PRINCIPLES OF SYMMETRY, DYNAMICS, AND SPECTROSCOPY

WILLIAM G. HARTER
University of Arkansas
Fayetteville, Arkansas

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To Margot, Alex, Thomas, and Daniel

PREFACE

This is a text for students of physics and physical chemistry on the principles and applications of symmetry analysis and spectroscopy to atomic and molecular systems. In the general physics and chemistry community, these subjects have come to be known as "group theory." However, this is a misnomer and there is relatively little group theory in this book. Group theory has become a well-established area of pure mathematics since sometime after the tragic death of its founder, Evariste Galois (1811–1832), in a duel. Mathematical treatments of group theory deal with abstract structures and classifications of groups that go well beyond what is found in the current text or most other books on applied group theory. Most of the latter follow the approach and subject contained in the pioneering 1928 work, *Group Theory and Quantum Mechanics*, by Hermann Weyl (Dover 1931) and the well-known texts, *Group Theory* by Eugene Wigner (Academic Press 1959), or *Group Theory and Its Application to Physical Problems* by Morton Hammermesh, (Addison-Wesley 1962).

Perhaps a better name for the mathematical part of our subject is applied group *representation* theory. This lies in the general mathematical areas of group *algebra* and *Fourier analysis*. Calling our subject by its proper name is important. The mathematical techniques of algebra and Fourier analysis are powerful ones. They lead to a more direct approach to the subject, beginning with Chapters 1 and 2. A simpler and more physical treatment of symmetry analysis, which respects its roots in algebra and wave mechanics, is perhaps one of the main things that distinguishes this text.

Ever since Schrödinger used the pejorative *gruppenpest*, the subject of group theory in physics has from time to time received a bad name and deservedly so. It is particularly obnoxious when it is used for taxonomy or mindless application of esoteric (but often meaningless) names that do not help in the understanding of physics or chemistry. It is *not* the intent of this text to encourage this sort of obscurantia.

Rather it is the physical description of the symmetry algebra and spectroscopy that is emphasized from the beginning and throughout this text. We attempt to present the mathematical analysis as a natural consequence of physical reality instead of the other way around. This approach clarifies the relation between mathematics and physics and motivates its own development. It is hoped this leads to increased understanding of physics as well as more computational power and results in not only better physics but also better mathematics.

The development begins by describing the smallest and simplest structures or symmetries which are later linked through *subgroup chains* to the larger ones. It is important to understand the smaller building blocks. Early in Chapter 2, considerable time is devoted to the double pendulum and the two-state system. This involves the elementary bilateral or C_2 symmetry which, incidentally, is the only symmetry our human bodies approximate. Two-fold symmetry provides a fundamental paradigm that recurs as the basis of U(2) symmetry in Chapter 5 and in analysis of spin resonance, optical polarization, and laser driven transitions in Chapters 7 and 8. It also introduces the key physical idea of symmetry; anything with symmetry must have at least two identical units and if these units are harmonic oscillators they must be precisely in *resonance* with each other.

Resonance is the basis of electromagnetic spectroscopy and probably the single most important phenomena in all of physics. Without it we would be deaf, dumb, and blind and physics as we know it would not exist. Most forces in nature are so weak they can be effective only if amplified by some resonance phenomenon. In typical atomic transitions, this amplification or quality factor is about 50 million; in molecules it can be more than 10^{10} or 10^{11}. Resonance between high quality oscillators requires that they match with a correspondingly high degree of precision or symmetry.

Given the importance of the relation between resonance and symmetry it seems worthwhile to describe its fundamental properties. This begins in Chapter 2 where the effects of symmetry breaking are introduced using both classical and quantum examples of resonance. The relation between classical and quantum resonance is continued with a discussion of the Lorentz theory for classical resonance of a *single* oscillator in Chapter 6. This provides a background for the modern SU(2) theory of two-level quantum resonance in Chapters 7 and 8.

Resonance between three, four, or more oscillators is described in later parts of Chapters 2 and in Chapters 3 and 4. Chapter 2 introduces the concept of symmetry-defined wave modes and shows how symmetry determines whether waves move or stand and where they stand. The concept of symmetry breaking and quenching of moving waves is introduced first for classical mechanical waves and then for quantum mechnical waves. All concepts are introduced by examples which range in complexity from simple pendulums, Bohr orbitals and 1-D lattice modes to more complex problems involving atomic orbitals in solids and rotations and vibrations of polyatomic molecules.

A unique feature of this test is its discussion and comparison of the two types of symmetry breaking. The standard type of external or *applied* symmetry breaking is exemplified by Zeeman or Stark splitting in which externally applied perturbation reduces the symmetry of a Hamiltonian and splits energy level degeneracy. The other type, which is called *internal* or *spontaneous* symmetry breaking, does the opposite; it unsplits or clusters energy levels into manifolds of greater degeneracy or near-degeneracy. These correspond to *induced* representations and the idea of the resonance effects in *local* and *global* symmetries which is introduced in Chapter 4.

Perhaps the simplest pedagogically unequivocal example of spontaneous symmetry breaking occurs in cubic or octahedral symmetry and is treated in Chapter 4. However, it is just as likely for symmetries as simple as for C_3 or C_2. The treatment of internal symmetry breaking arose from the author's work on laser molecular spectroscopy, however the general topic is having a much grander application in high energy physics.

Connected with the two kinds of symmetry breaking are the two kinds of symmetry groups. Chapter 3 and beyond show that there are two sides to the symmetry analysis of a physical body such as a molecule, atom, or nucleus. Roughly speaking there is an outside or *external* symmetry consisting of *laboratory* based operations, and an inside or *internal* symmetry consisting of *body* based operations. A detailed realization of this concept for spherical symmetry is treated in Chapter 5 in connection with rotor quantum states. However, the idea of what one calls the "inside" and "outside" or the observed and observer is a very general one that lies at the foundation of quantum theory and symmetry analysis.

A key mathematical object that embodies these ideas is the quantum symmetry *projection operator* P^{α}_{mn}. The P-operators are used in three ways in this book. First, they have well-known applications for computing quantum states. Second, (this is not so well known) they can be made to derive themselves and their related mathematical quantities. Third, (this is, seldom, if ever, used) the projection operators serve as conceptual objects which clearly delineate internal and external symmetry properties. The in and out of P-operators is first shown in Chapter 3. However, the most well known example is the quantum rotor projector P^{j}_{mn} introduced in Chapter 5 for which m and n are lab and body projections of angular momentum j.

Derivation of the algebra of matrix representations and projection operators begins in Chapter 1. Four axioms or postulates for the matrix approach to quantum mechanics are reviewed at the beginning of the first chapter. This approach to quantum theory is similar to that given in Volume III of the famous *Feynman Lectures* (Addison-Wesley 1965). These four physical axioms are related to the four mathematical axioms of group theory at the beginnning of the second chapter so the role of group theory in formulating quantum mechanics problems is seen immediately. However, it is group algebra and spectral decomposition by projection operators that helps to *solve* these problems and these techniques are the main topics of the first four chapters.

The mathematical development of representation theory in this text is backwards compared to that of most other applied symmetry treatments. According to the usual order one introduces Schur's lemmas, character or representation orthogonality, and finally the application of symmetry projection operators. Instead, this text develops projection operator and spectral decomposition first. Then the representation and character orthogonality follow more naturally and Schur's lemmas are trivial consequences. There is evidence in the literature that this is more like the way the subject was created even if it is not the way it is generally presented. (The standard approach is given in Appendix G.) This provides students with alternatives to an approach that just fights the last wars and may be a better way to prepare them for future engagements.

The current text has only brief discussions of the Pauli principle which is probably the single most mysterious principle or axiom in all of modern physics. Also relativistic spin and orbit theory is absent as are most of the author's research efforts on unitary and permutation groups involving multielectronic atoms and molecules and molecular spin–vibration–rotation interactions. Also, there is only a brief introduction to Racah recoupling coefficients.

A number of MacIntosh computer animation and simulation programs have been written by the author to accompany this text. Transformation matrix algebra and Dirac eignevector properties are displayed in a program called *MatrIt*. The properties of a driven and damped harmonic oscillator is simulated in a program called *OscillIt*. Two coupled oscillators, C_2 symmetry properties and the analogous two-state quantum systems are simulated in the program called *Color U(2)*. The latter contains a detailed development of Stokes–Poincaré polarization mechanics and Rabi spin resonance. Waves in multiple coupled oscillators and C_n symmetry analysis is the topic of the program *WaveIt*. Dispersion relations and elementary band theory are described there. Quantum wave mechanics and scattering in one-dimensional barriers, wells, and lattices are the subjects of the program called *BandIt*. Classical coulomb orbits for one- and two-center atomic and molcular systems are stimulated in a program call *CoulIt*. Hamilton's classical action ($S = \int p\,dq$) is displayed using color in *CoulIt* and *Color U(2)*. Finally, a program called *SpinIt* displays body and laboratory views (in stereo 3D) of rigid and semi-rigid rotors and coupled spins and rotors. The related chapters for these programs are listed below.

MatrIt	Chapter 1
OscillIt	Chapters 1, 2, and 6
Color U(2)	Chapters 2, 5, 7, and 8
WaveIt	Chapters 2 and 3
BandIt	Chapters 2 and 3
CoulIt	Chapters 5, 7, and 8
SpinIt	Chapters 5, 7, and 8

Information about where to obtain these programs can be obtained from the author.

WILLIAM G. HARTER

Fayetteville, Arkansas