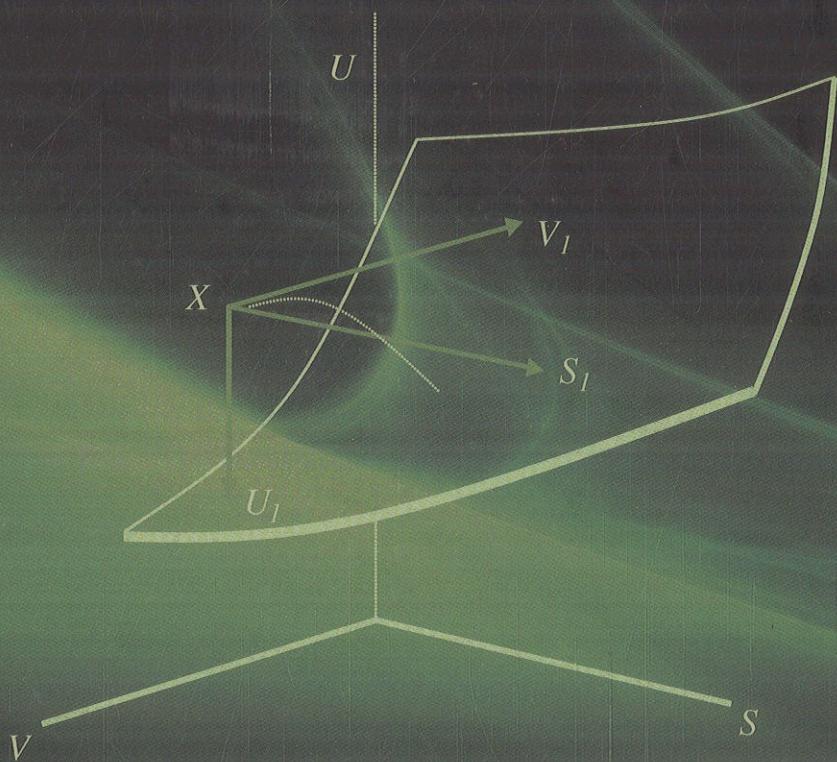


# Invitation to Physical Chemistry

Gopala Krishna Vemulapalli



Imperial College Press

# Contents

<i>Acknowledgments</i>	vii
<i>Preface</i>	ix
<b>Part A. Quantum Chemistry</b>	1
Chapter 1. The Schrödinger Equation, Waves and Wave Packets	3
1.1 Critical Experiment . . . . .	3
1.2 Wave Packets . . . . .	6
1.3 Wave Functions and Wave Packets: A Tutorial . . . . .	10
1.4 The de Broglie Principle . . . . .	14
1.5 Particle in a Box . . . . .	15
1.6 The Schrödinger Equation . . . . .	17
1.7 The Uncertainty Principle . . . . .	21
1.8 Interpretation of the Wave Function . .	22
1.9 Particle in a Three-Dimensional Box .	29
1.10 Quantum Wells, Wires and Dots . . . .	30
Chapter 2. Spectroscopy: Rotations and Vibrations	33
2.1 The Harmonic Oscillator Model . . . . .	35
2.2 The Rigid Rotor . . . . .	38
2.3 Diatomic Molecules . . . . .	40
2.4 Triatomic Molecules: Carbon Dioxide and Water . . . . .	47

2.5	Angular Momentum and the Dipole Moments . . . . .	50
2.6	Interstellar Molecules . . . . .	54
<b>Chapter 3.</b>	<b>Atoms</b>	<b>57</b>
3.1	The Hydrogen Atom . . . . .	57
3.2	Spin . . . . .	67
3.3	The Helium Atom . . . . .	70
3.4	Excited Terms of Helium . . . . .	75
3.5	Symmetry and Rotational Spectra . . . . .	77
<b>Chapter 4.</b>	<b>Molecules</b>	<b>79</b>
4.1	The $\text{H}_2^+$ Molecule . . . . .	79
4.2	Methodology of Quantum Calculations . . . . .	83
4.3	Homonuclear Diatomic Molecules . . . . .	86
4.4	Heteronuclear Diatomic Molecules . . . . .	92
4.5	The Valence Bond Theory . . . . .	94
4.6	Spectra of Diatomic Molecules . . . . .	94
<b>Part B. Chemical Thermodynamics</b>		<b>103</b>
<b>Chapter 5.</b>	<b>Entropy and Equilibrium</b>	<b>105</b>
5.1	Entropy: A Measure of Energy Shuffling . . . . .	107
5.2	Chemical and Physical Changes . . . . .	109
5.3	Entropy: Wider Context . . . . .	113
5.4	Entropy and Heat . . . . .	116
<b>Chapter 6.</b>	<b>The Fundamental Equation of Thermodynamics</b>	<b>118</b>
6.1	The Fundamental Equation . . . . .	118
6.2	A Brief History . . . . .	120
6.3	Intermolecular Energy . . . . .	126
6.4	Nature of Theory in Thermodynamics . . . . .	130
6.5	What is Actually Measured? . . . . .	131
6.6	What is Deduced? . . . . .	136

Chapter 7.	Thermodynamic Potentials	139
7.1	Important Functions . . . . .	139
7.2	Applications . . . . .	144
7.3	What Do They Mean? . . . . .	147
Chapter 8.	Chemical Potential	150
8.1	Chemical Potential and Equilibrium . . .	151
8.2	Derivation of Chemical Potential Equation . . . . .	155
8.3	Two Phases, One Component . . . . .	156
8.4	Two Phases, Two Components . . . . .	158
8.5	Reaction Equilibrium . . . . .	163
Chapter 9.	Statistical Thermodynamics	167
9.1	The Boltzmann Distribution Function . . . . .	167
9.2	Thermodynamic Properties . . . . .	169
9.3	Partition Functions . . . . .	171
9.4	Heat Capacities . . . . .	175
9.5	Chemical Equilibrium . . . . .	177
Chapter 10.	States of Matter	181
10.1	Non-Ideal Gases: Pair-Wise Interaction . . . . .	181
10.2	Continuity of the Fluid State . . . . .	183
10.3	The Liquid State . . . . .	186
<b>Part C. Kinetics</b>		<b>191</b>
Chapter 11.	The Kinetic Molecular Theory of Gases	193
11.1	Distribution of Speeds . . . . .	193
11.2	Collisions . . . . .	195
11.3	Transport . . . . .	198

Chapter 12. Chemical Kinetics	202
12.1 Unimolecular Reactions in the Gas Phase . . . . .	203
12.2 Testing Rate Laws . . . . .	207
12.3 Bimolecular Reactions in Solution . . . . .	209
12.4 Relaxation Method for Determining Rate Constants . . . . .	210
12.5 Comments on Rate Theories . . . . .	213
12.6 Radiation and Matter . . . . .	215
<i>Index</i>	221