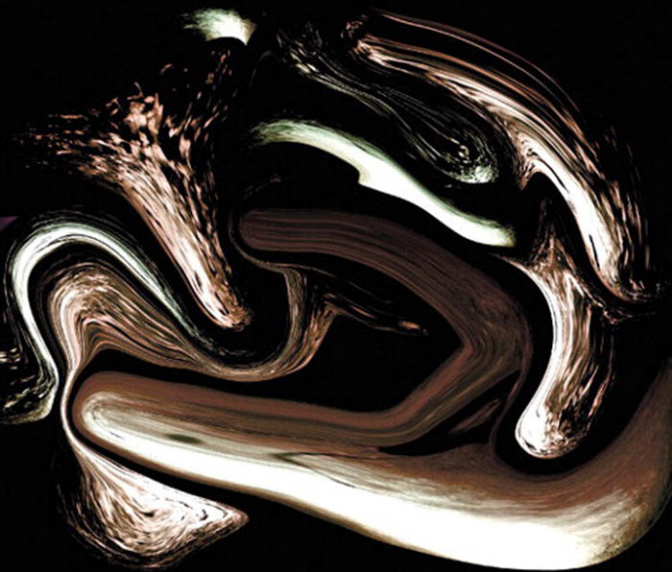


PHYSICAL CHEMISTRY

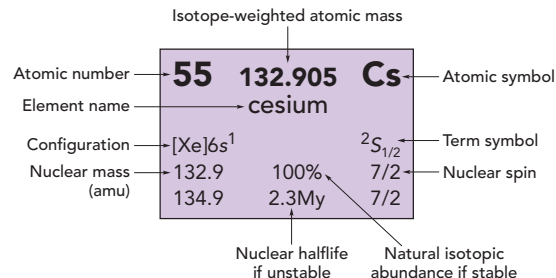
# Quantum Chemistry and Molecular Interactions



ANDREW COOKSY

## The Periodic Table of the Elements

1																														
1	1.00794 hydrogen	H																												
1s <sup>1</sup> 1.008 2.014	99.99% 0.01%	<sup>2</sup> S <sub>1/2</sub> 1/2 1																												
2																														
3	6.941 lithium	Li	4	9.01218 beryllium	Be																									
[He]2s <sup>1</sup> 7.016 6.015	<sup>2</sup> S <sub>1/2</sub> 3/2 1	3/2	[He]2s <sup>2</sup> 9.012 10.01	100% 1.5My	<sup>1</sup> S <sub>0</sub> 3/2 0																									
11	22.9898 sodium	Na	12	24.3050 magnesium	Mg																									
[Ne]3s <sup>1</sup> 22.99 21.99	<sup>2</sup> S <sub>1/2</sub> 3/2 3	3/2	[Ne]2s <sup>2</sup> 23.98 25.98	78.99% 11.01%	<sup>1</sup> S <sub>0</sub> 0 0																									
3		4		5		6		7		8		9																		
19	39.0983 potassium	K	20	40.078 calcium	Ca	21	44.9559 scandium	Sc	22	47.867 titanium	Ti	23	50.9415 vanadium	V	24	51.9961 chromium	Cr	25	54.9380 manganese	Mn	26	55.845 iron	Fe	27	58.9332 cobalt	Co				
[Ar]4s <sup>1</sup> 38.96 40.96	<sup>2</sup> S <sub>1/2</sub> 3/2 3/2	3/2	[Ar]4s <sup>2</sup> 39.96 43.95	96.94% 2.09%	<sup>1</sup> S <sub>0</sub> 0 0	[Ar]4s <sup>2</sup> 3d <sup>1</sup> 44.96 45.96	<sup>2</sup> D <sub>3/2</sub> 7/2 7/2	[Ar]4s <sup>2</sup> 3d <sup>2</sup> 47.95 49.95	<sup>3</sup> F <sub>2</sub> 0 0	[Ar]4s <sup>2</sup> 3d <sup>3</sup> 50.94 49.95	<sup>4</sup> F <sub>3/2</sub> 7/2 6/2	[Ar]4s <sup>1</sup> 3d <sup>5</sup> 51.94 52.94	<sup>7</sup> S <sub>3</sub> 83.79% 9.50%	5/2 3/2	[Ar]4s <sup>2</sup> 3d <sup>5</sup> 54.94 52.94	100% 3.7My	<sup>6</sup> S <sub>5/2</sub> 5/2 7/2	[Ar]4s <sup>2</sup> 3d <sup>6</sup> 55.93 53.94	91.8% 5.8%	<sup>5</sup> D <sub>4</sub> 0 0	[Ar]4s <sup>2</sup> 3d <sup>7</sup> 58.93 59.93	100% 5.27y	<sup>4</sup> F <sub>9/2</sub> 7/2 5				Ni			
37	85.468 rubidium	Rb	38	87.62 strontium	Sr	39	88.9059 yttrium	Y	40	91.224 zirconium	Zr	41	92.9064 niobium	Nb	42	95.94 molybdenum	Mo	43		Tc	44	101.07 ruthenium	Ru	45	102.906 rhodium	Rh				
[Kr]5s <sup>1</sup> 84.91 86.91	<sup>2</sup> S <sub>1/2</sub> 5/2 3/2	5/2	[Kr]5s <sup>2</sup> 87.91 85.91	82.6% 9.9%	<sup>1</sup> S <sub>0</sub> 0 0	[Kr]5s <sup>2</sup> 4d <sup>1</sup> 88.91 87.91	<sup>2</sup> D <sub>3/2</sub> 1/2 4	[Kr]5s <sup>2</sup> 4d <sup>2</sup> 89.91 93.91	<sup>3</sup> F <sub>2</sub> 51.45% 17.5%	<sup>5</sup> D <sub>1/2</sub> 9/2 7	[Kr]5s <sup>1</sup> 4d <sup>4</sup> 92.91 91.91	100% 37My	<sup>6</sup> D <sub>1/2</sub> 9/2 7	[Kr]5s <sup>1</sup> 4d <sup>5</sup> 97.91 95.91	24.1% 16.7%	<sup>7</sup> S <sub>3</sub> 0 0	[Kr]5s <sup>2</sup> 4d <sup>5</sup> 97.91 96.91	4.2My 2.6My	<sup>6</sup> S <sub>5/2</sub> 6 9/2	[Kr]5s <sup>1</sup> 4d <sup>7</sup> 101.9 103.9	31.6% 18.6%	<sup>5</sup> F <sub>5</sub> 0 0	[Kr]5s <sup>1</sup> 4d <sup>8</sup> 102.9 100.9	100% 3.3y	<sup>4</sup> F <sub>9/2</sub> 1/2 1/2				Pd	
55	132.905 cesium	Cs	56	137.327 barium	Ba	57	138.906 lanthanum	La	72	178.49 hafnium	Hf	73	180.948 tantalum	Ta	74	183.84 tungsten	W	75	186.207 rhenium	Re	76	190.23 osmium	Os	77	192.217 iridium	Ir				
[Xe]6s <sup>1</sup> 132.9 134.9	<sup>2</sup> S <sub>1/2</sub> 7/2 7/2	7/2	[Xe]6s <sup>2</sup> 137.9 136.9	71.7% 11.2%	<sup>1</sup> S <sub>0</sub> 3/2 3/2	[Xe]6s <sup>2</sup> 5d <sup>1</sup> 138.9 137.9	<sup>2</sup> D <sub>3/2</sub> 7/2 5	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>2</sup> 179.9 177.9	<sup>3</sup> F <sub>2</sub> 35.2% 27.1%	<sup>4</sup> F <sub>3/2</sub> 9/2 7	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>3</sup> 180.9 177.9	99.99% 0.01%	<sup>5</sup> D <sub>0</sub> 7/2 0	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>4</sup> 183.9 186.0	30.7% 28.6%	<sup>6</sup> S <sub>5/2</sub> 5/2 5/2	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>5</sup> 187.0 185.0	62.6% 37.4%	<sup>6</sup> S <sub>5/2</sub> 5/2 5/2	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>6</sup> 192.0 190.0	41.0% 26.4%	<sup>5</sup> D <sub>4</sub> 0 0	[Xe]6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>7</sup> 193.0 191.0	62.7% 37.3%	<sup>4</sup> F <sub>9/2</sub> 3/2 3/2				Pt	
87		Fr	88		Ra	89		Ac	104		Rf	105		Db	106		Sg	107		Bh	108		Hs	109		Mt				
[Rn]7s <sup>1</sup> 223.0 212.0	<sup>2</sup> S <sub>1/2</sub> 3/2 5	3/2	[Rn]7s <sup>2</sup> 226.0 228.0	1.6ky 5.76y	<sup>1</sup> S <sub>0</sub> 0 0	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 227.0 225.0	<sup>2</sup> D <sub>3/2</sub> 3/2 3/2	263 261	20m 75s	262.1 263.1	34s 27s	266 265	21s 16s	272 264	9.8s 0.44s	277 269	11.4m 9.3s	278 276	7.6s 0.72s										Ds	
58	140.115 cerium	Ce	59	140.908 praseodymium	Pr	60	144.24 neodymium	Nd	61		Pm	62	150.36 samarium	Sm	63	151.965 europium	Eu	64	157.25 gadolinium	Gd	65	158.925 terbium	Tb	66	162.50 dysprosium	Dy				
[Xe]6s <sup>2</sup> 4f <sup>1</sup> 5d <sup>1</sup> 139.9 141.9	<sup>3</sup> H <sub>1/2</sub> 0 0	5/2	[Xe]6s <sup>2</sup> 4f <sup>3</sup> 140.9 142.9	100% 13.6d	<sup>4</sup> I <sub>9/2</sub> 5/2 7/2	[Xe]6s <sup>2</sup> 4f <sup>4</sup> 141.9 143.9	<sup>5</sup> I <sub>9/2</sub> 0 0	[Xe]6s <sup>2</sup> 4f <sup>5</sup> 144.9 145.9	<sup>6</sup> H <sub>5/2</sub> 5/2 3	[Xe]6s <sup>2</sup> 4f <sup>6</sup> 151.9 153.9	<sup>7</sup> F <sub>0</sub> 0 0	[Xe]6s <sup>2</sup> 4f <sup>7</sup> 152.9 150.9	<sup>8</sup> S <sub>7/2</sub> 5/2 5/2	[Xe]6s <sup>2</sup> 4f <sup>8</sup> 157.9 159.9	52.2% 47.8%	<sup>8</sup> S <sub>7/2</sub> 5/2 5/2	[Xe]6s <sup>2</sup> 4f <sup>9</sup> 159.9 157.9	24.84% 180y	<sup>9</sup> D <sub>5</sub> 0 0	[Xe]6s <sup>2</sup> 4f <sup>10</sup> 163.9 161.9	100% 25.5y	<sup>6</sup> H <sub>15/2</sub> 3/2 3	[Xe]6s <sup>2</sup> 4f <sup>11</sup> 169.9 167.9	28.2% 25.5y	<sup>5</sup> I <sub>9</sub> 0 0				Ho	
90	232.038 thorium	Th	91		Pa	92	238.029 uranium	U	93		Np	94		Pu	95		Am	96		Cm	97		Bk	98		Cf				
[Rn]7s <sup>2</sup> 6d <sup>2</sup> 232.0 230.0	<sup>3</sup> F <sub>4</sub> 0 0	3/2	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>2</sup> 231.0 233.0	32ky 27.0d	<sup>4</sup> K <sub>11/2</sub> 3/2 3/2	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>3</sup> 238.1 235.0	<sup>5</sup> L <sub>11/2</sub> 0 7/2	[Rn]7s <sup>2</sup> 6d <sup>1</sup> 5f <sup>4</sup> 237.0 236.0	<sup>6</sup> L <sub>11/2</sub> 5/2 6	[Rn]7s <sup>2</sup> 5f <sup>6</sup> 244.1 242.1	82My 376ky	[Rn]7s <sup>2</sup> 5f <sup>7</sup> 243.1 241.1	7.4ky 432y	<sup>7</sup> F <sub>0</sub> 0 0	[Rn]7s <sup>2</sup> 5f <sup>8</sup> 248.1 248.1	16My 340ky	<sup>8</sup> S <sub>7/2</sub> 5/2 5/2	[Rn]7s <sup>2</sup> 5f <sup>9</sup> 247.1 249.1	1.4ky 320d	<sup>9</sup> D <sub>5</sub> 9/2 0	[Rn]7s <sup>2</sup> 5f <sup>10</sup> 251.1 249.1	900y 351y	<sup>6</sup> H <sub>15/2</sub> 3/2 7/2	[Rn]7s <sup>2</sup> 5f <sup>11</sup> 255.1 253.1	1.0y 9.7y	<sup>5</sup> I <sub>9</sub> 1/2 9/2				Es



Masses, natural terrestrial abundances or half-lives, and nuclear spins *I* are given for the two most abundant or longest-lived isotopes of the element. Numbers of significant digits vary among the elements.

Isotopes are listed in order of decreasing natural abundance (terrestrial abundance given in %), followed by order of decreasing half-life for those isotopes not found in nature. Units for half-life are ms (10<sup>-3</sup> s), s, m (minutes), h (hours), d (days), y (years), ky (10<sup>3</sup> years), My (10<sup>6</sup> years), and Gy (10<sup>9</sup> years).

Electron configurations and LS term symbols are given for the ground state atoms, if established. Elements that have no long-lived nuclei have often not been characterized as neutral atoms.

Atomic numbers and symbols in white type indicate elements found as gases under standard conditions at 298 K. Gray type indicates liquids. All others are solids.

Dashed outlines signify elements that occur only as radioactive isotopes.

At this writing, observations of elements 113, 115, 117, and 118 have been reported but not yet ratified by IUPAC.

For elements 104–112, 114, and 116, values for the longest-lived isotopes are in many cases uncertain.



PHYSICAL CHEMISTRY

# Quantum Chemistry

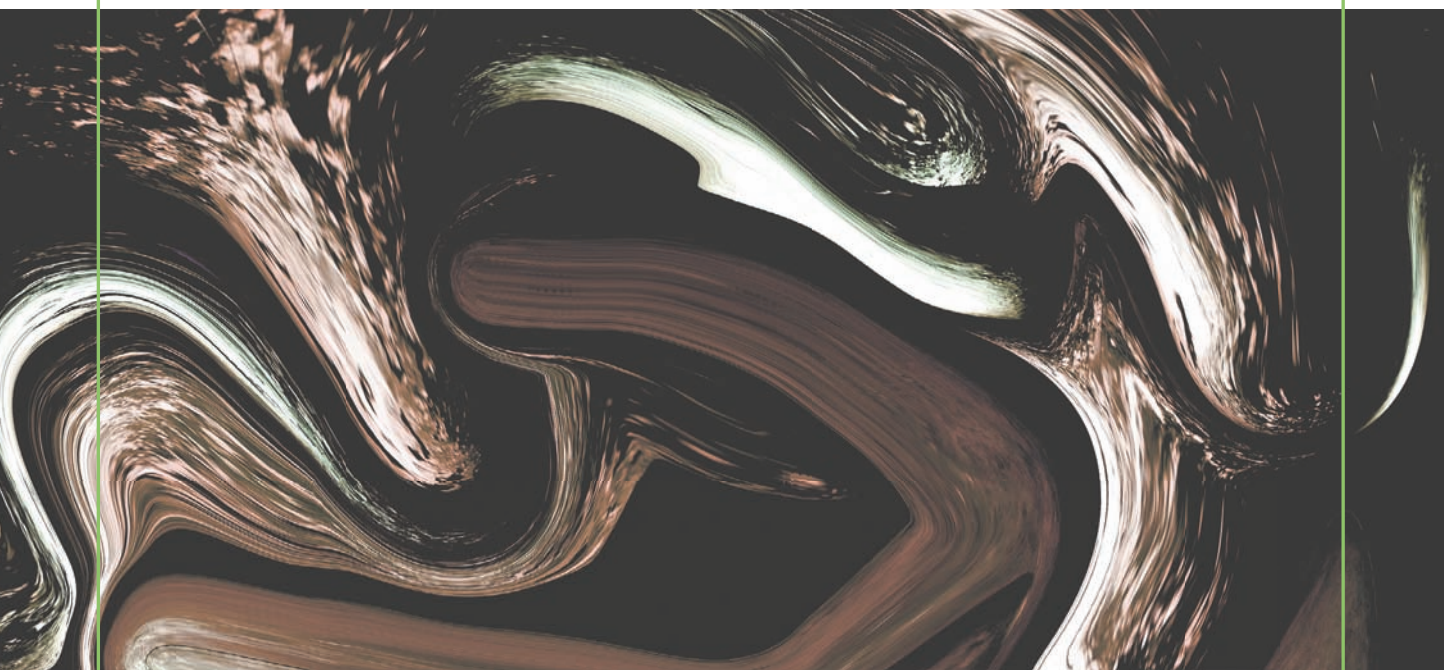
and Molecular Interactions

*This page intentionally left blank*

PHYSICAL CHEMISTRY

# Quantum Chemistry

## and Molecular Interactions



ANDREW COOKSY

**PEARSON**

Boston Columbus Indianapolis New York San Francisco Upper Saddle River  
Amsterdam Cape Town Dubai London Madrid Milan Munich Paris Montréal Toronto  
Delhi Mexico City São Paulo Sydney Hong Kong Seoul Singapore Taipei Tokyo

Editor in Chief: *Adam Jaworski*  
Executive Editor: *Jeanne Zalesky*  
Senior Marketing Manager: *Jonathan Cottrell*  
Project Editor: *Jessica Moro*  
Editorial Assistant: *Lisa Tarabokjia*  
Marketing Assistant: *Nicola Houston*  
Director of Development: *Jennifer Hart*  
Development Editor: *Daniel Schiller*  
Media Producer: *Erin Fleming*  
Managing Editor, Chemistry and Geosciences: *Gina M. Cheselka*  
Full-Service Project Management/Composition: *GEX Publishing Services*  
Illustrations: *Precision Graphics*  
Image Lead: *Maya Melenchuk*  
Photo Researcher: *Stephanie Ramsay*  
Text Permissions Manager: *Joseph Croscup*  
Text Permissions Research: *GEX Publishing Services*  
Design Manager: *Mark Ong*  
Interior Design: *Jerilyn Bockorick, Nesbitt Graphics*  
Cover Design: *Richard Leeds, BigWig Design*  
Operations Specialist: *Jeffrey Sargent*  
Cover Image Credit: *Tony Jackson/Getty Images*

Credits and acknowledgments borrowed from other sources and reproduced, with permission, in this textbook appear on the appropriate page within the text or in the back matter.

Copyright © 2014 Pearson Education, Inc. All rights reserved. Manufactured in the United States of America. This publication is protected by Copyright, and permission should be obtained from the publisher prior to any prohibited reproduction, storage in a retrieval system, or transmission in any form or by any means: electronic, mechanical, photocopying, recording, or likewise. To obtain permission to use material from this work, please submit a written request to Pearson Education, Inc., Permissions Department, 1 Lake Street, Department 1G, Upper Saddle River, NJ 07458.

Many of the designations used by manufacturers and sellers to distinguish their products are claimed as trademarks. Where those designations appear in this book, and the publisher was aware of a trademark claim, the designations have been printed in initial caps or all caps.

#### **Library of Congress Cataloging-in-Publication Data**

Cooksy, Andrew.

Physical chemistry : quantum chemistry and molecular interactions / Andrew Cooksy.

pages cm

Includes index.

ISBN-13: 978-0-321-81416-6

ISBN-10: 0-321-81416-9

1. Chemistry, Physical and theoretical--Textbooks. 2. Quantum chemistry--Textbooks. 3. Molecular dynamics--Textbooks. I. Title.

QD453.3.C655 2014

641--dc23

2012037314

1 2 3 4 5 6 7 8 9 10—RRD—16 15 14 13 12

**PEARSON**

[www.pearsonhighered.com](http://www.pearsonhighered.com)

ISBN-10: 0-321-81416-9  
ISBN-13: 978-0-321-81416-6

## DEDICATION

To Mary, Wesley, and Owen

...our great creative Mother, while she amuses us with apparently working in the broadest sunshine, is yet severely careful to keep her own secrets, and, in spite of her pretended openness, shows us nothing but results.

—*Nathaniel Hawthorne* (1804–1864) *The Birthmark*

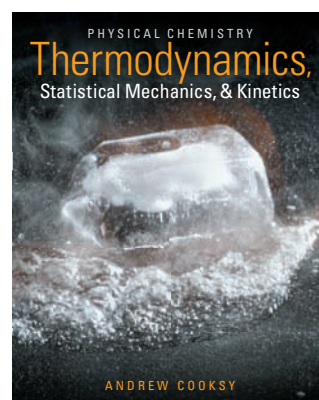


# Quantum Chemistry and Molecular Interactions

- A Introduction: Tools from Math and Physics
- 1 Classical and Quantum Mechanics
- 2 The Schrödinger Equation
- 3 One-Electron Atoms
- 4 Many-Electron Atoms
- 5 Chemical Bonds and Nuclear Magnetic Resonance
- 6 Molecular Symmetry
- 7 Electronic States and Spectroscopy
- 8 Vibrational States and Spectroscopy
- 9 Rotational States and Spectroscopy
- 10 Intermolecular Forces
- 11 Nanoscale Chemical Structure
- 12 The Structure of Liquids
- 13 The Structure of Solids

# Thermodynamics, Statistical Mechanics, & Kinetics

- A Introduction: Tools from Math and Physics
- 1 Classical Physical Chemistry Sets the Stage
- 2 Introduction to Statistical Mechanics: Building Up to the Bulk
- 3 Partitioning the Energy
- 4 Statistical Mechanics and Molecular Interactions
- 5 Mass Transport: Collisions and Diffusion
- 6 Energy Transport: Radiation and Matter
- 7 Introduction to Thermodynamics: Heat Capacity
- 8 The First Law: Expansion and Engines
- 9 The Second and Third Laws: Entropy
- 10 Phase Transitions and Phase Equilibrium
- 11 Solutions
- 12 The Thermodynamics of Chemical Reactions
- 13 Chemical Kinetics: Elementary Reactions
- 14 Chemical Kinetics: Multi-Step Reactions



## PHYSICAL CHEMISTRY

Quantum Chemistry and  
Molecular Interactions

## A Introduction: Tools from Math and Physics 3

A.1 Mathematics 3

A.2 Classical Physics 29

PROBLEMS 34

PART I  
ATOMIC STRUCTURE 37

## 1 Classical and Quantum Mechanics 38

1.1 Introduction to the Text 39

1.2 The Classical World 41

1.3 The Quantum World 44

TOOLS OF THE TRADE Low Energy Electron Diffraction 48

1.4 One-Electron Atoms 49

1.5 Merging the Classical and Quantum Worlds 57

PROBLEMS 63

## 2 The Schrödinger Equation 67

2.1 Mathematical Tools of Quantum Mechanics 68

BIOSKETCH Lene Vestergaard Hau 79

2.2 Fundamental Examples 86

PROBLEMS 99

### 3 One-Electron Atoms 103

**3.1** Solving the One-Electron Atom Schrödinger Equation 104

**BIOSKETCH** Peter Beiersdorfer 116

**3.2** The One-Electron Atom Orbital Wavefunctions 121

**3.3** Electric Dipole Interactions 135

**TOOLS OF THE TRADE** Atomic Absorption Spectroscopy 137

**3.4** Magnetic Dipole Interactions 138

**PROBLEMS** 149

### 4 Many-Electron Atoms 155

**4.1** Many-Electron Spatial Wavefunctions 157

**TOOLS OF THE TRADE** Photoelectron Spectroscopy 163

**4.2** Approximate Solution to the Schrödinger Equation 164

**BIOSKETCH** Sylvia Ceyer 179

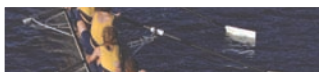
**4.3** Spin Wavefunctions and Symmetrization 179

**4.4** Vector Model of the Many-Electron Atom 186

**4.5** Periodicity of the Elements 190

**4.6** Atomic Structure: The Key to Chemistry 191

**PROBLEMS** 196



## PART II MOLECULAR STRUCTURE 205

### 5 Chemical Bonds and Nuclear Magnetic Resonance 206

**5.1** The Molecular Hamiltonian 208

**5.2** The Molecular Wavefunction 214

**5.3** Covalent Bonds in Polyatomic Molecules 223

**BIOSKETCH** Douglas Grotjahn 225

**5.4** Non-Covalent Bonds 231

**5.5** Nuclear Magnetic Resonance Spectroscopy 233

**TOOLS OF THE TRADE** Nuclear Magnetic Resonance Spectroscopy 234

**PROBLEMS** 253

- 6 Molecular Symmetry** 259
- 6.1** Group Theory 260
  - 6.2** Symmetry Representations for Wavefunctions 276
    - BIOSKETCH** James Rondinelli 280
  - 6.3** Selection Rules 290
    - TOOLS OF THE TRADE** Ramen Spectrometers 295
  - 6.4** Selected Applications 297
- PROBLEMS** 303
- 7 Electronic States and Spectroscopy** 311
- 7.1** Molecular Orbital Configurations 312
    - BIOSKETCH** Arthur Suits 319
  - 7.2** Electronic States 323
    - TOOLS OF THE TRADE** UV-vis Spectroscopy 328
  - 7.3** Computational Methods for Molecules 333
  - 7.4** Energetic Processes 338
- PROBLEMS** 345
- 8 Vibrational States and Spectroscopy** 355
- 8.1** The Vibrational Schrödinger Equation 356
  - 8.2** Vibrational Energy Levels in Diatomics 364
    - BIOSKETCH** Nathan Hammer 368
  - 8.3** Vibrations in Polyatomics 371
    - TOOLS OF THE TRADE** Fourier Transform Infrared (FTIR) Spectroscopy 374
  - 8.4** Spectroscopy of Vibrational States 382
- PROBLEMS** 389
- 9 Rotational States and Spectroscopy** 395
- 9.1** Rotations in Diatomics 396
  - 9.2** Rotations in Polyatomics 400
    - BIOSKETCH** Stewart Novick 402
  - 9.3** Spectroscopy of Rotational States 406
    - TOOLS OF THE TRADE** Radio Astronomy 408
- PROBLEMS** 416



**PART III**  
MOLECULAR INTERACTIONS 421

- 10 Intermolecular Forces** 422
- 10.1** Intermolecular Potential Energy 424
    - BIOSKETCH** Helen O. Leung and Mark D. Marshall 426
    - TOOLS OF THE TRADE** Molecular Beams 439
  - 10.2** Molecular Collisions 458
  - PROBLEMS** 466
- 11 Nanoscale Chemical Structure** 471
- 11.1** The Nanoscopic Scale 472
  - 11.2** Clusters 474
    - TOOLS OF THE TRADE** Scanning Tunneling and Atomic Force Microscopy 484
  - 11.3** Macromolecules 490
    - BIOSKETCH** James V. Coe 491
  - PROBLEMS** 498
- 12 The Structure of Liquids** 501
- 12.1** The Qualitative Nature of Liquids 502
  - 12.2** Weakly Bonded Pure Liquids 505
    - TOOLS OF THE TRADE** Neutron Diffraction 507
  - 12.3** Solvation 514
    - BIOSKETCH** Martina Havenith-Newen 516
  - PROBLEMS** 521
- 13 The Structure of Solids** 523
- 13.1** Amorphous Solids, Polymers, and Crystals 524
  - 13.2** Symmetry in Crystals 527
    - TOOLS OF THE TRADE** X-Ray Crystallography 534
  - 13.3** Bonding Mechanisms and Properties of Crystals 538
    - BIOSKETCH** Susan Kauzlarich 544
  - 13.4** Wavefunctions and Energies of Solids 546
  - PROBLEMS** 552
- Appendix: Character Tables for Common Point Groups 555
- Solutions to Objectives Review Questions 561
- Credits 563
- Index 565

This book is intended to provide students with a detailed guide to the reasoning that forms the basis for physical chemistry—the framework that unites all chemistry. The study of physical chemistry gives us the opportunity to look at our science as an integrated whole, with each concept connected to the next. My goal has been to trace those connections, step-by-step whenever possible, to show how each new concept makes sense given its place in the framework.

Because its ideas build upon each other in this way, physical chemistry can serve as the foundation for an intuitive understanding of chemistry in all its forms, whether synthesizing new compounds, analyzing samples in a forensic laboratory, or studying the properties of novel materials. To that end, this book emphasizes the shared, fundamental principles of chemistry, showing how we can justify the form and behavior of complex chemical systems by applying the laws of mathematics and physics to the structures of individual particles and then extrapolating to larger systems. We learn physical chemistry so that we can recognize these fundamental principles when we run into them in our other courses and in our careers. The relevance of this discipline extends beyond chemistry to engineering, physics, biology, and medicine: any field in which the molecular structure of matter is important.

A key step toward cultivating an intuition about chemistry is a thorough and convincing presentation of these fundamentals. When we see not only what the ideas are, but also how they link together, those ideas become more discernible when we examine a new chemical system or process. The following features of this text seek to achieve that objective.

- My aim is to provide a rigorous treatment of the subject in a relaxed style. A combination of qualitative summaries and annotated, step-by-step derivations illuminates the logic connecting the theory to the parameters that we can measure by experiment. Although we use a lot of math to justify the theory we are developing, the math will always make sense if we look at it carefully. We take advantage of this to strengthen our confidence in the results and our understanding of how the math relates to the physics. Nothing is more empowering in physical chemistry than finding that you can successfully predict a phenomenon using both mathematics *and* a qualitative physical argument. The manifestation of atomic and molecular structure in bulk properties of materials is a theme that informs the unhurried narrative throughout the text.

- To illustrate how our understanding in this field continues to advance, we take the time to examine several tools commonly used in the laboratory (“Tools of the Trade”), while profiles of contemporary scientists (“Biosketches”) showcase the ever-expanding frontiers of physical chemistry. Our intuition about chemistry operates at a deep level, held together by the theoretical framework, but these examples show how others are applying their understanding to solve real problems in the laboratory and beyond. They inspire us to think creatively about how the most fundamental chemical laws can answer our own questions about molecular structure and behavior.
- Our increasing appreciation and exploration of the interface between the molecular and the bulk scales has inspired a forward-looking coverage of topics that includes chapters dedicated to intermolecular interactions, nanoscale chemical structure, and liquid structure.

## Acknowledgments

I thank Kwang-Sik Yun and Andrew P. Stefani for providing the original inspiration and encouragement to carry out this project. My love of this field owes much to my mentors—William Klemperer, Richard J. Saykally, and Patrick Thaddeus—and to the many students and colleagues who have patiently discussed chemistry with me. I am particularly grateful to my fellow physical chemistry faculty—Steve Davis and Kwang-Sik Yun at Ole Miss, David Pullman and Karen Peterson at SDSU—for their many insights and limitless forbearance, and to William H. Green and the late John M. Brown for kindly hosting my sabbatical work in their research groups. An early prospectus for this book formed part of the proposal for an NSF CAREER grant, and I thank the agency for that support.

For helping me see this through, I thank my friends and mentors at Pearson, especially Nicole Folchetti, Adam Jaworski, Dan Kaveney, Jennifer Hart, Jessica Moro, and above all Jeanne Zalesky. A great debt is also owed to Dan Schiller for his patient and extensive work editing the manuscript. Thanks to Mary Myers for much work on the original manuscript, and to many in the open-source community for the tools used to assemble it. Finally, I thank all of our faculty and student reviewers for their careful reading and thoughtful criticisms. A textbook author could strive for no higher goal than to do justice to the fascination that we share for this subject.



## Reviewers

- Ludwik Adamowicz  
*University of Arizona*
- Larry Anderson  
*University of Colorado*
- Alexander Angerhofer  
*University of Florida*
- Matthew Asplund  
*Brigham Young University*
- Tom Baer  
*University of North Carolina*
- Russ Baughman  
*Truman State University*
- Nikos Benteinis  
*Southwestern University*
- John Bevan  
*Texas A&M University*
- Charles Brooks  
*University of Michigan*
- Mark Bussell  
*Western Washington University*
- Beatriz Cardelino  
*Spelman College*
- Donna Chen  
*University of South Carolina*
- Samuel Colgate  
*University of Florida*
- Stephen Cooke  
*Purchase College, the State University  
of New York*
- Paul Cooper  
*George Mason University*
- Phillip Coppens  
*University at Buffalo, the State  
University of New York*
- Biamxiao Cui  
*Stanford University*
- Alfred D'Agostino  
*University of Notre Dame*
- Paul Davidovits  
*Boston College*
- Borguet Eric  
*Temple University*
- Michelle Foster  
*University of Massachusetts*
- Sophya Garashchuk  
*University of South Carolina*
- Franz Geiger  
*Northeastern University*
- Kathleen Gilbert  
*New Jersey Institute of Technology*
- Derek Gragson  
*California Polytechnic State University*
- Hua Guo  
*University New Mexico*
- John Hagen  
*California Polytechnic State University*
- Cynthia Hartzell  
*Northern Arizona University*
- Bill Hase  
*Texas Tech University*
- Clemens Heske  
*University of Nevada, Las Vegas*
- Lisa Hibbard  
*Spelman College*
- Brian Hoffman  
*Northeastern University*
- Xiche Hu  
*University of Toledo*
- Bruce Hudson  
*Syracuse University*
- David Jenson  
*Georgia Institute of Technology*
- Benjamin Killian  
*University of Florida*
- Judy Kim  
*University of California, San Diego*
- Krzysztof Kuczera  
*University of Kansas*
- Joseph Kushick  
*University of Massachusetts, Amherst*
- Marcus Lay  
*University of Georgia, Athens*
- Lisa Lever  
*University of South Carolina*
- Louis Madsen  
*Virginia Polytechnic Institute and  
State University*

- Elache Mahdavian  
*Louisiana State University*
- Herve Marand  
*Virginia Polytechnic Institute and  
State University*
- Ruhullah Massoudi  
*South Carolina University*
- Gary Meints  
*Missouri State University*
- Ricardo Metz  
*University of Massachusetts*
- Kurt Mikkelsen  
*University of Copenhagen*
- Phambu Nsoki  
*Tennessee State University*
- Jamiu Odutola  
*Alabama A&M University*
- Jason Pagano  
*Saginaw Valley State University*
- James Patterson  
*Brigham Young University*
- James Phillips  
*University of Wisconsin*
- Simon Phillpot  
*University of Florida*
- Rajeev Prabhakar  
*Miami University*
- Robert Quandt  
*Illinois State University*
- Ranko Richert  
*Arizona State University*
- Tim Royappa  
*University of West Florida*
- Stephen Sauer  
*University of Copenhagen*
- G. Alan Schick  
*Missouri State University*
- Charles Schmuttenmaer  
*Yale University*
- Rod Schoonover  
*California Polytechnic State University*
- Alexander Smirnov  
*North Carolina State University*
- J. Anthony Smith  
*Walla Walla University*
- Karl Sohlberg  
*Drexel University*
- David Styers-Barnett  
*Indiana University*
- James Turner  
*Virginia Commonwealth University*
- Greg Van Patten  
*Ohio University*
- John Vohs  
*University of Pennsylvania*
- Michael Wagner  
*George Washington University*
- Brian Woodfield  
*Brigham Young University*
- Dong Xu  
*Boise State University*
- Eva Zurek  
*University at Buffalo, the State  
University of New York*



### **Andrew Cooksy**

B.A., chemistry and physics, Harvard College, 1984;  
Ph.D., chemistry, University of California, Berkeley, 1990;  
Postdoctoral Research Associate, Harvard-Smithsonian Center for Astrophysics and  
Harvard University Department of Chemistry, 1990-1993;  
Asst. and Assoc. Professor, University of Mississippi Department of Chemistry,  
1993-1999. Asst. and Assoc. Professor, San Diego State University Department  
of Chemistry, 1999-2010. Professor, San Diego State University Department of  
Chemistry, 2010-.  
Northrop-Grumman Excellence in Teaching Award, 2010  
Senate Excellence in Teaching Award, SDSU College of Sciences, 2011

# A Rigorous Standard with a Relaxed Style

“ A course in physical chemistry can describe the physical universe with uncommon depth, breadth, and clarity. The aim of this book is to help the reader make the most of the experience. ”

—Andrew Cooksy

**PHYSICAL CHEMISTRY** is the framework that unites all chemistry—providing powerful insight into the discipline as an integrated series of connected concepts.

As an instructor and author, Andrew Cooksy helps students uncover these connections while showing how they can be expressed in mathematical form and demonstrating the power that derives from such expressions.

The text's lively and relaxed narrative illuminates the relationship between the mathematical and the conceptual for students. By formulating the fundamental principles of physical chemistry in a mathematically precise but easily comprehensible way, students are able to acquire deeper insight—and greater mastery—than they ever thought possible.

This innovative approach is supported by several exclusive features:

- **Split quantum and thermodynamics volumes** can be taught in either order for maximum course flexibility.
- **A discrete chapter** (Chapter A) included in each volume summarizes the physics and mathematics used in physical chemistry.
- **Chapter opening sections** orient the students within the larger context of physical chemistry, provide an overview of the chapter, preview the physical and mathematical relationships that will be utilized, and set defined chapter objectives.
- **Unique pedagogical features** include annotations for key steps in derivations and an innovative use of color to identify recurring elements in equations.

# Uncovering connections between foundational concepts

Reflective of the author's popular lecture strategy, chapter opening and closing features ground each topic within the larger framework of physical chemistry and help students stay oriented as they follow the development of chapter concepts.

**Learning Objectives** outline the skills students should expect to acquire from their study of the chapter.

**Visual Roadmaps** help students see the relationship between the chapters in each part of the text and the topics in each chapter.

**PART I ATOMIC STRUCTURE**

**PART II MOLECULAR STRUCTURE**

**PART III MOLECULAR INTERACTIONS**

1 Classical and Quantum Mechanics  
2 The Schrödinger Equation  
3 One-Electron Atoms  
4 Many-Electron Atoms

## 1 Classical and Quantum Mechanics

**LEARNING OBJECTIVES**  
After reading this chapter, you will be able to do the following:

- 1 Convert between frequency, wavelength, and photon energy of electromagnetic radiation
- 2 Use the de Broglie wavelength to determine if quantum mechanics is needed to describe a particular system
- 3 Calculate the electronic energies of a one-electron atom and estimate other properties based on the Bohr model

**GOAL Why Are We Here?**  
The goal of this chapter is to introduce the general concepts of classical mechanics and quantum mechanics that pertain to atomic structure. In the process, it will demonstrate where and why we will need quantum mechanics to assemble an accurate theory of atomic and molecular structure.

**CONTEXT Where Are We Now?**  
For chemistry, the very smallest particles are electrons and atomic nuclei, and this is where we begin. Particle physicists divide matter into a more extensive library of particles comprising two families: *hadrons* (particles such as protons and neutrons that are composed of *quarks*) and *leptons* (non-quark matter, including electrons). But we have enough work ahead, and so we restrict ourselves to ordinary matter, except perhaps for an occasional example. This chapter introduces the concepts that guided our understanding of radiation and matter as we entered the twentieth century, and the preliminary results that forever enlarged that understanding. These ideas not only serve us as a springboard to the more advanced theory of today, but also provide a foundation that we will often return to for a better appreciation of how matter and energy work at all scales.

**SUPPORTING TEXT How Did We Get Here?**  
Throughout the book, we will call on results from physics and math to clear the path as we take the next step. This chapter, which starts with the smallest building blocks of chemistry, is no exception. The following principles will be useful to us in the work ahead:

- The kinetic energy  $K$  of a particle with mass  $m$  and speed  $v$  is given by Eq. A.36:

$$K = \frac{mv^2}{2}$$

38

**Context: Where Do We Go From Here?** sections at the end of each chapter afford students a perspective on what they have just learned, and how it provides the foundation for the material explored in the next chapter.

**Goal: Why Are We Here?** chapter openers prepare students for the work ahead using one to two simple sentences.

**Context: Where Are We Now?** helps students understand how the chapter they are starting is related to what has come before and its place in the unfolding development of physical chemistry.

**Supporting Text: How Did We Get Here?** reviews previously introduced concepts, mathematical tools, and topical relationships that the new chapter will draw on.

# Active research, tools, and techniques

Through learning about the instruments and methods of modern physical chemistry and meeting researchers at work today, students gain an appreciation for the practical applications of this science to many fields.

## TOOLS OF THE TRADE Photoelectron Spectroscopy

One of the early keys to quantum theory was Albert Einstein's explanation of the **photoelectric effect**. In 1887, Heinrich Hertz discovered that the generation of electricity at a metal surface could be enhanced by ultraviolet light. From the results of subsequent experiments by Philipp Lenard, Einstein concluded that the energy of electromagnetic radiation is carried in units of photons, and that the surface absorbs energy *one photon at a time*, with each interaction causing an energy change at the surface. If the photon energy surpasses a threshold value  $IE$  sufficient to expel an electron, any excess energy in the photon provides the kinetic energy of the ejected electron. Raising the intensity of the light merely provides more photons, increasing the number of interactions but not the energy of each interaction. If  $h\nu$  is not high enough to ionize the sample, no electrons will be ejected. In a gas, the  $IE$  is the first ionization energy, the energy difference between the ion and the neutral atom or molecule  $M$ ,  $IE = E(M^+) - E(M)$ . In a solid  $IE$  is called the **work function**.

We continue to take advantage of this technique in order to measure electronic transition energies by using a known photon energy  $h\nu$  and then measuring the kinetic energy of the electrons:

$$\Delta E = h\nu - \frac{m_e v^2}{2}$$

This principle established the foundation for **photoelectron spectroscopy**.

**What is photoelectron spectroscopy?** In photoelectron spectroscopy, we strike the sample with a burst of ionizing photons, all at energy  $h\nu$ , and then measure the distribution in kinetic energies of the electrons that reach the detector in order to generate the spectrum of  $\Delta E$  values.

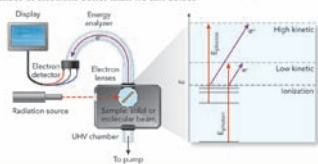
**Why do we use photoelectron spectroscopy?** Photoelectron spectroscopy has three advantages over absorption spectroscopy: (i) the sensitivity is much higher because we can detect the tiny currents generated by a small number of electrons better than we can detect

a tiny decrease in the intensity of radiation passing through a sample; (ii) ionizations are not subject to the  $\Delta l = \pm 1$  selection rule (Section 3.3), because the ejected electron can carry away the necessary angular momentum; (iii) in a many-electron atom or molecule, both the neutral  $M$  and the ion  $M^+$  have distinct quantum states, and the values of  $\Delta E$  we measure tell us about the energy levels of the neutral and the ion in the same experiment.

Photoelectron spectroscopy is a zero-background technique, meaning that the detector sees nothing (except a weak noise signal) until there is an interaction between the radiation and the sample. In addition, our ability to measure charged particles such as electrons or ions is usually much better than our ability to detect photons. For one thing, we can use electric fields to accelerate charged particles before they reach the detector, so that they hit the detector with considerably greater energy than they had originally, and with greater energy than a typical photon in the experiment would have.

**How does it work?** In photoelectron spectroscopy, a pulse of laser light at a known photon energy ionizes the sample in an ultrahigh vacuum chamber. The electrons are directed by magnetic fields down a drift tube toward a detector to separate the different velocities. Just before the detector, the electrons are rapidly accelerated and focused to amplify the signal. The raw measurements consist of electron signals—electrical currents at the detector—tabulated as a function of the time after the laser pulse. From the drift times  $\Delta t$  and the known length  $d$  of the drift tube, we can calculate the electron speeds  $v = d/\Delta t$  and convert the speeds into electron kinetic energies  $mv^2/2$ .

Gas-phase photoelectron spectroscopy is used chiefly for research into atomic and molecular energy levels. In addition, x-ray photoelectron spectroscopy is a common application of the technique, used on solid samples as a means of rapidly characterizing the elemental and molecular composition of materials or coatings.



Photoelectron spectroscopy.

**Tools of the Trade** sections highlight the design and operation of commonly used experimental apparatuses and how they relate to the principles discussed in the chapter.

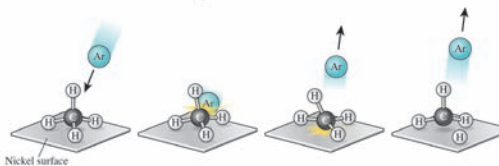
**Biosketches** highlight a diverse array of contemporary scientists and engineers and their current research relating to physical chemistry.

## BIOSKETCH Sylvia Ceyer



Sylvia Ceyer is the J. C. Sheehan Professor of Chemistry at MIT, where she and her research group investigate how molecules interact with solid surfaces. One of her goals has

been a better understanding of the pressure-dependence of chemical reactions that occur on a surface. Surface chemistry is normally investigated under ultra-high vacuum conditions, at pressures of  $10^{-13}$  bar or less, in order to allow methods like Auger spectroscopy (Example 4.3) and electron diffraction (Section 1.3) to characterize the reaction. These conditions make it difficult to study how pressure affects the reaction, however. The Ceyer group developed one technique that they christened "Chemistry with a Hammer." In this method, the reactant—methane, for example—is gently laid on the solid surface with too little energy to react. A high-speed beam of non-reactive noble gas atoms then strikes the surface, raising the effective temperature and pressure at the surface—simulating the reaction conditions the group wants to study, but only at the point at which the beam hits the surface. Overall, the pressure is still low enough to allow diagnostic tools like Auger spectroscopy and electron diffraction to function.



Nickel surface

▲ Chemistry with a hammer. (After an image by Tom Dunne, *American Scientist* 87, p. 21, 1999).

# Conceptual Insight and Mathematical Precision in a Real World Context

A discrete summary of the prerequisite mathematics and physics adds flexibility and convenience by incorporating the necessary math tools in a single chapter.

**TABLE A.5 Solutions to selected integrals.** In these equations,  $a$  and  $b$  are constants,  $n$  is a whole number, and  $C$  is the constant of integration.

$\int x^n dx = \frac{1}{n+1} x^{n+1} + C$	$\int dx = a(x + C)$
$\int \frac{1}{x} dx = \ln x + C$	$\int e^x dx = e^x + C$
$\int \ln x dx = x \ln x - x + C$	$\int \frac{dx}{x(a+bx)} = -\frac{1}{a} \ln \left( \frac{a+bx}{x} \right) + C$
$\int \sin x dx = -\cos x + C$	$\int \cos x dx = \sin x + C$
$\int \sin^2(ax) dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} + C$	$\int \cos^2(ax) dx = \frac{x}{2} + \frac{\sin(2ax)}{4a} + C$
$\int [f(x) + g(x)] dx = \int f(x) dx + \int g(x) dx$	$\int_a^b dx = x \Big _a^b = b - a$
$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$	$\int_0^\infty e^{-ax} dx = \frac{1}{a} \left( \frac{\pi}{a} \right)^{1/2}$
$\int_0^\infty x e^{-ax} dx = \frac{1}{a^2}$	$\int_0^\infty x^2 e^{-ax} dx = \frac{1}{a^3} \left( \frac{\pi}{a} \right)^{1/2}$
$\int_0^\infty x^{2n+1} e^{-ax} dx = \frac{n!}{2a^{n+1}}$	$\int_0^\infty x^{2n} e^{-ax} dx = \frac{[1 \cdot 3 \cdot 5 \cdots (2n-1)] \sqrt{\pi}}{2^{n+1} a^{n+1/2}}$
$\int_0^\infty x^p e^{-ax} dx = \frac{n!}{a^{n+1}} - e^{-ax} \sum_{i=0}^n \frac{n! a^{i-1}}{i!(n-i)!}$	

the value of  $C$  is lost. When we undo the derivative by taking the integral, we add an unknown constant of integration to the integrated expression. Omit this constant when solving definite integrals, because the limits of integration will determine its value.

- The function being integrated is the **integrand**, and it is multiplied by the incremental change along the coordinates, called the volume element.

Most of the algebraic solutions to integrals that we need appear in Table A.5.

## EXAMPLE A.4 Analytical Integration

**PROBLEM** Evaluate the numerical value for each of the following expressions.

- $\int_1^4 \frac{dx}{x}$
- $\int_0^\infty e^{-2x} dx$
- $\int_0^{\pi/3} (3 \cos^2 \theta - 1) \sin \theta d\theta$

**SOLUTION** These can be solved by substitution of the expressions in Table A.5.

- $\int_1^4 \frac{dx}{x} = \ln x \Big|_1^4 = \ln 4 - \ln 1 = 1.386 - 0 = 1.386$
- $\int_0^\infty e^{-2x} dx = -\frac{1}{2} e^{-2x} \Big|_0^\infty = -\frac{1}{2} (e^{-\infty} - e^0) = -\frac{1}{2} (0 - 1) = \frac{1}{2}$
- $\int_0^{\pi/3} (3 \cos^2 \theta - 1) \sin \theta d\theta = [-\cos^3 \theta + \cos \theta]_0^{\pi/3} = \left[ -\left(\frac{1}{2}\right)^3 + \left(\frac{1}{2}\right) \right] - [-(1)^3 + (1)] = \frac{3}{8}$

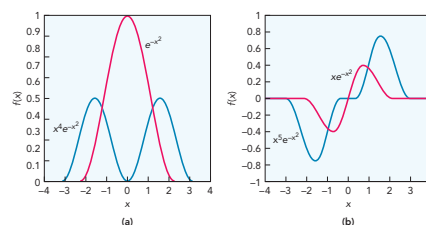
By the way, it is possible to apply rules of symmetry to extend some of the analytical solutions in Table A.5. For example, when the integrand is  $x^{2n} e^{-ax^2}$ , then the function is exactly the same from 0 to  $-\infty$  as from 0 to  $+\infty$  (Fig. A.3a). Therefore, the integral  $\int_{-\infty}^\infty x^{2n} e^{-ax^2} dx$  is equal to 2 times  $\int_0^\infty x^{2n} e^{-ax^2} dx$ . However, if the power of  $x$  is odd,  $2n + 1$ , then the function is negative when  $x < 0$  and positive when  $x > 0$  (Fig. A.3b). The integral from  $-\infty$  to 0 cancels the integral from 0 to  $+\infty$ , so  $\int_{-\infty}^\infty x^{2n+1} e^{-ax^2} dx = 0$ .

## Numerical Integration

Not all integrals have algebraic solutions, and some have algebraic solutions only between certain limits (such as 0 and  $\infty$ ). With suitable computers, any integral can be calculated without trying to cram it into some algebraic form. This is accomplished by going back to the definition in calculus,

$$\int_{x_i}^{x_N} f(x) dx = \lim_{\delta x \rightarrow 0} \left\{ \sum_{i=1}^N f[x_i + i \delta x] \delta x \right\} \quad (\text{A.20})$$

**FIGURE A.3 Symmetry and definite integrals.** (a) If a function  $f(x)$  is equal to  $f(-x)$  for all values of  $x$ , then the integral from  $-\infty$  to  $+\infty$  is equal to 2 times the integral from 0 to  $+\infty$ . (b) If  $f(x)$  is equal to  $-f(-x)$ , then the integral from  $-\infty$  to  $+\infty$  is 0.



**Chapter A** provides a comprehensive summary of the physical laws and mathematical tools used to develop the principles of physical chemistry.

The distinctive use of color in the text's mathematical narrative allows students to identify important equation elements (such as the Hamiltonian operator) even as they take on different mathematical forms.

$$\begin{aligned}
 \hat{L}^2\Theta(\theta) &= -\hbar^2 \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} - \frac{m_l^2}{\sin^2\theta} \right] A_\theta \sin^k\theta && \text{Eqs. 3.5 and 3.10} \\
 &= -A_\theta \hbar^2 \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta (k \sin^{k-1}\theta \cos\theta) - m_l^2 \sin^{k-2}\theta \right] && \text{take } \frac{\partial}{\partial\theta} \\
 &= -A_\theta \hbar^2 \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (k \sin^k\theta \cos\theta) - m_l^2 \sin^{k-2}\theta \right] && \times \sin\theta \\
 &= -A_\theta \hbar^2 \left[ \frac{1}{\sin\theta} (k^2 \sin^{k-1}\theta \cos^2\theta - k \sin^{k+1}\theta) - m_l^2 \sin^{k-2}\theta \right] && \text{take } \frac{\partial}{\partial\theta} \\
 &= -A_\theta \hbar^2 [(k^2 \sin^{k-2}\theta \cos^2\theta - k \sin^k\theta) - m_l^2 \sin^{k-2}\theta] && \times \sin^{-1}\theta \\
 &= -A_\theta \hbar^2 [(k^2 \sin^{k-2}\theta (1 - \sin^2\theta) - k \sin^k\theta) - m_l^2 \sin^{k-2}\theta] && \sin^2\theta + \cos^2\theta = 1 \\
 &= -A_\theta \hbar^2 [(k^2 \sin^{k-2}\theta - k^2 \sin^k\theta - k \sin^k\theta) - m_l^2 \sin^{k-2}\theta].
 \end{aligned}$$

Thoughtful **color-coding** in key equations makes it easier for students to follow the development of complex derivations as well as recognize common mathematical elements that appear in the representation of different physical situations.

## Derivations Demystified

$$\begin{aligned}
 \hat{p}_x \psi_\pm(x) &= \frac{\hbar}{i} \frac{\partial}{\partial x} \left[ \cos\left(\frac{2\pi x}{\lambda_{dB}}\right) \pm i \sin\left(\frac{2\pi x}{\lambda_{dB}}\right) \right] \\
 &= \frac{\hbar}{i} \left[ -\left(\frac{2\pi}{\lambda_{dB}}\right) \sin\left(\frac{2\pi x}{\lambda_{dB}}\right) \pm i \left(\frac{2\pi}{\lambda_{dB}}\right) \cos\left(\frac{2\pi x}{\lambda_{dB}}\right) \right] && \text{take } \frac{\partial}{\partial x} \\
 &= \frac{2\pi\hbar}{\lambda_{dB}} \left[ -\frac{1}{i} \sin\left(\frac{2\pi x}{\lambda_{dB}}\right) \pm \cos\left(\frac{2\pi x}{\lambda_{dB}}\right) \right] && \text{rearrange constants} \\
 &= \frac{\hbar}{\lambda_{dB}} \left[ i \sin\left(\frac{2\pi x}{\lambda_{dB}}\right) \pm \cos\left(\frac{2\pi x}{\lambda_{dB}}\right) \right] && 2\pi\hbar = h, \quad 1/i = -i \\
 &= p_x \left[ \pm \cos\left(\frac{2\pi x}{\lambda_{dB}}\right) + \sin\left(\frac{2\pi x}{\lambda_{dB}}\right) \right] && h/\lambda_{dB} = p_x, \text{ switch terms} \\
 &= \pm p_x \left[ \cos\left(\frac{2\pi x}{\lambda_{dB}}\right) \pm i \sin\left(\frac{2\pi x}{\lambda_{dB}}\right) \right] && \text{factor out } \pm 1, \\
 &= \pm |p_x| \psi_\pm(x). && (2.24)
 \end{aligned}$$

Derivations are made transparent and comprehensible to students without sacrifice of mathematical rigor. **Colored annotations** provide crucial help to students by explaining important steps in key derivations.

**DERIVATION SUMMARY The Angular Solution.** We chose a reasonable guess for the angular wavefunction, leaving several free parameters undecided, and just operated on the thing with  $\hat{L}^2$ , requiring that we get an eigenvalue equation. That equation was only satisfied by wavefunctions with a squared angular momentum value  $L^2$  of  $\hbar^2 l(l+1)$ , with  $l$  some whole number.

**Summaries** spell out the essential results of difficult derivations, making it easier to accommodate the needs of different courses, the preferences of different instructors, and the study and review habits of different students.



# Supporting students' quest for deeper understanding

With numerous worked examples, robust review support, a wealth of end-of-chapter problems and a solutions manual written by the text's author, students have everything they need to master the basics of physical chemistry.

## EXAMPLE 6.3 Point Group Operations

**CONTEXT** Problems in quantum mechanics can often be approached from different perspectives, and it becomes important to see when two processes, although described differently, are actually the same. For example, quantum mechanical tunneling has a dramatic impact on many chemical reactions that involve hydrogen transfer, because hydrogens are relatively light (which increases their tunneling probability). When there are several equivalent hydrogens in the same molecule, tunneling can also allow them to exchange places. In the 2-butyne molecule shown, it is possible for tunneling to exchange H atoms 1 and 2. A second tunneling exchange can then reverse the positions of atoms 2 and 3. Each of these exchanges is similar to a reflection of the methyl group through a mirror plane.



The combination of those two exchanges (switching atoms 1 and 2, and then switching 2 and 3) results in exactly the same arrangement as if the methyl group were rotated by  $120^\circ$ . The combination of two reflections in this case is equivalent to a single rotation by a third of a turn. This example illustrates in another way how we can determine that one combination of operations has the same result as another, single operation.

**PROBLEM** If  $\hat{C}_2(z)$  indicates rotation by  $\pi$  about the  $z$  axis,  $\hat{\sigma}_{xy}$  indicates reflection through the  $xy$  plane, and so on, then find the single operation that is identical to

$$\hat{\sigma}_{xy}\hat{C}_2(z)\hat{\sigma}_{yz}$$

**SOLUTION** Remembering to carry out the operations from right to left, we have

$$\begin{aligned}\hat{\sigma}_{xy}\hat{C}_2(z)\hat{\sigma}_{yz}\psi(x,y,z) &= \hat{\sigma}_{xy}\hat{C}_2(z)\psi(-x,y,z) \\ &= \hat{\sigma}_{xy}\psi(x,-y,z) = \psi(x,-y,-z) \\ &= \hat{C}_2(x)\psi(x,y,z) \\ \hat{\sigma}_{xy}\hat{C}_2(z)\hat{\sigma}_{yz} &= \hat{C}_2(x).\end{aligned}$$

Therefore, a point group that contains  $\hat{\sigma}_{xy}$ ,  $\hat{C}_2(z)$ , and  $\hat{\sigma}_{yz}$ , must also contain  $\hat{C}_2(x)$ .

**Worked Examples** provide students with context of the problem, clearly describe the parameters of the problem, and walk students step-by-step toward the solution.

KEY CONCEPTS AND EQUATIONS

KEY TERMS

OBJECTIVES REVIEW

PROBLEMS

A **comprehensive online solutions manual**, written by author Andrew Cooksy, is filled with unique solution sets emphasizing qualitative results to help students move beyond the math to a deeper conceptual understanding.

**End-of-chapter** materials bring students full circle, helping them assess their grasp of current chapter concepts and synthesize information from prior chapters.

# MasteringChemistry<sup>®</sup> for Students

www.masteringchemistry.com

MasteringChemistry provides dynamic, engaging experiences that personalize and activate learning for each student. Research shows that Mastering's immediate feedback and tutorial assistance helps students understand and master concepts and skills—allowing them to retain more knowledge and perform better in this course and beyond.

**Formation Reactions**

The standard heat of formation,  $\Delta H_f^\circ$ , is defined as the enthalpy change for the formation of one mole of substance from its constituent elements in their standard states. Thus, elements in their standard states have  $\Delta H_f^\circ = 0$ . Heat of formation values can be used to calculate the enthalpy change of any reaction.

Consider, for example, the reaction

$$2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$$

with heat of formation values given by the following table:

Substance	$\Delta H_f^\circ$ (kJ/mol)
$\text{NO}(g)$	90.2
$\text{N}(g)$	4
$\text{NO}_2(g)$	33.2

Then the heat of formation for the overall reaction is

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{products}) - \Delta H_f^\circ(\text{reactants}) = -2(33.2) - [2(90.2) + 0] = -113.6 \text{ kJ/mol}$$

**Part A**

For which of the following reactions is  $\Delta H_{\text{rxn}}^\circ$  equal to  $\Delta H_f^\circ$  of the product(s)?

You do not need to look up any values to answer this question.

Check all that apply.

- $\text{N}_2\text{O}(g) \rightarrow \frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g)$
- $\text{NaCl}(s) \rightarrow \frac{1}{2}\text{Na}_2\text{O}(s) + \frac{1}{2}\text{Cl}_2(g)$
- $\text{NaCl}(s) \rightarrow \frac{1}{2}\text{Na}_2\text{O}(s) + \frac{1}{2}\text{Cl}_2(g)$
- $\text{NaCl}(s) \rightarrow \frac{1}{2}\text{Na}_2\text{O}(s) + \frac{1}{2}\text{Cl}_2(g)$
- $2\text{H}_2\text{O}(l) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$
- $2\text{H}_2\text{O}(l) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$

**Part B**

The combustion of propane,  $\text{C}_3\text{H}_8$ , occurs in the reaction

$$\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$$

with heat of formation values given by the following table:

Substance	$\Delta H_f^\circ$ (kJ/mol)
$\text{C}_3\text{H}_8(g)$	-103.7
$\text{CO}_2(g)$	-393.5
$\text{H}_2\text{O}(l)$	-285.8

## Student Tutorials

Physical chemistry tutorials reinforce conceptual understanding. Over 460 tutorials are available in MasteringChemistry for Physical Chemistry, including new ones on The Cyclic Rule and Thermodynamic Relation of Proofs.

**Problem 13.4**

If an operator acts on a wave function as indicated by  $\hat{A}f(x)$ , it is important to carry out the operations in succession with the first operation being that nearest to the function. Mathematically,  $\hat{A}(\hat{B}f(x)) = \hat{A}\hat{B}f(x)$  and  $\hat{B}(\hat{A}f(x)) = \hat{B}\hat{A}f(x)$ .

**Part A**

Evaluate the following successive operations  $\hat{A}\hat{B}f(x)$ . The operators  $\hat{A}$  and  $\hat{B}$  are listed in the first two columns and  $f(x)$  is listed in the third column.

$\hat{A}$	$\hat{B}$	$f(x)$
$\frac{d}{dx}$	$\frac{d}{dx}$	$e^{-x}$

Express your answer in terms of some or all of the variables  $x, h$ .

**Part B**

Evaluate the following successive operations  $\hat{A}\hat{B}f(x)$ . The operators  $\hat{A}$  and  $\hat{B}$  are listed in the first two columns and  $f(x)$  is listed in the third column.

$\hat{A}$	$\hat{B}$	$f(x)$
$\frac{d}{dx}$	$\frac{d}{dx}$	$e^{-x}$

## End-of-Chapter Content Available in MasteringChemistry:

Selected end-of-chapter problems are assignable within MasteringChemistry, including:

- Numerical answer hints and feedback are only with tutorials in this course
- Equation and Symbolic answer types so that the results of a self-derivation can be entered to check for correctness, feedback, and assistance
- A Solution View that allows students to see intermediate steps involved in calculations of the final numerical result

**Problem 7.3**

Assume that the equation of state for a gas can be written in the form  $PV_m = RT(1 + B/P)$ .

**Part A**

Derive an expression for  $B = \frac{1}{P} \left( \frac{\partial^2 P}{\partial P^2} \right)_T$  for such a gas in terms of  $RT$ ,  $(\partial^2 P / \partial P^2)_T$ ,  $P$ , and  $V_m$ .

Express your answer in terms of the variables  $RT$ ,  $(\partial^2 P / \partial P^2)_T$ ,  $P$ , and  $V_m$ .

ANSWER

$$B = \frac{1}{P} \left( \frac{\partial^2 P}{\partial P^2} \right)_T$$

**Part B**

Derive an expression for  $B = -\frac{1}{P} \left( \frac{\partial^2 P}{\partial P^2} \right)_T$  for such a gas in terms of  $RT$ ,  $(\partial^2 P / \partial P^2)_T$ ,  $P$ , and  $V_m$ .

Express your answer in terms of the variables  $RT$ ,  $(\partial^2 P / \partial P^2)_T$ ,  $P$ , and  $V_m$ .

ANSWER

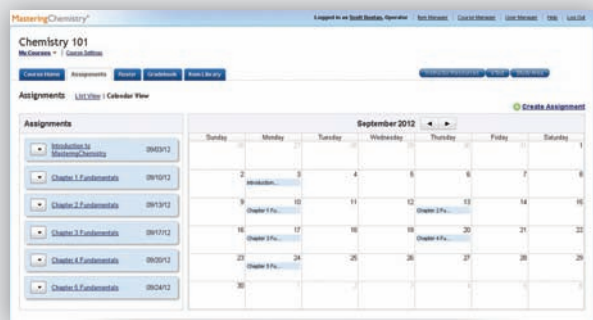
$$B = -\frac{RT}{P^2}$$

# MasteringChemistry<sup>®</sup> for Instructors

www.masteringchemistry.com

Easy to get started. Easy to use.

MasteringChemistry provides a rich and flexible set of course materials to get you started quickly, including homework, tutorial, and assessment tools that you can use *as is* or customize to fit your needs.



## NEW! Calendar Features

The Course Home default page now features a **Calendar View** displaying upcoming assignments and due dates.

- Instructors can schedule assignments by dragging and dropping the assignment onto a date in the calendar. If the due date of an assignment needs to change, instructors can drag the assignment to the new due date and change the “available from and to dates” accordingly.
- The calendar view gives students a syllabus-style overview of due dates, making it easy to see all assignments due in a given month.



## Gradebook

Every assignment is automatically graded. Shades of red highlight struggling students and challenging assignments at a glance.



## Gradebook Diagnostics

This screen provides you with your favorite diagnostics. With a single click, charts summarize the most difficult problems, vulnerable students, grade distribution, and even score improvement over the course.



## NEW! Learning Outcomes

Let Mastering do the work in tracking student performance against your learning outcomes:

- Add your own or use the publisher-provided learning outcomes.
- View class performance against the specified learning outcomes.
- Export results to a spreadsheet that you can further customize and share with your chair, dean, administrator, or accreditation board.



# Introduction: Tools from Math and Physics

## **GOAL** *Why Are We Here?*

The goal of this textbook is a concise and elegant exposition of the theoretical framework that forms the basis for all modern chemistry. To accomplish this, we are going to draw regularly on your knowledge of algebra, geometry, calculus, mechanics, electromagnetism, and chemistry. Physical chemistry is both rewarding and challenging in this way.

Mathematics of several varieties is our most valuable tool, and in this text we shall be interested in it only as a tool. It is not necessary, for example, that you remember how to derive the algebraic solution to the integral  $\int \ln x \, dx$ , but it will help if you know that an algebraic solution exists and how to use it (because with it we will obtain a useful equation for diffusion). This chapter is a summary of the math and physics that serve as our starting point as we explore the theory of chemistry. If you are embarking on this course, you may wish to review any of the following topics that appear alarmingly unfamiliar at first glance.

## **A.1** **Mathematics**

### **Algebra and Units**

#### **Basic Formula Manipulations**

The use of algebra in this text is similar to its use in introductory physics and chemistry courses. We will routinely encounter the basic manipulations of variables in equations, especially to solve for one unknown in terms of several known constants. A tough example would be to solve for  $n_B$  in the equation

$$T_B = T_B' \left[ \frac{V_T - V_A}{V_T - V_A'} \right]^{-n_B R / C_B}$$

The key is to see that a solution must be available, because the variable we are solving for appears in only one place, and a series of operations will allow us to isolate it on one side of the equation. Once we recognize that, then we can methodically undo the operations on one side of the equation to leave  $n_B$ : divide both sides by  $T'_B$ , take the logarithm of both sides to bring  $n_B$  down to earth from the exponent, and finally divide both sides by the factor that leaves  $n_B$  alone on one side of the equation. Those steps eventually bring us to

$$n_B = -\frac{C_B}{R} \frac{\ln\left(\frac{T_B}{T'_B}\right)}{\ln\left(\frac{V_T - V_A}{V_T - V'_A}\right)}.$$

One issue that makes the algebra something of a challenge is the notation. To put it mildly, we will use a lot of algebraic symbols. In fact, with the exception of “O,” which looks too much like a zero, we use the entire Roman alphabet at least twice, and most of the Greek.<sup>1</sup> The symbols have been chosen in hopes of an optimal combination of (a) preventing the same symbol from appearing with different meanings in the same chapter, (b) adherence to the conventional usage in the scientific literature, and (c) clarity of meaning. Unfortunately, these three aims cannot always be satisfied simultaneously. Physical chemistry is a synthesis of work done by pioneers in mathematics, physics, and chemistry, often without any intention that the results would one day become integrated into a general theory of chemistry. We bring together many fields that evolved independently, and the way these fields fit together is one of the joys of this course. Admittedly, the complexity of the notation is not.

The text provides guides to the notation used in long derivations and sample calculations to show how the notation is used. Please be aware, however, that no textbook gimmick can substitute for the reader’s understanding of the parameters represented by these symbols. If you recognize the difference between the fundamental charge  $e$  and the base of the natural logarithm  $e$ , you are in no danger of confusing the two, even though they are both represented by the letter “e,” sometimes appearing in the same equation.

### Unit Analysis and Reasonable Answers

One of the most helpful tools for checking algebra and for keeping these many symbols under control is unit analysis. If a problem asks you to solve for the value of some variable  $Y$ , and you’re not certain what units you will get in the end, then it’s likely that the meaning of  $Y$  has not been made entirely clear. In many cases, including viscosities and wavefunctions, the units are not obvious from the variable’s definition in words but are easily determined from an important equation in which the variable appears. Quick: how do you write the units for pressure in terms of mass and distance and time? If you recall the definition of the pressure as force per unit area

$$P = \frac{F}{A}$$

<sup>1</sup>If the lower case Greek letter upsilon ( $\upsilon$ ) didn’t look so much like an italic “v” ( $\nu$ ), there are at least two places it would have been used. It’s bad enough that  $\nu$  and the Greek nu ( $\nu$ ) are so similar and sometimes appear in the same equation.

and know that force has units of mass times acceleration, then pressure must have units of

$$\begin{aligned}\frac{\text{force}}{\text{distance}^2} &= \frac{\text{mass} \times \text{speed}/\text{time}}{\text{distance}^2} = \frac{\text{mass} \times \text{distance}/\text{time}^2}{\text{distance}^2} \\ &= \frac{\text{mass}}{\text{distance} \times \text{time}^2} = \text{kg m}^{-1} \text{s}^{-2}.\end{aligned}\quad (\text{A.1})$$

It will not be worthwhile to attempt a problem before understanding the variables involved.

Unit analysis is also a useful guard against algebraic mistakes. An error in setting up an algebraic solution often changes the units of the answer, and a check of the answer's units will show the mistake. This does not protect against many other mistakes, however, such as dividing instead of multiplying by  $10^{10}$  to convert a length from meters to angstroms. In such cases, there is no replacement for knowing what range of values is appropriate for the quantity. Recognizing a reasonable value for a particular variable is primarily a matter of familiarity with some typical parameters. The values given in Table A.1 are meant only to give common orders of magnitude for various quantities. Answers differing by factors of 10 from these may be possible, but not common.

**TABLE A.1** Some typical values for parameters in chemical problems. These are meant only as a rough guide to expected values under typical conditions.

Parameter	Value (in typical units)
chemical bond length	1.5 Å
chemical bond energy	400 kJ mol <sup>-1</sup>
molecular speed	200 m s <sup>-1</sup>
mass density (solid or liquid)	1 g cm <sup>-3</sup>

### EXAMPLE A.1 Unreasonable Answers

**PROBLEM** Unit analysis and recognition of a reasonable value can prevent errors such as those that resulted in the following answers. Identify the problem with these results for the requested quantity:

Quantity	Wrong answer
the density of NaCl(s)	$1.3 \cdot 10^{-24} \text{ g cm}^{-3}$
the density of NaCl(s)	$3.3 \cdot 10^7 \text{ g cm}^{-1}$
bond length of CsI	12.3 m
speed of a molecule	$4.55 \cdot 10^{11} \text{ m s}^{-1}$
momentum of electron	$5 \cdot 10^{-10} \text{ m s}^{-1}$

**SOLUTION** Each of those examples gives an answer of entirely the wrong magnitude (which could arise from using the wrong conversion factor, the wrong units, or both).

Quantity	Wrong answer	Why unreasonable
the density of NaCl(s)	$1.3 \cdot 10^{-24} \text{ g cm}^{-3}$	too small
the density of NaCl(s)	$3.3 \cdot 10^7 \text{ g cm}^{-1}$	wrong units
bond length of CsI	12.3 m	too big
speed of a molecule	$4.55 \cdot 10^{11} \text{ m s}^{-1}$	too big (greater than speed of light)
momentum of electron	$5 \cdot 10^{-10} \text{ m s}^{-1}$	wrong units

In many problems, the units themselves require some algebraic manipulation because several units are products of other units. For example, the unit of pressure,  $1 \text{ kg m}^{-1} \text{ s}^{-2}$ , obtained in Eq. A.1, is called the “pascal.” We shall also encounter an equation

$$E_n = -\frac{Z^2 m_e e^4}{2(4\pi\epsilon_0)^2 n^2 \hbar^2},$$

in which  $E_n$  has units of energy,  $Z$  and  $n$  are unitless,  $m_e$  has units of mass,  $e$  has units of charge,  $\epsilon_0$  has units of charge<sup>2</sup> energy<sup>-1</sup> distance<sup>-1</sup>, and  $\hbar$  has units of energy  $\times$  time. The units on each side of the equation must be identical, and this we can show by substituting in the appropriate units for mass, charge, and energy:

$$\begin{aligned} 1 \text{ J} &= 1 \frac{(\text{kg})(\text{C})^4}{(\text{C}^2 \text{ J}^{-1} \text{ m}^{-1})^2 (\text{J s})^2} \\ &= 1 \frac{(\text{kg})(\text{C})^4}{\text{C}^4 \text{ s}^2 / \text{m}^2} \\ &= 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ J}. \end{aligned} \quad (\text{A.2})$$

This may be a good place to remind you about that bothersome factor of  $4\pi\epsilon_0$  and some other aspects of the SI units convention.

## SI Units

The accepted standard for units in the scientific literature is the *Système International* (SI), based on the meter, kilogram, second, coulomb, kelvin, mole, and candela.<sup>2</sup> It is acceptable SI practice to use combinations of these units and to convert up or down by factors of 1000. So, for example, the SI unit of force should have units of (mass  $\times$  acceleration), or  $\text{kg m s}^{-2}$ , a unit commonly called the newton and abbreviated N. Energy has units of force  $\times$  distance, so the SI unit is  $\text{kg m}^2 \text{ s}^{-2}$ , also called the joule and abbreviated J. But the joule is inconveniently small for measuring, say, the energy released in a chemical reaction, so one could use the kilojoule ( $10^3 \text{ J}$ ) and remain true to the SI standard. We'll give special attention to energy units shortly.

A practical advantage of a single system for all physical units is that—if you're careful—the units take care of themselves. Allowing for the factors of 1000, if all the quantities on one side of an equation are in SI units, the value

<sup>2</sup>If you don't recall the candela, that's understandable. It's the unit of luminous intensity, and with that, makes its last appearance in this text.

on the other side will also be in SI units. If an object of mass 2.0 kg rests on a table, subject to the gravitational acceleration of  $9.8 \text{ m s}^{-2}$ , then I can calculate the force it exerts on the table by multiplying the mass and the acceleration,

$$F = ma = (2.0 \text{ kg})(9.8 \text{ m s}^{-2}) = 20 \text{ N},$$

and I can be certain that the final value is in SI units for force, namely newtons.

Standardization of units takes time, however, and you can be certain that the chemical data you encounter in your career will not adhere to one standard. One formerly common set of units, now widely discouraged, is the **Gaussian** or **CGS system**, similar to SI except that it replaces the meter, kilogram, and coulomb with the centimeter, gram, and electrostatic unit, respectively. Another convention, now on the rise, is the set of atomic units, for which all units are expressed as combinations of fundamental physical constants such as the electron mass  $m_e$  and the elementary charge  $e$ .

The SI system, while having some features convenient to engineering, suffers from one inconvenience in our applications: elementary calculations that include electric charges or magnetic fields require the use of constants called the permeability  $\mu_0$  and permittivity  $\epsilon_0$  of free space. Although these constants originally appeared with a physical meaning attached, for our purposes they are merely conversion factors. In particular, the factor  $4\pi\epsilon_0$  converts SI units of coulomb squared to units of energy times distance,  $\text{J} \cdot \text{m}$ . For example, the energy of repulsion between two electrons at a separation of  $d = 1.0 \cdot 10^{-10} \text{ m}$  is

$$\frac{e^2}{4\pi\epsilon_0 d} = \frac{(1.602 \cdot 10^{-19} \text{ C})^2}{(1.113 \cdot 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(1.0 \cdot 10^{-10} \text{ m})} = 2.306 \cdot 10^{-18} \text{ J}. \quad (\text{A.3})$$

In contrast, the atomic and CGS units fold this conversion into the definition of the charge, and the factor of  $4\pi\epsilon_0$  would *not* appear in the calculation. For all equations in this text involving the forces between charged particles, we conform to the standards of the day and use SI units and the associated factor of  $4\pi\epsilon_0$ .

In other cases, however, we will not adhere strictly to the SI standard. Even allowing for factors of 1000, I don't know any chemists who express molecular dipole moments in coulomb meters, a unit too large for its purpose by 30 orders of magnitude (not even prefixes like "micro-" and "nano-" are enough to save it). The conventional unit remains the debye, which is derived from CGS units (adjusted by 18 orders of magnitude, it must be said) and just the right size for measuring typical bond dipoles. The angstrom ( $\text{\AA}$ ) also remains in wide use in chemistry because it is a metric unit ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ) that falls within a factor of 2 of almost any chemical bond length.

Of all the physical parameters, energy has the greatest diversity in commonly used scientific units. There are several ways to express energy, even after excluding all sorts of nonmetric energy units (such as the British thermal unit, kilowatt-hour, foot-pound, ton of TNT, and—most beloved of chemists—the calorie). Other conventions appear when discussing the interaction of radiation with matter, for which it is common to quantify energy in terms of the frequency ( $\text{s}^{-1}$ ) or reciprocal wavelength ( $\text{cm}^{-1}$ ) of the radiation. Under the proper assumptions, it may also be informative to convert an energy to a corresponding



temperature, in units of kelvin. Typical laboratory samples of a compound have numbers of molecules in the range of  $10^{20}$  or more, and molecular energies are therefore often given in terms of the energy per mole of the compound (e.g.,  $\text{kJ mol}^{-1}$ ). These cases will be explained as they appear, and they are summarized in the conversion table for energies on this textbook's back endpapers.

Once these non-SI units are introduced, please make sure you are comfortable with the algebra needed to convert from one set of units to another. This one skill, mundane as it may seem, will likely be demanded of you in any career in science or engineering. Famous and costly accidents have occurred because this routine procedure was not given its due attention.<sup>3</sup>

## Complex Numbers

Complex numbers are composed of a real number and an imaginary number added together. For our purposes, a complex number serves as a sort of two-dimensional number; the imaginary part contains data on a measurement distinct from the data given by the real part. For example, a sinusoidal wave that varies in time may be described by a complex number in which the real part gives the shape of the wave at the current time and the imaginary part describes what the wave will look like a short time later.

The imaginary part of any complex number is a real number multiplied by  $i \equiv \sqrt{-1}$ . (The symbol “ $\equiv$ ” is used throughout this text to indicate a definition, as opposed to the “ $=$ ” symbol, used for equalities that can be proved mathematically.) This relationship between  $i$  and  $-1$  allows the imaginary part of a complex number to influence the real-number results of an algebraic operation. For example, if  $a$  and  $b$  are both real numbers, then  $a + ib$  is complex, with  $a$  the real part and  $ib$  the imaginary part. The **complex conjugate** of  $a + ib$ , written  $(a + ib)^*$ , is equal to  $a - ib$ , and the product of any number with its complex conjugate is a real number:

$$(a + ib)(a - ib) = a^2 - iba + iba - i^2b^2 = a^2 + b^2. \quad (\text{A.4})$$

Notice that the value of  $b$ —even though it was contained entirely in the imaginary parts of the two original complex numbers—contributes to the value of the real number quantity that results from this operation.

Many of the mathematical functions in the text are complex, but multiplication by the complex conjugate yields a real function, which can correspond directly to a measurable property. For that reason, we often judge the validity of the functions by whether we can integrate over the product  $f^*f$ . In this text, a well-behaved function  $f$  is single-valued, finite at all points, and yields a finite value when  $f^*f$  is integrated over all points in space. To be very well-behaved, the function and its derivatives should also be continuous functions, but we will use a few functions that are naughty in this regard.

---

<sup>3</sup>A prominent example is the loss in 1999 of the unmanned Mars Climate Orbiter, a probe that entered the Martian atmosphere too low and burned up because engineers were sending course correction data calculated using forces in pounds to an on-board system that was designed to accept the data in newtons.

**EXAMPLE A.2** Complex Conjugates

**PROBLEM** Write the complex conjugate  $f^*$  for each of the following expressions  $f$  and show that the value of  $f^*f$  is real.

- $5 + 5i$
- $-x/i$
- $\cos x - i \sin x$

**SOLUTION**

1.  $f^* = 5 - 5i$

$$f^*f = (5 + 5i)(5 - 5i) = 25 + 25 = 50$$

2. First we would like to put this in the form  $a + ib$ , so we multiply by  $\frac{i}{i}$  to bring the factor of  $i$  into the numerator:

$$f = -\frac{x}{i} \left( \frac{i}{i} \right) = -\frac{ix}{-1} = ix.$$

The real part of this function is zero, but for any complex conjugate, we change the sign on the imaginary term:  $f^* = -ix$

$$f^*f = (ix)(-ix) = -i^2x^2 = x^2$$

3.  $f^* = \cos x + i \sin x$

$$f^*f = \cos^2 x - i^2 \sin^2 x = \cos^2 x + \sin^2 x = 1$$

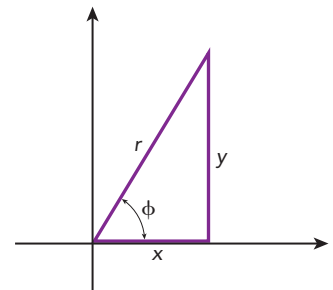
**Trigonometry**

Elementary results from trigonometry play an important role in our equations of motion, and therefore you should know the definitions of the sine, cosine, and tangent functions (and their inverses) as signed ratios of the lengths of the sides of a right triangle. Using the triangle drawn in Fig. A.1, with sides of length  $y$ ,  $x$ , and  $r$ , we would define these functions as follows:

$$\begin{aligned} \sin \phi &\equiv \frac{y}{r} & \csc \phi &\equiv \frac{1}{\sin \phi} = \frac{r}{y} \\ \cos \phi &\equiv \frac{x}{r} & \sec \phi &\equiv \frac{1}{\cos \phi} = \frac{r}{x} \\ \tan \phi &\equiv \frac{y}{x} & \cot \phi &\equiv \frac{1}{\tan \phi} = \frac{x}{y} \end{aligned} \quad (\text{A.5})$$

The sign is important. If  $\phi$  lies between  $90^\circ$  and  $270^\circ$ , then the  $x$  value becomes negative, so  $\cos \phi$  and  $\sec \phi$  would be less than zero. Similarly,  $\sin \phi$  and  $\csc \phi$  are negative for  $\phi$  between  $180^\circ$  and  $360^\circ$ .

Please also make sure you are comfortable using the trigonometric identities listed in Table A.2. These are algebraic manipulations that may allow us to simplify equations or to isolate an unknown variable.



**▲ FIGURE A.1** Right triangle used to define trigonometric functions of the angle  $\phi$ .