

ATOMS AND MOLECULES

Mitchel Weissbluth

ATOMS AND MOLECULES

Mitchel Weissbluth

*Department of Applied Physics
Stanford University
Stanford, California*



ACADEMIC PRESS New York San Francisco London 1978

A Subsidiary of Harcourt Brace Jovanovich, Publishers

COPYRIGHT © 1978, BY ACADEMIC PRESS, INC.

ALL RIGHTS RESERVED.

**NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY
INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT
PERMISSION IN WRITING FROM THE PUBLISHER.**

ACADEMIC PRESS, INC.

111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Weissbluth, Mitchel.

Atoms and molecules.

Bibliography: p.

1. Atoms. 2. Molecules. I. Title.

QC173.W433 539 76-55979

ISBN 0-12-744450-5

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE

Group theoretical methods in atomic and molecular physics were employed very early in the history of quantum mechanics, notably by H. Weyl, E. P. Wigner, and H. Bethe, although on the whole widespread acceptance was not achieved for some thirty years. An important impetus toward a renewed interest in group theory on the part of physicists was the work of G. Racah who introduced the formalism of irreducible tensor operators and demonstrated their utility in the evaluation of atomic matrix elements. Extensions to molecular systems followed within a relatively short time. It is the purpose of this book to discuss the basic properties of atoms and molecules, taking full advantage of these powerful methods.

Part I contains the essential mathematics pertaining to angular momentum properties, finite and continuous rotation groups, tensor operators, the Wigner-Eckart theorem, vector fields, and vector spherical harmonics. Part II provides the quantum mechanical background on specialized topics, it being assumed that the student has had at least an undergraduate course in quantum mechanics. Included are symmetry considerations, second quantization, density matrices, and several types of time-dependent and time-independent approximation methods. Discussion of atomic structure begins in Part III. Starting with the Dirac equation, its nonrelativistic approximation provides the basis for the derivation of the Hamiltonians for all important interactions, e.g., spin-orbit, external fields, hyperfine, etc. Multielectron atoms are discussed in Part IV, which treats multiplet theory and the Hartree-Fock formulation. Electromagnetic radiation fields and their interactions with atoms in first and higher orders are treated in Part V, which also includes topics of relevance to spectroscopy. Finally, Part VI is devoted to molecules and complexes, including such topics as the Born-Oppenheimer approximation, molecular orbitals, the self-consistent field

method, electronic states, vibrational and rotational states, molecular spectra, and ligand field theory.

The quantum mechanics of atoms and molecules, once the exclusive domain of physicists, has in recent years proliferated into other fields, primarily chemistry and several branches of engineering. In recognition of this wider interest, a full year graduate course in atomic and molecular physics has been taught in the Department of Applied Physics at Stanford University. Attendees consisted of students working in diverse fields such as spectroscopy, magnetic resonance, Mössbauer resonance, quantum electronics, solid state electronics, astrophysics, and biological physics. The present volume is an outgrowth of this course.

CONTENTS

Preface

xv

PART I MATHEMATICAL BACKGROUND

Chapter 1 Angular Momentum

1.1	Orbital Angular Momentum	1
1.2	Spherical Harmonics and Related Functions	3
1.3	Generalized Angular Momentum	13
1.4	Spin	20
1.5	Coupling of Two Angular Momenta	22
1.6	Coupling of Three Angular Momenta	36
1.7	Summary and Examples	42

Chapter 2 Rotations

2.1	Coordinate Rotations and Scalar Functions	48
2.2	Rotations and Angular Momenta	51
2.3	Transformation Properties of Angular Momentum Eigenfunctions	53

Chapter 3 Elements of Group Theory

3.1	Definitions and Basic Properties	60
3.2	Representations and Characters	66
3.3	Reducible and Irreducible Representations	68

vii

viii CONTENTS

3.4	Basis Functions	75
3.5	Projection Operators	78
3.6	Product Representations	83
3.7	Matrix Elements	88

Chapter 4 Continuous Rotation Groups

4.1	Rotation Group in Two Dimensions, C_∞	91
4.2	Rotation Group in Three Dimensions, $O^+(3)$	93
4.3	Special Unitary Group in Two Dimensions; $SU(2)$	95
4.4	Connection between $O^+(3)$ and $SU(2)$	98
4.5	Irreducible Representations of $O^+(3)$	100
4.6	Summary and Examples	104

Chapter 5 Finite Groups

5.1	Point Groups—Symmetry Operations and Nomenclature	111
5.2	Double Groups	121
5.3	The Groups O , D_4 and D_{6h}	124
5.4	Permutation Groups S_n — Young Diagrams	143

Chapter 6 Tensors

6.1	Irreducible Tensor Operators	151
6.2	Tensor Products	155
6.3	Wigner-Eckart Theorem	159
6.4	Cartesian Tensors	167
6.5	Tensors, Permutation Groups, Continuous Groups	175

Chapter 7 Vector Fields

7.1	Rotational Properties	182
7.2	Vector Spherical Harmonics	187
7.3	Plane Wave Expansion	193
7.4	Multipole Expansion of the Electromagnetic Field	196

PART II QUANTUM-MECHANICAL BACKGROUND

Chapter 8 Symmetry Elements of the Hamiltonian

8.1	Connection between Group Theory and Quantum Mechanics	203
-----	---	-----

8.2	Geometrical Symmetries	204
8.3	Time Reversal and Kramers' Theorem	207
8.4	Indistinguishability of Particles	213
Chapter 9 Time Development of a Quantum System		
9.1	Schrödinger Representation	216
9.2	Heisenberg Representation	220
9.3	Interaction Representation	221
9.4	Infinite Limits	227
Chapter 10 Harmonic Oscillator		
10.1	Schrödinger Solutions	233
10.2	Matrix Formulation	234
10.3	Heisenberg Representation	239
Chapter 11 Slater Determinants		
11.1	Matrix Elements—General	240
11.2	Matrix Elements—Special Cases	244
Chapter 12 Second Quantization		
12.1	Creation and Annihilation Operators	254
12.2	Matrix Elements of Operators	259
12.3	Diagrams	263
12.4	Field Operators	265
Chapter 13 Density Matrices		
13.1	General Properties	268
13.2	Spin States	271
13.3	Reduced Density Matrices	273
13.4	Thermal Equilibrium	276
13.5	Equation of Motion	278
13.6	Multielectron Systems	280
13.7	Fock–Dirac Density Matrices	283
13.8	Spinless Density Matrices	285
Chapter 14 Approximations		
14.1	Variational Methods	290
14.2	Time-Independent Perturbations	294

x **CONTENTS**

14.3	Time-Dependent Perturbations—Harmonic Potential	297
14.4	Fermi's Golden Rule	299
14.5	Density Matrices—Random Perturbations	301
14.6	Response Function; Susceptibility	305

PART III ONE-ELECTRON ATOMS

Chapter 15 Dirac Equation

15.1	Free Particle Equation	313
15.2	Dirac Equation with Electromagnetic Coupling	316

Chapter 16 Hydrogen Atom

16.1	Schrödinger Equation	322
16.2	One-Electron Wave Functions	334
16.3	Spin–Orbit Coupling	337
16.4	Other Interactions	341

Chapter 17 Static Fields

17.1	Magnetic Fields	346
17.2	Electric Fields	355

Chapter 18 Hyperfine Interactions

18.1	Hamiltonian for the Magnetic Hyperfine Interaction	358
18.2	Magnetic Hyperfine Interaction in One-Electron Systems	367
18.3	Electric Quadrupole Interaction	374

PART IV N-ELECTRON ATOMS

Chapter 19 Hartree–Fock Formulation

19.1	The Hamiltonian	385
19.2	Central Field Approximation	389
19.3	Hartree–Fock Equations	394

19.4	Properties of the Hartree–Fock Solutions	401
19.5	Computational Methods	407
19.6	Correlation Error and Configuration Interaction	410

Chapter 20 Multiplet Wave Functions

20.1	Two-Electron Multiplets	413
20.2	Terms from a Configuration of n Electrons	420
20.3	Construction of Multiplet Wave Functions	427
20.4	Symmetry Properties	435
20.5	jj Coupling	441

Chapter 21 Matrix Elements

21.1	Electrostatic Matrix Elements—Two Electrons	443
21.2	Some n -Electron Matrix Elements	454
21.3	Electrostatic Matrix Elements— n Electrons	457
21.4	Spin–Orbit Interaction	465
21.5	Conjugate Configurations	476
21.6	Other Interactions	478

PART V ELECTROMAGNETIC INTERACTIONS

Chapter 22 Interaction between Atoms and Radiation

22.1	Hamiltonian of the Radiation Field	483
22.2	Quantization of the Radiation Field	488
22.3	Interaction Hamiltonian and Matrix Elements	492
22.4	Selection Rules and Angular Distributions	500

Chapter 23 Absorption and Emission

23.1	Transition Probabilities	505
23.2	Einstein Coefficients and Planck's Law	510
23.3	Oscillator Strengths and Sum Rules	512
23.4	Numerical Computations	515
23.5	Line Broadening	517
23.6	Cross Sections	520
23.7	Photoelectric Effect	521
23.8	Survey of Atomic Spectra	525

Chapter 24 Higher Order Electromagnetic Interactions

24.1 The Kramers–Heisenberg Formula	536
24.2 Scattering—Special Cases	542
24.3 Diagrams	544
24.4 Optical Susceptibility and Nonlinear Effects	547

PART VI MOLECULES

Chapter 25 General Properties of Molecules

25.1 Born–Oppenheimer Approximation	551
25.2 Molecular Orbitals and the Self-Consistent Field Method	555
25.3 Computational Methods	561

Chapter 26 Electronic States of Molecules

26.1 Hydrogen Molecule Ion (H_2^+)	566
26.2 Symmetry Considerations— H_2^+	573
26.3 Hydrogen Molecule	579
26.4 Diatomic and Linear Molecules	584
26.5 Hybrid Orbitals	591
26.6 The π -Electron Approximation	596

Chapter 27 Molecular Spectra

27.1 Vibrations and Rotations of Diatomic Molecules	606
27.2 Transitions in Diatomic Molecules	615
27.3 Vibration of Polyatomic Molecules	631
27.4 Transitions in Polyatomic Molecules	641

Chapter 28 Ligand Fields

28.1 Basic Ideas	650
28.2 Single d Electron in an Octahedral and Tetragonal Field	655
28.3 Multielectron Configurations	666
28.4 Magnetic Fields and the Spin Hamiltonian	672
28.5 Molecular Orbitals	677

Appendix I Dirac Notation	681
----------------------------------	------------

<i>Appendix 2</i>	Operators	682
<i>Appendix 3</i>	Eigenvalues and Eigenfunctions	684
<i>Appendix 4</i>	Relationships among Unit Vectors	686
<i>Appendix 5</i>	Bessel Functions	689
<i>Appendix 6</i>	Laguerre Polynomials	692
<i>Appendix 7</i>	Hermite Polynomials	693
<i>Appendix 8</i>	Dirac δ-Functions	694
	References	697
	<i>Index</i>	705

Mathematical Background

CHAPTER 1

ANGULAR MOMENTUM

1.1 Orbital Angular Momentum

The orbital angular momentum operator \mathbf{L} is defined by

$$\mathbf{L} = \frac{1}{\hbar} (\mathbf{r} \times \mathbf{p}) \quad (1.1-1)$$

where \mathbf{r} is a vector whose components r_i are x, y, z (or x_1, x_2, x_3) and

$$\mathbf{p} = -i\hbar\nabla \quad (1.1-2)$$

is the linear momentum operator; the rectangular components of the gradient operator ∇ are $\partial/\partial x, \partial/\partial y, \partial/\partial z$. Expanding (1.1-1),

$$\begin{aligned} L_x &= \frac{1}{\hbar} (yp_z - zp_y) = -i \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ &= i \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right), \end{aligned} \quad (1.1-3a)$$

$$\begin{aligned} L_y &= \frac{1}{\hbar} (zp_x - xp_z) = -i \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ &= i \left(-\cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right), \end{aligned} \quad (1.1-3b)$$

$$\begin{aligned} L_z &= \frac{1}{\hbar} (xp_y - yp_x) = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \\ &= -i \frac{\partial}{\partial \varphi}. \end{aligned} \quad (1.1-3c)$$

2 1. ANGULAR MOMENTUM

In (1.1-1) the angles θ and ϕ are the polar and azimuth angles, respectively.

The operators L_x , L_y , and L_z are Hermitian, i.e.,

$$L_i^\dagger = L_i \quad (i = x, y, z), \quad (1.1-4)$$

and, as functions of the coordinates, L_x , L_y , and L_z are pure imaginary operators.

It will often be convenient to use *spherical components* of \mathbf{L} ; these are defined as

$$\begin{aligned} L_{+1} &= -\frac{1}{\sqrt{2}}(L_x + iL_y) = -\frac{1}{\sqrt{2}}e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right), \\ L_{-1} &= \frac{1}{\sqrt{2}}(L_x - iL_y) = -\frac{1}{\sqrt{2}}e^{-i\phi}\left(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi}\right), \end{aligned} \quad (1.1-5)$$

$$L_0 = L_z.$$

The inverse relations are

$$L_x = -\frac{1}{\sqrt{2}}(L_{+1} - L_{-1}), \quad L_y = \frac{1}{\sqrt{2}}(L_{+1} + L_{-1}), \quad L_z = L_0. \quad (1.1-6)$$

In contrast to the rectangular components of \mathbf{L} , L_{+1} and L_{-1} are *not* Hermitian since

$$L_{+1}^\dagger = -L_{-1}, \quad L_{-1}^\dagger = -L_{+1}. \quad (1.1-7)$$

The components of \mathbf{r} and \mathbf{p} satisfy certain commutation relations:

$$[r_i, p_j] = i\hbar \delta_{ij}, \quad (1.1-8a)$$

$$[r_i, r_j] = [p_i, p_j] = 0, \quad (1.1-8b)$$

$$[r_i, p^2] = 2i\hbar p_i, \quad (1.1-8c)$$

$$[p_i, p^2] = 0 \quad (1.1-8d)$$

in which $r_i, r_j = x, y, z$; $p_i, p_j = p_x, p_y, p_z$, and $p^2 = p_x^2 + p_y^2 + p_z^2$. The definition of \mathbf{L} (1.1-1) together with (1.1-8) imply that

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y. \quad (1.1-9)$$

These may be written in any of the compact forms:

$$[L_i, L_j] = i\hbar L_k \quad (i, j, k \text{ cyclic}), \quad (1.1-10a)$$

$$\mathbf{L} \times \mathbf{L} = i\hbar \mathbf{L}, \quad (1.1-10b)$$

$$[L_i, L_j] = i\epsilon_{ijk} L_k, \quad (1.1-10c)$$

in which ε_{ijk} is the antisymmetric unit tensor of rank 3 defined by

$$\varepsilon_{ijk} = \begin{cases} +1, & i, j, k \text{ in cyclic order,} \\ -1, & i, j, k \text{ not in cyclic order,} \\ 0, & \text{two indices alike.} \end{cases} \quad (1.1-11)$$

The three statements (1.1-10a)–(1.1-10c) are equivalent in all respects. Additional commutator relations among the components of \mathbf{L} , \mathbf{r} , and \mathbf{p} are

$$[L_i, r_j] = i\varepsilon_{ijk}r_k, \quad (1.1-12a)$$

$$[L_i, p_j] = i\varepsilon_{ijk}p_k, \quad (1.1-12b)$$

$$[L_0, L_{\pm 1}] = \pm L_{\pm 1}, \quad [L_{+1}, L_{-1}] = -L_0. \quad (1.1-13)$$

Another important operator is L^2 , also known as the *total orbital angular momentum operator*. It may be expressed in various equivalent forms:

$$\begin{aligned} L^2 &= L_x^2 + L_y^2 + L_z^2 \\ &= -\left[\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + (1 + \cot^2 \theta) \frac{\partial^2}{\partial \varphi^2} \right] \\ &= -\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \\ &= -L_{+1}L_{-1} + L_0^2 - L_{-1}L_{+1} \\ &= \sum_q (-1)^q L_q L_{-q} \quad (q = 1, 0, -1). \end{aligned} \quad (1.1-14)$$

Employing relations (1.1-13) we also have

$$L^2 = -2L_{+1}L_{-1} + L_0(L_0 - 1) = -2L_{-1}L_{+1} + L_0(L_0 + 1). \quad (1.1-15)$$

L^2 commutes with all components of \mathbf{L} , i.e.,

$$[L^2, L_\mu] = 0 \quad (1.1-16)$$

where L_μ refers to either rectangular components (L_x, L_y, L_z) or spherical components (L_{+1}, L_0, L_{-1}) of \mathbf{L} .

1.2 Spherical Harmonics and Related Functions

The spherical harmonics $Y_{lm}(\theta, \varphi)$ are defined by

$$Y_{lm}(\theta, \varphi) = \sqrt{(-1)^m + |m|} \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos \theta) e^{im\varphi} \quad (1.2-1)$$

TABLE 1.1

Spherical Harmonics^a

l	m	$r^l Y_{lm}(x, y, z)$	$Y_{lm}(\theta, \varphi)$
0	0	$\sqrt{\frac{1}{4\pi}}$	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}} z$	$\sqrt{\frac{3}{4\pi}} \cos \theta$
1	± 1	$\mp \sqrt{\frac{3}{8\pi}} (x \pm iy)$	$\mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\varphi}$
2	0	$\sqrt{\frac{5}{4\pi}} \sqrt{\frac{1}{4}} (3z^2 - r^2)$	$\sqrt{\frac{5}{4\pi}} \sqrt{\frac{1}{4}} (3 \cos^2 \theta - 1)$
2	± 1	$\mp \sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{2}} z(x \pm iy)$	$\mp \sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{2}} \cos \theta \sin \theta e^{\pm i\varphi}$
2	± 2	$\sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{8}} (x \pm iy)^2$	$\sqrt{\frac{5}{4\pi}} \sqrt{\frac{3}{8}} \sin^2 \theta e^{\pm 2i\varphi}$
3	0	$\sqrt{\frac{7}{4\pi}} \sqrt{\frac{1}{4}} z(5z^2 - 3r^2)$	$\sqrt{\frac{7}{4\pi}} \sqrt{\frac{1}{4}} (2 \cos^3 \theta - 3 \cos \theta \sin^2 \theta)$
3	± 1	$\mp \sqrt{\frac{7}{4\pi}} \sqrt{\frac{3}{16}} (x \pm iy)(5z^2 - r^2)$	$\mp \sqrt{\frac{7}{4\pi}} \sqrt{\frac{3}{16}} (4 \cos^2 \theta \sin \theta - \sin^3 \theta) e^{\pm i\varphi}$
3	± 2	$\sqrt{\frac{7}{4\pi}} \sqrt{\frac{15}{8}} z(x \pm iy)^2$	$\sqrt{\frac{7}{4\pi}} \sqrt{\frac{15}{8}} \cos \theta \sin^2 \theta e^{\pm 2i\varphi}$
3	± 3	$\mp \sqrt{\frac{7}{4\pi}} \sqrt{\frac{5}{16}} (x \pm iy)^3$	$\mp \sqrt{\frac{7}{4\pi}} \sqrt{\frac{5}{16}} \sin^3 \theta e^{\pm 3i\varphi}$
4	0	$\sqrt{\frac{9}{4\pi}} \sqrt{\frac{1}{64}} (35z^4 - 30z^2 r^2 + 3r^4)$	$\sqrt{\frac{9}{4\pi}} \sqrt{\frac{1}{64}} (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$
4	± 1	$\mp \sqrt{\frac{9}{4\pi}} \sqrt{\frac{5}{16}} (x \pm iy)(7z^3 - 3zr^2)$	$\mp \sqrt{\frac{9}{4\pi}} \sqrt{\frac{5}{16}} \sin \theta (7 \cos^3 \theta - 3 \cos \theta) e^{\pm i\varphi}$
4	± 2	$\sqrt{\frac{9}{4\pi}} \sqrt{\frac{5}{32}} (x \pm iy)^2 (7z^2 - r^2)$	$\sqrt{\frac{9}{4\pi}} \sqrt{\frac{5}{32}} \sin^2 \theta (7 \cos^2 \theta - 1) e^{\pm 2i\varphi}$
4	± 3	$\mp \sqrt{\frac{9}{4\pi}} \sqrt{\frac{35}{16}} z(x \pm iy)^3$	$\mp \sqrt{\frac{9}{4\pi}} \sqrt{\frac{35}{16}} \sin^3 \theta \cos \theta e^{\pm 3i\varphi}$
4	± 4	$\sqrt{\frac{9}{4\pi}} \sqrt{\frac{35}{128}} (x \pm iy)^4$	$\sqrt{\frac{9}{4\pi}} \sqrt{\frac{35}{128}} \sin^4 \theta e^{\pm 4i\varphi}$

^a In spectroscopic notation, functions that are proportional to Y_{lm} with $l = 0, 1, 2, 3, \dots$ are called s, p, d, f, ... functions.

with

$$l = 0, 1, 2, \dots, \quad (1.2-2a)$$

$$m = l, l-1, \dots, -l, \quad (1.2-2b)$$

and $P_l^m(\cos \theta)$ an associated Legendre polynomial. The phase convention in (1.2-1) is not universal: the one adopted here is known as the *Condon-Shortley convention*. Some of the commonly used spherical harmonics are listed in Table 1.1; among their properties are:

$$Y_{l-m}(\theta, \varphi) = (-1)^m Y_{lm}^*(\theta, \varphi), \quad (1.2-3a)$$

$$Y_{lm}(\pi - \theta, \pi + \varphi) = (-1)^l Y_{lm}(\theta, \varphi). \quad (1.2-3b)$$

The change from (θ, φ) to $(\pi - \theta, \pi + \varphi)$ corresponds to an inversion, that is, a change from (x, y, z) to $(-x, -y, -z)$. From (1.2-3b) it is seen that $Y_{lm}(\theta, \varphi)$ changes sign under inversion when l is an odd integer; when l is even, there is no change in sign. In the former case, $Y_{lm}(\theta, \varphi)$ is said to have *odd parity* and in the latter, *even parity*. The quantity $(-1)^l$, which is equal to $+1$ for l even and -1 for l odd is called the *parity factor*.

When $\theta = 0$,

$$Y_{lm}(0, \varphi) = \begin{cases} 0 & \text{for } m \neq 0, \\ \sqrt{\frac{2l+1}{4\pi}} & \text{for } m = 0. \end{cases} \quad (1.2-4)$$

The spherical harmonics satisfy an orthogonality relation

$$\int Y_{lm}^*(\theta, \varphi) Y_{l'm'}(\theta, \varphi) \sin \theta d\theta d\varphi \equiv \int Y_{lm}^*(\theta, \varphi) Y_{l'm'}(\theta, \varphi) d\Omega = \delta_{ll'} \delta_{mm'} \quad (1.2-5)$$

in which $d\Omega = \sin \theta d\theta d\varphi$ is an element of solid angle. An arbitrary function $f(\theta, \varphi)$, satisfying the usual criteria for expansion in terms of an orthonormal set, may be expanded in terms of spherical harmonics as

$$f(\theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm} Y_{lm}(\theta, \varphi), \quad (1.2-6a)$$

$$a_{lm} = \int Y_{lm}^*(\theta, \varphi) f(\theta, \varphi) d\Omega. \quad (1.2-6b)$$

It is often desirable to work with real functions constructed as linear combinations of the (complex) spherical harmonics. Several examples are listed in Table 1.2 and are shown in the form of polar diagrams in Fig. 1.1.

Orbital angular momentum operators and spherical harmonics are intimately related. This may be seen from the standpoint of a central force