Chapter 7 Quantum Theory of Light, the Atom, and Atomic Structure
(Sections 6.1, 6.2, and 6.3 in OpenStax)

Electromagnetic Radiation

- Electromagnetic radiation consists of oscillations in electric and magnetic fields. The oscillations can be described mathematically with a sine wave.
- Electromagnetic radiation has both wave-like and particle-like properties.
- Visible light is one form of electromagnetic radiation.
- The other forms of electromagnetic radiation are radio, microwave, infrared, ultraviolet, x-rays, and gamma rays.

Wavelength

- Symbolized by λ (lambda).
- Wavelength is the distance between two adjacent identical points on a wave. For example, the crest-to-crest distance is one wavelength.
- The units are those for length, such as nm (1 nm = 10^{-9} m).

Frequency

- Symbolized by ν (nu).
- Frequency is the number of wavelengths (cycles) per unit time, which is seconds (s).
- The units are Hertz (Hz), which are cycles/s.
  Cycles are normally omitted to give us s^{-1} (same as $\frac{1}{s}$).

Speed of Light (in a vacuum)

- Symbolized by c and is a constant: $c = 3.00 \times 10^{+8}$ m/s = length traveled per unit time
- Equal to wavelength times frequency: $c = \nu\,\lambda$ = (waves per unit time) × (length per wave)
- The equation can also be rearranged: $\lambda = \frac{c}{\upsilon}$ and $\nu = \frac{c}{\lambda}$

Example 7.01 If frequency is $4.55 \times 10^{+14}\ s^{-1}$, then what is the wavelength (and color)?

- Review how to use scientific notation here.
- $\lambda = \frac{c}{\upsilon} = \frac{(3.00 \times 10^{+8}\ \frac{m}{s})}{(4.55 \times 10^{+14}\ s^{-1})} = 6.59 \times 10^{-7}$ m
- $(6.59 \times 10^{-7}\ m)\left(\frac{10^{+9}\ nm}{1\ m}\right) = 659$ nm (orange)

Example 7.02 If wavelength is 554 nm, then what is the frequency (and color)?

- $\lambda = (554\ nm)\left(\frac{1\ m}{10^{+9}\ nm}\right) = 5.54 \times 10^{-7}$ m (green)
- $\nu = \frac{c}{\lambda} = \frac{(3.00 \times 10^{+8}\ \frac{m}{s})}{(5.54 \times 10^{-7}\ m)} = 5.42 \times 10^{+14}\ s^{-1}$

Electromagnetic Spectrum – The entire spectrum contains the full range of λ's and ν's.

- The equation for the energy of a cycle is $E = h\nu = hc/\lambda$, where h is Planck's constant (below).
- Radio waves have the lowest E, lowest ν, and highest λ.
- Gamma rays have the highest E, highest ν, and lowest λ.
- Visible is approximately in the middle, with wavelengths from 380 nm to 780 nm.

Diffraction

- Diffraction is a slight change in direction of a wave as it passes around the edge of an object. Objects make waves appear to "bend" or change their overall direction.
- Objects cause light to diffuse, or spread out in many directions.
- This shows that light can behave like a wave.

Vibrational Energy (Max Planck)

- Vibrational energy (E) of an atom causes it to oscillate back and forth like a spring.
- The energy can only have certain quantized values, and is not a continuous function.
- The atoms will have an oscillation frequency (ν), and E will be a function of ν.
- Max Planck found (in 1900) that $E = nh\nu$, where n is an integer called the vibrational quantum number, and h is Planck's constant: $h = 6.63 \times 10^{-34}$ J·s (or kg·m^2/s).

Photoelectric Effect (Albert Einstein)

- Light behaves not only like a wave, but also like a particle.
- Light can be absorbed by an e^{-1} and can cause the e^{-1} to be ejected from its atom.
- But for an e^{-1} to be ejected, the E_{photon} must be larger than the "threshold value" for that e^{-1}. So, frequency (ν) must be greater than the value of the spectral line in the emission spectrum.
- In this case, light is behaving like a particle, where each particle contains a specific quantity (quantum) of energy, which must be above the threshold value in order to eject the e^{-1}.
- The energy of the absorbed photon equals the change in the energy of the e^{-1}.
  $\Delta E_{electron} = E_{photon} = h\nu = hc/\lambda$.

Example 7.03 If wavelength is 456 nm, then what is the energy of the photon?

- $\lambda = (456\text{ nm})\left(\frac{1\text{ m}}{10^{+9}\text{ nm}}\right) = 4.56 \times 10^{-7}$ m $\qquad \nu = c / \lambda = \frac{3.00 \times 10^{+8}\ \frac{\text{m}}{\text{s}}}{4.56 \times 10^{-7}\text{ m}} = 6.58 \times 10^{+14}\text{ s}^{-1}$
- $E_{photon} = h\nu = (6.63 \times 10^{-34}\text{ J·s})(6.58 \times 10^{+14}\text{ s}^{-1}) = 4.36 \times 10^{-19}$ J

Niels Bohr's Theory of the Hydrogen Atom (1913)

- Stability of atom is due to quantization of E.
- The e^{-1} does not fall into the nucleus because it has kinetic E, which can only be gained or lost in certain quantized amounts.
- Emission of light by a heated gaseous element shows only specific λ's (lines), and this line spectrum is unique for each element.
- These λ's are those of specific transitions for e^{-1}'s going from one E level to another.

Rydberg formula

- In 1885, J.J. Balmer found a mathematical equation that fits the wavenumbers (m^{-1}) for the visible spectral lines emitted by hydrogen. In 1888, Johannes Rydberg found that Balmer's equation could be rewritten using integers.

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

- These wavenumbers are directly proportional to energy also, because $E = hc \times (1/\lambda)$.

Bohr's Postulates (1913)

1. An e^{-1} can only have specific E levels, such that $E = -\frac{R_H}{n^2}$.
   The n is an integer called the principal quantum #, and it corresponds to the primary E level.
2. An e^{-1} can change its E only by a transition from one E level to another, with a ΔE.

Bohr's Postulates explain why the Rydberg and Balmer formulas work for hydrogen

- The energy of an e^{-1} at energy level n is found by $E = -R_H/n^2$, where $\mathbf{R_H = 2.179 \times 10^{-18}\ J}$.
- When an e^{-1} goes from higher E to lower E, a photon is emitted.
- The energy of the emitted photon is equivalent to the energy of the transition.

  $$\mathbf{E_{photon} = -\Delta E_{electron} = -(E_f - E_i)}$$

  $$\mathbf{E_{photon} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)} \qquad \text{and} \qquad \mathbf{1/\lambda = \left(\frac{R_H}{hc}\right)\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)}$$

- R_H/hc is the Rydberg constant and equals $1.097 \times 10^{+7}\ m^{-1}$, as in the Rydberg equation above.
- E values are negative because bond energy between e^{-1} and nucleus stabilizes the atom. This is similar to the negative ΔH for exothermic reactions.
- The e^{-1} is ejected when there is no stabilization left, that is when $E = 0$.
- J.J. Balmer could only observe transitions that have visible λ's, which is where $n_f = 2$.

Example 7.04 Find λ and E_{photon} for a Transition (Where an e^{-1} Changes its Energy Level)

- The transition is from n = 4 to n = 2 for an e^{-1} in a hydrogen atom.
- $(1/\lambda) = \left(\frac{R_H}{hc}\right)\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = \left(\frac{R_H}{hc}\right)\left(\frac{1}{4} - \frac{1}{16}\right) = (1.097 \times 10^{+7}\ m^{-1})\left(\frac{3}{16}\right)$
- $\lambda = \left(\frac{1}{1.097 \times 10^{+7}\ m^{-1}}\right)\left(\frac{16}{3}\right) = 4.86 \times 10^{-7}\ m \times \left(\frac{10^{+9}\ nm}{1\ m}\right) = 486\ nm$ (blue-green)
- $E_{photon} = (R_H)\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = (2.179 \times 10^{-18}\ J)\left(\frac{3}{16}\right) = 4.086 \times 10^{-19}\ J$

Atomic Spectra (emission and absorption)

- Emission occurs when an e^{-1} goes from a higher E level to a lower E level, which causes a photon (or light) to be released.
- Absorption occurs when an e^{-1} absorbs a photon and goes to a higher E level (an excited state).

Quantum Mechanics

- Quantum mechanics describes the wave-like properties of submicroscopic particles.
- Louis de Broglie's relation is $\lambda = \frac{h}{mv}$, where m is mass and v is velocity.
- This shows that matter, like light, has wave-like properties.
- A smaller mass possesses a larger λ. As a result, a tiny e^{-1} can have a λ that is in the visible, ultraviolet, or x-ray ranges. For this reason, an electron microscope (image c) can work by using an x-ray detector to detect e^{-1}'s diffracted by the object being imaged.

Example 7.05 The de Broglie relation for a baseball (0.145 kg) and an electron (9.11×10^{-31} kg)

a. $v = (135\ \text{km/hr})\left(\frac{1\ \text{hr}}{3600\ \text{s}}\right)\left(\frac{1000\ \text{m}}{\text{km}}\right) = 37.5\ \text{m/s}$

$$\lambda = h/mv = \frac{6.63 \times 10^{-34}\ \text{J·s}}{(0.145\ \text{kg})\left(37.5\ \frac{\text{m}}{\text{s}}\right)} = = \frac{6.63 \times 10^{-34}\ (\text{kg·m}^2/\text{s}^2)\text{·s}}{(0.145\ \text{kg})\left(37.5\ \frac{\text{m}}{\text{s}}\right)} = 1.22 \times 10^{-34}\ \text{m}$$

b. $$\lambda = h/mv = \frac{6.63 \times 10^{-34}\ (\text{kg·m}^2/\text{s}^2)\text{·s}}{(9.11 \times 10^{-31}\ \text{kg})\left(3.45 \times 10^{6}\ \frac{\text{m}}{\text{s}}\right)} = 2.11 \times 10^{-10}\ \text{m}$$

$$\lambda = (2.11 \times 10^{-10}\ \text{m})\left(\frac{10^{12}\text{pm}}{1\ \text{m}}\right) = 211\ \text{pm (in the x-ray range)}$$

Heisenberg Uncertainty Principle

- An e^{-1} in an atom does not have a precise orbit, and we cannot simultaneously know its precise position (x) and momentum (p).
- The Δ's represent error magnitudes, and there is a minimum combined uncertainty.

$$(\Delta x)(\Delta p_x) \geq h/(4\pi)$$

- Also, momentum is mass times velocity (p = mv), so we can say $\Delta p_x = m(\Delta v_x)$.

$$(\Delta x)(\Delta v_x) \geq h/(4\pi m)$$

- If one value (x or v) is known precisely, the uncertainty for the other value must be large as a consequence.

Wave Function

- The wave equation describes position (x) and velocity (v) for a particle, like an electron, within a given energy level. The overall equation is symbolized by the Greek letter psi (Ψ).
- Ψ^2 gives the probability density function for finding the particle (e^{-1}) within a given volume around the nucleus. To obtain probability vs. distance from nucleus, we integrate:

$$\text{Probability} = \int (\Psi^2)\delta V, \text{ where V is volume.}$$

- Since $V = (4/3)\Pi r^3$ and $\delta V = (4\Pi r^2)\delta r$, we can put the equation in terms of atomic radius:

$$\text{Probability} = \int (\Psi^2)\,(4\Pi r^2)\delta r$$

- Integrating this equation for the hydrogen atom's one electron gives a simple curve with a single maximum probability.
- Volume is very small near the nucleus, so the probability of the electron being very near to the nucleus is very low. Probability approaches zero at the nucleus.
- Probability reaches a maximum at approximately 50 pm, then declines.
- Probability approaches 0 again near 200 pm.

Atomic Orbital

- An atomic orbital is a space around the nucleus where two electrons reside. That is, it is the space which has the highest probability for the e^{-1}'s locations.
- The wave function (Ψ) is the mathematical description of an atomic orbital.

Quantum Numbers and Atomic Orbitals

A wave function, which describes an atomic orbital, is determined by four quantum numbers.

1. Principle Q # is symbolized by n, where $n \in \{1, 2, 3\ldots\}$. All n values are positive integers.
   The n value determines most of the e^{-1}'s energy, and corresponds with its **shell number**.
   The shell number of the outermost e^{-1} corresponds with atom's **row** in periodic table.
2. Angular Momentum Q # is symbolized by L, where $L \in \{0, 1, 2, 3 \ldots (n - 1)\}$.
   L includes nonnegative integers up to $(n - 1)$ and $L < n$ for all values.
   L corresponds with **subshells** (**s**, **p**, **d**, **f**, and **g**) within a shell.
   The "s" subshell (where L = 0) has an orbital with a spherical shape.
   The "p" subshell (where L = 1) has orbitals with *two* elliptical lobes.
   The "d" subshell (where L = 2) has orbitals with *four* elliptical lobes.
3. Magnetic Q # is symbolized by m_L, where $m_L \in \{-L \ldots 0 \ldots +L\}$.
   The values include positive and negative integers with the absolute value $\leq$ L.
   m_L values correspond to **orbitals** in a subshell. The s subshell has only one orbital ($m_L = 0$), p has three orbitals ($m_L = -1, 0, +1$), and d has five orbitals ($m_L = -2, -1, 0, +1, +2$).
4. Spin Q # is symbolized by m_S, where $m_S \in \{-1/2$ and $+1/2\}$
   The two m_S values correspond to each of **two e^{-1}'s** in an orbital.
   No more than two e^{-1}'s can fit in an orbital, and they will have opposing spin directions.

This chart shows what values are allowed for electrons, according to their shells and subshells.

Example 7.06 Applying the Rules for the Four Quantum Numbers

a. n = 2 and L = 2: If n = 2 (shell 2), then L cannot be larger than n − 1, which is 2 − 1 = 1.
   This leaves only L = 0 (s subshell) and L = 1 (p subshell). So, L = 2 is not permissible.
b. n = 2, L = 1, and $m_L = -3$: If L = 1 (p subshell), then m_L can only be −1, 0, or +1.
   So, $m_L = -3$ is not permissible.
c. $m_S = 0$: Value for m_S can only be −1/2 or +1/2. So, $m_S = 0$ is never permissible.
d. n = 3, L = 2, and $m_L = -1$: If n = 3, then L = 2 (d subshell) is allowed because 3 − 1 = 2.
   If L = 2, then $m_L = -1$ is allowed because $m_L \in \{-2, -1, 0, +1, +2\}$ for L = 2.