Encyclopedia of Mathematics and its Applications 9

THE RACAH-WIGNER ALGEBRA IN QUANTUM THEORY

Lawrence C. Biedenharn
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The Racah–Wigner Algebra in Quantum Theory

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Section: Mathematics of Physics
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The Racah–Wigner Algebra in Quantum Theory

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Editor's Statement

A large body of mathematics consists of facts that can be presented and described much like any other natural phenomenon. These facts, at times explicitly brought out as theorems, at other times concealed within a proof, make up most of the applications of mathematics, and are the most likely to survive changes of style and of interest.

This ENCYCLOPEDIA will attempt to present the factual body of all mathematics. Clarity of exposition, accessibility to the non-specialist, and a thorough bibliography are required of each author. Volumes will appear in no particular order, but will be organized into sections, each one comprising a recognizable branch of present-day mathematics. Numbers of volumes and sections will be reconsidered as times and needs change.

It is hoped that this enterprise will make mathematics more widely used where it is needed, and more accessible in fields in which it can be applied but where it has not yet penetrated because of insufficient information.

GIAN-CARLO ROTA

Foreword

The study of the symmetries of physical systems remains one of the principal contemporary theoretical activities. These symmetries, which basically express the geometric structure of the physical system in question, must be clearly analyzed in order to understand the dynamical behavior of the system. The analysis of rotational symmetry, and the behavior of physical quantities under rotations, is the most common of such problems. Accordingly, every professional physicist must achieve a good working knowledge of the "theory of angular momentum."

In addition, the theory of angular momentum is the prototype of continuous symmetry groups of many types now found useful in the classification of the internal symmetries of elementary particle physics. Much of the intuition and mathematical apparatus developed in the theory of angular momentum can be transferred with little change to such research problems of current interest.

If there is a single essential book in the arsenal of the physicist, it is a good book on the theory of angular momentum. I have worn out several earlier texts on this subject and have spent much time checking signs and Clebsch-Gordan coefficients. Such books are the most borrowed and least often returned. I look forward to a long association with the present fine work.

A good book on the theory of angular momentum needs to be thoroughly reliable yet must develop the material with insight and good taste in order to lay bare the elegant texture of the subject. Originality should not be erected in opposition to current practices and conventions if the text is to be truly useful.

The present text, written by two well-known contributors to the field, satisfies all these criteria and more. Subtleties and scholarly comments are presented clearly yet unobtrusively. Moreover, the footnotes contain fascinating historical material of which I was previously unaware. The two chapters on the "theory of turns" and "boson calculus" are significant new additions to the pedagogical literature on angular momentum. Much of the theory of turns presented here was developed by the authors. By means of this approach the concept of "double group" is made very clear. The development of the boson calculus employs Gel'fand patterns in an essential way, in addition to the more traditional Young tableaux. This section provides an excellent prototype for the analysis of all compact groups.

The representation theory is developed in the complete detail required for physical applications. This exposition of the lore of rotation matrices is especially thorough, including the Euler angle parametrization as well as others of practical value.

The text ends with a long chapter on applications well chosen to illustrate the power of the general techniques. The book concludes with a masterly development of the group theoretical description of the spectra of spherical top molecules. To my mind the recent experimental confirmation of this theory in high resolution laser spectrometry experiments is one of the most spectacular confirmations of quantum theory.

The present text is really a book for physicists. Nevertheless, the theory generates substantial material of interest for mathematicians. Recent research (for example in non-Abelian gauge field theory) has produced topics of common interest to both mathematicians and physicists. Some of the more interesting mathematical outgrowths of the theory of angular momentum are developed in the companion volume currently in press.

PETER A. CARRUTHERS
General Editor, Section on Mathematics of Physics

Preface

"The art of doing mathematics," Hilbert[1] has said, "consists in finding that *special* case which contains all the germs of *generality*." In our view, angular momentum theory plays the role of that "special case," with symmetry—one of the most fruitful themes of modern mathematics and physics—as the "generality." We would only amend Hilbert's phrase to include physics as well as mathematics. In the Preface to the second edition of his famous book *Group Theory and its Applications to the quantum Mechanics of Atomic Spectra*, Wigner[2] records von Laue's view of how remarkable it is that "almost all the rules of [atomic] spectroscopy follow from the symmetry of the problem." The symmetry at issue is *rotational symmetry*, and the spectroscopic rules are those implied by *angular momentum conservation*. In this monograph, we have tried to expand on these themes.

The fact that this monograph is part of an encyclopedia imposes a responsibility that we have tried to take seriously. This responsibility is rather like that of a library. It has been said that a library must satisfy two disparate needs: One should find the book one is looking for, but one should also find books that one had no idea existed. We believe that much the same sort of thing is true of an encyclopedia, and we would be disappointed if the reader did not have both needs met in the present work. To accomplish this objective, we have found it necessary to split our monograph into two volumes, one dealing with the "standard" treatment of angular momentum theory and its applications, the other dealing in depth with the fundamental concepts of the subject and the interrelations of angular momentum theory with other areas of mathematics.

Fulfilling this responsibility further, we have made an effort to address readers who seek *very* detailed answers on *specific* points—hence, we have a large index, and many notes and appendices—as well as readers who seek an overview of the subject, especially a description of its unique and appealing aspects. This accounts for the uneven level of treatment which varies from chapter to chapter, or even within a chapter, quite unlike a

[1]Quoted in M. Kac, "Wiener and Integration in Function Spaces," *Bull. Amer. Math. Soc.* **72** (1966), p. 65. (The italics are in the original; Kac notes that the statement may be apocryphal.)

[2]E. P. Wigner, *Group Theory and Its Applications to the Quantum Mechanics of Atomic Spectra*, Academic Press, New York, 1959, p. v. (We have added in brackets the word "atomic," since this was clearly von Laue's intended meaning.)

textbook with its uniformly increasing levels of difficulty. The variation in the treatment applied particularly to the Remarks. Quite often these Remarks contain material that has not been developed or explained earlier. Such material is intended for the advanced reader, and it can be disregarded by others. We urge the reader to browse and skip, rather than trying, at first, any more systematic approach.

These considerations apply also to the applications. Some applications may be almost too elementary, whereas others are at the level of current research. The field of applications is so broad that we have surely failed to do justice in many cases, but we do hope that the treatment of some applications is successful.

In discussing a particular subject, we have given more detail than is usual in mathematical books, where terseness is considered the cardinal virtue. Here we have followed the precepts of Littlewood[3] who points out that "*two* trivialities omitted can add up to an *impasse*."

Let us acknowledge one idiosyncrasy of our treatment: We have not explicitly used the methods of group theory, per se, but have proceeded algebraically so that the group theory, if it appears at all, appears naturally as the treatment develops. No doubt this method of treatment is an overreaction to the censure—(now disappearing?)—with which many physicists greeted the *Gruppenpest*.[4] In any event, we think that this treatment does make the material more accessible to some readers.

Let us make some brief suggestions as to how to use the first volume, *Angular Momentum in Quantum Physics* (AMQP). Part I: (i) Chapters 2 and 3 and parts of Chapter 6 constitute the standard treatment of angular momentum theory and will suffice for many readers who wish to learn the mechanics of the subject. The methods used are elementary (but by no means imprecise), and the whole treatment flows from the fundamental commutation relations of angular momentum. (ii) Chapters 4 and 5 are recommended to the reader who wishes a general overview of the subject with methods capable of great generalization. Paradoxically, although these two chapters contain much new material, this material also belongs to the very beginnings of the subject—in the multiplication of forms of Clebsch and Gordan, and in the ξ-η calculus of Weyl—all of which are now incorporated under the rubric of the "boson calculus." Part II: The applications given in Chapter 7 are totally independent of one another, and can be understood from the results given in Chapter 3.

The second volume, *Racah–Wigner Algebra in Quantum Theory* (RWA), is also presented in two parts. (The Contents for RWA appears also at the

[3] J. E. Littlewood, *A Mathematician's Miscellany*, Methuen and Co., London, 1953, p. 30. (The italics are in the original.)

[4] B. G. Wybourne, "The Gruppenpest yesterday, today, and tomorrow," *International Journal of Quantum Chemistry*, Symposium No. 7 (1973), pp. 35–43.

beginning of AMQP.) Part I: In Chapters 2, 3, and 4 the algebra of the operators associated with the two basic quantities in angular momentum theory—the Wigner and Racah coefficients—is developed within the framework of the algebra of bounded operators acting in Hilbert space. These chapters are intended to rephrase the concept of a "Wigner operator" (tensor operator) in algebraic terms, using methods from Gel'fand's development of Banach algebras. This approach to angular momentum theory is rather new, and is intended for the reader who wishes to pursue the subject from the viewpoint of mathematics. Part II: The twelve topics developed in Chapter 5 establish diverse interrelations between concepts in angular momentum theory and other areas of mathematics. These topics are independent of one another, but do draw for their development on the material of Chapter 3 of AMQP, and to a lesser extent on Chapters 1–3 of RWA. This material should be of interest to both mathematicians and physicists.

Acknowledgments

This monograph could not have been completed without the extensive help of friends and colleagues. Professor L. P. Horwitz performed the vital chore of a thorough reading and criticism of the entire two volumes; his help is gratefully acknowledged.

Other colleagues who have helped us by reading and criticizing particular chapters, the applications, or topics in *Angular Momentum in Quantum Physics* and in *Racah–Wigner Algebra in Quantum Theory* are: (i) AMQP. D. Giebink, Chapters 2–4; Professors H. Bacry and B. Wolf, Chapter 4; Professor R. Rodenberg and Dr. M. Danos, Chapters 2–6; Professor B. R. Judd, Chapter 7, Section 5; Drs. H. W. Galbraith, C. W. Patterson, and B. J. Krohn, Chapter 7, Section 10; (ii) RWA. Professor L. Michel, Chapters 2–4; Drs. H. Ruch and R. Petry, Topic 2; Dr. M. M. Nieto, Professors M. Reed, N. Mukunda, and H. Bacry, Topic 7; Professor T. Regge, Topic 9; Dr. B. J. Krohn, Topic 10; Dr. C. W. Patterson and Professor J. Paldus, Topic 12. Dr. W. Holman read both volumes to assist us with the indexing and suggested many improvements. Further acknowledgment of help from those not mentioned here is indicated in the relevant chapters.

In a more general way, we are indebted also to Professors H. van Dam, E. Merzbacher, A. Bohm, and Dr. N. Metropolis for discussions and help extending over several years.

This monograph is dedicated to Professor Eugene P. Wigner, whose picture (courtesy of the Niels Bohr Library of the American Institute of Physics) appears as the frontispiece. We not only acknowledge the inspiration of Wigner's research, but also record his personal encouragement and help, and we are honored that he has accepted this dedication. We wish also to acknowledge our great indebtedness to the late Professor Giulio Racah, who encouraged our work at its most critical time, the very beginning. Professor Ugo Fano also helped us greatly in this same period.

Special thanks are due to Professor Gian-Carlo Rota, editor of this Encyclopedia, for encouraging us to write at length on the subject of this monograph.

Most monographs begin as course notes and lectures series. The present monograph is no exception and evolves from such notes and lectures given over the years. We are particularly indebted to Dr. H. William Koch for urging us to write up the lectures on angular momentum theory (based on

the concept of the turn) given at the National Bureau of Standards. This was finally achieved many years later, when a much expanded version was presented at Canterbury University (Christchurch, New Zealand, in 1973) and supported by an Erskine Fellowship arranged by Professor Brian Wybourne.

Without the patience and helpful attitude of the editorial and production staffs of the Advanced Book Program of Addison-Wesley, and the free-lance copy editor, Dorothea Thorburn, it would not have been possible to split our original manuscript into the present two volumes.

The entire typing of the original manuscript and several of its revisions were carried through, courageously and without flinching, by Nancy Simon. Her loyalty to this task, extending over several years, is especially appreciated. Thanks are also given to Lena Diehl for typing many of the final revisions. We are also indebted to Graphic Arts and Illustration Services of the Los Alamos Scientific Laboratory for the figures and reproductions.

The writing of a monograph can be traumatic to others besides the authors. We wish to thank our wives, Sarah Biedenharn and Marge Louck, for their unfailing support and encouragement in keeping us at our task.

L. C. BIEDENHARN
J. D. LOUCK

Introduction

1. This book is a sequel to its authors' recently published *Angular momentum in quantum physics*: *Theory and application*; it treats various advanced topics that could not be covered in the earlier volume without making it inconveniently long. My purpose is to explain the subject matter from a mathematician's point of view, but it would be awkward and difficult to do this without taking into account the contents of both books. Thus, in spite of its tardy appearance, this essay will, in effect, be an introduction to the two-volume work as a whole.

When a physicist speaks of "angular momentum theory," he is alluding to a theory that a mathematician would be more likely to describe as "the theory of rotational invariance." This theory, whatever we call it, is concerned (*a*) with a technique for exploiting the fact that many physical laws are independent of orientation in space and (*b*) with the many important consequences of this fact.

The physicists' choice of the words "angular momentum theory" illustrates a tendency that is one of the many factors inhibiting communication between mathematicians and physicists. This is the tendency physicists have to avoid thinking in the abstract and instead to keep a concrete physical problem constantly in mind and use physical terminology whenever possible. From the mathematician's point of view, the physicist is behaving like a beginner who will not take the step from "two oranges and two oranges is four oranges" to "two plus two equals four." The physicist is much less practiced in abstract thinking and is quite properly reluctant to give up an important source of intuition and inspiration.

But what is the connection between rotational invariance and angular momentum that inspires this terminology? It derives from a fundamental

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theorem in mechanics—both classical and quantum—setting up a natural one-to-one correspondence between certain "one-parameter symmetry groups" on the one hand, and "integrals of the motion" on the other. The group $\mathfrak{E}$ of all rigid motions of Euclidean space defines an action of $\mathfrak{E}$ on the phase space Ω of an n-particle system, and for each x in $\mathfrak{E}$ the associated one-to-one map of Ω on Ω is a "symmetry" of the system in an obvious sense. If $s \to \alpha_s$ is any one-parameter subgroup of $\mathfrak{E}$—that is, any continuous homomorphism of the additive group of the real line into $\mathfrak{E}$—then this homomorphism composed with the action of $\mathfrak{E}$ defines an action of the real line on Ω, each map of which is a symmetry. Thus, one has an integral of the motion that is, a function on Ω that is constant in time) for each one-parameter subgroup α of $\mathfrak{E}$. These integrals, which are evidently of special interest, are called momentum integrals. Given a line l in space, let α_s^l denote the rotation about l through an angle of s radians. The integral of the motion corresponding to this one-parameter symmetry group is called the *total angular momentum* about the axis l. Linear momentum is defined similarly, with one-parameter groups of translations. Although the linear and angular momentum integrals were discovered long before anyone thought in terms of groups of symmetries, it is gratifying to have such an elegant a priori reason for their existence.

2. Before proceeding further, it will be useful to recall the basic structure of quantum mechanics in the rigorous form given it by von Neumann. This can be done quite concisely and completely, and a reader unfamiliar with quantum mechanics (at least in this formulation) should not hesitate to make a serious effort to understand it.

In classical mechanics the future of a system of n particles in uniquely determined by the positions and velocities of these particles at any instant of time t. The $6n$-dimensional space Ω of all possible positions and velocities of the particles is called the *phase space* of the system, and its points ω are called the *states* of the system. (For reasons that need not concern us, one actually uses positions and momenta; the momentum of a particle being the mass times its velocity.) For each positive real number t and each $\omega \in \Omega$, let $\alpha_t(\omega)$ denote that point ω' of Ω such that the positions and velocities corresponding to ω' are precisely those that describe the system t time units after it was described by the positions and velocities corresponding to ω. Then in all "reversible" systems (and we consider no others), each α_t is a one-to-one map of Ω on Ω, and setting $\alpha_{-t} = \alpha_t^{-1}$ we obtain a one-parameter group $t \to \alpha_t$ of one-to-one transformations of Ω into itself. Let us call this the *dynamical group* of the system. The parameterized curves $t \to \alpha_t(\omega)$ are the *trajectories* of the system, and we obtain a vector field X^α in Ω by assigning to each point ω the tangent vector to the unique trajectory through ω. This vector field is called the *infinitesimal generator* of the dynamical group α, and via uniqueness theorems for systems of ordinary differential

equations it determines α uniquely. The unique determination of α by X^α is of the greatest importance for physics, because in most cases X^α can be written down explicitly, whereas α cannot. Thus, nontrivial mathematical problems remain to be solved after the physical law has been precisely formulated. Real valued functions on Ω—that is, functions of the coordinates and velocities—are called *observables* or *dynamical variables*. If f is an observable and $\omega \in \Omega$, then $f(\omega)$ is said to be the *value of the observable* in *the state defined by* ω. Since ω varies with time, the value of any observable f will also vary with time according to the formula $t \to f(\alpha_t(\omega))$. However, there are certain observables g that are such that $t \to g(\alpha_t(\omega))$ is a constant for all ω. These are called *integrals of the motion*, and they are precisely those functions g on Ω that are constants on the trajectories.

In quantum mechanics the states (points of Ω) are replaced by the one-dimensional subspaces of a separable complex Hilbert space $\mathcal{H}$, and the dynamical group is replaced by a continuous one-parameter group $t \to V_t$ of unitary operators mapping $\mathcal{H}$ onto $\mathcal{H}$. By a celebrated theorem of M. H. Stone (inspired by the needs of quantum mechanics), every one-parameter unitary group $t \to V_t$ may be put uniquely in the form $V_t = e^{iHt}$, where H is a (not necessarily bounded) self-adjoint operator. This operator H is the analog of the vector field X^α in classical mechanics and is what one can write down explicitly. If ϕ is a unit vector in the one-dimensional subspace specifying a state at time 0, then this state will be specified t time units later by the one-dimensional subspace containing $V_t(\phi)$, and the variable vector $t \to V_t(\phi) = \phi_t$ will satisfy the differential equation $d\phi_t/dt = iH(\phi_t)$. This (in abstract form) is the Schrödinger equation—the quantum mechanical substitute for the equations of motion of a classical mechanical system. Just as in classical mechanics, the state of a system at a future time t is uniquely determined by t and the state at time 0.

The key difference between quantum mechanics and classical mechanics lies in the fact that the number $f(\omega)$, which the state defined by ω assigns to the observable f, is replaced in quantum mechanics by a probability distribution. In every quantum mechanical state there will be observables that do not have a well-determined value. If one makes the appropriate measurements, one gets different values, but some occur much more frequently than others, and one does have a well-defined probability measure on the line. Our task now is to explain how to calculate the probability distribution of an observable $\mathcal{O}$ in a state s when we know the self-adjoint operator A defining $\mathcal{O}$ and the one-dimensional subspace L of $\mathcal{H}$ defining s. This will be the quantum mechanical substitute for $f(\omega)$. The task is quite trivial when the operator A has a pure point spectrum—that is, when $\mathcal{H}$ admits an orthonormal basis $\phi_1, \phi_2, \ldots$ such that $A(\phi_j) = \lambda_j \phi_j$ for $j = 1, 2, \ldots$. Let ψ be any unit vector in L. Then $\psi = \sum_{j=1}^{\infty} c_j \phi_j$, where $c_j = (\psi \cdot \phi_j)$ and

$\sum_{j=1}^{\infty} |c_j|^2 = 1$. Also, $|c_j|$ is independent of the choice of ψ in L. Setting $\mu_L(E) = \sum_{\lambda_j \in E} |c_j|^2$, we obtain a probability measure on the real line, and this is the probability measure assigned to the observable $\mathcal{O}$ defined by A when the system is in the state s defined by L. Note that the probability that the measurement of $\mathcal{O}$ is not one of the eigenvalues λ_j of the operator A is zero. Of course, self-adjoint operators may have continuous spectra, and then the associated probability measures will not be concentrated in countable sets—not all quantum mechanical observables are "quantized." To compute μ_L when A has a (partially or totally) continuous spectrum, it is necessary to resort to the spectral theorem. We shall not attempt to explain the spectral theory here. Readers who are familiar with the theorem will have no difficulty in adapting the above.

Although it is necessary to diagonalize A in order to compute the probability distribution of the corresponding $\mathcal{O}$ in the various states, the "expected value" of $\mathcal{O}$ can be computed directly from A and ψ. When A has a pure point spectrum so that $\mu_L(E) = \sum_{\lambda_j \in E} |c_j|^2$, it follows at once from the definition that the expected value of $\mathcal{O}$ is $\sum_{j=1}^{\infty} \lambda_j |c_j|^2$. On the other hand, if $\psi = \sum_{j=1}^{\infty} c_j \phi_j$, then

$$A(\psi) = \sum_{j=1}^{\infty} c_j A(\phi_j) = \sum_{j=1}^{\infty} c_j \lambda_j \phi_j,$$

so

$$(A(\psi) \cdot \psi) = \sum_{j=1}^{\infty} c_j \overline{c_s} \lambda_j (\phi_j \cdot \phi_j) = \sum_{j=1}^{\infty} \lambda_j |c_j|^2.$$

Thus, the expected value is just $(A(\psi) \cdot \psi)$. This result can be shown to hold even where A does not have a pure point spectrum.

Finally, let A be the self-adjoint operator defining an observable $\mathcal{O}$. Under what conditions on A shall we say that $\mathcal{O}$ is an "integral of the motion"? In classical mechanics we required that $f(\alpha_t(\omega))$ be independent of t for every ω in Ω. The obvious analog is that the probability distribution defined by A and $V_t(\psi)$ be independent of t for every unit vector ψ. This is equivalent to demanding that the probability distribution defined by $V_t A V_t^{-1}$ and ψ be independent of t for every unit vector ψ: This can be shown to happen if and only if $V_t A V_t^{-1}$ is independent of t—that is, if and only if A commutes

with all V_t. Accordingly, an integral of the motion in quantum mechanics is an observable whose corresponding self-adjoint operator A commutes with all V_t. Recall that $V_t = e^{iHt}$ for some self-adjoint operator H. Evidently the observable corresponding to H is an integral of the motion and, moreover, one that plays a special role. It is a constant multiple of the quantum mechanical analog of the energy integral of classical mechanics. Note that the state defined by the unit vector ψ will be stationary—that is, independent of the time—if and only if $V_t(\psi) = e^{i\lambda t}\psi$ for some real λ and all t. On the other hand, it is easy to see that $V_t(\psi) = e^{i\lambda t}\psi$ if and only if $H(\psi) = \lambda\psi$. Thus, the stationary states are precisely the states in which the energy observable has a definite value with probability 1, the possible values being constant multiples of the eigenvalues of H. As will be explained more fully below, this fact is the key to the quantum mechanical explanation of atomic spectra. In particular, it largely reduces the problem of predicting spectral lines to finding the eigenvalues of certain self-adjoint operators.

3. With the abstract structure of quantum mechanics before us, it is possible to explain the correspondence between one-parameter symmetry groups and integrals of the motion alluded to in section 1. By definition, a symmetry of a quantum mechanical system is a pair α, β consisting of a one-to-one mapping α of the states on the states and a one-to-one mapping β of the observables on the observables such that the following two conditions are satisfied:

*For all states s and all observables $\mathcal{O}$, the probability measure in the line assigned to $\beta(\mathcal{O})$ by $\alpha(s)$ is the same as that assigned to $\mathcal{O}$ by s.

**For all states s and all real numbers t, $\tilde{V}_t(\alpha(s)) = \alpha(\tilde{V}_t(s))$, where $\tilde{V}_t$ is the map of states into states defined by the unitary operator V_t.

It is a theorem that any pair α, β that satisfies (*) is defined by an operator U that is either unitary or anti-unitary. If s corresponds to the one-dimensional subspace L, and $\mathcal{O}$ to the self-adjoint operator A, then $\alpha(s)$ corresponds to $U(L)$, and $\beta(\mathcal{O})$ to UAU^{-1}. The operator U is uniquely determined up to multiplication by a complex number of modulus 1. In order that (**) should also be satisfied, it is evidently necessary and sufficient that for each real t we have $UV_tU^{-1} = c(t)V_t$, where $c(t)$ is a complex number of modulus 1. Since the square of an anti-unitary operator is always unitary, an obvious argument shows that only unitary operators occur in one-parameter symmetry groups. A less easy argument allows one to eliminate the constant $c(s_1, s_2)$ in $\overline{U}_{s_1+s_2} = U_{s_1}U_{s_2}c(s_1, s_2)$ and to show that every one-parameter symmetry group is implemented by a one-parameter unitary group $s \to U_s$. By Stone's theorem, $U_s = e^{iAs}$ for some self-adjoint operator A. The operator A is determined by the symmetry group up to an additive constant. Condition (**) is satisfied if and only if $U_sV_t = c(s, t)V_tU_s$

for all s and t, and unless V has a very special form this can be shown to imply that the U_s and V_t commute. This special form seldom if ever arises in actual physical problems. In other words, the one-parameter symmetry groups are defined by those one-parameter unitary groups $s \to U_s$ such that $U_s V_t = V_t U_s$ for all s and t. Now $U_s = e^{iAs}$, where A is a self-adjoint operator, and one shows easily that $U_s V_t = V_t U_s$ for all s and t if and only if $V_t A = A V_t$ for all t. This last condition, however, is precisely the condition that the observable corresponding to A be an integral of the motion. In other words, the one-parameter symmetry groups are just those of the form $s \to e^{iAs}$, where A varies over the self-adjoint operators corresponding to those observables that are integrals of the motion.

4. The fact that the laws of physics are independent of position and orientation in space implies the existence of certain symmetries for an isolated physical system. Let $\mathfrak{S}$ be the group generated by the translations and rotations in space. Then there will be a symmetry for each member α of $\mathfrak{S}$. Since every member of $\mathfrak{S}$ is the square of another member, these symmetries will be implemented by unitary operators, and there will exist a certain natural map $\alpha \to U_\alpha$ of $\mathfrak{S}$ into the unitary operators of the Hilbert space $\mathfrak{H}$ of the system—uniquely determined up to multiplication of each U_α by a complex number c_α such that $|c_\alpha| = 1$. This mapping will be a homomorphism of $\mathfrak{S}$ into the group of symmetries and hence will have the property that $U_{\alpha\beta} = U_\alpha U_\beta \sigma(\alpha, \beta)$. Here, for each α and β, $\sigma(\alpha, \beta)$ is a complex number of modulus 1. As such, it is a so-called "projective unitary representation of $\mathfrak{S}$ with multiplier σ." If we replace each U_α by $c_\alpha U_\alpha$, then σ changes to σ', where $\sigma'(\alpha, \beta) = \sigma(\alpha, \beta) c_{\alpha\beta} / c_\alpha c_\beta$, and it is natural to try to eliminate σ by choosing the c_α properly. This can almost be done, but not quite. There is a multiplier σ_0, taking on only the values ± 1 that cannot be eliminated in this fashion. It can be shown, however, that every other σ can either be eliminated or be changed into σ_0 by suitably choosing the c_α. Actually, the most convenient way to proceed is to replace $\mathfrak{S}$ by its simply connected covering group $\tilde{\mathfrak{S}}$. This has a two-element normal subgroup Z and a homomorphism ψ onto $\mathfrak{S}$ whose kernel is Z. Defining $\tilde{U}_\alpha = U_{\psi(\alpha)}$ for all α in $\tilde{\mathfrak{S}}$, one can always choose the c_α so that $\tilde{U}_{\alpha\beta} = \tilde{U}_\alpha \tilde{U}_\beta$ for all α, β in $\tilde{\mathfrak{S}}$. When this is done, the $\tilde{U}_s$ are uniquely determined. Thus, to every "isolated" physical system one has a canonically associated unitary representation of the group $\tilde{\mathfrak{S}}$. Mild and plausible physical assumptions make it possible to prove that this representation is *continuous* in the sense that for each vector ϕ in $\mathfrak{H}$ the mapping $\alpha \to \tilde{U}_\alpha(\phi)$ is a continuous function from $\tilde{\mathfrak{S}}$ to $\mathfrak{H}$. Thus, the theorems of the theory of unitary group representations apply.

One can also show that $V_t \tilde{U}_\alpha = \tilde{U}_\alpha V_t$ for all t and α—that is, that the constant that the definition of symmetry permits is actually 1 for all t and α. It follows that V and $\tilde{U}$ can be combined to yield a natural unitary

representation of the product group $\mathfrak{S} \times T$, where T is the group of all translations in time.

5. Let us now introduce a rectangular coordinate system in space with origin 0, and let $\tilde{K}$ denote the subgroup of $\tilde{\mathfrak{S}}$ consisting of all elements that leave 0 fixed. Then $\tilde{K}$ is the simply connected covering group of the group K of all rotations about 0, and there is a natural homomorphism of $\tilde{K}$ on K whose kernel is the two-element center of K. The group $\tilde{K}$ is isomorphic to the group $SU(2)$ of all 2×2 unitary matrices of determinant 1, and its center consists of $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and $\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$. With respect to our rectangular coordinate system, we may distinguish three one-parameter subgroups of $\tilde{K}$; they are the groups of rotations about the x-, y-, and z-axes. Let α_θ^x denote the rotation through θ radians about the x-axis in some fixed sense. Then $\theta \to \alpha_\theta^x$ will be a continuous homomorphism of the additive group of the real line into $\tilde{K}$—that is, a one-parameter subgroup of $\tilde{K}$. In a similar fashion, one defines the one-parameter subgroups $\theta \to \alpha_\theta^y$ and $\theta \to \alpha_\theta^z$. Of course, if $\theta \to \beta_\theta$ is any one-parameter subgroup of $\tilde{K}$ (or, more generally, of $\tilde{\mathfrak{S}}$), then $\theta \to \tilde{U}_{\beta_\theta}$ will define a one-parameter symmetry group of our system, and by the considerations of section 3 there will correspond a well-defined integral of the motion. The integrals of the motion thus defined by the one-parameter subgroups α^x, α^y, and α^z (multiplied by a universal constant) are called the x-, y-, and z-components of the *total angular momentum* of the system. This constant is the same as the one relating the operator H in $V_t = e^{iHt}$ to the operator defining the energy observable. It occurs because in quantum mechanics, unlike classical mechanics, there is a "natural" unit of mass. More precisely, such a unit exists once units have been chosen for time and distance. If one makes use of this unit, the constant turns out to be 1 and can be ignored. However, physicists are conservative and stick to old traditions as much as possible. They still use the arbitrary mass unit of classical physics and need a conversion factor to carry them from the "natural" measures of energy and momentum to the classical ones. This constant is usually denoted by $\hbar$ and is $h/2\pi$, where h is the celebrated constant introduced by Planck in the theory of "black-body radiation," which he formulated in 1900.

Of course, every one-parameter subgroup of $\tilde{K}$ leads to an integral of the motion just as α^x, α^y, and α^z do. We do not get anything essentially new in this way, however. Every such integral is a linear combination with real coefficients of the x-, y-, and z-components of the total angular momentum. Equivalently, it is equal to a constant multiple of the total angular momentum about some axis through 0.

6. A fact about the operators describing the angular momentum observables that is of great significance for the whole theory is that they satisfy

certain simple identities called commutation relations. Specifically,

$$M_x M_y - M_y M_x = i\hbar M_z,$$
$$M_y M_z - M_z M_y = i\hbar M_x,$$
$$M_z M_x - M_x M_z = i\hbar M_y,$$

where M_x, M_y, and M_z denote the self-adjoint operators associated, respectively, with the x-, y-, and z-components of the angular momentum about 0. Note that the second and third commutation relations can be obtained from the first by cyclical permutations of x, y, and z.

From the point of view of pure mathematics, these identities are immediate consequences of the definition of M_x, M_y, and M_z and the application to the rotation group of some of the fundamental ideas of Lie's theory of continuous groups. Consider the group $GL(n, R)$ of all $n \times n$ matrices with real coefficients and determinant different from zero. If A is *any* $n \times n$ real matrix, then e^{At} is defined by the convergent infinite series $1 + At + (A^2t^2/2!) + \ldots$ for all real t, and $t \to e^{At}$ is a continuous one-parameter subgroup of $GL(n, R)$. Conversely, every continuous one-parameter subgroup of $GL(n, R)$ can be obtained from a unique A. This one-to-one correspondence between matrices A and one-parameter subgroups of $GL(n, R)$ permits one to define an "infinitesimal version" of the group $GL(n, R)$ that is easier to analyze than the group itself but reflects many of its most important properties. Moreover, the construction of this "infinitesimal version" is capable of vast generalization and is applicable to any group locally describable by finite sets of real numbers in such a way that the group operations are continuous.

Consider two one-parameter subgroups, $t \to e^{At}$ and $t \to e^{Bt}$. Their product, $t \to e^{At}e^{Bt}$, is not a one-parameter subgroup but becomes more and more like one as t is restricted to smaller and smaller values. Indeed, $e^{At}e^{Bt} = (1 + At + At^2/2! + \ldots)(1 + Bt + Bt^2/2! + \ldots) = 1 + (A + B)t + (t^2/2!)(A^2 + 2A + B^2) + \ldots$, so that $e^{At}e^{Bt}$ is approximated by $e^{(A+B)t}$ for small t. Thus, we may associate a unique "sum" $t \to e^{(A+B)t}$ to each pair of one-parameter subgroups $t \to e^{At}$ and $t \to e^{Bt}$, and under this sum the set of all one-parameter subgroups is itself a group. This group is commutative and becomes a real vector space under a definition of real multiplication that is easily defined for arbitrary one-parameter subgroups of arbitrary groups without any need for infinitesimal considerations. One simply uses the trivial fact that, if $t \to \psi(t)$ is a one-parameter subgroup, then $t \to \psi(\lambda t)$ is also a one-parameter subgroup for every real λ, and defines this to be $\lambda\psi$.

The fact that the one-parameter subgroups of $GL(n, R)$ can be made into an n^2-dimensional real vector space is not very interesting in itself. This vector space tells us nothing but the number of parameters describing the group. The significant fact is that one can define a kind of product that

captures much more of the structure of the group. Consider $t \to e^{At}e^{Bt}(e^{At})^{-1}(e^{Bt})^{-1} = e^{At}e^{Bt}e^{-At}e^{-Bt}$. This also is not a one-parameter subgroup, but it becomes more and more like one as t is restricted to smaller and smaller values. Indeed, replacing e^{At} by $1+At+A^2t^2/2!+\ldots$ and e^{Bt} by $1+B^t+B^2t^2/2!+\ldots$, one finds that $e^{At}e^{Bt}e^{-At}e^{-Bt} = 1+(AB-BA)t+t^2(\ldots)+\ldots$, so that, for small t, $t \to e^{At}e^{Bt}e^{-At}e^{-Bt}$ is approximated by the one-parameter subgroup $t \to e^{(AB-BA)t}$. This one-parameter subgroup uniquely determined by $t \to e^{At}$ and $t \to e^{Bt}$ is called the *commutator product* of these two one-parameter subgroups.

The key idea in Sophus Lie's theory of continuous groups is that for any such group one can convert the one-parameter subgroups into a finite-dimensional vector space with a "commutator product" in a strictly analogous fashion and that the resulting object, the so-called Lie algebra of the group, reflects many of its most important properties. In the particular case of the group $GL(n, R)$, the above considerations show that the Lie algebra of the group is isomorphic to the vector space of all $n \times n$ real matrices, with the commutator product $[A, B]$ being defined by $[A, B] = AB - BA$. It is easy to check that this product obeys the distributive laws

$$[A, B+C] = [A, B] + [A, C],$$
$$[A+B, C] = [A, C] + [B, C],$$

but is neither commutative nor associative. Instead of commutativity one has anticommutativity, $[A, B] = -[B, A]$, and instead of associativity one has the so-called Jacobi identity,

$$[[A, B], C] + [[C, A], B] + [[B, C], A] = 0.$$

These properties persist in the general case and in fact characterize Lie algebras.

Now consider the group of rotations in three-dimensional space. It is three-dimensional and has a three-dimensional Lie algebra $\mathfrak{L}$ spanned by the one-parameter subgroups $\alpha_x, \alpha_y, \alpha_z$. Thus, every element of $\mathfrak{L}$ is uniquely of the form $\lambda_1\alpha_x + \lambda_2\alpha_y + \lambda_3\alpha_z$, and by the distributive law the commutator product may be completely described by specifying the nine products of the basis elements. Since $[A, A] = -[A, A]$, $[A, A] = 0$ for all A, and it suffices to specify $[\alpha_x, \alpha_y]$, $[\alpha_y, \alpha_z]$, and $[\alpha_z, \alpha_x]$. A computation shows that

$$[\alpha_x, \alpha_y] = \alpha_z, \qquad [\alpha_y, \alpha_z] = \alpha_x, \qquad [\alpha_z, \alpha_x] = \alpha_y,$$

in evident analogy with the commutation relations for the operators defining the angular momentum observables.

Quite generally, if one has a continuous unitary representation $x \to U_x$ of a continuous group G, and $\mathfrak{L}$ is the Lie algebra of G, then each α in $\mathfrak{L}$ defines a

one-parameter group of unitary operators $t \to U_{\alpha(t)}$. By Stone's theorem, one has $U_{\alpha(t)} = e^{iT_\alpha t}$, where T_α is a self-adjoint operator depending on α, and one proves easily that $(iT_\alpha)(iT_\beta) - (iT_\beta)(iT_\alpha) = iT_{[\alpha,\beta]}$ for all α and β in $\mathfrak{L}$. This implies that $T_\alpha T_\beta - T_\beta T_\alpha = (1/i)T_{[\alpha,\beta]}$ for all α and β in $\mathfrak{L}$. The commutation relations for the angular momentum operators result from applying this theorem to the commutation relations defining the Lie algebra of the rotation group.

7. It is not difficult to show that the unitary operators e^{iT}, where T varies over all angular momentum operators about a given 0, coincide exactly with the operators U_x, where $x \to U_x$ is the associated unitary representation of the rotation group. Thus, in exploiting rotational symmetry, it is often a matter of indifference whether one argues from the theory of group representations or from properties of the angular momentum operators. One arrives at much the same conclusions in either case. Physicists tend to prefer calculations with matrices—especially when these have a direct physical interpretation—to arguments involving the more abstract and conceptually more difficult theory of group representations. They refer to using "algebraic methods" to eliminate group theory, much to the astonishment of mathematicians, for whom group theory is one of the principal branches of algebra. To a physicist, however, "algebra" means computing with symbols, not the abstract conceptual arguments dear to the hearts of mathematicians.

8. The first and one of the most important applications of angular momentum theory to quantum mechanics is to the analysis of atomic spectra. Let $\mathcal{H}$ be the Hilbert space of states for the quantum mechanical system that models an atom consisting of a nucleus surrounded by N electrons. Just as in classical mechanics, one can separate the motion of the center of gravity of the system from motion relative to the center of gravity and replace the problem by one in which N electrons move in a central force field. With this reduction the problem of calculating the frequencies of the spectral lines emitted by the atom becomes that of computing the eigenvalues of that multiple of the dynamical operator that corresponds to the total energy of the system. Indeed, if $E_1 \leqslant E_2 \leqslant \ldots$ are these eigenvalues, then the possible frequencies are included among the numbers $(E_i - E_j)/h$, where h is Planck's constant. This is because a light quantum of energy $E_i - E_j$ is emitted when a "perturbation" causes the atom to shift from a stationary state with energy E_i to a continuous state of energy $E_j < E_i$ (see the last half of the last paragraph in section 2 above) and the frequency ν of the light in a quantum of energy E is such that $E = h\nu$.

In the special case in which there is only one electron (the hydrogen atom) and one neglects the effects of "spin," the operator whose eigenvalues must be found is a relatively simple partial differential operator in three

variables. It is the (densely defined) operator in $\mathfrak{L}^2(R^3)$ that takes ψ into

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-\frac{e^2\psi}{\sqrt{x^2+y^2+z^2}}.$$

Here m and $-e$ are, respectively, the mass and charge of the electron, and h is Planck's constant. For the helium atom (two electrons) the operator is only slightly more complicated. It is (densely) defined in $\mathfrak{L}^2(R^6)$ and takes ψ into

$$\begin{aligned}-\frac{h^2\psi}{8\pi^2 m}&\left(\frac{\partial^2\psi}{\partial x_1^2}+\frac{\partial^2\psi}{\partial y_1^2}+\frac{\partial^2\psi}{\partial z_1^2}+\frac{\partial^2\psi}{\partial x_2^2}+\frac{\partial^2\psi}{\partial y_2^2}+\frac{\partial^2\psi}{\partial z_2^2}\right)\\&-\frac{2e^2\psi}{\sqrt{x_1^2+y_1^2+z_1^2}}-\frac{2e^2\psi}{\sqrt{x_2^2+y_2^2+z_2^2}}\\&+\frac{e^2\psi}{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}}.\end{aligned}$$

The reader should now be able to guess the form that the operator takes when there are N electrons. The Hilbert space is $\mathfrak{L}^2(R^{3N})$, and the operator H takes ψ into

$$\begin{aligned}&-\frac{h^2}{8\pi^2 m}\sum_{j=1}^{N}\left(\frac{\partial^2\psi}{\partial x_j^2}+\frac{\partial^2\psi}{\partial y_j^2}+\frac{\partial^2\psi}{\partial z_j^2}\right)\\&-Ne^2\psi\sum_{j=1}^{N}\frac{1}{\sqrt{x_j^2+y_j^2+z_j^2}}\\&+e^2\psi\sum_{i>j}\frac{1}{\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}}.\end{aligned}$$

When $N=1$, the eigenvalues can be found exactly by relatively easy arguments. They are the numbers $-2\pi^2e^4m/h^2n^2$, where $n=1,2,3,\ldots$; m, e, and h are as described above; and the eigenvalue $-2\pi^2e^4m/h^2n^2$ occurs with multiplicity n^2. This formula for the energy levels of the hydrogen atom was announced by Bohr in 1913 a dozen years before the discovery of quantum mechanics. He obtained it as a consequence of the assumption that the electron in a hydrogen atom moves in a circular orbit about the nucleus and that only certain "quantized" orbits occur—those in which the angular momentum is an integer multiple of $h/2\pi$. [In a circular orbit of radius r, the velocity v is a constant and is such that $e^2/r^2=mv^2/r$

(because the attraction of the nucleus for the electron must balance the centrifugal force). Thus, $mv^2=e^2/r$. Now Bohr's quantization hypothesis implies that $mvr=nh/2\pi$, and eliminating v from these two equations yields the formula $r=n^2h^2/4\pi^2e^2m$ for the radii of the allowed orbits. The total energy $mv^2/2-e^2/r=-e^2/2r$ is thus limited to the values $\dfrac{-e^2}{2(n^2h^2/4\pi^2e^2m)}=\dfrac{-2\pi^2e^4m}{h^2n^2}$ as stated.]

When N is 2 or greater, no such simple formula exists, and approximate methods have to be used. Although rotational symmetry can be effectively utilized in discovering the simple formula for the eigenvalues in the $N=1$ case, the arguments are relatively simple and elementary. It is in dealing with more than one electron that one has to make use of the more advanced and interesting parts of angular momentum theory.

9. The approximation method that one uses is based on the fact that, if only the electrons did not repel one another, the eigenvalues of an N-electron atom could be written down at once. Indeed, in that case the final term

$$e^2\psi\sum_{i>j}\frac{1}{\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}}$$

in the formula for H would be missing, and one checks easily that, if $\psi_1,\psi_2,\ldots,\psi_n$ are any N eigenfunctions of the operator ${}_1H$,

$$\psi\to-\left(\frac{h^2}{8\pi^2m}\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-N\frac{e^2\psi}{\sqrt{x^2+y^2+z^2}},$$

with eigenvalues $\lambda_1,\lambda_2,\ldots,\lambda_N$, then

$$x_1,y_1,z_1,\ldots,x_N,y_N,z_N\to\psi_1(x_1,y_1,z_1)\psi_2(x_2,y_2,z_2)\ldots\psi_N(x_N,y_N,z_N)$$

is an eigenfunction of the modified H with eigenvalue $\lambda_1+\lambda_2+\cdots+\lambda_N$. Moreover, it is also easy to see that every eigenfunction is a finite linear combination of such, all having the same eigenvalue. The operator H' differs from the operator H in the one-electron case only in that the coefficient e^2 has been replaced by e^2N. Thus, the eigenvalues of H' can be obtained from those of H by replacing e by $e\sqrt{N}$; they are the numbers $-2\pi^2N^2e^4m/h^2n^2$.

Of course, one cannot neglect the mutual repulsion of the electrons, and one obtains a second approximation to the desired eigenvalues by using the

following device. Define a family of operators H_ε by replacing the term

$$e^2\psi \sum_{i>j} \frac{1}{\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}}$$

$$\varepsilon e^2\psi \sum_{i>j} \frac{1}{\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}},$$

where ε is a real parameter. Then $H_1=H$, and H_0 is an operator whose eigenvalues have just been described and whose eigenfunctions are known. Assume that the eigenvalues and eigenfunctions of H_ε vary analytically with ε. Let λ_j be one of the known eigenvalues of H_0, and suppose that it occurs with multiplicity 1. Let ψ_j be a corresponding eigenfunction (determined up to a multiplicitive constant). Then there exist constants $\lambda_j^1, \lambda_j^2, \ldots$ and functions $\psi_j^1, \psi_j^2, \ldots$ so that, for every sufficiently small $\varepsilon, \psi_j+\varepsilon\psi_j^1+\varepsilon^2\psi_j^2+\ldots$ is an eigenfunction for H_ε with eigenvalue $\lambda_j(\varepsilon)=\lambda_j+\varepsilon\lambda_j^1+\varepsilon^2\lambda_j^2+\ldots$. Thus, if the radius of convergence of these paired series exceeds 1, $\lambda(1)=\lambda_j+\lambda_j^1+\lambda_j^2+\ldots$ will be an eigenvalue of H that one thinks of as a "perturbation" of the eigenvalue λ_j of H_0.

When our assumptions are valid, the problem reduces to computing the coefficients $\lambda_j^1, \lambda_j^2, \ldots$ of the power series expansion of $\lambda_j(\varepsilon)$. This turns out to be quite easy—at least in principle. Let us write $H_\varepsilon=H_0+\varepsilon J$, where $J=H-H_0$, and consider the equation

$$(H_0+\varepsilon J)\left(\psi_j+\varepsilon\psi_j^1+\varepsilon^2\psi_j^2+\ldots\right)$$
$$=\left(\lambda_j+\varepsilon\lambda_j^1+\varepsilon^2\lambda_j^2+\ldots\right)\left(\psi_j+\varepsilon\psi_j^1+\varepsilon^2\psi_j^2+\ldots\right).$$

Expanding and equating coefficients of corresponding powers of ε, one obtains equations that may be solved iteratively to obtain explicit expressions for the λ_j^k in terms of the matrix elements of J. These are rather complicated for large k, but for $k=1$ one has the very simple expression

$$\lambda_j^1=\left(J(\psi_j)\cdot\psi_j\right).$$

Correspondingly, one thinks of $\lambda_j+\lambda_j^1$ as a first approximation to the perturbation of the eigenvalue λ_j of H_0.

Unfortunately, the assumption that λ_j has multiplicity 1 is quite unrealistic, and the simple formula $\lambda_j^1=(J(\psi_j)\cdot\psi_j)$ can seldom be used. For reasons that will be explained below, the highly symmetrical character of the operator H_0 not only makes it easy to determine its eigenvalues and eigenfunctions but also forces most of the eigenvalues to have rather high multiplicities. Although it is not difficult to modify the above argument and

find an elegant generalization of the formula $\lambda_j^1=(J(\psi_j)\cdot\psi_j)$, using this generalization leads to difficult new problems.

The perturbation J is much less symmetrical than the operator H_0, and this causes some of the multiplicities to decrease. Thus, an eigenvalue λ_j of H_0 whose multiplicity is ρ_j may break up into ρ_j different eigenvalues or at least into several eigenvalues of lower multiplicities when H_0 is perturbed by εJ. There will be a number of different functions of λ, all of which reduce to λ_j when $\varepsilon=0$, and one has to find not just λ'_j but perhaps as many as ρ_j different numbers $\lambda'_{j,1}\lambda'_{j,2},\ldots,\lambda'_{j,\rho_j}$. The algorithm for finding these is simple in principle. One introduces an orthonormal basis $\psi_j^1,\psi_j^2,\ldots,\psi_j^{\rho_j}$ in the ρ_j-dimensional vector space of all the eigenfunctions of H_0 of eigenvalue λ_j and calculates the matrix $\|(J(\psi_j^k)\cdot\psi_j^{k'})\|$. The eigenvalues of this matrix are then the $\lambda'_{j,k}$. Since ρ_j can be quite large, diagonalizing this matrix presents practical problems of considerable magnitude. However, J retains some of the symmetry of H_0, and this can be exploited to make extensive simplifications in the diagonalization problem. Working this out has led to a considerable body of theory, and this theory is a major part of the content of angular momentum theory insofar as it applies to atomic spectra. We shall describe it in some detail beginning in section 12 below.

10. Although little if anything has been done in the direction of extending the theory to be described below to simplify the calculation of higher-order terms, there is a way of making the approximation of first-order perturbation theory a bit less crude. Instead of writing $H=H_0+\varepsilon J$, with H_0 and J defined as above, one replaces the term $-Ne^2\psi\sum_{j=1}^{N}\frac{1}{\sqrt{x_j^2+y_j^2+z_j^2}}$ in the definition of H_0 by a term of the form $\sum_{j=1}^{N} g_N\left(\sqrt{x_j^2+y_j^2+z_j^2}\right)$, where g_N is chosen in such manner that the resulting new H_0 is a much better approximation to H. We need not discuss here the details of how g_N is chosen. The basic idea is to diminish the attractive force of the nucleus by a force representing the average repulsion of all the other electrons. We shall denote this modification of H_0 by H'_0 and define J' as $H-H'_0$.

Of course, once H_0 has been replaced by H'_0, our determination of the eigenvalues of H_0 is no longer relevant, and it must be replaced by a determination of the eigenvalues of H'_0. Just as with H_0, this reduces to determining the eigenvalues of an operator ${}_1H'_0$ in three-dimensional space, the eigenvalues of H_0 being sums $\lambda_1+\lambda_2+\cdots+\lambda_N$ of eigenvalues of ${}_1H'_0$. The operator ${}_1H'_0$ in three-dimensional space is that which takes ψ into

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-g_N\left(\sqrt{x^2+y^2+z^2}\right)\psi.$$

Unlike the special case considered above in which $g_N(\sqrt{x^2+y^2+z^2})$ is $Ne^2/\sqrt{x^2+y^2+z^2}$, there is no explicit, exact formula for the eigenvalues of ${}_1H_0'$. However, they can be shown to be eigenvalues of certain *ordinary* second-order differential operators, and good approximate values can be obtained quite easily.

This reduction to ordinary differential operators is worth looking at in some detail, as it is an excellent illustration of the exploitation of rotational invariance and leads directly to an important classification of the eigenvalues of ${}_1H_0'$, which is insensitive to the exact choice of g_N. It can perhaps be understood most easily by looking first at a two-dimensional analog in which the corresponding rotation group is commutative and the application of the theory of group representations reduces to ordinary Fourier analysis.

Consider, then, the differential operator

$$\psi \to -A\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)-g\left(\sqrt{x^2+y^2}\right)\psi,$$

where A is a positive constant, and h is a real valued function defined on the nonnegative real axis. Let ψ be an eigenfunction with eigenvalue λ. For each $r>0$, the restriction of ψ to the circle $x=r\cos\theta$, $y=r\sin\theta$, is a function $\theta\to\psi_r(\theta)$, which may be expanded into a Fourier series $\psi_r(\theta)=\sum_{l=-\infty}^{\infty} a_l(r)e^{il\theta}$. In this way the determination of ψ_r is reduced to the determination of the countably many functions of one variable $r\to a_l(r)$, and for each l these satisfy an ordinary differential equation. Indeed, one computes without difficulty that for any $l=0,\pm1,\pm2,\ldots$ and any differentiable f, one has

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\left(f(r)e^{il\theta}\right)=e^{il\theta}\left(\frac{d^2f}{dr^2}+\frac{1}{r}\frac{df}{dr}-\frac{l^2f}{r^2}\right).$$

Thus, our differential operator takes $\sum_{l=-\infty}^{\infty} a_l(r)e^{il\theta}$ into

$$\sum_{l=-\infty}^{\infty}\left(-A\frac{d^2a_l}{dr^2}-\frac{A}{r}\frac{da_l}{dr}+\frac{Al^2}{r^2}a_l-ga_l\right)e^{il\theta},$$

and this will equal $\lambda\sum_{l=-\infty}^{\infty} a_l(r)e^{il\theta}$ if and only if, for each $l=0,\pm1,\pm2,\ldots$, the function a_l is an eigenfunction with eigenvalue λ for the second-order ordinary differential operator

$$f\to\left(-A\frac{d^2f}{dr^2}-\frac{A}{r}\frac{df}{dr}+\frac{Al^2}{r^2}f-gf\right)=K^l(f).$$

Usually a given λ will be an eigenvalue for only one of the differential operators K^l, and thus it forces the corresponding eigenfunction to have the form $f(r)e^{il\theta}$, where f is the λ eigenfunction for K^l. In any case, eigenfunctions of the form $f(r)e^{il\theta}$, where f is an eigenfunction of K^l, will constitute a basis for the space spanned by all eigenfunctions.

Thus, one sees that there is a natural division of the eigenfunctions and eigenvalues of our partial differential operator into classes, with one class for each integer l, in which the members of the class l are obtained by finding the eigenfunctions and eigenvalues of the ordinary differential operator K^l.

To apply the same method to the partial differential operator of actual concern to us, we need a substitute for the functions $e^{il\theta}$ on the unit circle. For each $l=0,1,2,\ldots$, let S^l denote the complex vector space of all homogeneous polynomials of the lth degree in three variables that satisfy Laplace's equation $\partial^2P/\partial x^2+\partial^2P/\partial y^2+\partial^2P/\partial z^2=0$. It is almost trivial to see that this vector space is $(2l+1)$-dimensional and is invariant under rotations. Moreover every element may be written uniquely in the form

$$\left(\sqrt{x^2+y^2+z^2}\right)^l P\left(\frac{x}{\sqrt{x^2+y^2+z^2}}, \frac{y}{\sqrt{x^2+y^2+z^2}}, \frac{z}{\sqrt{x^2+y^2+z^2}}\right).$$

The functions $\left(1/\sqrt{x^2+y^2+z^2}\right)^l P(x, y, z)$, where P is in S^l, thus define a $(2l+1)$-dimensional vector space $\tilde{S}^l$ of functions on the unit sphere called surface harmonics. This vector space can be shown to be irreducible under rotations, and the corresponding representation of the group R of all rotations in three-space is customarily denoted by the symbol D^l. Toward the end of the eighteenth century, two decades before Fourier's famous first memoir on heat conduction was sent to the French Academy, Laplace and Lagrange studied surface harmonics and showed how to write more or less general functions defined on the sphere as infinite linear combinations of surface harmonics. It turns out that surface harmonics of different degrees l are orthogonal functions, and, choosing an arbitrary orthonormal basis is each $\tilde{S}^l$, one obtains functions that in the aggregate form an orthonormal basis in the Hilbert space of all square-summable functions on the unit sphere.

Using expansions in surface harmonics as a substitute for Fourier expansions of functions on the circle, one can easily adapt the arguments given in the two-dimensional case and show that the eigenfunctions of our three-dimensional partial differential operator ${}_1H_0$ are all linear combinations of functions of the special form

$$f\left(\sqrt{x^2+y^2+z^2}\right)P\left(\frac{x}{\sqrt{x^2+y^2+z^2}}, \frac{y}{\sqrt{x^2+y^2+z^2}}, \frac{z}{\sqrt{x^2+y^2+z^2}}\right),$$

where P is a surface harmonic of some degree $l=0,1,2,\ldots$, and f is an eigenfunction of an ordinary second-order differential operator $\bar{K}^l$ depending on l (and also on N and g). For a given such l and f, P can be *any* surface harmonic of degree l, and so the corresponding eigenvalue will occur with multiplicity at least equal to $2l+1$.

In understanding the final result, obtained by finding the eigenvalues of the ordinary differential operators $\bar{K}^l$, it is useful to consider first the special case in which $g_N(r)=Ne^2/r$, so that $H_0'=H_0$. One finds in this case that the eigenvalues of $\bar{K}^l$ can be exactly and explicitly determined; they are equal to the numbers $-2\pi^2N^2me^4/h^2(k+l+1)^2$, where $k=0,1,2,3\ldots$, and each occurs with multiplicity 1. Correspondingly, H_0 has eigenvalues depending on the two parameters k and l, and for each l the eigenvalue $-2\pi^2N^2me^4/h^2(k+l+1)^2$ occurs $(2l+1)$ times. The actual value of the eigenvalue depends only on the sum of k and l, so that eigenvalues belonging to different l's can be equal. For a given value of $n=k+l+1$, the possible l values vary from 0 up to $n-1$. Thus, the total multiplicity of the eigenvalue $-N^2me^4/2h^2n^2$ is $1+3+5+\cdots+(n-1)=n^2$, as announced in section 8 for the case $N=1$.

When Ne^2/r is replaced by a function $g_N(r)$ that yields an H_0' giving a better approximation to H than H_0, the eigenvalues $-2\pi^2N^2me^4/h^2(k+l+1)^2$ are perturbed slightly in a manner that varies with l. However, the change is small enough so that each can be unambiguously associated with the particular $-2\pi^2N^2me^4/h^2(k+l+1)^2$ from which it came. The value of $k+l+1=n$ is called the *principal quantum number* and the value of l is called the *azimuthal quantum number* for the eigenvalue in question. We need not concern ourselves with the exact value of the eigenvalue with given quantum numbers n and l. It suffices to know that it may be written in the form $-2\pi^2N^2me^4/h^2(n+\varepsilon(l))^2$, where $|\varepsilon(l)|$ is small and does vary with l and that it occurs with multiplicity $2l+1$.

11. Before returning to the role of symmetry in carrying out perturbation theory for an N-electron atom alluded to at the end of section 9, we shall continue the considerations of section 10 by relating the analysis given there to the general theory of unitary group representations. This will make it possible (a) to see the methods used in the two- and three-dimensional cases from a unified point of view, (b) to understand that these methods work because of the rotational symmetry of the operators, and (c) to explain the physical significance of the azimuthal quantum number l.

Let G be a compact group, and let $\alpha\to U_\alpha$ be a continuous unitary representation of G in the separable Hilbert space $\mathcal{H}$. It follows from the compactness of G and the general theory of unitary representations that U is a discrete direct sum of subrepresentations each of which is irreducible and finite-dimensional. This means that $\mathcal{H}$ admits a sequence $\mathcal{H}_1,\mathcal{H}_2,\ldots$ of mutually orthogonal subspaces having the following properties: (a) Each $\mathcal{H}_j$

is *invariant* in the sense that $U_\alpha(\mathcal{H}_j)=\mathcal{H}_j$ for all α, and *irreducible* in the sense that no proper subspace is invariant. (*b*) Every element ϕ in $\mathcal{H}$ is expressible as the sum of an infinite series $\phi_1+\phi_2+\dots$, where each $\phi_j\in\mathcal{H}_j$. Although the decomposition is not unique, it is "essentially" unique in the following sense. If $\mathcal{H}'_1,\mathcal{H}'_2,\dots$ is a second such decomposition, then there exists a permutation π of the integers such that the subrepresentation of G defined by restricting U to $\mathcal{H}_j$ is for all j "equivalent" to the subrepresentation defined by restricting U to $\mathcal{H}'_{\pi(j)}$. In this connection one says that two representations V and V' in Hilbert spaces $\mathcal{H}(V)$ and $\mathcal{H}(V')$ are *equivalent* if there exists a unitary operator W mapping $\mathcal{H}(V)$ on $\mathcal{H}(V')$ such that $WV_\alpha W^{-1}=V'_\alpha$ for all α in G. In particular, it follows that for each irreducible unitary representation W the number of j for which W is equivalent to U restricted to $\mathcal{H}_j$ is the same for all decompositions. This number is called the *multiplicity* of W in U, and the representation U is said to be *multiplicity-free* if this number is 0 or 1 for all W.

There is another element of uniqueness in the decomposition of U into irreducibles. For each irreducible W whose multiplicity in U is not zero, let $\mathcal{H}_W$ denote the closed subspace spanned by *all* irreducible invariant subspaces that define subrepresentations equivalent to W. Then $\mathcal{H}_W$ is clearly invariant, and $\mathcal{H}_W$ and $\mathcal{H}_{W'}$ are orthogonal whenever W and W' are inequivalent. Evidently $\mathcal{H}$ is *uniquely* a direct sum of invariant subspaces of the form $\mathcal{H}_W$. The corresponding decomposition of U is called the canonical decomposition into primary representations—a primary representation being (by definition) a direct sum of mutually equivalent irreducible representations. Any decomposition into irreducibles is clearly a refinement of the canonical decomposition into primaries. Moreover, it is obvious that the multiplicity-free representations are precisely those in which the decomposition into irreducibles is unique and coincides with the canonical decomposition into primary representations.

At this point it is possible to make a simple, easily proved general statement whose truth is fundamental for the application of group representations to the theory of atomic spectra.

Theorem. Let U be a continuous unitary representation of the compact group G in the Hilbert space $\mathcal{H}$, and let $\mathcal{H}=\mathcal{H}_{W^1}\oplus\mathcal{H}_{W^2}\oplus\dots$ define the canonical decomposition of U into primary representations. Let T be any self-adjoint operator in $\mathcal{H}$ that lies in the commuting algebra of U in the sense that $TU_\alpha=U_\alpha T$ for all α in G. Then (*a*) for each W^j, $\mathcal{H}_{W^j}$ is carried into itself by T. (*b*) If λ is any eigenvalue for the restriction T^j of T to $\mathcal{H}_{W^j}$, and $\mathfrak{M}_\lambda\subseteq\mathcal{H}_{W^j}$ is the corresponding eigenspace, then $\mathfrak{M}_\lambda$ is invariant under all U_α and hence is a direct sum of irreducible U-invariant subspaces in each of which U defines a representation equivalent to W^j. In particular, the dimension of $\mathfrak{M}_\lambda$ is a multiple of the dimension $d(W^j)$ of the space in which W^j acts.

It follows at once from (a) that a partial diagonalization of a self-adjoint operator is provided by the canonical decomposition into primaries of any unitary group representation that commutes with it, and from (b) that this diagonalization is essentially complete whenever the unitary group representation is multiplicity-free. It also follows from (b) that the operator is forced to have multiple eigenvalues whenever the group representation has irreducible constituents which are not one-dimensional irreducible constituents.

In this section we shall be concerned only with the applications of the theorem to the interpretation of the results of section 10. Later we shall exploit it heavily in simplifying the diagonalization of the finite-dimensional matrices that arise in the perturbation theory of many-electron atoms.

Returning to the two- and three-dimensional partial differential operators of section 10, let $M=2$ or 3, and let $\mathcal{H}$ be the Hilbert space of all square-summable complex-valued functions on Euclidean M space E^M. Let G be the group of all rotations α about the origin, and let U be the unitary representation of G such that $U_\alpha(f)(p)=f(\alpha(p))$ for each $p\in E^M$. The operators considered in section 10 are all rotationally invariant in the sense that they commute with all U_α. Thus, the theorem stated above applies, and in particular it provides a natural division of the eigenfunctions and the eigenvalues of these operators into families parameterized by those equivalence classes of irreducible unitary representations of G that actually occur in the decomposition of U.

When $M=2$, G is commutative and is isomorphic to the multiplicative group of all complex numbers of modulus 1. All irreducible unitary representations of a commutative group are one-dimensional and hence are of the form $\alpha\to\chi(\alpha)I$, where I is the identity operator, and χ is a continuous function with $|\chi(\alpha)|=1$ such that $\chi(\alpha_1\alpha_2)=\chi(\alpha_1)\chi(\alpha_2)$. For each integer l, $\chi_l(e^{i\theta})=e^{il\theta}$ is such a function, and it can be shown that there are no others. One checks easily that the decomposition of U into irreducibles contains each χ_l and contains it with multiplicity ∞. Thus, the canonical decomposition of U into primary representations carries with it a direct sum decomposition of $\mathcal{H}$ into subspaces parameterized by l and each invariant under our operator. Our original diagonalization problem is replaced by countably many others. As shown in section 10, these are much simpler, since they involve finding the eigenvalues of *ordinary* differential operators.

When $M=3$, the situation is much the same. The only added complication is that G is noncommutative and has irreducible unitary representations that are more than one-dimensional. As explained in section 10, the natural action of G on the surface harmonics of degree l gives a $(2l+1)$-dimensional example D^l of an irreducible unitary representation of G for each $l=0,1,2,\ldots$. It turns out that there are no others—every irreducible unitary representation of G is equivalent to some D^l. These all occur with multiplicity ∞, and the theorem applies as when $M=2$. Now, however, conclusion (b) comes into play and tells us that the eigenvalues in the primary

component corresponding to D^l must have a multiplicity that is a multiple of $2l+1$, the dimension of D^l.

Keeping $M=3$, consider an arbitrary eigenspace $\mathfrak{M}_\lambda$ of ${}_1H_0'$. Unless the function g_N is very special, the restriction of U to the invariant subspace $\mathfrak{M}_\lambda$ will be irreducible and thus equivalent to D^l for some $l=0,1,2\ldots$, where l is the azimuthal quantum number for the eigenvalue λ. Since the subspace $\mathfrak{M}_\lambda$ is U-invariant, it is in particular invariant under all $U_{\alpha(t)}$, where $t\to\alpha(t)$ is an arbitrary one-parameter subgroup of G. Hence it is invariant under all angular momentum operators and consequently under the operator $\Omega_x^2+\Omega_y^2+\Omega_z^2=\Omega$, where Ω_x, Ω_y, and Ω_z give the angular momenta about the x-, y-, and z-axes, respectively. It is natural to think of the corresponding observable as the square of the total angular momentum. It is not surprising to find it to be independent of the orientation of the axes and equivalently that it commutes with all U_α. This and the irreducibility of U in $\mathfrak{M}_\lambda$ imply that Ω restricted to $\mathfrak{M}_\lambda$ is just multiplication by a constant. In other words, in the $(2l+1)$-dimensional vector space of state vectors having a given definite energy value with azimuthal quantum number l, the square of the total angular momentum also has a definite value. A simple computation shows that this value depends only on l and is equal to $(h^2/4\pi^2)l(l+1)$. Thus, the physical significance of the azimuthal quantum number is that it determines the total angular momentum in the associated stationary states. The principal quantum number determines the *approximate* energy.

12. Now let us return to the line of thought begun at the end of section 9 and discuss the manner in which rotational symmetry can be used to simplify the problem of diagonalizing the matrices that arise when one attempts to apply perturbation theory to the N-electron atom. Our first observation is that the relationship between the unitary representation U of the rotation group $G=SO(3)$ and the eigenspaces of ${}_1H_0'$ considered in the last section has an obvious generalization in which $SO(3)$ is replaced by a group containing $SO(3)\times SO(3)\times\cdots\times SO(3)$ (N factors) and ${}_1H_0'$ is replaced by H_0'. Let $\alpha_1,\alpha_2,\ldots,\alpha_N$ be any N members of $SO(3)$. Then there is a unique unitary operator $W^0_{\alpha_1,\alpha_2,\ldots\alpha_N}$, which takes $f_1(x_1,y_1,z_1)$, $f_2(x_2,y_2,z_2),\ldots,f_N(x_N,y_N,z_N)$ into $f_1(\alpha_1(x_1,y_1,z_1))$, $f_2(\alpha_2(x_2,y_2,z_2)),\ldots,f_N(\alpha_N(x_N,y_N,z_N))$ whenever the f_j are square-summable. The mapping $\alpha_1,\alpha_2,\ldots,\alpha_N\to W^0_{\alpha_1,\alpha_2,\ldots\alpha_N}$ is then a continuous unitary representation of $G^0=SO(3)\times SO(3)\times\cdots\times SO(3)$, and it is clear that $W^0_\alpha H^1_0=H^1_0W^0_\alpha$ for all $\alpha=\alpha_1,\alpha_2,\ldots,\alpha_N\in G^0$. In the language of the general theory of group representations, W^0 is the "outer tensor product" $U\times U\times\cdots\times U$ of N copies of U. However, W^0 is not quite the N-electron generalization of U that we need. When $N>1$, there are further symmetries. Indeed, let π be any permutation of the N integers $1,2,3,\ldots,N$. Then there is a unique unitary operator in our Hilbert space that takes

$\phi(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$ into $\phi(x_{\pi(1)}, y_{\pi(1)}, z_{\pi(1)}, x_{\pi(2)}, y_{\pi(2)}, z_{\pi(2)}, \ldots, x_{\pi(N)}, y_{\pi(N)}, z_{\pi(N)})$ for all square-summable ϕ. Let us denote it by W'_π. One sees at once that $\pi \to W'_\pi$ is a unitary representation of S_N, the symmetric group on N objects, and that H'_0 also commutes with all W^0_π. The two representations W^0 and W^1 of G^0 and S^N can now be combined into a single representation W of a compact group G containing both G^0 and S_N as subgroups. The group G consists of all pairs α, π, where $\alpha = \alpha_1, \alpha_2, \ldots, \alpha_N \in G_0$ and $\pi \in S_N$. The multiplication law in G is given by $(\alpha_1, \alpha_2, \ldots, \alpha_N, \pi)(\alpha'_1, \alpha'_2, \ldots, \alpha'_N, \pi') = \alpha''_1, \alpha''_2, \ldots, \alpha''_N, \pi\pi'$, where $\alpha''_j = \alpha_j \alpha'_{\pi(j)}$, and G^0 and S^N may be identified with the subgroups of G defined by setting α (respectively π) equal to the identity. The representation W of G is then defined by setting $W_{\alpha,\pi} = W^0_\alpha W'_\pi$.

Evidently H'_0 commutes with all $W_{\alpha,\pi}$, and the representation W of $G = SO(3) \times SO(3) \times \cdots \times SO(3) \textcircled{S} S_N$ is the analog of the representation U of $SO(3)$, whose relationship to the eigenspaces of ${}_1H'_0$ was analyzed in section 11. Just as in the one-electron case, the commutativity of H'_0 and the $W_{\alpha,\pi}$ implies that each eigenspace of H'_0 is invariant under all $W_{\alpha,\pi}$ and hence defines a subrepresentation of the representation W. Moreover, when there are no "accidental degeneracies"—that is, whenever $\lambda_1 + \lambda_2 + \cdots + \lambda_N \neq \lambda'_1 + \lambda'_2 + \cdots + \lambda'_N$—unless there is a permutation π such that $\lambda'_j = \lambda_{\pi(j)}$ for all j (and certain other conditions hold), then this subrepresentation of W can be shown to be an *irreducible* unitary representation of G. Each eigenspace and eigenvalue of H'_0 has a "label" that is an equivalence class of (often irreducible) unitary representations of the compact group G and plays the role in the N-electron case played by the azimuthal quantum number l in the one-electron case.

Our next observation is that a certain closed subgroup $\tilde{G}$ of G has the property that not only H'_0 but also J' and H all lie in the commuting algebra of the representation $\tilde{W}$ of $\tilde{G}$ obtained by restricting W to $\tilde{G}$. This is the group of all $\alpha_1, \alpha_2, \ldots, \alpha_N, \pi$ for which $\alpha_1 = \alpha_2 = \cdots = \alpha_N$ and is obviously isomorphic to $SO(3) \times S_N$. Consider now an eigenspace $\mathfrak{M}_{\lambda_1 + \cdots + \lambda_N}$ of H'_0, and let P be the projection operator whose range it is. Then P lies in the commuting algebra of W and *a fortiori* in that of $\tilde{W}$. Thus, $PJ'P$ lies in the commuting algebra of $\tilde{W}$. But $PJ'P$ restricted to the range of P is precisely the operator whose matrix we must diagonalize to find the first-order approximations to those eigenvalues of H obtained by perturbing $\lambda_1 + \lambda_2 + \cdots + \lambda_N$. (See the end of section 9.)

The key point may now be formulated as follows. Each eigenspace $\mathfrak{M}$ of H'_0 is the space of a (usually irreducible) unitary representation W of $G = SO(3) \times SO(3) \times \cdots \times SO(3) \textcircled{S} S_N$, and the operator $J'_{\mathfrak{M}}$ = restriction to $\mathfrak{M}$ of $PJ'P$ (whose eigenvalues must be found in order to determine first-order approximations to the corresponding values of H) is in the commuting algebra of the restriction $\tilde{W}$ of W to a subgroup $\tilde{G}$ of G isomorphic to $SO(3) \times S_N$.

13. Because of the facts summarized at the end of the preceding section, one can apply the theorem of section 11 and use the decomposition of W to facilitate determining the eigenvalues of $J'_{\mathfrak{M}}$. It is time to explain just how this is done and just what one needs to know about the unitary representation theory of $SO(3)\times S_N$ in order to do it. It will be convenient to proceed abstractly and consider an arbitrary self-adjoint operator T, which lies in the commuting algebra of an arbitrary finite-dimensional unitary representation V of an arbitrary separable locally compact group K.

Let $L^1, L^2, \ldots, L^r$ denote the irreducible representations into which V decomposes, let m_j denote the multiplicity with which L^j occurs, and let $\mathfrak{M}_j$ denote the unique invariant subspace in which V is equivalent to L^j repeated m_j times. According to the theorem of section 11, T must take each $\mathfrak{M}_j$ into itself, and the eigenvalues of the restriction T_j of T to $\mathfrak{M}_j$ must have multiplicities that are integer multiples of the dimension d_j of the space of L^j. Let $\lambda_1^j, \lambda_2^j, \ldots, \lambda_{m_j}^j$ be the eigenvalues of T_j, each repeated as many times as its multiplicity divided by d_j. We now make the important observation that for each j one can compute the sum

$$\lambda_1^j+\lambda_2^j+\cdots+\lambda_{m_j}^j$$

as a linear combination of the matrix elements $t_{i,i'}$ of T with respect to any convenient orthonormal basis $\phi_1, \phi_2, \ldots, \phi_d$, the coefficients being determined by the properties of the group representation V. Indeed, let $\theta_1^j, \theta_2^j, \ldots, \theta_{m_j d_j}^j$ be any orthonormal basis for $\mathfrak{M}_j$. Then the trace of T_j is equal on the one hand to

$$d_j\left(\lambda_1^j+\lambda_2^j+\cdots+\lambda_{m_j}^j\right) \tag{$*$}$$

and on the other to

$$\sum_{l=1}^{m_j d_j}\left(T\left(\theta_l^j\right)\cdot\theta_l^j\right). \tag{$**$}$$

Now, expanding θ_l^j in terms of the basis $\phi_1, \phi_2, \ldots, \phi_d$ yields

$$\theta_l^j=\sum_i\left(\theta_l^j\cdot\phi_i\right)\phi_i \tag{$***$}$$

and

$$T\left(\theta_l^j\right)=\sum_{i'}\left(\theta_l^j,\phi_{i'}\right)T(\phi_{i'}), \tag{$****$}$$

equating ($*$) and ($**$) and substituting ($***$) and ($****$) into ($**$), one

finds that

$$d_j\left(\lambda_1^j+\lambda_2^j+\cdots+\lambda_{m_j}^j\right)=\sum_{l=1}^{m_j d_j}\left(\sum_{i,i'}\left(T(\phi_{i'})\cdot\phi_i\right)\overline{\left(\theta_l^j\cdot\phi_i\right)}\left(\theta_l^j\cdot\phi_{i'}\right)\right),$$

and this evidently implies that

$$\left(\lambda_1^j+\lambda_2^j+\cdots+\lambda_{m_j}^j\right)=\sum_{i,i'}\left(T(\phi_i)\cdot\phi_{i'}\right)c_{i,i'}^j, \tag{†}$$

where the coefficients $c_{i,i'}^j$ are computed from the formula

$$c_{i,i'}^j=\frac{1}{d_j}\sum_{l=1}^{m_j d_j}\left(\theta_l^j\cdot\phi_i\right)\overline{\left(\theta_l^j\cdot\phi_{i'}\right)}. \tag{††}$$

The two equations (†) and (††) are fundamental. They make it possible to compute the sums $\lambda_1^j+\lambda_2^j+\cdots+\lambda_{m_j}^j$ for the eigenvalues of T directly from the matrix elements of T as soon as one knows the expansion coefficients $(\theta_l^j\cdot\phi_i)$ for the members of the basis $\{\theta_l^j\}$ relative to the basis $\{\phi_i\}$. The determination of these coefficients is a purely group-representational problem that is a substantial part of the entire theory. It does not become definite until one has chosen the bases in question, but it is important to realize that it cannot be trivialized by choosing the ϕ_i to coincide with the θ_l^j. This would beg the question. To be able to compute the matrix elements $(T(\phi_i)\cdot\phi_{i'})$, the ϕ_i must be chosen in a way that takes no cognizance of the $\mathfrak{M}_j$. This "coefficient problem" will be described in some detail below. The rest of the present section will be devoted to the problem of passing from the sums $\lambda_1^j+\cdots+\lambda_{m_j}^j$ to the individual eigenvalues.

Evidently, when V is multiplicity-free—that is, when each m_j is equal to 1—there is no problem. Each sum has just one term, and formula (†) gives the actual eigenvalues. In the general case one notices that, when T is in the commuting algebra of V, so is every power of T, and also that the eigenvalues of T^k are just $\lambda_1^k, \lambda_2^k, \ldots$, where $\lambda_1, \lambda_2, \ldots$ are the eigenvalues of T. Knowing the matrix elements of T, one can compute those of $T^2, T^3, \ldots$ by matrix multiplication and so use formula (†) (with T replaced by its various powers) to find explicit expressions for $(\lambda_1^j)^2+\cdots+(\lambda_{m_j})^2$, $(\lambda_1^j)^3+(\lambda_2^j)^3+\cdots+(\lambda_{m_j})^3$, etc. From these one can obtain the eigenvalues $\lambda_1^j, \lambda_2^j, \ldots, \lambda_{m_j}^j$ as the roots of a polynomial equation of degree m_j. Indeed, if $m_j=2$, one will have two unknown eigenvalues a and b but will know both $a+b$ and a^2+b^2. Now a and b are the roots of the quadratic equation $x^2-(a+b)x+ab=0$, and $ab=[(a+b)^2-(a^2+b^2)]/2$. Thus, knowing $a+b$

and a^2+b^2 permits one to find a and b by solving a quadratic equation. Similarly, one can find a cubic equation whose roots are a, b, and c whenever $a+b+c$, $a^2+b^2+c^2$, $a^3+b^3+c^3$, etc., are known for all possible values of m_j.

The point of the reduction is that it is much easier to solve r polynomial equations of degrees $m_1, m_2, \ldots, m_r$ than one polynomial equation of degree $m_1d_1+\cdots+m_rd_r$. From another point of view, the polynomial of degree $m_1d_1+\cdots+m_rd_r$, which must be factored into linear factors in order to solve the equation, is partially factored by the method into $P_1^{d_1}P_2^{d_2}\cdots P_r^{d_r}$, where each P_j is a polynomial of degree m_j, and it remains only to factor the P_j.

14. At this point it will be useful to descend from the abstract to the concrete and consider the actual V's that arise in the theory of atomic spectra in the special case in which $N=2$. In that case the general eigenvalue of H_0' will be of the form $\lambda_1+\lambda_2$, where λ_1 and λ_2 are eigenvalues of ${}_1H_0'$ with principal quantum numbers n_1 and n_2 and azimuthal quantum numbers l_1 and l_2. With no "accidental" degeneracies, the corresponding eigenspace will have dimension $2(2l_1+1)(2l_2+1)$, and an orthonormal basis for it will consist of all functions of the form $\phi(x_1, y_1, z_1)\psi(x_2, y_2, z_2)$ and all functions of the form $\psi(x_1, y_1, z_1)\,\phi(x_2, y_2, z_2)$, where ϕ ranges over the $2l_1+1$ members of some orthonormal basis for the λ_1 eigenspace of ${}_1H_0'$, and ψ ranges over the $2l_2+1$ members of some orthonormal basis for the λ_2 eigenspace of ${}_1H_0'$. However, in the special case in which $m_1=m_2$ and $l_1=l_2$, so that the two eigenspaces coincide, the dimension is only $(2l_1+1)(2l_2+2)$-dimensional, since interchanging ϕ and ψ does not lead to a different eigenfunction.

In any case, the eigenspace is the space of an irreducible unitary representation of the group $SO(3)\times SO(3)\textcircled{S}S_2$, which is irreducible unless $n_1\neq n_2$ and $l_1=l_2$ hold simultaneously. In the latter event the representation in the eigenspace decomposes into two inequivalent subrepresentations. Fortunately, these two subeigenspaces are easily shown to be carried with themselves by the operator J' and so can be treated as separate eigenspaces —just as though $E_1+E_2\neq E_2+E_1$. Making the appropriate modification in the definition of eigenspace, one may say that in all cases the eigenspace is the space of an *irreducible* unitary representation of the group $SO(3)\times SO(3)$ $\textcircled{S}$ S_2 and that the coefficient problem is a problem about the restriction of this irreducible representation to the subgroup of all x, y, π, with $x=y$. It is useful to analyze this restriction by looking first at the restriction to the intermediate subgroup $SO(3)\times SO(3)$. It is almost evident that this restriction is irreducible when $l_1=l_2$ and otherwise is a direct sum of the two inequivalent irreducibles $D^{l_1}\times D^{l_2}$ and $D^{l_2}\times D^{l_1}$, whose spaces are interchanged by the unitary map defined by the nontrivial member of S_2. The

coefficient problem in either case thus reduces to the corresponding problem in which $SO(3)\times SO(3)\textcircled{S}S_2$ is replaced by $SO(3)\times SO(3)$ and the subgroup is the set of all x, y with $x=y$.

To revert to the abstract for the moment, let G_1 and G_2 be any two compact groups, let L be any finite-dimensional unitary representation of G_1, and let M be any finite-dimensional unitary representation of G_2. One can then prove that there exists a finite-dimensional unitary representation V of $G_1\times G_2$ that is uniquely determined up to equivalence by the fact that $\text{trace}(V_{x,y})=\text{trace}(L_x)\,\text{trace}(M_y)$ for all x in G_1 and all y in G_2. It is called the *tensor product* of L and M and is denoted by the symbol $L\times M$. Its dimension is the product of the dimensions of L and M. One proves that $L\times M$ is irreducible if and only if *both* L and M are irreducible and that every irreducible unitary representation of $G_1\times G_2$ is equivalent to one of the form $L\times M$, where L and M are uniquely determined up to equivalence. In this way the problem of finding the irreducible unitary representations of a product group is completely reduced to the corresponding problem for the factors. Evidently there is a step-by-step procedure permitting one to deal in an analogous fashion with the irreducible unitary representations of any finite product of compact groups $G_1\times G_2\times\cdots\times G_m$.

In the special case in which $G_1=G_2=G$, one can identify G with a subgroup of $G\times G$—namely, the diagonal subgroup of all x, y with $x=y$. Given any two irreducible unitary representations L and M of G, one can form $L\times M$ and by restricting to the diagonal form a new unitary representation of G. This representation is sometimes called the *inner tensor product* of L and M, and it is seldom irreducible. When one has found the possible irreducible unitary representations of a compact group G, another important problem that presents itself is that of determining their inner tensor products. For each triple L, M, N of irreducible unitary representations of G, one wants the (possibly zero) multiplicity with which N is contained in the inner tensor product $L\otimes M$.

Returning now to the concrete problem set by the two-electron atom, one sees that the representation V occurring in the coefficient problem is just the inner tensor product $D^l\otimes D^{l'}$ of two irreducible unitary representatives of $SO(3)$. The structure of this representation is easily determined by using an important fact about the restrictions of D^l and $D^{l'}$ to the subgroup A_z of all rotations about the z-axis. The group A_z is commutative and isomorphic to the multiplicative group of all complex numbers of modulus 1—that is, all $e^{i\theta}$, with θ real. The irreducible unitary representations are all one-dimensional and correspond one-to-one to the integers, the representation L^k for $k=0,\pm1,\pm2,\ldots$ being $e^{i\theta}\to e^{ik\theta}$. Moreover, it follows easily from the definition of D^l in terms of surface harmonics that D^l restricted to A_z is multiplicity-free and equivalent to the direct sum $L^{-l}\oplus L^{-l+1}\oplus\cdots\oplus L^{l-1}\oplus L^l$. It follows at once from the relevant definitions that $D^l\otimes D^{l'}$ restricted to A_z must be the direct sum of all $L^{k+k'}$, where k and k' are integers and

$-l \leqslant k \leqslant l$, $-l' \leqslant k' \leqslant l'$. Since $L^{l+l'}$ occurs just once in this sum and $l+l'$ is the maximum integer that occurs, it follows that $D^{l+l'}$ occurs once and only once in the decomposition of $D^l \otimes D^{l'}$. Continuing in this vein, one deduces the truth of the celebrated Clebsch–Gordan formula

$$D^l \otimes D^{l'} = D^{|l-l'|} \oplus D^{|l-l'|+1} \oplus D^{|l-l'|+2} \oplus \cdots \oplus D^{l+l'}$$

and in particular that $D^l \otimes D^{l'}$ is multiplicity-free for all l and l'. It follows that the formula of section 13 gives the eigenvalues of J' directly without the necessity of factoring any nonlinear polynomials.

To use the formula of section 13, one must choose an orthonormal basis in the space of $D^l \otimes D^{l'}$ and another in the space of each irreducible constituent. A useful and natural choice is suggested by the fact that each D^k has the property that its restriction to A_z is multiplicity-free and so defines a direct sum decomposition of the space of D^k into one-dimensional A_z-invariant subspaces. Choosing the basis elements to lie in these subspaces determines them up to multiplication by a complex number of modulus 1. The properties of surface harmonics make it possible to write down these basis elements quite explicitly, and from the physicist's point of view they have the added advantage of having a simple physical interpretation. They are eigenvectors of the operator representing the z-component of an angular momentum and hence represent states in which this angular momentum component has a definite value. This natural (modulo a choice of z-axis) basis in the space of each D^l carries with it a corresponding basis in the space of each product $D^l \otimes D^{l'}$ and in the space of each component $D^{|l-l'|+k}$ in the reduction of $D^l \otimes D^{l'}$. The basis $\{\phi_i\}$ of section 13 is thus parameterized by pairs of integers k_1, k_2, where $-l \leqslant k_1 \leqslant l$ and $-l' \leqslant k_2 \leqslant l'$, and the basis $\{\theta_\rho^j\}$ by pairs of integers j, ρ, where $|l-l'| \leqslant j \leqslant l+l'$ and $-j \leqslant \rho \leqslant j$. In the physical interpretation the z-components of angular momentum corresponding to k_1, k_2, and ρ are those of the two electrons individually and of the total system. The coefficients of section 13 for $SO(3) \times SO(3)$ and its diagonal subgroup with the bases chosen as indicated are known as *Clebsch–Gordan coefficients*, and their determination and detailed study is one of the major topics in angular momentum theory. They not only solve the problem in the two-electron case but serve as building blocks in solving the coefficient problem for more than two electrons. They are functions of six integer variables—l, l', j, k_1, k_2, and ρ—where $0 \leqslant l$, $0 \leqslant l'$, and j, k_1, k_2, and ρ are restricted as indicated above.

At this point the better-informed reader will be protesting that in fact the variables are not integers but half-integers. He is correct, but half-integers appear only when the effect of "electron spin" has been taken into account and the group $SO(3)$ has been replaced by the group $SU(2)$ of all 2×2 unitary matrices of determinant 1. The quotient of this group by its two-element center is isomorphic to $SO(3)$, and its irreducible unitary

representations include those of $SO(3)$ as well as a supplementary family $D^{1/2}, D^{3/2}, \ldots$, which reduce on the center to the negative of the identity and so may be regarded as "double-valued" representations of $SO(3)$. For all l, integral or not, the dimension of D^l is $2l+1$.

The Clebsch–Gordan coefficients (and slight variants thereof) are also known as Wigner coefficients, as Wigner 3-j symbols, and as vector coupling coefficients. The literature on them is extensive, including tables of values, explicit formulas, and formulas for computing them recursively.

15. The case $N=2$, although fundamental, is rather special in that $D^l \otimes D^{l'}$ is multiplicity-free and also in that S_2 is a commutative group with a very trivial representation theory. It is accordingly necessary to take a look at the three-electron case as well as the two-electron case in order to get an adequate introduction to the complexities of the general case.

When $N=3$, the group whose irreducible unitary representations help to label the eigenvalues of H_0' is $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$. We begin by describing the irreducible unitary representations of this group. Let V be any such representation, and consider the restriction to $SO(3)\times SO(3)\times SO(3)$. This will be a finite direct sum of irreducible unitary representations of $SO(3)\times SO(3)\times SO(3)$—that is, of representations of the form $D^{l_1}\times D^{l_2}\times D^{l_3}$. Moreover, it is easy to prove that, whenever $D^{l_1}\times D^{l_2}\times D^{l_3}$ occurs, then the others that occur are precisely those obtainable by permuting l_1, l_2, and l_3 in all possible ways. The number of inequivalent ones depends, of course, upon how many equalities there are between l_1, l_2, and l_3 and is either 1, 3, or 6. The (unordered) triple l_1, l_2, l_3 "almost" determines the irreducible unitary representation V. Indeed, when l_1, l_2, and l_3 are distinct, it does determine it. On the other hand, when $l_1 \neq l_2 = l_3$, there are two inequivalent V's for each l_1, l_2, l_3, and when $l_1 = l_2 = l_3$, there are three inequivalent V's for each. To analyze these possibilities, consider the restriction of V to S_3, and let $H(V) = \mathfrak{M}_1 \oplus \mathfrak{M}_2 \oplus \cdots \oplus \mathfrak{M}_f$ be the decomposition of $H(V)$ into orthogonal subspaces corresponding to the distinct irreducibles in the restriction of V to $SO(3)\times SO(3)\times SO(3)$. By the above, $f=1$, 3, or 6. One sees easily that for π in S_3 the V_π permute the $\mathfrak{M}_i$ among themselves so that the decomposition defines a "system of imprimitivity" for V and for its restriction to S_3. Let S be the subgroup of S_3 consisting of all π in S_3 such that $V_\pi(\mathfrak{M}_1) = \mathfrak{M}_1$. It is not hard to show that, when V is restricted to $\mathfrak{M}$ and at the same time to S, one obtains a representation of S that is a multiple of an *irreducible* unitary representation L of S. It is (the equivalence class of) this representation L that one needs to know in addition to the (unordered) triple l_1, l_2, l_3 in order to determine the equivalence class of V. Every irreducible unitary representation of S (up to equivalence) actually occurs. Thus, depending upon whether none, two, or three of the l's are equal, S will be S_1, S_2, or S_3, and there will be correspondingly one, two, or three inequivalent unitary V's for each triple l_1, l_2, l_3.

In order to pass from a given unitary representation L of S back to the corresponding unitary representation V of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$, one employs a general construction in group representation theory that is a sort of inverse to restricting a representation to a subgroup. In the special case in which the subgroup has only a finite number of cosets, this construction is quite easy to describe. Let G' be a closed subgroup of a topological group G, and let there be only a finite number of right G' cosets $G'x$ (x in G). Let W be an arbitrary continuous finite-dimensional unitary representation of G'. One constructs a unitary representation U^W of the whole group G as follows. Its space is the vector space F of all functions g from G to the Hilbert space $\mathcal{H}(W)$ in which W acts, which satisfy the equation

$$g(\xi x)=W_\xi g(x) \qquad (*)$$

for all ξ in G' and all x in G. Note that $(*)$ implies that g is uniquely determined throughout the coset $G'x_0$ as soon as its value at x is determined and that this value can be assigned arbitrarily. It follows that the dimension of F is finite and equal to the number of right G' cosets in G multiplied by the dimension of $\mathcal{H}(W)$. It is obvious that, whenever $(*)$ holds for g, one has also $g(\xi xy)=W_\xi g(xy)$ for all y, and hence that the right translates by y of every g in F is also in F. We define U_y^W by setting $U_y^W(g)(x)=g(xy)$. Evidently $y\to U^W$ is a representation of G whose space is F. It is called the *representation of G induced by W*.

Returning to the problem at hand and given l_1, l_2, l_3 and the appropriate subgroup S of S_3, let L be an arbitrary irreducible unitary representation of S. Recall that the representation $D^{l_1}\times D^{l_2}\times D^{l_3}$ of $SO(3)\times SO(3)\times SO(3)$ has a "natural" extension to an irreducible unitary representation $(D^{l_1}\times D^{l_2}\times D^{l_3})^e$ of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$. (Compare the relationship between W^0 and W in section 12.) On the other hand, $\alpha_1, \alpha_2, \alpha_3, \pi\to L_\pi$, is an irreducible unitary representation L' of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S$. One shows easily that the inner tensor product of L' with the restriction to $SO(3)\times SO(3)\times SO(3)\textcircled{S}S$ of $(D^{l_1}\times D^{l_2}\times D^{l_3})^e$ is irreducible. Denote it by $A^{l_1,l_2,l_3,L}$. The unitary representation $U^{A^{l_1,l_2,l_3,L}}$ of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S$, induced by the representation $A^{l_1,l_2,l_3,L}$ of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S$ is irreducible and is the desired representation associated with l_1, l_2, l_3, L.

The fact that V can be so induced from an irreducible representation of a subgroup is intimately related to the existence of the system of imprimitivity $\mathfrak{M}_1\oplus\mathfrak{M}_2\oplus\cdots\oplus\mathfrak{M}_f$. Returning to the general group G considered above, let V be any unitary representation of G, and let $\mathcal{H}(V)$, the space of V, be a direct sum of a finite number of orthogonal subspaces $\mathfrak{M}_1\oplus\mathfrak{M}_2\oplus\cdots\oplus\mathfrak{M}_f$ such that $V_x(\mathfrak{M}_j)=\mathfrak{M}_k$ for each j and x and some k depending on x and j. Suppose also that this system of imprimitivity is "transitive" in the sense that for each j and k there exists x, with $V_x(\mathfrak{M}_j)=\mathfrak{M}_k$. Let G' be the

subgroup of G consisting of all x with $V_x(\mathfrak{M}_1)=\mathfrak{M}_1$. Then the simultaneous restriction of V to G' and $\mathfrak{M}_1$ defines a unitary representation W of G', and it is easy to see that V can be reconstructed from W and the way in which G permutes the $\mathfrak{M}_j$. Actually $G'x \to V_x(\mathfrak{M}_1)$ sets up a one-to-one correspondence between the right G' cosets and the $\mathfrak{M}_j$, and one can show that V is equivalent to the induced representation U^w.

The determination of the irreducible unitary representations of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$ just described has a straightforward generalization in which 3 is replaced by an arbitrary positive integer N. To construct the most general irreducible unitary representation (up to equivalence) of $SO(3)\times SO(3)\times\cdots\times SO(3)\textcircled{S}S_N$, one chooses an N-tuple $l_1, l_2, l_3, \ldots, l_N$ of nonnegative integers l and standardizes the arbitrary ordering by requiring $l_1\leqslant l_2\leqslant l_3\leqslant\cdots\leqslant l_N$. Next one chooses an irreducible unitary representation L of the subgroup S of S_N consisting of all permutations π of the superscripts such that $l_{\pi(j)}=l_j$ for $j=1,2,\ldots,N$ and forms a representation $A^{l_1,l_2,\ldots,l_N,L}$ of $SO(3)\times SO(3)\times\cdots\times SO(3)\textcircled{S}S$ by direct analogy with what was done above in the case $N=3$. The induced representation $U^{A^{l_1,l_2,\ldots,l_N,L}}$ is then an irreducible unitary representation of $SO(3)\times SO(3)\times\cdots\times SO(3)\textcircled{S}S_N$. To within equivalence it is the most general possible, and two such are equivalent if and only if the l_j are the same and the representations L of S are equivalent. Note that S is always isomorphic to a group of this form $S_{f_1}\times S_{f_2}\times\cdots\times S_{f_r}$, where S_j is the symmetric group on j objects and $f_1+f_2+\cdots+f_r=N$. Thus, to find all irreducible unitary representations for every S that arises, one need only know the irreducible unitary representations of the symmetry groups S_k for all k.

16. Having described the irreducible unitary representations of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$, we have paved the way for generalizing the considerations of section 14 to the case of three electrons. Each eigenspace will now be determined by an (unordered) triple of eigenvalues of H_0' with quantum numbers n_1, l_1, n_2, l_2, and n_3, l_3. The dimensions of this eigenspace will be $k(2l_1+1)(2l_2+1)(2l_3+1)$, where $k=1$, 3, or 6 according to whether the number of equalities among the pairs n_i, l_i is 3, 1, or 0. Moreover, if $n_i=n_j$ whenever $l_i=l_j$, this eigenspace will be the space of an irreducible unitary representation of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S$—namely, that induced by the representation $(D^{l_1}\times D^{l_2}\times D^{l_3})^e$ restricted back to $SO(3)\times SO(3)\times SO(3)\textcircled{S}S$. Here $S=S_3$ if $l_1=l_2=l_3$, and otherwise is isomorphic to S_2 or S_1. If $l_i=l_j$ and $n_i\neq n_j$ for one or more pairs i, j with $i\neq j$, the situation is more complicated in that the representation in the eigenspace is no longer irreducible. In the extreme case in which $l_1=l_2=l_3=l$ while all n_j are distinct, this representation is that induced by $D^l\times D^l\times D^l$ and is a direct sum of four irreducible representations of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$, two of which are equivalent. The three inequivalent ones exhaust the irreducible

unitary representations of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$ associated with the triple l, l, l and correspond to the three inequivalent irreducible representations of S_3. In all cases the situation can be described by introducing the subgroup S' of all permutations, leaving the pairs n_1, l_1, n_2, l_2, n_3, l_3 fixed, as well as the subgroup S leaving l_1, l_2, l_3 fixed. Of course $S'\subseteq S$, and one forms the representation B of S induced by the identity of S'. The reduction of B exactly parallels that of the representation of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$ defined by the eigenspace. In particular, it has at most four irreducible constituents and is multiplicity-free except in the extreme case discussed above.

Whatever the actual representation of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$ in the eigenspace is, one can collect the irreducible components and obtain the canonical decomposition into primary parts. The corresponding subspaces of the eigenspaces are J'-invariant and so (as in the case $N=2$) may be treated as though they belonged to distinct eigenvalues. Unlike the case $N=2$, the associated unitary representations need not be irreducible. Instead they will be primary—that is, direct sums of *equivalent* irreducibles. However, the multiplicity will always be either 2 or 1 and will be 2 only when $l_1=l_2=l_3$ and n_1, n_2, and n_3 are all distinct. In any case the problem is to carry out the program of section 14 with the irreducible representations of $SO(3)\times SO(3)\textcircled{S}S_2$ replaced by primary representations of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$. Whether the primary representation is irreducible or not, the major part of the problem concerns the corresponding irreducible representation. Thus, to solve the coefficient problem in most cases and most of the problem in all cases, one must restrict an irreducible unitary representation V of $G=SO(3)\times SO(3)\times SO(3)\textcircled{S}S_3$ to the subgroup G_3 of all x, y, z, π with $x=y=z$ and seek two orthonormal bases for $\mathcal{H}(V)$, the space of V, as well as the expansion coefficients of one basis with respect to the other. One of these bases must be defined and be readily computable without the knowledge of how V reduces when restricted. The other must reduce the restriction of V to G_3 in the sense that each basis element must lie in one of the irreducible subspaces of some fixed restriction.

Finding the first basis is easily reduced to finding a basis for the space of the inducing representation $A^{l_1,l_2,l_3,L}$ of $SO(3)\times SO(3)\times SO(3)\textcircled{S}S$, since inducing commutes with the taking of direct sums. When l_1, l_2, and l_3 are all distinct, $S=S_1$ and may be ignored. In that case (and more generally whenever L is one-dimensional), it suffices to choose a convenient basis in the space of $D^{l_1}\times D^{l_2}\times D^{l_3}$, and this is carried out by considering the subgroup $A_z\times A_z\times A_z$ of $SO(3)\times SO(3)$ in evident generalization of what was done in section 14 for the case in which $N=2$.

A straightforward analysis shows that, when the induced representation $U^{A^{l_1,l_2,l_3,L}}$ is restricted back to G_3 (and G_3 is identified with $SO(3)\times S_3$), it coincides with the representation of $SO(3)\times S_3$ induced by a certain repre-

sentation of $SO(3)\times S$. When $S=S_1$ (as it does when l_1, l_2, and l_3 are all distinct), $SO(3)\times S$ is just $SO(3)$, and the inducing representation is just $D^{l_1}\otimes D^{l_2}\otimes D^{l_3}$, the inner tensor product of three irreducible representations D^{l_1}, D^{l_2}, D^{l_3} of $SO(3)$. Since inducing commutes with the taking of direct sums, it suffices in finding the second basis to find an orthonormal basis in the space of $D^{l_1}\times D^{l_2}\times D^{l_3}$ that reduces $D^{l_1}\otimes D^{l_2}\otimes D^{l_3}$. If one attempts to use the method that was used above for $D^{l_1}\times D^{l_2}$, one runs into difficulty because $D^{l_1}\otimes D^{l_2}\otimes D^{l_3}$ is multiplicity-free only in rather special cases. To overcome this difficulty, one effects the reduction in two stages. In the first stage one restricts $D^{l_1}\times D^{l_2}\times D^{l_3}$ to the subgroup of all x, y, z in $SO(3)\times SO(3)\times SO(3)$ with $x=y$, and in the second one restricts further to the subsubgroup of all x, y, z with $x=y=z$. At the first stage the restriction may be identified with $D^{l_1}\otimes D^{l_2}\times D^{l_3}=(D^{|l_1-l_2|}\oplus D^{|l_1-l_2|+1}\oplus D^{|l_1-l_2|+2}\oplus\cdots\oplus D^{l_1+l_2})\times D^{l_3}=(D^{|l_1-l_2|}\times D^{l_3})\oplus(D^{|l_1-l_2|+1}\times D^{l_3})\oplus\cdots\oplus(D^{l_1+l_2}\times D^{l_3})$, which is a multiplicity-free representation of $SO(3)\times SO(3)$ and so defines a unique direct sum decomposition of the space of $D^{L_1}\otimes D^{l_2}\otimes D^{l_3}$. The kth summand in this decomposition is the space of the representation $D^{|l_1-l_2|+k-1}\times D^{l_3}$, and in the second stage this becomes the multiplicity-free representation $D^{|l_1-l_2|+k-1}\otimes D^{l_3}=D^{|l_1-l_2|+k-1+l_3}\oplus D^{|l_1-l_2|+k+l_3}\oplus\cdots\oplus D^{|l_1-l_2|+k-1+l_3}$ of $SO(3)$. Thus, each summand has a uniquely determined direct sum decomposition into spaces of irreducible representations of $SO(3)$. Putting them together, one has a well-defined direct sum decomposition of $D^{l_1}\otimes D^{l_2}\otimes D^{l_3}$ into irreducible components.

One obtains the second basis by restricting each of these to A_z, as in the case in which $N=2$. To designate a member of the second basis, given l_1, l_2, l_3, one chooses first an integer l_4, with $|l_1-l_2|\leqslant l_4\leqslant l_1+l_2$, denoting the particular component of $D^{l_1}\otimes D^{l_2}$ that is to be combined with D^{l_3}. Then one chooses an integer l^5, with $|l_4-l_3|\leqslant l_5\leqslant l_4+l_3$, denoting the component of $D^{l_4}\otimes D^{l_3}$ whose space is to contain the basis element. Finally one chooses an integer m_5, with $-l_5\leqslant m_5\leqslant l_5$, to select a basis element in the space of l_5. The ordered triple l_4, l_5, m_5 determines the basis element (once suitable corrections have been made about "phase factors"—that is, arbitrary constants of absolute value 1).

The members of the first basis are indexed by the triples m_1, m_2, m_3, where $-l_1\leqslant m_1\leqslant l_1-l_2\leqslant m_2\leqslant l_2-l_3\leqslant m_3\leqslant l_3$. The coefficients that must be computed in the $N=3$ case (when L is one-dimensional) are thus functions of the nine integer variables l_1, l_2, l_3, m_1, m_2, m_3, l_4, l_5, and m_5, which vary independently subject to the restrictions listed above. To carry out the computation, one introduces a third basis and proceeds in two steps. In the first step, members of the second basis are expressed in terms of those of the third, and in the second step, members of the third basis are expressed in terms of those of the first. The members of the third basis are defined by using the method of the $N=2$ case to introduce a second basis in the space of $D^{l_1}\times D^{l_2}$ and then combining this with the A_z basis for D^{l_3} by the tensor

product construction. It is almost obvious that all coefficients involved in expressing members of the third basis in terms of members of the second are Clebsch–Gordan coefficients as defined in section 14 (whenever they are not zero) and that the same is true of the coefficients involved in expressing members of the second basis in terms of the third. It follows immediately that the coefficients that replace the Clebsch–Gordan coefficients when $N=3$ can all be explicitly given as sums of products of pairs of Clebsch–Gordan coefficients.

The nondegenerate cases for any N can be treated by a straightforward (although tedious to describe) generalization of the method just described for $N=3$. The coefficients involved can all be computed from the Clebsch–Gordan coefficients; they are complicated sums of $(N-1)$-fold products of them.

17. The analysis given so far is incomplete in several important respects. First, it has concentrated on the strongly nondegenerate cases in which $l_1, l_2, \ldots, l_N$ are all distinct, whereas in practice the most interesting and most frequently encountered cases are those in which there are coincidences among the l_j as well as among the n_j. Second, nothing has been said about how one computes the matrix elements of J' with respect to the first basis. This can be a formidable problem—especially since there are so many of them—and rotational symmetry can be as useful in simplifying the solution as it is in facilitating the diagonalization of the matrix after it has been found. Finally, no account has yet been taken of two fundamental physical facts: the so-called "spin" of the electron, and the "Pauli exclusion principle."

It is clear from the discussion in sections 14, 15, and 16 that an analysis of the degenerate cases along the lines indicated there demands considerable involvement with the representation theory of the symmetric group S_N. This fact was quite disturbing to most physicists of the late 1920s. They disliked the idea of having to learn to think in terms of an unfamiliar "unphysical" and abstract subject like group theory, and the device of passing to the operators occurring in the corresponding Lie algebra representation was not available. The symmetric group S_N is discrete, and its Lie algebra is consequently trivial. There was thus considerable relief when it was realized that the Pauli exclusion principle excluded so many eigenvectors and eigenvalues from consideration that only relatively easy parts of the representation theory of S_N continued to play a role. Indeed, if the electron did not have a "spin," this representation theory (effectively) would not be involved at all. Finally in 1929, only two or three years after Wigner, Weyl, and von Neumann introduced group-theoretic methods, J. C. Slater published a remarkable and extremely influential paper entitled "The Theory of Complex Spectra," in which he apparently got rid of the "group pest" altogether. In addition, he attacked and partially solved the problem of

computing the matrix elements of J' with respect to the first basis. In brief, he outlined a practical procedure for computing first-order perturbations to energy levels that made no explicit use of the representation theory of either $SO(3)$ or S_N and in particular no explicit use of Clebsch–Gordan coefficients. Its only limitations were that it sometimes yielded only finite sums of energy levels and that it required very lengthy (but elementary) computations except when N and the l_j were small.

Before explaining what Slater did in detail, it will be necessary to say a few words about the nature of spin and the Pauli exclusion principle and how they affect our mathematical model. In the discussion up to now it has been assumed that the Hilbert space of states for an N-electron atom is the space $\mathfrak{L}^2(E^{3N})$ of all square-summable complex-valued functions on $3N$-dimensional Euclidean space, or equivalently the tensor product $\mathfrak{H}\times\mathfrak{H}\times\cdots\times\mathfrak{H}$ of N copies of the one-electron space $\mathfrak{L}^2(E^3)$. The Pauli exclusion principle, in the more general and sophisticated form given it (independently) by Heisenberg and Dirac, changes this assumption by replacing $\mathfrak{L}^2(E^{3N})$ by a certain closed subspace invariant under the energy operator H. This subspace is the subspace of all functions f in $\mathfrak{L}^2$ that are *antisymmetric* in the sense that

$$f(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N) \equiv f(x_2, y_2, z_2, x_1, y_1, z_1, \ldots, x_N, y_N, z_N)$$

and more generally that the analogous identity holds for the interchange of any two pairs $x_i, y_i, z_i; x_j, y_j, z_j$. This statement can be put into a different form, which relates it to the symmetric group S_N by considering the unitary representation W' of S_N introduced in section 12. If one forms the canonical decomposition of W' into primary parts, one obtains an H-invariant subspace for each equivalence class of irreducible representations of S_N, and the subspace of antisymmetric functions is precisely that associated with the so-called "alternating representation" of S_N. The latter is the unique one-dimensional representation other than the identity; it may be described explicitly by the assertion that it is -1 times the identity on every permutation that interchanges two distinct integers while fixing the rest.

The replacement of $\mathfrak{H}^N=\mathfrak{H}\times\mathfrak{H}\times\cdots\times\mathfrak{H}$ by its antisymmetric subspace $\mathfrak{H}_A^N$ has the effect of eliminating many of the stationary states and energy levels that would be predicted by the more naïve theory. As already explained in earlier sections, each eigenspace of the approximate energy operator is associated with an irreducible unitary representation of $SO(3)\times SO(3)\times\cdots\times SO(3)\textcircled{S}S_N$, and one has a different first-order perturbed energy level associated with each irreducible representation of $SO(3)\times S_N$, which occurs in the restriction of the eigenspace representation to the subgroup of all $x_1, x_2, \ldots, x_N$, with $x_1=x_2=\cdots=x_N$. In particular, every perturbed eigenvalue is canonically associated with an irreducible unitary