Chapter 7. Quantum Theory and Atomic Structure

• A problem arose in Rutherford’s nuclear model. A nucleus and electron attract each other; to remain apart the electron must move.

• The energy of the electron’s movement must balance the energy of attraction.

• Physics established that a charged particle moving in a curved path such as an electron in an atom must give off energy.

• Why doesn’t the electron continuously lose energy and spiral into the nucleus?

• Subatomic matter seemed to violate common experience. A new model was needed to describe atoms.
Concept 7-1. The wave characteristics of light (frequency, wavelength, and speed; the meaning of amplitude) and a general overview of the electromagnetic spectrum

- Visible light is one type of electromagnetic (EM) radiation.
- Electromagnetic radiation travels as waves—the result of oscillating electric and magnetic fields moving simultaneously through space.
- The wave properties of electromagnetic radiation are described by two interdependent variables, frequency and wavelength.
Frequency (ν, Greek nu) is the number of cycles the wave makes per second, expressed in units of 1/second (s⁻¹), or hertz (Hz).
• Wavelength (\( \lambda \), Greek lambda) is the distance between any point on a wave and the corresponding point on the next wave.

\( \lambda \) is expressed in meters, nanometers (nm, \( 10^{-9} \) m), picometers (pm, \( 10^{-12} \) m), and angstroms (Å, \( 10^{-10} \) m).

• The speed of the wave (m/s) is the product of its frequency (cycles per second) and its wavelength (meters per cycle):

\[
\text{Speed} = \frac{\text{cycles}}{s} \times \frac{\text{m}}{\text{cycle}} = \frac{\text{m}}{s}
\]

• In a vacuum, all electromagnetic radiation travels at \( 3.00 \times 10^8 \) m/s, a constant called the speed of light (c):

\[
c = \nu \lambda
\]

• Radiation of high frequency has a short wavelength, and vice versa.
Skill 7-1. Interconverting frequency and wavelength

Problem: A dentist uses x-rays (λ=1.00 Å) while a patient listens to an FM radio station (λ=325 cm) and looks out the window at blue sky (λ=473 nm). What is the frequency (s⁻¹) of the EM from each?
Plan:

<table>
<thead>
<tr>
<th>1 Å = 10^{-10} m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cm = 10^{-2} m</td>
</tr>
<tr>
<td>1 nm = 10^{-9} m</td>
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</tbody>
</table>

\[ \nu = \frac{c}{\lambda} \]

Wavelength (given units) \[\rightarrow\] Wavelength (m) \[\rightarrow\] Frequency (s\(^{-1}\))

Solution: For x-rays. Converting from Angstroms to meters:

\[ \lambda = 1.00 \, \text{Å} \times \frac{10^{-10} \, \text{m}}{1 \, \text{Å}} = 1.00 \times 10^{-10} \, \text{m} \]

Calculating the frequency:

\[ \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \, \text{m/s}}{1.00 \times 10^{-10} \, \text{m}} = 3.00 \times 10^{18} \, \text{s}^{-1} \]

For the radio station. Combining steps to calculate the frequency:

\[ \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \, \text{m/s}}{325 \, \text{cm} \times 10^{-2} \, \text{m/1 cm}} = 9.23 \times 10^{7} \, \text{s}^{-1} \]

For the sky. Combining steps to calculate the frequency:

\[ \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \, \text{m/s}}{473 \, \text{nm} \times 10^{-9} \, \text{m/1 nm}} = 6.34 \times 10^{14} \, \text{s}^{-1} \]
**Concept 7-2.** How particles and waves differ in terms of the phenomena of refraction, diffraction, and interference

**Wave Diffraction**

- If a wave passes through a slit about as wide as its wavelength, it forms a semi-circular wave on the other side of the opening.

- A stream of particles aimed at a small opening behaves quite differently:

- Some particles hit the edge and stop; those going through continue linearly in a narrower stream.
• If light waves pass through **two adjacent** slits, the emerging circular waves interact through **interference** creating a **diffraction pattern**.

• A diffraction pattern produced by X-rays.
The Particulate Nature of Light

Blackbody radiation

• As an object is heated, it begins to emit visible light, first as a red glow, then orange, then white light.
• Attempts to use electromagnetic theory to predict wavelengths of the emitted light failed.
• Max Planck proposed that the hot, glowing object could emit (or absorb) only certain amounts of energy: $E = n\hbar\nu$

-where $E$ is the radiation energy, $\nu$ is its frequency, $n$ is a positive integer called a quantum number, and $\hbar$ is Planck’s constant.
• With $E$ in joules (J) and frequency in s$^{-1}$, $\hbar$ has units of J·s: 

$$\hbar = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$$
Concept 7-3. The quantization of energy and the fact that an atom changes its energy by emitting or absorbing quanta of radiation

• If atoms can emit only fixed amounts of energy, it follows that atoms can have only fixed electronic energy values: \( E = nh\nu \), \( 2nh\nu \), ..

• This constraint means that the energy of an atom is not continuous but quantized: it can exist only in certain fixed amounts.

• Each change in energy results from a “packet” of energy being gained or lost by the atom. This energy packet is called a quantum.

• Thus, an atom changes its energy state by emitting or absorbing a quantum of energy.

\[
\Delta E_{\text{atom}} = E_{\text{emitted (or absorbed) radiation}} = \Delta nh\nu
\]

• The smallest possible energy change for an atom is from one energy state to an adjacent one (\( \Delta n = 1 \)):

\[
\Delta E = h\nu
\]
**Concept 7-4.** How the photon theory explains the photoelectric effect; the relation between photon absorbed and electron released

The **photoelectric effect**—when monochromatic light of sufficient energy hits the metal plate, an electric current flows.

1. Presence of a **threshold frequency**. Light shining on the metal must have a minimum frequency (which varies with the metal), or no current flows.

2. Absence of a time lag. Current flows the moment that light of high enough frequency shines on the metal, regardless of its intensity.
Albert Einstein offered his **photon theory** to help explain the photoelectric effect.

He proposed that radiation is **particulate**, occurring as quanta of electromagnetic energy, later called **photons**.

An atom changes its energy when it absorbs/emits a photon, a “piece” of light whose energy is fixed by its frequency:

\[ E_{\text{photon}} = h\nu = \Delta E_{\text{atom}} \]

How does Einstein’s photon theory explain the photoelectric effect?

1. Presence of a threshold frequency:

• A beam of light is composed of enormous numbers of photons.

• An electron is freed only when one photon of a certain minimum energy is absorbed. Energy depends on frequency \((h\nu)\), so a threshold frequency is to be expected.
2. Absence of a time lag. An electron is freed the instant the atom absorbs a photon of enough energy. It doesn’t accumulate energy.

- Current will be less in dim light than in bright light since fewer photons with enough energy eject fewer electrons per unit time.

**Skill 7-2.** Interconverting the energy of a photon with its frequency and/or wavelength

**Problem:** A microwave oven has a frequency of $2.45 \times 10^9 \text{ s}^{-1}$. What is the energy of one photon of this microwave radiation?

**Solution:**

$$E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.45 \times 10^9 \text{ s}^{-1})$$

$$= 1.62 \times 10^{-24} \text{ J}$$

- The quantum and photon theories ascribed features to radiation that had been reserved for matter: **fixed amount** and **discrete particles**.
**Concept 7-5.** How the Bohr theory explained line spectra of the H atom; the importance of discrete atomic energy levels

- When an element is vaporized and thermally or electrically excited, it emits light. Hydrogen gas gives a pinkish color.
- Produces a **line spectrum**, a series of fine lines of individual colors.
Atomic spectra video clip by Philip Morrison
• Spectroscopists discovered several series of H spectral lines in other regions of the electromagnetic spectrum.

• Each series showed a similar pattern.

• Equations of the form below, (Rydberg equation) were found to predict the position and wavelength of any line in a given series:

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

Where \( n_1 \) and \( n_2 \) are positive integers with \( n_2 > n_1 \), and \( R \) is the Rydberg constant (1.096776 x 10\(^7\) m\(^{-1}\)).
• For the series of spectral lines in the visible range, $n_1 = 2$:

\[
\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right), \text{ with } n_2 = 3, 4, 5, \ldots
\]

• Rydberg equation is empirical, based on data rather than theory.

**Why do the spectral lines of hydrogen follow this pattern?**

• Rutherford’s nuclear model did not predict the existence of atomic line spectra. It had to be modified or replaced.

• Niels Bohr, working in Rutherford’s laboratory, suggested a model for the hydrogen atom that predicted the observed line spectra.
The Bohr Model of the Hydrogen Atom

- Bohr used Planck’s and Einstein’s ideas about quantized energy proposing that hydrogen atoms had only certain fixed energy states.

- Each of these states was associated with a fixed circular orbit of the electron around the nucleus.

- Bohr proposed that atoms do not radiate energy while in one of their fixed (stationary) energy states.

- When the electron moves to a different orbit, the atom changes to another energy state.

- This happens only by the atom absorbing or emitting a photon.

- The photon energy equals the difference in energy between the two stationary states:

$$E_{\text{photon}} = \Delta E_{\text{stationary states}} = h\nu$$
• Spectral lines represent emission of a photon of specific energy ($\nu$) as an electron drops from a higher energy state to a lower one.

• An atomic spectrum consists of lines instead of a continuum because the atom’s energy has only certain discrete levels, or states.
• In Bohr’s model, the quantum number $n$ determines the radius of the electron’s orbit and is directly related to the atom’s energy.

• The lower the value of $n$, the smaller is the radius of the orbit and the lower is the energy level of the atom.

• When the electron is in the $n = 1$ orbit, the atom is in its lowest (first) energy level, called the ground state.

• The second energy level (second stationary state) and all higher levels are called excited states.

• A hydrogen atom in the 2nd energy level can return to the ground state by emitting a photon of a particular frequency:

$$E_{\text{photon}} = h\nu = E_{\text{first excited state}} - E_{\text{ground state}}$$
When a sample of atomic hydrogen absorbs energy, different H atoms absorb different amounts.

In various atoms all the allowable energy levels (orbits) are populated by electrons.

Transitions from outer orbits to $n = 3$ gives the **infrared series** of spectral lines.

Transitions from outer orbits to $n = 2$ gives the **visible series** of spectral lines.

Transitions from outer orbits to $n = 1$ gives the **ultraviolet series** of lines.
The Energy States of the Hydrogen Atom

• Bohr obtained an equation giving the energies of the stationary states of the hydrogen atom:

\[ E = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n^2} \right) \]

• The energy of the ground state (n = 1) is:

\[ E = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{1^2} \right) = -2.18 \times 10^{-18} \text{ J} \]

• He defined zero energy (E = 0) as the state when the electron is totally removed from the nucleus; in other words, when n = \infty.

• So E < 0 (i.e. negative) for any smaller n values.

• The energy difference between any two energy levels is given by:

\[ \Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \]
How much energy is needed to completely remove the electron from the hydrogen atom; that is, what is \( \Delta E \) for the following change?

\[
H(g) \rightarrow H^+(g) + e^-
\]

Calculate this by substituting \( n_{\text{final}} = \infty \) and \( n_{\text{initial}} = 1 \):

\[
\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18} \, \text{J} \left( \frac{1}{\infty^2} - \frac{1}{1^2} \right)
\]

\[
= 2.18 \times 10^{-18} \, \text{J}
\]

\( \Delta E \) is positive because energy must be absorbed to remove the electron from the positive nucleus.

For one mole of H atoms,

\[
\Delta E = \left( 2.18 \times 10^{-18} \, \frac{\text{J}}{\text{atom}} \right) \left( 6.022 \times 10^{23} \, \frac{\text{atoms}}{\text{mol}} \right) \left( \frac{1 \, \text{kJ}}{10^3 \, \text{J}} \right)
\]

\[
= 1.31 \times 10^3 \, \text{kJ/mol}
\]

This is the ionization energy of the hydrogen atom.
Despite its success in accounting for spectral lines of the H atom, the Bohr model failed to predict the spectrum of any other element.

The model worked well for one-electron species, but not for atoms or ions with more than one electron.

The existence of discrete atomic energy levels is retained from Bohr’s model in the current atomic model.

Concept 7-6. The wave-particle duality of matter and energy and the relevant theories and experiments that led to it

The Wave-Particle Duality of Matter and Energy

- Louis de Broglie proposed a surprising reason for the existence of fixed energy levels in Bohr’s model atoms.

- He said atoms are like other systems that display only certain allowed states, such as the wave created by a plucked guitar string.
A \quad L = n\left(\frac{\lambda}{2}\right)

B

\[ L = 1\left(\frac{\lambda}{2}\right) \]

\[ L = 2\left(\frac{\lambda}{2}\right) \]

\[ L = 3\left(\frac{\lambda}{2}\right) \]

\[ n = 3 \]

\[ n = 5 \]

\[ \text{Forbidden} \quad n = 3.3 \]
• DeBroglie suggested suggested that particles of matter such as electrons have some properties of waves.

• If electrons were wavelike and restricted to orbits of fixed radii, only certain possible frequencies and energies would be allowed.

• From mass-energy equivalence \((E = mc^2)\) and the equation for the energy of a photon \((E = h \nu = hc/\lambda)\), de Broglie derived:

\[
\lambda = \frac{h}{mu}
\]

where \(m\) is the mass and \(u\) is the velocity.

• An object’s wavelength is inversely proportional to its mass; heavy objects have wavelengths that are very much smaller than the object

• Fast moving electrons have wavelengths close to the size of an atom \((\sim 10^{-10} \text{ m})\).
• If de Broglie’s concept is correct, electrons should exhibit the wave properties of **diffraction** and **interference**.

• A good “slit” could be the spacings between atoms in a crystal.

• In 1927, C. Davisson and L. Germer guided a beam of electrons at a nickel crystal and obtained an **electron diffraction pattern**.

• This observation proves that electrons behave as waves under some conditions.
Concept 7-7. The meaning of the uncertainty principle and how it limits our knowledge of electron properties

- If an electron has both particle and wave properties, its position in an atom can’t be readily determined.
- Werner Heisenberg postulated the uncertainty principle: it is impossible to know simultaneously the exact position and velocity of a particle like an electron.
- The uncertainty principle is expressed mathematically as:

\[ \Delta x \cdot m\Delta u \geq \frac{h}{4\pi} \]

\(\Delta x\) is the uncertainty in position. \(\Delta u\) is the uncertainty in velocity.

- We cannot prescribe exact paths for electrons, such as the circular orbits of Bohr’s model.
- At best, the probability of finding an electron in a given volume of space can be determined.
The Quantum-Mechanical Model of the Atom

• Applying wave mathematics to the electron wave, Erwin Schrödinger derived an equation that is the basis for the quantum-mechanical model of hydrogen atom.

• The allowed wave-like motion of the electron leads to an atom with certain fixed energy states much like Bohr assumed.

• The electron’s exact location cannot be determined.

• Solutions of Schrödinger’s wave equation are functions, ψ, that describe atomic orbitals.

• Each ψ describes a fixed-energy state the electron can occupy and ψ^2 gives the probability of finding it in a given 3-dimensional space.
Concept 7-8. The distinction between $\psi$ (atomic orbital) and $\psi^2$ (probability of the electron being at a distance $r$ from the nucleus)

- This probability can be shown pictorially by means of an electron probability density diagram, or simply, an electron density diagram.
- Electron probability density in the H atom ground state.
**Concept 7-9.** How electron density diagrams and radial distribution plots depict the probability of electron location within the atom

- Dividing the volume of atom into thin, concentric, spherical layers and calculating $\psi^2$ in each, the variation of electron density with radial distance is found.

- The probability of the electron being far from the nucleus is very small, but not zero.

A 90% contour depiction of the ground state; the volume in which the electron spends 90% of its time.
• The maximum radial probability for the ground-state of H atom appears at (0.529 Å, or $5.29 \times 10^{-10}$ m), the same as 1st Bohr orbit.

• The electron spends most of its time at the same distance that the Bohr model predicted it spent all of its time.

• Each atomic orbital, $\psi$, has a distinctive radial probability distribution and probability contour diagram.

**Concept 7-10.** The hierarchy of the quantum numbers that describe the size ($n$, energy), shape ($l$), and orientation ($m_l$) of an orbital

**Quantum Numbers of an Atomic Orbital**

• An atomic orbital is specified by three quantum numbers.

• These determine the orbital’s size, shape, and orientation in space.
Concept 7-11. The distinction between level (shell), sublevel (subshell), and orbital

- The principal quantum number \( n \) is a positive integer (1, 2, 3, etc).

  \( n \) indicates the relative size of the orbital (the distance from the nucleus of the peak in the radial probability distribution plot).

  \( n \) specifies the energy level of the H atom: the higher the \( n \) value, the greater the energy.

- The azimuthal quantum number, \( l \), is an integer from 0 to \( n - 1 \).

  \( l \) is related to the shape of the orbital.

  For orbitals with \( n = 2 \), \( l \) can have a value of 0 or 1; with \( n = 3 \), \( l \) can be 0, 1, or 2; etc.

  The number of possible \( l \) values equals the value of \( n \).
• The magnetic quantum number \( (m_l) \) is an integer from \(-l\) through 0 to \(+l\).

\( m_l \) prescribes the **orientation** of the orbital in the three-dimensional space about the nucleus.

The possible values of an orbital’s magnetic quantum number are set by its azimuthal quantum number.

An orbital with \( l = 0 \) can have only \( m_l = 0 \).

An orbital with \( l = 1 \) can have \( m_l \) values of \(-1, 0, \) or \(+1\).

The number of possible \( m_l \) values, or orbitals, for a given \( l \) value is \( 2l + 1 \).
Determining Quantum Numbers for a Given Energy Level

**Problem**: (a) What values of the azimuthal and magnetic quantum numbers are allowed for a principal quantum number of 3? (b) How many orbitals are allowed for \( n = 3 \)?

**Solution**: Determining \( l \) values:

\( l \) takes values from 0 to \( n-1 \). For \( n = 3 \), \( l = 0, 1, 2 \).
Determining $m_l$ for each $l$ value:

For $l = 0$, $m_l = 0$

For $l = 1$, $m_l = +1, 0, -1$

For $l = 2$, $m_l = +2, +1, 0, -1, -2$

Since there are nine $m_l$ values, there are nine orbitals with $n = 3$.

- The total number of orbitals for a given $n$ value is $n^2$.
- The atom’s energy levels, or shells, are given by the $n$ value.
- The $n = 1$ shell has lower energy and a greater probability of the electron being closer to the nucleus than higher shells.
- The atom’s sublevels, or subshells, are given by the $n$ and $l$ values. Each shell contains subshells that designate the shape of the orbital.
Each subshell is designated by a letter:

- $l = 0$ indicates an \textbf{s subshell}.
- $l = 1$ indicates a \textbf{p subshell}.
- $l = 2$ indicates a \textbf{d subshell}.
- $l = 3$ indicates an \textbf{f subshell}.

Subshells are named by using the $n$ value and the letter designation.

The subshell with $n = 2$ and $l = 0$ is called the \textbf{2s subshell}.

The only orbital in the 2s subshell has $n = 2$, $l = 0$, and $m_l = 0$.

The subshell with $n = 3$ and $l = 1$ is the \textbf{3p subshell}.

It has three orbitals: $n = 3$, $l = 1$, and $m_l = +1, 0$ and $-1$.

Each of an atom’s orbitals is specified by a set of $n$, $l$, and $m_l$ values.

These fix the orbital’s size, energy, shape, and spatial orientation.
Skill 7-5. Determining quantum numbers and sublevel designations

**Problem:** Give the name, magnetic quantum numbers, and number of orbitals for each subshell with the quantum numbers shown:

(a) \( n = 3, l = 2 \)  
(b) \( n = 2, l = 0 \)  
(c) \( n = 5, l = 1 \)  
(d) \( n = 4, l = 3 \)

**Solution:**

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>subshell name</th>
<th>possible ( m_\ell )</th>
<th>No. of orb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 3</td>
<td>2</td>
<td>3d</td>
<td>-2, -1, 0, +1, +2</td>
<td>5</td>
</tr>
<tr>
<td>(b) 2</td>
<td>0</td>
<td>2s</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(c) 5</td>
<td>1</td>
<td>5p</td>
<td>-1, 0, +1</td>
<td>3</td>
</tr>
<tr>
<td>(d) 4</td>
<td>3</td>
<td>4f</td>
<td>-3, -2, -1, 0, +1, +2, +3</td>
<td>7</td>
</tr>
</tbody>
</table>
Identifying Incorrect Quantum Numbers

Problem: What is wrong with each of the following quantum number designations and/or subshell names?

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</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1p</td>
</tr>
<tr>
<td>(b)</td>
<td>4</td>
<td>3</td>
<td>+1</td>
<td>4d</td>
</tr>
<tr>
<td>(c)</td>
<td>3</td>
<td>1</td>
<td>-2</td>
<td>3p</td>
</tr>
</tbody>
</table>

Solution: (a) A sublevel of \( n = 1 \) can have only \( l = 0 \), not \( l = 1 \). The only possible subshell is 1s.
(b) A subshell with \( l = 3 \) is an f subshell, not a d subshell. The subshell name should be 4f.
(c) A subshell with \( l = 1 \) can have only \( m_l \) of -1, 0, +1, not -2.
Concept 7-12. The shapes and nodes of s, p, and d orbitals

- Each subshell of the H atom has orbitals with a characteristic shape.
- s orbitals ($l = 0$) are spherically symmetrical around the nucleus.
• The p orbital (with $l = 1$) has **two** regions of higher probability that lie on either side of the nucleus.

• The nucleus lies at a **nodal plane** of p orbitals.

• The max. value of $l$ is $n - 1$, so only shells with $n \geq 2$ can have p orbitals.

• Energies of p orbitals: $2p < 3p < 4p ...$
• The three possible \( m_l \) values: +1, 0, and –1, which lead to three **mutually perpendicular** p orbitals: \( p_x \), \( p_y \), \( p_z \).

• The three p orbitals are equivalent in size, shape, and energy, differing only in orientation.
The d orbitals

- Orbitals with $l = 2$ are called d orbitals. There are five possible $m_l$ values for the $l = 2$ sublevel: +2, +1, 0, –1, and –2.

- d orbitals can have any one of five different orientations.

Actual shape of $d_{yz}$

simplified shape of $d_{yz}$
• In accord with the quantum number rules, a d orbital must have a principal quantum number of at least \( n = 3 \).

• The 4d orbitals extend farther from the nucleus than the 3d, and the 5d orbitals extend still farther.
Energy Levels of the Hydrogen Atom

- In the ground state the electron is in the $n = 1$ shell (1s orbital)
- Photons of the correct energies can promote the electron to higher shells.
- The excited atom can return to the ground state by emitting a photon of the same energy.

$n = 4$ (4s, 4p, 4d, 4f)
$n = 3$ (3s, 3p, 3d)
$n = 2$ (2s, 2p)
$n = 1$ (1s)