (J·s)

With this equation, you can calculate the wavelength of a baseball or the mass of a photon.(moving, of course, at speed of light)

An observation was made in 1800's by Rydberg and others: when electric current was passed through a gas at low pressure, emission lines were produced, called "bright line spectra." None of the earlier theories of the atom could account for this.

Bohr (1913) explained this observation with his theory of the atom:

(1) the atom has a number of definite discrete energy levels,

(2) an electron may move from one energy level to another but it must emit or absorb energy. (radiation)

$$\Delta E = h\nu$$
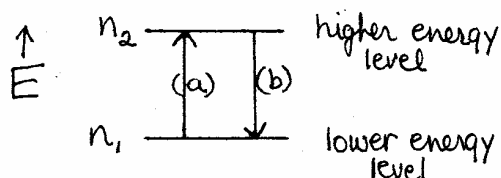
(a) energy is absorbed (as photon)

(b) energy is released (as photon)

Example: If an atom absorbs a photon of green light ($\lambda = 5200$ Å)
  (a) what is frequency of radiation
  (b) how much energy does the atom gain?

(a) $c = \lambda \nu$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{\left(5200 \text{ Å} \times \frac{1 \times 10^{-10} \text{ m}}{1 \text{ Å}}\right)} = 5.77 \times 10^{14} \text{ s}^{-1}$$

(b) $\Delta E = h\nu = 6.63 \times 10^{-34}$ J·s $\times$ 5.77×10^{14} s^{-1}

$$= 3.83 \times 10^{-19} \text{ J/atom}$$

OR

$$\Delta E = \frac{3.83 \times 10^{-19} \text{ J}}{1 \text{ atom}} \times \frac{6.02 \times 10^{23} \text{ atoms}}{1 \text{ mol}} = 2.30 \times 10^5 \text{ J/mol}$$

(3) electrons move in circular paths (orbits) around the nucleus. Their motions are restricted by laws of mechanics and electrostatics.

However, electrons, atoms and molecules do not behave like golfballs, according to classical Newtonian mechanics. We must use a different kind of mechanics : QUANTUM MECHANICS - which treats electrons as waves!

An underlying principle of Quantum Mechanics is the Heisenburg Uncertainty Principle (1927): It is impossible to determine both the momentum (mass × velocity) and the position of an electron at the same time.

Measurement and the Uncertainty Principle

Whenever any measurement is made, some uncertainty exists. Our experience with objects of ordinary dimensions, like balls or trains or laboratory equipment, indicates that the uncertainty of a measurement can be decreased by using more precise instruments. In fact, we might expect that the uncertainty in a measurement can be made indefinitely small. However, the uncertainty principle states that there is an actual limit to the accuracy of measurements. This limit is not a restriction on how well instruments can be made; rather, it is inherent in nature. This limit has no practical consequences when we are dealing with ordinary-sized objects, but its implications are enormous when we are dealing with subatomic particles, such as electrons.

To measure an object, we must disturb it, at least a little, with our measuring device. Imagine that you use a flashlight to locate a large rubber ball in a dark room. You see the ball when the light from the flashlight bounces off the ball and strikes your eyes. When a beam of photons strikes an object of this size, it does not alter its position or momentum to any practical extent. Imagine, however, that you wish to locate an electron by similarly bouncing light off it into some detector. Objects can be located to an accuracy no greater than the wavelength of the radiation used. Thus if we want an accurate position measurement for an electron, we must use a short wavelength. This means that photons of high energy must be employed. The more energy the photons have, the more momentum they impart to the electron when they strike it, which changes the electron's motion in an unpredictable way. The attempt to accurately measure the electron's position introduces considerable uncertainty in its momentum; the act of measuring the electron's position at one moment makes our knowledge of its future position inaccurate.

Suppose, then, that we use photons of longer wavelength. Because these photons have lower energy, the momentum of the electron is not so appreciably changed during measurement, but its position will be correspondingly less accurately known. This is the essence of the uncertainty principle: *There is an uncertainty in either the position or the momentum of the electron that cannot be reduced beyond a certain minimum level.* The more accurately one is known, the less accurately the other is known. Although we can never know with certainty the exact position and motion of the electron, we can talk about the probability of the electron being at certain locations in space. In the next section we introduce a model of the atom that provides the probability of finding electrons of specific energies at certain positions in atoms.

Brown + Lemay

Therefore, we talk about the probability of finding an electron in a certain space; we resort to a statistical approach.

An atomic orbital is a region in space where the probability of finding an electron is high. We treat each electron in an atom as a standing wave - a wave that does not travel and has at least one point where it has zero amplitude.

The tenets of Quantum Mechanics are
(1),(2) similar to Bohr model
(3) the allowed energy states of atoms and molecules can be described by sets of numbers called quantum numbers (solutions to the Schrödinger equation based on electrons as wave-like)

Four Quantum Numbers – uniquely describe each electron in an atom

1. Principle quantum number (n) : describes the major energy level and volume of the region in which an electron can be found.

$$n = 1, 2, 3 \cdots$$
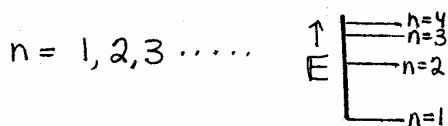
2. Subsidiary (or azimuthal) quantum number (ℓ) : designates the energy sublevel and the geometric <u>shape</u> of the region occupied by an electron. The letters s, p, d, f are code letters for shapes of orbitals.

$$\ell = 0, 1, 2, 3 \cdots (n-1)$$
$$\quad \downarrow \ \downarrow \ \downarrow \ \downarrow$$
$$\quad s \ \ p \ \ d \ \ f$$
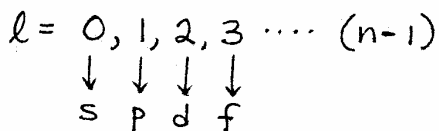
3. Magnetic quantum number (m_ℓ) : designates the spatial orientation (how the shape is oriented) of the orbital

$$m_\ell = -\ell, (-\ell+1), \cdots 0 \cdots +\ell$$

The number of values of m_ℓ is the number of orbitals in a particular sublevel. eg when $\ell = 1$ (referring to p orbitals), $m_\ell = -1, 0 +1$. There are 3 values of m_ℓ, ∴ there are 3 p orbitals.

4. Spin quantum number (m_s) : refers to the spin and orientation of the magnetic field produced by the motion of the electron in an orbital.

$$m_s = +\tfrac{1}{2}, -\tfrac{1}{2}$$

The first 3 quantum numbers: n, ℓ, m_ℓ define an atomic orbital.
All 4 quantum numbers define an electron in an orbital.

<u>Pauli Exclusion Principle</u> : No two electrons in an atom may have identical sets of 4 quantum numbers.

And so we know:
- An atomic orbital is the probability of finding an electron in a certain space.
- It is defined by the first 3 quantum numbers : n, ℓ, m_ℓ
- Each orbital can have no more than 2 electrons in it.

① Lets look at the lowest major energy level an electron can occupy: $n = 1$

$\therefore \ell$ must be 0   since $\ell = 0 \cdots n-1$ and $n-1 = 1-1 = 0$
$\therefore m_\ell$ must be 0   since $m_\ell = -\ell \cdots 0 \cdots +\ell$ and $\ell = 0$

This is a $\underset{\substack{\nearrow \\ n=1}}{1} \underset{\substack{\uparrow \\ \ell=0}}{s}$ orbital

The 1s orbital is spherical centered on the nucleus. The probability of finding an electron is highest near nucleus.

The maximum number of an electrons a major energy level can hold is calculated by

$$\text{maximum } \# e\text{'s} = 2n^2 = 2(1)^2 = 2$$

② The next higher major energy level: $n = 2$.   Therefore $\ell = 0$ or $\underline{1}$

ℓ	0	1		
m_ℓ	0	-1	0	+1
orbital	$\underset{\substack{\nearrow \quad \uparrow \\ n=2 \quad \ell=0}}{2s}$	$2p_x$	$\underset{\substack{\nearrow \quad \uparrow \\ n=2 \quad \ell=1}}{2p_y}$	$2p_z$

Note: When $\ell = 1$, there are 3 values of m_ℓ and so there are 3 p orbitals (p_x, p_y, p_z). But p_x does not necessarily correspond to $m_\ell = -1$, etc. We may say so only for bookkeeping's sake.

For $n = 2$, maximum $\# e\text{'s} = 2n^2 = 2(2)^2 = 8$.   The p orbitals are dumbbell shaped Fig 7.16 with p_x on x axis, p_y on y axis, p_z on z axis.

③ The n=3 major energy level: ℓ can be 0 or 1 or 2.

ℓ	0	1			2				
m_ℓ	0	-1	0	+1	-2	-1	0	+1	+2
orbital	3s ↗↑ n=3 ℓ=0	$3p_x$	$3p_y$ ↗↑ n=3 ℓ=1	$3p_z$	$3d_{x^2-y^2}$	$3d_{z^2}$	$3d_{xy}$ ↗↑ n=3 ℓ=2	$3d_{xz}$	$3d_{yz}$

maximum # e's in n=3 energy level = $2n^2 = 2(3)^2 = 18$ e's
The d orbitals are shown in Fig 7.15 Memorize!

④ The n=4 major energy level: ℓ can be 0 or 1 or 2 or 3
4s↗ 4p↗ 4d↗ 4f↗

When ℓ = 3, m_ℓ = -3, -2, -1, 0, +1, +2, +3

The maximum # e's in n=4 energy level = $2n^2 = 2(4)^2 = 32$ e's
Refer to Fig. 5-25 for pictures of the f orbitals - do not memorize, only appreciate

The spin quantum number, m_s, says that each atomic orbital (n, ℓ, m_ℓ) can have 2 electrons, each spinning in opposite directions, creating magnetic fields which attract each other.

We are now going to examine the electronic structures of different elements using their ground state (as opposed to excited state) election configuration. In building up ground state electron configurations, we use the Aufbau Principle : which says that electrons fill orbitals from the lowest energy up.

- the orbitals increase in energy with increasing n (in general)
- within n, energy increases with increasing values of ℓ

s < p < d < f in energy.