Chapter 7

Quantum Theory and Atomic Structure

7.1 The Nature of Light

7.2 Atomic Spectra

7.3 The Wave-Particle Duality of Matter and Energy

7.4 The Quantum-Mechanical Model of the Atom
The Wave Nature Of Light

Frequency and wavelength.

\[ c = \lambda \nu \]
\[ c = 2.998 \times 10^8 \text{ m/sec} \]

Amplitude (intensity) of a wave.

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Regions of the electromagnetic spectrum.

Interconverting Wavelength and Frequency

PROBLEM: A dental hygienist uses x-rays ($\lambda = 1.00 \text{ Å}$) to take a series of dental radiographs while the patient listens to a radio station ($\lambda = 325 \text{ cm}$) and looks out the window at the blue sky ($\lambda = 473 \text{ nm}$). What is the frequency (in $s^{-1}$) of the electromagnetic radiation from each source? (Assume that the radiation travels at the speed of light, $3.00 \times 10^8 \text{ m/s}$.)

PLAN: Use $c = \lambda \nu$

\begin{align*}
1 \text{ Å} &= 10^{-10} \text{ m} \\
1 \text{ cm} &= 10^{-2} \text{ m} \\
1 \text{ nm} &= 10^{-9} \text{ m}
\end{align*}

\begin{align*}
\nu &= \frac{c}{\lambda} \\
\text{Frequency (s}^{-1} \text{ or Hz)}
\end{align*}
Interconverting Wavelength and Frequency: Solution

\[ c = \lambda \nu \]

1.00 Å \( \times \) \( \frac{10^{-10} \text{ m}}{1 \text{ Å}} \) = 1.00 \( \times \) \( 10^{-10} \text{ m} \)

\[ \nu = \frac{3 \times 10^8 \text{ m/s}}{1.00 \times 10^{-10} \text{ m}} = 3 \times 10^{18} \text{ s}^{-1} \]

325 cm \( \times \) \( \frac{10^{-2} \text{ m}}{1 \text{ cm}} \) = 325 \( \times \) \( 10^{-2} \text{ m} \)

\[ \nu = \frac{3 \times 10^8 \text{ m/s}}{325 \times 10^{-2} \text{ m}} = 9.23 \times 10^7 \text{ s}^{-1} \]

473 nm \( \times \) \( \frac{10^{-9} \text{ m}}{1 \text{ nm}} \) = 473 \( \times \) \( 10^{-9} \text{ m} \)

\[ \nu = \frac{3 \times 10^8 \text{ m/s}}{473 \times 10^{-9} \text{ m}} = 6.34 \times 10^{14} \text{ s}^{-1} \]

Different behaviors of waves and particles.
The diffraction pattern caused by light passing through two adjacent slits.

Particle Nature of Light: Blackbody Radiation

Three phenomena could not be explained by classical physics: blackbody radiation, photoelectric effect, and atomic spectra. A new picture of energy was required.

Blackbody Radiation: Heat a solid object: at 1000 K it begins to emit soft red light; at 1500 K it begins to glow orange and is brighter; at 2000 K it is still brighter and white. How to explain?

Planck: proposed that only certain quantities of energy could be emitted or absorbed:

\[ E = nh\nu = \frac{nhc}{\lambda} \]

These packets of energy are called quantum, and \( n \) is a quantum number. Since it was (correctly) assumed that most transitions occur between adjacent states, \( \Delta n = 1 \) and the change in energy is:

\[ \Delta E = h\nu = \frac{hc}{\lambda} \]
Demonstration of the photoelectric effect.

NOT a function of light intensity;

IS a function of light wavelength (and therefore frequency) “Threshold frequency”;

NO time lag.

Calculating the Energy of Radiation from Its Wavelength

**PROBLEM:** A cook uses a microwave oven to heat a meal. The wavelength of the radiation is 1.20 cm. What is the energy of one photon of this microwave radiation?

**PLAN:** After converting cm to m, we can use the energy equation, \( E = h\nu \)
combined with \( \nu = c/\lambda \), to find the energy.

**SOLUTION:**

\[
E = \frac{h\nu}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{sec})(3.00 \times 10^8 \text{ m/ sec})}{1.20 \times 10^{-2} \text{ m}} = 1.66 \times 10^{-23} \text{ J}
\]
Atomic Spectra: A Problem to Solve!

(a) “Continuum”: Classical Physics

(b) Balmer series

The line spectra of several elements.

Chap 7-14 Quantum Mechanics
Rydberg equation for emission

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

*R* is the Rydberg constant = \( 1.096776 \times 10^7 \) m\(^{-1}\)

Three series of spectral lines of atomic hydrogen.

for the visible series, \( n_1 = 2 \) and \( n_2 = 3, 4, 5, ... \)

Quantum staircase.
The Bohr explanation of the three series of spectral lines.

Wave motion in restricted systems.
Wave-Particle Duality

- Energy (electromagnetic radiation) behaves like waves (diffraction, wavelength, frequency) but also possesses particle behavior (photons in photoelectric effect). Invoke wave-particle duality of EMR to explain.
- If energy can exhibit both particle and wave natures, what about matter?
- deBroglie: “Matter Waves”

\[ \lambda = \frac{h}{mv} = \frac{h}{p} \]

- Large items have very small wavelengths
- Electrons are small enough however to exhibit measurable wave properties

<table>
<thead>
<tr>
<th>Substances</th>
<th>Mass (g)</th>
<th>Speed (m/s)</th>
<th>( \lambda ) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow electron</td>
<td>( 9 \times 10^{-28} )</td>
<td>1.0</td>
<td>( 7 \times 10^{-4} )</td>
</tr>
<tr>
<td>Fast electron</td>
<td>( 9 \times 10^{-28} )</td>
<td>( 5.9 \times 10^{6} )</td>
<td>( 1 \times 10^{-10} )</td>
</tr>
<tr>
<td>Alpha particle</td>
<td>( 6.6 \times 10^{-24} )</td>
<td>( 1.5 \times 10^{7} )</td>
<td>( 7 \times 10^{-15} )</td>
</tr>
<tr>
<td>One-gram mass</td>
<td>1.0</td>
<td>0.01</td>
<td>( 7 \times 10^{-29} )</td>
</tr>
<tr>
<td>Baseball</td>
<td>142</td>
<td>25.0</td>
<td>( 2 \times 10^{-34} )</td>
</tr>
<tr>
<td>Earth</td>
<td>( 6.0 \times 10^{27} )</td>
<td>( 3.0 \times 10^{4} )</td>
<td>( 4 \times 10^{-63} )</td>
</tr>
</tbody>
</table>
Determining $\Delta E$ and $\lambda$ of an Electron Transition

**PROBLEM:** A hydrogen atom absorbs a photon of visible light and its electron enters the $n = 4$ energy level. Calculate (a) the change in energy of the atom and (b) the wavelength (in nm) of the photon.

**PLAN:**
(a) The H atom absorbs visible light, so the electron is going from $n = 2$ to $n = 4$. Calculate $\Delta E$. (b) $\Delta E = h\nu = hc/\lambda$.

**SOLUTION:**
(a) $\Delta E = -2.18 \times 10^{-18} \text{ J} \left( \frac{Z^2}{n_{\text{final}}^2} - \frac{Z^2}{n_{\text{initial}}^2} \right) = -2.18 \times 10^{-18} \text{ J} \left( \frac{1^2}{4^2} - \frac{1^2}{2^2} \right)$

$\Delta E = 4.09 \times 10^{-18} \text{ J}$

(b) $\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{4.09 \times 10^{-18} \text{ J}} = 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm}$

Comparing diffraction patterns of x-rays and electrons.

X-ray diffraction of aluminum

Electron diffraction of aluminum
Summary of the major observations and theories leading from classical theory to quantum theory.

Wave-Particle Duality: Problems

- Classical mechanics: particles have trajectories and can precisely be described according to location \( (x) \) and linear momentum \( (p) \)
- Quantum mechanics: can’t think like this: waves are spread out as they oscillate
- Duality denies the ability of knowing the trajectory of particles (complementarity)
- Heisenberg Uncertainty principle:

\[
(\Delta x)(m\Delta p) = (\Delta x)(\Delta p) \geq \hbar/4\pi \quad \text{or} \quad (\Delta x)(\Delta p) \geq \hbar/2
\]

- Important for wave equations
The Heisenberg Uncertainty Principle

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

Schrödinger Equation

- The SWE relates the second derivative of \( \Psi \) to the value of \( \Psi \) at each point; impossible to solve exactly (except simple cases)
- One simple solution: particle in a box

\[ \psi_{\nu} (x) = \sqrt{\frac{2}{L_x}} \sin \left( \frac{n\pi x}{L_x} \right) \]

\[ \Lambda = \text{length of box} \]
\[ \nu = 1, 2, 3, \ldots \]
\[ \xi = \text{distance between 0 and } \Lambda \]

- Solution of SWE using this yields:

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]

Since \( n \) is an integer, \( E \) is quantized with discrete values of \( E \)

and, since \( \Delta E = h \nu \) and \( \Delta E = E_{n+1} - E_n \)

\[ h\nu = \frac{hc}{\lambda} = \frac{(2n+1)\hbar^2}{8mL^2} \]
SWE: Particle in a Rectangular Box

• What if the box is 3-dimensional?

\[ \psi_n(x) = \frac{2}{\sqrt{L}} \sin \left( \frac{n\pi x}{L} \right) \]

\[ \psi_{n,n,n}(x,y,z) = (\psi_n(x))^* (\psi_n(y))^* (\psi_n(z))^* \]

• Solution of SWE using this yields:

\[ E_{n,n,n} = \frac{\hbar^2}{8m} \left[ \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right] \]

\[ E_{n,n,n} = \frac{\hbar^2}{8ml^2} \left[ n_x^2 + n_y^2 + n_z^2 \right] \]

Electron probability density in the ground-state H atom.
Hydrogen Wavefunctions

<table>
<thead>
<tr>
<th>n</th>
<th>l</th>
<th>( R_n(r) )</th>
<th>0</th>
<th>0</th>
<th>( Y_{00}(\theta, \phi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>( \frac{2}{a_0} \left( \frac{Z}{a_0} \right)^{3/2} e^{-r/a_0} )</td>
<td>1</td>
<td>( \frac{1}{2\pi} )</td>
<td>Angle independent</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( \frac{1}{2\sqrt{2}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) e^{-r/a_0} )</td>
<td>1</td>
<td>( \frac{1}{4\pi} )</td>
<td>sin ( \theta ) cos ( \phi )</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>( \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z}{a_0} \right) e^{-r/a_0} )</td>
<td>1</td>
<td>( \frac{1}{4\pi} )</td>
<td>sin ( \theta ) sin ( \phi )</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>( \frac{1}{9\sqrt{3}} \left( \frac{Z}{a_0} \right)^{3/2} \left( 3 - \frac{Zr}{a_0} \right) \left( \frac{Zr^2}{a_0^2} \right) e^{-r/a_0} )</td>
<td>1</td>
<td>( \frac{3}{4\pi} )</td>
<td>cos ( \theta )</td>
</tr>
<tr>
<td>1</td>
<td>( \frac{1}{2\sqrt{2}} )</td>
<td>( \left( \frac{Z}{a_0} \right)^{3/2} \left( 2 - \frac{Zr}{a_0} \right) \left( \frac{Zr^2}{a_0^2} \right) e^{-r/a_0} )</td>
<td>1</td>
<td>( \frac{15}{16\pi} )</td>
<td>sin(^2) ( \theta ) cos ( 2\phi )</td>
</tr>
<tr>
<td>2</td>
<td>( \frac{1}{8\sqrt{10}} )</td>
<td>( \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z^2}{a_0^2} \right) e^{-r/a_0} )</td>
<td>1</td>
<td>( \frac{15}{4\pi} )</td>
<td>cos ( \theta ) sin ( \theta ) sin ( \phi )</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>( \frac{1}{8\sqrt{10}} )</td>
<td>( \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z^2}{a_0^2} \right) e^{-r/a_0} )</td>
<td>1</td>
<td>( \frac{15}{4\pi} )</td>
</tr>
<tr>
<td>3</td>
<td>( \frac{1}{3\cos^2 \theta - 1} )</td>
<td>( \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Z^2}{a_0^2} \right) e^{-r/a_0} )</td>
<td>2</td>
<td>( \frac{15}{16\pi} )</td>
<td>sin(^2) ( \theta ) sin ( 2\phi )</td>
</tr>
</tbody>
</table>

Note: In each case, \( a_0 = 4\pi\varepsilon_0/m_e^2 \), or close to 52.9 pm; for hydrogen itself, \( Z = 1 \).

*In all cases except \( m_l = 0 \), the orbitals are sums and differences of orbitals with specific values of \( m_l \).

Quantum Numbers and Atomic Orbitals

An atomic orbital is specified by three quantum numbers.

\( n \) the principal quantum number - a positive integer (1, 2, 3, ……)

\( l \) the angular momentum quantum number - an integer from 0 to \((n - 1)\)

\( m_l \) the magnetic moment quantum number - an integer from \(-l\) to \(+l\)
Determining Quantum Numbers for an Energy Level

**PROBLEM:** What values of the angular momentum \(l\) and magnetic \(m_l\) quantum numbers are allowed for a principal quantum number \(n\) of 3? How many orbitals exist for \(n = 3\)?

**PLAN:** Follow the rules for allowable quantum numbers found in the text.

\(l\) values can be integers from 0 to \((n - 1)\); \(m_l\) can be integers from \(-l\) through 0 to \(+l\).

**SOLUTION:**

For \(n = 3\), \(l = 0, 1, 2\)

For \(l = 0\), \(m_l = 0\)

For \(l = 1\), \(m_l = -1, 0, +1\)

For \(l = 2\), \(m_l = -2, -1, 0, +1, +2\)

There are 9 \(m_l\) values and therefore, 9 orbitals with \(n = 3\).
## Determining Sublevel Names and Orbital Quantum Numbers

**PROBLEM:** Give the name, magnetic quantum numbers, and number of orbitals for each sublevel with the following quantum numbers:

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

**PLAN:** Combine the \( n \) value and \( l \) designation to name the sublevel. Knowing \( l \), we can find \( m_l \) and the number of orbitals.

**SOLUTION:**

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>sublevel name</th>
<th>possible ( m_l ) values</th>
<th># of orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3</td>
<td>2</td>
<td>-2, -1, 0, +1, +2</td>
<td>5</td>
</tr>
<tr>
<td>(b)</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(c)</td>
<td>5</td>
<td>1</td>
<td>-1, 0, +1</td>
<td>3</td>
</tr>
<tr>
<td>(d)</td>
<td>4</td>
<td>3</td>
<td>-3, -2, -1, 0, +1, +2, +3</td>
<td>7</td>
</tr>
</tbody>
</table>

The 1s, 2s, and 3s orbitals.
The 2p orbitals.

The 3d orbitals.
One of the seven possible $4f$ orbitals.