CHEMSTRY Gilbert An atoms-focused approach Foster



Chapteb Atomic Structure Explaining the Properties of Elements

Chapter Outline

3.1 Waves of Light

- 3.2 Atomic Spectra
- 3.3 Particles of Light: Quantum Theory
- 3.4 The Hydrogen Spectrum and the Bohr Model
- 3.5 Electrons as Waves
- 3.6 Quantum Numbers
- 3.7 The Sizes and Shapes of Atomic Orbitals
- 3.8 The Periodic Table and Filling Orbitals
- 3.9 Electron Configurations of Ions
- 3.10 The Sizes of Atoms and Ions
- **3.11 Ionization Energies**
- 3.12 Electron Affinities

Electromagnetic Spectrum













Visible light



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Electromagnetic Radiation

Perpendicular oscillating fields:

- a) Electric
- b) Magnetic



Wave Properties of Light

- Wavelength (λ) :
 - Distance from crest to crest or trough to trough
- Frequency (v):
 - The number of times a wave passes a point per unit of time
- Amplitude:
 - The height of the crest or depth of the trough



Wave Properties of Light

- Wavelength and frequency related by $\lambda_{v} = c$
 - Where λ is wavelength (in meters), v is frequency (in hertz, or s⁻¹), and c is the speed of light in vacuum
 - c is a constant and in a vacuum equals
 2.99792458 × 10⁸ m/s

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a) Fraunhofer lines (dark spectra)



b) Sodium emission (bright line spectra)



Atomic Emission Spectra

 Bright line emission spectra of other elements.







Atomic Spectra: Dark Lines



(a)



Hydrogen Helium

Neon

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Particles vs. Waves

- Incandescence not consistent with Maxwell equations, wave theory.
 - Most intense emissions in the infrared region.
 - Little or no emissions in UV.



Quantum Theory

- Radiant energy is "quantized"
 - Having values restricted to whole-number multiples of a specific base value
- Quantum = smallest discrete quantity of energy
- Photon = a quantum of electromagnetic radiation
- Energy of photon: $E = h_V$ or $E = hc/\lambda$
 - $h = 6.6260755 \times 10^{-34}$ J•s (Planck's constant)

Quantized States

- Quantized states: Discrete energy levels (e.g., steps)
- Continuum states: Smooth transition between levels (e.g., ramp)



Photoelectric Effect

- Photoelectric Effect:
 - Phenomenon of light striking a metal surface and producing an electric current (flow of electrons)





- Explained by quantum theory
 - Photons of sufficient energy (*h_V*) dislodge e⁻ from metal surface
 - Work function (Φ) amount of energy needed to dislodge an electron from the surface of a metal:

 $\Phi = h_{V_o}$

where Φ = work function; v_o = threshold frequency

• Kinetic energy of ejected electrons: $KE_{electron} = h_V - \Phi$

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What is the wavelength of the line in the visible spectrum corresponding to $n_1 = 2$ and $n_2 = 4$?

- Collect and Organize:
- Analyze:
- Solve:
- Think about It:





- Ground State: Lowest energy state available to an electron in an atom
- Excited State: Any energy state above the ground state
- Electron Transition: Movement of an electron between energy states

Energy Level Diagram

- Shows electron transitions (i.e., movement of electrons between energy levels)
- \downarrow = emission of energy





Bohr Model



- Strengths:
 - Accurately predicts energy needed to remove an electron from an atom (ionization)
 - Allowed scientists to begin using quantum theory to explain matter at atomic level
- Limitations:
 - Does not account for spectra of multielectron atoms
 - Movement of electrons in atoms is less clearly defined than Bohr allowed

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Particles or Waves?



- De Broglie (1892–1987)
 - If electromagnetic radiation behaves as a particle, could a particle in motion, such as an electron, behave as a wave?
- De Broglie's Equation:
 - $\lambda = hc/E = hc/mc^2 = h/mc$ (or = h/mv)
 - λ = De Broglie wavelength, m = mass of electron (in kg), v = velocity (in m/s), and h = Plank's constant.

Linear Waves

- Nodes = regions of standing waves that experience no displacement
- Wavelength, $\lambda = 2L$
- Harmonic frequencies:
 - $L = n \lambda/2$
 - For n = 2¹/₂ : no nodes, so no standing wave





- Electrons behave like circular waves oscillating around nucleus.
 - No defined stationary ends
- Stable circular waves of circumference





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Electron Wave Equations

- Erwin Schrödinger (1925)
 - Developed mathematical equations to describe behavior of electron waves; became the basis of quantum mechanics
- Wave functions (ψ)
 - ψ = describes the motion of electron waves as they vary with location and time
 - ψ² defines an **orbital**, or region of high probability for locating an electron

Wave Equations and Quantum Numbers

• Quantum Numbers:

- Principle quantum number (*n*); indicates the overall energy level (shell). *n* = 1, 2, 3,...
- Angular momentum quantum number (l); shows number of sublevels (subshells). $l = 0 \rightarrow (n 1)$
- Magnetic quantum number $(m_{|})$; indicates number of orbitals in each sublevel. $m_{|} = -\ell \rightarrow + \ell$
- Spin quantum number ();indicates that each orbital can only hold two electrons.



Quantum Numbers



Energy Shells (or Levels)

- 3D regions around the nucleus where electrons may be found
- Shells are distinguished by quantum numbers:
 n = 1, 2, 3, 4, ...
- All electrons in a particular shell have similar energies (shells may overlap slightly in energy)



- Each Shell has a maximum # of electrons it can hold
- Lower # shells:
 - Are physically smaller
 - Have lower energy electrons
 - Are usually filled up before higher energy shells

Each shell has at least one sub-shell (or sub-level)

Sub-shells are also labeled by quantum numbers: I = 0, 1, 2, 3, 4.... (n-1)but letters are usually used to avoid confusion: I = s, p, d, f, g,

 1^{st} shell – only one sub-shell – s 2^{nd} shell – only two sub-shells – s, p 3^{rd} shell – only three sub-shells – s, p, d 4^{th} shell – only four sub-shells – s, p, d, f

.

Each sub-shell has a fixed number of orbitals (from 3rd quantum number):

- s 1 orbital (spherically shaped)
- p 3 orbitals (lobed shaped, along each axis)
- d 5 orbitals
- f 7 orbitals

g – 9 orbitals

Quantum Numbers



TABLE 3.1 Quantum Numbers of the Orbitals in the First Four Shells					
Value	Allowed Values	Subshell		NUMBER OF ORBITALS IN:	
of <i>n</i>	of ℓ	Letter	Allowed Values of \pmb{m}_ℓ	Subshell	Shell
1	0	S	0	1	1
2	0	S	0	1	
	1	P	-1, 0, +1	3	4
3	0	S	0	1	
	1	P	-1, 0, +1	3	
	2	d	-2, -1, 0, +1, +2	5	9
4	0	S	0	1	
	1	P	-1, 0, +1	3	
	2	d	-2, -1, 0, +1, +2	5	
	3	f	-3, -2, -1, 0, +1, +2, +3	7	16



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Shapes and Sizes of Orbitals



Comparison of s Orbital


Comparison of s Orbital



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The Three 2p Orbitals



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The Five 3d Orbitals



Five *d* orbitals in each shell with $n \ge 3$; nodes at nucleus.

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Aufbau Principle



Aufbau Principle:

- Method of building electron configurations by adding one electron at a time as atomic number increases
- When adding electrons to an atom:
 - Electrons always go in lowest energy orbitals available
 - Maximum of two electrons per orbital

Each orbital can hold a maximum of two electrons (from 4th quantum number)

- •Electrons in an orbital must have opposite spins
 - "Spin up" or "spin down" (+1/2 or -1/2)

•This determines the maximum # of electrons a sub-shell and shell can hold:

- s 1 orbital 2 electrons
- p 3 orbitals 6 electrons
- d 5 orbitals 10 electrons
- f 7 orbitals 14 electrons

shell	sub- orbitals per shells subshell		electrons per sub-shell	maximum possible electrons		
1	S	1	2	2		
2	S	1	2	8		
<u> </u>	р	3	6			
	S	1	2			
3	р	3	6	18		
	d	5	10			
	S	1	2			
4	р	3	6	20		
	d	5	10	32		
	f	7	14			

- •Electrons want to occupy the lowest available energy state.
- •Some shells overlap, so the lowest <u>state</u> is not always in the lowest <u>shell (level)</u>.

Orbital Energies in Multielectron Atoms



- •We can use the periodic table to determine which subshells should be filled up first.
- •The periodic table also shows how many electrons each sub-shell can hold.
- •The periodic table can be split into 4 blocks: s, p, d, and f blocks

Periodic Table: *s*, *p*, *d*, and *f* Orbitals



•Each box can hold one electron, so fill up the boxes, starting in the upper left, until all electrons have been used

•The sub-shells are labeled with the energy level (shell) first, then the sub-shell: e.g. 1s, 2p, 4d....

•Superscripts after each sub-shell tell how many electrons are in that sub-shell: e.g. 1s², 3p⁴,....



- •The shell of each s and p sub-shell is the same as the period on the PT, but not so for d and f:
- •The simplest way to determine energy shell is:
 - The first s is 1s
 - The first p is 2p
 - The first d is 3d
 - The first f is 4f





•Electron Configuration

- Use shells, sub-shells, and superscripts to show where all electrons are positioned
 - Ground state electrons occupy lowest available states
 - Excited state electrons are at higher energy states due to added energy

l Group IA	1																18 Group VIIIA	
1 H 1.01	2 Group IIA											13 Group IIIA	14 Group IVA	15 Group VA	16 Group VIA	17 Group VIIA	2 He 4.00	
3	4											5	6	7	8	9	10	
Li	Be											B	С	N	0	F	Ne	
6.94	9.01											10.81	12.01	14.01	16.00	19.00	20.18	
11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Na	Mg	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Al	Si	P	8	CI	Ar	
22.99	24.31	IIIB	IVB	VB	VIB	VIIB	~	VIIIB		IB	IIB	26.98	28.09	30.97	32.07	35.45	39.95	
19 V	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36 V	
ĸ	Ca	Sc	11	V	Cr	Nin	re	Co	INI INI	Cu	Zn	Ga	Ge	AS	Se	Br	Kr	
39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38	69.72	72.64	74.92	78.96	79.90	83.80	
37 Dh	38	39	40	41 NIL	42	43 To	44 D	45 Db	40 Dd	47	48	49	50 Sm	51 Ch	52 To	53	54 Vo	
KD	Sr	X		IND	NIO	IC	Ku	Kn	Pa	Ag	Ca	In	Sn	50	le	1000	Ae	
85.47	87.62	88.91	91.22	92.91	95.96	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29	
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122.01	Da	129.01	179.40	120.05	102.04	196.21	100.22	102.22	105.09	106.07	200.50	204.29	207.2	208.08	(200)	(210)	(222)	
152.91	137.33	158.91	1/8.49	180.95	185.84	180.21	190.25	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	118	
Fr	Ra	Ac	Rf	Db	Sa	Rh	He	Mt	De	Ra	112	115	114	115	110		110	
(223)	(226)	(227)	(267)	(268)	(271)	(272)	(270)	(276)	(281)	(280)	(285)	(284)	(289)	(288)	(293)		(294)	
(225)	(220)	(227)	(207)	(200)	(271)	(272)	(270)	(270)	(201)	(200)	(205)	(204)	(20))	(200)	(275)		(2)4)	
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																	meta	als
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				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
				140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.05	174.97	
				90	91	92	93	94	95	96	97	98	99	100	101	102	103	
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
				232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)	

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- There are exceptions to expected config.
 - Electrons may shift from one subshell to another subshell of similar energy
 - Fully filled or half filled subshells may be preferable to other fractions.

- Noble Gas configuration
 - Shorthand only shows outer electrons
 - Brackets around Noble Gas represents the <u>electron configuration</u> of that gas
 - e.g. [Ar] = $1s^2 2s^2 2p^6 3s^2 3p^6$



- Use boxes, lines, or circles to show individual orbitals
- Usually only orbitals of outer sub-shells are shown
- In a given sub-shell:
 - Place one electron per orbital before pairing
 - All single electrons must have same spin
 - Paired electrons must have opposite spin

Orbital Diagrams for Hydrogen and Helium



(filled n = 1 shell!)

Orbital Diagrams for Multielectron Atoms



	C	Prbital diag	ram	Electron configuration	Condensed electron configuration				
	1 <i>s</i>	2 <i>s</i>	2р						
Li	1	1		$1s^22s^1$	$[He]2s^1$				
Be	1	1,		$1s^2 2s^2$	$[He]2s^2$				
В	1/	1,	1	$1s^2 2s^2 2p^1$	$[He]2s^{2}2p^{1}$				
С	1/	1,	11	$1s^2 2s^2 2p^2$	$[He]2s^22p^2$				
Ν	1/	1,	1111	$1s^2 2s^2 2p^3$	$[He]2s^{2}2p^{3}$				
0	1/	1,	1, 1, 1	$1s^2 2s^2 2p^4$	$[He]2s^{2}2p^{4}$				
F	1,	1,	1, 1, 1	$1s^2 2s^2 2p^5$	$[\text{He}]2s^22p^5$				
Ne	1,	1,		$1s^2 2s^2 2p^6$	$[\mathrm{He}]2s^22p^6 = [\mathrm{Ne}]$				



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Electron Configuration of Ions

- Formation of lons:
 - Gain/loss of valence electrons to achieve stable electron configuration (filled shell)
 - Cations:
 - $Na(g) \rightarrow Na^{+}(g) + e^{-}$
 - [He] $3s^1 \rightarrow$ [He] + e⁻
 - Anions:
 - $Cl(g) + e^{-} \rightarrow Cl^{-}(g)$
 - [Ne] $3s^23p^5$ + e⁻ \rightarrow [Ne] $3s^23p^6$ = [Ar]

Isoelectronic Atoms/Ions

- Main Group Elements:
 - Form ions by gain/loss of e⁻ to obtain noble gas configuration:
 - Mg \rightarrow Mg²⁺ + 2e⁻ = [Ar]
 - O + $2e^{-} \rightarrow O^{2-}$ = [Ne]
- Isoelectronic: Describes atoms/ions having identical electron configurations
 - Na⁺, Mg²⁺, O²⁻, F⁻, Ne = 1s²2s²2p⁶ (= [Ne])
 - K⁺, Cl⁻, Ca²⁺, Ar = $1s^22s^22p^63s^23p^6$ (= [Ar])

Cations of Transition Metals

- Transition Metal Cations:
 - Loss of valence electrons (s) and, in some cases, d electrons:
 - Fe: [Ar]3*d*⁶4*s*²
 - Fe^{2+} : [Ar] $3d^{6}4s^{27}$ = [Ar] $3d^{6}$ (loss of valence e⁻)
 - Fe³⁺: [Ar]3^d = [Ar]3^d (loss of one 3^d = half-filled ^d subshell!)



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Sizes of Atoms/Ions



 Half the distance between identical nuclear centers in a molecule

Metallic Radius

 half the distance between nuclear centers in the crystal of a metal

Ionic Radius

 Derived from the distance between nuclear centers in ionic crystals

Atomic, Metallic, Ionic Radii



Atomic Radius Trends

- Atomic Radii:
 - Increase going down a family
 - "Shielding" by inner shell electrons decreases effective nuclear charge (z_{eff})
 - <u>Decrease</u> going across a row
 - Increased nuclear charge (z) moving across row
 - Increased attraction for electrons in inner orbitals → atomic size decreases

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122.01	Da	129.01	179.40	120.05	102.04	196.21	100.22	102.22	105.09	106.07	200.50	204.29	207.2	208.08	(200)	(210)	(222)	
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				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
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Atomic Radii (pm)



	1	2	13	14	15	16	17	18
<i>n</i> = 1	H 37							He 32
<i>n</i> = 2	Li 	Be	B () 88	C • 77	N 0 75	0 0 73	F 0 71	Ne 69
<i>n</i> = 3	Na 186	Mg 160	Al	Si 0 117	P 0 110	S 03	C1 99	Ar 97
<i>n</i> = 4	227	Ca 197	Ga 135	Ge 122	As	Se 119	Br 114	Kr 110
<i>n</i> = 5	Rb 247	Sr 215	In () 167	Sn 140	Sb 141	Te 143	I 133	Xe 130
<i>n</i> = 6	265	Ba 222	TI 170	Рь 154	Bi	Po 167	At 140	Rn 145

Radii of Atoms and Ions





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- 3.12 Electron Affinities

Ionization Energy (IE)

- Ionization Energy:
 - Amount of energy needed to remove 1 mole of e⁻ from 1 mole of the ground-state atoms or ions in the gas phase (kJ/mole)
 - $X(g) \rightarrow X^{+}(g) + e^{-}(g)$
 - 1st Ionization Energy (IE₁): Mg(g) → Mg⁺(g)
 + e⁻
 - 2nd Ionization Energy (IE₂): Mg⁺(g) → Mg²⁺(g)
 + e⁻
 - Note: $IE_2 > IE_1$

Ionization Energy (IE)



• Periodic Trend:

- Ionization energy increases going up a group
- Ionization energy tends to increase going across a period
- Note: Lower ionization energy indicates that the atom more easily forms a cation

First Ionization Energies


Successive Ionization Energies (kJ/mol)

\checkmark	

TABLE 3.2	Successive Ionization Energies® of the First 10 Elements											
Element	z	IE,	IE ₂	IE ₃	IE4	IE _s	IE ₆	IE,	IE ₈	IE,	IE ₁₀	
Н	1	1312										
He	2	2372	5249									
Li	3	520	7296	12040								
Be	4	900	1758	15050	21070							
В	5	801	2426	3660	24682	32508						
С	6	1086	2348	4617	6201	37926	46956					
Ν	7	1402	2860	4581	7465	9391	52976	64414				
0	8	1314	3383	5298	7465	10956	13304	71036	84280			
F	9	1681	3371	6020	8428	11017	15170	17879	92106	106554		
Ne	10	2081	3949	6140	9391	12160	15231	19986	23057	115584	131236	
"In kJ/mol.												



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Electron Affinities (EA)

• Electron Affinity:

- Energy change that occurs when 1 mole of electrons combine with 1 mole of atoms or ions in the gas phase
- $Cl(g) + e^{-} \rightarrow Cl^{-}(g) = A_1 = -349 \text{ kJ/mol}$
- Periodic Trends
 - EA values become more negative moving to the right and up in the periodic table
 - A more negative EA means a stronger attraction for electrons

Periodic Trends in EA



1							18
Н -72.6	2	13	14	15	16	17	He (0.0) ^a
Li	Be	В	C	N	0	F	Ne
-59.6	>0	-26.7	-122	+7	-141	-328	(+29) ^a
Na	Mg	A1	Si	Р	S	C1	Ar
-52.9	>0	-42.5	-134	-72.0	-200	-349	(+35) ^a
К	Ca	Ga	Ge	As	Se	Br	Kr
-48.4	-2.4	-28.9	-119	-78.2	-195	-325	(+39) ^a
Rb	Sr	In	Sn	Sb	Te	I	Xe
-46.9	-5.0	-28.9	-107	-103	-190	-295	(+41) ^a
Cs	Ba	T1	Рь	Bi	Po	At	Rn
-45.5	–14	-19.2	-35.2	-91.3	-183.3	-270 ^a	(+41) ^a

^aCalculated values.



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This concludes the Lecture PowerPoint presentation for Chapter 3



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