

The Bohr Theory of the Hydrogen Atom

• Atomic Line Spectra

- In 1885, J. J. Balmer showed that the wavelengths, λ , in the visible spectrum of hydrogen could be reproduced by a simple formula.

$$\frac{1}{\lambda} = 1.097 \times 10^7 \text{ m}^{-1} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

- The known wavelengths of the four visible lines for hydrogen correspond to values of $n = 3$, $n = 4$, $n = 5$, and $n = 6$

1

Figure 7.10: Energy-level diagram for the electron in the hydrogen atom.

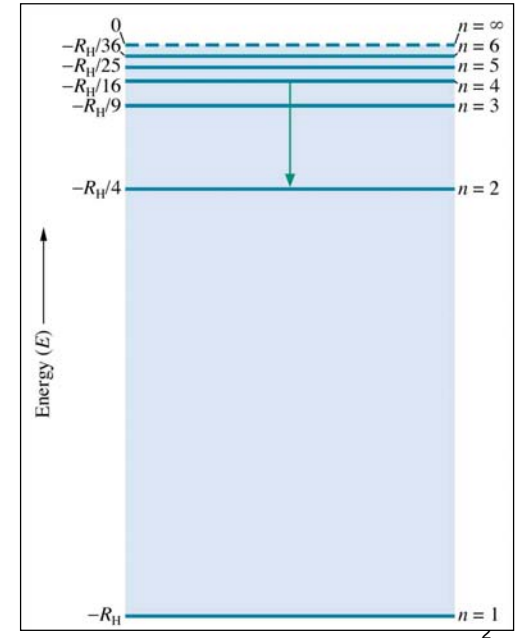
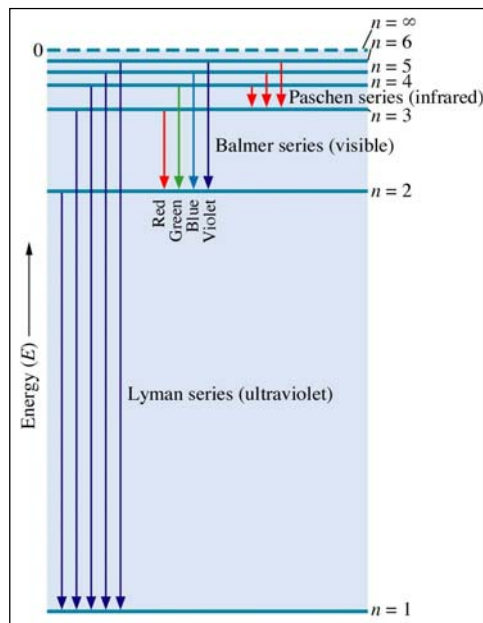


Figure 7.11: Transitions of the electron in the hydrogen atom.



2

The Bohr Theory of the Hydrogen Atom

• Bohr's Postulates

- Bohr set down postulates to account for (1) the stability of the hydrogen atom and (2) the line spectrum of the atom.

1. **Energy level postulate** An electron can have only specific energy levels in an atom.

2. **Transitions between energy levels** An electron in an atom can change energy levels by undergoing a "transition" from one energy level to another.

- Bohr derived the following formula for the energy levels of the electron in the hydrogen atom.

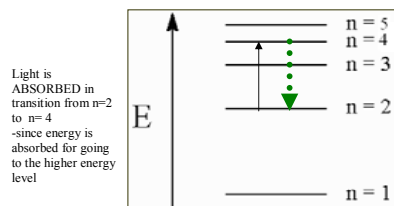
$$E = -\frac{R_h}{n^2} \quad n = 1, 2, 3 \dots \infty \quad (\text{for H atom})$$

- R_h is a constant (expressed in energy units) with a value of $2.18 \times 10^{-18} \text{ J}$.

4

Typical problem that we solved in class:

What is the wavelength of the light emitted (or absorbed?) when an electron undergoes transition from the 2nd to the 4th level in the hydrogen atom?



Light is ABSORBED in transition from $n=2$ to $n=4$ -since energy is absorbed for going to the higher energy level

Note: this transition is the reverse of the GREEN line transition in Balmer's series

Given: $n(\text{initial}) = 2$, $n(\text{final}) = 4$, $\lambda = ?$

Relevant Equations/ solution outline:
 $E = h\nu$, $\nu\lambda = c$ → so, if we find energy E (or change of energy ΔE) and then frequency ν → we can find the wavelength λ .
 $\Delta E = (-R_H/n_f^2) - (-R_H/n_i^2)$ - this is energy change in the transition between n_i (initial) and n_f (final) levels
 Constants: $R_H = 2.179 \times 10^{-18} \text{ J}$ (Ridberg constant), $h = 6.63 \times 10^{-34} \text{ J s}$ (Planks constant)
Calculations: step 1: $\Delta E = (-R_H/n_f^2) - (-R_H/n_i^2) = (-R_H/4^2) - (-R_H/2^2) = R_H \cdot 3/16$
 Step 2: $\nu = E/h$, $\nu = R_H/h \times 3/16 = 2.179 \times 10^{-18} \text{ J} / (6.63 \times 10^{-34} \text{ J s}) \times 3/16 = 6.17 \times 10^{14} \text{ s}^{-1}$
 Step 3: $\lambda = c/\nu$, $\lambda = 3 \times 10^8 \text{ m/sec} / (6.17 \times 10^{14} \text{ s}^{-1}) = 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm}$
Answer: $\lambda = 486 \text{ nm}$

Bonus question: what is the energy needed for transition of electron from the 1st level ($n_{\text{initial}} = 1$) to complete loss of electron (that is $n_{\text{final}} = \text{infinity}$)?

Note: you could use Balmer's formula to answer this question too! Just note that it gives you $1/\lambda$, not λ !

Quantum Mechanics

- Bohr's theory established the concept of atomic energy levels but did not thoroughly explain the "wave-like" behavior of the electron.
 - Current ideas about atomic structure depend on the principles of **quantum mechanics**, a theory that applies to subatomic particles such as electrons.
 - In 1923, Louis de Broglie reasoned that if light exhibits particle aspects, perhaps particles of matter show characteristics of waves.
 - He postulated that a particle with mass m and a velocity v has an associated wavelength.
 - The equation $\lambda = h/mv$ is called the **de Broglie relation**.
 - (m and v here are mass and velocity of **any** moving object). Since Planks constant h is very small ($\sim 10^{-34}$!) the waves generated by moving objects can be observed only at microscopic level, that is when the mass is very small, - such as in case of moving electrons, - with mass $\sim 10^{-31}$ kilograms.
 - (The wave-like property of electrons is the ground principle of **working electron microscopes!**)

Uncertainty principle:

- Quantum mechanics** is the branch of physics that mathematically describes the wave properties of submicroscopic particles.
 - We can no longer think of an electron as having a precise orbit in an atom. To describe such an orbit would require knowing its exact position and velocity. In 1927, Werner Heisenberg showed (from quantum mechanics) that it is impossible to know both simultaneously.

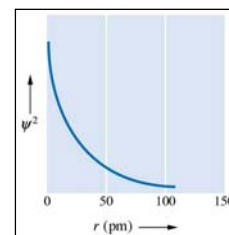
$$(\Delta x)(m\Delta v_x) \geq \frac{h}{4\pi}$$

Heisenberg's uncertainty principle states that the product of the uncertainty in position (Δx) and the uncertainty in momentum ($m \Delta v_x$) of a particle can be no larger than $h/4\pi$.

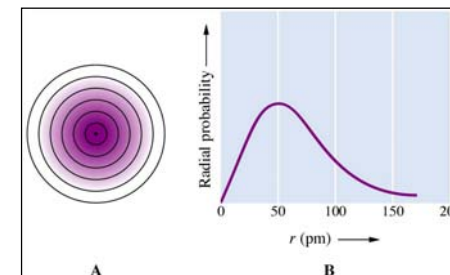
- When m is large (for example, a baseball) the uncertainties are small (again, remember that $h \sim 10^{-34}$!),
- but for electrons, high uncertainties forbid defining an exact orbit/position.

Wave functions

- Although we cannot precisely define an electron's orbit, we can obtain the **probability** of finding an electron at a given point around the nucleus.
 - Erwin Schrodinger defined this probability in a mathematical expression called a **wave function**, denoted ψ (psi).
 - The probability of finding a particle in a region of space is defined by ψ^2 .



Plot of ψ^2 for the lowest energy level of the hydrogen atom.



Probability of finding an electron in a spherical shell about the nucleus

Quantum Numbers and Atomic Orbitals

- According to quantum mechanics, each electron is described by four quantum numbers:

Principal quantum number (n); Angular momentum quantum number (l); Magnetic quantum number (m_l); Spin quantum number (m_s)

- The first three define the wave function for a particular electron. The fourth quantum number refers to the magnetic property of electrons.
- The **principal quantum number (n)** represents the “shell number” in which an electron “resides.”
 - The smaller n is, the smaller the orbital.
 - The smaller n is, the lower the energy of the electron.
- The **angular momentum quantum number (l)** distinguishes “sub shells” within a given shell that have different shapes.
 - Each main “shell” is subdivided into “sub shells.” Within each shell of quantum number n, there are n sub shells, each with a distinctive shape. l can have any integer value from 0 to (n - 1) The different subshells are denoted by letters.

Letter	s	p	d	f	g	...
l	0	1	2	3	4

9

Quantum Numbers and Atomic Orbitals (continuation)

- The **magnetic quantum number (m_l)** distinguishes orbitals within a given sub-shell that have different shapes and orientations in space.
 - Each sub shell is subdivided into “orbitals,” each capable of holding a pair of electrons.
 - m_l can have any integer value from -l to +l.
 - Each orbital within a given sub shell has the same energy.
- The **spin quantum number (m_s)** refers to the two possible spin orientations of the electrons residing within a given orbital.
 - Each orbital can hold only two electrons whose spins must oppose one another.
 - The possible values of m_s are +1/2 and -1/2.

10

Table 7.1

Permissible Values of Quantum Numbers for Atomic Orbitals

n	l	m _l *	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	-1, 0, +1	2p	3
3	0	0	3s	1
3	1	-1, 0, +1	3p	3
3	2	-2, -1, 0, +1, +2	3d	5
4	0	0	4s	1
4	1	-1, 0, +1	4p	3
4	2	-2, -1, 0, +1, +2	4d	5
4	3	-3, -2, -1, 0, +1, +2, +3	4f	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.

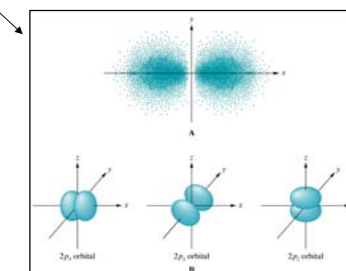
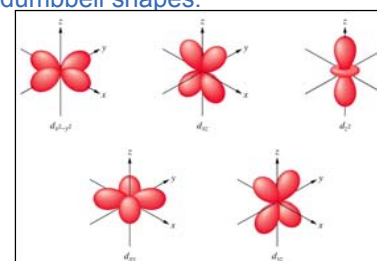
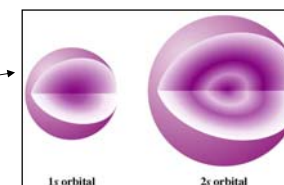
You should be able to fill in the whole table by using the rules on the previous 2 pages!

11

Quantum Numbers and Atomic Orbitals

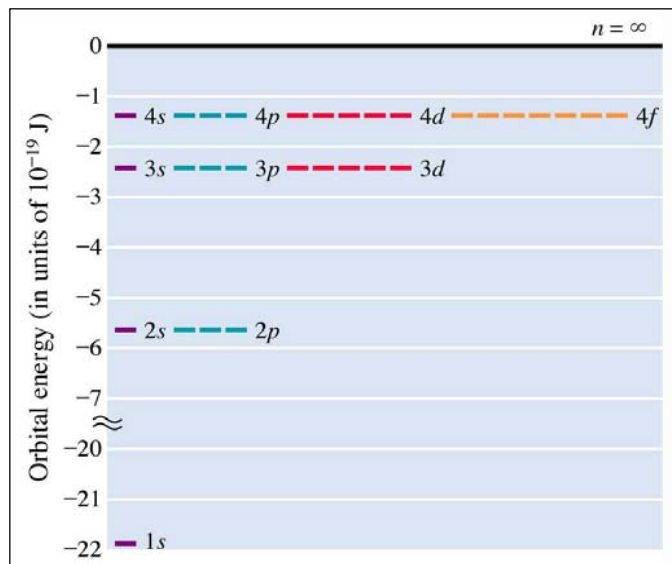
- Using calculated probabilities of electron “position,” the shapes of the orbitals can be described.

- The **s** sub shell orbital (there is only **one**) is spherical.
- The **p** sub shell orbitals (there are **three**) are dumbbell shape.
- The **d** sub shell orbitals (there are **five**) are a mix of cloverleaf and dumbbell shapes.



12

Figure 7.23: Orbital energies of the hydrogen atom.



13

Operational Skills for Chapter 7

- Relating wavelength and frequency of light.
- Calculating the energy of a photon.
- Determining the wavelength or frequency of a hydrogen atom transition.
- Using the rules for quantum numbers.

14