7.4 The Wavelike properties of the Electron

- **de Broglie's hypothesis –** all matter has wavelike properties
  - for a particle with mass, ***m***, and velocity, ***v***, the wavelength is:

$$l = h/mv$$

- Wave-particle duality of matter - de Broglie's relation combines particle properties (***m, v***) with wave properties (l)

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

$$l(e^-) = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\mathrm{J\cdot s}}{9.109\times10^{-31}\,\mathrm{kg}\times2.2\times10^{6}\,\mathrm{m/s}}$$

$$= 3.3\times10^{-10}\,\mathrm{m} = 0.33\ \mathrm{nm} \rightarrow \text{comparable to atomic sizes}$$

$$l(bul) = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\mathrm{J\cdot s}}{5.0\times10^{-3}\,\mathrm{kg}\times700.\ \mathrm{m/s}} =$$

$$= 1.9\times10^{-34}\,\mathrm{m} \quad \rightarrow \text{very short, undetectable}$$

- Experimental evidence (Davisson and Germer)
  - **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

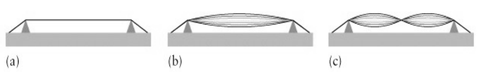

Fig. 7.12

- **Heisenberg's uncertainty principle** – the exact position and momentum (velocity) of a particle can not be known simultaneously
  - consequence of the wave-particle nature of matter
  - the exact location of very small particles is not well known due to their wave properties
  - the probability to find a particle at a particular location depends on the amplitude (intensity) of the wave at this location

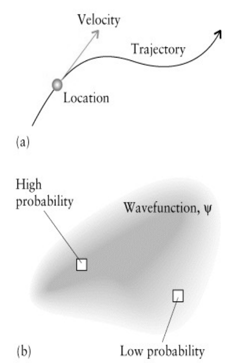

Fig. 7.14

Models of atoms

- Bohr's model of the **H** atom
  - the electron travels in circular orbits around the nucleus
  - 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

7.5 Atomic Orbitals

- **Schrödinger's 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)

$$-\frac{\hbar}{2m}\nabla^2\Psi + V\Psi = E\Psi$$

- 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, **Ψ²**, in this point
- The atomic orbitals (**Ψ**) can be graphically expressed by three-dimensional plots of the probability to find the electron (**Ψ²**) around the nucleus **– electron clouds** (electron density)
- **Boundary surfaces** – surround the densest regions of the electron cloud

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- Orbitals differ by their shapes, sizes and orientations in space (**s, p, d, f, … -orbitals**)

s-orbitals

– spherical shape

– highest density in the center at the nucleus (density decreases away from the nucleus)

– size increases with the energy of the orbital

–higher energy orbitals have more complex distribution of the electron density

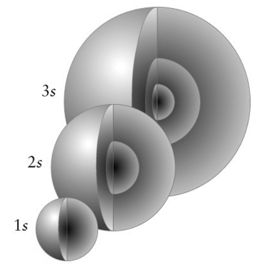

Fig. 7.18

- **p-orbitals**
  - figure-eight shaped
  - 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 (**p_x**, **p_y**, **p_z**)

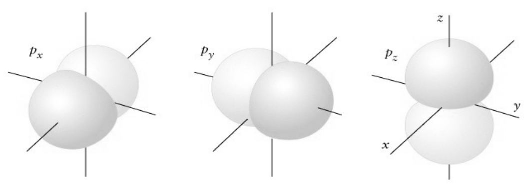

Fig. 7.19

- **d-orbitals**
  - two figure-eight shapes perpendicular to each other
  - opposite signs of **Ψ** in the lobes laying beside each other
  - **node** at the nucleus (zero probability to find the electron)
  - five possible orientations in space (**d_{z^2}**, **$d_{x^2-y^2}$**, **d_{xy}**, **d_{zx}**, **d_{yz}**)

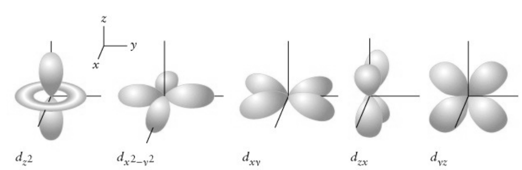

Fig. 7.20

7.6 Energy Levels in the H-atom

- Solutions of Schrödinger's equation for the energy of the electron in the **H** atom

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

- ***E*** is negative (***E*** becomes zero when the **e⁻** and the nucleus are infinitely separated)
- ***R_H*** is Rydberg's constant (3.29×10^{15} Hz)
- **Principal quantum number** (***n***) – used to label the ***E*** levels (***E_n*** increases with increasing ***n***)

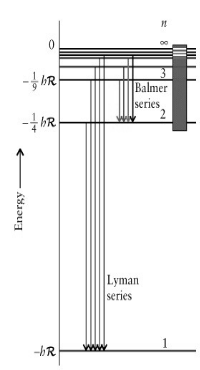

Fig. 7.22

- 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, ***DE***:

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

$$= hR_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = E_{ph} = hn$$

$$\Rightarrow n = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \text{Rydberg's eq.}$$

7.7 Quantum Numbers

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

Atomic orbitals $\rightarrow$ Ψ_{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 ($\uparrow n \Rightarrow \uparrow E$, $\uparrow n \Rightarrow \uparrow r$)

- **Angular momentum quantum number (*l*)** – specifies the shape of the orbital (s, p, d, …)
- **Magnetic quantum number (*m_l*)** – specifies the orientation of the orbital (p_x, p_y, p_z, ...)
- 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, …, ∞

  l = 0, 1, 2, …, n-1

  m_l = -l, -(l-1), …, -1, 0, 1, …, l-1, 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 shell**
- All orbitals with the same value of ***l*** form a **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 → s, l=1 → p, l=2 → d, l=3 → f, l=4 → g, …

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

n = 3 l=2 → d ⇒ 3d subshell

# of orbitals in a subshell = 2*l*+1

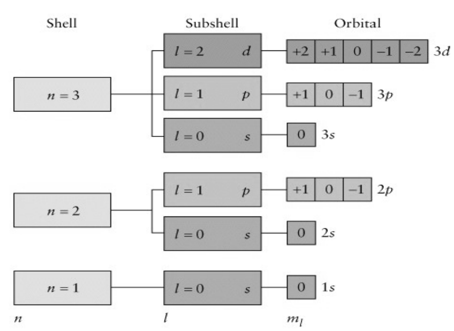

Fig. 7.23