Unit 2: Atomic Structure
(Estimated instructional time: 6 hours)

Atoms are the fundamental building blocks of matter. Understanding their internal structure, the arrangement of electrons, and the experimental evidence that led to modern atomic theory is crucial for all branches of chemistry and physics. In this chapter, we will examine in depth:

1. **Subatomic particles and isotopes**
2. **Electron configurations and energy levels**
3. **Spectroscopic evidence for atomic models**

Each section will develop concepts step by step, providing thorough explanations, illustrative examples, and ample detail to ensure a deep grasp of the material. No external links or references are included; all content is self-contained.

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1. Subatomic Particles and Isotopes

1.1 Historical Context: From Indivisible Atoms to Subatomic Particles

- **Ancient “Atomos”**
    - **Democritus (circa fifth century BCE) proposed that all matter consisted of tiny, indivisible particles called “atomos” (meaning “uncuttable”). Although insightful, this idea lacked experimental support at the time.**
- **Dalton’s Atomic Theory (Early 1800s)**
    - **John Dalton formulated the first scientifically based atomic theory:**
        - **Each element is composed of tiny, indivisible particles called atoms.**
        - **All atoms of a given element are identical in mass and properties; atoms of different elements differ.**
        - **Atoms cannot be created, divided, or destroyed in chemical processes.**

        - **Atoms combine in simple whole-number ratios to form compounds.**
        - **In reactions, atoms are rearranged, separated, or combined, but their identities do not change.**
    - **Dalton's theory explained conservation of mass and simple stoichiometry, but did not yet know about the internal structure of atoms.**
- **Discovery of Electrons (1897)**
    - **J. J. Thomson's cathode-ray experiments demonstrated that cathode rays were streams of negatively charged particles—later named electrons.**
    - **He measured the ratio of charge to mass (e/m) of the electron and showed that atoms were divisible and contained smaller charged components.**
- **Discovery of the Nucleus (1911)**
    - **Ernest Rutherford's gold foil experiment involved firing alpha particles (positively charged helium nuclei) at a thin sheet of gold foil.**
        - **Most alpha particles passed straight through.**
        - **A small fraction were deflected at large angles, and a very few bounced directly back.**
    - **Rutherford concluded that the positive charge and most of the mass of an atom are concentrated in a tiny, dense nucleus; electrons occupy the relatively vast empty space around that nucleus.**
- **Discovery of Neutrons (1932)**
    - **James Chadwick bombarded beryllium with alpha particles and detected neutral radiation.**
    - **He demonstrated the existence of a neutral particle nearly equal in mass to the proton, which he named the neutron.**

By 1932, the modern picture of an atom—protons and neutrons in a dense nucleus with electrons arranged around it—was firmly established.

1.2 Subatomic Particles: Protons, Neutrons, and Electrons

Every atom is made up of three principal types of subatomic particles:

1. Proton
    - Charge: +1 elementary charge (that is +1.602 × 10^(-19) coulombs).
    - Mass: 1.6726 × 10^(-27) kilograms (about 1.0073 mass-units, where one mass-unit is defined as one-twelfth the mass of a carbon-12 atom).
    - Location: Inside the nucleus.
    - Role: Determines the positive charge of the nucleus; the number of protons (called the atomic number, Z) defines which element an atom is.
2. Neutron
    - Charge: zero (electrically neutral).
    - Mass: 1.6749 × 10^(-27) kilograms (about 1.0087 mass-units).
    - Location: Inside the nucleus, alongside protons.
    - Role: Contributes to the mass of the atom and provides stability by offsetting electrostatic repulsion between protons. Variations in neutron number give rise to different isotopes of the same element.
3. Electron
    - Charge: –1 elementary charge (that is –1.602 × 10^(-19) coulombs).
    - Mass: 9.109 × 10^(-31) kilograms (about 0.0005486 mass-units).
    - Location: Distributed around the nucleus in regions of high probability called orbitals (as defined by quantum mechanics).
    - Role: Participate in chemical bonding, determine chemical properties, and occupy quantized energy levels around the nucleus.

1.2.1 Relative Masses and Charges

Particle	Symbol	Charge (in elementary units)	Charge (coulombs)	Mass (kilograms)	Mass (mass-units)
Proton	p	+1	+1.602 × 10^(-19) C	1.6726 × 10^(-27) kg	1.0073

Neutron	n	0	0	1.6749 × 10^(-27) kg	1.0087
Electron	e–	–1	–1.602 × 10^(-19) C	9.109 × 10^(-31) kg	0.0005486

Because one mass-unit is defined as one-twelfth the mass of a carbon-12 atom, both protons and neutrons are very close to one mass-unit. The electron is about one-one-thousand eight-hundred thirty-sixth the mass of a proton. That means almost all of an atom's mass is in its nucleus.

1.2.2 Nuclear Composition and Notation

An atomic nucleus is described by:

- Atomic number (Z): the number of protons.
- Mass number (A): the total number of protons plus neutrons (so A = Z + N, where N is the number of neutrons).

We write an isotope with the notation:

A
Ž X

where X is the chemical symbol, A is the mass number (protons plus neutrons), and Z is the atomic number (number of protons). For example:

- Carbon with 6 protons and 6 neutrons is written as
  12
  6 C
  This is called carbon-12 (A = 12, Z = 6).
- Uranium with 92 protons and 146 neutrons is written as
  238
  92 U
  This is uranium-238 (A = 238, Z = 92).

Often in tables the atomic number Z is omitted if the element symbol X already tells us Z. So people simply write "^12C" for carbon-12. When writing an isotope, if the element's name or symbol already implies Z, you may see just the superscript A, as in "^14N" or "^64Zn."

1.3 Isotopes

1.3.1 Definition and General Properties

- **Isotopes are atoms of the same element (same number of protons, so same Z) that differ in mass number A because of different numbers of neutrons.**
    - **Example: Carbon has three naturally occurring isotopes:**
        - **Carbon-12 (6 protons, 6 neutrons)**
        - **Carbon-13 (6 protons, 7 neutrons)**
        - **Carbon-14 (6 protons, 8 neutrons; this one is radioactive).**
- **Chemical Properties**
    - **All isotopes of an element have nearly identical chemical behavior because chemistry depends on electron arrangement, which depends on the number of protons (Z).**
    - **Small differences in reaction rates can occur when hydrogen is replaced by its heavier isotope (deuterium or tritium) because the vibrational frequencies of bonds change with mass. This is called a kinetic isotope effect.**
- **Physical Properties**
    - **Physical properties such as density, rates of diffusion, and vibrational spectra differ slightly from isotope to isotope because of the change in mass.**
    - **Some isotopes are stable; others are radioactive and decay over time, emitting radiation.**

1.3.2 Relative Atomic Mass (Atomic Weight)

- **Definition: The relative atomic mass of an element is the weighted average of the masses of its naturally occurring isotopes, weighted by their percent abundances. To calculate it, multiply each isotope's mass by its fraction of natural abundance, then add all those products.**

  For example, chlorine consists mostly of two stable isotopes:

    - **Chlorine-35, with a mass of 34.9688527 mass-units and an abundance of 75.78%.**

    - **Chlorine-37, with a mass of 36.9659026 mass-units and an abundance of 24.22%.**

- **To calculate chlorine's atomic weight:**

    - **Convert percentages to fractions (75.78% = 0.7578; 24.22% = 0.2422).**

    - **Multiply each isotope's mass by its fraction:**
      • For chlorine-35: 0.7578 × 34.9688527 = 26.5073 (mass-units)
      • For chlorine-37: 0.2422 × 36.9659026 = 8.9458 (mass-units)

    - **Add them: 26.5073 + 8.9458 = 35.4531 (mass-units).**

- **Therefore, the average atomic mass of chlorine is about 35.45 mass-units, which is why periodic tables list chlorine's atomic weight as 35.45.**

- **Mass Spectrometry**

    - **A technique that separates isotopes based on their mass-to-charge ratio (m/z).**

    - **Atoms or molecules are ionized, accelerated through electromagnetic fields, and deflected based on their mass-to-charge ratio. The deflection pattern shows the different isotopes and their relative abundances.**

    - **Mass spectrometry provides precise values for atomic masses and isotopic abundances.**

1.3.3 Nuclear Stability and Isotopic Distribution

- **Stable vs. Radioactive Isotopes**

    - **Stable isotopes do not undergo spontaneous nuclear decay.**

    - **Radioactive isotopes (also called radioisotopes) have unstable nuclei. They emit radiation—alpha particles, beta particles, or gamma rays—to reach a more stable configuration.**

- **For example:**

    - **Carbon-12 and carbon-13 are stable.**

    - **Carbon-14 is radioactive, with a half-life of about 5,730 years. It decays by beta emission into nitrogen-14.**

- **Neutron-to-Proton Ratio (N/Z)**

  - For light elements (up to about atomic number 20), stability usually means the number of neutrons N is roughly equal to the number of protons Z.
  - For heavier elements, more neutrons than protons are needed to offset the greater electrostatic repulsion between protons. In other words, N/Z increases as Z increases for stability.
  - A chart of N versus Z shows a "band of stability." If an isotope lies outside that band it is typically radioactive:
    - Too few neutrons (low N/Z) → the nucleus is proton-rich; it may emit a positron (beta-plus decay) or undergo electron capture to turn a proton into a neutron.
    - Too many neutrons (high N/Z) → the nucleus is neutron-rich; it may undergo beta-minus decay to turn a neutron into a proton.
- Applications of Specific Isotopes
  - Radiometric Dating (Geochronology):
    - Carbon-14 dating for organic materials up to about 50,000 years old.
    - Uranium-238 dating (half-life 4.468 billion years) for geological formations and rocks.
  - Medical Diagnostics and Therapy:
    - Technetium-99m (a metastable isotope of technetium) is used in imaging (SPECT scans).
    - Iodine-131 is used in diagnosing and treating thyroid conditions.
  - Tracer Studies:
    - Deuterium (hydrogen-2) and tritium (hydrogen-3) are used to trace chemical and biological pathways.
    - Radioactive tracers help track movement of substances in the environment.

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2. Electron Configurations and Energy Levels

The arrangement of electrons in quantized energy levels around the nucleus determines an atom's chemical behavior. In this section, we develop the concept of energy levels, sublevels, and detailed electron configuration notation—essential for understanding periodic trends, bonding, and reactivity.

2.1 Early Atomic Models: From Bohr to the Quantum Mechanical Model

2.1.1 Rutherford’s Nuclear Model (Post-1911)

- Rutherford’s experiments proved that:
  • An atom’s positive charge and most of its mass are concentrated in a small, dense nucleus.
  • Electrons move around this nucleus in otherwise empty space.

- Limitation: According to classical physics, an accelerating charged particle (like an electron in circular orbit) should continuously emit radiation, lose energy, and spiral into the nucleus. Yet atoms are stable; electrons do not collapse into the nucleus.

2.1.2 Bohr Model (1913)

Niels Bohr proposed a semi-classical model for the hydrogen atom (and other hydrogen-like ions) that successfully explained the stability of atoms and the discrete line spectrum of hydrogen:

1. Quantized Orbits: Electrons orbit the nucleus in circular orbits but do not emit radiation while in those orbits. Each allowed orbit corresponds to a fixed energy level “E sub n” (for n = 1, 2, 3, …).

2. Angular Momentum Quantization: Only orbits in which the electron’s angular momentum is an integer multiple of the reduced Planck constant (denoted “h-bar”) are allowed. That is, m × v × r = n × h-bar, where:

   - m is the electron’s mass (9.109 × 10^(–31) kg).

   - v is the electron’s speed in that orbit.

   - r is the orbit’s radius.

   - n is a positive integer called the principal quantum number.

   - h-bar is Planck’s constant divided by 2π (approximately 1.0546 × 10^(–34) joule-seconds).

3. Energy of the n-th Level: For hydrogen (nucleus charge +1), the energy of an electron in the n-th orbit equals
   –(13.6 electron-volts) divided by n squared. In general, for a nucleus of charge +Z (Z protons), the energy is –(13.6 electron-volts times Z squared) divided by n squared. The negative sign indicates that the electron is bound to the nucleus; as n approaches infinity, the energy approaches zero (meaning the electron is effectively free or ionized).

4. Photon Emission or Absorption: When the electron jumps from a higher level (n_i) to a lower level (n_f), it emits a photon whose energy equals the difference

between the two levels:
Energy of photon = E□$_i$ – E□_f.
Conversely, if the electron absorbs a photon whose energy matches that difference, it can jump from a lower level to a higher one.

5. Limitations of the Bohr Model:
   • It accurately predicts hydrogen-like spectra (one-electron systems such as H, He^+, Li^{2+}), but fails for multi-electron atoms.
   • It cannot explain fine structure (small splittings in spectral lines) or the effect of external fields (Zeeman or Stark effects).
   • It does not incorporate the electron's intrinsic spin.

2.1.3 Quantum Mechanical Model (Wave Mechanics)

Building on De Broglie's matter waves and Schrödinger's wave equation, the modern quantum mechanical model replaces fixed circular orbits with three-dimensional probability distributions known as orbitals:

1. De Broglie Hypothesis (1924)
   - A particle of mass m moving at speed v can be described as a wave with wavelength lambda = Planck's constant divided by (m × v).
   - Applying this to electrons implies that allowed orbitals correspond to standing waves around the nucleus.
2. Schrödinger Equation (1926)
   - The time-independent form for a single electron in a central electric potential V(r) is:
     –(h-bar squared over two times electron mass) times the Laplacian of the wavefunction psi(r, θ, φ) plus V(r) times psi(r, θ, φ) equals E times psi(r, θ, φ), where E is the energy of that electron.
   - For hydrogen-like atoms, V(r) equals –(Z × e squared) divided by (4 π × vacuum permittivity × r). Solving this equation yields quantized energies that agree with Bohr's results for energy levels, and also defines three quantum numbers:
     • Principal quantum number n (n = 1, 2, 3, …).
     • Azimuthal (angular momentum) quantum number ℓ (ℓ = 0, 1, …, n–1).
     • Magnetic quantum number m_ℓ (m_ℓ = −ℓ, −ℓ+1, …, +ℓ).
3. Spin Quantum Number
   - Discovered by Goudsmit and Uhlenbeck in 1925: electrons have intrinsic angular momentum called spin, denoted s = 1/2.

    - Associated with the spin magnetic quantum number m_s, which can be +1/2 or −1/2.

4. Atomic Orbitals and Probability Densities
    - Each allowed set of quantum numbers (n, ℓ, m_ℓ) defines an orbital with a characteristic shape and energy (for hydrogen-like atoms, energy depends only on n; for multi-electron atoms, energy depends on both n and ℓ).
    - The wavefunction psi(r, θ, φ) has a square magnitude $|psi|^2$ that gives the probability density of finding the electron at each point in space.
    - The radial part of $|psi|^2$ gives how likely the electron is to be at a certain distance from the nucleus, and the angular part gives the shape (s orbitals are spherical; p orbitals look like dumbbells; d orbitals look like cloverleafs; f orbitals are more complex).

Key Insight: The quantum mechanical model shows that electrons are not tiny planets circling the nucleus; instead, each electron occupies an orbital—a region in which there is a certain probability of finding it. The allowed energy levels are quantized, and each energy level can have one or more orbitals associated with it.

2.2 Principal Energy Levels, Sublevels, and Orbitals

In a multielectron atom, electrons occupy energy levels (shells) and sublevels (subshells), filling from lowest energy upward. Each electron is uniquely described by the four quantum numbers (n, ℓ, m_ℓ, m_s).

2.2.1 Principal Quantum Number (n)

- Indicates the main energy level or “shell” of the electron, roughly correlating with the average distance of the electron from the nucleus.
- Allowed values: n = 1, 2, 3, ….
- As n increases, the orbital’s average radius and energy both increase.

2.2.2 Azimuthal (Angular Momentum) Quantum Number (ℓ)

- Defines the subshell and orbital shape.
- ℓ can be any integer from 0 to n−1.

- The letter designations are:
  - ℓ = 0 → s subshell (spherical)
  - ℓ = 1 → p subshell (dumbbell-shaped)
  - ℓ = 2 → d subshell (cloverleaf or complex shapes)
  - ℓ = 3 → f subshell (even more complex shapes)
  - For ℓ ≥ 4, one would use g, h, etc., but elements up to atomic number 118 fill only up to f orbitals.

- Number of orbitals in each subshell:
  - s (ℓ = 0): 2ℓ + 1 = 1 orbital
  - p (ℓ = 1): 2ℓ + 1 = 3 orbitals
  - d (ℓ = 2): 2ℓ + 1 = 5 orbitals
  - f (ℓ = 3): 2ℓ + 1 = 7 orbitals

Each orbital can hold up to two electrons (with opposite spins).

2.2.3 Magnetic Quantum Number (m_ℓ)

- Specifies the orientation of the orbital in space.

- For a given ℓ, m_ℓ can be any integer from –ℓ up to +ℓ.
  - For s (ℓ = 0): m_ℓ can only be 0 (one orientation).
  - For p (ℓ = 1): m_ℓ can be –1, 0, or +1 (three orientations, often labeled p_x, p_y, p_z).
  - For d (ℓ = 2): m_ℓ can be –2, –1, 0, +1, +2 (five orientations).
  - For f (ℓ = 3): m_ℓ can be –3, –2, –1, 0, +1, +2, +3 (seven orientations).

2.2.4 Spin Quantum Number (m_s)

- Specifies the direction of the electron's intrinsic spin.

- Allowed values: +½ (spin up) or –½ (spin down).

- Pauli Exclusion Principle: No two electrons in the same atom can have identical sets of all four quantum numbers (n, ℓ, m_ℓ, m_s). Thus, each orbital can hold at most two electrons, and those two must have opposite spins.

2.3 Aufbau Principle, Pauli Exclusion Principle, and Hund's Rule

When building the ground-state (lowest-energy) electron configuration of an atom:

1. Aufbau Principle ("Building Up")

    - **Electrons occupy the lowest-energy orbitals available before filling higher-energy ones.**

    - **The typical order of orbital energies (for many-electron atoms) is as follows:**
      1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, …

    - **Notice that 4s is filled before 3d because 4s is slightly lower in energy than 3d for neutral atoms. However, once electrons occupy 3d, the energy ordering can shift.**

2. **Pauli Exclusion Principle**

    - **Each orbital can hold at most two electrons, and those two must have opposite spins. In other words, no two electrons in an atom can simultaneously have the same four quantum numbers (n, ℓ, m_ℓ, and m_s).**

3. **Hund's Rule of Maximum Multiplicity**

    - **When electrons occupy a set of degenerate orbitals (orbitals of exactly the same energy, such as the three 2p orbitals), they fill each orbital singly first, all with parallel spins (same m_s), before any orbital gets a second electron. This arrangement minimizes electron-electron repulsion and leads to a lower total energy for the atom.**

Example: Carbon (Z = 6)

- **Carbon has 6 electrons to place.**

- **Fill in order:**

    1. **1s can hold 2 electrons → $1s^2$.**

    2. **2s can hold 2 electrons → $2s^2$.**

    3. **2p can hold up to 6 electrons, but only 2 remain to place: by Hund's rule, one goes into each of two different 2p orbitals, with parallel spins.**

- **So carbon's ground-state configuration is written as $1s^2\ 2s^2\ 2p^2$. In an orbital diagram, the three 2p orbitals would each be drawn as a separate line, with one upward arrow in two of them and none in the third.**

2.4 Writing Electron Configurations

2.4.1 Standard Notation

- **We write orbitals in order of increasing energy, indicating how many electrons occupy each subshell with a superscript. For example:**
  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ …
- **Each superscript reflects the number of electrons in that subshell.**

Examples:

- **Hydrogen (Z = 1): $1s^1$**
- **Helium (Z = 2): $1s^2$**
- **Oxygen (Z = 8): $1s^2\ 2s^2\ 2p^4$**
- **Neon (Z = 10): $1s^2\ 2s^2\ 2p^6$**
- **Sodium (Z = 11): $1s^2\ 2s^2\ 2p^6\ 3s^1$**
- **Argon (Z = 18): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$**

2.4.2 Noble Gas Core Notation

- **For elements with higher atomic numbers, writing out every occupied subshell from 1s upward becomes lengthy. Instead, we use the configuration of the preceding noble gas in brackets, then list only the additional orbitals. For example:**
  • Chlorine (Z = 17) has the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. Since $1s^2\ 2s^2\ 2p^6$ is the same as neon (Ne), we write chlorine as [Ne] $3s^2\ 3p^5$.
  • Iron (Z = 26) would be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$, but since $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ is argon (Ar), we write iron as [Ar] $4s^2\ 3d^6$.
  • Copper (Z = 29) actually has a slight exception (see below), but naively one would write [Ar] $4s^2\ 3d^9$.

Note on Exceptions:
• Transition metals sometimes deviate from the naïve filling order because the energy difference between an ns orbital (for example, 4s) and a (n–1)d orbital (for example, 3d) is very small. A filled d subshell (d^{10}) or a half-filled d subshell (d^5) is unusually stable. This can cause one electron to move from the ns orbital into the (n–1)d orbital.
• For example, chromium (Z = 24) would be expected to be [Ar] $4s^2\ 3d^4$, but actually it is [Ar] $4s^1\ 3d^5$, because having a half-filled 3d subshell plus one electron in 4s is more stable.
• Similarly, copper (Z = 29) is not [Ar] $4s^2\ 3d^9$ but rather [Ar] $4s^1\ 3d^{10}$—one 4s electron has moved into 3d, giving a completely filled 3d subshell.

2.5 Energy Level Diagrams and Orbital Filling Order

2.5.1 Aufbau Order Diagram

A handy way to remember the order in which orbitals are filled is to draw a diagonal (Madelung) diagram:

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```
   1s
    2s    2p
    3s    3p    3d
    4s    4p    4d    4f
    5s    5p    5d    5f    5g
    6s    6p    6d    6f    6g    6h
```

Then draw diagonal arrows from top right to bottom left. Following each arrow shows the sequence:

1s → 2s → 2p → 3s → 3p → 4s → 3d → 4p → 5s → 4d → 5p → 6s → 4f → 5d → 6p → 7s → … and so on.

2.5.2 Relative Energies of Orbitals

- Within a given principal quantum number n, the energy of subshells generally goes s < p < d < f.

- However, because of the way electron penetration (how close the electron's probability cloud comes to the nucleus) and shielding (how inner electrons block nuclear charge) work, an orbital with a higher n but lower ℓ (for example, 4s) can be lower in energy than an orbital with a lower n but higher ℓ (for example, 3d) for neutral atoms.

2.5.3 Writing Energy Level Diagrams

- On paper, you draw each subshell as a horizontal line, label it with its orbital notation (for example, 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, …).

- Then you write small upward (↑) and downward (↓) arrows on each line to represent the electrons, filling from lowest to highest energy, and obeying Pauli's exclusion (max two arrows per line, one up and one down) and Hund's rule (in degenerate lines, put one up arrow in each before pairing them).

Example: Iron (Z = 26)

1. The Aufbau sequence up to 26 electrons is:
   1s → 2s → 2p → 3s → 3p → 4s → 3d → 4p → …

2. Place electrons one by one:
   - $1s^2$ (2 electrons)
   - $2s^2$ (2 more; total 4)
   - $2p^6$ (6 more; total 10)
   - $3s^2$ (2 more; total 12)
   - $3p^6$ (6 more; total 18)
   - $4s^2$ (2 more; total 20)
   - $3d^6$ (6 more; total 26)

3. The resulting electron configuration is [Ar] $4s^2\ 3d^6$.

In an orbital-diagram form, you would draw lines for each subshell:

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```
4p  |
3d  | ↑↓  ↑↓  ↑↓  ↑   ↑    (six electrons; five orbitals, so four are unpaired until pairing begins)
4s  | ↑↓
3p  | ↑↓  ↑↓  ↑↓
3s  | ↑↓
2p  | ↑↓  ↑↓  ↑↓
2s  | ↑↓
1s  | ↑↓
```

2.6 Quantum Numbers and Orbital Shapes

2.6.1 Principal Quantum Number (n) and Energy Levels

- For hydrogen-like (one-electron) atoms, the energy of each level depends only on n. In multi-electron atoms, the energy depends on both n and ℓ because of electron–electron repulsions.

- The maximum number of electrons that can fit in the nth shell is $2n^2$:
  - n = 1 → 2 electrons
  - n = 2 → 8 electrons
  - n = 3 → 18 electrons
  - n = 4 → 32 electrons, and so on.

2.6.2 Subshells, Orbital Shapes, and Radial Distribution

- **s Orbitals ($\ell = 0$)**
  - **Spherical shape. No angular nodes (region where probability is zero due to angular part).**
  - **For 1s, the highest probability of finding the electron (the peak in the radial probability distribution) is at one Bohr radius from the nucleus (1 Bohr radius ≈ 0.529 angstroms).**
  - **The number of radial nodes (spherical shells where probability is zero) equals $n - 1$. For 1s, there are 0 radial nodes; for 2s, 1 radial node; for 3s, 2 radial nodes; etc.**
- **p Orbitals ($\ell = 1$)**
  - **Dumbbell shape, with two lobes separated by a nodal plane passing through the nucleus.**
  - **Three orientations: p_x, p_y, p_z (corresponding to $m_\ell = -1, 0, +1$).**
  - **Number of radial nodes equals $n - 2$. For 2p, there are 0 radial nodes; for 3p, 1 radial node; etc.**
- **d Orbitals ($\ell = 2$)**
  - **Four of them look like a cloverleaf (four lobes), and one (the d_{z^2} orbital) looks like a dumbbell with a donut-shaped ring around the middle.**
  - **Five orientations: $m_\ell = -2, -1, 0, +1, +2$.**
  - **Number of radial nodes equals $n - 3$.**
- **f Orbitals ($\ell = 3$)**
  - **Even more complex lobed shapes; seven orientations ($m_\ell = -3, -2, -1, 0, +1, +2, +3$).**
  - **Number of radial nodes equals $n - 4$.**

Bohr Radius (a_0)
Defined as the most probable distance of the 1s electron from the nucleus in a hydrogen atom, equal to about 0.529×10^{-10} meters.

2.7 Effective Nuclear Charge and Shielding

2.7.1 Shielding (Screening) Effect

- **Inner electrons partially block (or shield) the positive nuclear charge from outer electrons.**
- **An outer electron does not feel the full nuclear charge Z; instead, it feels an effective nuclear charge, Z_eff, which is less than Z.**

2.7.2 Slater's Rules for Estimating Z_eff

To estimate the effective nuclear charge felt by a certain electron, you can use Slater's empirical rules:

1. **Write the electron configuration in order of orbital groups:**
   (1s); (2s, 2p); (3s, 3p); (3d); (4s, 4p); (4d); (4f); (5s, 5p); and so on.
2. **For the electron of interest (call it the "target electron"):**
   - **Electrons in higher principal shells (larger n) or the same shell but a higher subshell (same n but higher ℓ) do not shield at all (contribution = 0).**
   - **Electrons in the same group (same n and same ℓ) each contribute 0.35 to the shielding, except when the group is 1s, in which case the other 1s electron contributes 0.30.**
   - **Electrons in the n–1 shell (one shell inward) each contribute 0.85 to shielding.**
   - **Electrons two or more shells inward (n–2, n–3, etc.) each contribute 1.00 to shielding.**
   - **For d and f electrons:**
     • Electrons in the same group (for example, both in 3d) each contribute 0.35.
     • Electrons in any lower shell (n–1, n–2, etc.) each contribute 1.00.
3. **Sum all the shielding contributions from other electrons; call that total S. Then Z_eff ≈ Z – S.**

Example: Sodium (Z = 11), estimate Z_eff for the 3s electron

- **Sodium's electron configuration: ($1s^2$) ($2s^2$ $2p^6$) ($3s^1$).**

- **The target electron is the single 3s electron.**
- **Electrons in the same shell and subshell: there are none, because there is only one electron in 3s.**
- **Electrons in shell n–1 = 2 (that is, the 2s and 2p electrons). There are 2 in 2s and 6 in 2p, total 8 electrons. Each contributes 0.85: 8 × 0.85 = 6.80.**
- **Electrons in shell n–2 = 1 (that is, the two 1s electrons). Each contributes 1.00: 2 × 1.00 = 2.00.**
- **Total shielding S = 6.80 + 2.00 = 8.80.**
- **Therefore, Z_eff = Z – S = 11 – 8.80 = 2.20.**

That means the 3s electron "feels" an effective nuclear charge of about +2.20 rather than the full +11.

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3. Spectroscopic Evidence for Atomic Models

Spectroscopy—the study of the interaction between electromagnetic radiation and matter—provided pivotal experimental evidence for quantized energy levels in atoms and underlies the modern quantum mechanical model. In this section, we will cover:

1. **Emission and absorption spectra**
2. **The hydrogen line spectra (e.g., Lyman, Balmer, Paschen series)**
3. **Fine structure and line broadening**
4. **Spectra of multi-electron atoms**
5. **How spectral observations support or challenge historical atomic models**

3.1 Emission and Absorption Spectra: Basic Principles

- **Discrete Spectral Lines: When atoms or ions transition between quantized energy levels, they absorb or emit photons whose energies correspond exactly to the difference between levels. As a result, we see discrete spectral lines rather than a continuous spectrum.**

3.1.1 Emission Spectra

- **Emission Process:**

  1. **An atom in an excited state (higher energy level E□$_i$) may spontaneously—or be stimulated to—emit a photon and drop to a lower energy state (lower energy level E□_f), where n_i > n_f.**

  2. **The energy of the emitted photon is E□$_i$ minus E□_f.**

  3. **The wavelength λ of that photon is given by the relationship: energy = Planck's constant (h) times frequency (v), and frequency = speed of light (c) divided by wavelength. In plain terms:**
     photon energy (in joules) equals h times c divided by λ.

  4. **When light from these photons is passed through a prism or diffraction grating, we see specific bright lines at those wavelengths in the spectrum (called an emission spectrum).**

3.1.2 Absorption Spectra

- **Absorption Process:**

  1. **An atom in a lower energy state E□_f can absorb a photon whose energy exactly matches E□$_i$ minus E□_f, causing the electron to jump from the lower level up to the higher level.**

  2. **If white (continuous) light passes through a gas of the element, specific wavelengths get absorbed, leaving dark lines at those wavelengths in the transmitted spectrum (called an absorption spectrum).**

  3. **Fraunhofer lines in the solar spectrum are famous examples: they are dark lines corresponding to wavelengths absorbed by elements in the Sun's atmosphere (for instance, hydrogen, sodium, magnesium).**

3.2 Hydrogen Atom Spectral Series

Hydrogen, being the simplest one-electron atom, provides a clear example of discrete line spectra. The formula for the wavenumber (which is 1 divided by wavelength) of any line in hydrogen's spectrum can be written in plain words as:

> **"The wavenumber equals the Rydberg constant for hydrogen, multiplied by [one divided by the square of the final energy level number minus one divided by the square of the initial energy level number]."**

We write that as:

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Wavenumber = R_H times (1 ÷ (n_f squared) − 1 ÷ (n_i squared)),
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where R_H is the Rydberg constant for hydrogen (about 1.0968 × 10^7 per meter), n_f is the lower principal quantum number (for example 1, 2, 3, …), and n_i is the higher principal quantum number (n_i > n_f).

Then, once you have the wavenumber (that is, 1 ÷ wavelength), you can find the wavelength by taking the reciprocal (wavelength = 1 ÷ wavenumber), or find the photon energy by multiplying Planck's constant h (6.626 × 10^(–34) joule-seconds) times the speed of light (3.00 × 10^8 meters per second), and dividing by wavelength in meters.

3.2.1 Named Spectral Series

Depending on the value of the final energy level n_f, you get different series of lines:

1. Lyman Series (n_f = 1)
   - These lines lie in the ultraviolet.
   - For example:
     • Transition from n_i = 2 down to n_f = 1 produces a wavelength of about 121.6 nanometers.
     • Transition from n_i = 3 down to n_f = 1 produces about 102.6 nm.
     • Transition from n_i = 4 down to n_f = 1 produces about 97.3 nm, and so on.
2. Balmer Series (n_f = 2)
   - These lines lie in the visible region (and near-ultraviolet).
   - Examples:
     • n_i = 3 → n_f = 2 gives a wavelength of 656.3 nm (red line, known as H-alpha).
     • n_i = 4 → n_f = 2 gives 486.1 nm (blue-green line, H-beta).
     • n_i = 5 → n_f = 2 gives 434.0 nm (blue-violet line, H-gamma).
     • n_i = 6 → n_f = 2 gives 410.2 nm (violet line, H-delta).
     • As n_i increases further, the lines get closer together and approach a limit at 364.6 nm (just into the ultraviolet).
3. Paschen Series (n_f = 3)
   - These lines lie in the infrared.

  - For instance:
    • n_i = 4 → n_f = 3 gives about 1,875 nm.
    • n_i = 5 → n_f = 3 gives about 1,282 nm.
    • n_i = 6 → n_f = 3 gives about 1,094 nm, and so on.

4. Brackett Series (n_f = 4)

   - Also in the infrared (longer wavelengths).

   - For example: n_i = 5 → n_f = 4 gives 4,051 nm; n_i = 6 → n_f = 4 gives 2,625 nm; etc.

5. Pfund Series (n_f = 5)

   - Farther out in the infrared (like 7,460 nm for n_i = 6 → n_f = 5).

6. Humphreys Series (n_f = 6)

   - Even farther into the infrared.

In each series, there is a "series limit" obtained by letting n_i approach infinity. Then one divided by (n_i squared) goes to zero, and the wavenumber approaches R_H divided by (n_f squared). The corresponding wavelength limit equals (n_f squared) divided by R_H. For example, Balmer series (with n_f = 2) has a series limit at 364.6 nm, which is where 1 ÷ wavelength equals R_H times (1 ÷ 4).

3.3 Experimental Observation of Atomic Spectra

3.3.1 Emission Spectroscopy: Discharge Lamps and Flame Tests

- Gas Discharge Tubes

  - A low-pressure gas (for example hydrogen, helium, neon, or mercury vapor) is enclosed in a sealed glass tube. Electrodes at each end apply a high voltage, causing a current through the gas.

  - Electrons colliding with gas atoms excite them to higher energy levels. As atoms relax back to lower levels, they emit photons at characteristic wavelengths.

  - When this emitted light is sent through a prism or diffraction grating, discrete bright lines appear at particular wavelengths—each element has a unique pattern of lines.

- **Flame Tests**
  - **A small sample of a solid salt (for instance, sodium chloride, potassium chloride, calcium chloride, etc.) is placed in a hot flame.**
  - **Thermal energy excites the electrons in the metal atoms. As those electrons relax back to lower levels, they emit photons. The colors seen are characteristic of the element:**
    • Sodium gives a bright yellow color around 589 nm (actually a closely spaced doublet known as the D-lines).
    • Potassium gives a lilac or light purple color (around 766.5 nm and 769.9 nm).
    • Calcium gives a brick-red color (around 622 nm and 616 nm).
    • Barium gives a yellow-green color.
    • Copper gives a blue-green color.

3.3.2 High-Resolution Spectroscopy and Fine Structure

- **Fine Structure Splitting arises from two main quantum mechanical effects:**
  - **Spin–Orbit Coupling: Interaction between the electron's spin magnetic moment and the magnetic field caused by its orbital motion around the nucleus. This interaction slightly changes the energy of the level depending on whether the electron's spin is aligned with or against its orbital angular momentum. The resulting energy differences are typically on the order of 10^(–4) electron-volts.**
  - **Relativistic Corrections: As electrons in inner shells move at speeds approaching a significant fraction of the speed of light, relativistic effects change their effective mass and alter the energy of their orbit, adding small corrections.**
- **Hyperfine Structure Splitting**
  - **Even smaller splitting (on the order of 10^(–6) electron-volts) arises from the interaction between the electron's magnetic moment and the nuclear magnetic moment (nuclear spin).**
  - **A famous hyperfine transition in hydrogen is the 21-centimeter line observed in radio astronomy. It corresponds to the electron flipping its spin with respect to the proton's spin (a spin-flip transition).**
- **Zeeman Effect**
  - **If atoms are placed in an external magnetic field, their spectral lines split into multiple components. This "Zeeman splitting" occurs because**

the external field lifts the degeneracy in m_ℓ and m_s.

- **There are two types:**
  • Normal Zeeman Effect: Splitting into three equally spaced lines, observed when the nuclear spin is zero or where spin–orbit coupling is negligible.
  • Anomalous Zeeman Effect: More complex patterns occur in atoms where spin–orbit coupling is significant.

- **Stark Effect**
  - **When subjected to an external electric field, spectral lines shift and split. This arises because the field perturbs the energies of the electron orbitals in a way that depends on their orientation relative to the field.**

3.4 Spectroscopic Evidence: Supporting or Challenging Atomic Models

3.4.1 Support for the Bohr Model

- **Balmer Series (Visible) Fit**
  - **The measured wavelengths of hydrogen's Balmer lines (for example 656.3 nm, 486.1 nm, 434.0 nm, 410.2 nm) match Bohr's predictions for energy levels of hydrogen (within experimental error). This agreement was a major success of Bohr's model.**
- **Ionized Helium (He^+) and Lithium (Li^{2+})**
  - **Bohr's formula predicts that if the nucleus has charge +Z, the energy levels scale as Z^2. For He^+ (Z = 2) or Li^{2+} (Z = 3), observed spectra indeed show that scaling. For instance, the energy difference between n = 2 and n = 3 in He^+ is four times that in hydrogen.**
- **Rydberg Constant**
  - **The empirical Rydberg formula (written before Bohr's theory) gave the wavenumbers of hydrogen lines as R times (1 ÷ (n_f squared) – 1 ÷ (n_i squared)). Bohr's theory derived the Rydberg constant from first principles, showing that**
    R = m_e × e^4 ÷ [8 × ε_0^2 × h^3 × c],
    which matches the measured value of about 1.0968 × 10^7 per meter. This successful derivation was a strong confirmation of Bohr's postulates.

3.4.2 Limitations Revealed by Spectroscopy

- **Multi-Electron Atoms**
    - **Observed spectra of atoms with more than one electron (such as lithium, beryllium, etc.) do not fit Bohr's simple Z^2/n^2 energy pattern because Bohr's model neglects electron–electron repulsion and does not account for the fact that energy depends on both n and ℓ.**
- **Fine Structure**
    - **Spectral lines exhibit small splittings (fine structure) that Bohr's model cannot explain. These arise from spin–orbit coupling and relativistic corrections, which require quantum mechanics with spin to handle correctly.**
- **Zeeman and Stark Effects**
    - **The way spectral lines split under magnetic or electric fields follows specific patterns consistent with quantum selection rules for angular momentum and spin. Bohr's model has no way to predict those rules; a full quantum mechanical treatment is needed.**

3.5 Spectra of Multi-Electron Atoms

While hydrogenic spectra (one-electron system) are simplest, real atoms typically have many electrons. Electron–electron interactions, spin–orbit coupling, and other effects make their spectra more complex. To describe energy levels in multi-electron atoms, we use term symbols and selection rules.

3.5.1 Term Symbols and Level Multiplicity

A term symbol takes the form ^(2S+1)L_J, where:

- **S is the total spin quantum number (sum of the individual electron spins).**
- **2S+1 is called the multiplicity. If S = 1, for example, multiplicity = 3, and we write a superscript 3.**
- **L is the total orbital angular momentum quantum number (sum of the individual ℓ values), designated by letters:**
    - **L = 0 → S**
    - **L = 1 → P**
    - **L = 2 → D**
    - **L = 3 → F**
    - **L = 4 → G**

… etc.

- J is the total angular momentum quantum number (vector sum of L and S). Possible values of J go from |L – S| up to L + S in integer steps.

Example: Carbon atom (6 electrons) in its ground state:

- Configuration: $1s^2 2s^2 2p^2$.
- The two electrons in 2p can couple their orbital angular momenta and spins. By applying Hund's rules and coupling rules, one finds the ground term is ^3P_0 (meaning multiplicity 3, L = 1, J = 0).

3.5.2 Selection Rules

For electric dipole transitions (the most common type responsible for strong spectral lines), the selection rules are:

- The total spin must not change: $\Delta S = 0$.
- The total orbital angular momentum must change by one unit: $\Delta L = +1$ or -1.
- The total angular momentum J may change by 0 or ±1, except that a transition from J = 0 to J = 0 is forbidden.
- Parity must change: the electron must go from an orbital of one parity to an orbital of the opposite parity (for example from s to p, which is even → odd, or from p to d, which is odd → even).

3.5.3 Example: Sodium D Lines

- Sodium atom (Z = 11) ground configuration: [Ne] $3s^1$.
- The first excited states involve the 3p orbitals.
- Due to spin–orbit coupling, the 3p level is split into two sublevels: 3p_(1/2) and 3p_(3/2).
- Transitions from those two sublevels down to the 3s_(1/2) ground sublevel produce two very close wavelengths: 589.0 nm (called D_2) and 589.6 nm (D_1). Together they are the famous "sodium D lines," which give flame-test sodium its bright yellow color.

4. Integrative Examples and Practice Problems

4.1 Example 1: Identifying an Element from Spectral Lines

Problem:
A gas discharge experiment on a poorly labeled tube shows emission lines at wavelengths 656.3 nm, 486.1 nm, and 434.0 nm. Which element is present in the tube?

Solution:

- **Those wavelengths correspond exactly to three lines in the Balmer series of hydrogen:**
  • Transition from n = 3 to n = 2 → 656.3 nm (Hα).
  • Transition from n = 4 to n = 2 → 486.1 nm (Hβ).
  • Transition from n = 5 to n = 2 → 434.0 nm (Hγ).
- **Therefore, the gas must be hydrogen (Z = 1).**

4.2 Example 2: Writing the Ground-State Electron Configuration of Chromium (Z = 24)

Problem:
Predict the ground-state electron configuration of chromium (atomic number 24).

Solution (step by step):

1. **Write down the Aufbau filling order up to 24 electrons: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, …**
2. **Start filling:**
   - **$1s^2$ (2 electrons)**
   - **$2s^2$ (2 more; total 4)**
   - **$2p^6$ (6 more; total 10)**
   - **$3s^2$ (2 more; total 12)**
   - **$3p^6$ (6 more; total 18)**
   - **$4s^2$ (2 more; total 20)**

   - **Now 3d can hold up to 10, but we only have 4 left to reach 24. So naïvely, one would fill $3d^4$, yielding [Ar] $4s^2$ $3d^4$.**

3. **However, experimental evidence shows that chromium's actual ground state is [Ar] $4s^1$ $3d^5$, not $4s^2$ $3d^4$.**
   - **A half-filled d subshell ($3d^5$) is especially stable due to exchange energy and symmetry.**
   - **Promoting one electron from 4s into 3d gives a completely half-filled 3d subshell plus one electron in 4s. That lowers the total energy slightly compared to $4s^2$ $3d^4$.**
4. **Therefore, chromium's ground-state electron configuration is:**

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Chromium (Z = 24): [Ar] 4s¹ 3d⁵
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4.3 Example 3: Estimating Effective Nuclear Charge for a 3p Electron in Silicon (Z = 14)

Problem:
Using Slater's rules, estimate the effective nuclear charge felt by a 3p electron in a silicon atom (Z = 14).

Solution:

1. **Write silicon's configuration by group:**
   ($1s^2$) ($2s^2$ $2p^6$) ($3s^2$ $3p^2$)
2. **The target electron is one of the two 3p electrons.**
   - **Electrons in the same group ($3s^2$ $3p^2$):**
     • There is one other 3p electron, which contributes 0.35 to shielding.
     • There are two 3s electrons, each contributing 0.35 to shielding (total 0.70).
     • So total from same group = 0.35 + 0.70 = 1.05.
   - **Electrons in the n–1 shell (n = 3 → n–1 = 2): that is the two 2s and six 2p electrons, total 8 electrons; each contributes 0.85. So 8 × 0.85 = 6.80.**
   - **Electrons in the n–2 shell (n = 3 → n–2 = 1): that is the two 1s electrons, each contributing 1.00; total = 2.00.**

3. Sum of shielding S = 1.05 + 6.80 + 2.00 = 9.85.

4. Z_eff ≈ Z – S = 14 – 9.85 = 4.15.

So a 3p electron in silicon feels an effective nuclear charge of about +4.15.

4.4 Practice Questions

1. Isotopic Abundance Calculation:
   Naturally occurring chlorine has two main stable isotopes: chlorine-35 (mass = 34.9688527 u, abundance = 75.78%) and chlorine-37 (mass = 36.9659026 u, abundance = 24.22%). Calculate the average atomic mass of chlorine.

2. Ionization Energy Trend:
   Explain why the first ionization energy of sodium (Z = 11) is much lower than that of magnesium (Z = 12), even though magnesium has a greater nuclear charge.

3. Spectral Calculation:
   Compute the wavelength of light emitted when an electron in a hydrogen atom transitions from n = 4 down to n = 2. Use the Rydberg constant R_H = 1.0968 × 10^7 per meter, and the fact that wavelength = 1 ÷ [R_H × (1 ÷ 2^2 – 1 ÷ 4^2)]. Give your answer in nanometers.

4. Electron Configuration Exception:
   Provide the ground-state electron configuration of copper (Z = 29) and explain why it deviates from the naïve Aufbau filling order.

5. Spin–Orbit Coupling in Hydrogen:
   Without detailed calculation, explain qualitatively why the hydrogen 2p level splits into two energy levels called $2p_{1/2}$ and $2p_{3/2}$ due to spin–orbit coupling.

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5. Summary of Key Concepts

1. Atom as Composite of Subatomic Particles
   - Proton (mass ~1 mass-unit, charge +1), neutron (mass ~1 mass-unit, charge 0), electron (mass ~0.00055 mass-unit, charge –1).
   - Atomic number Z = number of protons; mass number A = Z + N (where N is the number of neutrons).

2. Isotopes
    - Atoms with the same Z but different N.
    - Atomic weight (relative atomic mass) is the weighted average of isotopic masses based on natural abundance.
3. Quantum Mechanical Model of the Atom
    - Electrons are described by wavefunctions $\psi(n,\ell,m_\ell)$ that give the probability of finding an electron at a given position.
    - Four quantum numbers (n, ℓ, m_ℓ, m_s) uniquely define each electron in an atom.
    - Pauli Exclusion Principle, Hund's Rule, and the Aufbau Principle govern how electrons fill the orbitals.
4. Electron Configuration Notation
    - Standard notation lists orbitals in increasing energy order with superscripts for how many electrons occupy each.
    - Noble gas core notation uses the preceding noble gas in square brackets, followed by any additional occupied orbitals.
    - Transition-metal exceptions occur when energy differences between ns and (n–1)d shells are small; half-filled or filled d subshells are especially stable.
5. Shielding and Effective Nuclear Charge (Z_{eff})
    - Inner electrons shield outer electrons from the full nuclear charge.
    - Slater's Rules provide an empirical method for estimating Z_{eff}.
6. Atomic Spectra
    - Emission (bright-line) and absorption (dark-line) spectra demonstrate that electrons occupy quantized energy levels.
    - Hydrogen's spectral lines (Lyman, Balmer, Paschen, etc.) follow the Rydberg formula:
      $\text{Wavenumber} = R_H \times (1 \div (n_f^2) - 1 \div (n_i^2))$.
    - Fine and hyperfine structure (small splittings) arise from spin–orbit coupling, relativistic effects, and nuclear spin interactions.

  - Zeeman and Stark effects show how external magnetic or electric fields split spectral lines according to quantum selection rules.

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6. Glossary of Terms

- Atomic Number (Z): Number of protons in an atom’s nucleus; defines the element.
- Mass Number (A): Total number of protons plus neutrons in the nucleus.
- Isotope: Atoms with the same Z but different A (different number of neutrons).
- Relative Atomic Mass (Atomic Weight): Weighted average of an element’s isotopic masses based on natural abundances.
- Orbital: A region in space (described by a wavefunction) where there is a high probability of finding an electron. Orbitals are labeled by (n, ℓ, m_ℓ).
- Principal Quantum Number (n): Specifies the main energy level (shell) of an electron (n = 1, 2, 3, …).
- Azimuthal Quantum Number (ℓ): Defines the subshell and orbital shape (ℓ = 0 for s, ℓ = 1 for p, ℓ = 2 for d, ℓ = 3 for f).
- Magnetic Quantum Number (m_ℓ): Specifies the orientation of the orbital in space (m_ℓ = –ℓ, …, 0, …, +ℓ).
- Spin Quantum Number (m_s): Specifies the direction of the electron’s spin; can be +½ or –½.
- Aufbau Principle: Electrons occupy the lowest-energy orbitals available first.
- Pauli Exclusion Principle: No two electrons in an atom can have the same set of four quantum numbers.
- Hund’s Rule: When filling degenerate orbitals (same energy), electrons occupy each orbital singly with parallel spins before pairing.
- Effective Nuclear Charge (Z_eff): The net positive charge “felt” by an electron in a multi-electron atom, equal to actual nuclear charge Z minus shielding S from other electrons.

- **Rydberg Formula: For hydrogenic atoms,**
  Wavenumber = R_H × (1 ÷ (n_f²) – 1 ÷ (n_i²)).
- **Bohr Model: An early atomic model in which electrons move in fixed circular orbits without radiation, with quantized angular momentum.**
- **Spin–Orbit Coupling: Interaction between an electron's spin magnetic moment and the magnetic field due to its motion around the nucleus, causing small energy shifts (fine structure).**

7. Practice Problems and Solutions

7.1 Problem 1: Chlorine's Average Atomic Mass

Given:

- **Chlorine-35, mass = 34.9688527 mass-units, abundance = 75.78%**
- **Chlorine-37, mass = 36.9659026 mass-units, abundance = 24.22%**

Compute: The average atomic mass of chlorine.

Solution:

1. **Convert percentages to fractions: 75.78% → 0.7578; 24.22% → 0.2422.**
2. **Multiply each isotope's mass by its fraction:**
   • 0.7578 × 34.9688527 = 26.5073 mass-units
   • 0.2422 × 36.9659026 = 8.9458 mass-units
3. **Add them: 26.5073 + 8.9458 = 35.4531 mass-units.**

Therefore, the average atomic mass of chlorine is about 35.45 mass-units.

7.2 Problem 2: Ionization Energy of Na vs. Mg

Question: Why is the first ionization energy (the energy needed to remove the outermost electron) of sodium (Z = 11) much lower than that of magnesium (Z = 12), even though magnesium has a higher nuclear charge?

Solution:

1. Electronic Configurations:
   - Sodium’s ground state is [Ne] $3s^1$. Removing its single 3s electron leaves the stable neon core [Ne]. That is relatively easy because you remove the only electron in the 3s orbital.
   - Magnesium’s ground state is [Ne] $3s^2$. Removing one 3s electron leaves [Ne] $3s^1$. That is not as easy, because the remaining 3s electron is now held more tightly (it feels more of the nuclear charge once its partner is gone).
2. Shielding and Z_eff:
   - For sodium’s 3s electron, the 10 inner electrons ($1s^2$ $2s^2$ $2p^6$) shield most of the nuclear charge. Its effective nuclear charge is about +2.20, so it is not held very tightly.
   - For magnesium’s 3s electrons, after removing one, the second 3s electron in Mg^+ feels a higher effective nuclear charge (roughly +2.7). Therefore, more energy is required to remove that first 3s electron (about 737.7 kJ/mol) than for sodium’s 3s electron (about 495.8 kJ/mol).
3. Result: The first ionization energy of sodium is lower because removing its 3s electron produces a closed, stable neon core, whereas removing one 3s electron from magnesium leaves a less stable $3s^1$ configuration and leaves a more tightly held electron behind.

7.3 Problem 3: Hydrogen 4→2 Transition Wavelength

Given:

- A hydrogen atom’s electron drops from n = 4 down to n = 2.
- Rydberg constant R_H = 1.0968 × 10^7 per meter.

Compute: The wavelength λ in nanometers.

Solution:

1. Use the plain-language Rydberg formula for the wavenumber (which is 1 divided by λ):
   Wavenumber = R_H × (1 ÷ (2^2) – 1 ÷ (4^2)).

2. Compute $1 \div (2^2) = 1 \div 4 = 0.25$; $1 \div (4^2) = 1 \div 16 = 0.0625$; the difference is 0.1875.

3. Multiply by R_H: 0.1875 × 1.0968 × 10^7 per meter = 2.0565 × 10^6 per meter.

4. That is the wavenumber, so the wavelength in meters is 1 ÷ (2.0565 × 10^6) = 4.861 × 10^(–7) meter. Converting to nanometers (×10^9) gives 486.1 nm.

Therefore, the wavelength of the photon emitted in the n = 4 to n = 2 transition of hydrogen is 486.1 nanometers (called the Hβ line of the Balmer series).

7.4 Problem 4: Copper's Electron Configuration Exception

Question: Provide copper's (Z = 29) actual ground-state electron configuration and explain why it deviates from the naïve Aufbau filling order.

Solution:

1. The naïve filling order up to Z = 29 would be:
   $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$ (that is, [Ar] $4s^2\ 3d^9$).

2. However, copper's actual ground state is [Ar] $4s^1\ 3d^{10}$. In other words, one electron from the 4s orbital has moved into the 3d orbital to fill it completely with 10 electrons.

3. Why? Because a fully filled d subshell (d^{10}) is especially stable due to exchange energy and symmetry considerations. The small energy difference between 4s and 3d allows that one electron to shift into 3d, giving copper a configuration with a full 3d subshell and a single 4s electron. The total energy is slightly lower than if the configuration remained $4s^2\ 3d^9$.

So copper's ground-state configuration is:

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Copper (Z = 29): [Ar] 4s¹ 3d¹⁰
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7.5 Problem 5: Spin–Orbit Coupling in Hydrogen's 2p Level

Question: Explain qualitatively why the hydrogen 2p energy level is split into two slightly different energies called $2p_{1/2}$ and $2p_{3/2}$.

Solution:

1. When an electron moves around the nucleus in a p orbital ($\ell = 1$), in the electron's own rest frame the positively charged nucleus appears to orbit around it, creating a tiny magnetic field.

2. The electron itself has an intrinsic magnetic moment due to its spin (spin quantum number $s = 1/2$). That magnetic moment can be aligned parallel or antiparallel to the magnetic field produced by the orbital motion.

3. The interaction energy of the electron's spin with that magnetic field depends on whether the spin is aligned with or opposed to the orbital angular momentum. That changes the energy slightly.

4. Total angular momentum J can be $\ell + s = 1 + 1/2 = 3/2$, or $\ell – s = 1 – 1/2 = 1/2$. These two possibilities are called $2p_{3/2}$ and $2p_{1/2}$, respectively. Because of spin–orbit coupling, $2p_{3/2}$ lies slightly lower in energy than $2p_{1/2}$. That small energy difference leads to two closely spaced spectral lines rather than a single line.

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8. Further Exploration and Connections

1. Periodic Trends and Atomic Structure
    - Trends such as ionization energy, atomic radius, electron affinity, and electronegativity across a period can be explained by changes in effective nuclear charge and shielding.
    - For example, across the third period (sodium → argon), atomic radius decreases because Z_eff increases while shielding stays relatively constant; thus electrons are pulled closer to the nucleus. Ionization energy increases accordingly.
2. From Atomic to Molecular Orbitals
    - Atomic orbitals of individual atoms combine to form molecular orbitals when atoms bond to form molecules. Understanding how electrons occupy atomic orbitals is essential to predicting how molecular orbitals form, what their energies are, and how stable the resulting molecule will be.
3. Spectroscopy in Analytical Chemistry
    - Atomic Emission Spectroscopy: Identifies elements by their characteristic emission lines.

- **Absorption Spectroscopy (UV-Vis): Probes electronic transitions in molecules and ions.**

- **Photoelectron Spectroscopy (PES): Measures the binding energies of electrons in atoms or molecules by ejecting electrons with high-energy photons and analyzing their kinetic energy. PES can map out the energy levels of multi-electron atoms, showing how subshell energies differ.**

4. **Nuclear Magnetic Resonance (NMR)**

    - **Although not directly about electron energy levels, NMR techniques rely on nuclear spins (for example, protons in hydrogen or carbon-13 nuclei). These spins interact with an external magnetic field, splitting nuclear energy levels in a way analogous to the electronic Zeeman effect. NMR is a powerful tool for determining molecular structure, and it connects logically to concepts of nuclear spin and magnetic interactions in atoms.**

5. **Quantum Numbers and Periodic Table Structure**

    - **The shape of the periodic table arises because of how orbitals fill:**
      • s-block (Groups 1 & 2) fill s orbitals.
      • p-block (Groups 13–18) fill p orbitals.
      • d-block (Transition metals) fill d orbitals.
      • f-block (Lanthanides and actinides) fill f orbitals.

    - **Understanding quantum numbers explains why the periodic table has its familiar shape and why elements in the same group share similar properties.**

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9. Chapter Review

- **Subatomic Particles:**

    - **Protons and neutrons reside in the atomic nucleus (each about 1 mass-unit; proton has charge +1, neutron has no charge).**

    - **Electrons (mass about 1/1836 of a proton, charge –1) occupy orbitals around the nucleus.**

- **Isotopes:**

  - Atoms with the same number of protons but different numbers of neutrons.

  - Atomic weight (relative atomic mass) equals the weighted average of isotopic masses.

  - Radioactive isotopes decay via alpha, beta, or gamma emission to reach more stable configurations.

- Quantum Mechanical Model of the Atom:

  - Electrons are described by wavefunctions and occupy orbitals labeled by quantum numbers n, ℓ, m_ℓ, and m_s.

  - Four quantum numbers specify each electron uniquely; the Pauli Exclusion Principle forbids two electrons from having the same four quantum numbers.

- Electron Configurations:

  - Electrons fill orbitals following the Aufbau principle (lowest energy first), Pauli exclusion (max two per orbital, opposite spins), and Hund's rule (in degenerate orbitals, fill singly first with parallel spins).

  - Exceptions occur for certain transition metals where half-filled or fully filled d subshells yield extra stability (for example, Cr: [Ar] $4s^1\ 3d^5$; Cu: [Ar] $4s^1\ 3d^{10}$).

- Shielding and Effective Nuclear Charge:

  - Inner electrons shield outer electrons from the full nuclear charge.

  - Use Slater's rules to estimate the shielding constant S, then $Z_{eff} \approx Z - S$.

- Atomic Spectra:

  - Discrete emission and absorption lines arise because electrons occupy quantized energy levels.

  - Hydrogen's line spectra (Lyman, Balmer, Paschen, etc.) follow the Rydberg formula:
    Wavenumber (in reciprocal meters) = $R_H \times (1 \div (n_f^2) - 1 \div (n_i^2))$.

  - Fine structure, hyperfine structure, Zeeman and Stark effects reveal deeper quantum mechanical interactions (spin–orbit coupling, nuclear spin interaction, external field effects).

- **Spectroscopic Support for Atomic Models:**
  - **Bohr's model explained hydrogen's line spectra and derived the Rydberg constant from theory.**
  - **Discrepancies in multi-electron atoms and the presence of fine structure led to the development of full quantum mechanics.**

10. Key Concepts and Plain-Language Formulas

1. **Planck's Constant (h): 6.626 × 10^(–34) joule-seconds.**
2. **Reduced Planck's Constant (h-bar): h divided by 2π, about 1.055 × 10^(–34) J·s.**
3. **Speed of Light (c): 2.998 × 10^8 meters per second.**
4. **Elementary Charge (e): 1.602 × 10^(–19) coulombs.**
5. **Vacuum Permittivity (ε_0): 8.854 × 10^(–12) coulomb^2 per (newton·meter^2).**
6. **Bohr Radius (a_0): Approximately 0.529 × 10^(–10) meters (distance of highest probability for a hydrogen 1s electron).**
7. **Rydberg Constant for Hydrogen (R_H): 1.0968 × 10^7 per meter.**
8. **Bohr Energy Levels (for hydrogenic atoms):**
   "Energy of the nth level = –(13.6 electron-volts × Z^2) ÷ n^2, where Z is the nuclear charge and n is the principal quantum number."
9. **Rydberg Formula (plain words):**
   "Wavenumber (which is 1 divided by wavelength) equals the Rydberg constant times [1 divided by (the square of the final quantum number) minus 1 divided by (the square of the initial quantum number)]."
10. **Energy–Wavelength Relationship (plain words):**
    "Photon energy in joules = Planck's constant times speed of light divided by wavelength." Or conversely, "wavelength in meters = Planck's constant times speed of light divided by photon energy in joules."

11. Flashcards

1. **Q: What is the charge and mass of a neutron?**
   A: Charge = zero; mass ≈ 1.6749 × 10^(–27) kilograms (about 1.0087 mass-units).

2. **Q: Define an isotope.**
   A: Atoms with the same number of protons (same Z) but different numbers of neutrons (different A).

3. **Q: What are the four quantum numbers and their allowed values?**
   A:

   - ○ **n (principal quantum number): 1, 2, 3, …**

   - ○ **ℓ (azimuthal quantum number): 0 up to n–1 (ℓ = 0 for s; 1 for p; 2 for d; 3 for f)**

   - ○ **m_ℓ (magnetic quantum number): integer values from –ℓ to +ℓ**

   - ○ **m_s (spin quantum number): +½ or –½**

4. **Q: State the Pauli Exclusion Principle.**
   A: No two electrons in the same atom can have the same set of all four quantum numbers (n, ℓ, m_ℓ, m_s).

5. **Q: What is Hund's rule?**
   A: When filling orbitals of equal energy, place one electron in each orbital with parallel spins before pairing them up.

6. **Q: How is effective nuclear charge (Z_eff) defined?**
   A: Z_eff = Z – S, where Z is the actual nuclear charge (number of protons) and S is the shielding constant due to other electrons.

7. **Q: Write the ground-state electron configuration of sodium.**
   A: $1s^2\ 2s^2\ 2p^6\ 3s^1$ (or [Ne] $3s^1$).

8. **Q: What is the wavelength of the Hα line (n = 3 → n = 2) in hydrogen?**
   A: 656.3 nanometers.

9. **Q: What is spin–orbit coupling?**
   A: Interaction between an electron's spin magnetic moment and the magnetic field produced by its orbital motion, causing small shifts in energy (fine structure).

10. **Q: Why do chromium and copper have "exceptional" electron configurations?**
    A: Because a half-filled or fully filled d subshell is especially stable, causing one electron to move from the ns orbital into the (n–1)d orbital, which lowers the total energy slightly.

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12. Memory Aids

1. **“Pauli’s Perfect Pairs”:**
   - **Each orbital can hold a “perfect pair” of electrons with opposite spins; no two electrons can share the same set of quantum numbers.**
2. **“Aufbau’s Waterfall”:**
   - **Visualize the diagonal (Madelung) arrows as a cascading waterfall guiding electrons from lower to higher energy levels.**
3. **“nℓ Mnemonic—‘Some People Drink Franly’”:**
   - **Remember the letters for ℓ = 0, 1, 2, 3 correspond to s, p, d, f. A silly phrase—“Some People Drink Freely”—helps recall s-p-d-f.**
4. **“Balmer’s Beautiful Blue-Green”:**
   - **The Balmer lines include 486.1 nm (blue-green, Hβ) and 434.0 nm (blue-violet, Hγ) in the visible region.**
5. **“Shielding—Strong Inside, Slight at Side”:**
   - **Inner electrons (n–2, n–3, etc.) shield strongly (contribution of 1 each); electrons in the same subshell shield only slightly (contribution of 0.35 each).**

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13. Estimated Study Time

- **Introduction & Historical Context: 30 minutes**
- **Subatomic Particles & Isotopes: 60 minutes**
  - **Reading text, isotope abundance calculations, discussing radioactive decay.**
- **Quantum Mechanical Model & Bohr Model: 90 minutes**
  - **Derivations of Bohr energy levels, conceptual Schrödinger equation, orbital shapes.**

- **Electron Configuration & Periodic Trends: 60 minutes**
    - **Aufbau principle, Pauli exclusion, Hund's rule, effective nuclear charge calculations.**
- **Spectroscopic Evidence: 90 minutes**
    - **Emission/absorption principles, calculating wavelengths, exploring fine and hyperfine structures, selection rules.**
- **Summary & Problem Solving: 60 minutes**
    - **Reviewing key formulas, solving practice problems, using flashcards.**

Total: Approximately 6 hours.

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14. Key Takeaways

- **Atoms consist of a dense nucleus (protons, neutrons) surrounded by electrons in quantized energy levels.**
- **Isotopes are atoms with the same number of protons but different numbers of neutrons. Atomic weight is a weighted average of isotopic masses.**
- **Bohr's model was a breakthrough for hydrogen-like atoms but failed for multi-electron systems and fine structure. Quantum mechanics (Schrödinger, Heisenberg) provided the modern wavefunction description.**
- **Electrons occupy orbitals labeled by quantum numbers (n, ℓ, m_ℓ, m_s). The Pauli Exclusion Principle, Hund's Rule, and the Aufbau Principle dictate how electrons fill these orbitals.**
- **Effective nuclear charge explains why outer electrons in multi-electron atoms feel less than the full nuclear charge, affecting atomic size, ionization energy, and chemical behavior.**
- **Spectroscopy—emission and absorption lines—gives direct experimental evidence of quantized energy levels. Hydrogen's spectral series follow the Rydberg formula, while multi-electron atoms exhibit fine, hyperfine, Zeeman, and Stark splittings requiring quantum mechanics to explain.**
- **Certain transition metals (for example, chromium and copper) have "exceptional" electron configurations because half-filled or fully filled d**

subshells are particularly stable.