ATOMS AND MOLECULES

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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 evaulation 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 mometum 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.

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PART I

Mathematical Background

CHAPTER 1

ANGULAR MOMENTUM

1.1 Orbital Angular Momentum

The orbital angular momentum operator **L** is defined by

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

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

$$\mathbf{p} = -i\hbar\nabla \tag{1.1-2}$$

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),

$$L_x = \frac{1}{\hbar}(yp_z - zp_y) = -i\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$= i\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right), \tag{1.1-3a}$$

$$L_y = \frac{1}{\hbar}(zp_x - xp_z) = -i\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$= i\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right), \tag{1.1-3b}$$

$$L_z = \frac{1}{\hbar}(xp_y - yp_x) = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$= -i\frac{\partial}{\partial\varphi}. \tag{1.1-3c}$$

In (1.1-3) 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.,

$$L_i^{\dagger} = L_i \qquad (i = x, y, z), \tag{1.1-4}$$

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 **L**; these are defined as

$$\begin{aligned} L_{+1} &= -\frac{1}{\sqrt{2}}(L_x + iL_y) = -\frac{1}{\sqrt{2}} e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\varphi}\right), \\ L_{-1} &= \frac{1}{\sqrt{2}}(L_x - iL_y) = -\frac{1}{\sqrt{2}} e^{-i\varphi}\left(\frac{\partial}{\partial\theta} - i\cot\theta \frac{\partial}{\partial p}\right), \\ L_0 &= L_z. \end{aligned} \tag{1.1-5}$$

The inverse relations are

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

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

$$L_{+1}^{\dagger} = -L_{-1}, \qquad L_{-1}^{\dagger} = -L_{+1}. \tag{1.1-7}$$

The components of **r** and **p** satisfy certain commutation relations:

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

$$[r_i, r_j] = [p_i, p_j] = 0, \tag{1.1-8b}$$

$$[r_i, p^2] = 2i\hbar p_i, \tag{1.1-8c}$$

$$[p_i, p^2] = 0 \tag{1.1-8d}$$

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 **L** (1.1-1) together with (1.1-8) imply that

$$[L_x, L_y] = iL_z, \qquad [L_y, L_z] = iL_x, \qquad [L_z, L_x] = iL_y. \tag{1.1-9}$$

These may be written in any of the compact forms:

$$[L_i, L_j] = iL_k \qquad (i, j, k \text{ cyclic}), \tag{1.1-10a}$$

$$\mathbf{L} \times \mathbf{L} = i\mathbf{L}, \tag{1.1-10b}$$

$$[L_i, L_j] = i\varepsilon_{ijk}L_k, \tag{1.1-10c}$$

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

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

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

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

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

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

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

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

Employing relations (1.1-13) we also have

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

L^2 commutes with all components of **L**, i.e.,

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

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

1.2 Spherical Harmonics and Related Functions

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

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

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	$\sqrt{\frac{9}{4\pi}}\sqrt{\frac{1}{64}}(35z^4 - 30z^2r^2 + 3r^4)$	$\sqrt{\frac{9}{4\pi}}\sqrt{\frac{1}{64}}(35\cos^4\theta - 30\cos^2\theta + 3)$
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 $l = 0, 1, 2, 3, \ldots$ are called s, p, d, f, . . . functions.

with

$$l = 0, 1, 2, \ldots, \tag{1.2-2a}$$

$$m = l, l-1, \ldots, -l, \tag{1.2-2b}$$

and $P_l^{|m|}(\cos\theta)$ an associated Legendre polynomial. The phase convection 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:

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

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

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 $\theta = 0$,

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

The spherical harmonics satisfy an orthogonality relation

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

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

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

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

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