CHAPTER 27

Early Quantum Theory and Models of the Atom

Discovery and Properties of the Electron

When a high voltage is applied to electrodes attached to a glass tube containing a rarefied gas, a glow appears on one end, as though emitted by the negative electrode.

- The position of the glow, caused by **cathode rays,** was observed to change in response to an electric or magnetic field, implying the cathode rays were charged particles. J. J. Thompson used this behavior to measure the **charge-to-mass ratio** of these particles, $e/m = E/B^2r$, where E represents an electric field, B represents a magnetic field, and r is the radius of curvature of the particle's path.
- Cathode rays are beams of **electrons,** whose individual charge to mass ratio is 1.76×10^{11} C/kg.
- Robert A. Millikan's **oil-drop experiment** measured the electric field necessary to suspend charged oil drops, and Millikan used this to determine the charge of a single electron as $e = 1.6 \times 10^{-19}$ C.
- A value for the electron mass could be calculated when Millikan's result was combined with Thompson's charge-to-mass ratio. Millikan's experiment also showed that electric charges are all integer multiples of e, and are thus quantized.

Planck's Quantum Hypothesis

Heated objects produce a spectrum of light whose peak wavelength is a function of temperature in **Wein's law,** $\lambda_p T = 2.90 \times 10^{-3}$ m·K, where T is temperature in kelvins.

- This phenomenon, as idealized in blackbody radiation, was explained by Max Planck—by assuming that the energy of the charge oscillations within molecules producing such radiation is quantized in relation to its wavelength, such that $E_{\text{min}} = hf$, where Planck's constant $h = 6.626 \times 10^{-34}$ J·s.
- Therefore, the energy of molecular vibration is quantized in discrete values, given by $E = nhf$, for $n = 1, 2, 3 \ldots$. Planck's assumption is called **Planck's quantum hypothesis.**

Photon Theory of Light and the Photoelectric Effect

Following Planck's work, Albert Einstein proposed that light must also be quantized, where $E = hf$, gives the energy of individual **photons,** which are particles rather than waves.

- This was confirmed in the **photoelectric effect,** in which electrons are released from a metal surface when light is directed at it. This can be demonstrated with a **photocell,** which consists of a metal plate and a separate electrode at opposite ends of an evacuated glass tube, which is attached to a circuit containing an ammeter. When light having a sufficiently high energy (frequency) strikes the metal plate, electrons are knocked loose and a current flows in the circuit. The reverse voltage necessary to prevent a flow of current (that is, to stop emitted electrons from having enough kinetic energy to reach the electrode), is called the **stopping voltage** V_0. It can be experimentally determined. From this, $KE_{max} = eV_0$.
- Photon theory suggests that each electron is released after being struck by a photon, which no longer exists after transferring its energy in the collision. The **work function,** W_0, is the minimum energy needed to extricate the electron from the metal, such $hf = KE + W$ that where hf is the energy of the photon, W is the energy necessary to release the electron, and KE is the kinetic energy of the electron after its release.
- Kinetic energy after release is maximized for the electrons which have the smallest energy keeping them bound to the metal, where $hf = KE_{max} + W_0$.
- Contradicting the predictions of wave theory and confirming those of photon theory, experiments by Millikan demonstrated that maximum kinetic energy of electrons is unchanged when intensity is increased. Further, an increase of frequency produces a linear increase in the maximum kinetic energy of electrons, such that $KE_{max} = hf - W_0$, and frequencies below the cutoff frequency f_0 do not cause electron release, regardless of intensity.

Photon Interactions; Compton Effect and Pair Production

Further evidence for the photon theory came from the **Compton effect,** which describes the behavior of a photon that has struck an electron at rest.

- The photon's frequency decreases after the collision, and when the final angles are taken into account, the results agree with the conservation laws of momentum and energy. The wavelength of the scattered photon is given by $\lambda' = \lambda + (h/m_0c)[1 - \cos\theta']$, where θ' is the angle between the initial and final directions of the photon and m_0 is the rest mass of the electron.
- There are four ways that photons can interact with matter: 1) the Compton effect; 2) the photoelectric effect; 3) knocking an atomic electron to a higher energy level; and 4) **pair production,** which creates matter in the form of two new particles.

Wave-Particle Duality; The Principle of Complementarity; Wave Nature of Matter

The resolution between the competing particle and wave theories is to accept **wave-particle duality** such that one of the theories—but not both—can explain any observed phenomenon. Both theories are needed for a complete understanding of the behavior of light. Louis de Broglie applied wave-particle duality to matter, believing particles would exhibit properties of waves. The **de Broglie wavelength** of matter is a function of its mass and velocity, such that $\lambda = h/mv$.

Early Models of the Atom

Rutherford's bombardment of a thin gold foil with alpha particles resulted in occasional large-angled deflections, indicating a concentrated positively charged mass in each atom taking up a small portion of its size, as opposed to a homogenous atomic structure. This tiny nucleus has a radius of 10^{-14} m or 10^{-15} m, whereas the atom has a radius of 10^{-10} m.

Atomic Spectra: Key to the Structure of the Atom

The spectra of light produced by excited rarefied gases are discrete, represented by a **line spectrum.** The **emission spectrum** produced by each gas is distinctive.

- The spectrum produced by a hydrogen atom demonstrates groups of line patterns: The **Balmer series** represents the set of lines whose wavelengths are given by $1/\lambda = R(1/2^2 - 1/n^2)$, for $n = 3, 4, \ldots$ where $R = 1.097 \times 10^7\ \text{m}^{-1}$. The **Lyman series** represents the set of lines whose wavelengths are given by $1/\lambda = R(1/1^2 - 1/n^2)$, for $n = 2, 3$. The **Paschen series** is another set of lines whose wavelengths are given by $1/\lambda = R(1/3^2 - 1/n^2)$, for $n = 4, 5, \ldots.$
- These results contradicted the Rutherford model of the atom, which said that atoms should emit a continuous spectrum.

The Bohr Model

Bohr hypothesized that electrons travel in discrete circular orbits, called **stationary states,** and experience only quantized changes in energy.

- An electron emits light as it moves from an orbit of higher energy, E_u, to an orbit of lower energy, E_l, such that the energy of the photon released is given by $hf = E_u - E_l$.
- From the Balmer formula, Bohr derived a relation between electron orbit and energy by first determining the relation between electron orbit and angular momentum known as the **quantum condition,** in which $L = mvr_n = nh/2\pi$ for $n = 1, 2, 3 \ldots$ where r_n is the radius of the nth orbit, and n is called the orbit's **quantum number.** The nth orbital radius is defined as

$$r_n = \frac{n^2h^2}{4\pi^2mkZe^2} = \frac{n^2r_l}{Z},$$

where $r_l = \dfrac{h^2}{4\pi^2mke^2} = 0.529 \times 10^{-10}$ m, called the **Bohr radius.**

- From this, energy levels are defined as

$$E_n = \frac{-2\pi^2Z^2e^4mk^2}{h^2n^2} = \frac{Z^2E_l}{n^2} = \frac{-13.6\ \text{eV}}{n^2}$$

for $n = 1, 2, 3 \ldots . E_1$ is referred the **ground state,** while subsequent iterations of the **energy level** equation are called **excited states.** These energy levels are negative due to the relative assignment of zero for potential energy to show that energy must be added to free an electron. **Binding energy** is the minimum energy necessary for removing an electron from the ground state.

de Broglie's Hypothesis Applied to Atoms

Louis de Broglie proposed that electron orbits are resonant circular standing waves, which were consistent with Bohr's theoretical quantum condition because they allowed for quantized orbits. However, Bohr's theory could not account for the energy levels of atoms beyond hydrogen. A new theory, known as quantum mechanics, was needed to explain the fine structure of emission lines, the differing brightness of spectral lights, or other forms of molecular bonding.

CHAPTER 28

Quantum Mechanics of Atoms

Quantum Mechanics—A New Theory; the Wave Function and Its Interpretation; The Double-Slit Experiment

- **Quantum mechanics** serves to fuse wave-particle duality.
- While classical mechanics is a sufficient approximation for macroscopic phenomenon involving speeds much less than the speed of light, only quantum mechanics can precisely explain atomic phenomenon.
- The amplitude of a matter wave, ψ, is determined from **Schroedinger's wave equation** and is a function of time and position. For a particle, Ψ^2 is the probability of an electron being located at a specific time and position.

The Heisenberg Uncertainty Principle

Quantum mechanics predicts a limit to the accuracy of certain measurements due to the interaction between the phenomena being studied and the process of measuring.

- Because of its necessary interaction with a photon, an electron cannot be observed without changing its momentum, thereby altering its motion and/or position.

- **Heisenberg's uncertainty principle** quantifies the limit to the accuracy of measuring position and momentum in $(\Delta x)(\Delta p) \geq h/2\pi$. Restated in terms of the limit to the accuracy of measuring energy and time, $(\Delta E)(\Delta t) \geq h/2\pi$.

Philosophic Implications; Probability versus Determinism

Quantum mechanics gives probabilistic values for phenomena as opposed to discrete values. Classical mechanics represents the overwhelmingly most probable outcome for larger scale phenomena.

Quantum-Mechanical View of Atoms

Due to their probabilistic location, electrons are thought to approximate a cloud surrounding a nucleus. These clouds are **probability distributions,** not an indication of the paths taken by these electrons.

Quantum Mechanics of the Hydrogen Atom; Quantum Numbers

- As in the Bohr model, energy levels for the hydrogen atom are given by $E_n = -13.6 \text{ eV}/n^2$ for $n = 1, 2, 3 \ldots$, where n is called the **principle quantum number.**
- The magnitude of angular momentum of an electron is quantified in the **orbital quantum number,** l, whose value can consist of integers from 0 to $n - 1$. The **selection rule** states values of l nearly always change by plus or minus one unit following photon emission or absorption.
- The direction of the electron's angular momentum, m_1, is quantified in the **magnetic quantum number,** and it allows for a range of integer values from $-l$ to $+l$.
- The **spin quantum number,** m_s, can have values of $+1/2$ or $-1/2$ to describe the direction of spin angular momentum for an electron.

Complex Atoms; The Exclusion Principle

Energy levels for complex atoms differ from those of hydrogen atoms due to electron interactions. The **atomic number** of an atom, Z, represents the number of protons which equals the number of electrons necessary for a neutral charge. It determines the distinguishing properties of each element. The **Pauli exclusion principle** states that the set of values for n, l, m_l, and m_s cannot be shared by two different electrons, and therefore any quantum state can only be occupied by one electron.

For Additional Review

Correlate the historical debate over light as a wave or particle with the development of the atomic model, and note how these developments interacted.

Multiple-Choice Questions

1. A value for the mass of an electron was derived from
   I. Thompson's cathode ray experiments
   II. Millikan's oil drop experiments
   III. Rutherford's gold foil bombardments

   (A) I only
   (B) II only
   (C) III only
   (D) I and II only
   (E) II and III only

2. What is the peak wavelength of the spectrum produced by an object with a surface temperature of 4637°F?
   (A) 1.02×10^{-6} m
   (B) 2.15×10^{-5} m
   (C) 1.45×10^{-4} m
   (D) 9.10×10^{-2} m
   (E) None of the above

3. According to Planck's quantum hypothesis, which of the following could be the energy of molecular vibrations in a radiating object with a wavelength of λ?
   (A) $4\lambda hc$
   (B) $hc/2\lambda$
   (C) $4hc/\lambda$
   (D) $2\lambda c/h$
   (E) $\lambda hc/2$

4. What is the work function when monochromatic light of frequency 4.5×10^{15} Hz releases the least tightly held electrons from a metal with a maximum kinetic energy of 13.10 eV?
   (A) 1.4 eV
   (B) 5.5 eV
   (C) 13 eV
   (D) 19 eV
   (E) 32 eV

5. What is the de Broglie wavelength of a 0.050 gram projectile fired at 180 m/s?
   (A) 2.4×10^{-24} m
   (B) 2.4×10^{-27} m
   (C) 1.8×10^{-30} m
   (D) 7.4×10^{-32} m
   (E) 7.4×10^{-35} m

6. According to Heisenberg's uncertainty principle, the limit to precision for the product of position and momentum is given by
   (A) 1.06×10^{-34} J·s
   (B) 3.32×10^{-34} J·s
   (C) 6.63×10^{-34} J·s
   (D) 13.4×10^{-34} J·s
   (E) 37.9×10^{-34} J·s

7. The results of Rutherford's gold foil experiment suggested that
   (A) the atom is a homogenized sphere
   (B) nearly all of the mass of an atom is centrally located
   (C) electrons have discrete orbital pathways
   (D) electron orbits are analogous standing waves
   (E) all of the above are true

8. Which of the following is not a possible energy value for an excited state of an electron orbital in the Bohr model of the atom?
   (A) −3.4 eV
   (B) −1.5 eV
   (C) −0.85 eV
   (D) −0.54 eV
   (E) −0.27 eV

9. What is the minimum uncertainty in position of a 0.15 gram object traveling at 20 m/s measured with a precision of 1%?
   (A) 9.11×10^{-23} m
   (B) 2.11×10^{-26} m
   (C) 3.52×10^{-30} m
   (D) 1.06×10^{-34} m
   (E) 3.17×10^{-39} m

10. The Pauli exclusion principle states that the electrons in an atom cannot
    (A) share an identical set of quantum state values
    (B) jump orbital states of more than one unit
    (C) share values of spin quantum number
    (D) simultaneously have up and down spin
    (E) have their locations accurately determined

Free-Response Questions

1. In the hydrogen line spectrum, the set of wavelengths referred to as the Balmer series is modeled by the equation, $1/\lambda = R(1/2^2 - 1/n^2)$ for $n = 3, 4, 5 \ldots$.
   (a) If 656 nm is the largest wavelength of the Balmer series, given by $1/\lambda = R(1/2^2 - 1/n^2)$ for $n = 3, 4, 5 \ldots$, derive a value for the Rydberg constant.

(b) What is the limit to the smallest possible wavelength of the Balmer series?
(c) What part of the spectrum does this range of values span?
(d) How do the lines of the Balmer series contradict the Rutherford model of the atom?

2. Bohr's model of the atom improved on Rutherford's earlier proposition.
   (a) Numerically and theoretically distinguish the ground state and excited states as defined in the Bohr model of the atom.
   (b) State an advantage of the Bohr model over the Rutherford model of the atom.
   (c) State the problems with the Bohr model that led to new atomic models.
   (d) Which aspect of the Bohr model was incorporated into quantum mechanics?

ANSWERS AND EXPLANATIONS

Multiple-Choice Questions

1. **(D) is correct.** A value for the mass of an electron was derived from two experiments. First, Thompson's cathode ray experiments provided the ratio of charge to mass for an electron. Next, Millikan's oil drop experiments determined the charge. Using both expressions, the mass can be derived.
2. **(A) is correct.** After converting to kelvins, Wien's law can be applied, $\lambda_p T = 2.90 \times 10^{-3}$ m·K, so $\lambda_p = 2.90 \times 10^{-3}$ m·K/2831 K $= 1.02 \times 10^{-6}$ m.
3. **(C) is correct.** Planck's quantum hypothesis suggests that values for energy are whole number multiples of the product of frequency and Planck's constant. Frequency is related to wavelength by $f = c/\lambda$. To fit the criteria, $E = nhf = nhc/\lambda$, where n is a whole number.
4. **(B) is correct.** Rearranging the relation $hf = KE_{max} + W_0$,

$$W_0 = hf - KE_{max} = \frac{(6.63 \times 10^{-34}\ \text{J·s})(4.5 \times 10^{15}\ \text{s}^{-1})}{(1.6 \times 10^{-19}\ \text{J/eV})} - 13.1\ \text{eV}$$

$= 18.6$ eV $- 13.1$ eV $= 5.5$ eV to two significant figures.
Note that for the units to match, the value in joules has to be converted to electron volts.

5. **(D) is correct.** The de Broglie wavelength is given by the ratio of Planck's constant to momentum. Here, $\lambda = h/mv$
$= (6.63 \times 10^{-34}\ \text{J·s})/(.000050\ \text{kg})(180\ \text{m/s})$
$= 7.4 \times 10^{-32}$ m to two significant figures.
6. **(A) is correct.** Heisenberg's uncertainty principle relates the limits to determining energy and time or momentum and location as being less than $h/2\pi = 6.63 \times 10^{-34}$ J s$/2\pi = 1.06 \times 10^{-34}$ J·s.
7. **(B) is correct.** Rutherford's experiment showed a wide angle of deflection for some alpha particles directed at a gold foil. This suggested a large positively charged central mass, contradicting the plum pudding model of the atom, (answer *A*). Answers *C* and *D* were later conceptualizations for the atom.

8. (E) is correct. According to the Bohr model, excited states are given by $E_n = -13.6\ \text{eV}/n^2$ for integer values of n greater than 1. Of the values given, only -0.27 eV is not an even square factor of the ground state of -13.6 eV (to two significant figures).

9. (C) is correct. The Heisenberg uncertainty principle states that the product of the uncertainties in measuring position and momentum is greater than $h/2\pi$, so $(\Delta x)(\Delta p) \geq 1.055 \times 10^{-34}$ J·s. The momentum $p = mv = (0.00015\ \text{kg})(20\ \text{m/s}) = 0.003$ kg·m/s, which means
$\Delta p = (0.003\ \text{kg·m/s})(0.01) = (0.00003\ \text{kg m/s})$,
so $\Delta x \geq (1.055 \times 10^{-34}\ \text{J·s})/(0.00003\ \text{kg m/s})$,
so Δx must be greater than or equal to 3.52×10^{-30} m.

10. (A) is correct. Some of the answers provided are true of quantum mechanics (for instance, answer *B* references so called "forbidden transitions"), but only answer A states the Pauli exclusion principle—that identical values for the set of four quantum numbers (principle, orbital, magnetic, spin) cannot be shared by two electrons.

Free-Response Questions

1. (a) As the wavelength of the Balmer series is given by $1/\lambda = R(1/2^2 - 1/n^2)$ for $n = 3, 4, 5 \ldots$, clearly 656 nm (as the largest wavelength) corresponds to $n = 3$, because for this equation the larger n gets, the smaller λ gets. Solving for R and substituting these values,

$$R = \frac{\frac{1}{\lambda}}{\left(\frac{1}{2^2} - \frac{1}{n^2}\right)} = \frac{\frac{1}{656 \times 10^{-9}\ \text{m}}}{\left(\frac{1}{4} - \frac{1}{9}\right)} = 1.098 \times 10^7\ \text{m}^{-1},$$

which is close to the experimental value of $1.097 \times 10^7\ \text{m}^{-1}$.

(b) As n gets larger, the value of $1/n^2$ becomes increasingly smaller. The limit of wavelength would be as the $1/n^2$ approaches 0, such that $1/\lambda = R(1/2^2)$ and $\lambda = 2^2/R = 365 \times 10^{-9}$ m or 365 nm.

(c) Since the range of visible light ranges from 400 nm to 750 nm, 656 would be in the visible range while 365 nm would be in the ultraviolet range.

(d) The lines of the Balmer series are part of the line spectrum given off by a hydrogen atom, whereas the Rutherford model predicts a continuous spectrum.

The relation between values of n and the trends of wavelength are correctly interpreted and utilized for the responses to parts a and b. The value for R is determined in the response to part a, and it is applied in the response to part b to determine a specific wavelength. The response to part c demonstrates an understanding of the electromagnetic spectrum and the different groups determined by wavelength. The response to part d shows an historical understanding of how the Rutherford model failed to account for the hydrogen line spectrum.

2. (a) In the Bohr atom, the ground state represents the lowest energy level for its smallest orbit, whereas the excited states represent the energy levels

associated with larger orbits. The values for energy are given by the equation $E_n = -13.6 \text{ eV}/n^2$, where the ground state corresponds with $n = 1$, and excited states correspond to higher whole number values of n.

(b) The Bohr model successfully explained why atoms emit line spectrum instead of a continuous spectrum.

(c) The Bohr model was not accurate at predicting line spectra for atoms beyond hydrogen.

(d) Quantum mechanics uses the same value of n for energy levels, but it incorporates three other values to define quantum state.

This response follows the development of the Bohr atomic model—from its advantages over Rutherford's earlier model to its failings, which led to the development of quantum mechanics. The response to part a correctly defines the terms for energy levels numerically and in words, which ties in to the response for part d and relates it to quantum mechanics. The responses to parts b and c demonstrate an historical and theoretical perspective on the Bohr model.