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

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**

**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)

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

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

\[ \Psi_{n,l,m_l} \]

- 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:
  - \(n = 1, 2, 3, \ldots, \infty\)
  - \(l = 0, 1, 2, \ldots, n-1\) (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 \(l\)
    - \(l=0 \rightarrow s, \ l=1 \rightarrow p, \ l=2 \rightarrow d, \ l=3 \rightarrow f, \ l=4 \rightarrow g, \ldots\)
    - Each value of \(m_l\) specifies an orbital in a subshell

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

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

- **Possible values**:
  - 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:

\[ E_n = -\frac{B}{n^2} \quad n = 1, 2, 3, ... \]

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

- Same as Bohr’s energy levels ($B = 2.18 \times 10^{-18}$ 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 ($1s < 2s < 3s ...$)
  - Higher energy orbitals have several maxima in the radial distribution and one or more spherical nodes (regions with zero probability to find the electron) $2s \rightarrow 2$ max, 1 node; $3s \rightarrow 3$ max, 2 nodes ...

- $p$-Orbitals $\rightarrow l = 1$
  - 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 2nd and higher principal shells
  - The orbital size increases with increasing the energy of the orbital ($2p < 3p < 4p ...$)
• **$d$-Orbitals $\rightarrow l = 2$**
  - 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$^{\text{rd}}$ and higher principal shells
  - The orbital size increases with increasing the energy of the orbital ($3d < 4d < 5d \ldots$)

• **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
  
  ![Energy Levels Graph](image.png)