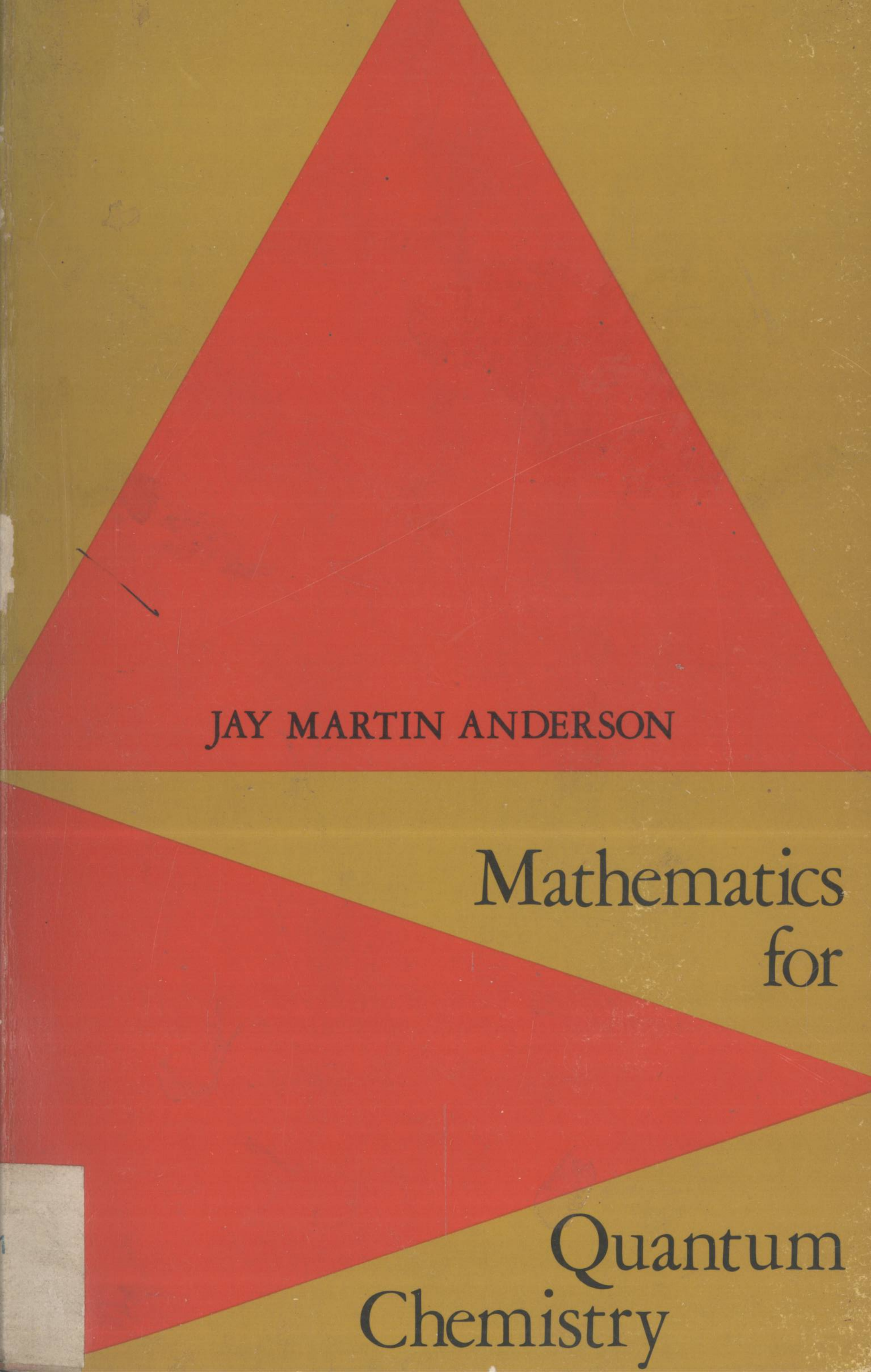

JAY MARTIN ANDERSON

Mathematics for Quantum Chemistry

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Mathematics for Quantum Chemistry

With the fondest of memories, to my first class:

BARBARA, CANDY, ELLEN, LYNNE, MARCIA, ROBERTA, AND ROWENA

Preface

Recent trends in chemical education force students of chemistry into contact with the applications of quantum mechanics at an earlier and earlier point in their development. This direction of undergraduate chemistry curricula is important for several reasons: the wealth of physico-chemical information which is gleaned from molecular spectroscopy and other techniques which are based on quantum mechanics; the trend of descriptive chemistry to rely on concepts taken from quantum mechanics; the growing concern in theoretical chemistry to adequately explain molecular phenomena by means of quantum mechanics.

The rush to introduce the student to these bold and exciting studies often leaves him uncomfortable in the mathematical formalism in which these studies are couched, unsure of the connection between the conventional Newtonian world to which he is accustomed and the world of molecular phenomena, and unable to apply his new-found theoretical knowledge to problems of molecular structure and motion.

In the present work I shall attempt to present only two main topics from mathematics, and two from physics. These are the calculus of orthogonal functions and the algebra of vector spaces from mathematics, and the Lagrangian and Hamiltonian formulation of classical mechanics and its applications to molecular motion from physics. I have selected these four topics because of their relevance to modern quantum chemistry, especially in the application of quantum mechanics to molecular spectroscopy. This emphasis on molecular spectroscopy betrays my personal interest and excitement in this growing and popular field of endeavor; it also eliminates from the pages of this brief book a consideration of other topics which may be equally stimulating to my colleagues and to their students. Relativity, electricity, magnetism, and radiation physics were eliminated because they are generally better treated elsewhere and in greater depth than this work allows; similarly, group theory and differential equations, including approximate methods of solution, are left to other treatises.

This book attempts to lay down a central core of physical and mathematical background for quantum chemistry in general, but for molecular spectroscopy in particular. It assumes a knowledge of calculus through partial derivatives and multiple integration (usually about one and one-half years), a year of physics, and chemistry through a year of physical chemistry. This material has been used as the basis of a one-semester course at Bryn Mawr College entitled "Applied Mathematics for Chemists" for students with approximately the indicated background; this course immediately precedes the first course in quantum mechanics.

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JAY MARTIN ANDERSON

Bryn Mawr, Pennsylvania
October 1965

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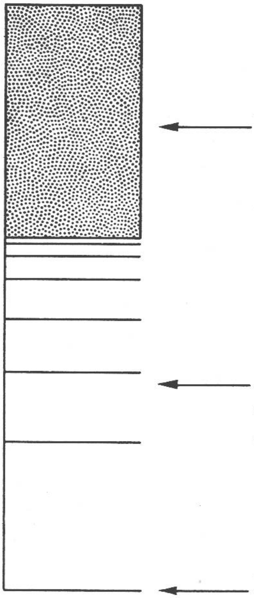
1

Introduction

1–1 EIGENVALUE PROBLEMS IN QUANTUM MECHANICS

The mathematics and physics that are relevant to quantum chemistry are, almost without exception, oriented toward the solution of a particular kind of problem, the calculation of properties of a molecular system from the fundamental properties (charge, mass) of the particles composing the system. A good example of this is the calculation of the *energy* of the electrons in a molecule, using only the charge of the electron, Planck's constant, and so forth. The reader is probably already aware of the nature of the answer to this problem. There are a number of discrete values for the energy which the electrons in the molecule can assume up to a point, but higher values for the electronic energy occur in a continuous range. These energy values are shown qualitatively in Fig. 1–1. Quantum mechanics does provide the result that some physical quantities may take on only *some* values, not *all* values, as experiments indicated. The allowed values for a physical quantity are called *eigenvalues*, from the German for *characteristic values*. A particular physical quantity may assume an eigenvalue from a continuum, or perhaps from a finite or infinite discrete set of eigenvalues. The energy of an atom, for instance, may take on one of an



Continuum, or range of continuous eigenvalues, of energy. Corresponds to an ionizing molecule.

Range of discrete eigenvalues of energy. Corresponds to electronically excited molecule.

Lowest eigenvalue of energy. Corresponds to ground state of molecule.

Figure 1–1 Eigenvalues of the energy of a molecule.

infinite number of discrete values, as well as values from a higher-lying range of continuous eigenvalues, called the *continuum*. More often than not, chemistry is concerned with the discrete eigenvalues of a quantity, rather than its continuum of eigenvalues.

The mathematical problem of finding the eigenvalues of a quantity is called an *eigenvalue problem;* it is usually cast in the form of an equation called an *eigenvalue equation*. An eigenvalue equation for a physical quantity Q has the deceptively simple appearance

$$\mathcal{Q}f = qf \tag{1–1}$$

In this equation, f is a function, called the *eigenfunction* for the quantity Q, with the eigenvalue q. The element $\mathcal{Q}$ is called an *operator*, and the statement $\mathcal{Q}f$ tells us to change the function f into a new function, according to a set of instructions implicit in the definition of the operator $\mathcal{Q}$. The eigenvalue equation, Eq. 1–1, then informs us that, by applying these "instructions" of the operator $\mathcal{Q}$ to f, we get merely a multiple, q, of the function f. The function $\mathcal{Q}f$ differs from the function f by a multiplicative constant q. It may very well be the case that several eigenfunctions have the same eigenvalue; that is, $\mathcal{Q}f_1 = qf_1$, $\mathcal{Q}f_2 = qf_2$, and so forth. If this is the case, the eigenvalue q is said to be *degenerate*, and the number of eigenfunctions that have the same eigenvalue is called the *degree of degeneracy*.

Operators may simply be numbers or functions; for example, the operator $\mathcal{X}$ may be defined by the instruction "multiply the operand function by x"; thus, $\mathcal{X}\, x^2 = x^3$. On the other hand, operators may be more complex than just numbers or functions. For example, the student has already used the operator (although probably not by that name) Δ, which means, or is defined by the instructions, "evaluate the change in." For example, if we operate Δ on the thermodynamic function H, the enthalpy, we get a new function ΔH, the change in the enthalpy, $\Delta H = H_2 - H_1$. Another operator that is familiar is d/dx, meaning, "evaluate the derivative with respect to x."

It is the job of quantum mechanics to tell us how to form operators corresponding to the physical quantities which we wish to measure. Our task for the moment will be to learn how to solve the eigenvalue equations for such operators, and especially the vocabulary and concepts that are used to discuss the solutions. Quantum mechanics itself, however, grew up from two different points of view, which represent two analogous mathematical formulations of eigenvalue problems.

The first of these points of view is the *wave mechanics* of Schrödinger In wave mechanics, operators are differential expressions, such as the operator d/dx referred to above, and the eigenvalue equation then takes the form of a differential equation, and relies on the calculus for its solution. The second formulation is the *matrix mechanics* of Heisenberg, in which operators are represented by algebraic entities called *matrices;* instead of a function in the eigenvalue equation, the matrix operator operates on a *vector* ξ to transform ξ into a vector parallel to ξ, but q times as long:

$$\mathcal{Q}\xi = q\xi \tag{1–2}$$

Equation 1–2 is the matrix-mechanical formulation of the eigenvalue problem. Matrices and vectors are defined and discussed in detail in Chapter 3. As in Eq. 1–1, q is the eigenvalue of the quantity Q, ξ is the *eigenvector*, and $\mathbb{Q}$ is the operator represented as a matrix. The solution of this form of the eigenvalue problem relies on algebra.

These apparently different mathematical and physical approaches to quantum mechanical problems are really deeply interrelated; the work of Dirac shows the underlying equivalence of the two points of view, as well as of the corresponding mathematical techniques.

1–2 EIGENVALUE PROBLEMS IN CLASSICAL MECHANICS

We have briefly discussed the role of eigenvalue equations in quantum mechanics. But a number of problems of classical mechanics may also be expressed in a simple and meaningful way as eigenvalue problems. Among these are the problems of the vibrations and rotations of a mechanical system, such as a molecule. These physical problems are of importance to the chemist concerned with molecular motion and spectroscopy. In vibrations, the normal modes and frequencies of oscillation appear as eigenvectors and eigenvalues; in rotations, the principal axes and moments of inertia emerge from an eigenvalue problem. It should be noted, however, that a correct description of these systems on the molecular level nearly always requires quantum mechanics, not classical mechanics.

1–3 SCOPE OF THIS BOOK

With our course thus determined by the kinds of problems we wish to be able to set up, solve, and understand, we shall proceed first to a study of a certain class of functions germane to eigenfunction problems, then to a number of aspects of vector algebra and matrix algebra, finally to a synthesis of the two points of view of eigenvalue problems. We shall conclude with a study of classical mechanics to see how the vibrations of a mechanical system, such as a molecule, may be formulated as an eigenvalue problem. We shall also attempt to formulate Newtonian mechanics in such a way that the connection to quantum mechanics is clear.

Along the way, we shall learn some methods of solving eigenvalue problems, and take up applications of interest in chemistry. Our emphasis throughout will be primarily on concepts, secondarily on methods, and only lastly on the detailed proofs of the mathematical theorems. At the end of each chapter, a set of problems is given. Answers and hints for solution for many of the problems are found at the back of the book.

Problem

1. Find the eigenfunctions of the operator d/dx.

2

Orthogonal Functions

Two properties are, almost without exception, possessed by the eigenfunctions of operators corresponding to important physical quantities: *orthogonality* and *normality*. The purpose of this chapter is to develop these concepts in detail and to illustrate a number of their applications. Of primary usefulness is the idea of an *expansion in orthogonal functions*. As an example of this technique, we shall examine the *Fourier series* in some detail. We shall also learn how to construct orthogonal functions by the *Schmidt orthogonalization procedure*, and how orthogonal functions arise from the solution of particular differential equations. To illustrate the latter concepts, we shall investigate the properties of the *Legendre polynomials*, and briefly mention other of the important "special functions" which arise in quantum chemistry. A brief discussion of some of the elements of the calculus and of complex variables are given in the Appendix. The reader would be wise to check his familiarity with this material before advancing into the present chapter.

2-1 INTRODUCTORY CONCEPTS: ORTHOGONALITY AND NORMALIZATION

We may best begin our discussion of orthogonal functions by reviewing the concept of *function*. The concept of function has three essential ingredients. We agree first to define a function on a particular region of the number scale, say, from a to b. Second, we agree that there exists a variable (say, x) that can independently assume values in the region from a to b. Third, we agree by some prescribed rule that for any value of x there exists a *definite* value of y. Then we say that y is a function of x on the range $a \leq x \leq b$. This definition may be modified in a number of ways—so as to include more than one independent variable—but these three essential ingredients persist: an independent variable; a range on which the independent variable assumes its values; a dependent variable related to the independent variable by a prescribed rule.

The simplest way of notating the statement "y is a function of x" is to write $y = y(x)$. This notation is compact, yet may be misleading. The left side of the equation is simply the name of a variable—we do not know it is the dependent variable until we see the right side of the equation. The right side uses the letter y again, but here the symbol $y(\ )$ means something different than just the name of the variable. The meaning of $y(\ )$ is that y is a dependent variable whose value may be found by some prescribed rule from the quantity inside the parentheses. Left out of the notation $y = y(x)$ is the interval, or range, of the independent variable x for which the functional relationship is defined. This is not always of importance in elementary considerations of the idea of function, but it is of supreme importance to the notion of expansion of a function. Hence, we introduce a definition.

Definition *Expansion interval* (or, simply, *interval*). The expansion interval is the range of the independent variable assumed by the functions under consideration. This does not imply that the function may not be defined for other values of the independent variable; we just decline to consider those other values.

The expansion interval is usually notated $[a, b]$, meaning that the independent variable x is allowed values on the range $a \leq x \leq b$. We proceed now to four definitions in rapid succession.

Definition *Inner product*. The inner product of the two (in general, complex-valued) functions f and g of a continuous variable on their expansion interval $[a, b]$ is

$$\langle f \mid g \rangle = \int_a^b f(x)^* g(x)\, dx \qquad \text{(2–1)}$$

The inner product of two functions is defined *on their expansion interval*. The inner product is notated by some authors (f, g), but this can easily be confused with the notation for two-dimensional coordinates or for an open interval. We shall use the notation $\langle f \mid g\rangle$. The order is quite important:

$$\begin{aligned}\langle g \mid f\rangle &= \int g(x)^* f(x)\,dx = \left(\int f(x)^* g(x)\,dx\right)^* \\ &= \langle f \mid g\rangle^* \end{aligned} \tag{2–2}$$

For real-valued functions, the order is not important. Equation 2–2 illustrates an important feature of the inner product that arises again and again: “turning around,” or *transposing an inner product gives the complex conjugate of that inner product*. Constants may be removed at will from the inner product symbol: if b and c are (complex) numbers, $\langle bf \mid cg\rangle = b^*c\langle f \mid g\rangle$.

The inner product is a concept of no small significance. It has a geometrical analog, that of the *dot product* or *scalar product* of vectors that may already be familiar, which we shall discuss in Chapter 3.

In analogy to the geometrical property of perpendicularity of vectors, both functions and vectors afford the sweeping and general concept of *orthogonality*.

Definition Two functions, $f(x)$ and $g(x)$, are said to be *orthogonal* on the interval $[a, b]$ if their inner product on $[a, b]$ is zero:

$$\langle f \mid g\rangle = \int_a^b f^* g = 0 = \int_a^b g^* f = \langle g \mid f\rangle \tag{2–3}$$

If the inner product is to be zero, it does not matter which function “comes first” in the inner product, so the orthogonality of f and g may be expressed by either $\langle f \mid g\rangle = 0$ or $\langle g \mid f\rangle = 0$. The perpendicularity of two vectors is related to this definition of orthogonality: two vectors are perpendicular if their dot product is zero.

Definition The *norm* of a function on the interval $[a, b]$ is the inner product of the function with itself, and may be symbolized by N:

$$N(f) = \langle f \mid f\rangle = \int_a^b f^* f \tag{2–4}$$