Chapter 7. Quantum Theory and the Electronic Structure of Atoms

7.1 From Classical to Quantum Theory

- 1900 - classical physics (describing molecules simply as bouncing marbles and balls) was not explaining all observations
- Planck discovered that atoms and molecules emit energy in discrete quantities

Properties of waves (Fig. 7.2)

- wavelength (λ)
- frequency (ν)
- travel at 3.00×10^8 meters/second (m/s)
  (186,000 miles/second in English units)

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

$\lambda\nu = c$ = speed of light = 3.00×10^8 m/sec

units: λ = distance (m, cm, nm, etc.)
ν = 1/sec = s^{-1} { 1 s^{-1} = 1 Hertz }

electromagnetic spectrum -- range of frequencies / wavelengths (Fig. 7.4)

7.2. Planck's Quantum Theory and the Photoelectric Effect

Energy of electromagnetic radiation

Radiation interacts with matter in discrete "packets" of energy called "quanta" or "photons". (light as "particles")

$$E = h\nu$$

where h = Planck's Constant = 6.63×10^{-34} J· s

E is the energy of ONE photon. Will eject one electron, break one bond, etc.

always get energy in multiples of $h\nu$ (2 $h\nu$, 3 $h\nu$, but not 1.3 $h\nu$)

7.3. Bohr's Theory of the Hydrogen Atom

Emission Spectra: (Figs. 7.6, 7.8)

- excited atoms only emit radiation in discrete energies
- electron moving from a higher to a lower energy ***orbit*** (electronic energy levels)
  - analogous to a ball on stairs (Fig. 7.10): ball only stops on steps, never in between
- ***n*** is a "quantum number" with values of 1, 2, 3...
- **Rydberg equation** - calculate energy differences between levels with different ***n*** values
  - Fig. 7.11: compare to lines for hydrogen on Fig 7.6 and 7.8

7.4 The Dual Nature of the Electron

electrons behave as both waves and matter;
particles with wavelike properties

7.5 Quantum Mechanics

- Bohr's model only explained emission spectra for hydrogen
- Bohr's model did not explain the wavelike properties of electrons
- wavelike properties mean locating an electron is not easy
- ***Heisenberg Uncertainty principle***: It is impossible to know simultaneously both the momentum and the position of a particle with certainty.
- ***Schrödinger equation***: complicated mathematical techniques used to describe the behavior and energies of subatomic particles.
- This launched a new era in physics and chemistry - ***quantum mechanics***
  - electron density: probability that an electron will be found in a particular region of an atom
  - atomic ***orbital***
    - the wave function of an electron or the distribution of electron density (Fig 7.15 - hydrogen atom)
    - solution to Schrödinger equation
  - electrons in atoms with many electrons are assumed to behave as the single electron in hydrogen, i.e., the Schrödinger equation can only be solved for hydrogen

7.6 Quantum Numbers

- describe the distribution of electrons in hydrogen (and other atoms)
- Electrons in multi-electron atoms can be classified into a series of:

shells ⟶ **subshells** ⟶ **orbitals**

- Each orbital can be described mathematically by a "wave function" that is characterized by a set of ***quantum numbers***.

A. Principle Quantum number -- *n*

- related to energy of the ***shell*** and to distance from nucleus (size)
- possible values of ***n*** = 1, 2, 3, 4, ...

B. Secondary Quantum Number -- ℓ

- related to shape of various ***subshells*** within a given ***shell***
- possible values of ℓ = 0 1 2 3 4 ... *n* - 1
  letter designation: *s* *p* *d* *f* *g* ....*h*, *i*.

values of *n*	values of ℓ	orbitals
1	0	1*s*
2	0, 1	2*s*, 2*p*
3	0, 1, 2	3*s*, 3*p*, 3*d*

C. Magnetic Quantum Number -- m_ℓ

- related to spatial orientation of ***orbitals*** within a given ***subshell***
- possible values of m_ℓ = $-\ell$, ... 0, ..., $+\ell$
- the number of m_ℓ values = number of orbitals within a subshell

within subshell ℓ = 2, there are 5 orbitals corresponding to the 5 possible values of m_ℓ (- 2, -1, 0, +1, +2)

d orbitals come in sets of 5 (- 2, -1, 0, +1, +2)
p orbitals in sets of 3 (-1, 0, +1)
s orbitals in sets of 1 (0)

D. Electron Spin and the Pauli Exclusion Principle

- electrons have intrinsic angular momentum -- "**spin**" -- m_s
- only two possible values: m_s = +½ and -½

(compare to front and back side of a page of paper)

7.7 Atomic Orbitals

A. **Summary** of above -- electronic quantum numbers and orbitals

n	ℓ	m_ℓ	**subshell**	**# orbitals**
1	0	0	1*s*	**1**
2	0	0	2*s*	**1**
	1	-1. 0, +1	2*p*	**3**
3	0	0	3*s*	**1**
	1	-1, 0, +1	3*p*	**3**
	2	-2, -1, 0, +1, +2	3*d*	**5**
4	0	0	4*s*	**1**
	1	-1, 0, +1	4*p*	**3**
	2	-2, -1, 0, +1, +2	4*d*	**5**
	3	-3, -2, -1, 0, +1, +2, +3	4*f*	**7**

B. Shapes of orbitals See Figure 7.19 - 7.21 for boundary surface diagrams of the *s, p* and *d* orbitals:

See Figure 7.18 for electron density plots of *s* orbital

best viewed as "clouds of electron density" with the density thinning or diminishing with distance from the nucleus

C. Energy of Orbitals

1. Hydrogen: Figure 7.22

2. Other atoms: Figure 7.23

7.8 Electron Configurations

A. *Pauli Exclusion Principle*: *No two electrons in an atom can have identical values of all 4 quantum numbers -- maximum of 2 electrons per orbital*.

a single orbital can hold a "pair" of electrons with opposite "spins"

e.g., the 3rd shell (n = 3) can hold a maximum of 18 electrons:

n = 3	ℓ =	0	1	2	
	subshell	3*s*	3*p*	3*d*	
	# orbitals	1	3	5	
	# electrons	2	6	10	= 18 total

a single electron in an orbital is called "unpaired"

B. Paramagnetism and Diamagnetism

- atoms with 1 or more *unpaired* electrons are ***paramagnetic***, (attracted by a magnetic)
- atoms with all spins *paired* are ***diamagnetic*** (repelled by magnet)

C. The Shielding Effect (many electron atoms)

- Electrons in the smaller orbitals (lower energy) are closer to nucleus (e.g., 1*s*) than electrons in larger orbitals (e.g., 2*p*, 3*s*)
- Thus they are "shielded" from the attractive forces of the nucleus
- This causes slight increase in energy of the more distant electrons.

  (see Figure 7.23 again)
- thus 4*s* orbital is lower in energy than the 3*d* orbital (see below)

7.9 The Aufbau Principle (Building-Up)

A. atomic # = # protons = # electrons (in neutral atom)
add electrons to atomic orbitals, two per orbital, from the bottom up

#	Atom	Electron Configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	$1s^2\ 2s^1$
4	Be	$1s^2\ 2s^2$
5	B	$1s^2\ 2s^2\ 2p^1$
6	C	$1s^2\ 2s^2\ 2p^2$
7	N	$1s^2\ 2s^2\ 2p^3$
8	O	$1s^2\ 2s^2\ 2p^4$
9	F	$1s^2\ 2s^2\ 2p^5$
10	Ne	$1s^2\ 2s^2\ 2p^6$
11	Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$

B. Hund's Rule - *the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins*. (i.e., don't pair electrons until all orbitals of that type in the same energy level, e.g., 2*p*, have one electron.)

orbital diagrams:

C ↑↓ ↑↓ ↑ ↑ __
1*s* 2*s* 2*p*

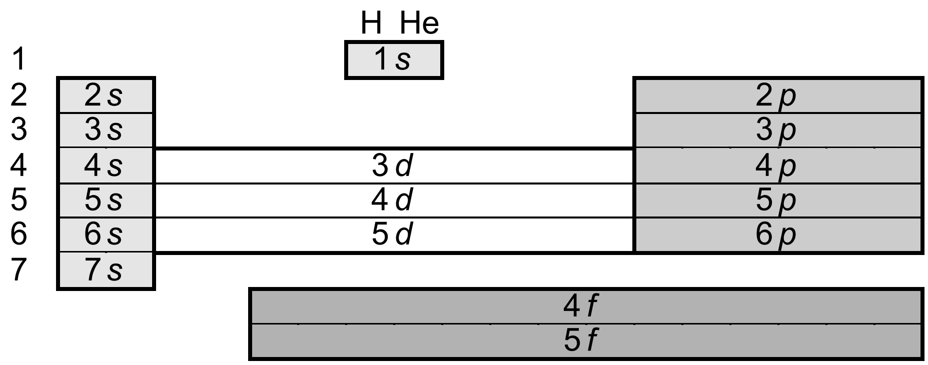
N ↑↓ ↑↓ ↑ ↑ ↑
1*s* 2*s* 2*p*

O ↑↓ ↑↓ ↑↓ ↑ ↑
1*s* 2*s* 2*p*

K ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑
1*s* 2*s* 2*p* 3*s* 3*p* 4*s*

Sc ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑ __ __ __ __
1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d*

C. Relationship to Periodic Table (see Figure 7.27)



e.g., electronic configuration of Ge (# 32, group IV)

Ge $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$

alkali metals and *alkaline earth metals* fill the *s* orbitals last
main group elements fill the *p* orbitals last
transition metals fill the *d* orbitals last
lanthanides (4*f*) and *actinides* (5*f*) fill the *f* orbitals last

Short-hand notation -- show preceding inert gas configuration plus the additional electrons

Ge $[Ar]^{18}\ 3d^{10}\ 4s^2\ 4p^2$ where $[Ar]^{18} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Valence Shell Configurations

valence shell -- largest value of *n* (e.g., for Ge, *n* = 4)

Ge $4s^2\ 4p^2$ (valence shell electron configuration)

Ge ↑↓ (4*s*) ↑ ↑ __ (4*p*) (valence shell orbital diagram)

Elements in same group have same valence shell e⁻ configurations

e.g., group V:

N	$2s^2\ 2p^3$
P	$3s^2\ 3p^3$
As	$4s^2\ 4p^3$
Sb	$5s^2\ 5p^3$
Bi	$6s^2\ 6p^3$