7.4 The Quantum-Mechanical Model of the Atom

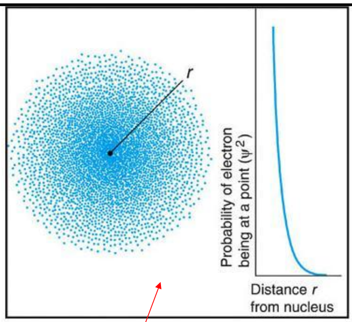
- Bohr's model of the **H** atom
  - Assumes the quantization without explanation
  - Does not take into account Heisenberg's uncertainty principle
  - Limited success only for the **H** atom
- Schrödinger's model
  - Based on the wave-particle duality of the electron
  - The quantization is logically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

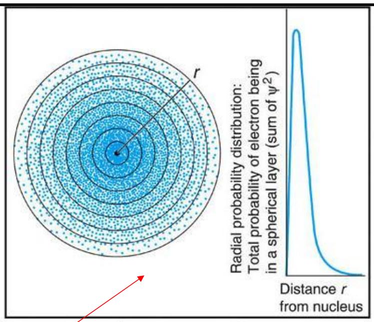
Atomic Orbitals

- **The Schrödinger equation**
  - The electron wave is described by a **wavefunction (Ψ)** – 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)

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

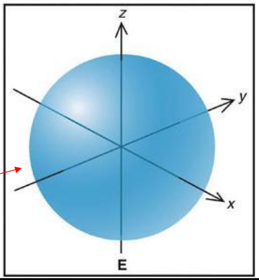
- The solutions for the wavefunction, Ψ, in the **H** atom are called **atomic orbitals**
- **Born's interpretation** of the wavefunction – the probability to find the electron at a certain point (x, y, z) in space is proportional to the square of the wave function, Ψ^2, in this point
- **Electron density diagrams** – three-dimensional plots of the probability to find the electron (Ψ^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**





Probability plot (ground state of H)

Radial distribution plot (probability to find the electron in a given spherical layer)



90% probability contour

Quantum Numbers

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

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

  - 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)

$$\uparrow n \Rightarrow \uparrow E_n \qquad \uparrow n \Rightarrow \uparrow r$$

- **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** (Ψ_{n,l,m_l})
- **Possible values** of the quantum numbers:

$n = 1, 2, 3, \ldots, \infty$

$l = 0, 1, 2, \ldots, n-1$ (restricted by n)

$m_l = -l, \ldots, -1, 0, 1, \ldots, l$ (restricted by l)

$\Psi_{3,2,-1}$ **(possible)** $\Psi_{2,2,2}$ **and** $\Psi_{3,0,1}$ **(impossible)**

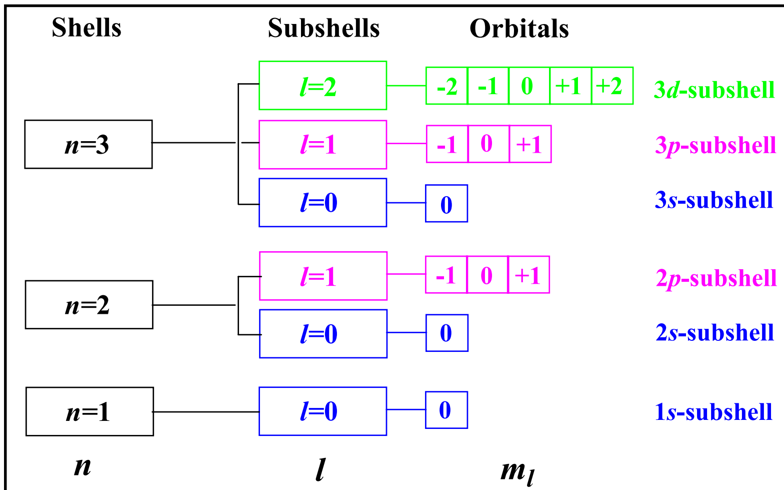
- All orbitals with the same value of n form a **principal level (shell)**
- All orbitals with the same value of l form a **sublevel (subshell)** within a principal shell
  - Subshells are labeled with the value of n followed by a letter corresponding to the value of l

$l=0 \rightarrow$ s, $l=1 \rightarrow$ p, $l=2 \rightarrow$ d, $l=3 \rightarrow$ f, $l=4 \rightarrow$ g, …

  - Each value of m_l specifies an **orbital** in a subshell

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

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



\# 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.

$4f \rightarrow n = 4, l = 3 \rightarrow 2l + 1 = 7$ **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:

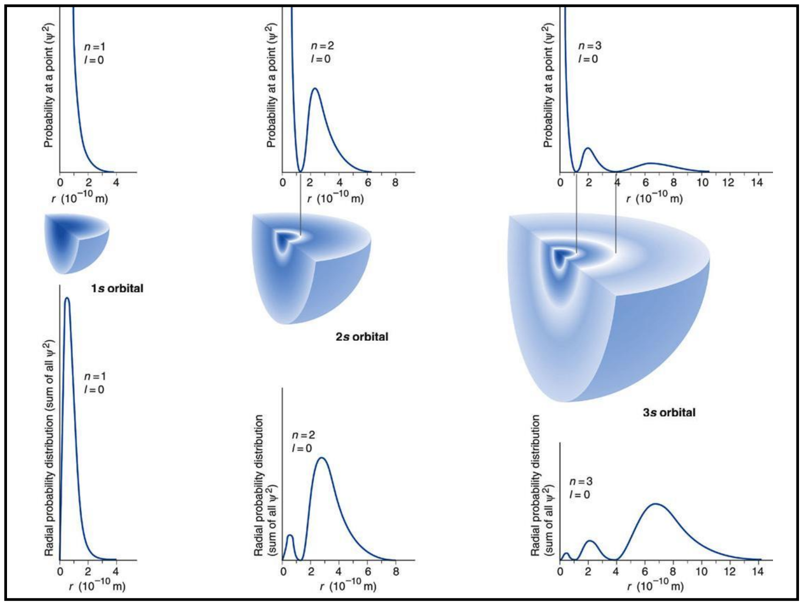
$$E_n = -\frac{B}{n^2} \qquad n = 1, 2, 3, \ldots$$

⇒The **energy levels** of **H** depend only on the principal quantum number, n

- Same as Bohr's energy levels ($B = 2.18\times10^{-18}$ **J**)
- E_n increases with increasing n

Shapes of Orbitals

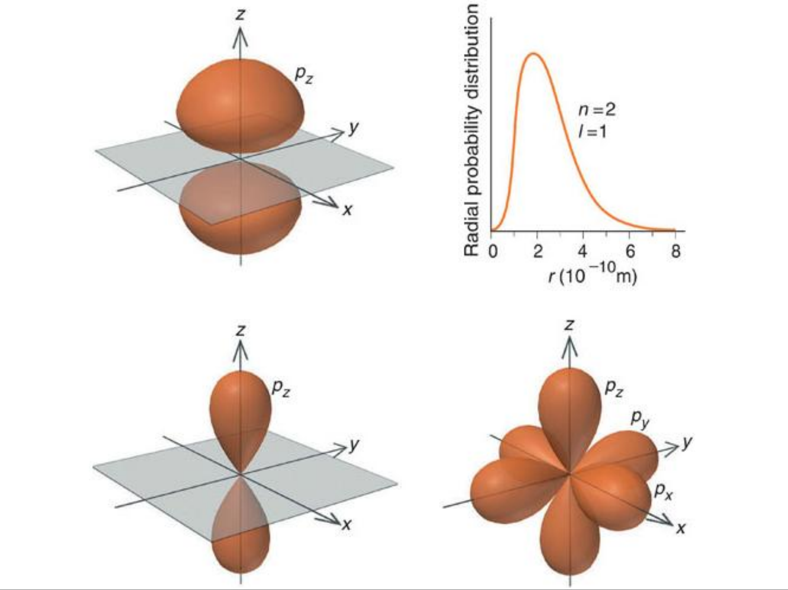
- ***s*-Orbitals** $\rightarrow l = 0$
  - Spherical shape
  - The electron density is highest at the nucleus (density decreases away from the nucleus)
  - The radial distribution has a maximum slightly away from the nucleus
  - The orbital size increases with increasing the energy of the orbital (**1*s* < 2*s* < 3*s* …**)
  - Higher energy orbitals have several **maxima** in the radial distribution and one or more spherical **nodes** (regions with zero probability to find the electron) **2*s* → 2 max, 1 node; 3*s* → 3 max, 2 nodes …**



- ***p*-Orbitals** $\rightarrow l = 1$
  - Dumbbell-shaped (two-lobed)
  - Positive sign of Ψ 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:

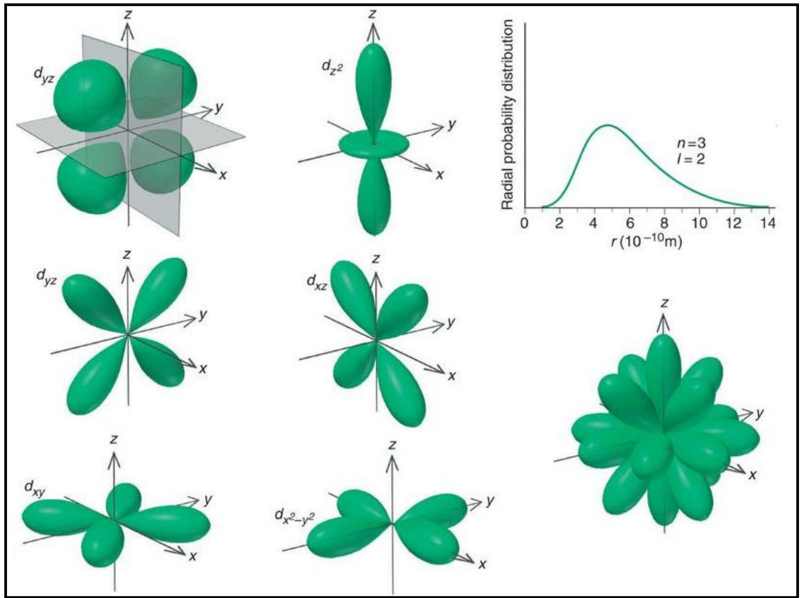
$$m_l = -1, 0, +1 \quad \rightarrow \quad p_x, p_y, p_z$$

  - *p*-orbitals are possible only in the 2nd and higher principal shells
  - The orbital size increases with increasing the energy of the orbital (**2*p* < 3*p* < 4*p* …**)



- ***d*-Orbitals → *l* = 2**
  - **Cloverleaf-shaped** (four-lobed, except d_{z^2})
  - Opposite signs of Ψ 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** → d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{zx}, d_{yz}
  - ***d*-orbitals are possible only in the 3[rd] and higher principal shells
  - The orbital size increases with increasing the energy of the orbital (**3*d* < 4*d* < 5*d* …**)



- **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