

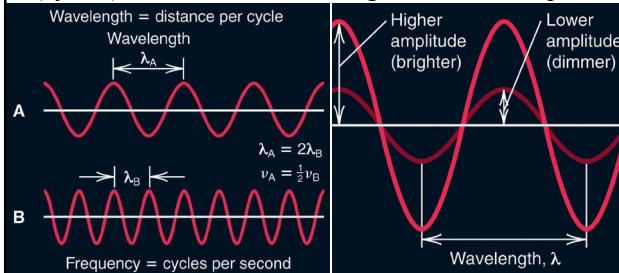


## Quantum Theory and Atomic Structure

- **Nuclear atom** – small, heavy, positive nucleus surrounded by a negative electron cloud
- **Electronic structure** – arrangement of the electrons around the nucleus
- **Classical mechanics** – fails in describing the electronic motion
- **Quantum mechanics** – designed to describe the motion of microscopic particles

### 7.1 The Nature of Light

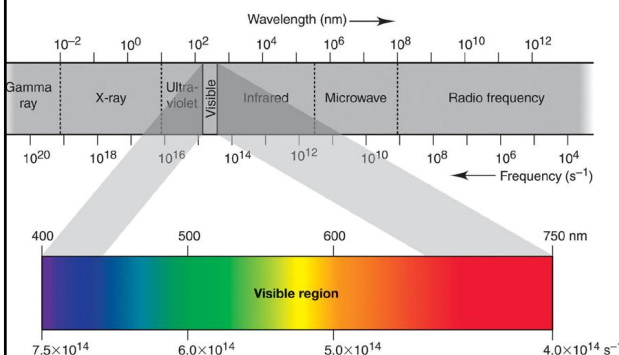
- Light is **electromagnetic radiation** – a stream of energy in the form waves
- **Electromagnetic waves** – periodic oscillations (cycles) of the electric and magnetic fields in space



- **Wavelength ( $\lambda$ )** – distance between two adjacent minima or maxima of the wave
- **Frequency ( $\nu$ )** – number of oscillations of the electric (or magnetic) field per second  
– units - hertz (Hz)  $\rightarrow 1 \text{ Hz} = 1 \text{ s}^{-1}$
- **Amplitude** – strength of the oscillation (related to the intensity of the radiation)
- **Speed of light ( $c$ )** – rate of travel of all types of electromagnetic radiation ( $3.00 \times 10^8 \text{ m/s}$ )

$$\lambda \nu = c \quad \uparrow \lambda \rightarrow \downarrow \nu$$

- **Electromagnetic spectrum** – classification of light based on the values of  $\lambda$  and  $\nu$



### Example:

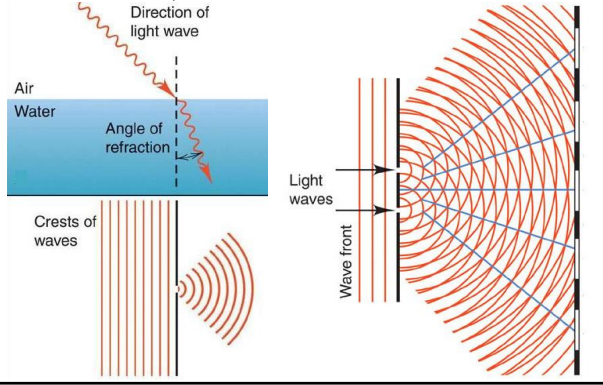
What is the wavelength of light with frequency **98.9 MHz**.

$$98.9 \text{ MHz} = 98.9 \times 10^6 \text{ Hz} = 98.9 \times 10^6 \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{98.9 \times 10^6 \text{ s}^{-1}} = 3.03 \text{ m}$$

• **Differences between waves and particles**

– Refraction, diffraction and interference of waves



**The particle nature of light**

- **Blackbody radiation** – light emitted from solid objects heated to incandescence
  - The energy profile of the emitted light could not be explained by the classical mechanics which assumes that the energy of an object can be continuously changed
  - **Planck** (1900) explained the energy profiles by assuming that the energy of an object can be changed only in discrete amounts (**quanta**) → **quantization of energy**

$$\Delta E = n(h\nu)$$

$h$  – Planck’s constant  $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

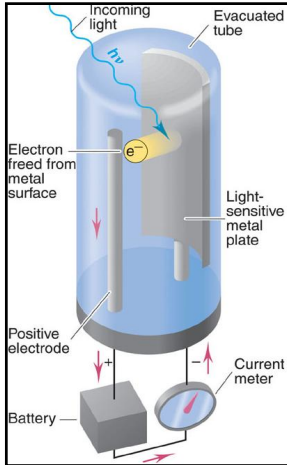
$\nu$  – frequency of the emitted light

$n$  – quantum number (positive integer – 1, 2, 3, ...)

$h\nu$  – the energy of one quantum

• **Photoelectric effect** – ejection of  $e^-$  from metals by irradiation with light

- Ejection of  $e^-$  begins only above a certain **threshold frequency** (below this frequency, no ejection occurs no matter how intense the light is)
- Ejection of  $e^-$  begins with no time delay
- Can’t be explained by treating light as waves



- Explanation (**Einstein, 1905**) – the ejection of  $e^-$  is caused by particles (**photons**) with energy proportional to the frequency of the radiation
  - ⇒ Only photons with enough energy and therefore high enough frequency can eject electrons
  - ⇒ Ejection results from an encounter of an  $e^-$  with a single photon (not several photons), so no time delay is observed

- Energy of the photon ( $E_{ph}$ ):

$$E_{ph} = h\nu \quad \nu = c/\lambda \quad E_{ph} = hc/\lambda$$

⇒ The photon is the **electromagnetic quantum** – the smallest amount of energy atoms can emit or absorb

• **Dual nature of light** – light has both wave and particle like properties

- wave (refraction, interference, diffraction)
- particle (photoelectric effect)

**Example:**

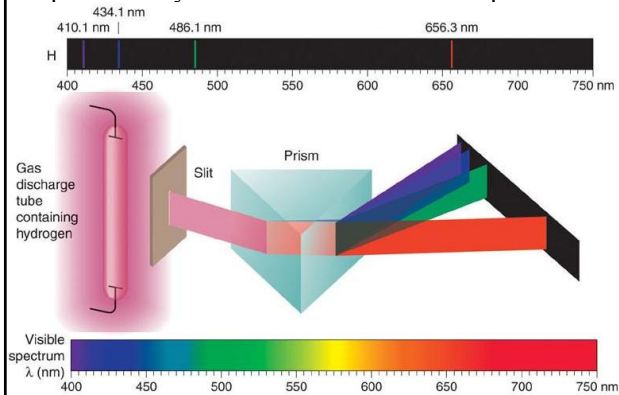
Calculate the energy of a photon of light with wavelength **514 nm**.

$$E_{ph} = h \frac{c}{\lambda} = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} \frac{3.00 \times 10^8 \text{ m/s}}{514 \times 10^{-9} \text{ m}} = 3.87 \times 10^{-19} \text{ J}$$

**7.2 Atomic Spectra**

- **Spectroscopy** – studies the interaction of light with matter (emission, absorption, scattering, ...)
- **Spectrometer** – instrument that separates the different colors of light and records their intensities
- **Spectrum** – intensity of light as a function of its color (wavelength or frequency)
- **Atomic emission spectrum** – the spectrum emitted by the atoms of an element when they are excited by heating to high temperatures (very characteristic for each element; used for identification of elements)

- **Spectral lines** – images of the spectrometer entrance slit produced by the different colors in the spectrum

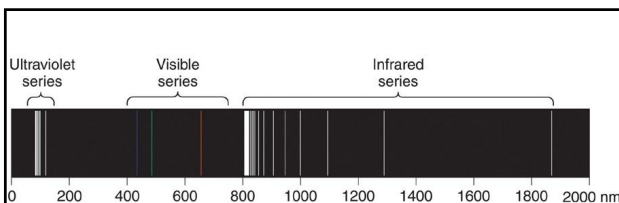


- Atomic emission spectra are **line spectra** – consist of discrete frequencies (lines)
  - Can't be explained by classical physics
- The **Rydberg equation** – fits the observed lines in the hydrogen atomic emission spectrum

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$n_1, n_2$  – positive integers (1, 2, 3, ...) and  $n_1 < n_2$

$R$  – the **Rydberg constant** ( $1.096776 \times 10^7 \text{ m}^{-1}$ )



- Lyman series (UV) –  $n_1 = 1$  and  $n_2 = 2, 3, 4, \dots$
- Balmer series (VIS) –  $n_1 = 2$  and  $n_2 = 3, 4, 5, \dots$
- Paschen series (IR) –  $n_1 = 3$  and  $n_2 = 4, 5, 6, \dots$

### The Bohr model of the H atom (1913)

- Explains the hydrogen atomic emission spectrum by using the idea of quantization
- **Postulates:**
  - The electron travels around the nucleus in **circular orbits** without loss of energy
  - The angular momentum of the electron is quantized → **only certain orbits are allowed**
- **Consequences:**
  - The energy of the H atom is quantized → only **certain discrete energy levels** (stationary states) are allowed
  - Each circular orbit corresponds to one  $E$ -level

### Consequences (cont.):

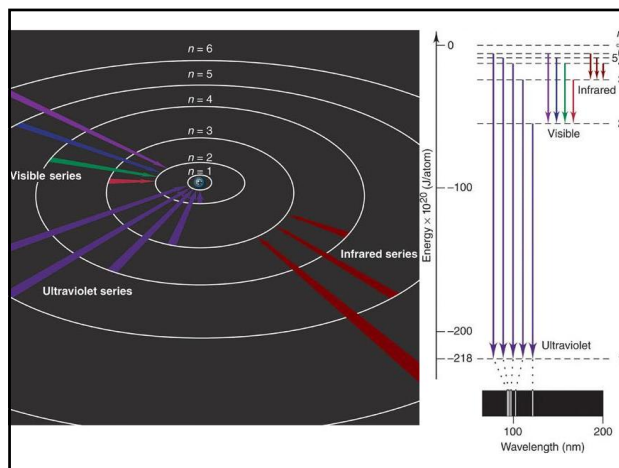
– A transition between two energy states generates a **photon** with energy equal to the difference between the two levels ( $\Delta E$ )

$$E_{ph} = E_{state\ 2} - E_{state\ 1} = h\nu \Rightarrow \Delta E = h\nu$$

– A photon with a specific (discrete) frequency is emitted for each transition from a higher to a lower  $E$ -level

⇒ **Atomic emission spectra consist of discrete lines**

- Each orbit is labeled with a number,  $n$ , starting from the orbit closest to the nucleus ( $n = 1, 2, \dots$ )
- The same number is used to label the energy levels →  $n$  is the **quantum number**



- **Energy states of the H atom**

$$E_n = -B \left( \frac{Z^2}{n^2} \right) \quad n = 1, 2, 3, \dots, \infty$$

$B$  is a constant ( $B = 2.18 \times 10^{-18} \text{ J}$ )

$Z$  is the nuclear charge (For H:  $Z = 1 \rightarrow E_n = -B/n^2$ )

- **Ground state** – the lowest energy state ( $n = 1$ )

$$E_1 = -B/1^2 = -B = -2.18 \times 10^{-18} \text{ J}$$

- **Excited states** – higher energy levels ( $n > 1$ )

- The energy increases with increasing  $n$

- The highest possible energy is for  $n = \infty$  (the electron is completely separated from the nucleus)

$$E_\infty = -B/\infty^2 = 0$$

- A transition between two  $E$ -levels with quantum numbers  $n_1$  and  $n_2$  will produce a photon with energy equal to the  $E$ -difference between the levels,  $\Delta E$ :

$$\Delta E = E_{n_2} - E_{n_1} = \left( -\frac{B}{n_2^2} \right) - \left( -\frac{B}{n_1^2} \right) = B \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = E_{ph} = h\nu = \frac{hc}{\lambda} = B \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow \frac{1}{\lambda} = \frac{B}{hc} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \leftarrow \text{Rydberg eq.} \left( \frac{B}{hc} = R \right)$$

- **Ionization energy ( $I$ )** of the H atom – the energy needed to completely remove the electron from a H atom in its ground state (can be viewed as the energy change from  $E_1$  to  $E_\infty$ )

$$\Delta E = E_\infty - E_1 = \left( -\frac{B}{\infty^2} \right) - \left( -\frac{B}{1^2} \right) = 0 - (-B) = B$$

$$\Rightarrow I = B = 2.18 \times 10^{-18} \text{ J/atom}$$

- **Limitations of the Bohr Model**

- Applicable only to **H-like** atoms and ions (having a single electron) in the absence of strong electric or magnetic fields (H,  $\text{He}^+$ ,  $\text{Li}^{2+}$ , ...)

### 7.3 The Wave-Particle Duality of Matter and Energy

- **Mass-energy equivalency** (Einstein)

$$E = mc^2$$

- For a photon with energy  $E = h\nu = hc/\lambda$ :

$$E = mc^2 = hc/\lambda \Rightarrow mc = h/\lambda \Rightarrow \lambda = h/mc$$

$$\Rightarrow \lambda = h/p \quad p - \text{photon momentum}$$

- The equation shows that the wave-like photons have particle-like mass and momentum

- Experimental evidence (Compton, 1923)

- **De Broglie's hypothesis** (1924) – all matter has wave-like properties (just as waves have particle-like properties)

- For a particle with mass,  $m$ , and velocity,  $u$ , the wavelength is:

$$\lambda = h/mu$$

- De Broglie's equation is equivalent to that for a photon ( $\lambda = h/mc$ )

- De Broglie's equation combines particle properties ( $m, u$ ) with wave properties ( $\lambda$ )

$\Rightarrow$  Matter and energy exhibit wave-particle duality

- **Example:** Calculate the wavelengths of an electron ( $m = 9.109 \times 10^{-31} \text{ kg}$ ) with velocity  $2.2 \times 10^6 \text{ m/s}$  and a bullet ( $m = 5.0 \text{ g}$ ) traveling at  $700. \text{ m/s}$ .

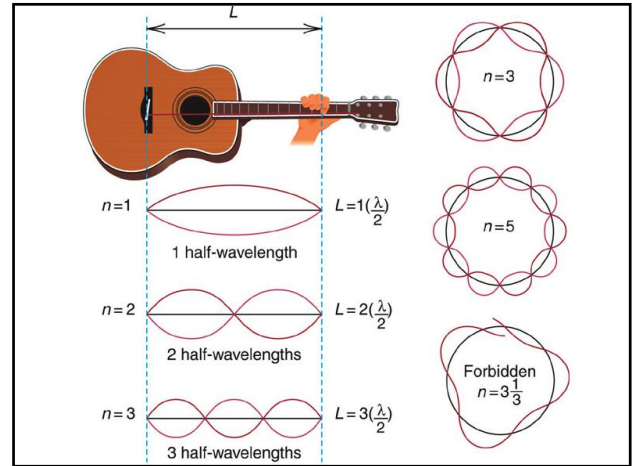
$$\lambda(e^-) = \frac{h}{mu} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{9.109 \times 10^{-31} \text{ kg} \times 2.2 \times 10^6 \text{ m/s}}$$

$$= 3.3 \times 10^{-10} \text{ m} = 0.33 \text{ nm} \rightarrow \text{comparable to atomic sizes}$$

$$\lambda(\text{bul}) = \frac{h}{mu} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{5.0 \times 10^{-3} \text{ kg} \times 700. \text{ m/s}}$$

$$= 1.9 \times 10^{-34} \text{ m} \rightarrow \text{very short, undetectable}$$

- **Experimental evidence** (Davisson and Germer, 1927)
  - **Diffraction of electrons** by crystal surfaces
  - Diffraction patterns are consistent with the wavelength predicted by de Broglie's relation
- The electron can be treated as a wave with a very short wavelength (similar to the wavelength of x-rays)
- The electron confined in the **H** atom can be treated as a **standing wave** having discrete frequencies (energies) like a guitar string



- **Heisenberg's uncertainty principle** (1927) – the exact position and momentum (velocity) of a particle can not be known simultaneously

$$\Delta x \cdot \Delta p \geq h/4\pi$$

$\Delta x$  and  $\Delta p = m\Delta u$  – uncertainty in position and momentum, respectively

- A consequence of the wave-particle duality of matter
- The exact location of very small particles is not well known due to their wave-like properties
- The probability to find a particle at a particular location depends on the amplitude (intensity) of the wave at this location

## 7.4 The Quantum-Mechanical Model of the Atom

- Bohr's model of the **H** atom
  - Assumes the quantization without explanation
  - Does not take into account Heisenberg's uncertainty principle
  - Limited success only for the **H** atom
- Schrödinger's model
  - Based on the wave-particle duality of the electron
  - The quantization is logically derived from the wave properties of the electron
  - Formalism applicable to other atoms

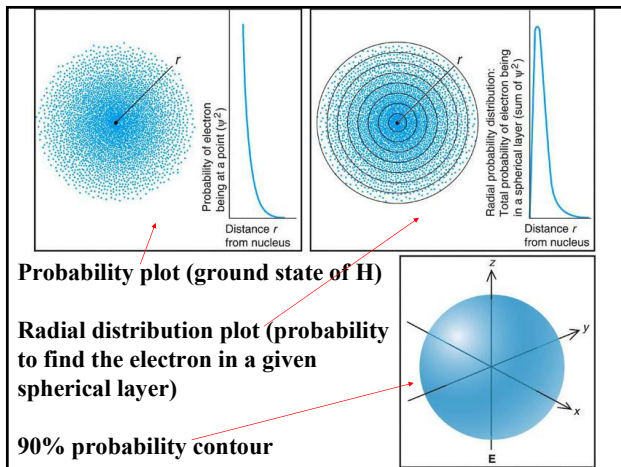
### Atomic Orbitals

- **The Schrödinger equation**
  - The electron wave is described by a **wavefunction** ( $\Psi$ ) – a mathematical function of the wave's amplitude at different points (x, y, z) in space
  - The equation provides solutions for the possible wavefunctions and energies of the electron
  - Only certain solutions for the energy are allowed (waves fit in the atom only for certain energy values)

$$-\frac{\hbar}{2m} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V\Psi = E\Psi$$

- The solutions for the wavefunction,  $\Psi$ , in the **H** atom are called **atomic orbitals**
- **Born's interpretation** of the wavefunction – the probability to find the electron at a certain point (x, y, z) in space is proportional to the square of the wave function,  $\Psi^2$ , in this point
- **Electron density diagrams** – three-dimensional plots of the probability to find the electron ( $\Psi^2$ ) around the nucleus → **electron clouds**
- **Contour diagrams** – surround the densest regions of the electron cloud – usually 90% of the total probability → **90% probability contour**





## Quantum Numbers

- Solutions of the Schrödinger equation for the wavefunction of the electron in the H atom:

$$\text{Atomic orbitals} \rightarrow \Psi_{n,l,m_l}$$

- Depend on three quantum numbers used as labels of each solution ( $n, l, m_l$ )
- Principal quantum number ( $n$ )** – specifies the energy ( $E_n$ ) of the electron occupying the orbital and the average distance ( $r$ ) of the electron from the nucleus (size of the orbital)

$$\uparrow n \Rightarrow \uparrow E_n \quad \uparrow n \Rightarrow \uparrow r$$

- Angular momentum quantum number ( $l$ )** – specifies the shape of the orbital
  - Magnetic quantum number ( $m_l$ )** – specifies the orientation of the orbital
  - A set of three quantum numbers ( $n, l, m_l$ ) unambiguously specifies an **orbital** ( $\Psi_{n,l,m_l}$ )
  - Possible values** of the quantum numbers:
    - $n = 1, 2, 3, \dots, \infty$
    - $l = 0, 1, 2, \dots, n-1$  (restricted by  $n$ )
    - $m_l = -l, \dots, -1, 0, 1, \dots, l$  (restricted by  $l$ )
- $\Psi_{3,2,-1}$  (possible)       $\Psi_{2,2,2}$  and  $\Psi_{3,0,1}$  (impossible)

- All orbitals with the same value of  $n$  form a **principal level (shell)**
- All orbitals with the same value of  $l$  form a **sublevel (subshell)** within a principal shell
  - Subshells are labeled with the value of  $n$  followed by a letter corresponding to the value of  $l$
  - $l=0 \rightarrow s, l=1 \rightarrow p, l=2 \rightarrow d, l=3 \rightarrow f, l=4 \rightarrow g, \dots$
  - Each value of  $m_l$  specifies an **orbital** in a subshell

**Example:** Label the subshell containing the orbital  $\Psi_{3,2,-1}$

$$n = 3 \quad l = 2 \rightarrow d \Rightarrow 3d\text{-subshell}$$

Shells	Subshells	Orbitals	
$n=3$	$l=2$	-2   -1   0   +1   +2	3d-subshell
	$l=1$	-1   0   +1	3p-subshell
	$l=0$	0	3s-subshell
$n=2$	$l=1$	-1   0   +1	2p-subshell
	$l=0$	0	2s-subshell
$n=1$	$l=0$	0	1s-subshell
$n$	$l$	$m_l$	

# of orbitals in a shell =  $n^2$   
 # of orbitals in a subshell =  $2l + 1$

**Example:** What is the # of orbitals in the 4f subshell? Give the  $m_l$  values of these orbitals.

$$4f \rightarrow n = 4, l = 3 \rightarrow 2l + 1 = 7 \text{ orbitals}$$

$$l = 3 \rightarrow m_l = -3, -2, -1, 0, +1, +2, +3$$

- Solutions of the Schrödinger equation for the energy of the electron in the H atom:

$$E_n = -\frac{B}{n^2} \quad n = 1, 2, 3, \dots$$

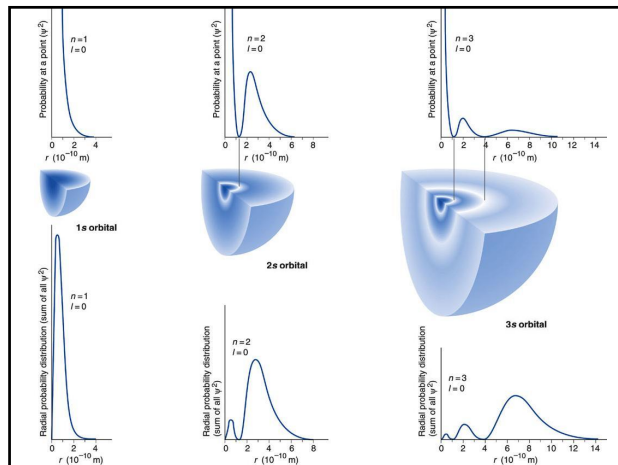
$\Rightarrow$  The **energy levels** of H depend only on the principal quantum number,  $n$

- Same as Bohr's energy levels ( $B = 2.18 \times 10^{-18} \text{ J}$ )
- $E_n$  increases with increasing  $n$

## Shapes of Orbitals

### • *s*-Orbitals → $l = 0$

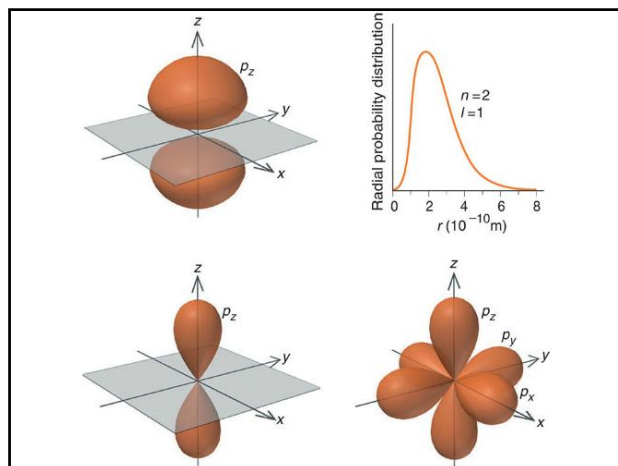
- Spherical shape
- The electron density is highest at the nucleus (density decreases away from the nucleus)
- The radial distribution has a maximum slightly away from the nucleus
- The orbital size increases with increasing the energy of the orbital ( $1s < 2s < 3s \dots$ )
- Higher energy orbitals have several **maxima** in the radial distribution and one or more spherical **nodes** (regions with zero probability to find the electron)  $2s \rightarrow 2 \text{ max, } 1 \text{ node}; 3s \rightarrow 3 \text{ max, } 2 \text{ nodes} \dots$



### • *p*-Orbitals → $l = 1$

- Dumbbell-shaped (two-lobed)
- Positive sign of  $\Psi$  in one of the lobes of the orbital and negative in the other lobe
- **Nodal plane** going through the nucleus (surface with zero probability to find the electron)
- **Three** possible orientations in space:  

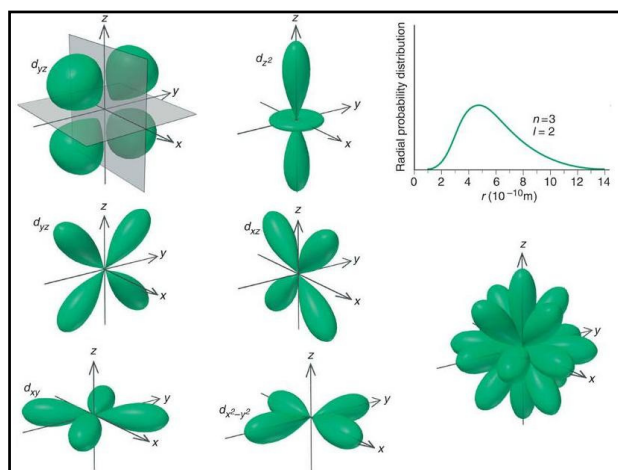
$$m_l = -1, 0, +1 \rightarrow p_x, p_y, p_z$$
- *p*-orbitals are possible only in the 2<sup>nd</sup> and higher principal shells
- The orbital size increases with increasing the energy of the orbital ( $2p < 3p < 4p \dots$ )



### • *d*-Orbitals → $l = 2$

- **Cloverleaf-shaped** (four-lobed, except  $d_{z^2}$ )
- Opposite signs of  $\Psi$  in the lobes laying beside each other
- Two perpendicular **nodal planes** going through the nucleus
- **Five** possible orientations in space:  

$$m_l = -2, -1, 0, 1, 2 \rightarrow d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{zx}, d_{yz}$$
- *d*-orbitals are possible only in the 3<sup>rd</sup> and higher principal shells
- The orbital size increases with increasing the energy of the orbital ( $3d < 4d < 5d \dots$ )



### • Energy levels of the H atom

- Electronic energy depends only on the principal quantum number ( $n$ ) – all subshells in a given shell have the same energy

