CHAPTER 6

Electronic Structure and the Periodic properties of element

From Classical Physics to Quantum Theory

- Planck discovered that atoms and molecules emit energy only in certain discrete quantities, or ***quanta***.
- *Classical electromagnetism, energy* is thought of as continuous, which meant that any amount of energy could be released in a radiation process.
- ***Electromagnetic radiation is*** *the emission and transmission of energy in the form of electromagnetic waves.*

Planck's Quantum Theory

- Classical physics assumed that atoms and molecules could emit (or absorb) any arbitrary amount of radiant energy.
- Planck said that atoms and molecules could emit (or absorb) energy only in discrete quantities, like small packages or bundles.
- Planck gave the name ***quantum to the smallest quantity of energy that*** *can be emitted (or absorbed) in the form of electromagnetic radiation.*
- *The energy E* of a single quantum of energy is given by

$$E = h\nu$$

where *h is called Planck's constant and n is the frequency of radiation. The value of* Planck's constant is 6.63×10^{-34} J . s.

PHOTOELECTRIC EFFECT

a phenomenon in which electrons are ejected from the surface *of certain metals exposed to light of at least a certain minimum frequency, called the threshold frequency.*

- *The **number of** electrons ejected was proportional to **the intensity (or brightness)** of the light, but the **energies** of the ejected electrons were **not**.*
- Below the threshold frequency no electrons were ejected no matter how intense the light.
- Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period.
- This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

- ***photoelectric effect, a phenomenon in which electrons are ejected from the surface*** *of certain metals exposed to light of at least a certain minimum frequency, called the threshold frequency.*
- Below the threshold frequency no electrons were ejected no matter how intense the light.
- if ***hv*** *is exactly equal to the energy that binds* the electrons in the metal, then it knocks electrons.
- if ***hv*** *is higher it* acquire some kinetic energy. This situation is summarized by the equation.

$$hv = KE + W$$

Example

1. Calculate the energy (in joules) of (a) a photon with a wavelength of 3.75×10^{4} nm (infrared region) and (b) a photon with a wavelength of 3.75×10^{-2} nm (X ray region).
2. The work function of magnesium metal is 5.86×10^{-19} J. (a) Calculate the minimum frequency of light required to release electrons from the metal. (b) Calculate the kinetic energy of the ejected electron if light of frequency 2.00×10^{15} s-1 is used for irradiating the metal.

Bohr's Theory of the Hydrogen Atom

Emission Spectra

- ***emission spectra is expressed as either*** *continuous or line spectra of radiation emitted by substances.*

Emission Spectrum of the Hydrogen Atom

- **Bohr** postulated that the electron is allowed to occupy only certain orbits of specific energies.
- In other words, the ***energies of the electron are quantized***.

$$E_n = -R_H\left(\frac{1}{n^2}\right)$$

- The lower energy state may be either a less excited state or the ground state. The difference between the energies of the initial and final states is

$$\Delta E = E_f - E_i$$

$$E_f = -R_H\left(\frac{1}{n_f^2}\right)$$

$$E_i = -R_H\left(\frac{1}{n_i^2}\right)$$

$$\Delta E = \left(\frac{-R_H}{n_f^2}\right) - \left(\frac{-R_H}{n_i^2}\right)$$

$$= R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

The Dual Nature of the Electron

- De Broglie reasoned that if light waves can behave like a stream of particles (photons), then perhaps particles such as electrons can possess wave properties.
- According to de Broglie, an electron bound to the nucleus behaves like a *standing* ***wave***.
- De Broglie deduced that the ***particle and wave properties*** are related by the expression:

$$\lambda = h/mu$$

where λ, *m, and u are the wavelengths associated with a moving particle, its mass,*

Quantum Mechanics

- The quantum hypothesis explained the observed rate of emission of radiation from hot bodies very well, but its implications for determinism were not realized until 1926, when another German scientist, Werner Heisenberg, formulated his famous **uncertainty principle**.
- *In order to predict the future position and velocity of a particle, one has to be able to measure its present position and velocity accurately.*
- The obvious way to do this is to shine light on the particle. Some of the waves of light will be scattered by the particle and this will indicate its position.
- However, one will not be able to determine the position of the particle more accurately than the distance between the wave crests of light, so one needs to use light of a short wavelength in order to measure the position of the particle precisely.

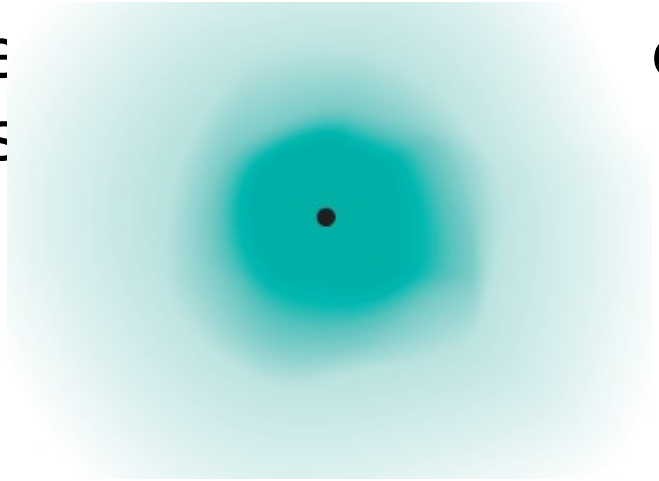
- Now, by Planck’s quantum hypothesis, one cannot use an arbitrarily small amount of light; one has to use at least one quantum.
- This quantum will disturb the particle and change its velocity in a way that cannot be predicted.
- Moreover, the more accurately one measures the position, the shorter the wavelength of the light that one needs and hence the higher the energy of a single quantum.
- So the velocity of the particle will be disturbed by a larger amount. In other words, the more accurately you try to measure the position of the particle, the less accurately you can measure its speed, and vice versa.

- Heisenberg showed that the uncertainty in the position of the particle times the uncertainty in its velocity times the mass of the particle can never be smaller than a certain quantity, which is known as Planck's constant.
- 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 the momentum (mass times velocity) and the position of a particle with certainty.*

$$\Delta x \Delta p \geq h$$

The Quantum Mechanical Description of the Hydrogen Atom

- the probability of finding the electron in a certain region in space is proportional to the square of the wave function, ψ^2.
- *The square of the wave function, ψ^2, defines the distribution* of electron density in three e around the nucleus



The Structure of Many-Electron Atoms

- An atomic orbital is specified by *three quantum numbers.*
- One is related to the orbital's **size**, another to its **shape**, and the third to its **orientation** in space.
- * The quantum numbers have a hierarchical relationship:

the size-related number limits the shape-related number, which limits the orientation-related number.

1. **The principal quantum number (n)**

is a positive integer (1, 2, 3, and so forth). It indicates the relative size of the orbital and therefore the relative distance from the nucleus of the peak in the radial probability distribution plot.

2. The angular momentum quantum number (*l*)

- related to shape and is sometimes called orbital-shape or azimuthal quantum number.
- is an integer from 0 to n-1.

3. The magnetic quantum number (ml)

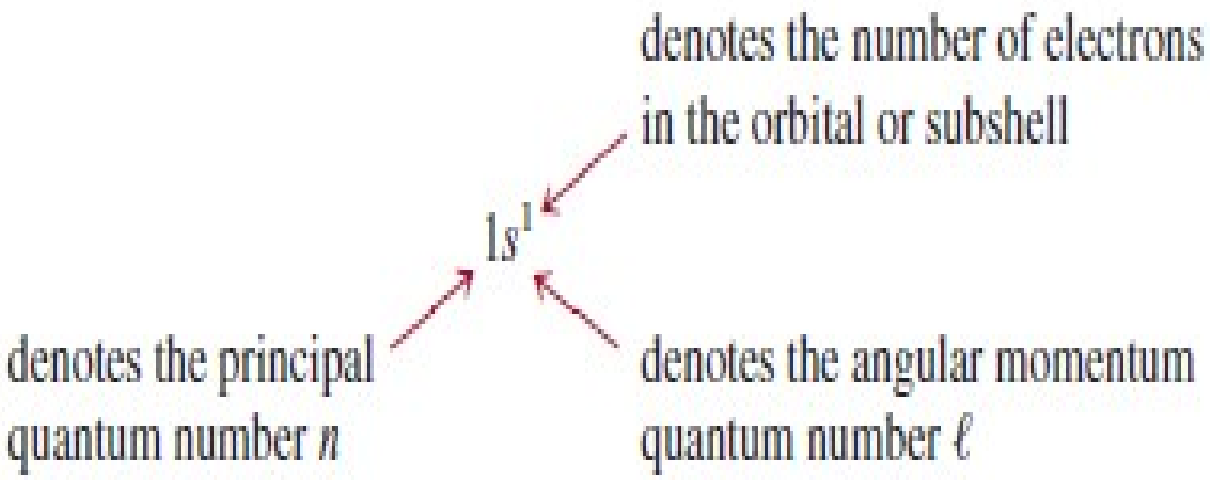
- is an integer from -*l* through 0 to + *l*.
- Prescribes the orientation of the orbital.
- Note that the number of possible *ml* values equals the number of orbitals, which is ***2l*+ 1** for a given *l* value.

4. The spin quantum number (m_s)

- may have values of +1/2 or -1/2; Indicates electron spinning direction.

Ex.

Decide the values of n, *l*, and *ml* for 3d atomic orbital!



- The energy states of **many-electron** atoms arise from **nucleus-electron** attractions, and **electron-electron** repulsions.
- For example, with lithium (Li; Z = 3) in its ground state, the first two electrons fill the ls orbital because the electrons of an atom in its ground state occupy the orbitals of lowest energy.
- Then the third Li electron must go into the n = 2 level, which has 2s and 2p sublevels.
- The 2s is lower in energy than the 2p. The reasons for this energy difference are based on three factors-**nuclear charge, electron repulsions, and orbital shape** (more specifically, radial probability distribution).

The Effect of Nuclear Charge (Z) on Orbital Energy Nuclear protons create an ever-present pull on the electrons.

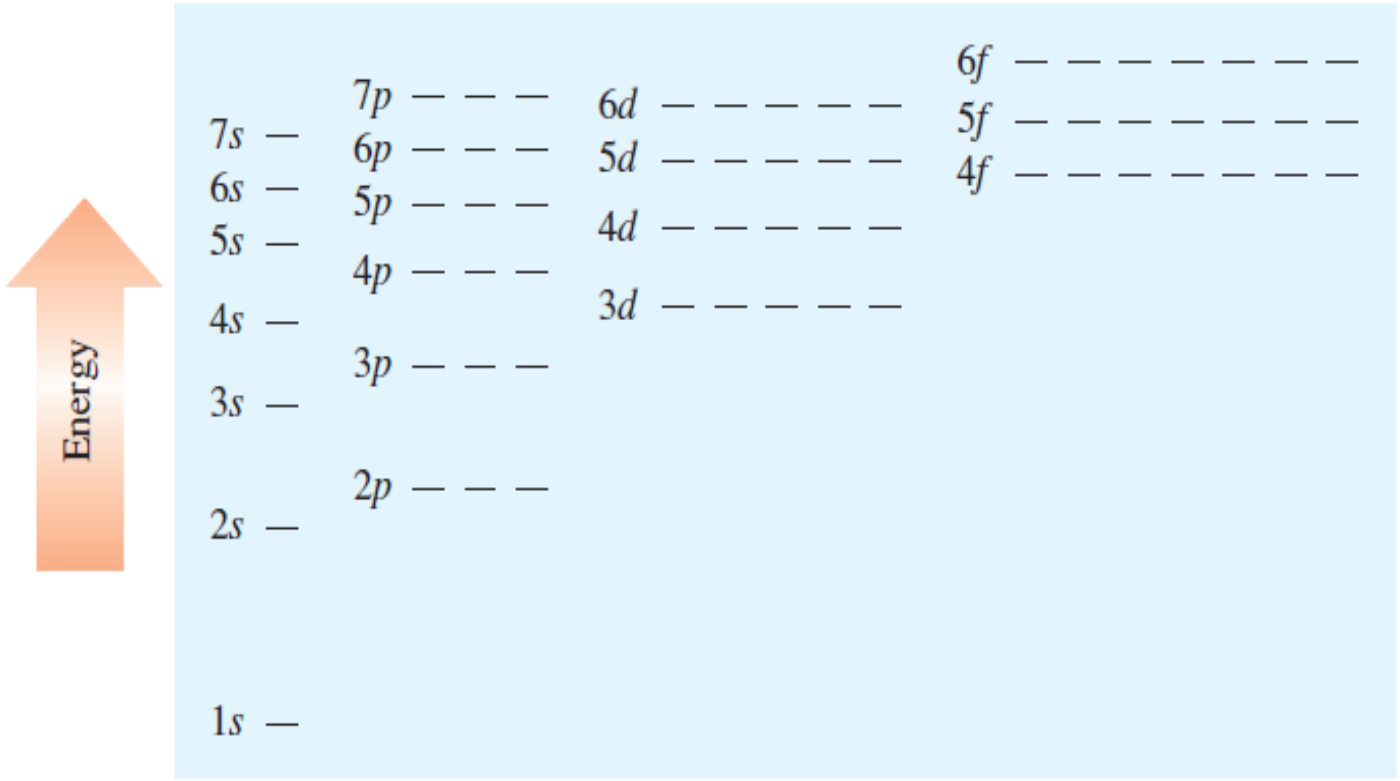
- Higher charges attract each other more strongly than lower charges.
- Therefore, higher nuclear charge lowers orbital energy (stabilizes the system) by increasing nucleus-electron attractions.

Shielding: The Effect of Electron Repulsions on Orbital Energy In many-electron atoms, each electron "feels" not only the attraction to the nucleus but also the repulsion from other electrons.

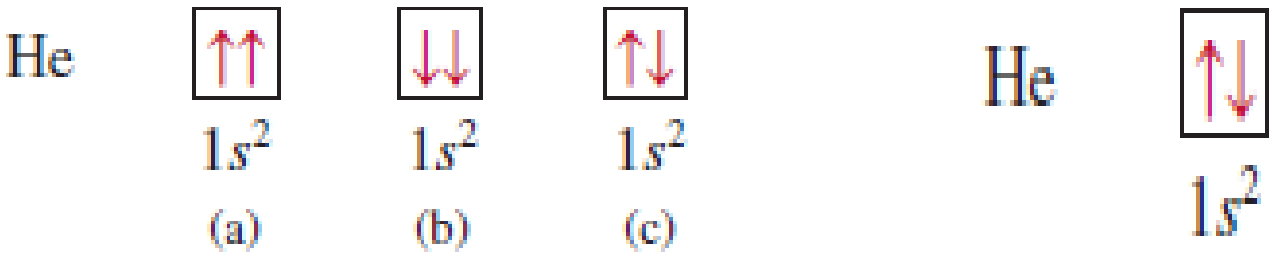
- This repulsion counteracts the nuclear attraction somewhat, making each electron easier to remove by, in effect, helping to push it away.
- We speak of each electron "shielding" the other electrons somewhat from the nucleus. Shielding (also called screening) ***reduces the full nuclear charge to an effective nuclear charge (Zeff)***, the nuclear charge an electron actually experiences. This lower nuclear charge makes the electron easier to remove.

Order of sublevel energies: s < p < d < f

- **An energy level diagram, or orbital diagram**, is a diagram that represents the re

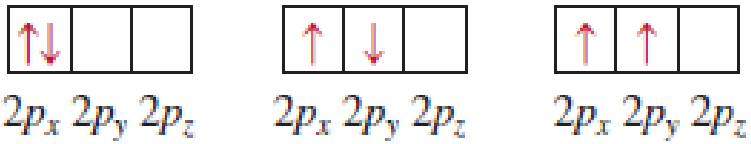


- For multi-electron elements, **the Pauli exclusion principle** applies; *no two electrons in an atom can have the same four quantum numbers*.



- **Hund's Rule:** *the most stable arrangement of the electrons in sub-shells is the one with the greatest number of parallel spins.*

The electron configuration of carbon ($Z = 6$) is $1s^2 2s^2 2p^2$. The following are different ways of distributing two electrons among three p orbitals:



The Building-up Principle (aufbau) helps determine the electron configuration

- Electrons fill the lowest-energy orbital that is available first.

A Survey of Periodic Table

Blocks, Periods, and Groups

- **Blocks**: s-block, p-block, d-block & f-block.
- **Group** (family): vertical column in the periodic table 18 groups.
- Elements in a group have similar configurations of the outermost shells, leading to similar properties.
- **Period**: The horizontal row in a periodic table.
- There are 7 periods.
- Elements of the same period have the same number of electron shells.

Trends in the Periodic Table

- **Atomic Radius**
- ½ the distance between the nuclei of 2 like atoms in a diatomic molecule
- **In a period, left to right**

1. n (number of shells) remain constant.
2. Z increases (by one unit)

So atomic radius decrease left to right

- **In a group, top to bottom**

1. n increases
2. Z increases

So atomic radius increases moving down the group.

Ionization Energy (IE)

- IE: *the amount of energy required to lose an electron from an atom in its gaseous state.*
- The minimum energy needed to remove an electron from a gas phase atom depends on

(a) Size of the atom - IE decreases as the size of the atom increases

(b) Nuclear Charge - IE increases with increase in nuclear charge

(c) The type of electron - Shielding effect

- **On moving down a group**

1. nuclear charge increases
2. number of shells increases, hence atomic size increases.
3. there is increase in the number of inner electrons which shield the valence electrons from the nucleus

- Thus IE decreases down the group

- **On moving across a period**

1. the atomic size decreases
2. nuclear charge increases

- Thus IE increases along a period

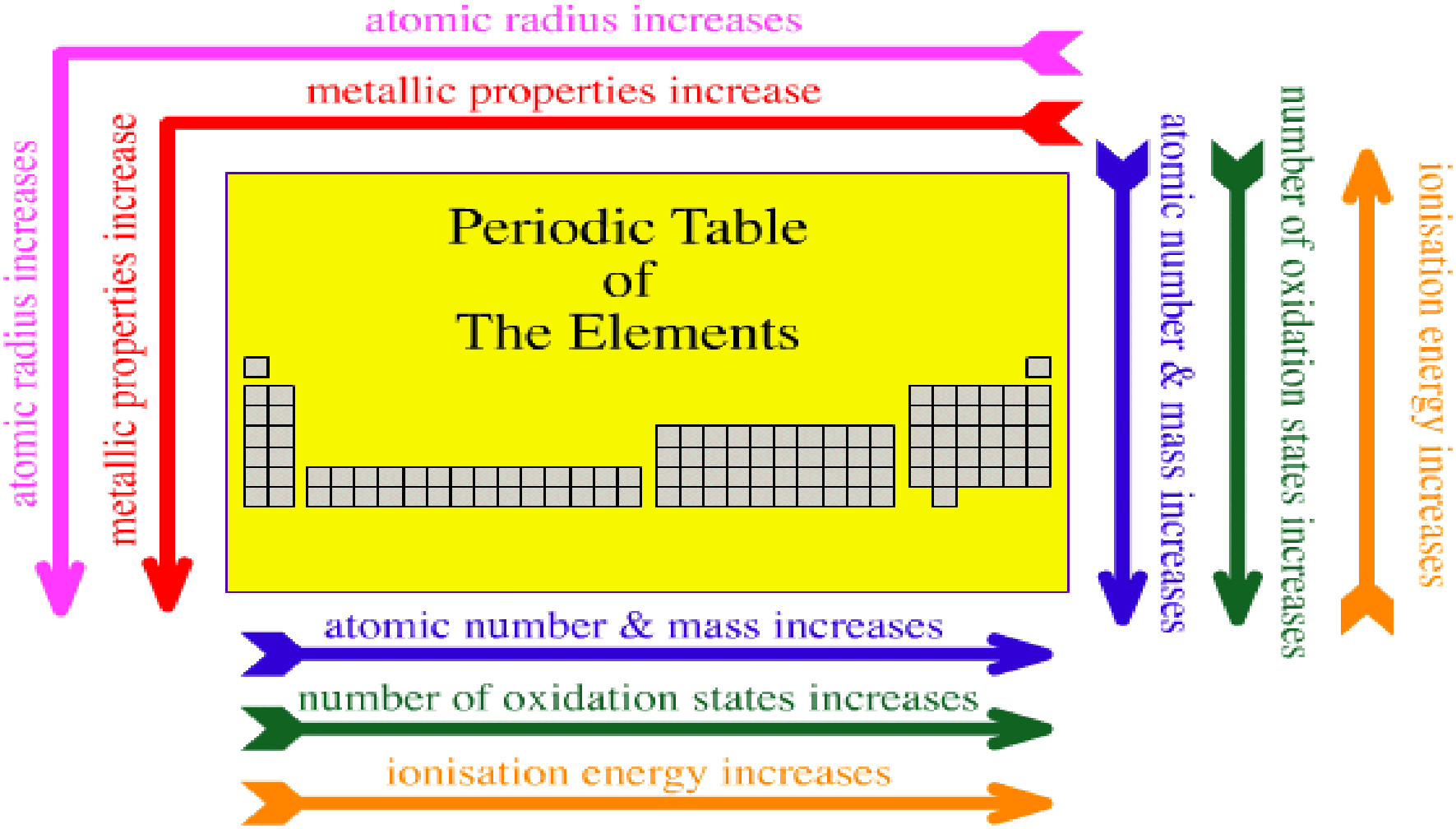
Electron affinity (EA)

- EA *is the amount of energy change when an atom gain an electron*.
- **On moving across a period**,
- The atomic size decreases and hence the force of attraction exerted by the nucleus on the electrons increases.
- Consequently, the atom has a greater tendency to attract additional electron i.e., its electron affinity increases

- **On moving down a group**,
- - The atomic size increases and therefore, the effective nuclear attraction decreases and thus electron affinity decreases

Electronegativity

- *is the tendency for an atom to attract electrons to itself when it is chemically combined with another element.*
- As you go down a group the electronegativity decreases because, the further down a group, the farther the electron is away from the nucleus, thus, more willing to share.
- As you move across a period, electronegativity generally increases from left to right because, at the right end are the nonmetals. They want more electrons.


atomic radius increases
metallic properties increase
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Periodic Table
of
The Elements
atomic number & mass increases
number of oxidation states increases
ionisation energy increases
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