Unit 9: Atomic Structure And Quantum Mechanics
The Nature of Light

James Clerk Maxwell: Mathematician

★ Derived the first wave equations describing propagation of light
  • Derived equations for electric and magnetic fields independently
  • Calculations revealed that electric and magnetic fields travel at the same speed through space
  • Maxwell concluded that this could not be a coincidence and considered both together to be “electromagnetic radiation,” the same phenomenon as visible light.
The Nature of Light

Standing waves

★Amplitude: The distance between “zero” magnitude and a crest (“high point”) or trough (“low point”) on a wave

★Wavelength: The distance in space between two crests or two troughs on a wave

★Frequency: How many waves (wavelengths) pass through a point in space per second. Usually expressed in “cycles per second,” s\(^{-1}\) or Hz (Hertz)

Speed of electromagnetic radiation (light) propagating through a vacuum:

\[2.998 \times 10^8 \text{ m s}^{-1}\]
Electric and magnetic fields are orthogonal (perpendicular) to each other and propagating through space on the same axis.
The Nature of Light

The Electromagnetic Spectrum

[Diagram showing the spectrum with various wavelengths and examples of technologies]
The Nature of Light

The Ultraviolet Catastrophe: A problem that can’t be solved using classical physics to describe how hot objects emit light

★ Rayleigh-Jeans Law: “Classical Theory” deriving the spectrum of blackbody radiation based on movement of charged particles. It only works if the object is at a reasonably low temperature

★ At higher temperatures, the light emitted is predicted to approach infinite intensity, which is forbidden by the Law of Conservation of Energy
The Nature of Light
Max Planck (1858-1947, Nobel Prize in Physics 1918)
Quantum Theory

★ Observed blackbody radiation, which is light emitted by hot objects
★ Prevailing theories of the day (based on statistical mechanics and movement of charged particles) could not predict the energy of light emitted by very hot objects (visible and ultraviolet)
★ Planck derived the spectrum of blackbody radiation correctly by rejecting the assumption that light is a continuous spectrum of energies
★ “Light is quantized”: it exists as discrete packets of energy
Planck’s Constant is an empirical “fudge factor” that makes the correct derivation of the blackbody radiation spectrum possible. Effectively, Planck’s constant expresses the size of a “quantum” or packet of electromagnetic radiation at a given frequency.

\[ h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \]

\[ E = h \nu = h \times \frac{c}{\lambda} \]

- **E**: Energy of the “packet”
- **h**: Planck’s Constant
- **\( \nu \)**: Frequency (s\(^{-1}\) or Hz)
- **c**: Speed of Light, m\( \cdot \)s\(^{-1}\)
- **\( \lambda \)**: Wavelength, m
The Nature of Light
Albert Einstein (1879-1955, Nobel Prize in Physics 1921)
The photoelectric effect: light acting as a particle

★ When light shines on a metal, it emits “photoelectrons”
★ Photoelectrons are only emitted if the light is above a certain frequency (below a certain wavelength) so it has enough energy to “bounce” the electrons from the metal
★ The intensity of the light (number of light waves) only controlled how many electrons were emitted, not their kinetic energy
★ Kinetic energy of emitted electrons depended on frequency of the light:

\[ E = h\nu = W + E_k \]

“Work function” or amount of energy to eject electrons from the metal
The Nature of Light

Albert Einstein (1879-1955, Nobel Prize in Physics 1921)
First noteworthy contribution to physics

★ Light waves could act like particles, bouncing electrons off of metals with a measurable kinetic energy related to the energy of the light waves: light waves can act like particles

★ Einstein coined the term “photons” to refer to light “particles”

★ Einstein’s particle/wave “duality” of light is key to quantum physics and quantum chemistry as we know it today
Interaction of Light With Matter

Johannes Rydberg (1884-1919)
Emission spectra of gaseous elements

★Built on the observations of Charles Balmer to predict the “line spectra” of discrete wavelengths of light that gaseous elements emitted when a high voltage passed through them

Empirical derivation of line spectra:

\[ \frac{1}{\lambda} = R_\infty \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \]

Wavelength Emitted

“Rydberg’s constant For heavy atoms”
1.097 x 10^7 m^{-1}

Small empirically derived integers
Interaction of Light With Matter

Niels Bohr (1885-1962, Nobel Prize in Physics 1922)

The Bohr Model of the atom

★ Derived Rydberg’s constant using known physical constants

\[ R_z = \frac{2\pi^2 z^2 m_e e^4}{h^3} \]

- \( R_z \): Rydberg’s constant for an atom with atomic number “z”
- Usually \( z = 1 \) or “hydrogen-like”
- Mass of the electron in kg
- Elementary charge of the electron in coulombs
- Planck’s constant

★ This is significant because it means that emission is related to energy of electrons
Interaction of Light With Matter
Niels Bohr (1885-1962, Nobel Prize in Physics 1922)
The Bohr Model of the atom
(educated guess on the meanings of integer orbits)

★ Electrons “orbit” atoms like planets orbit the sun: physicists of the time accepted the model because it looked “ordered”
★ An electron the is “excited” to a higher orbit emits light at a discrete energy (wavelength) when it falls into an orbit closer to the nucleus
★ The values for “n” now have physical meaning: they are integers representing orbits of electrons, spanning from “1” to infinity.
★ Although not very accurate, the Bohr model is still the picture of the atom found in introductory chemistry classrooms
Modern Quantum Mechanics

Louis de Broglie (1892-1987, Nobel Prize in Physics 1929)

Matter, like energy, can be treated like a wave

★ Built on Einstein’s new Theory of Special Relativity where he derived that energy and mass are equivalent \(E=mc^2\)

★ If energy and mass are equivalent, then the properties of matter can be substituted for light:

\[ E = mc^2 \]

Replace “c” with “u” because matter cannot move at the speed of light

\[ E = mu^2 \]

Substitute in Planck’s Quantum theory

\[ E = h\nu = mu^2 \]

Use the relationship between frequency and wavelength

\[ h\nu = h \times \frac{u}{\lambda} = mu^2 \]

Simplify the equation

\[ hu = mu^2 \lambda \]

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

Matter has a wavelength!
Modern Quantum Mechanics

DeBroglie: Matter, like energy, can be treated like a wave
Implications: Wave mechanics apply to matter

Demonstration:

Sound clip will start in 5 seconds

Constructive Interference
★ When two waves are “in phase,” meaning they are superimposed, their amplitudes add up at all points

Destructive Interference
★ When two waves are “out of phase,” meaning they are not superimposed, their amplitudes cancel when added together because one is the negative of the other.
Modern Quantum Mechanics

Matter, like energy, can be treated like a wave.

Implications: Wave mechanics apply to matter

★ If the electron is considered to be a “wave” of matter, then its “orbit” is analogous to a standing wave wrapped around an atom’s nucleus.

★ If the number of “wavelengths per orbit” is not an integer like 1, 2, 3, etc, then the electron could destructively interfere with itself because it “ends” at a different point from where it “begins” so it’s out of phase with itself.

★ This explains where the integer in the Bohr model comes from: if there aren’t an integral number of wavelengths around the nucleus (controlled by the distance of the orbit from the nucleus) then the electron would destroy itself from interference.
Modern Quantum Mechanics

Erwin Schrödinger (1887-1961, Nobel Prize in Physics 1933)

The Schrödinger equation: wave functions for electrons

★ If the electron is a wave, then it must have a function much like “y = sin(x)” is a simple function for a standing wave

★ Schrödinger’s equation combines mathematical properties of a particle and a wave (using classical and quantum physics) to describe an electron as a mathematical function

\[
\frac{-\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U(x) \psi(x) = E \psi(x)
\]
Modern Quantum Mechanics

Werner Heisenberg (1901-1976, Nobel Prize in Physics 1932)

Heisenberg’s Uncertainty Principle

★ You can’t find both the exact position and momentum of an electron
★ Deriving the functions describing position and momentum of an electron introduces a certain degree of uncertainty in “where they are” dictated by the mathematical properties of the functions. The math derives to:

\[ \Delta x \Delta p \geq \frac{\hbar}{4\pi} \]

★ An electron as a “wave function” can only be located with a limited amount of certainty as to where it “probably is.”
Electronic Structure of the Hydrogen Atom

Quantum numbers: variables plugged into 3-D wave functions that describe energy and location properties of electrons to describe where they “are”

★ Principal quantum number (n): how far from the nucleus the electron is, or “which shell” (think “Bohr model). Possible values are theoretically 1 to infinity but really **1 to 7**

★ Angular momentum quantum number (l): how much angular (“orbiting”) momentum the electron has as it “orbits” the nucleus. **Values range from 0 to n-1**

★ Magnetic quantum number (ml): several electrons can have the same principle and angular momentum quantum numbers. The magnetic quantum number specifies which of the possible positions the electron occupies. **Values range from -l to +l**

★ Spin quantum number (ms): describes the orientation of the electron’s magnetic field from its “intrinsic angular momentum” which is usually referred to as “spin.” **Values are +1/2 and -1/2**
Electronic Structure of the Hydrogen Atom

Wolfgang Pauli (1900-1958, Nobel Prize in Physics 1945)

The Pauli Exclusion Principle

★ If electrons are described by wave functions, then no two electrons on the same atom can have the same set of four quantum numbers; otherwise, they have the same wave function and they will interfere with each other
Electronic Structure of the Hydrogen Atom

Plugging quantum numbers into wave functions: what does it all mean?

★ Atomic orbitals: regions where there is a 90% chance of finding an electron, based on its quantum numbers

★ Squaring a wave function and graphing its solution results in a 3-D “probability surface” describing where there’s a 90% chance of finding an electron. The surface is called an atomic orbital.
Quantum Mechanics and the Periodic Table

Plugging quantum numbers into wave functions to find electrons: what does it all mean? (Look at the periodic table)

★“s” orbitals have \( l=0 \), so the only possible value for \( m_l \) is 0. That means in a period there can only be one “s” orbital holding two electrons; one with \( m_s=+\frac{1}{2} \) and one with \( m_s=-\frac{1}{2} \)
Plugging quantum numbers into wave functions: what does it all mean? (Look at the periodic table)

★“p” orbitals have \( l = 1 \), so \( m_l \) could be \{-1,0,1\} meaning there are three p orbitals in each period that has them. Each could hold two electrons for a total of six in each p subshell.

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Quantum Mechanics and the Periodic Table

Columbus State Community College

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Plugging quantum numbers into wave functions: what does it all mean? (Look at the periodic table)

“d” orbitals have l=2, so $m_l$ could be $\{-2,-1,0,1,2\}$ meaning there are five d orbitals in each period that has them. Each could hold two electrons for a total of 10.
Plugging quantum numbers into wave functions: what does it all mean? (Look at the periodic table)

★“f” orbitals have l=3, so \( m_l \) could be \{-3,-2,-1,0,1,2,3\} meaning there are seven f orbitals in each period that has them. Each could hold two electrons for a total for 14.
Quantum Mechanics and the Periodic Table

Behavior of electrons in a multi-electron atom

★ If there is only one electron, then all of the orbitals in a shell are degenerate (the same in energy) and its energy can be determined by the Rydberg equation.

★ In multi-electron atoms, electrons in different orbitals shield each other from nuclear charge, so different orbitals penetrate further in toward the nucleus.

★ Example: “s” orbitals with l=0 are lower in energy than “p” orbitals with l=1 in the same shell because they penetrate more toward the nucleus and shield the p orbitals, allowing the “p” electrons to be further from the nucleus and thus higher in energy.
Quantum Mechanics and the Periodic Table

Building atoms electron by electron: the aufbau principle

- Build atoms by assigning each electron an “address” related to its quantum numbers
- Locations of an atom’s electrons are expressed as an electron configuration for the atom
- Atoms with similar electron configurations have similar chemical properties

Example: Neon has 10 electrons

Ne: $1s^2 \ 2s^2 \ 2p^6$
Quantum Mechanics and the Periodic Table

Building atoms electron by electron: the aufbau principle

Electron configurations are built electron by electron, by moving across each period of the periodic table. Use the periodic table as a guide and count your way across the four blocks:

Examples:

Carbon (C) \( z=6 \)
\[ 1s^22s^22p^2 \]

Iron (Fe) \( z=26 \)
\[ 1s^22s^22p^63s^23p^64s^23d^6 \]

Wait, what?
Quantum Mechanics and the Periodic Table

Shielding and penetration: “Principal quantum number” is not the same as “period”

★ “d” orbitals are very large, and “f” are even larger than d (“larger” meaning “extending farther out”)
★ This means that smaller orbitals the next shell out are sometimes more penetrating (lower energy) than larger orbitals in the previous shell.

★ Example: the electrons appear in the order $6s^24f^{14}5d^{10}6p^6$ in the sixth period because $d$ and $f$ orbitals in lower shells extend far out and thus have higher energy.
Quantum Mechanics and the Periodic Table

Recap: full electron configuration example for a very heavy atom

Pb: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s\(^2\) 3d\(^{10}\) 4p\(^6\) 5s\(^2\) 4d\(^{10}\) 5p\(^6\) 6s\(^2\) 4f\(^{14}\) 5d\(^{10}\) 6p\(^2\)

“Full” configurations can be very long, tedious, and contain information that’s not needed. Abbreviating is usually more appropriate.
Quantum Mechanics and the Periodic Table

Abbreviating electron configurations by only listing valence electrons

Pb: \([\text{Xe}]6s^24f^{14}5d^{10}6p^2\)

These electrons are the Xe “core” of Pb and don’t affect its chemical behavior. They can be called “Xe”

Only the “valence” electrons need to be listed explicitly. The core is just “Xe”
Quantum Mechanics and the Periodic Table

How to make cations by removing electrons

Pb^{2+}: [Xe]6s^2 4f^{14} 5d^{10} 6p^2

Pb^{4+}: [Xe]6s^2 4f^{14} 5d^{10} 6p^2

★ A period’s p electrons are always easiest to remove because they are the highest in energy
★ A period’s s electrons are second easiest because they are in a higher shell than the d electrons
★ A period’s d electrons are always the last to go because they’re in a lower shell (and a filled d subshell)
Quantum Mechanics and the Periodic Table

Orbital diagrams: showing how a subshell fills with electrons

Filled s subshell

Filled p subshell

Filled d subshell

Filled f subshell
Quantum Mechanics and the Periodic Table

Order of filling a subshell with electrons:
Using Hund’s rule and the Pauli Exclusion Principle

Oxygen: \([\text{He}]2s^22p^4\)

Not possible:
Violates Pauli Exclusion Principle

Possible but not ground state:
Not following Hund’s Rule

Ground State:
Place one electron in each orbital before pairing
Anomalous Electron Configurations

Electron configurations aren’t always predictable: things to remember

1) Shells get closer to each other as they are added to the outside of atoms. As a result, they “blur” together, causing some of the penetration and shielding effects that make subshells from lower shells poke through subshells from higher shells.

2) Symmetrically filled subshells (half-filled or full) are particularly stable. These anomalies are common on the periodic table:
   - An electron from the s subshell in the nth shell moves into the d subshell in the (n-1) shell to make a “d⁴” configuration “d⁵” or to make a “d⁹” configuration “d¹⁰”.
   - An electron in the f subshell in the nth shell moves into the d subshell in the (n-1) shell to make a “d⁸” configuration “d⁷”.
   - The nd subshell takes one electron before the (n-1)f subshell begins to populate because they are nearly identical in energy.