

CHEM 115

Spectroscopy and Electron Configurations

Lecture 19
Prof. Sevian



1

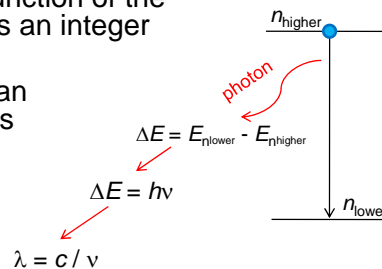
Agenda

- How the quantum mechanical model explains electrons in atoms
 - Four parameters in the equations that describe electron wave functions
 - Principal quantum number, n
 - Azimuthal quantum number, l
 - Magnetic quantum number, m_l
 - Spin quantum number, m_s
- Electron configurations
 - Ground state vs. excited state

2

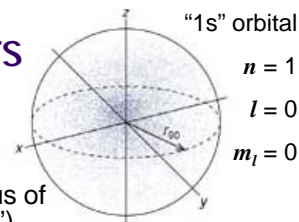
Key points from last lecture

- Emission spectrum of hydrogen has distinct lines at different colors (specific wavelengths λ)
 - Note that you can also describe the lines in terms of their frequencies using $c = \lambda\nu$ and solving for $\nu = c / \lambda$
- These lines correspond to energies of the photons that are emitted because $E = h\nu$
- The energies of these photons are the differences in energy when the electron inside the atom falls from a higher (excited) energy state to a lower energy state
- In the de Broglie model, E_n is a function of the energy level number n , where n is an integer
 - Rydberg equation: $E_n = -Rhc (1/n^2)$
- So the energy of a photon when an electron falls from n_{higher} to n_{lower} is given by the formula:
 - Δ always means “final - initial”
 - $\Delta E = E_{n_{\text{lower}}} - E_{n_{\text{higher}}}$



Meaning of the quantum numbers

(simulation we played with at Lecture 18)



- **n : energy level**
 - tells about average radius away from nucleus of the electron density cloud (called an “orbital”)
 - also tells how many nodes (places where electron density equals zero) are in the electron density cloud = $n-1$
- **l : shape of the electron density cloud**
 - tells about the planes of symmetry the electron density cloud has
 - when $l=0$, there are no planes of symmetry (sphere)
 - when $l=1$, there is one plane of symmetry cutting the electron density into two equal halves (like two balloons whose ties touch in middle)
 - when $l=2$, there are two planes of symmetry
- **m : orientation of the electron density cloud**
 - tells about which way the electron density cloud is turned
 - when $l=0$, there is only one way (can't turn a sphere and make it look different), so there is only one possible m value ($m=0$)
 - when $l=1$, there are three ways to orient the two equal halves, either top-bottom, left-right, or front-back, so there are three possible m values ($m=0, -1, +1$)

What does an atom look like?

More than anything else, it depends on the electrons

Model 4 Schrodinger, Heisenberg, Bohr, de Broglie and some others, 1912-1924

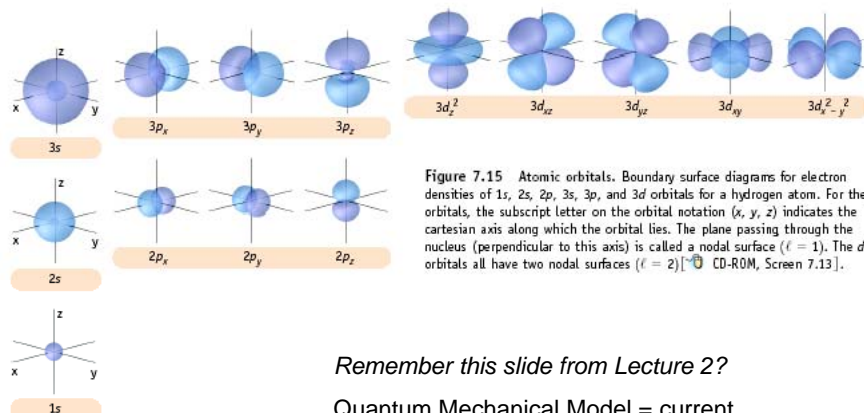


Figure 7.15 Atomic orbitals. Boundary surface diagrams for electron densities of 1s, 2s, 2p, 3s, 3p, and 3d orbitals for a hydrogen atom. For the p orbitals, the subscript letter on the orbital notation (x, y, z) indicates the cartesian axis along which the orbital lies. The plane passing through the nucleus (perpendicular to this axis) is called a nodal surface ($l = 1$). The d orbitals all have two nodal surfaces ($l = 2$) [© CD-ROM, Screen 7.13].

Remember this slide from Lecture 2?

Quantum Mechanical Model = current working model (stay tuned until chapter 7 for more information...)

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Spectroscopy

Macroscopic observations

- When energy enters atoms, atoms give off light at discrete wavelengths (line emission spectrum)
- Line emission is fingerprint of an element (demonstrations in class)
- Entire periodic table at

<http://jersey.uoregon.edu/vlab/elements/Elements.html>

Particle level explanation

- Electrons are so small that their quantum mechanical properties become important (Heisenberg uncertainty principle)
- Electrons can reside in various different quantum mechanical potential energy states, only one of which is the lowest energy ground state
- For a very nice, short summary explanation with helpful pictures, see

<http://www.avogadro.co.uk/light/bohr/spectra.htm>

Symbolic representation (mathematical model)

6

Quantum Mechanical Theory

- Bohr model correctly predicts hydrogen spectrum, but no theoretical basis for “quantization postulate” needed in the mathematical model
- de Broglie uses converse of Einstein’s “light can be described as a particle” to say “a very small particle like an electron can be described as a wave.”
- Schrödinger equation models hydrogen spectrum and quantization occurs as a mathematical solution, resulting from the wavelike behavior of electrons.
- Schrödinger equation involves electromagnetic interaction between a single electron and a positive point charge at the nucleus
- Therefore, Schrödinger equation can be solved exactly only when there is a single electron (H atom, He⁺ ion, H₂⁺ ion, Li²⁺ ion)
- However, Schrödinger equation serves as a good first approximation for other elements (ch. 7 and structure of the Periodic Table)

The Schrodinger equation and wave functions that obey it

$$H\psi_{nlm}(\theta, \phi, r) = E_n\psi_{nlm}(\theta, \phi, r) \quad \text{where } H|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

$$\psi_{nlm}(\theta, \phi, r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{l,m}(\theta, \phi)$$

ψ_{nlm} are a set of functions that are mathematical solutions in three-dimensional space (radial coordinates θ, ϕ, r instead of Cartesian coordinates x, y, z) that depend on three quantum numbers n, l, m

$$a_0 \text{ is the "Bohr radius" given by } a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c \alpha}$$

ρ, L and Y are just special functions that depend on the parameters shown

Implications of Quantum Mechanical Model

- Energy of electron is quantized (only certain states are allowed)
- Due to Heisenberg uncertainty principle, it is impossible to identify both position of electron and its energy, so if energy is given by the S equation, then equation can only predict *probability* of locating electron within a given region of space (orbital), also called electron density
- Orbitals (solutions to S equation) are specified mathematically by quantum numbers: n , l , m_l , which are interdependent

The “Game” of Quantum Numbers

Principal quantum number ($n = 1, 2, 3, \dots \infty$)

Meaning: Specifies energy of the electron

Sometimes called “shell”, in reference to Bohr model

$$E_n = -Rhc/n^2 \text{ (same as Bohr/Rydberg)}$$

Azimuthal (angular momentum) quantum number ($l = 0, 1, 2, \dots n-1$)

Meaning: Specifies 3-D shape of probability map of electron density

Sometimes called “subshell”

Often coded by letters corresponding to different values for l

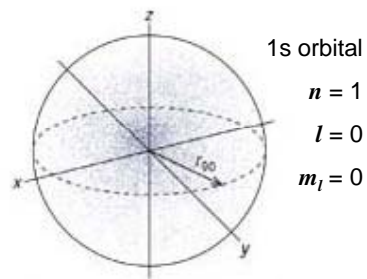
$$l = 0, 1, 2, 3, \dots \text{ corresponds to } s, p, d, f, \dots$$

Magnetic quantum number ($m_l = 0, \pm 1, \pm 2, \pm 3, \dots \pm l$)

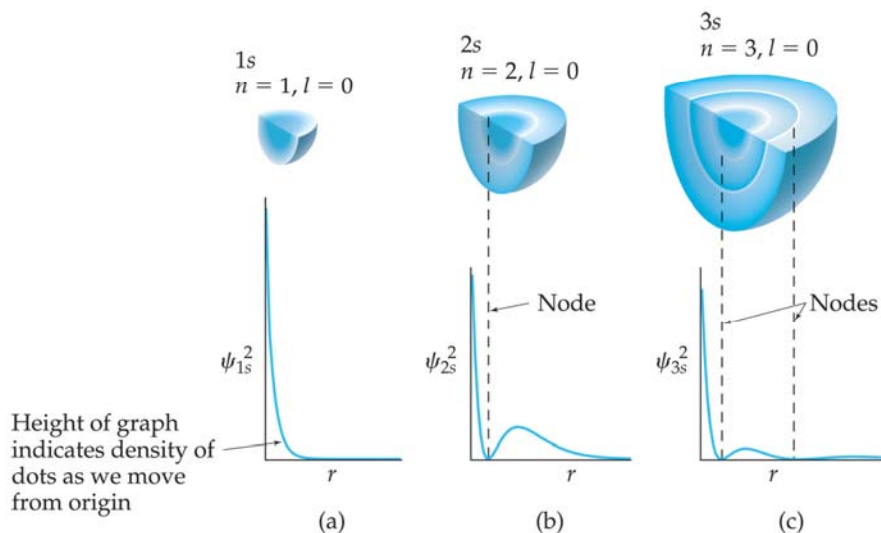
Meaning: Orientation of orbitals (mathematical solutions to Schrodinger equation) within a subshell

What Orbitals Are

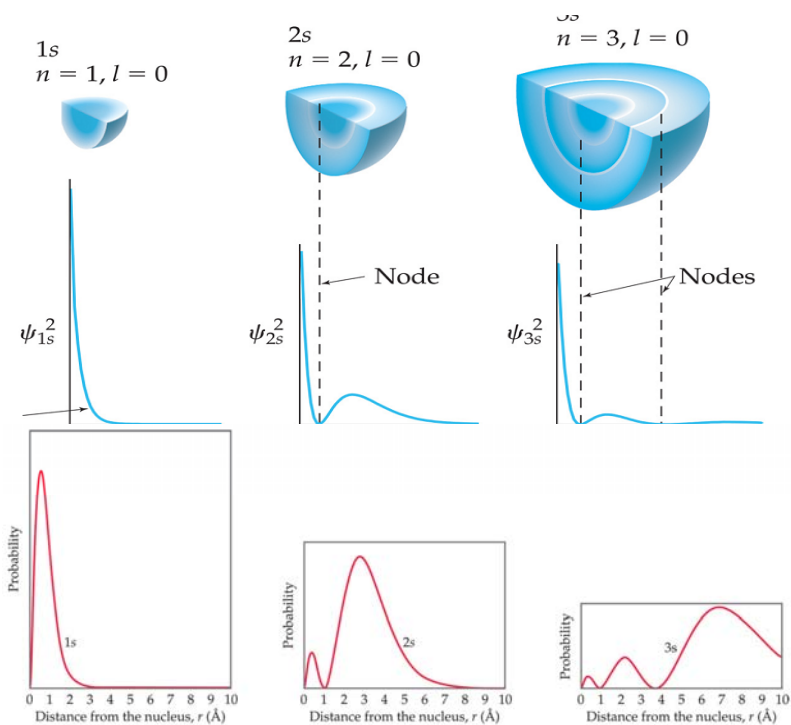
- Electron cloud pictures
- Probability density describing where electron is located
- Proportional to the square of the wave function with specific quantum numbers (wave function symbolized by Greek letter ψ)
- Think of a bird at a bird feeder, and a time-lapse photo



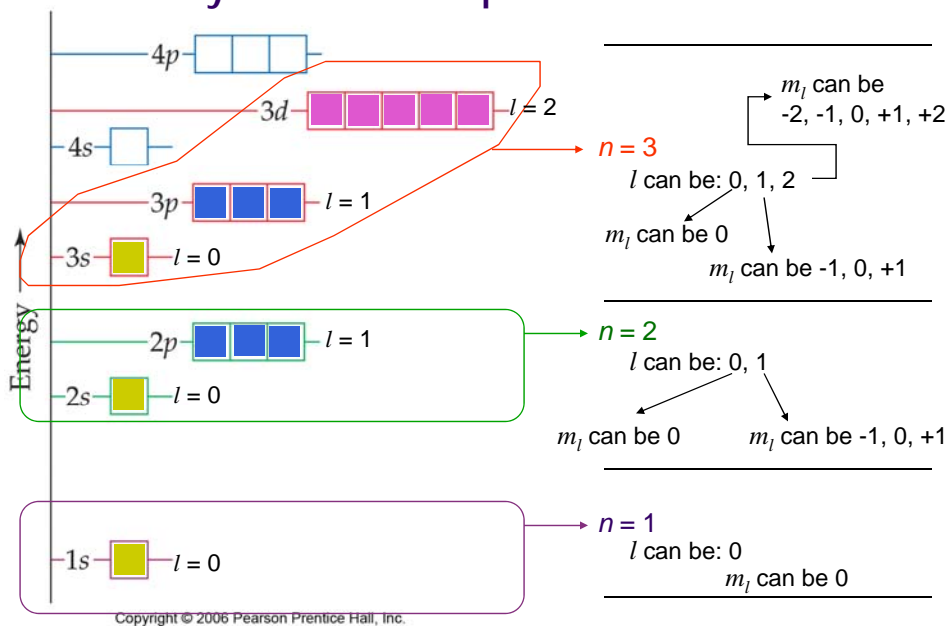
Comparing 1s, 2s, and 3s orbitals



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Summary of the first 3 quantum numbers

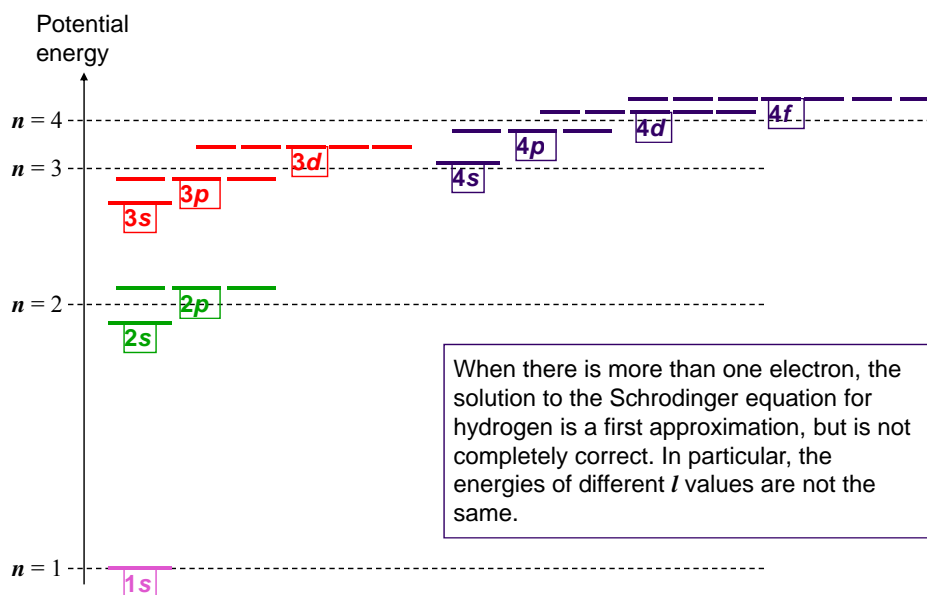


How do the Bohr model and the Quantum Mechanical model compare?

- Both quantitatively predict hydrogen emission spectrum
- Bohr model is completely wrong for atoms with more than one electron
- Quantum mechanical model is impossible to solve exactly for atoms with more than one electron, but:
 - Qualitatively predicts correct atomic emission spectra
 - Explains arrangement of atoms in the periodic table
 - Approximate mathematical solutions come close to correct quantitative predictions for atomic emission spectra

16

Orbital Energies in Multielectron Atoms



Magnetism of Materials

Macroscopic Evidence for a 4th Quantum Number

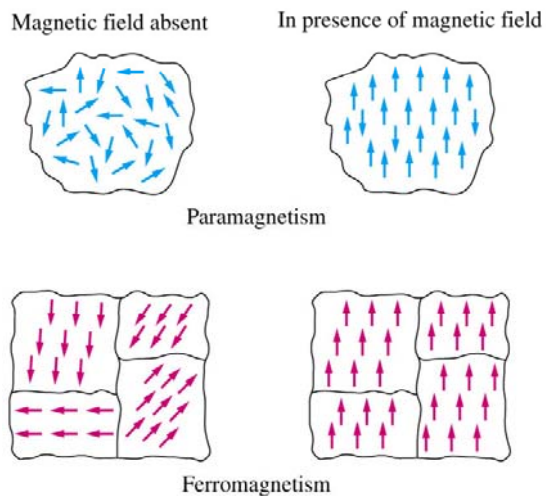
- Substances are either:
 1. Diamagnetic: slightly repelled by a strong magnet
 2. Paramagnetic: attracted to a magnetic field
- Usually undetectable unless strong field
- Some paramagnetic substances (iron, cobalt, nickel) are ferromagnetic (strongly attracted to a magnetic field)
- Some ferromagnetic substances (particularly mixtures, such as AlNiCo) can set up permanent magnetic character
- Atomic emission spectra of paramagnetic substances show splitting of spectral lines

19

Magnetism of Materials

Particle Level Behavior


- Ferromagnets contain regions of magnetic “strength” in the material
- Some regions have slightly different magnetic moments than other regions




From http://cwx.prenhall.com/petrucci/medialib/media_portfolio/24.html

Magnetism of Materials

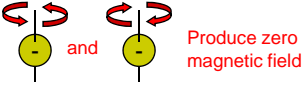
Symbolic/Mathematical Representation

- Recall that an electric field in motion creates a magnetic field, and vice versa
- Electron is charged particle that spins 
- Two spins possible, therefore two directions of magnetic field possible

Some unpaired electrons

- If spins of two electrons are aligned, then magnetic field strengthened 

All electrons are paired

- If spins of two electrons are opposed, then magnetic field cancelled 

- Define a fourth quantum number: magnetic spin, m_s , which can take two possible values $+\frac{1}{2}$ or $-\frac{1}{2}$

Adding a fourth quantum number: magnetic spin of the electron, m_s

Electrons are mathematical wave functions (orbitals) specified by:

- Principal quantum number, n
 - Can take values 1, 2, 3, 4, ...
 - Radial distance from the nucleus (shell #)
- Azimuthal quantum number, l
 - Can take values up to but not including n value
 - Shape of orbital (when $l=0$ has s -shape, when $l=1$ has p -shape, when $l=2$ has d -shape, etc.)
- Magnetic quantum number, m_l
 - Can take values ranging from $-l$ up to $+l$
 - Orientation of the orbital
- Spin quantum number, m_s
 - Can take one of two values ($+\frac{1}{2}$ or $-\frac{1}{2}$), does not depend on other quantum numbers

22

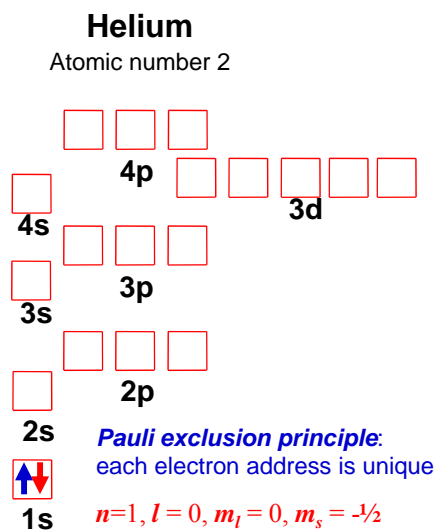
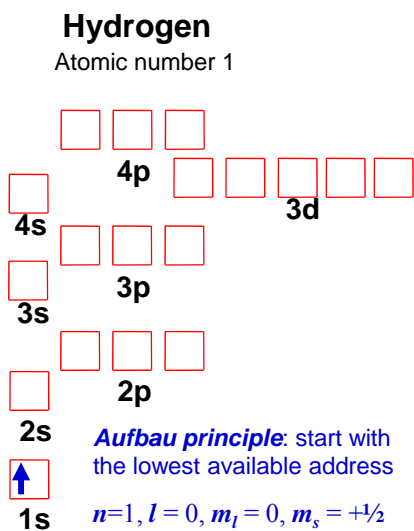
The “game” of QM: What you need to know

- Study pp. 232-233 (10th ed.) or pp. 226-227 (11th ed.) in the text to learn the rules
- Know what information the first three quantum numbers tell about the electron density cloud's size (n), shape (l) and orientation (m_l)
- Know the difference between s, p, d and f orbitals (these are codes for the “ l ” values of 0, 1, 2 and 3)
- Be able to tell which combinations of quantum numbers (n, l, m_l) are allowed and which combinations are not allowed
- Given a particular electron address, determine a set of quantum numbers (n, l, m_l) that correspond to it
- Given an atom with a specific number of electrons, determine the electronic “ground state” configuration
- Know the vocabulary: level, shell, orientation, node, subshell, orbital, and names of the quantum numbers (principal, azimuthal, magnetic, spin)

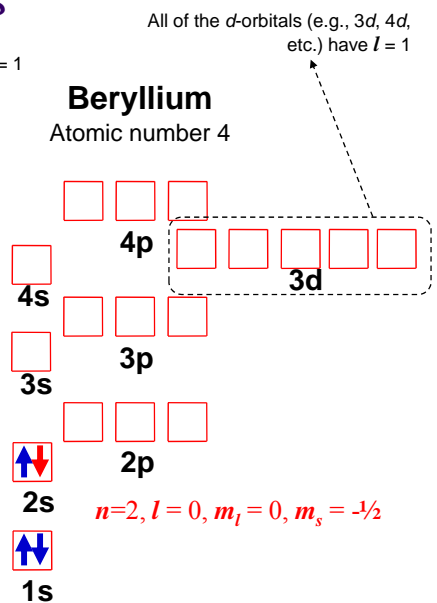
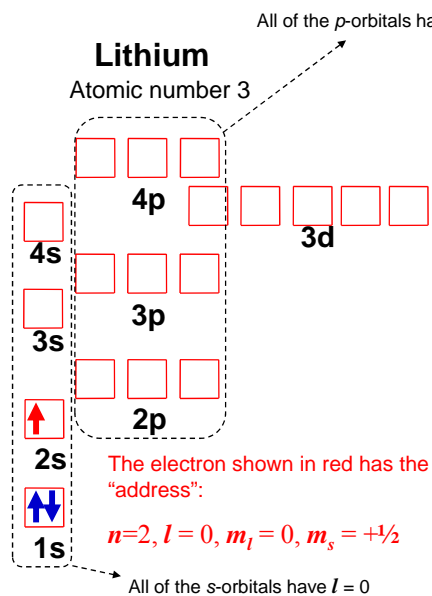
How to find ground state electron configuration for an element

1. Aufbau (“building up/assembly”) principle
Add electrons sequentially from lowest energy orbitals on upward.
2. Pauli exclusion principle
Electrons are uniquely specified. If two electrons have the same first three quantum numbers (same orbital), then their fourth quantum number (m_s) must differ.
3. Hund's rule
Electrons that are in the same subshell (same l value) tend to distribute so that they are in different orbitals (different m_l values) and have parallel spin (same m_s values).

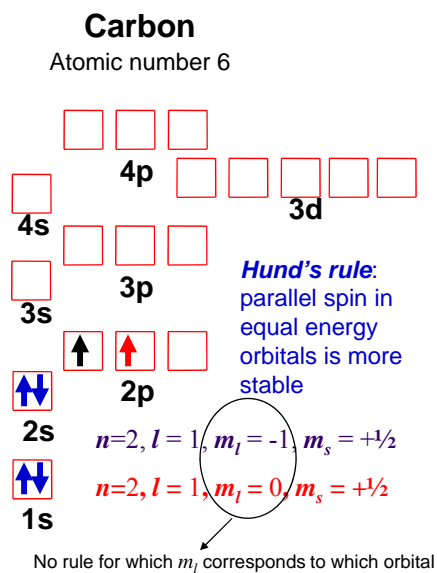
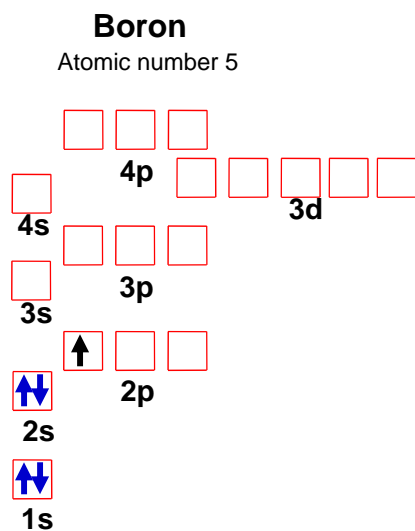
Aufbau (Building) Elements



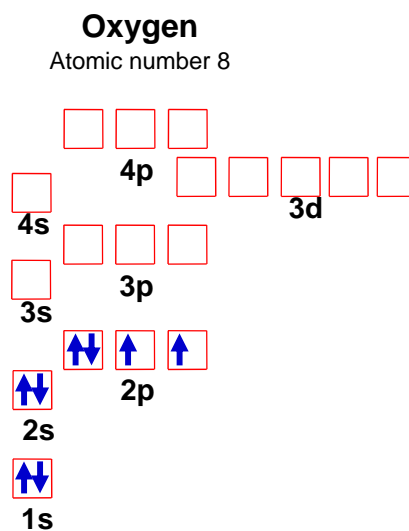
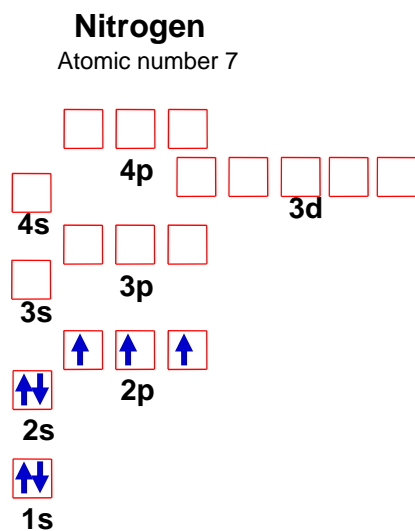
Aufbau (Building) Elements



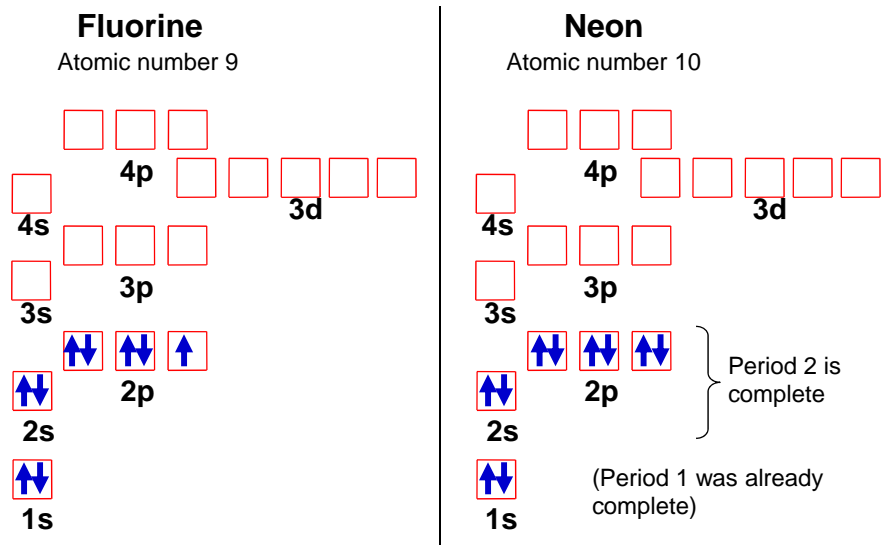
Aufbau (Building) Elements



Aufbau (Building) Elements



Aufbau (Building) Elements



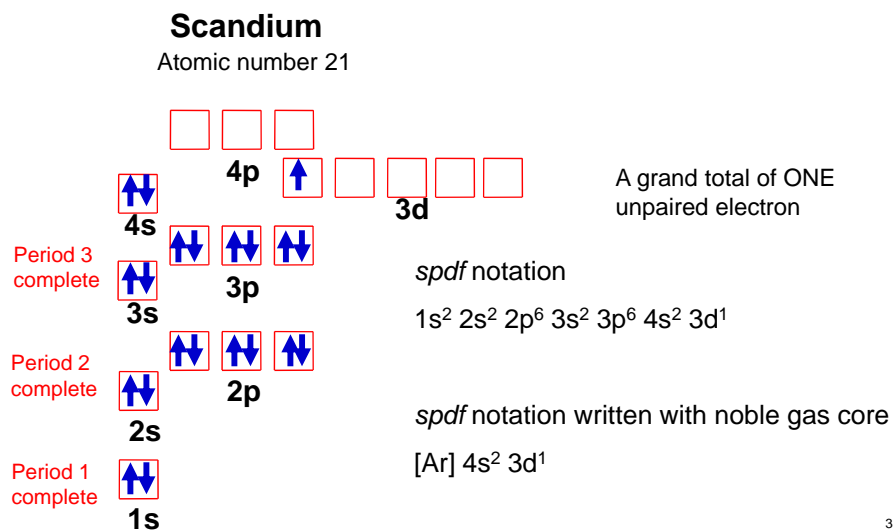
Book's representation

TABLE 6.3 Electron Configurations of Several Lighter Elements							
Element	Total Electrons	Orbital Diagram				Electron Configuration	
		1s	2s	2p		3s	
Li	3	$\uparrow\downarrow$	\uparrow				$1s^2 2s^1$
Be	4	$\uparrow\downarrow$	$\uparrow\downarrow$				$1s^2 2s^2$
B	5	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow			$1s^2 2s^2 2p^1$
C	6	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow		$1s^2 2s^2 2p^2$
N	7	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	$1s^2 2s^2 2p^3$
Ne	10	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$1s^2 2s^2 2p^6$
Na	11	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$1s^2 2s^2 2p^6 3s^1$

Shorthand notation

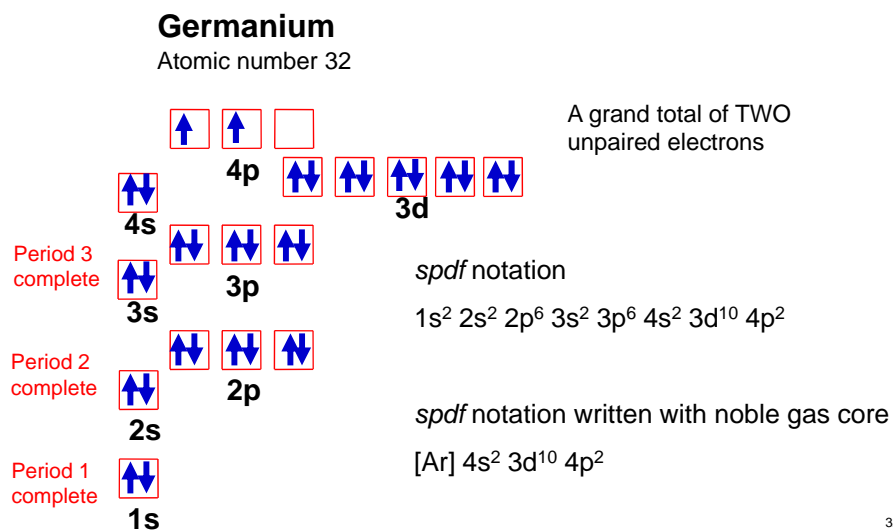
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Aufbau (Building) Elements



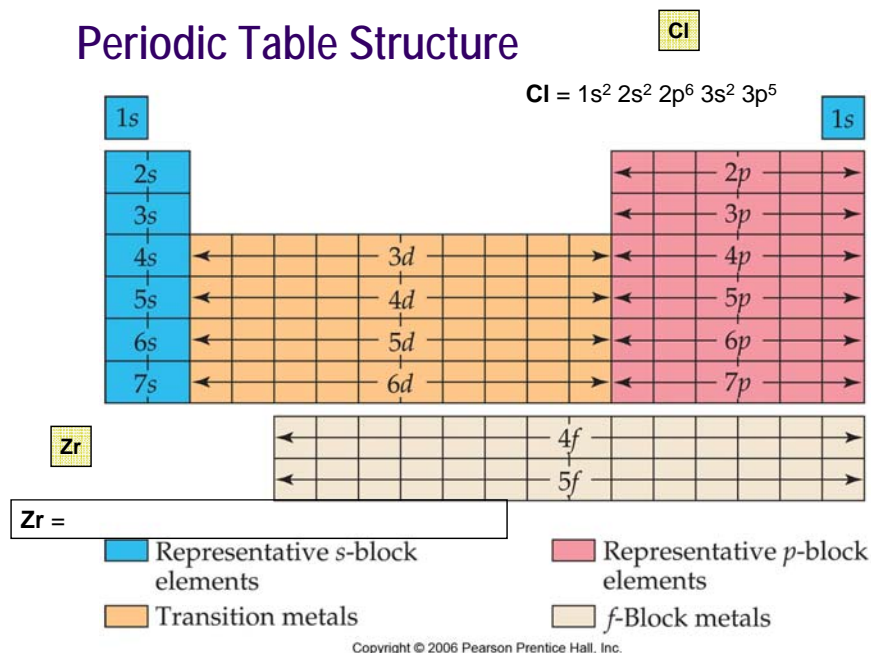
31

Aufbau (Building) Elements



32

Periodic Table Structure



Clicker question #1

What is the electron configuration for the ground state of vanadium (V)?

- (A) $1s^2 2s^2 2p^3$
 (B) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
 (C) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
 (D) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

Hint: it is element #23

Second hint: there are two correct answers in this list

34



Clicker question #2

What is a possible excited state electron configuration for nitrogen?

- (A) $1s^2 2s^2 2p^3$
- (B) $1s^2 2s^2 2p^3 3s^1$
- (C) $1s^2 2s^2 2p^2 3s^1$
- (D) $1s^2 2s^2 2p^2 3s^2$

35



Clicker question #3

What is the ground state electron configuration for the chloride ion, Cl^- ?

- (A) $1s^2 2s^2 2p^6 3s^2 3p^4$
- (B) $1s^2 2s^2 2p^6 3s^2 3p^5$
- (C) $1s^2 2s^2 2p^6 3s^2 3p^6$
- (D) $1s^2 2s^2 2p^6 3s^1 3p^6$

36