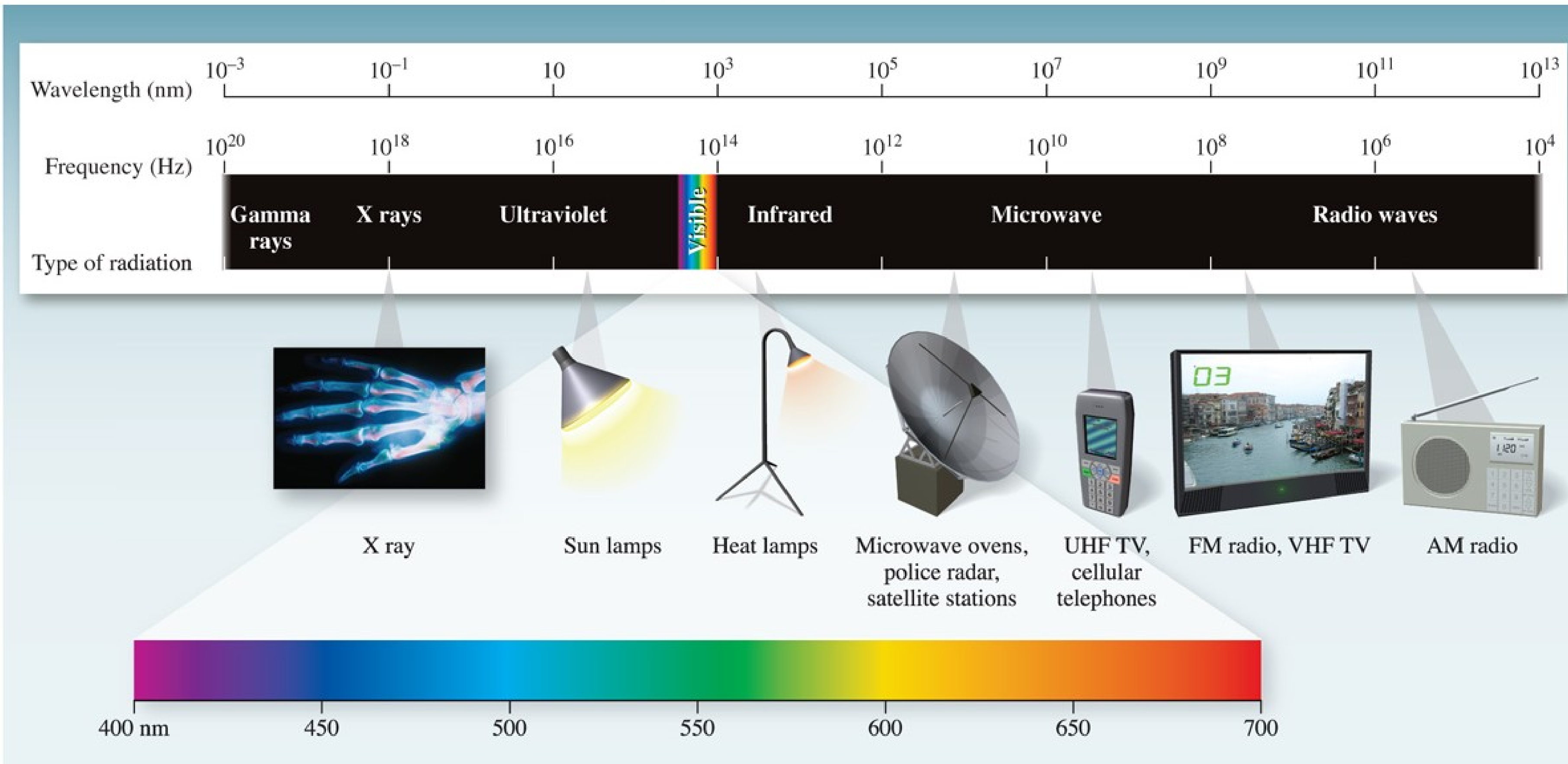
Chapter 6

Quantum Theory and the Electronic Structure of Atoms

6.1 The Nature of Light

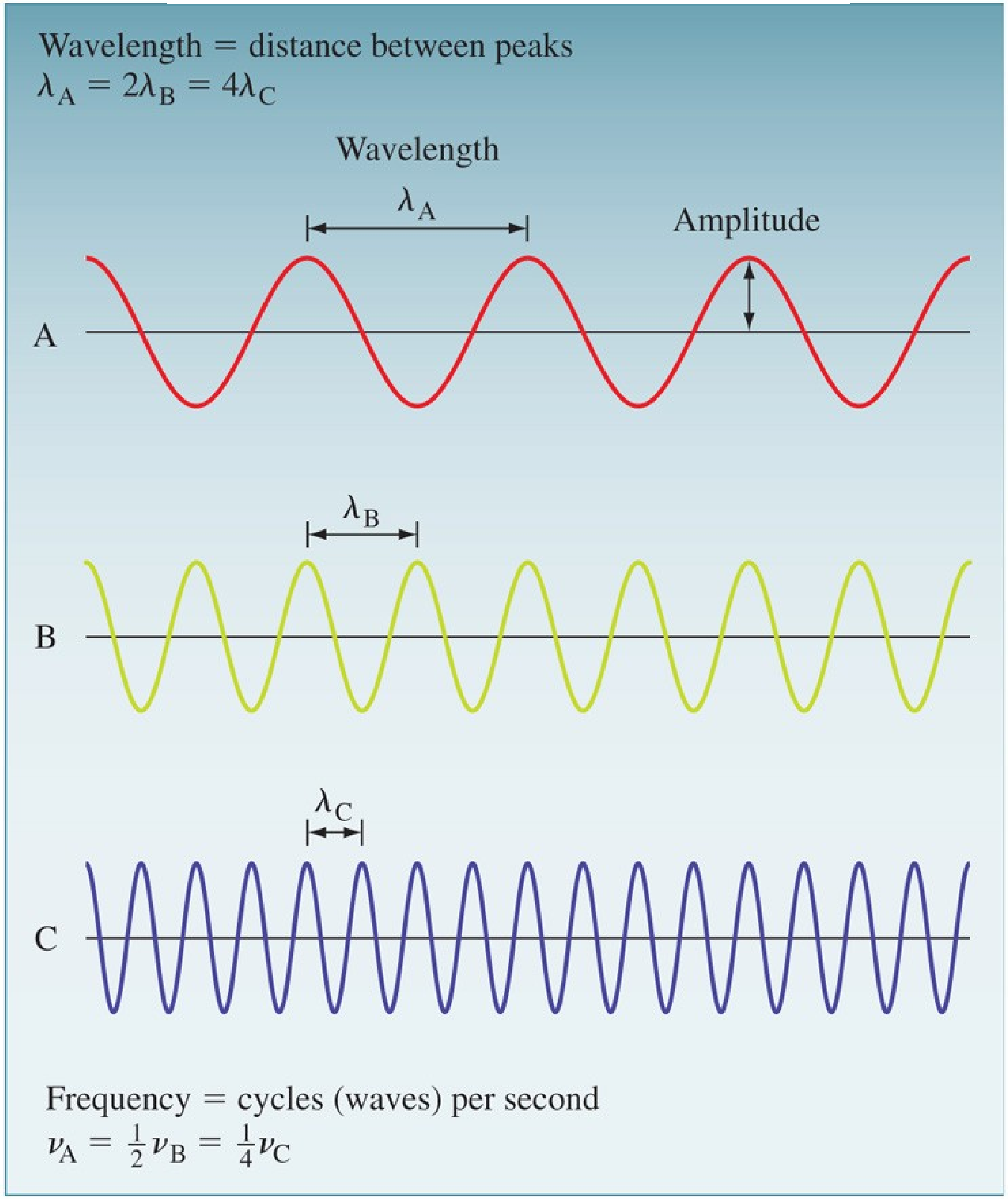
- The electromagnetic spectrum includes many different types of radiation.
- Visible light accounts for only a small part of the spectrum
- Other familiar forms include: radio waves, microwaves, X rays
- All forms of light travel in waves

Electromagnetic Spectrum



Wave Characteristics

- **Wavelength**: λ (lambda) distance between identical points on successive waves…peaks or troughs
- **Frequency**:ν (nu) number of waves that pass a particular point in one second
- **Amplitude**: the vertical distance from the midline of waves to the top of the peak or the bottom of the trough


Wavelength = distance between peaks
$\lambda_A = 2\lambda_B = 4\lambda_C$
Wavelength
λ_A
Amplitude
A
λ_B
B
λ_C
C
Frequency = cycles (waves) per second
$\nu_A = \frac{1}{2}\nu_B = \frac{1}{4}\nu_C$

Wave Characteristics

- Wave properties are mathematically related as:

$$c = \lambda\nu$$

where

c = 2.99792458 x 10^8 m/s (speed of light)

λ = wavelength (in meters, m)

ν = frequency (reciprocal seconds, s^{-1})

Wave Calculation

The wavelength of a laser pointer is reported to be 663 nm. What is the frequency of this light?

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The wavelength of a laser pointer is reported to be 663 nm. What is the frequency of this light?

$$\upsilon = \frac{c}{\lambda}$$

$$\lambda = 663\,\text{nm} \times \frac{10^{-9}\,\text{m}}{\text{nm}} = 6.63 \times 10^{-7}\,\text{m}$$

$$\upsilon = \frac{3.00 \times 10^{8}\,\text{m/s}}{6.63 \times 10^{-7}\,\text{m}} = 4.52 \times 10^{14}\,\text{s}^{-1}$$

Your Turn!

Calculate the wavelength of light, in nm, of light with a frequency of $3.52 \times 10^{14}\ s^{-1}$.

Calculate the wavelength of light, in nm, of light with a frequency of 3.52×10^{14} s^{-1}.

$$\lambda = \frac{c}{\upsilon}$$

$$\lambda = \frac{3.00 \times 10^{8}\,\text{m/s}}{3.52 \times 10^{14}\,\text{s}^{-1}} = 8.52 \times 10^{-7}\,\text{m}$$

$$\lambda = 8.52 \times 10^{-7}\,\text{m} \times \frac{10^{9}\,\text{nm}}{\text{m}} = 852\,\text{nm}$$

6.2 Quantum Theory

- 1900 - Max Planck
- Radiant energy could only be emitted or absorbed in discrete quantities
- Quantum: packets of energy
- Correlated data from blackbody experiment to his quantum theory
- Revolutionized way of thinking (energy is quantized)

Quantum Theory

- Energy of a single quantum of energy

$$E = h\upsilon$$

where

E = energy (in Joules)

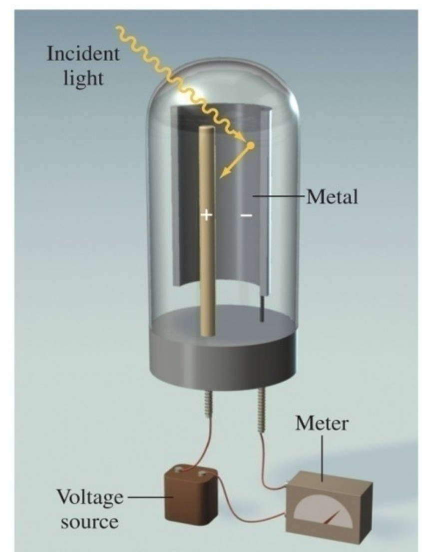
h = Planck's constant 6.63×10^{-34} J $\cdot$ s

ν = frequency

Photoelectric Effect

- Electrons ejected from a metal's surface when exposed to light of certain frequency
- Einstein proposed that particles of light are really **photons** (packets of light energy) and deduced that

$$E_{\text{photon}} = h\nu$$



- Only light with a frequency of photons such that $h\nu$ equals the energy that binds the electrons in the metal is sufficiently energetic to eject electrons.
- If light of higher frequency is used, electrons will be ejected and will leave the metal with additional kinetic energy.
  - (what is the relationship between energy and frequency?)
- Light of at least the threshold frequency **and** of greater *intensity* will eject *more* electrons.

Calculate the energy (in joules) of a photon with a wavelength of 700.0 nm

Calculate the energy (in joules) of a photon with a wavelength of 700.0 nm

$$\lambda = 700.0\,\text{nm} \times \frac{10^{-9}\,\text{m}}{\text{nm}} = 7.00 \times 10^{-7}\,\text{m}$$

$$\upsilon = \frac{3.00 \times 10^{8}\,\text{m/s}}{7.00 \times 10^{-7}\,\text{m}} = 4.29 \times 10^{14}\,\text{s}^{-1}$$

$$E = (6.63 \times 10^{-34}\,\text{J} \cdot \text{s})(4.29 \times 10^{14}\,\text{s}^{-1})$$

$$E = 2.84 \times 10^{-19}\,\text{J}$$

Your Turn!

Calculate the wavelength (in nm) of light with energy 7.85×10^{-19} J per photon. In what region of the electromagnetic radiation does this light fall?

Calculate the wavelength (in nm) of light with energy 7.83 x 10^{-19} J per photon. In what region of the electromagnetic radiation does this light fall?

$$\upsilon = \frac{7.83\times10^{-19}\,\mathrm{J}}{6.63\times10^{-34}\,\mathrm{J\cdot s}} = 1.18\times10^{15}\,\mathrm{s}^{-1}$$

$$\lambda = \frac{3.00\times10^{8}\,\mathrm{m\cdot s^{-1}}}{1.18\times10^{15}\,\mathrm{s}^{-1}} = 2.53\times10^{-7}\,\mathrm{m}\quad \text{or } 253\,\mathrm{nm}$$

Ultraviolet region

Photoelectric Effect

- Dilemma caused by this theory - is light a wave or particle?
- Conclusion: Light must have particle characteristics as well as wave characteristics

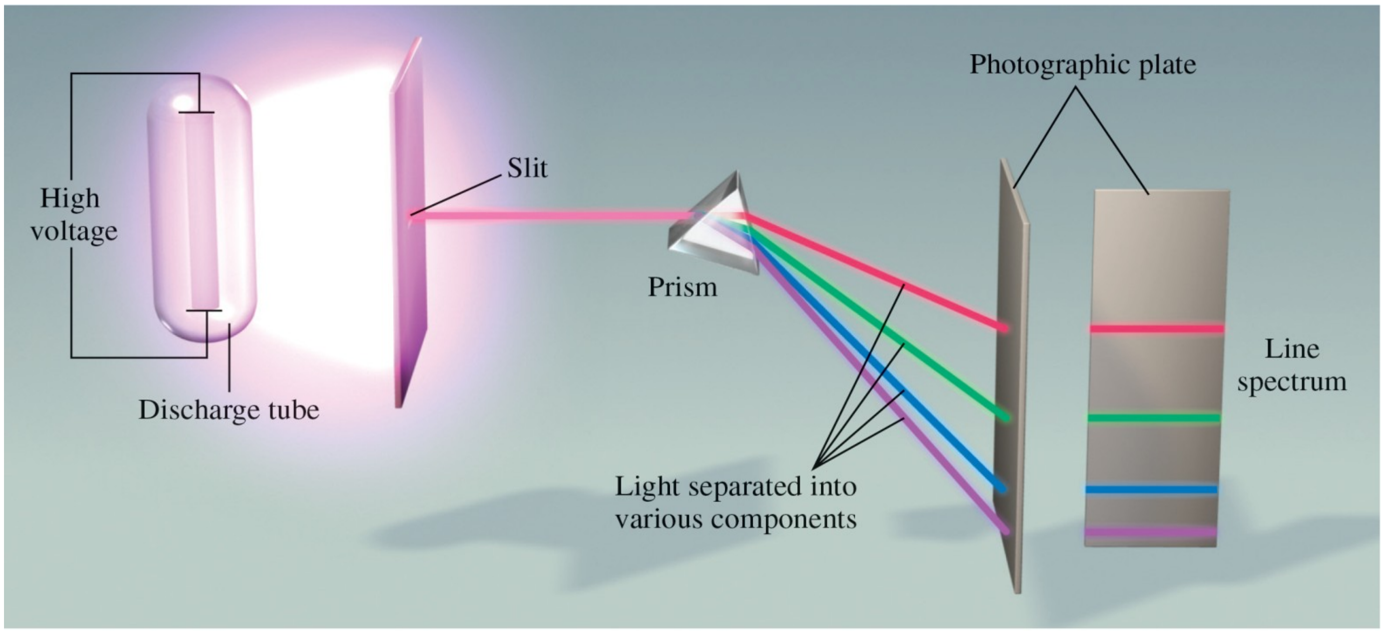
6.3 Bohr's Theory of the Hydrogen Atom

- Planck's theory along with Einstein's ideas not only explained the photoelectric effect, but also made it possible for scientists to unravel the idea of atomic line spectra

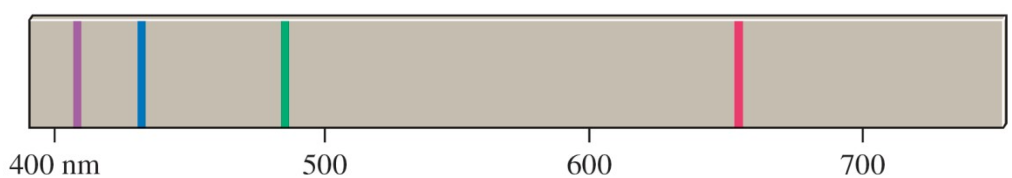
Atomic Line Spectra

- ***Line spectra***: emission of light only at specific wavelengths
- Every element has a unique emission spectrum
- Often referred to as “fingerprints” of the element

Atomic Line Spectra

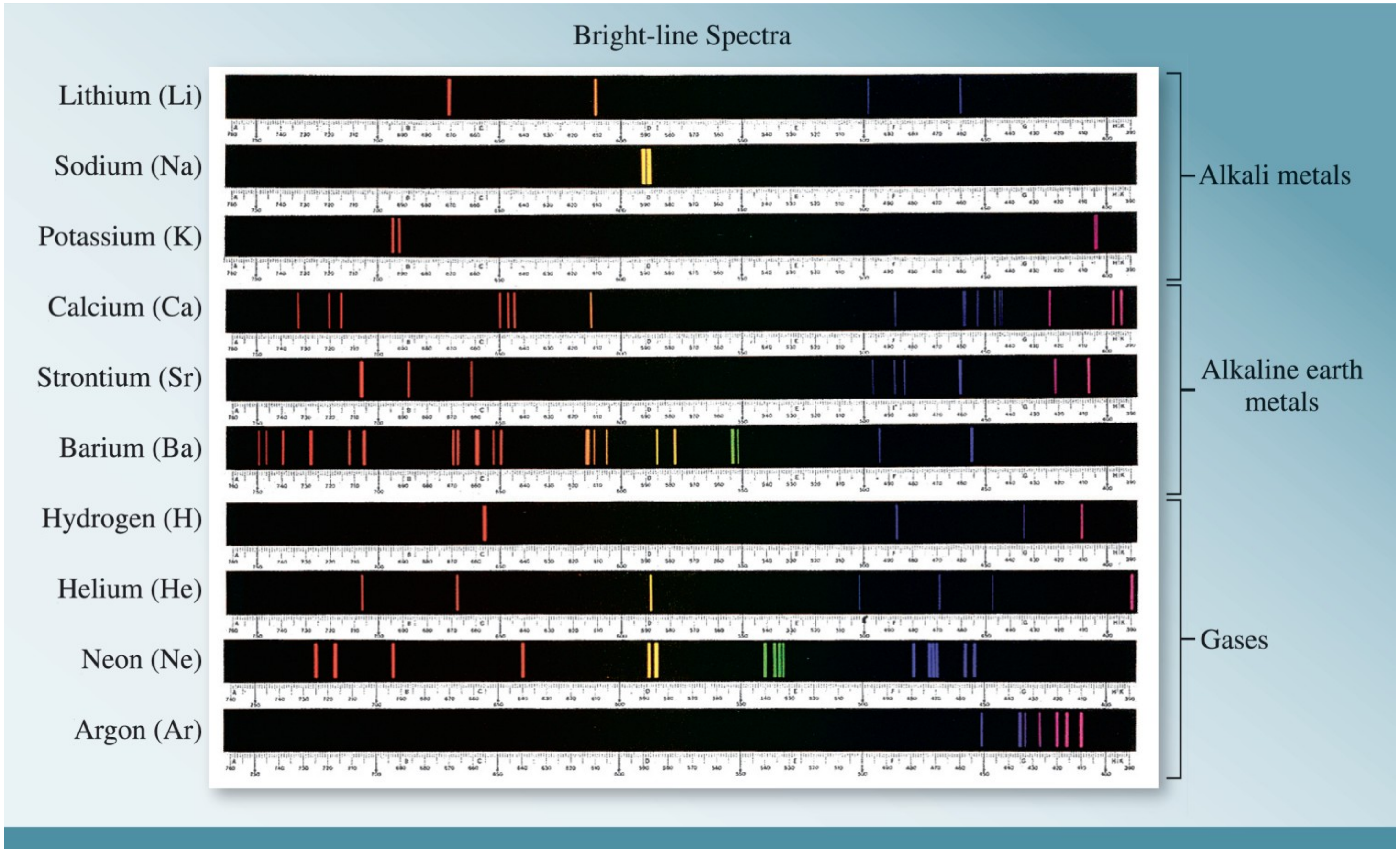


(a)



(b)

Bright-line Spectra



Line Spectra of Hydrogen

- The *Rydberg equation*:

$$\frac{1}{\lambda} = R_{\infty}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- Balmer (initially) and Rydberg (later) developed the equation to calculate all spectral lines in hydrogen

Line Spectra of Hydrogen

- Bohr's contribution:

  showed only valid energies for hydrogen's electron with the following equation

$$E_n = 2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{n^2}\right)$$

Line Spectra of Hydrogen

- As the electron gets closer to the nucleus, E_n becomes larger in absolute value but also more negative.
- Ground state: the lowest energy state of an atom
- Excited state: each energy state in which $n > 1$

Line Spectrum of Hydrogen

- Each spectral line corresponds to a specific transition
- Electrons moving from ground state to higher states require energy; an electron falling from a higher to a lower state releases energy
- Bohr's equation can be used to calculate the energy of these transitions within the H atom

Energy Transitions

Calculate the energy needed for an electron to move from $n = 1$ to $n = 4$.

Energy Transitions

Calculate the energy needed for an electron to move from n = 1 to n = 4.

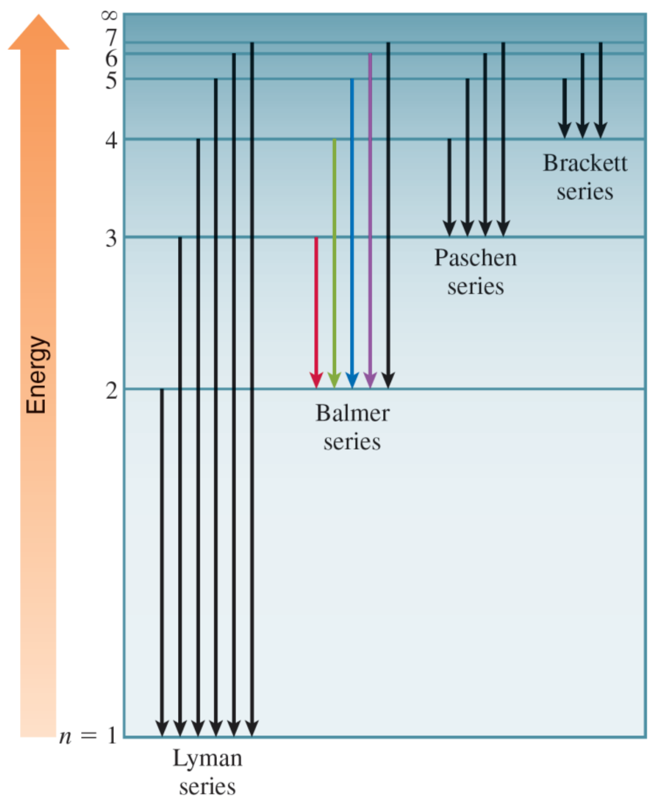
$$\Delta E = 2.18\times10^{-18}\,\mathrm{J}\left(\frac{1}{4^2}-\frac{1}{1^2}\right)$$

$$\Delta E = 2.04\times10^{-18}\,\mathrm{J}$$

Note: final – initial levels

TABLE 6.1 Emission Series in the Hydrogen Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared



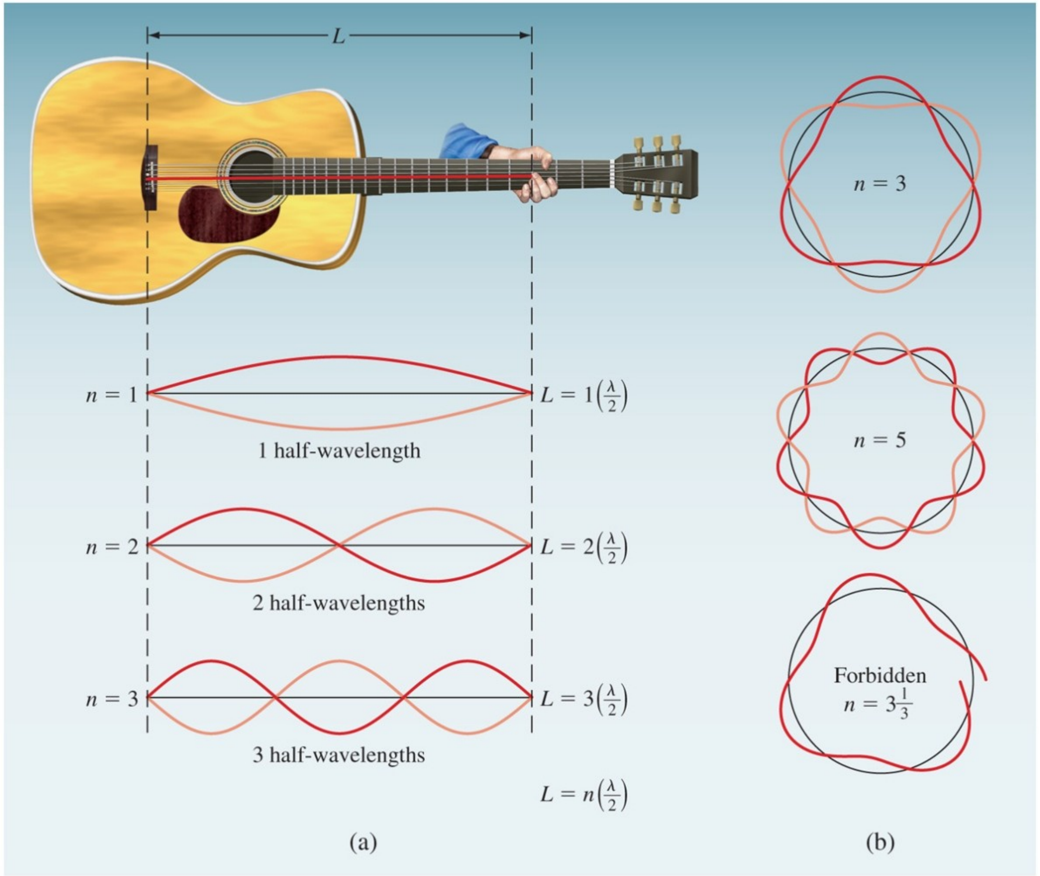
6.4 Wave Properties of Matter

- Bohr could not explain why electrons were restricted to fixed distances around the nucleus
- Louis de Broglie (1924) reasoned that if energy (light) can behave as a particle (photon) then perhaps particles (electrons) could exhibit wave characteristics

Wave Properties of Matter

- De Broglie proposed that electrons in atoms behave as standing waves (like the wave created when a guitar string is plucked)
- There are some points called nodes (where the wave exhibits no motion at all)

Wave Properties of Matter



Wave Properties of Matter

- De Broglie's idea of particle and wave properties are related by the following

$$\lambda = \frac{h}{mu}$$

where λ = wavelength

m = mass (kg)

u = velocity (m/s)

Calculate the de Broglie wavelength of the "particle" in the following two cases:

A 25.0 g bullet traveling at 612 m/s

An electron (mass = 9.109×10^{-31}kg) moving at 63.0 m/s

Note: 1 Joule = 1 kg $\cdot$ m^2/s^2

A 25.0 g bullet traveling at 612 m/s

$$\lambda = \frac{6.63\times10^{-34}\text{kg}\cdot\text{m}^2/\text{s}}{(0.025\text{ kg})(612\text{ m/s})} = 4.3\times10^{-35}\text{ m}^*$$

An electron (mass = 9.109 x 10^{-31} kg) moving at 63.0 m/s

$$\lambda = \frac{6.63\times10^{-34}\text{kg m}^2/\text{s}}{(9.109\times10^{-31}\text{ kg})(63.0\text{ m/s})} = 1.16\times10^{-5}\text{ m}$$

* Wavelengths of macroscopic particles are imperceptibly small and really have no physical significance.

6.5 Quantum Mechanics

- Scientists yearned to understand exactly where electrons are in an atom.
- Heisenberg's uncertainty principle mathematically described the position and velocity of an electron. The more you know about one, the less you are sure about the other quantity.

Quantum Mechanics

- Heisenberg's equation disproved Bohr's model of defined orbits for electrons
- Bohr's theory did not provide a clear description
- Erwin Schrödinger, derived a complex mathematical formula to incorporate wave and particle characteristics

Quantum Mechanics

- Quantum mechanics (wave mechanics)
- Does not allow us to specify exact location of electrons, we can predict high probability of finding an electron
- Use the term atomic orbital instead of “orbit” to describe the electron’s position within the atom

6.6 Quantum Numbers

- Each atomic orbital in an atom is characterized by a unique set of three quantum numbers (from Schrödinger's wave equation)
- n, l, and m_l

Quantum Numbers

- ***Principal quantum number*** **(*n*)** - designates size of the orbital
- **Integer values**: 1,2,3, and so forth
- The larger the "*n*" value, the greater the average distance from the nucleus
- Correspond to quantum numbers in Bohr's model

Quantum Numbers

- ***Angular momentum quantum number*** **(*l*)** - describes the shape of the atomic orbital
- **Integer values**: 0 to $n - 1$
- 0 = *s* sublevel; 1 = *p*; 2 = *d*; 3 = *f*

Quantum Numbers

- ***Magnetic quantum number*** **(m_l)** - describes the orientation of the orbital in space (think in terms of *x*, *y* and *z* axes)
- **Integer values**: – l to 0 to + l

Quantum Numbers

TABLE 6.2	Allowed Values of the Quantum Numbers n, ℓ, and m_ℓ		
When n is	**ℓ can be**	**When ℓ is**	**m_ℓ can be**
1	only 0	0	only 0
2	0 or 1	0 1	only 0 -1, 0, or $+1$
3	0, 1, or 2	0 1 2	only 0 -1, 0, or $+1$ -2, -1, 0, $+1$, or $+2$
4	0, 1, 2, or 3	0 1 2 3	only 0 -1, 0, or $+1$ -2, -1, 0, $+1$, or $+2$ -3, -2, -1, 0, $+1$, $+2$, or $+3$
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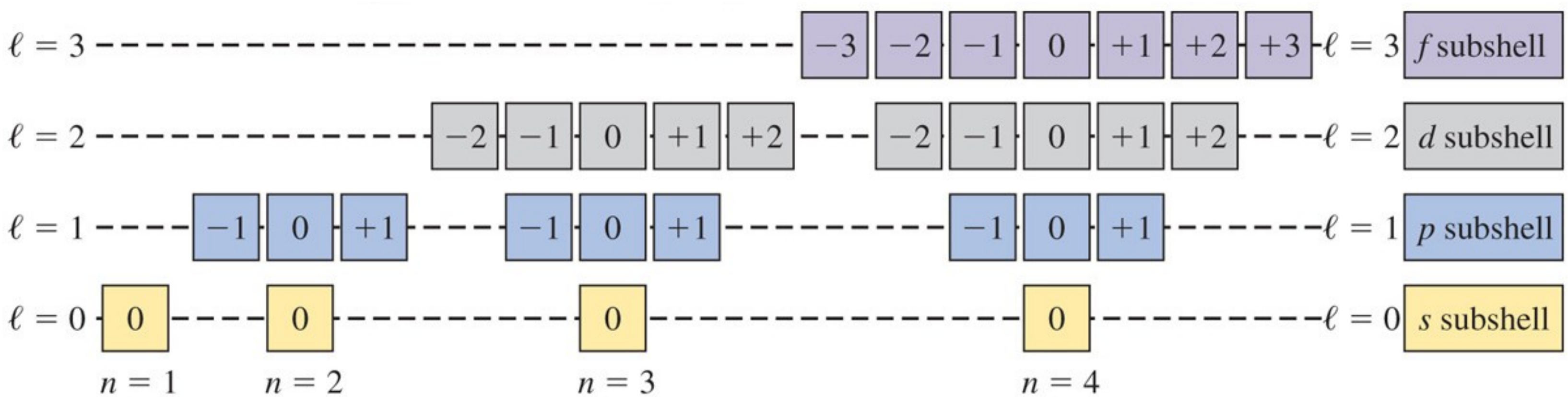
.	.	.	.
.	.	.	.

Quantum Numbers



Quantum Numbers

- ***Electron spin quantum number*** **(m_s)** - describes the spin of an electron that occupies a particular orbital
- **Values**: +1/2 or –1/2
- Electrons will spin opposite each other in the same orbital

Quantum Numbers

Which of the following are possible sets of quantum numbers?

a) 1, 1, 0, +1/2

b) 2, 0, 0, +1/2

c) 3, 2, –2, –1/2

Quantum Numbers

Which of the following are possible sets of quantum numbers?

a) 1, 1, 0, +1/2 l value not possible

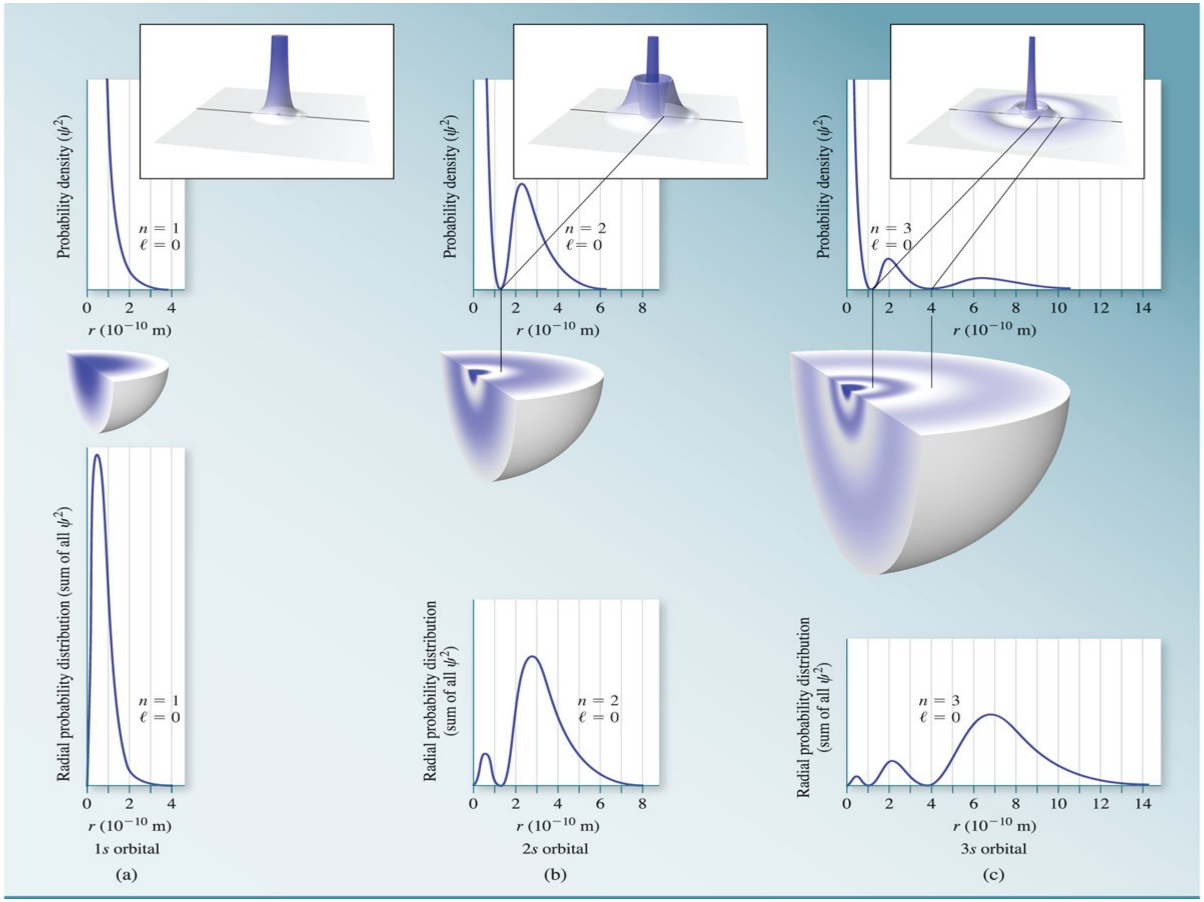
b) 2, 0, 0, +1/2 possible

c) 3, 2, –2, –1/2 possible

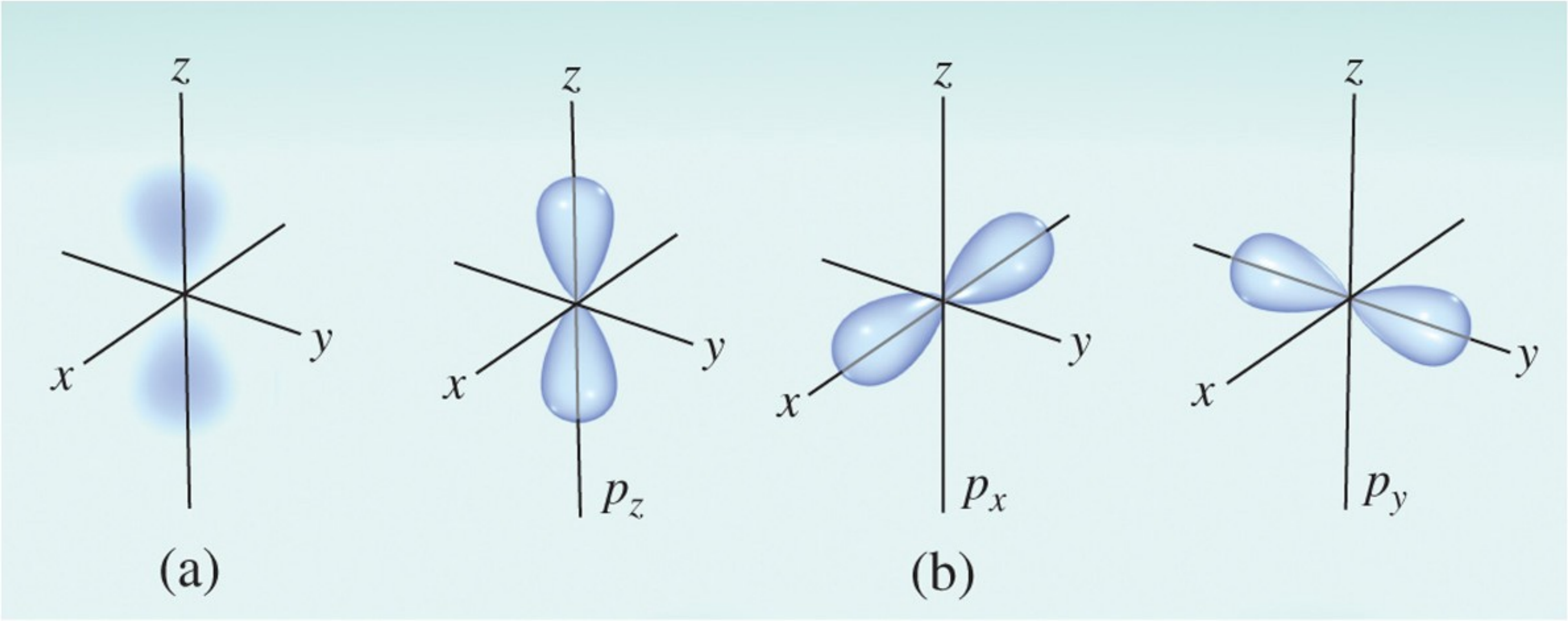
6.7 Atomic Orbitals

- "Shapes" of atomic orbitals
- "*s*" orbital - spherical in shape
- "*p*" orbitals - two lobes on opposite sides of the nucleus
- "*d*" orbitals - more variations of lobes
- "*f*" orbitals - complex shapes

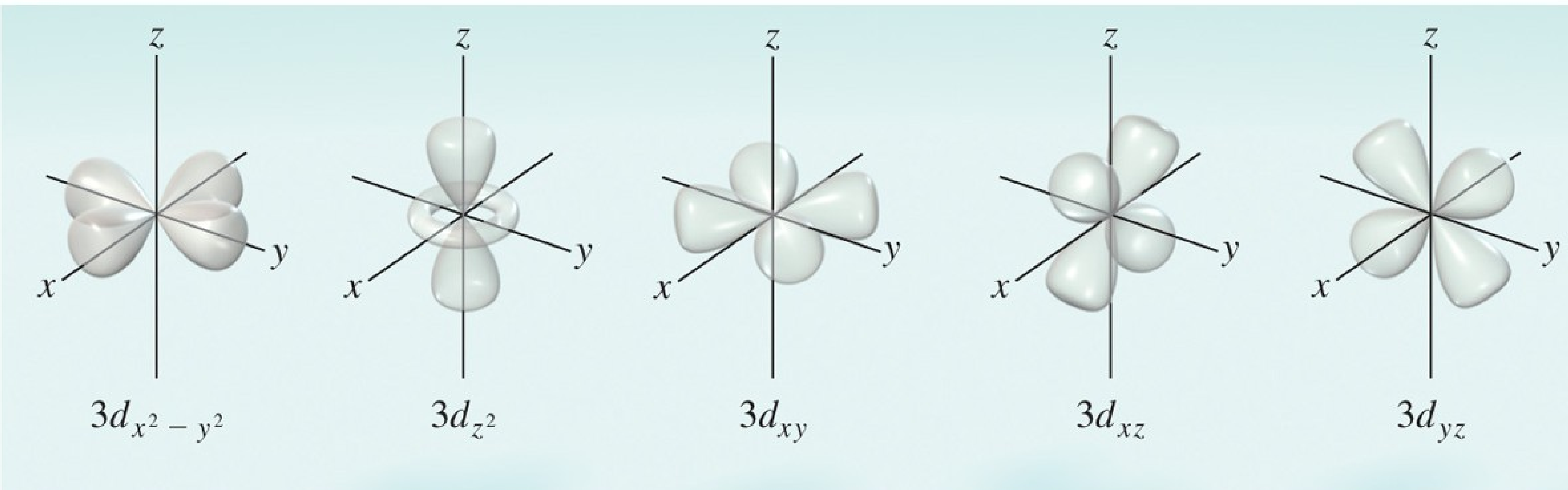
Probability Density and Radial Probability for "*s*" Orbitals



Atomic Orbitals for “*p*”



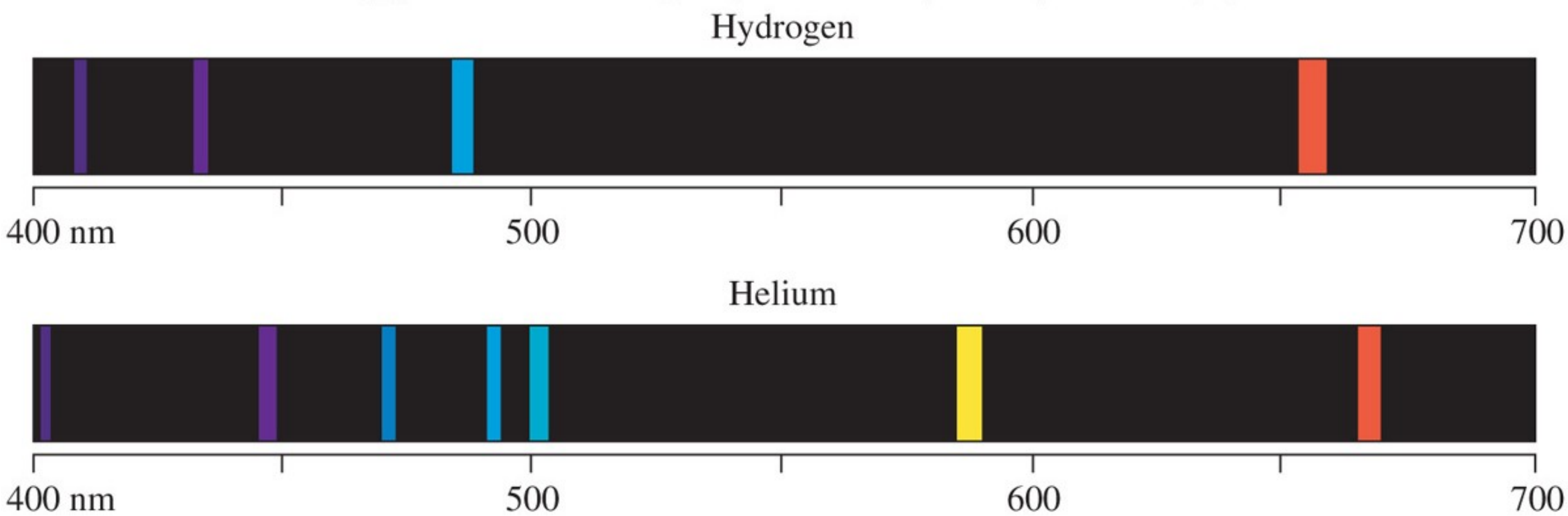
Atomic Orbitals for "*d*"



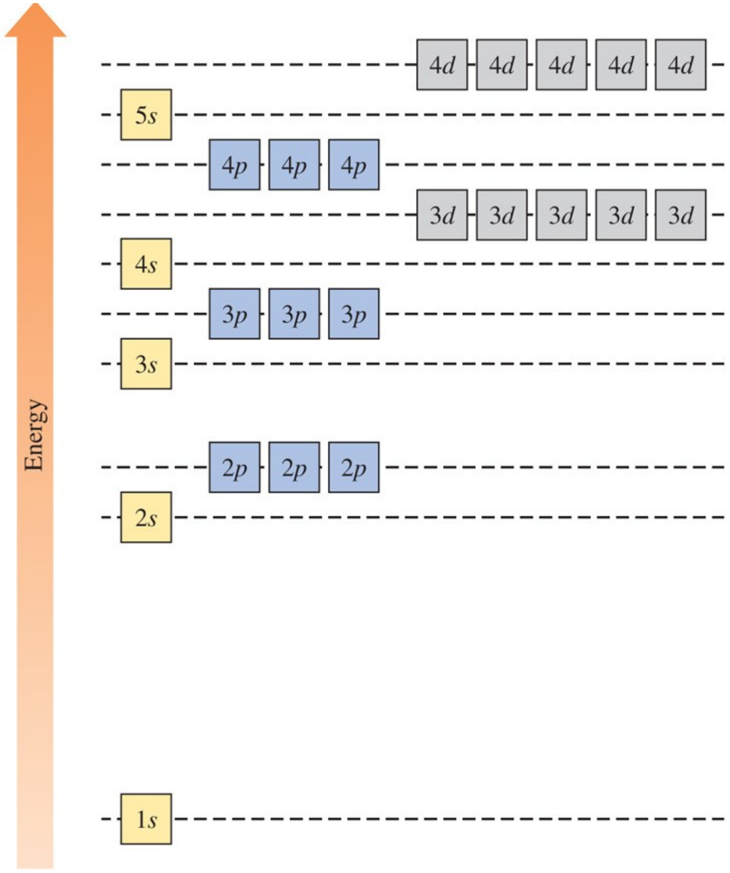
6.8 Electron Configuration

- ***Ground state*** - electrons in lowest energy state
- ***Excited state*** - electrons in a higher energy orbital
- ***Electron configuration*** - how electrons are distributed in the various atomic orbitals

Compare the Following Emission Spectra



Electron Configuration - Notice the Energy for Each Orbital



Electron Configuration

- ***Pauli Exclusion Principle*** - no two electrons in an atom can have the same four quantum numbers; no more than two electrons per orbital
- ***Aufbau Principle*** - electrons fill according to orbital energies (lowest to highest)

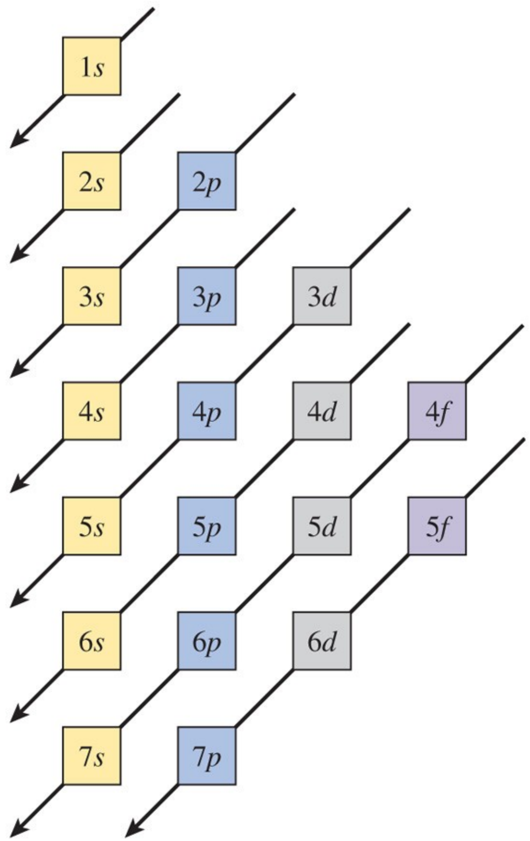
Electron Configuration

- ***Hund's Rule*** - the most stable arrangement for electrons in orbitals of equal energy (degenerate) is where the number of electrons with the same spin is maximized
- Example: Carbon - 6 electrons
- $1s^2 2s^2 2p^2$

Rules for Writing Electron Configurations

- Electrons reside in orbitals of lowest possible energy
- Maximum of 2 electrons per orbital
- Electrons do not pair in degenerate orbitals if an empty orbital is available
- Orbitals fill in order of earlier slide (or an easy way to remember follows)

The Diagonal Rule



Practice Electron Configuration and Orbital Notation

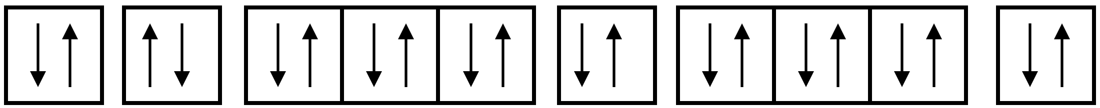
Write the electron configuration and orbital notation for each of the following

$Z = 20$

$Z = 35$

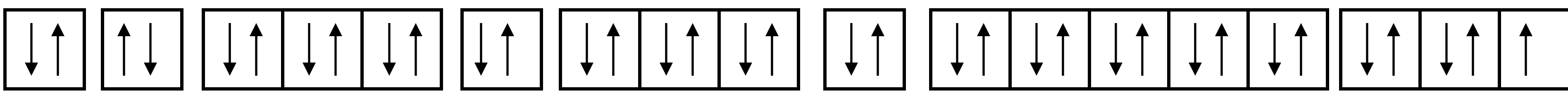
$Z = 26$

$Z = 20 \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ (Ca)



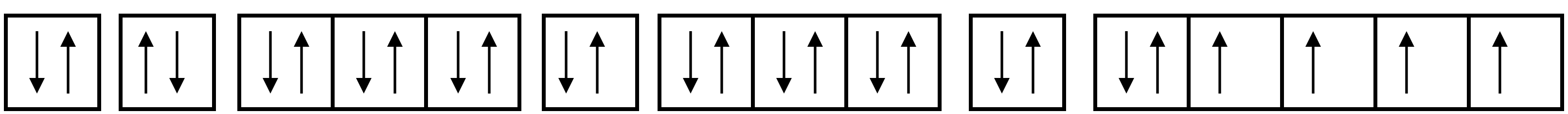
$1s \quad 2s \quad 2p \quad 3s \quad 3p \quad 4s$

$Z = 35 \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3\mathrm{d}^{10} 4\mathrm{p}^5$ (Br)



$1s \quad 2s \quad 2p \quad 3s \quad 3p \quad 4s \quad 3d \quad 4p$

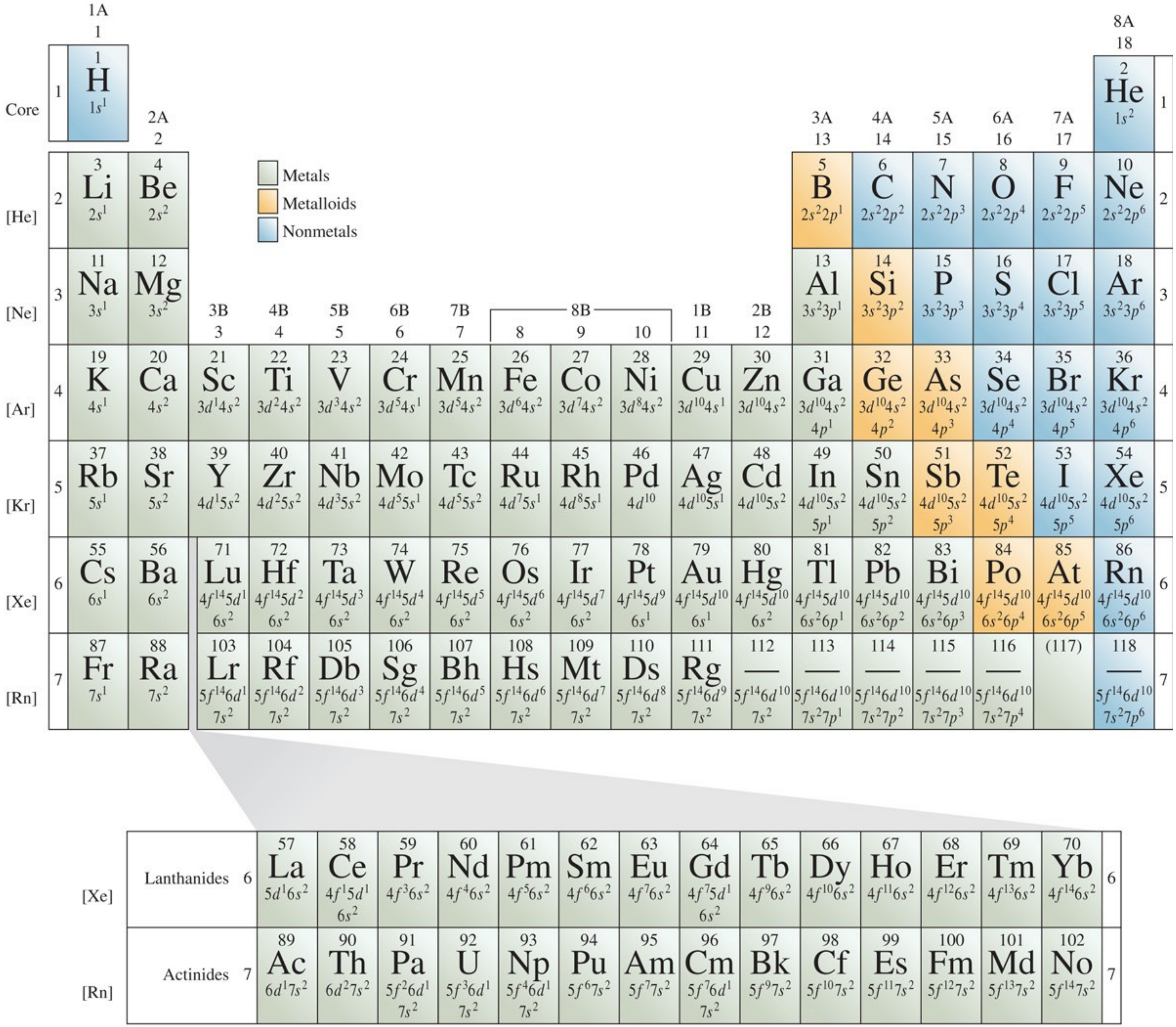
$Z = 26 \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3\mathrm{d}^6$ (Fe)



$1s \quad 2s \quad 2p \quad 3s \quad 3p \quad 4s \quad 3d$

6.9 Electron Configurations and the Periodic Table

- Position on the periodic table indicates electron configuration
- What similarities are found within groups on the table?


1A 1
2A 2
3A 13 4A 14 5A 15 6A 16 7A 17
8A 18
3B 3 4B 4 5B 5 6B 6 7B 7 8B 8 9 10 1B 11 2B 12
Metals
Metalloids
Nonmetals
Core [He] [Ne] [Ar] [Kr] [Xe] [Rn]
1 H 2 He
3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne
11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
55 Cs 56 Ba 71 Lu 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
87 Fr 88 Ra 103 Lr 104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt 110 Ds 111 Rg 112 113 114 115 116 (117) 118
Lanthanides 6 57 La 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb
Actinides 7 89 Ac 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No

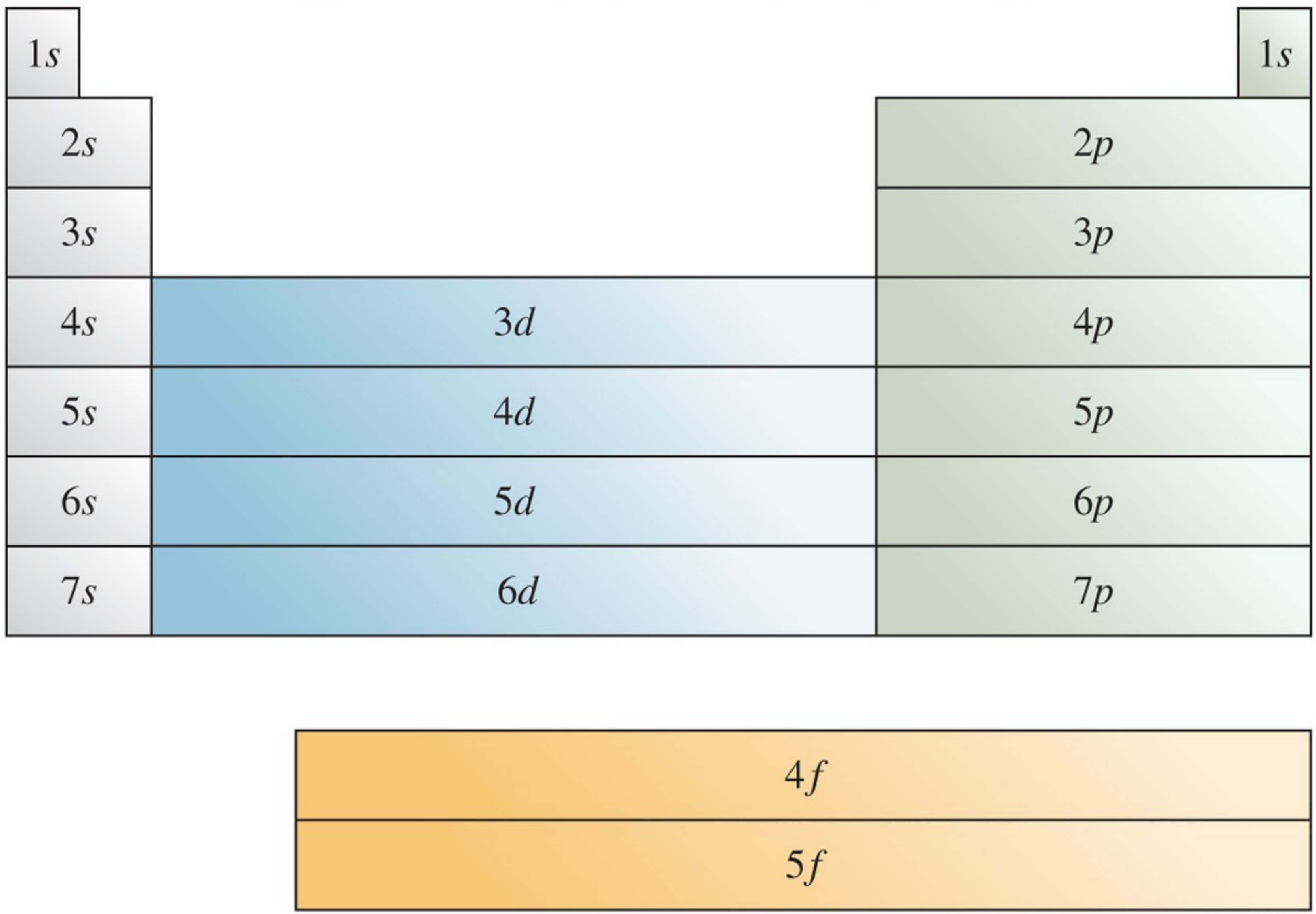
Electron Configurations and the Periodic Table

- ***Noble gas core configuration*** - can be used to represent all elements but H and He

Example:

Z = 15 [$1s^2 2s^2 2p^6$]$3s^2 3p^3$ (P)

[Ne] $3s^2 3p^3$ (P)


1s
1s
2s
2p
3s
3p
4s
3d
4p
5s
4d
5p
6s
5d
6p
7s
6d
7p
4f
5f

Too Good to Be True?

- Not all elements follow the "order" of the diagonal rule
- Notable exceptions: Cu (Z = 29) and Cr (Z = 24)

$$Cu = [Ar]4s^1 3d^{10}$$

$$Cr = [Ar]4s^1 3d^5$$

Reason: slightly greater stability associated with filled and half-filled *d* subshells

Key Points

- Electromagnetic spectrum
- Wavelength, frequency, energy (calculate)
- Quanta (of light - photon)
- Photoelectric effect
- Emission spectra
- Ground state vs excited state
- Heisenberg uncertainty principle

Key Points

- Quantum numbers (n, l, m_l, m_s) predict values and possible sets
- Electron configuration - identify and write (also noble gas core)
- Pauli exclusion principle, Hund's rule, Aufbau principle