Focus 1 ATOMS

Topic 1A: INVESTIGATING ATOMS

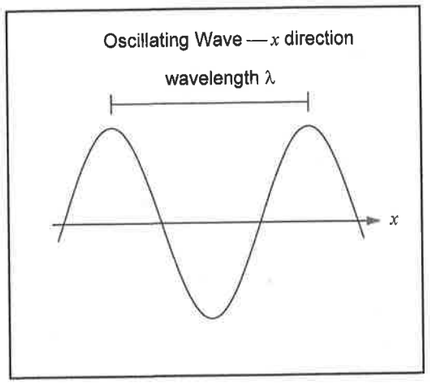
1A.1 The Nuclear Model of the Atom

- **Background**
  - → J. J. Thomson found that charged cathode-ray particles, which are now called **electrons**, were the same regardless of the metal used for the cathode. He concluded that they are part of the foundation of all atoms.
  - → Thomson measured a value of e/m_e, the ratio of the magnitude of the electron's charge e to its mass m_e. Values for e and m_e were not known until the physicist Robert Millikan carried out experiments that enabled the calculation of the value of e.
  - → Fundamental unit of charge: $e = 1.602 \times 10^{-19}$ C. Mass of the electron: 9.109×10^{-31} kg.
  - → The charge of $-e$ is "one unit" of negative charge, and the charge of e is "one unit" of positive charge.
  - → Based on the scattering of alpha particles on platinum foil, Ernest Rutherford proposed a nuclear model of the atom. Later work showed that the nucleus of an atom contains particles called **protons,** each of which has a charge of $+e$ (responsible for the positive charge), and **neutrons** (uncharged particles).
  - → The number of protons in the nucleus is different for each element and is called the **atomic number,** Z, of the element (*Fundamentals* B). The total charge on an atomic nucleus of atomic number Z is $+Ze$ and, for the atoms to be electrically neutral, there must be Z electrons around it.
- **Subatomic particles**
  - → Electron: mass ($m = 9.109\,383 \times 10^{-31}$ kg) charge ($-e = -1.602\,177 \times 10^{-19}$ C)
  - → Proton: mass ($m = 1.672\,622 \times 10^{-27}$ kg) charge ($e = 1.602\,177 \times 10^{-19}$ C)
  - → Neutron: mass ($m = 1.674\,927 \times 10^{-27}$ kg) charge = 0
- **Nucleus**
  - → *Nucleons* (protons and neutrons) occupy a small volume at the center of the atom. The binding energy of the nucleus is attributed to a strong force (nuclear) acting over a very short distance.
  - → The radius of the nucleus (assumed to be spherical) is given roughly by $r_{nuc} = r_0 A^{1/3}$, where $r_0 \approx 1.3 \times 10^{-15}$ m = 1.3 fm and A is defined below.
- **Atom**
  - → Atomic number: $Z = N_p$ = number of protons in the nucleus
  - → Atomic mass number: $A = N_p + N_n$ = number of protons and neutrons in the nucleus
  - → Uncharged atom: $N_p = N_e$ (number of protons equals the number of electrons)
  - → *Electrons* occupy a much larger volume than the nucleus and define the "size" of the atom. The binding energy of the electrons is attributed to a weak force (coulomb) acting over a much longer distance than the strong force.

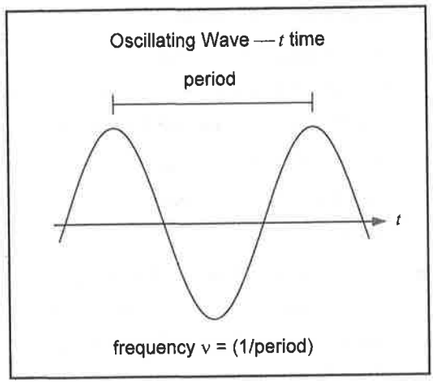
1A.2 Electromagnetic Radiation

- **Oscillating amplitude of electric and magnetic field**
  - → Waves are characterized by *wavelength* λ (lambda) and *frequency* ν (nu).
  - → Waves always travel at the speed of light (constant for a given medium)
  - → No known upper or lower limit of frequency or wavelength

Distance Behavior (fixed time *t*)



Time Behavior (fixed position *x*)



Speed of light (distance / time) = wavelength / period = wavelength × frequency

$\boxed{c = \lambda\nu}$ speed of light = wavelength × frequency

SI units: $(m \cdot s^{-1})$ (m) (s^{-1}) [1 Hz (hertz) = 1 s^{-1}]

- → The speed of light c (c_0 in vacuum $\approx 3.00 \times 10^8$ $m \cdot s^{-1}$) depends on the medium it travels in. Medium effects on wavelength in the visible region are small (beyond three significant figures).
- → Visible radiation or visible light: 700 nm to 400 nm.
- → Ultraviolet radiation: < 400 nm (< 200 nm vacuum ultraviolet)
- → Infrared radiation: > 700 nm
- → Infrared radiation: > 700 nm
- → Visible spectrum colors (pneumonic): ROY G BIV (red, orange, yellow, green, blue, indigo, violet)
- → See **Table 1A.1** in the text: Color, Frequency, and Wavelength of Electromagnetic Radiation

1A.3 Atomic Spectra

- **Spectral lines**
  - → Discharge lamp of hydrogen

    H_2 + electrical energy → H + H^* (* ≡ asterisk denotes excited atom)

    H^* → $H^{(*)} + h\nu$ ($^{(*)}$ ≡ denotes a less excited atom)

- **Lines form a discrete pattern**
  - → Discrete energy levels
- **Hydrogen atom spectral lines**
  - → Spectral lines imply discrete energy level for electrons in atoms
  - → Johann Rydberg's general equation
  - → $n_2 = n_{upper}$ and $n_1 = n_{lower}$

$$\boxed{\nu = \mathcal{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad n_1 = 1,\ 2,\ \ldots \quad n_2 = n_1 + 1,\ n_1 + 2,\ \ldots}$$

$\mathcal{R} = 3.29 \times 10^{15}$ Hz
Rydberg constant

- → Rydberg expression reproduces pattern of lines in H atom emission spectrum. The value of $\mathcal{R}$ is obtained empirically. (Font: Monotype Corsiva)

Note: Lines with a common n_1 can be grouped into a *series* and some have special names:

	n_1 = 1 (Lyman),	2 (Balmer),	3 (Paschen),	4 (Brackett),	5 (Pfund)
	121.6 nm	656.3 nm (red)	1.875 μm	4.05 μm	7.46 μm
	102.6 nm	486.1 nm (blue)	1.282 μm	2.62 μm	4.65 μm
	97.3 nm	434.0 nm (indigo)	1.094 μm	2.16 μm	3.74 μm
	95.0 nm	410.2 nm (violet)	1.005 μm	1.94 μm	3.30 μm
	.....	.....	.....	.....	.....
series limit: $n_2 = \infty$	91.2 nm	364.7 nm	0.820 μm	1.46 μm	2.28 μm
spectrum:	vacuum UV	vis → UV	IR	IR	IR

Infrared: ***near*** **(0.8 μm to 20 μm)** **and** ***far*** **(50 μm to 1000 μm)**
(0.7 μm to 50 μm) **(50 μm to 100 μm)**

Note: Different limits for the infrared are determined mainly by instrumentation and/or the light source used.

Topic 1B: QUANTUM THEORY

1B.1 Radiation, Quanta, and Photons

- **Black body**
  - → Perfect absorber and emitter of radiation
  - → Intensity of radiation for a series of temperatures leads to two laws (Stefan–Boltzmann and Wien's).

→ Stefan–Boltzmann law: $\boxed{\dfrac{\text{Power emitted (watts)}}{\text{Surface area (meter}^2\text{)}} = \text{constant} \times T^4}$

→ Wien's law: $\boxed{T\lambda_{max} = \text{constant}}$ where constant = 2.88 K·mm

Wavelength corresponding to maximum intensity = λ_{max}

At higher temperature, maximum intensity of radiation shifts to lower wavelength.

- **Energy of a quantum (packet) of light (generally called a photon)**
  - → Postulated by Max Planck to explain black body radiation
  - → Resolved the "ultraviolet catastrophe" of classical physics, which predicted intense ultraviolet radiation for all heated objects ($T > 0$)
  - → Quantization of electromagnetic radiation

$\boxed{E = h\nu}$ Photon energy = Planck's constant × photon frequency

SI units: (J) ($h = 6.6261 \times 10^{-34}$ J·s) (s^{-1})

- **Photoelectric effect**
  - → Ejection of electrons from a metal surface exposed to photons of sufficient energy
  - → Indicates that light behaves as a particle

$\boxed{E_K = h\nu - \Phi}$ E_K = kinetic energy of the ejected electron, Φ = threshold energy (work function) required for electron ejection from the metal surface, and $h\nu$ = photon energy

→ $h\nu \geq \Phi$ required for electron ejection

- **Bohr frequency condition**

$\boxed{h\nu = E_{upper} - E_{lower}}$ Relates photon energy to energy difference between two energy levels in an atom

1B.2 The Wave–Particle Duality of Matter

- **Wave behavior of light**
  - → Diffraction and interference effects of superimposed waves (*constructive* and *destructive*)
- **Wave behavior of matter**
  - → Proposed by Louis de Broglie, who considered the properties of matter of mass m traveling with velocity v.
  - → Such matter behaves as a wave with a characteristic wavelength.
  - → de Broglie wavelength λ for a particle with linear momentum $p = mv$ $\boxed{\lambda = \dfrac{h}{mv}}$
  - → Wave character of electrons is verified by electron diffraction.

1B.3 The Uncertainty Principle

- **Complementarity of location (x) and momentum (p)**
  - → Uncertainty in x is Δx; uncertainty in p is Δp.
  - → Limitation of knowledge (p and x cannot be determined simultaneously)

$\boxed{\Delta p \Delta x \geq \hbar/2}$ Heisenberg uncertainty principle, where $\hbar = h/2\pi$

→ $\boxed{\hbar \text{ is called "h bar"}}$ $\hbar = 1.0546 \times 10^{-34}$ J·s

→ Refutes classical physics on the atomic scale

Topic 1C: WAVEFUNCTIONS AND ENERGY LEVELS

1C.1 The Wavefunction and Its Interpretation

- **Classical trajectories**
  - → Precisely defined paths

- **Wavefunction ψ**
  - → Gives *probable* position of particle with mass m
- **Born interpretation**
  - → Probability of finding particle in a region is proportional to ψ^2.
- **Schrödinger equation in one-dimension**
  - → Allows calculation of ψ by solving a differential equation
  - → $H\psi = E\psi$; H is called the Hamiltonian
  - → H represents the sum of kinetic energy and potential energy in a system

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi = E\psi} \qquad \boxed{\nabla^2 = \frac{d^2}{dx^2}}$$

1C.2 The Quantization of Energy

- **Particle in a box**
  - → Mass m confined between two rigid walls a distance L apart
  - → $\psi = 0$ outside the box and at the walls (boundary condition)
  - → The *operator* for a one-dimensional system is $\boxed{\nabla^2 = \dfrac{d^2}{dx^2}}$

→ In the box, $V(x) = 0$. The resulting differential equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

→ Solving with the boundary condition and normalizing the function yields

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1,\ 2,\ \ldots$$

→ $\psi_n(x)$ = wavefunction that satisfies the Schrödinger equation between the box limits.

→ n is a *quantum number* (n = 1, 2, 3, 4, 5, …)

Note: A node is a point in the box where $\psi = 0$ and ψ *changes* sign. $\psi^2 \geq 0$, always

→ The resulting energy levels follow

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where E_n = allowed energy values of a particle in a one-dimensional box

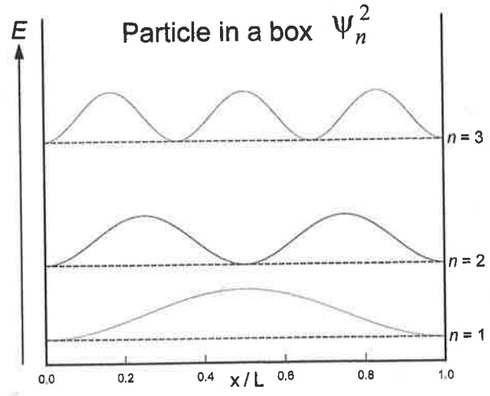
Note: n = 1 gives the zero-point energy E_1. $E_1 \neq 0$ implies residual motion (consistent with the *uncertainty principle*).

→ The energy difference between two neighboring levels is

$$\Delta E = E_{n+1} - E_n = \frac{(2n+1)h^2}{8mL^2}$$

- **Probability as a function of position in the box**

→ Plot is shown for the first three levels, ψ^2 as a function of the dimensionless variable x/L



Topic 1D: THE HYDROGEN ATOM

1D.1 Energy Levels

- **Charge on an electron**

→ $q = -e = -1.602\,177\,33 \times 10^{-19}$ C

- **Vacuum permittivity**

→ $\varepsilon_0 = 8.854\,187\,817 \times 10^{-12}\ C^2 \cdot N^{-1} \cdot m^{-2}$

- **Coulomb potential energy** $V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$

$$V(r) = \frac{\text{product of charges on particles}}{4\pi \times \text{permittivity of free space} \times \text{distance between charges}} \qquad \text{(SI system)}$$

Units of $V(r)$: $\mathrm{J} = \frac{C^2}{(C^2 \cdot N^{-1} \cdot m^{-2})\ m} = N \cdot m = (kg \cdot m \cdot s^{-2})\ m = kg \cdot m^2 \cdot s^{-2}$

→ For the H atom, $V(r) = \frac{(-e)(+e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r}$

→ Solution of the Schrödinger equation using $V(r)$ above leads to energy levels E_n given below.

- **H atom and one-electron ion energy levels (He^+, Li^{2+}, Be^{3+}, etc.)**

→ Solutions to the Schrödinger equation

$$E_n = -h\mathcal{R}\left(\frac{Z^2}{n^2}\right) \qquad Z = 1 \ \&\ n = 1, 2, 3, \ldots \qquad (n \text{ is dimensionless})$$

$$\mathcal{R} = \frac{m_e e^4}{8h^3\varepsilon_0^2} = 3.289\,842 \times 10^{15}\ \text{Hz} \qquad \text{Units: } \frac{kg \cdot C^4}{(J \cdot s)^3 (C^2 \cdot N^{-1} \cdot m^{-2})^2} = s^{-1} \equiv \text{Hz}$$

→ All quantum numbers are dimensionless. With $\mathcal{R}$ in units of frequency, the H atom energy-level equation has the same form as the Planck equation, $E = h\nu$.

→ E_n = energy levels (states) of the H atom. Note the *negative* sign.

→ $\mathcal{R}$ = Rydberg constant, calculated exactly using Bohr theory *or* the Schrödinger equation

→ Z = atomic number, equal to 1 for hydrogen

→ n = principal quantum number

→ As n increases, energy increases, the atom becomes less stable, and energy states become more closely spaced (more dense).

→ Integer n varies from 1 (ground state) to higher integers (excited states) to ∞ (ionization).

→ Energies of H atom states vary from $-h\mathcal{R}(n = 1)$ to 0 ($n = \infty$). States with $E > 0$ are possible and correspond to an ionized atom in which the energy > 0 equals the kinetic energy of the electron.

1D.2 Atomic Orbitals (AOs)

- **Definition of AO**
  - → Wavefunction (Ψ, psi) describes an electron in an atom.
  - → Orbital (Ψ^2) holds 0, 1, or 2 electrons.
  - → Orbital can be viewed as a *cloud* within which the point density represents the *probability* of finding the electron at that point.
  - → Orbital is specified by *three* quantum numbers (n, ℓ, m_ℓ).
- **Wavefunction**
  - → Fills all space
  - → Depends on the *three* spherical coordinates: r, θ, ϕ
  - → Written as a product of a radial [$R(r)$] and an angular [$Y(\theta,\phi)$] wavefunction; mathematically, $\Psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$
- **Wavefunction for the H atom 2s orbital** → $n = 2$, $\ell = 0$, and $m_\ell = 0$

$$R(r) = \frac{\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}}{(2a_0)^{3/2}} \qquad Y(\theta,\phi) = (4\pi)^{-1/2} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = \left\{\begin{array}{c} 5.29177\times10^{-11}\ \text{m} \\ \text{(Bohr radius)} \end{array}\right\}$$

$$\text{Units: } R(r) = \text{m}^{-3/2} \qquad Y(\theta,\phi) = \text{none} \qquad a_0 = \frac{(\text{C}^2\cdot\text{N}^{-1}\cdot\text{m}^{-2})\,(\text{J}\cdot\text{s})^2}{\text{kg}\cdot\text{C}^2} = \text{m}$$

1D.3 Quantum Numbers, Shells, and Subshells

Three Quantum Numbers [n, ℓ, m_ℓ] Specify an Atomic Orbital

Symbol	Name	Allowed Values	Constraints
n	Principal quantum number	= 1, 2, 3, …	Positive integer
ℓ	Orbital angular momentum quantum number	= 0, 1, 2, … , $n-1$	Each value of n corresponds to n allowed values of ℓ.
m_ℓ	Magnetic quantum number	= ℓ, $\ell-1$, $\ell-2$, … ,$-\ell$ = 0, ±1, ±2, … , ±ℓ	Each value of ℓ corresponds to $(2\ell+1)$ allowed values of m_ℓ.

- → Quantum number n is related to the energy and "size" of the orbital.
- → Quantum number ℓ is related to the shape of the orbital.
- → Quantum number m_ℓ is related to the orientation of the orbital in space.

- **Terminology (nomenclature)**

  shell: AOs with the same n value

  subshell: AOs with the same n and ℓ values;

  ℓ = 0, 1, 2, 3 equivalent to s-, p-, d-, f-subshells, respectively, or

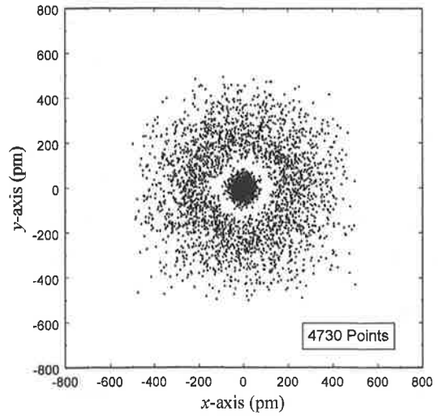
  s-orbital ⇒ $\ell = 0$ $m_\ell = 0$

  p-orbital ⇒ $\ell = 1$ $m_\ell = -1$, 0, or +1

  d-orbital ⇒ $\ell = 2$ $m_\ell = -2$, −1, 0, +1, or +2

  f-orbital ⇒ $\ell = 3$ $m_\ell = -3$, −2, −1, 0, +1, +2, or +3
- **Physical significance of the wavefunction $\psi(r,\theta,\phi)$**
  - → For all atoms and molecules, the square of the wavefunction, $\psi^2(r, \theta, \phi)$, is proportional to the probability of finding the electron at a point r, θ, ϕ. We can also regard $\psi^2(r, \theta, \phi)$ as the electron density at point r, θ, ϕ.
- **Plot of electron density for the 2*s*-orbital of hydrogen**

Computer-generated electron density dot diagram for the hydrogen atom 2s-orbital. The nucleus is at the center of the square and the density of dots is proportional to the probability of finding the electron. Notice the location of the spherical node.



- **Concept of AOs** → Two interpretations are useful:
  1. Visualize an AO as a *cloud of points,* with the density of points in a given volume proportional to the probability of finding the electron in that volume.
  2. Visualize an AO as a *surface* (boundary surface) within which there is a given probability of finding the electron. For example, the 95% boundary surface, within which the probability of finding an electron is 95%.

1D.4 The Shapes of Orbitals

- **Boundary surfaces** → *Shapes* of atomic orbitals

  s-orbital *spherical*

  p-orbital *dumbbell* or *peanut*

  d-orbital *four-leaf clover* or *dumbbell* with equatorial *torus* (doughnut)

- **Number and type of orbitals** → Follow from allowed values of quantum numbers

s-orbitals: *s* means that $\ell = 0$; if $\ell = 0$, then $m_\ell = 0$. So, for each value of n, there is *one* *s*-orbital.

one for each n : 1s, 2s, 3s, 4s, …

p-orbitals: *p* means that $\ell = 1$; if $\ell = 1$, then $m_\ell = -1, 0, +1$, and $n > 1$. So, for each value of $n > 1$, there are *three* *p*-orbitals, p_x, p_y, p_z.

three for each $n > 1$: $2p_x, 2p_y, 2p_z$; $3p_x, 3p_y, 3p_z$; …

The *np*-orbitals are referred to collectively as the 2p-orbitals, 3p-orbitals, and so on.

d-orbitals: d means that $\ell = 2$; if $\ell = 2$, then $m_\ell = -2, -1, 0, +1, +2$, and $n > 2$. So, for each value of $n > 2$, there are *five* d-orbitals, d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2}.

five for each $n > 2$: $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$, and $3d_{z^2}$; $4d_{xy}$, $4d_{xz}$, $4d_{yz}$, $4d_{x^2-y^2}$, and $4d_{z^2}$; …

The *n*d-orbitals are referred to collectively as the 3d-orbitals, 4d-orbitals, and so on.

- **Wavefunction Properties**

→ Positive and negative regions are designated as + and – on orbital diagrams

($n > 1$ (radial node), $\ell > 0$ (angular node))

→ Possess nodal surfaces defined by $\psi = 0$ (wavefunction changes sign).

Example: All 2p orbitals have positive and negative lobes separated by a nodal plane.

1D.5 Electron Spin

- **Spin states**

→ An electron has *two* spin states in an atom, represented as ↑ and ↓ **or** α and β.

→ In the atom, spin states are described by the spin magnetic quantum number, m_s

→ For any electron in an atom, only two values of m_s are allowed: $+\frac{1}{2}, -\frac{1}{2}$.

→ Spin is an intrinsic property of an electron. The spin quantum number for a free electron is given by $s = ½$.

1D.6 The Electronic Structure of Hydrogen

- **Degeneracy of orbitals**

In the H atom, orbitals in a given shell are *degenerate* (have the same energy).

For many-electron atoms, this is not true and the energy of a given orbital depends on n and ℓ.

- **Ground and excited states of H**

In the ground state, $n = 1$, and the electron is in the 1s-orbital. The first excited state corresponds to $n = 2$, and the electron occupies one of the *four* possible orbitals with $n = 2$ ($2s$, $2p_x$, $2p_y$, or $2p_z$). Similar considerations hold for higher excited states.

- **Ionization of H**

Absorption of a photon with energy ≥ $h\mathcal{R}$ ionizes the atom, creating a free electron and a free proton. Energy in excess of $h\mathcal{R}$ appears as kinetic energy of the system.

- **Summary**

The state of an electron in a H atom is defined by four quantum numbers $\{n, \ell, m_\ell, m_s\}$. As the value of n increases, the "size" of the H atom increases.

Topic 1E: MANY-ELECTRON ATOMS

1E.1 Orbital Energies

- **Many-electron atoms**

→ Atoms with more than one electron

→ Coulomb potential energy equals the sum of *nucleus-electron* **attractions** and *electron-electron* **repulsions**.

→ Schrödinger equation cannot be solved exactly.

→ Accurate wavefunctions are obtained numerically by using computers.

- **Variation of energy of orbitals**

→ For orbitals in the same shell but in different subshells, a combination of *nucleus-electron* attraction and *electron-electron* repulsion influences the orbital energies.

- **Shielding and penetration**

→ Qualitative understanding of orbital energies in atoms

- **Shielding**

→ Each electron in an atom is *attracted* by the nucleus and *repelled* by all the other electrons. In effect, each electron feels a *reduced* nuclear charge ($Z_{eff}\,e$ = effective nuclear charge). The electron in an occupied orbital is *shielded* to some extent from the nuclear charge and its energy is raised accordingly.

- **Penetration**

→ The **s-, p-, d-, … orbitals** have different shapes and different electron density distributions. For a given *shell* (same value of the principal quantum number n), **s-electrons** tend to be closer to the nucleus than **p-electrons**, which are closer than **d-electrons**. We say that, other things equal, **s-electrons** are more *penetrating* than **p-electrons**, and **p-electrons** are more *penetrating* than **d-electrons**.

Note: Shielding and penetration can be understood qualitatively on the basis of the nucleus-electron potential energy term: $-(Ze)e/4\pi\varepsilon_0 r$, where Ze is the nuclear charge and r the nucleus-electron distance. *Shielded* electrons have the equivalent of a reduced Z value ($Z_{eff} < Z$) and therefore

higher energy; *penetrating* electrons have the equivalent of a reduced value of r and therefore *lower* energy.

- **Review**
  - → Z has three equivalent meanings:
    Nuclear charge (actually, Ze)
    Atomic number
    Number of protons in the nucleus
- **Consequences of *shielding* and *penetration* in many-electron atoms**
  - → Orbitals with the same n and different ℓ values have *different* energies.
  - → For a given *shell* (n), *subshell* energies *increase* in the order: $ns < np < nd < nf$.
    Example: A 3s-electron is lower in energy than a 3p-electron, which is lower than a 3d-electron.
  - → Orbitals within a given *subshell* have the *same* energy.
    Example: The five 3d-orbitals are degenerate for a given atom.
  - → *Penetrating* orbitals of higher shells may be lower in energy than less *penetrating* orbitals of lower shells.
    Example: A penetrating 4s-electron may be lower in energy than a less penetrating 3d-electron.

1E.2 The Building-Up Principle

- **Pauli exclusion principle**
  - → No more than *two* electrons per orbital
  - → *Two* electrons occupying a single orbital must have paired spins: ↑↓
  - → *Two* electrons in an atom may *not* have the same *four* quantum numbers.
- **Terminology**

closed shell:	Shell with maximum number of electrons allowed by the exclusion principle
valence electrons:	Electrons in the outermost occupied shell of an atom; they occupy the shell with the largest value of n and are used to form chemical bonds.
electron configuration:	List of all occupied *subshells* or *orbitals*, with the number of electrons in each indicated as a numerical superscript. **Example:** Li: $1s^2 2s^1$.

- **Building-Up (*Aufbau*) Principle**
  - → Order in which electrons are added to *subshells* and *orbitals* to yield the *electron configuration* of atoms
  - → **The ($n + \ell$) rule:** Order of filling subshells in *neutral atoms* is determined by filling those with the *lowest* values of ($n + \ell$) first. Subshells in a group with the same value of ($n + \ell$) are filled in the order of increasing n (*topic not covered in the text*).
- **Usual filling order of subshells ($n + \ell$ rule):** $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < \ldots$

Note: Ionization or subtle differences in shielding and penetration can change the order of the energy of subshells. *Thus, energy ordering of subshells is not fixed absolutely, but may vary from atom to atom or from an atom to its ion.*

- **Orbitals within a subshell**
  - → Hund's rule
  - → Electrons add to *different* orbitals of a subshell with spins *parallel* until the subshell is half full.
- **Applicability**
  - → The building-up principle in combination with the *Pauli exclusion principle* and *Hund's rule* accounts for the *ground-state* electron configurations of atoms.
  - → The principle is generally valid, **but there are exceptions** (see the periodic table on SG page 14).

Topic 1F: Periodicity

1F.1 The General Structure of the Periodic Table

- **Order of filling subshells**
  - → Understanding the organization of the periodic table
  - → Straightforward determination of (most) electron configurations
- **Terminology** → See the following two tables

Groups:	Columns in the periodic table, labeled 1–18 horizontally
s-block elements:	Groups 1, 2; s-subshell fills
p-block elements:	Groups 13–18; p-subshell fills
d-block elements:	Groups 3–12; d-subshell fills
Transition elements:	Groups 3–11; d-subshell fills
Main-group elements:	Groups 1, 2 and 13–18
Lanthanides:	4f-subshell fills
Actinides:	5f-subshell fills

Note: A transition element has a partially filled d-subshell either as the element or in any commonly occurring oxidation state. Thus, Zn, Cd, and Hg with completely filled d-subshells are not transition elements. The $(n-1)$d electrons of the d-block elements are considered to be valence electrons. Groups 1, 2, and 13–18 are alternatively labeled with Roman numerals I–VIII, which correspond to the number of valence electrons in the element.

Valence shell:	Outermost occupied shell (highest n)
Period:	Row of the periodic table
Period number:	Principal quantum number of valence shell
Period 1:	H, He; 1s-subshell fills
Period 2:	Li through Ne; 2s-, 2p-subshells fill
Period 3:	Na through Ar; 3s-, 3p-subshells fill
Period 4:	K through Kr; 4s-, 3d-, 4p-subshells fill

- **Periodic table** → Two forms are displayed (one below, the other on the next page):
  The one below shows the elements, the other shows the *final* subshell filled.
  Look at the tables to understand the terminology.

Periodicity of Elements in the Periodic Table

Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	*Cr*	Mn	Fe	Co	Ni	*Cu*	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	*Nb*	*Mo*	Tc	*Ru*	*Rh*	***Pd***	*Ag*	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	*Pt*	*Au*	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
Lanthanides			*La*	*Ce*	Pr	Nd	Pm	Sm	Eu	*Gd*	Tb	Dy	Ho	Er	Tm	Yb		
Actinides			*Ac*	***Th***	*Pa*	*U*	*Np*	Pu	Am	*Cm*	Bk	Cf	Es	Fm	Md	No		

- **Electron configurations of the elements** → See the Appendix section on *Ground-State Electron Configurations* in the text.

- **17 italicized elements**
  → Exceptions to the $(n+\ell)$ rule
  → Differ by the placement of *one* electron
  Example: Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ = [Ar] $4s^1 3d^5$ (not [Ar] $4s^2 3d^4$ as might be expected)

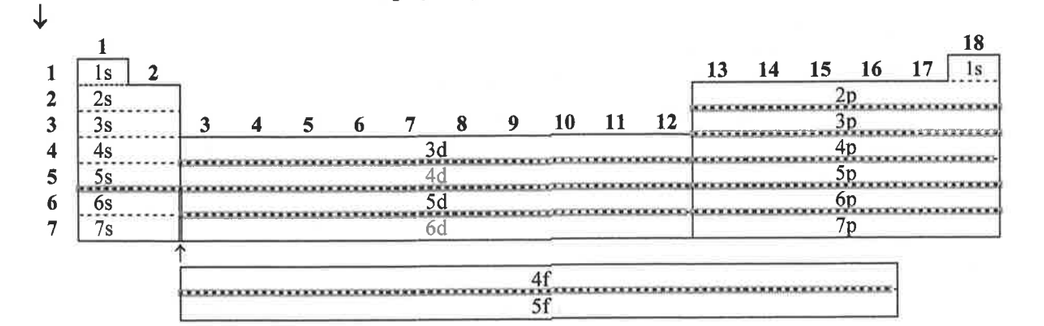
- **2 bold, italicized elements**
  → Differ by the placement of *two* electrons (Pd, Th)
  → **Pd** We expect [Kr] $4d^8 5s^2$, but *actually* find [Kr] $4d^{10}$ with *no* 5s-subshell electrons.
  → **Th** We expect [Rn] $5f^2 7s^2$, but *actually* find [Rn] $6d^2 7s^2$ with *no* 5f-subshell electrons.

- **Recently named elements**
  → **Rg** = Roentgenium ($Z = 111$) [in honor of Wilhelm Röntgen (Roentgen)]
  → **Cn** = Copernicium ($Z = 112$) [in honor of Nicolaus Copernicus]
  → **Fl** = Flerovium ($Z = 114$) [in honor of Georgiy Flerov (1913-1990), a Russian physicist]
  → **Lv** = Livermorium ($Z = 116$) [in honor of the Lawrence Livermore Lab]

  Note: **Cn** was originally given the symbol **Cp**, but that symbol was previously associated with the name *cassiopeium*, now know as lutetium (Lu). The symbol Cp is also used in organometallic chemistry to denote the cyclopentadienyl ligand. For these reasons, IUPAC disallowed the use of Cp as a future element symbol.

  Note: There is evidence for the existence of certain isotopes of Elements 113, 115, 117, and 118. The claims require ratification.

Order of Filling Subshells in the Periodic Table



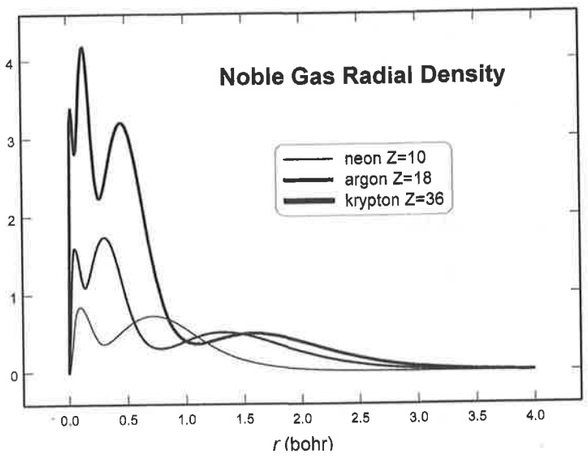
1F.2 Atomic Radius (r)

- **Definition of atomic radius**
  → Half the distance between the centers of neighboring atoms (nuclei).
  → For metallic elements, r is determined for the solid.
  Example: For solid Zn, 274 pm between nuclei, so r (atomic radius) = 137 pm
  → For nometallic elements, r is determined for diatomic molecules (covalent bond).
  Example: For I_2 molecules, 266 pm between nuclei, so r (covalent radius) = 133 pm

- **General trends in radius with atomic number**
  - → r decreases from *left* to *right* across a period (*effective* nuclear charge increases)
  - → r increases from *top* to *bottom* down a group (change in valence electron principal quantum number and size of valence shell)

Note: The atomic radius of noble-gas atoms can be obtained from low-temperature solids (high pressure for helium). These atoms are held together by weak, van der Waals forces (Focus 6), so their size defined in this way is actually *larger* than the covalent radius of the neighboring halogen atom. There are other definitions of size. If *all* atomic sizes are defined from *atomic wavefunctions*, then each noble-gas atom is *smaller* than its neighboring halogen atom.

- **Spatial plot of atomic wavefunctions for several noble gas atoms ($r^2\psi^2$)**



Notes:

Radial density $\propto r^2\psi^2$

1 bohr = $a_0 \approx 52.9$ pm

Observe the appearance of shell structure.

Note: Kr has the highest curve due to its greater noble gas radial density, followed by Ar and then Ne. The "size" of the atom is given by the most probable value of r for the valence shell.

1F.3 Ionic Radius

- **An ion's share of the distance between neighbors in an ionic solid (cation to anion)**
  - → Distance between the nuclei of a neighboring cation and anion is the sum of two ionic radii
  - → Radius of the oxide anion (O^{2-}) is 140 pm.

    Example: Distance between Zn and O nuclei in zinc oxide is 223 pm; therefore, the ionic radius of Zn^{2+} is 83 pm [$r(Zn^{2+}) = 223\text{ pm} - r(O^{2-})$].
  - → Cations are **smaller** than parent atoms, for example, Zn (133 pm) and Zn^{2+}(83 pm).
  - → Anions are **larger** than parent atoms, for example, O (66 pm) and O^{2-}(140 pm).
- **Isoelectronic atoms and ions**
  - → Atoms and ions with the same number of electrons

    Example: Cl^-, Ar, K^+, and Ca^{2+}

1F.4 Ionization Energy (I)

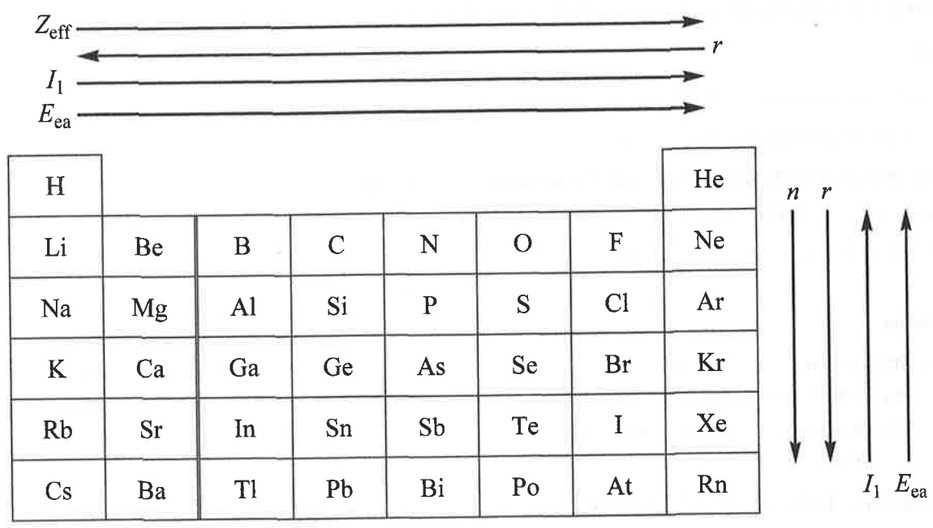
- I
  - → Energy needed to remove an electron from a gas-phase atom in its lowest energy state.
- **Symbol**
  - → Number subscripts (*e.g.*, I_1, I_2) denote removal of successive electrons. For a given species, $I_2 > I_1$ always.
- **General periodic table trends in I_1 for the main-group elements**
  - → Increases from *left* to *right* across a period (Z_{eff} increases)
  - → Decreases from *top* to *bottom* down a group (increase in principal quantum number n of valence electron)
- **Exceptions**
  - → For Groups 2 and 15 in Periods 2–4, I_1 is *larger* than the neighboring *main group element* in Groups 13 and 16, respectively. Repulsions between electrons in the same orbital and/or extra stability of completed and half completed subshells are responsible for these exceptions to the general trends.
- **Metals toward the lower left of the periodic table (e.g., Cs, Ba)**
  - → Have low ionization energies.
  - → Readily lose electrons to form cations.
- **Nonmetals toward the upper right of the periodic table (e.g., F, O)**
  - → Have high ionization energies.
  - → Do not readily lose electrons.

1F.5 Electron Affinity (E_{ea})

- **Energy *released* when an electron is *added* to a gas-phase atom**
- **Periodic table trends in E_{ea} for the main-group elements**
  - → Increases from *left* to *right* across a period. (Z_{eff} increases)
  - → Decreases from *top* to *bottom* down a group. (increase in principal quantum number n of valence electron)
  - → Generally, the same as for I_1 with the major exceptions displayed in **Figure 1F.12**
- **Summary of trends in r, I_1, and E_{ea}**
  - → All depend on Z_{eff} and n of outer subshell electrons.
  - → Recall that there are *many* exceptions to the general trends.

    Example: For electron affinity, the value for N is actually less than that for O.
  - → The diagram on the next page indicates the general behavior of the three properties (r, I_1, and E_{ea}) with respect to both Z_{eff} and n (exceptions ignored, many in the case of electron affinity). The wavefunction definition for atomic size is used if noble gas atoms are included.

Main-Group Elements in the Periodic Table



1F.6 The Inert-Pair Effect

- **Tendency to form ions two units lower in charge than expected from the group number relation**
  - → Most pronounced in p-block elements near the bottom of the groups
  - → Due in part to the different energies of the valence p- and s-electrons
  - → Important for the *heavier* two members of Groups 13, 14, and 15; for example, Pb(IV) & Pb (II) or Sb(V) & Sb(III)
  - → Valence s-electrons are called a "lazy pair."

1F.7 Diagonal Relationships

- **Diagonally related pairs of main-group elements often show similar chemical properties.**
  - → Diagonal band of metalloids dividing metals from nonmetals
  - → Similarity of Li and Mg (react directly with N_2 to form nitrides, N^{3-})
  - → Similarity of Be and Al (both react with acids and bases)

1F.8 The General Properties of the Elements

- **s-block elements (Groups 1 and 2)**
  - → All are reactive metals (except H); they form *basic* oxides (O^{2-}), peroxides (O_2^{2-}), or superoxides (O_2^-).
- **Compounds of s-block elements are ionic, except for beryllium.**

Notes: *Hydrogen* (a nonmetal) is placed by itself, or *more usually* in Group 1, because its electronic configuration ($1s^1$) is similar to those of the alkali metals: [noble gas] ns^1.

Helium, with electronic configuration $1s^2$, is placed in Group 18 because its properties are similar to those of neon, argon, krypton, and xenon, all with filled subshells.

- **p-block elements (Groups 13–18)**
  - → Members are metals, metalloids, and nonmetals.

Metals: Group 13 (Al, Ga, In, Tl); Group 14 (Sn, Pb); Group 15 (Bi)

Note: These metals have relatively low I_1, but *larger* than those of the *s* block and *d* block.

Metalloids: Group 13 (B); Group 14 (Si, Ge); Group 15 (As, Sb); Group 16 (Te, Po)

Note: Metalloids have the *physical* appearance and properties of *metals* but behave *chemically* as *nonmetals*.

Nonmetals: Group 14 (C); Group 15 (N, P); Group 16 (O, S, Se); Groups 17 & 18 (All)

Notes: High E_{ea} in Groups 13–17; these atoms tend to *gain* electrons to complete their subshells.

Group 18 noble-gas atoms are generally *nonreactive*, except for Kr and Xe, which form a few compounds.

- **d-block elements (Groups 3–12)**
  - → All are metals (*most* are transition metals), with properties intermediate to those of s-block and p-block metals.

Note: *All* Group 12 cations retain the filled d-subshell. For this reason, these elements (Zn, Cd, Hg) are *not* classified as transition metals. Recall that in this text d-orbital electrons are considered to be valence electrons for *all* the d-block elements.

- **Transition metals**
  - → Form compounds with a variety of oxidation states (oxidation numbers)
  - → Form alloys
  - → Facilitate subtle changes in organisms
- **f-block elements (lanthanides and actinides)**
  - → Rare on Earth
  - → Lanthanides are incorporated in *superconducting* materials.
  - → Lanthanides are used in electronic devices such as plasma TVs, disk drives, and mobile phones.
  - → Actinides are all *radioactive* elements, most do not occur naturally on Earth.