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PREFACE

In investigating the highly different phenomena in nature, scientists have always tried to find some fundamental principles that can explain the variety from a basic unity. Today they have not only shown that all the various kinds of matter are built up from a rather limited number of atoms, but also that these atoms are constituted of a few basic elements or building blocks. It seems possible to understand the innermost structure of matter and its behavior in terms of a few elementary particles: electrons, protons, neutrons, photons, etc., and their interactions. Since these particles obey not the laws of classical physics but the rules of modern quantum theory or wave mechanics established in 1925, there has developed a new field of "quantum science" which deals with the explanation of nature on this ground.

Quantum chemistry deals particularly with the electronic structure of atoms, molecules, and crystalline matter and describes it in terms of electronic wave patterns. It uses physical and chemical insight, sophisticated mathematics, and high-speed computers to solve the wave equations and achieve its results. Its goals are great, but perhaps the new field can better boast of its conceptual framework than of its numerical accomplishments. It provides a unification of the natural sciences that was previously inconceivable, and the modern development of cellular biology shows that the life sciences are now, in turn, using the same basis. "Quantum biology" is a new field which describes the life processes and the functioning of the cell on a molecular and submolecular level.

Quantum chemistry is hence a rapidly developing field which falls between the historically established areas of mathematics, physics, chemistry, and biology. As a result there is a wide diversity of backgrounds among those interested in quantum chemistry. Since the results of the research are reported in periodicals of many different types, it has become increasingly difficult both for the expert and the nonexpert to follow the rapid development in this new borderline area.

The purpose of this serial publication is to try to present a survey of the current development of quantum chemistry as it is seen by a number of the internationally leading research workers in various countries. The authors have been invited to give their personal points of view of the subject freely and without severe space limitations. No attempts have been made to avoid overlap—on the contrary, it has seemed desirable to have certain important research areas reviewed from different points of view. The response from the authors has been so encouraging that a fifth volume is now being prepared.

The editor would like to thank the authors for their contributions which give an interesting picture of the current status of selected parts of quantum chemistry. The topics covered in this volume range from pure mathematics — the theory of Hilbert space and group theory — over the quantum theory of atoms, molecules, and inorganic complexes to applications in molecular biology.

It is our hope that the collection of surveys of various parts of quantum chemistry and its advances presented here will prove to be valuable and stimulating, not only to the active research workers but also to the scientists in neighboring fields of physics, chemistry, and biology, who are turning to the elementary particles and their behavior to explain the details and innermost structure of their experimental phenomena.

January, 1968 PER-OLOV LÖWDIN

Functional Analysis for Quantum Theorists

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Introduction

The abstract methods of functional analysis provide an essential insight in the mechanism of the mathematical manipulations employed in quantum theory. The initial penetration of this abstract world requires an effort from a physicist which at first may seem too exacting and too far removed from his direct interests. Nevertheless, the intellectual effort invested in learning the abstract language of functional analysis is rewarding in the long run even for one who values mathematics only as a practical tool for organizing experiences pertaining to the physical world. By adapting an abstract point of view one rises above the details of computational work and perceives the motivation for many mathematical procedures. One also recognizes the conceptual unity of the apparently distinct approaches employed in quantum theory. In fact, it was the recognition of the unity of two separate quantum theories developed parallel in the 1920's that led John von Neumann to the abstract formulation of Hilbert space.

Hilbert space is one of the many abstract spaces studied by mathematicians who like to view these spaces with due regard to their interdependence and interrelation. The books written on Hilbert space by mathematicians naturally emphasize interrelationships of various mathematical constructions. They present the mathematical conclusions in the most general form possible, laying stress on the complete logical structure of the development with particular emphasis on the problems which present the greatest mathematical difficulties. The lectures from which this article derives had a different purpose. They were intended to introduce physicists and chemists to the concepts and terminology of the theory of Hilbert space and to make available to them some of the basic results useful in applications to quantum theory. In order to accomplish this purpose within the relatively short time available during a summer institute, some basic propositions, whose proofs are of interest to mathematicians, had to be stated without proof.

The notation in this article is that employed universally in the mathematical literature with one notable exception: The dagger† instead of the star* is used to indicate an adjoint operator. The customary symbols of set theory, $\in$ and $\subset$, are employed to indicate that an element is a member of a set and that a set is included in another set, respectively.

Some exercises which were found useful in the course were retained in this article. Their inclusion perhaps unnecessarily emphasizes the tutorial character of this article which the editor quite charitably decided to include in a volume devoted to advances of quantum chemistry.

I. The Basic Structure of Hilbert Space

A. Linear Spaces

Hilbert space is an abstract space, one of the many obtained by generalization from the ordinary three-dimensional vector space. Before discussing Hilbert space, it is of advantage to contemplate a more general concept: that of linear space.

A collection of mathematical entities is called a *linear space* if it has the following elementary properties of ordinary vectors:

(i) An operation of addition is defined; to every pair of elements $\mathbf{X}$, $\mathbf{Y}$, there is ordered an element $\mathbf{X} + \mathbf{Y}$. This operation is commutative and associative: $\mathbf{X} + \mathbf{Y} = \mathbf{Y} + \mathbf{X}$, $\mathbf{X} + (\mathbf{Y} + \mathbf{Z}) = (\mathbf{X} + \mathbf{Y}) + \mathbf{Z}$.

(ii) Every element $\mathbf{X}$ may be multiplied by a complex number α, the resulting element being denoted by $\alpha\mathbf{X}$. Scalar multiplication follows the distributive law: $\alpha(\mathbf{X} + \mathbf{Y}) = \alpha\mathbf{X} + \alpha\mathbf{Y}$, and the associative law: $\alpha(\beta\mathbf{X}) = (\alpha\beta)\mathbf{X}$.

(iii) There is a null element $\mathbf{O}$, with the properties: $\alpha\mathbf{O} = \mathbf{O}$, for every α, $\mathbf{X} + \mathbf{O} = \mathbf{X}$, for every $\mathbf{X}$ and $0\mathbf{X} = \mathbf{O}$.

In elementary geometry, the scalar multipliers α, β, etc., are real. For the sake of generality and with a view to applications to quantum theory, however, we permit α to be complex. In the case of ordinary (three-dimensional) vectors, the elements of the linear space are the ordered triplets of numbers, $\mathbf{X} = (x_1, x_2, x_3)$, where x_1, x_2, x_3 are the rectangular components of the vector $\mathbf{X}$. The sum $\mathbf{X} + \mathbf{Y}$ is a vector with components $x_1 + y_1$, $x_2 + y_2$, $x_3 + y_3$, and $\alpha\mathbf{X}$ is one with components $\alpha x_1, \alpha x_2, \alpha x_3$.

There are many collections which qualify as linear spaces. Clearly, all ordered n-tuples of complex numbers satisfy (i), (ii), and (iii) if vector addition and scalar multiplication are defined as they are in the three-dimensional space. All infinite sequences with complex elements form a linear space also. The collection of all polynomials in x with complex coefficients affords another example of a linear space, since the sum of two polynomials is again one, and so is any complex multiple of a polynomial. The polynomial zero is the zero element of this space. The validity of the commutative, associative, and distributive laws is obvious. Though further examples of linear spaces are easy to construct, we mention only the set of continuous functions and the set of integrable functions on a given interval. In view of the fact that the concept of linear space covers such a wide variety of collections of mathematical elements of diverse character, it is rather surprizing that quite a few statements may be proved about linear spaces in general.

The elements $\mathbf{X}_1, \ldots, \mathbf{X}_n$ of a linear space are said to be *linearly dependent* if n complex numbers $\alpha_1, \ldots, \alpha_n$, not all zero, exist such that $\alpha_1\mathbf{X}_1 + \cdots + \alpha_n\mathbf{X}_n = \mathbf{O}$. If, however, this last equation implies that $\alpha_1 = \alpha_2 = \cdots \alpha_n = 0$, the elements $\mathbf{X}_1, \ldots, \mathbf{X}_n$ are called *independent*. An infinite set is called independent if every finite subset of the set is independent.

A set of $\mathbf{S}$ of independent elements is called a *basis* of the linear space $\mathbf{L}$ if every element of $\mathbf{L}$ is linearly dependent on the elements of $\mathbf{S}$. This means that given $\mathbf{X} \in \mathbf{L}$, one can find a finite number of elements $\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_n$ all in $\mathbf{S}$, so that for suitable $\alpha_1\ \alpha_2, \ldots, \alpha_n$

$$\mathbf{X} = \sum_{i=1}^{n} \alpha_i \mathbf{X}_i. \tag{I.1}$$

A linear space will be called n-dimensional if it contains n independent elements, but any $n + 1$ elements in this space are linearly dependent. If the number of independent elements is unlimited, the space will be called infinite-dimensional. In an n-dimensional space, n independent elements $\mathbf{X}_1, \ldots, \mathbf{X}_n$ always form a basis, since any element $\mathbf{X}$ not contained among them satisfies an equation of the type $\alpha_1\mathbf{X}_1 + \cdots + \alpha_n\mathbf{X}_n + \alpha_{n+1}\mathbf{X} = \mathbf{O}$, where the last coefficient α_{n+1} is not zero. Hence $\mathbf{X}$ is a linear combination of $\mathbf{X}_1, \ldots, \mathbf{X}_n$. It can be shown that all bases of the same space have the same number of elements.

Starting with an arbitrary set $\mathbf{S}$ in a linear space we can form the set $[\mathbf{S}]$ consisting of all elements linearly dependent on $\mathbf{S}$. This set is a linear space; it is called the subspace spanned by $\mathbf{S}$.

It is easy to prove that the following collections form a linear space:

(a) All complex polynomials of the variable x of degree $\leqq n$.

(b) All complex polynomials of x.

(c) All complex sequences.

(d) All complex sequences which contain only a finite number of non-zero terms.

(e) All continuous functions on the interval $0 \leqq x \leqq 1$ which vanish on both ends.

(f) All complex sequences for which $\sum_{n=1}^{\infty} |x_n|^2 < \infty$.

B. Normed Spaces and Inner Product Spaces

With the introduction of the concept of magnitude, or norm, a linear space becomes a metric space, or a normed linear space. The two terms have identical meaning. Given a linear space, the norm of an element may be defined in a variety of ways. It is only necessary that the norm satisfy the following formal requirements:

The norm $\|\mathbf{X}\|$ of every element must be a positive number, only the null element has the norm 0. Moreover, for every complex number α and every pair of elements $\mathbf{X}$ and $\mathbf{Y}$,

$$\|\alpha\mathbf{X}\| = |\alpha|\;\|\mathbf{X}\|, \tag{I.2}$$

$$\|\mathbf{X}+\mathbf{Y}\| \leqq \|\mathbf{X}\| + \|\mathbf{Y}\|. \tag{I.3}$$

The last inequality is called the *triangle inequality*. The variety of choices available for defining a norm in a given space is illustrated on the linear space formed by all complex polynomials. The norm of $p_n(x)$ may be chosen as

(a) $\|p_n\| = \max|p_n(x)|, \quad \text{for} \quad 0 \leqq x \leqq 1;$

(b) $\|p_n\| = \int_0^1 |p_n(x)|\,dx;$

(c) $\|p_n\| = \left[\int_0^1 |p_n(x)|^2\,dx\right]^{1/2}.$

Each of these choices is consistent with the relations (I.2) and (I.3). Nevertheless, polynomials "large" in the sense of one norm may be "small" in the sense of another norm.

The distance of two elements $\mathbf{X}$ and $\mathbf{Y}$ is defined as $\|\mathbf{X}-\mathbf{Y}\|$, where $\mathbf{X}-\mathbf{Y} = \mathbf{X} + (-1)\mathbf{Y}$. Once the space has been "metrized" by the introduction of the norm, the convergence of a sequence $\{\mathbf{X}_n\}$ to an element $\mathbf{X}_0$ is defined by the requirement that $\|\mathbf{X}_n - \mathbf{X}_0\|$ tends to 0 as n tends to ∞. It makes sense now to talk about a set being closed; which means that it contains all its limit points.

In the special case of greatest interest to us, the norm can be introduced by the way of a scalar, or inner product defined for every pair of elements in the space. The procedure is the generalization of the definition of the length of a vector as the square root of the scalar product of the vector with itself. Naturally, the scalar product must be defined in such a manner that the product of each vector with itself is positive.

A linear space is called an *inner product space*, or a generalized vector space, if a scalar product may be defined in it to satisfy the following requirements:

To every pair of elements $\mathbf{X}$ and $\mathbf{Y}$ there is ordered a complex number

(X,Y) with the following properties:

$$(\alpha\mathbf{X}, \mathbf{Y}) = \alpha(\mathbf{X}, \mathbf{Y}) \tag{I.4}$$

for every complex α. Moreover

$$(\mathbf{X}_1 + \mathbf{X}_2, \mathbf{Y}) = (\mathbf{X}_1, \mathbf{Y}) + (\mathbf{X}_2, \mathbf{Y}), \tag{I.5}$$

$$(\mathbf{Y}, \mathbf{X}) = (\mathbf{X}, \mathbf{Y})^* \tag{I.6}$$

where * denotes the complex conjugate. Finally $(\mathbf{O}, \mathbf{O}) = 0$, and

$$(\mathbf{X}, \mathbf{X}) > 0 \tag{I.7}$$

for all $\mathbf{X} \neq \mathbf{O}$.

From Eqs. (I.4), (I.5), and (I.6), it is easy to derive the following equations:

$$(\alpha_1\mathbf{X}_1 + \alpha_2\mathbf{X}_2, \mathbf{Y}) = \alpha_1(\mathbf{X}_1, \mathbf{Y}) + \alpha_2(\mathbf{X}_2, \mathbf{Y}), \tag{I.8}$$

$$(\mathbf{X}, \beta_1\mathbf{Y}_1 + \beta_2\mathbf{Y}_2) = \beta_1{}^*(\mathbf{X}, \mathbf{Y}_1) + \beta_2{}^*(\mathbf{X}, \mathbf{Y}_2), \tag{I.9}$$

$$(\alpha\mathbf{X}, \alpha\mathbf{X}) = |\alpha|^2(\mathbf{X}, \mathbf{X}). \tag{I.10}$$

In an inner product space the norm is defined as

$$\|\mathbf{X}\| = [(\mathbf{X}, \mathbf{X})]^{1/2}. \tag{I.11}$$

The norm as defined by (I.11) clearly satisfies (I.2). It remains to be shown that (I.3) is also satisfied. The proof of this proposition depends on Schwarz's inequality:

$$|(\mathbf{X}, \mathbf{Y})| \leqq \|\mathbf{X}\| \, \|\mathbf{Y}\|, \tag{I.12}$$

which must be proven first. For $\mathbf{Y} = \mathbf{O}$ its validity is clear, for $\mathbf{Y} \neq \mathbf{O}$ we introduce $\mathbf{X}_1 = \mathbf{X} - \beta\mathbf{Y}$, where $\beta = (\mathbf{X}, \mathbf{Y})/\|\mathbf{Y}\|^2$. Then

$$(\mathbf{X}_1, \mathbf{Y}) = (\mathbf{X}, \mathbf{Y}) - \beta\|\mathbf{Y}\|^2 = (\mathbf{X}, \mathbf{Y}) - (\mathbf{X}, \mathbf{Y}) = 0, \tag{I.13}$$

therefore $(\mathbf{X}_1, \mathbf{X}_1) = (\mathbf{X}, \mathbf{X}_1)$, and hence

$$\|\mathbf{X}_1\|^2 = (\mathbf{X}, \mathbf{X} - \beta\mathbf{Y}) = \|\mathbf{X}\|^2 - (\mathbf{X}, \mathbf{Y})(\mathbf{X}, \mathbf{Y})^*/\|\mathbf{Y}\|^2. \tag{I.14}$$

Since the left side of (I.11) is never negative,

$$\|\mathbf{X}\|^2 - |(\mathbf{X}, \mathbf{Y})|^2/\|\mathbf{Y}\|^2 \geqq 0, \tag{I.15}$$

which we were to prove. Equality holds in (I.12) and (I.15) only when $\mathbf{X}_1 = \mathbf{O}$; i.e., when $\mathbf{X} = \beta\mathbf{Y}$.

With the aid of (I.5) we obtain readily

$$\begin{aligned}\|\mathbf{X}+\mathbf{Y}\|^2 &= (\mathbf{X},\mathbf{X}) + (\mathbf{X},\mathbf{Y}) + (\mathbf{Y},\mathbf{X}) + (\mathbf{Y},\mathbf{Y}) \\ &= \|\mathbf{X}\|^2 + \|\mathbf{Y}\|^2 + 2\,\mathrm{Re}(\mathbf{X},\mathbf{Y}). \end{aligned} \tag{I.16}$$

The last term in (I.16) can be estimated using Schwarz's inequality

$$|\mathrm{Re}(\mathbf{X},\mathbf{Y})| \leqq |(\mathbf{X},\mathbf{Y})| \leqq \|\mathbf{X}\|\ \|\mathbf{Y}\|. \tag{I.17}$$

Hence

$$\|\mathbf{X}+\mathbf{Y}\|^2 \leqq \|\mathbf{X}\|^2 + \|\mathbf{Y}\|^2 + 2\|\mathbf{X}\|\ \|\mathbf{Y}\| = [\|\mathbf{X}\| + \|\mathbf{Y}\|]^2, \tag{I.18}$$

and the triangle inequality is satisfied. On replacing **Y** by −**Y** in (I.16), we obtain

$$\|\mathbf{X}-\mathbf{Y}\|^2 = \|\mathbf{X}\|^2 + \|\mathbf{Y}\|^2 - 2\,\mathrm{Re}(\mathbf{X},\mathbf{Y}). \tag{I.19}$$

From (I.16) and (I.19) follows the important *parallelogram relation*:

$$\|\mathbf{X}+\mathbf{Y}\|^2 + \|\mathbf{X}-\mathbf{Y}\|^2 = 2\|\mathbf{X}\|^2 + 2\|\mathbf{Y}\|^2. \tag{I.20}$$

Although only norms appear in this relation, its validity is a consequence of the definition of the norm in terms of an inner product. The parallelogram relation is a specific property of inner product spaces. Whenever (I.20) holds in a normed linear space, there exists a scalar product definable uniquely in terms of the norms, the space is an inner product space. It is easy to show that of the three definitions proposed for the norm of a polynomial only one (c) is consistent with Eq. (I.20).

In three-dimensional geometry, we define the inner product of the vectors $\mathbf{X} = \{x_1, x_2, x_3\}$ and $\mathbf{Y} = \{y_1, y_2, y_3\}$ as

$$(\mathbf{X},\mathbf{Y}) = x_1y_1 + x_2y_2 + x_3y_3. \tag{I.21}$$

but we could define another scalar product, for example

$$(\mathbf{X},\mathbf{Y})' = x_1y_1 + 2x_2y_2 + 3x_3y_3. \tag{I.22}$$

The requirements embodied in (I.4)–(I.7) are not violated by this new definition. It leads, however, to a new norm, a different determination of distance in space.

Many physicists prefer to write the scalar product in a slightly different form. In their notation

$$(\mathbf{X},\mathbf{Y}) = \langle \mathbf{Y} | \mathbf{X} \rangle. \tag{I.23}$$

Then equation (I.4) becomes:

$$\langle \mathrm{Y} \mid \alpha \mathrm{X} \rangle = \alpha \langle \mathrm{Y} \mid \mathrm{X} \rangle \tag{I.24}$$

Clearly $\langle \beta \mathrm{Y} \mid \mathrm{X} \rangle = \beta^* \langle \mathrm{Y} \mid \mathrm{X} \rangle$.

An inner product space may be finite-dimensional or infinite-dimensional. When it is finite dimensional, it always possesses the property of *completeness* which is defined as follows: Whenever an infinite sequence of elements satisfies Cauchy's convergence condition $\lim \|\mathrm{X}_n - \mathrm{X}_m\| = 0$ as n and m tend to ∞, then there is a limit element X_0 to which the sequence converges in the sense that $\lim \|X_n - X_0\| = 0$ as n tends to ∞. The theorem is proven for any finite-dimensional space in the manner it is proven when X's represent ordinary complex numbers. The theorem is no longer true in a general, infinite-dimensional inner product space. Such a space may be incomplete. When it is complete, it is by definition a Hilbert space.

C. Hilbert Space

By definition, the Hilbert space is an infinite-dimensional, complete, inner product space. For convenient reference we repeat the axioms or postulates defining Hilbert space in their customary form:

A set of elements $f, g, h, \ldots$ forms a Hilbert space $\mathfrak{H}$ if it possesses the following properties:

(a) $\mathfrak{H}$ is a linear space. There is defined a commutative and associative addition of its elements and a multiplication of these elements by complex numbers. These operations obey the rules of vector algebra. There exists a null element $\mathbf{O}$ so that $0f = \mathbf{O}$. Moreover, the following equations hold:

$$\alpha(f + g) = \alpha f + \alpha g, \qquad (\alpha + \beta)f = \alpha f + \beta f,$$
$$\alpha(\beta f) = (\alpha\beta)f, \qquad 1 \cdot f = f,$$

for every f and g in $\mathfrak{H}$ and for any complex numbers α and β.

(b) There is a scalar product in $\mathfrak{H}$. To every pair $\{f, g\}$ in $\mathfrak{H}$ belongs a complex number denoted by (f, g) with the following properties:

$$(\alpha f, g) = \alpha(f, g), \qquad (g, f) = (f, g)^*,$$
$$(f_1 + f_2, g) = (f_1, g) + (f_2, g), \qquad (f, f) \geqq 0,$$

the equality holds only for $f = \mathbf{O}$. The norm of an element f is defined as $\|f\| = [(f, f)]^{1/2}$

(c) $\mathfrak{H}$ is an infinite dimensional space.

(d) $\mathfrak{H}$ is complete. Whenever a sequence of elements $\{f_n\}$ satisfies

Cauchy's convergence condition $\|f_n - f_m\| \to 0$ as $n \to \infty$, the sequence converges toward some element $f_0 \in \mathfrak{H}$.

The idea of the abstract Hilbert space defined by these axioms arose when J. von Neumann recognized that two mathematical objects have identical structure: The classical Hilbert space, which is defined as the collection of complex sequences $\{x_n\}$ such that $\Sigma\, |x_n|^2$ is convergent, and the space $\mathfrak{L}_2$, which is the collection of complex functions $f(x)$ integrable over an interval $[a, b]$ and such that $\int_a^b |f(x)|^2\, dx$ is finite. (Integration is defined in Lebesgue's sense, thus permitting the inclusion of more functions than are integrable in the ordinary, Riemann sense.) The identical structure—isomorphism—of these two spaces accounts for the equivalence of the two formulations of quantum theory, one in terms of infinite matrices, the other in terms of Schrödinger's equation (von Neumann, 1932).

In the classical or *sequential Hilbert space*, the scalar product is defined as $\Sigma x_n y_n^*$. Convergence of this product is assured because

$$|x_n y_n| \leqq \tfrac{1}{2}\{|x_n|^2 + |y_n|^2\}. \tag{I.25}$$

Multiplication by a complex number α is defined as $\alpha\{x_n\} = \{\alpha x_n\}$, and addition by a complex number as $\{x_n\} + \{y_n\} = \{x_n + y_n\}$. It is relatively simply to verify that this sequential Hilbert space satisfies the postulates (a)–(d), but the last postulate requires more than elementary manipulations.

In space $\mathfrak{L}_2$ the scalar product is defined as

$$(f, g) = \int_a^b f(x) g(x)^*\, dx. \tag{I.26}$$

The sum of two elements is the ordinary sum of the functions. The demonstration of the fact that this space is complete requires the techniques of Lebesgue integration. That this should be so is made plausible by the observation that if one restricts oneself to continuous functions or even to Riemann-integrable functions, axioms (a), (b), and (c) are readily seen to be satisfied. Axiom (d) is not satisfied, however, because the limiting process takes one outside of the set of functions restricted to be continuous or Riemann integrable (Riesz and Sz.-Nagy, 1955).

The two spaces mentioned have an additional property called *separability* which will not be of a great consequence to us. Separability means that there exists in the space a sequence $\{f_n\}$ which is everywhere dense, the latter term meaning that given any $\varepsilon > 0$, and any fixed element f_0, there is an element f_m in the sequence such that $\|f_0 - f_m\| < \varepsilon$. The only consequence of this property is that the space and its every linear subspace can be built up, or spanned, in a way to be explained, by at most an infinite sequence of elements $f_1, f_2, \ldots, f_n, \ldots$. Proofs of these statements are found in all standard treatises on Hilbert space (Akhiezer and Glazman, 1961, 1963; Halmos, 1951; von Neumann, 1932; Riesz and Sz.-Nagy, 1955; Stone, 1932).

The simplest form of the space $\mathfrak{L}_2$ is built on a finite interval $[a, b]$ of a single variable. It is possible to show, however, that the finiteness of the interval is of no consequence, and in place of a single variable we may consider Lebesgue-integrable functions in a space of n (finite) variables. The structures of all these spaces are alike.

For the sake of simplicity we contemplate $\mathfrak{L}_2$ of a single variable and introduce a sequence of orthonormal functions in $\mathfrak{L}_2$; i.e., functions $\varphi_n(x)$ such that

$$\int_a^b \varphi_n(x)\varphi_m(x)^* \, dx = \delta_{nm}. \tag{I.27}$$

Then one can show that given any element f in $\mathfrak{L}_2$, the numbers

$$a_n = \int_a^b f(x)\varphi_n(x)^* \, dx \tag{I.28}$$

are finite, $\Sigma\, |a_n|^2$ is convergent, and in fact

$$\sum_{n=1}^{\infty} |a_n|^2 \leqq \int_a^b |f(x)|^2 \, dx. \tag{I.29}$$

When the orthonormal sequence is complete; i.e., when the only function orthogonal to the entire sequence is identically 0 (up to a set of measure 0), then equality sign prevails in (I.29). Equation (I.28) establishes a correspondence which orders to every element f of $\mathfrak{L}_2$ an element of the sequential Hilbert space. When the orthonormal sequence is complete, the element in $\mathfrak{L}_2$ and its image in the sequential space have the same norms. It is true, but not easy to show, that this is a one-to-one correspondence (Riesz and Sz.-Nagy, 1955, pp. 66–70). Every element in the sequential Hilbert space corresponds to exactly one element in $\mathfrak{L}_2$ provided two functions $f_1(x)$ and $f_2(x)$ are regarded identical when

$$\int_a^b |f_1(x) - f_2(x)|^2 \, dx = 0. \tag{I.30}$$

The statement about this one-to-one correspondence is called the *Riesz-Fischer theorem.*

We return now to the abstract space $\mathfrak{H}$ using the concrete spaces just discussed for illustration.

A subset L of $\mathfrak{H}$ is called a *linear manifold* if it contains all elements of the form $\alpha f + \beta g$ whenever it contains f and g. The set of all complex sequences which contain only a finite number of nonzero terms is a linear manifold in the sequential Hilbert space. This set is not closed, since it does not contain all its limit points.

A linear manifold which contains all its limit points is called a *closed linear manifold*, or a *subspace.*

Two elements f and g are called orthogonal if $(f, g) = 0$; an element f is called normalized if $\|f\| = 1$. A set S is called orthonormal if it consists only of normalized elements which are orthogonal to each other. It is the consequence of the separability axiom that an orthonormal set is either finite or it is an infinite sequence.

Given a set S in $\mathfrak{H}$, the set of all elements linearly dependent on S forms a linear manifold, it is called the linear manifold spanned by S. If S contains only a finite number of independent elements, the linear manifold spanned by S is finite-dimensional and therefore a closed linear manifold. When the set S is an infinite sequence we can replace S by an orthonormal sequence which spans the same linear manifold. This replacement, or orthogonalization, may be accomplished in several ways. In principle it is the simplest to make use of the following method called the *Schmidt orthogonalization process*:

All O's are dropped from the sequence. Let f_1 be the first element of the remaining sequence, then $\varphi_1 = f_1/\|f\|$ is the first element of the orthonormal sequence. Let f_2 be the first element in S not linearly dependent on φ_1 and let $g_2 = f_2 - (f_2, \varphi_1)\varphi_1$. Then $g_2 \neq \mathbf{O}$ and we define $\varphi_2 = g_2/\|g_2\|$. Having found the first $k-1$ orthonormal elements $\varphi_1, \varphi_2, \ldots, \varphi_{k-1}$, the kth one is given by

$$g_k = f_k - \sum_{j=1}^{k-1} (f_k, \varphi_j)\varphi_j; \qquad \varphi_k = g_k/\|g_k\|. \tag{I.31}$$

In each step it is assumed that elements of S which are found to be linearly dependent on earlier elements are omitted. As a result of the process described, either an infinite orthonormal sequence is obtained, or the process terminates because the number of independent elements in S is exhausted.

When the set S is not a sequence, one makes use of the separability postulate to replace it by a sequence before attempting orthogonalization.

In nonseparable spaces it is, of course, possible to obtain an orthonormal set which is not a sequence.

An o.n. (orthonormal) set S is said to be *complete* when there is no element in $\mathfrak{H}$ orthogonal to every element of S. The word complete as used in this sense corresponds to the German word vollständig. Its meaning is not related to that of the same word used in connection with postulate (d). The latter meaning is rendered in German by the word abgeschlossen.

Given any element f in $\mathfrak{H}$ and an o.n. set S, we form the numbers

$$a_n = (f, \varphi_n), \qquad n = 1, 2, 3, \ldots,^1 \tag{I.32}$$

which are called the expansion coefficients of f according to the o.n. set S. We now prove *Bessel's inequality*:

$$\sum_{n=1}^{N} |a_n|^2 \leqq \|f\|^2, \tag{I.33}$$

where N is any number.

$$\left\| f - \sum_{n=1}^{N} a_n \varphi_n \right\|^2 = \|f\|^2 + \sum_{n=1}^{N} a_n a_n^* - \sum_{n=1}^{N} (f, a_n \varphi_n) - \sum_{n=1}^{N} (a_n \varphi_n, f). \tag{I.34}$$

The left-hand side of (I.34) is ≥ 0 and the right-hand side simplifies to

$$\|f\|^2 - \sum_{n=1}^{N} |a_n|^2,$$

therefore (I.33) must hold. The inequality establishes the convergence of the infinite series $\Sigma\ |a_n|^2$, and from this fact we deduce that the sequence in $\mathfrak{H}$,

$$f_N = \sum_{n=1}^{N} a_n \varphi_n, \tag{I.35}$$

must tend to a limit. In fact, for $N > M$

$$\|f_N - f_M\|^2 = \left\| \sum_{n=M+1}^{N} a_n \varphi_n \right\|^2 = \sum_{n=M+1}^{N} |a_n|^2. \tag{I.36}$$

The right-hand side of (I.36) tends to zero as $M \to \infty$, therefore axiom (d) assures that f_N tends to a limit g. The expansion coefficients of this element g with respect to the o.n. set S must be the same as those of f given by

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[1] In a nonseparable space, one cannot order the coefficients (f, φ_t) into a sequence directly, but one can prove that, at most, a countable set of coefficients of a given f can be different from zero. Then it is possible to arrange these nonzero coefficients in sequence.

(I.32), because $(f_N, \varphi_n) = a_n$ for $N \geqq n$ and $(g, \varphi_n) = \lim(f_N, \varphi_n)$ according to the following continuity argument which utilizes Schwarz's inequality:

$$|(g, \varphi_n) - (f_N, \varphi_n)| = |(g - f_N, \varphi_n)| \leqq \|g - f_N\| \, \|\varphi_n\|. \tag{I.37}$$

Thus we have shown that, for every $f \in \mathfrak{H}$, there is an element

$$g = \sum_{n=1}^{\infty} a_n \varphi_n, \tag{I.38}$$

where the a_n's are defined by (I.32). Moreover, $(f - g, \varphi_n) = 0$ for every $\varphi_n \in \mathbf{S}$.

When S *is complete,* $f - g$ must be **O**, therefore

$$f = \sum_{n=1}^{\infty} a_n \varphi_n. \tag{I.39}$$

The left-hand side of (I.34) tends to 0 as $N \to \infty$, and therefore Bessel's inequality is replaced by *Parseval's equation*:

$$\sum_{n=1}^{\infty} |a_n|^2 = \|f\|^2. \tag{I.40}$$

The interpretation of (1.39) in the space $\mathfrak{L}_2$ asserts the *convergence in the mean* of every generalized Fourier expansion, not its point-by-point convergence.

It is easy to show that given a complete o.n. set S, and two elements f and g with expansion coefficients a_n and b_n, then

$$\sum_{n=1}^{\infty} a_n b_n^* = (f, g), \tag{I.41}$$

where the convergence of the series is always assured.

Two important properties of the Hilbert space are readily demonstrated with the aid of o.n. functions. These properties are not shared by finite-dimensional spaces:

(1) An infinite o.n. set—complete or not—is a bounded set. Each of its elements has the norm 1. Yet this bounded set contains no convergent subsequence, because $\|\varphi_n - \varphi_m\|^2 = 2$ for every $n \neq m$. Ordinary finite-dimensional space is compact; the term means that every bounded infinite set contains a convergent sequence.

(2) Starting with an infinite o.n. set S we generate a linear manifold consisting of all elements linearly dependent on S. Every element in this

linear manifold is of the form

$$f = \sum_{n=1}^{N} a_n \varphi_n. \tag{I.42}$$

The linear manifold so generated is not closed, because the set S spans the closed linear manifold containing all elements of the form

$$f = \sum_{n=1}^{\infty} a_n \varphi_n, \tag{I.43}$$

where

$$\sum_{n=1}^{\infty} |a_n|^2 < \infty. \tag{I.44}$$

In contrast, linear manifolds in a finite dimensional space are always closed.

The significance of the last two properties is best understood if one examines the role of compactness and closure in the proofs of basic propositions in analysis. The reader is urged to think through the proof of the theorem that a function continuous on a closed, finite interval assumes its maximum on this interval.

Exercises

1. Consider the functions $1, x, x^2, x^3, \ldots,$ in the space $\mathfrak{L}_2$ on the real interval $[0, 1]$.
   (a) What linear manifold is spanned by these functions?
   (b) Is the function e^{inx} (n arbitrary integer) included in the linear manifold, or the closed linear manifold spanned?
   (c) Are all continuous functions of x on $[0, 1]$ included in the closed linear manifold spanned?
2. Orthogonalize the sequence in exercise 1, obtaining the first three orthonormal functions.
3. Show that a convergent sequence in $\mathfrak{H}$ is always bounded.
4. Show that if f_n converges to f, and g_n to g, then $\lim(f_n, g_n) = (f, g)$.

D. Linear Manifolds and Projections

We will discuss the properties of certain subsets of the Hilbert space. These properties do not depend on the separability of the space, their discussion can be carried out without introducing o.n. sequences.

Given a set S, the set of all elements orthogonal to S is called the *orthogonal complement* of S and is denoted by $S^{\perp}$.

The term "complement" is justified by the fact that **O** is the only common element in **S** and $\mathbf{S}^{\perp}$ because $f \in \mathbf{S}$ and $f \in \mathbf{S}^{\perp}$ together imply that $(f, f) = 0$.

The set $\mathbf{S}^{\perp}$ is clearly a linear manifold. It is also closed. The closure of $\mathbf{S}^{\perp}$ is demonstrated as follows: Let f_n be a sequence in $\mathbf{S}^{\perp}$ whose limit is f^*. To show that f^* is contained in $\mathbf{S}^{\perp}$, we note first that $(f_n, g) = 0$ holds for all n and all elements of **S**, therefore $\lim(f_n, g)$ is 0 for all $g \in \mathbf{S}$. Hence $(f^*, g) = (\lim f_n, g) = \lim(f_n, g) = 0$ since the continuity of the inner product permits us to move the "lim" out of the parenthesis. The set $\mathbf{S}^{\perp\perp}$ is a closed linear manifold which contains **S**, because if $f \in \mathbf{S}$, then $(f, g) = 0$ for every $g \in \mathbf{S}$ and therefore f is in the orthogonal complement of $\mathbf{S}^{\perp}$. In symbols $\mathbf{S} \subset \mathbf{S}^{\perp\perp}$.

The following theorem is of fundamental importance. We shall call it *the basic projection theorem.*

Given a closed linear manifold **M**, any element $f \in \mathfrak{H}$ can be uniquely decomposed in the form $f = f_0 + f_1$, where $f_0 \in \mathbf{M}$ and $f_1 \in \mathbf{M}^{\perp}$.

If the decomposition is possible at all, its uniqueness follows from the fact that from $f = f_0 + f_1 = f_0' + f_1'$, it follows that $f_0 - f_0' = f_1' - f_1$ is an element of both **M** and $\mathbf{M}^{\perp}$, and therefore **O**. When $f \in \mathbf{M}$, the decomposition is clearly $f_0 = f$, $f_1 = 0$. When f is not in **M**, we prove the existence in **M** of an element nearest to f; i.e., an element g_0 such that

$$\|f - g_0\| \leqq \|f - g\| \tag{I.45}$$

for all $g \in \mathbf{M}$.

Let d be the lower bound of $\|f - g\|$. There is then a sequence $g_n \in \mathbf{M}$ such that $\lim\|f - g_n\| = d$. We apply the parallelogram relation (I.20) to the elements $f - g_n$ and $f - g_m$. Then

$$\|2f - g_n - g_m\|^2 + \|g_n - g_m\|^2 = 2\|f - g_n\|^2 + 2\|f - g_m\|^2. \tag{I.46}$$

Hence

$$\|g_n - g_m\|^2 = 2\{\|f - g_n\|^2 + \|f - g_m\|^2 - 2\,\|f - \tfrac{1}{2}(g_n + g_m)\|^2\}. \tag{I.47}$$

According to the definition of g_n, we can choose n and m so large that $\|f - g_n\|^2 < d^2 + \varepsilon$, $\|f - g_m\|^2 < d^2 + \varepsilon$. Therefore

$$\|g_n - g_m\|^2 \leqq 2(d^2 + d^2 + 2\varepsilon - 2d^2) = 4\varepsilon. \tag{I.48}$$

Thus the convergence of g_n is assured and the assumption that **M** is closed guarantees that the limit element g_0 lies in **M**. We prove now that $f - g_0 \in \mathbf{M}^{\perp}$. Let h be an arbitrary element of **M**. Then according to (I.45)

$$\|f - g_0\|^2 \leqq \|f - g_0 + \alpha h\|^2 \tag{I.49}$$

for any number α. Consequently

$$2 \operatorname{Re} \alpha^*(f - g_0, h) + |\alpha|^2 \|h\|^2 \geqq 0 \tag{I.50}$$

for all α. This is possible only when

$$(f - g_0, h) = 0, \tag{I.51}$$

and since the relation holds for every $h \in \mathbf{M}$, the element $f - g_0$ belongs to $\mathbf{M}^\perp$. The decomposition is thus accomplished with $f_0 = g_0$, $f_1 = f - g_0$.

The relation

$$\|f\|^2 = \|f_0\|^2 + \|f_1\|^2 \tag{I.52}$$

follows immediately from $(f_0, f_1) = 0$. The element f_0 is called the projection of f on $\mathbf{M}$; it is denoted by the symbol Pf, where P is called the *projection operator* of $\mathbf{M}$.

It is easy to prove the following relations valid for any closed linear manifold and any element of $\mathfrak{H}$:

(a) $\|Pf\| \leqq \|f\|$, (b) $Pf + Pg = P(f + g)$, (c) $P(Pf) = Pf$.

By means of the basic projection theorem, we can show that, if the closed linear manifold $\mathbf{M}$ is a proper subset of the closed linear manifold $\mathbf{N}$, there exists an element $h \in \mathbf{N}$ which is orthogonal to $\mathbf{M}$. To verify this proposition we select an element of $\mathbf{N}$ which is not in $\mathbf{M}$ and subtract from it its projection on $\mathbf{M}$.

Let us assume that $\mathbf{S}$ is a closed linear manifold. We can now show that $\mathbf{S} = \mathbf{S}^{\perp\perp}$. We know already that $\mathbf{S} \subset \mathbf{S}^{\perp\perp}$. If the set $\mathbf{S}$ were a proper subset of $\mathbf{S}^{\perp\perp}$ we could find an $h \in \mathbf{S}^{\perp\perp}$ which is orthogonal to $\mathbf{S}$ and therefore contained in $\mathbf{S}^\perp$. But the relations $h \in \mathbf{S}^\perp$ and $h \in \mathbf{S}^{\perp\perp}$ together imply that $h = \mathbf{O}$.

If, on the other hand, $\mathbf{S}$ is not originally a closed linear manifold, we can enlarge it first to a linear manifold by adding all linear combinations of the elements contained in $\mathbf{S}$, and finally, we could add to the set so enlarged all its limit points. So ultimately we arrive at a closed linear manifold $\bar{\mathbf{S}}$. During the process of enlarging the original set $\mathbf{S}$, the set $\mathbf{S}^\perp$ does not change because of the linearity and continuity of the inner product. Thus we have $\bar{\mathbf{S}}^\perp = \mathbf{S}^\perp$ and therefore also $\bar{\mathbf{S}}^{\perp\perp} = \mathbf{S}^{\perp\perp}$. But since $\bar{\mathbf{S}} = \bar{\mathbf{S}}^{\perp\perp}$, it follows that $\mathbf{S}^{\perp\perp} = \bar{\mathbf{S}}$. In words: The least closed linear manifold spanned by the set $\mathbf{S}$ is $\mathbf{S}^{\perp\perp}$.

It is clear now that whenever we are dealing with closed linear manifolds, if $\mathbf{A}$ is the orthogonal complement of $\mathbf{B}$, then $\mathbf{B}$ is the orthogonal complement of $\mathbf{A}$.

Closed linear manifolds are frequently called subspaces because they possess essentially all the properties of the original space.

II. Bounded Linear Operators

A. Definitions

Our objective is to study functions in Hilbert space. These functions are defined in a subset of the space called the *domain* of the function. Two kinds of functions must be considered; those which assign numbers as values to elements of the domain, and those which assign elements of the Hilbert space. The former are called *functionals*, the latter *operators*. Examples of functionals are the norm and the scalar product of a variable element with a fixed element. Examples of operators are easy to construct in the space $\mathfrak{L}_2$. An important operator is one which assigns to every differentiable function its derivative. Functionals will be denoted by Greek capital letters; e.g., $x = \Phi(f)$ means that the functional Φ orders to the element f the number x. Operators will be denoted by Roman capital letters; $g = Tf$ means that the operator T orders the element g to the element f. Sometimes it is said that T transforms f into g, and T is called a *transformation* of the Hilbert space.

The domain of the operator T is denoted by $\mathbf{D}_T$, the set of elements $g = Tf$ obtained as f varies through $\mathbf{D}_T$ is called the *range* of T.

An operator T_2 is called an *extension* of T_1 if $\mathbf{D}_{T_2} \supset \mathbf{D}_{T_1}$, and $T_2 f = T_1 f$ for every $f \in \mathbf{D}_{T_1}$. An extension of a functional is defined similarly.

An operator T is called *linear* when $\mathbf{D}_T$ is a linear manifold and

$$T(\alpha_1 f_1 + \alpha_2 f_2) = \alpha_1 T f_1 + \alpha_2 T f_2 \tag{II.1}$$

for all f_1 and f_2 in $\mathbf{D}_T$. For a *linear functional* we have:

$$\Phi(\alpha_1 f_1 + \alpha_2 f_2) = \alpha_1 \Phi(f_1) + \alpha_2 \Phi(f_2). \tag{II.2}$$

Clearly $T\mathbf{O} = \mathbf{O}$, and $\varphi(\mathbf{O}) = 0$.

An operator T is called *bounded* if there exists a number K such that $\|Tf\| \leqq K\|f\|$ for every $f \in \mathbf{D}_T$. The least suitable K is called *the bound* or *the norm* of the operator.

An operator T is called *continuous* at the point f_0 ($f_0 \in \mathbf{D}_T$) if $Tf_n \to Tf_0$ for every sequence $f_n \in \mathbf{D}_T$, such that $f_n \to f_0$. A linear operator continuous at one point is continuous at every point in its domain.

In fact, if T is known to be continuous at g_0 and the continuity at another point $f_0 \in \mathbf{D}_T$ is to be proven, we introduce $g = f + g_0 - f_0$. Then, $f \in \mathbf{D}_T$ implies $g \in \mathbf{D}_T$. From the linearity of the operator it follows that

$Tg - Tg_0 = Tf - Tf_0$. Therefore $\|g - g_0\| = \|f - f_0\| < \delta$ implies $\|Tg - Tg_0\| = \|Tf - Tf_0\| < \varepsilon$.

For linear operators, continuity and boundedness are equivalent concepts. To prove that continuity implies boundedness, we proceed as follows: Continuity at $\mathbf{O}$ requires that $\|Tf\| \leqq \varepsilon$ whenever $\|f\| \leqq \delta(\varepsilon)$ for every $f \in \mathbf{D}_T$. In particular, it requires the existence of a positive number $\delta = \delta(1)$, so that $\|Tf\| \leqq 1$ for $\|f\| \leqq \delta$. For a general element $g \in \mathbf{D}_T$, we write $f = \delta g/\|g\|$. Then $\|f\| = \delta$, and

$$\|Tg\| = \frac{\|g\|}{\delta} \|Tf\| \leqq \frac{1}{\delta} \|g\|. \tag{II.3}$$

Therefore T is bounded with a bound not greater than $1/\delta$.

Boundedness and continuity of functionals are defined in a similar manner, and it is easy to show that in the case of linear functionals boundedness and continuity are equivalent.

A bounded linear operator and a bounded linear functional can be extended without increasing their bounds until their domains coincide with the space $\mathfrak{H}$. We prove this statement for bounded linear operators. If $\mathbf{D}$ is not already closed, the operator is extended over $[\mathbf{D}]$, the closed linear manifold spanned by $\mathbf{D}$, by means of a simple continuity argument. Let $f^* \in [\mathbf{D}]$, then every sequence $f_n \in \mathbf{D}$ which tends to f^* has the property that $\|f_n - f_m\| \to 0$. Therefore $\|Tf_n - Tf_m\|$ also tends to 0, the sequence Tf_n converges to an element g which is independent from the particular sequence chosen. We set $T_e f^* = g$, where T_e is the extended operator. It is easy to show that the bound of T_e is the same as that of T. If $[\mathbf{D}]$ is not $\mathfrak{H}$, we define $T_e h = \mathbf{O}$ for every $h \in \mathbf{D}^\perp$, or in other words, we set

$$T_e f = T_e P f,$$

where Pf is the projection of f on $[\mathbf{D}]$.

As a consequence of the extension theorem just proven, it is permissible to assume that every bounded linear operator and every bounded linear functional is defined over the entire space. An unbounded linear operator cannot be so defined. The discussion of unbounded operators is a great deal more difficult, largely because of the care that must be exercised with regard to their domains.

If A and B are bounded linear operators, there is no difficulty involved in the definition of such operators as $C = A + B$, or $D = AB$. Clearly $Cf = Af + Bf$, and $Df = A(Bf)$. When A and B are unbounded, it is conceivable that $\mathbf{D}_A$ and $\mathbf{D}_B$ have only the $\mathbf{O}$ element in common, then $\mathbf{D}_C$ can consist only of the $\mathbf{O}$ element. Similarly, the range of B and the domain of A may only have the $\mathbf{O}$ element in common, resulting in a rather restricted operator AB.

The operator whose domain is $\mathfrak{H}$ and which orders every element to itself is called the *identity operator*. It is designated by I. The *null operator* O also has $\mathfrak{H}$ as its domain, and $Of = \mathbf{O}$.

Exercises

1. Define boundedness and continuity of functionals, and show that for linear functionals these concepts are equivalent.

2. Consider the space $\mathfrak{L}_2[-1, +1]$. Let the domain of Φ be the set of all polynomials and let

$$\Phi(p) = \int_{-1}^{+1} p\, dx.$$

Prove that Φ is a linear functional. Is it bounded? Can it be extended? If so, how? What is the subspace S over which $\Phi(p) = 0$? What is $S^{\perp}$?

3. Consider the sequential Hilbert space, and let Φ order to every sequence in the space its first element. Is this a linear functional? Is it bounded?

4. Consider the space $\mathfrak{L}_2[-1, +1]$, and define the operator T for $1, x, x^2, \ldots$, by $Tx^n = nx^{n-1}$, then fix its domain as the set of polynomials demanding linearity. Is this a bounded linear operator? Can its domain be extended to include functions other than polynomials?

5. Let g_0 be a fixed element of $\mathfrak{H}$. Show that $\Phi(f) = (f, g_0)$ is a bounded linear functional. What is its bound?

6. Prove that the inequality $|Tf, g)| \leqq K\|f\|\;\|g\|$ valid for every f and g in $\mathfrak{H}$ implies $\|Tf\| \leqq K\|f\|$ for every f.

B. Bounded Linear Functionals

A bounded linear functional Φ satisfies Eq. (II.2) as well as the inequality $|\Phi(f)| \leqq K\|f\|$ for some constant K.

Given a fixed element g_0, the inner product (f, g_0) is a bounded linear functional of f; its bound is readily calculated from Schwarz's inequality

$$|(f, g_0)| \leqq \|f\|\;\|g_0\|. \tag{II.4}$$

Thus $K \leqq \|g_0\|$, and substituting $f = g_0$, we obtain $K = \|g_0\|$.

According to a theorem of F. Riesz, every bounded linear functional is of the form

$$\Phi(f) = (f, g_0). \tag{II.5}$$

The bound of the functional is $\|g_0\|$, and the element g_0 is uniquely determined by the functional. This interesting theorem has the following consequences: It reveals that all bounded linear functionals are really very simple in their structure. It establishes an isomorphism (one-to-one correspondence) between bounded linear functionals and the elements of the Hilbert space. This correspondence preserves norm in the sense that it orders to each element of the space a linear functional whose bound is equal to the norm of the element.

Proof: Let us assume that Φ is extended so that it is defined over the entire space, and let $\mathbf{G}$ be the set of all elements f for which $\Phi(f) = 0$. The linearity of Φ ensures that $\mathbf{G}$ is a linear manifold, the boundedness of Φ that $\mathbf{G}$ is closed. If $\mathbf{G} = \mathfrak{H}$ then $\Phi(f) \equiv 0$, therefore $g_0 = \mathbf{O}$. If $\mathbf{G} \neq \mathfrak{H}$, there is a nonzero element $g \in \mathbf{G}^\perp$. Consider now the element

$$u = \Phi(f)g - \Phi(g)f, \tag{II.6}$$

while f varies over $\mathfrak{H}$. Since $\Phi(u) = 0$ for every f, therefore $u \in \mathbf{G}$. Consequently

$$(u, g) = \Phi(f)(g, g) - \Phi(g)(f, g) = 0. \tag{II.7}$$

Hence

$$\Phi(f) = \frac{\Phi(g)}{(g, g)} (f, g) \tag{II.8}$$

is valid for every f. The element $g_0 = \Phi(g)^* g / \|g\|^2$ has the property required by the theorem. Its uniqueness follows from the fact that if a second element h_0 would also generate the same linear functional, then the equation $(f, g_0) = (f, h_0)$ would hold for every f. Therefore $(f, g_0 - h_0) = 0$, and for $f = g_0 - h_0$ it follows that $g_0 - h_0 = \mathbf{O}$.

The theorem of Riesz provides a method for extending a bounded linear functional not defined everywhere originally, without increasing its bound. Let the functional be defined over a proper subspace $\mathbf{L}$ of $\mathfrak{H}$. This subspace is again either a Hilbert space or a finite-dimensional inner product space. In either case, Riesz' theorem is applicable in this space; it provides an element $g_0 \in \mathbf{L}$ such that $\Phi(f) = (f, g_0)$ for every $f \in \mathbf{L}$. The bound of Φ is $\|g_0\|$. The extension of Φ is accomplished by setting $\Phi_e(f) = (f, g_0)$ for every $f \in \mathfrak{H}$. The bound remains the same.

C. The Adjoint of a Bounded Linear Operator

In this section, we consider only bounded linear operators defined over the entire Hilbert space, therefore we will not repeat this qualification every time. Clearly sums and products of a finite number of such operators can be formed without complications, one must, of course, keep in mind that AB is in general not equal to BA.

Given an operator A, the expression (Af, g) is a linear functional in both f and g. Let us keep g fixed, then the theorem of F. Riesz asserts the existence of an element g^* such that

$$(Af, g) = (f, g^*) \tag{II.9}$$

for all $f \in \mathfrak{H}$. This procedure can be applied to any $g \in \mathfrak{H}$, therefore we obtain a mapping of the space as g runs through all elements of $\mathfrak{H}$. This mapping serves as the definition of the operator

$$A^\dagger g = g^*, \tag{II.10}$$

called the operator *adjoint* to A. Clearly $A^\dagger$ is a linear operator. It is bounded, because from

$$(Af, g) = (f, A^\dagger g) \tag{II.11}$$

follows

$$|(f, A^\dagger g)| = |(Af, g)| = \|Af\| \; \|g\| = K\|f\| \; \|g\|, \tag{II.12}$$

where K is the bound of A. This inequality is valid for every f and g, therefore also for $f = A^\dagger g$. Hence $\|A^\dagger g\|^2 \leqq K\|A^\dagger g\| \; \|g\|$, and therefore

$$\|A^\dagger g\| \leqq K\|g\|. \tag{II.13}$$

Thus the bound of $A^\dagger$ does not exceed that of A. Since (II.11) implies that $(A^\dagger)^\dagger = A$, the bounds of A and $A^\dagger$ must be equal.

The following propositions are easily proven: $(\alpha I)^\dagger = \alpha^* I$; $(A + B)^\dagger = A^\dagger + B^\dagger$; and $(AB)^\dagger = B^\dagger A^\dagger$.

When $A^\dagger = A$ the operator is called *self-adjoint*. For bounded operators the expressions self-adjoint, symmetric, or Hermitean symmetric mean the same thing.

The operator $AA^\dagger$ and $A^\dagger A$ are always self-adjoint, whatever A, but these two operators are generally not equal. The operators $A + A^\dagger$ and $i(A - A^\dagger)$ are also self-adjoint.

Let H be a self-adjoint operator with bound K. Then

$$(Hf, f) = (f, Hf) = (Hf, f)^*, \tag{II.14}$$

therefore (Hf, f) is real. Moreover

$$|(Hf, f)| \leqq \|Hf\| \; \|f\| \leqq K\|f\|^2, \tag{II.15}$$

so that $(Hf, f)/\|f\|^2$ varies between $-K$ and $+K$. Conversely, it is possible to prove, that

$$|(Hf, f)| \leqq K\|f\|^2, \tag{II.16}$$

for every f implies that H is bounded, and its bound is not greater than K (Stone, 1932, pp. 54–55).

When $(Hf, f) \geqq 0$ for every f, then H is called a *positive, self-adjoint operator*. If the self-adjoint operators A and B are such that $H = A - B$ is a positive operator, then A is said to be greater than B.

The proofs of the following propositions may be easily worked out by the reader:

(1). The operators $AA^\dagger$ and $A^\dagger A$ are always positive.
(2). A projection operator is always positive.
(3). If H is a positive operator, so is H^n, where n is any positive integer.

D. Matrix Representation of Linear Operators

Before attempting the representation of linear operators in Hilbert space by means of matrices, we summarize the situation that prevails in a finite-dimensional space where the relation between operator theory and matrix algebra is direct and simple.

Let us call a linear operator in a finite-dimensional vector space a transformation. It transforms an element $\mathbf{X}$ into $\mathbf{Y} = A\mathbf{X}$. Such a transformation is completely determined once it is known what elements the unit vectors

$$\begin{aligned} e_1 &= \{1, 0, 0, \dots, 0\}, \\ e_2 &= \{0, 1, 0, \dots, 0\}. \\ &\cdot \\ &\cdot \\ &\cdot \\ e_n &= \{0, 0, 0, \dots, 1\} \end{aligned} \tag{II.17}$$

are transformed into. Let these be

$$g_k = Ae_k = \sum_{i=1}^{n} a_{ik} e_i. \tag{II.18}$$

The general vector $\mathbf{X} = \sum_{k=1}^{n} x_k e_k$ is transformed into $\mathbf{Y} = A\mathbf{X}$, where the components of $\mathbf{Y} = \{y_1, y_2, \dots, y_n\}$ are given by

$$y_i = \sum_{k=1}^{n} a_{ik} x_k, \quad i = 1, 2, \dots, n. \tag{II.19}$$

Thus every $n \times n$ matrix corresponds to a linear transformation and the algebra of transformations is the ordinary matrix calculus. We recall from elementary algebra that, if the determinant of the matrix $\{a_{ik}\}$ is zero, the system of equations

$$\sum_{k=1}^{n} a_{ik} x_k = 0, \quad i = 1, 2, \ldots, n \tag{II.20}$$

has a nontrivial solution, but when $\det\{a_{ik}\} \neq 0$, the equations (II.19) have a unique solution for every $\mathbf{Y} = \{y_1, y_2, \ldots, y_n\}$. In this latter case, the transformation $\mathbf{Y} = A\mathbf{X}$ is a one-to-one transformation of the n-dimensional vector space. It can be inverted; i.e., there is a transformation $B = A^{-1}$, such that

$$AA^{-1} = A^{-1}A = I \tag{II.21}$$

holds. The matrix form of (II.21) is

$$\sum_{k=1}^{n} a_{ik} b_{kj} = \sum_{k=1}^{n} a_{ki} b_{jk} = \delta_{ij}. \tag{II.22}$$

The situation is considerably more complicated in Hilbert space. Let us contemplate the sequential Hilbert space first. The n unit vectors (II.17) are replaced by an infinite sequence

$$e_1 = \{1, 0, 0, \ldots\}, \qquad e_2 = \{0, 1, 0, \ldots\}, \tag{II.23}$$

and so on *ad infinitum*. As in n-dimensional space, we may define

$$g_k = Ae_k = \sum_{i=1}^{\infty} a_{ik} e_i, \tag{II.24}$$

but now the a_{ik}'s are no longer arbitrary. They must be so restricted that $\sum_{i=1}^{\infty} |a_{ik}|^2$ converges for every k, otherwise the g_k are not elements of the sequential Hilbert space. With this restriction the a_{ik}'s determine the transform of every element $\mathbf{X}$ in the linear manifold spanned by the vectors (II.23). More precisely, whenever

$$\mathbf{X} = \sum_{k=1}^{N} x_k e_k, \tag{II.25}$$

then the components of $\mathbf{Y} = A\mathbf{X}$ are given by

$$y_i = \sum_{k=1}^{N} a_{ik} x_k, \quad i = 1, 2, \ldots. \tag{II.26}$$

Note, however, that the summations in (II.25) and (II.26) should be confined to finite number of terms, otherwise convergence difficulties may arise. One cannot assert that the transformation A is always definable over the *closed* linear manifold spanned by the vectors e_1, e_2, etc. In principle, a matrix only defines a linear operator whose domain is the linear manifold **L** spanned by the vectors e_1, e_2, etc. Some operators permit extension over a larger domain, perhaps even over the entire space.

The following examples illustrate what might happen:

(a) Let the linear operator A be defined over the unit vectors by means of the equations $Ae_k = e_k$, or equivalently, by $a_{ik} = \delta_{ik}$. Within the linear manifold spanned by $\{e_n\}$, the operator A is the same as the identity operator I. The latter is an extension of A.

(b) Let H be defined by the equations $He_k = ke_k$, $k = 1, 2, \ldots$. The domain of this operator can be extended to include the set of sequences $\{x_n\}$ for which $\Sigma|kx_k|^2$ is convergent. This set forms a linear manifold **M** which contains **L**.

A linear transformation T, whose domain **D** is not closed, can frequently be extended by the following continuity argument: If there is a limit point f of **D** which is not in **D**, it may happen that, whenever $f_n \to f$, the sequence Tf_n is a convergent sequence which tends to an element g. Then we assign f to the domain of the extended operator T, and say that $Tf = g$. The new transformation is called a closed extension of T. Its domain is still not necessarily a closed linear manifold. It is practical to consider the matrix as the representative of this extended operator T.

The following theorem is proven in mathematical texts:

If the matrix a_{ik} is such that there is a constant K with the property that

$$\sum_{i=1}^{\infty} \left| \sum_{k=1}^{\infty} a_{ik} x_k \right|^2 \leqq K^2 \sum_{k=1}^{\infty} |x_k|^2 \qquad \text{(II.27)}$$

for every sequence $\{x_n\}$ in the sequential Hilbert space, then the matrix a_{ik} defines a bounded linear operator A which, after proper extension, is defined over the entire Hilbert space. The adjoint operator $A^\dagger$ has the matrix a_{ki}^*, the bounds of A and $A^\dagger$ are equal and do not exceed K.

Conversely, if a linear operator A and its adjoint $A^\dagger$ are defined over the entire Hilbert space, then A may be represented by a matrix a_{ik} which satisfies (II.27). Such an operator is therefore bounded. This last proposition is one of the deeper theorems of functional analysis. It implies that a self-adjoint operator defined over the entire space is bounded. (For proof see Akhiezer and Glazman, 1963, p. 48, or Stone, 1932, p. 61.)

The construction of the matrix representation of an operator given in abstract space begins with the introduction of a complete o.n. sequence $\{\varphi_n\}$. Then we define

$$a_{ik} = (A\varphi_k, \varphi_i) \tag{II.28}$$

for all pairs i and k. Clearly $A\varphi_k = \sum_{i=1}^{\infty} a_{ik}\varphi_i$, and for any element f in the linear manifold **L** spanned by $\{\varphi_n\}$:

$$f = \sum_{k=1}^{N} x_k\varphi_k, \qquad Af = \sum_{i=1}^{\infty}\left(\sum_{k=1}^{N} a_{ik}x_k\right)\varphi_i. \tag{II.29}$$

Here

$$\|Af\|^2 = \sum_{i=1}^{\infty}\left|\sum_{k=1}^{N} a_{ik}x_k\right|^2, \tag{II.30}$$

while $\|f\|^2 = \sum_{k=1}^{N} |x_k|^2$. The original operator A may have had a larger domain than **L** and this domain may be regained by extending the matrix operator. However, only such elements $f = \sum_{k=1}^{\infty} x_k\varphi_k$ may be included in the extended domain which do not cause the expression (II.30) to become infinite as $N \to \infty$.

The physicist obtains his matrix elements on transition from the space $\mathfrak{L}_2$ to the sequential Hilbert space. In this transition, Eq. (II.28) takes the form

$$a_{ik} = \int (A\varphi_k)\varphi_i^*\,dx = \int \varphi_i^* A\varphi_k\,dx. \tag{II.31}$$

The physicist keeps track of his functions by means of indices, which in the applications are usually quantum numbers. He prefers not to write the function symbol φ, only its index i, k, etc. Thus he writes:

$$a_{ik} = \langle i|A|k\rangle. \tag{II.32}$$

Here the symbols $\langle i\,|$ and $|\,k\rangle$ stand for functions. If α is a complex number and the function $\langle i\,|$ is multiplied by α, then a_{ik} is multiplied by α^*, because the complex conjugate of φ_i enters into (II.31). Actually, the second bar in the physicist's notation is unnecessary, because using the Dirac bracket introduced in Section I, B,

$$a_{ik} = \langle i\,|\,Ak\rangle, \tag{II.33}$$

where $|Ak\rangle$ is to be interpreted as the transform by A of the function having index k.

The matrix elements which describe a linear operator depend on the choice of the o.n. set φ_n. Change to a new set is equivalent to a coordinate transformation in n-dimensional vector space. One of the important tasks in operator theory is to find for a given operator the o.n. set which provides a particularly simple description of the operator.

Exercises

1. A linear operator T is defined by the equations $T\varphi_n = \varphi_{n+1}$, $n = 1, 2, 3, \ldots$. Show that T can be extended so that T is defined over $\mathfrak{H}$. Write down the matrix of T and that of $T^\dagger$. Prove that $T^\dagger T = I$, but that $TT^\dagger \neq I$. (Note: T is the extended operator, I is the identity.)

2. The functions $e^{2\pi i n x}$ ($n = 0, \pm 1, \pm 2, \ldots$) form orthonormal functions in $\mathfrak{L}_2$ over the interval $[0, 1]$. Find the matrix of the operator d/dx in this o.n. system. Note: It is simplest to number the rows and columns of the matrix from $-\infty$ to $+\infty$ in this case.

What is the matrix of the same operator for the o.n. system obtained after normalization of the sequence 1, $\cos 2\pi x$, $\sin 2\pi x$, $\cos 4\pi x$, $\sin 4\pi x$, etc.?

3. In the text it was said that the set of sequences $\{x_n\}$ for which $\Sigma\, |kx_k|^2$ is convergent is a linear manifold. Verify this statement. Is this manifold closed?

E. Projection Operators

We have seen in Section I,D that given a closed linear manifold $\mathbf{M}$, every element $f \in \mathfrak{H}$ can be decomposed in the following manner:

$$f = f_0 + f_1, \tag{II.34}$$

where $f_0 \in \mathbf{M}$ and $f_1 \in \mathbf{M}^\perp$. Moreover, we found that this decomposition is unique. The relationship

$$f_0 = Pf \tag{II.35}$$

defines the *projection operator* P associated with $\mathbf{M}$. The domain of P is $\mathfrak{H}$, its range is $\mathbf{M}$. The linearity of P is readily proven by multiplying equations of the type of (II.34) by complex constants and arriving at

$$\alpha f + \beta g = (\alpha f_0 + \beta g_0) + (\alpha f_1 + \beta g_1), \tag{II.36}$$

where the first expression in parenthesis belongs to $\mathbf{M}$, the second to $\mathbf{M}^\perp$. Every projection is a bounded operator with the bound 1. Moreover $P^2 = P$, because $Pf_0 = f_0$. For arbitrary f and g we have $(Pf, g) = (f_0, g) = (f_0, g_0) = (f, g_0) = (f, Pg)$, because $(f_1, g_0) = (f_0, g_1) = 0$. Therefore $P^\dagger = P$.

Conversely, given a bounded, self-adjoint operator P, such that $P^2 = P$, there is always a closed linear manifold $\mathbf{M}$ of which P is the projection operator.

Proof: The equation $Pg = \mathbf{O}$ defines a closed linear manifold N. Since $P(f - Pf) = \mathbf{O}$ for every f, therefore $f - Pf \in \mathrm{N}$. Moreover Pf is orthogonal to N, because $(f, Pg) = (Pf, g) = 0$ for every g in N, Pg being $\mathbf{O}$. Therefore $\mathbf{M} = \mathrm{N}^{\perp}$ is the desired manifold.

If P is a projection of $\mathbf{M}$, $I - P$ is also a projection. It is the projection of the orthogonal complement $\mathbf{M}^{\perp}$.

Let $\mathbf{M}_1$ and $\mathbf{M}_2$ be two closed linear manifolds, P_1 and P_2 the corresponding projections. Then $\mathbf{M}_1$ and $\mathbf{M}_2$ are orthogonal to each other, if and only if $P_1P_2 = P_2P_1 = \mathrm{O}$. (Note that $P_1P_2 = \mathrm{O}$ implies that $P_2P_1 = (P_1P_2)^\dagger = \mathrm{O}^\dagger = \mathrm{O}$.)

Proof. Let $\mathbf{M}_1$ and $\mathbf{M}_2$ be orthogonal, then

$$(P_2P_1f, g) = (P_1f, P_2g) = 0 \tag{II.37}$$

for every f and g. We choose in particular $g = P_2P_1f$, then $\|P_2P_1f\|^2 = 0$ for arbitrary f. Hence $P_2P_1 = \mathrm{O}$. Conversely, if $P_2P_1 = \mathrm{O}$ holds, then (II.37) is valid for arbitrary f and g. Take an arbitrary element $f_0 \in \mathbf{M}_1$ and another $g_0 \in \mathbf{M}_2$. For these elements $P_1f_0 = f_0$, $P_2g_0 = g_0$; therefore from (II.37) it follows that $(P_1f_0, P_2g_0) = (f_0, g_0) = 0$, the manifolds $\mathbf{M}_1$ and $\mathbf{M}_2$ are orthogonal to each other.

The sum of two projections is a projection, if and only if the corresponding manifolds are orthogonal.

If $P_1 + P_2$ is a projection, then $(P_1 + P_2)^2 = P_1{}^2 + P_2{}^2 + P_1P_2 + P_2P_1 = P_1 + P_2$, therefore

$$P_1P_2 + P_2P_1 = \mathrm{O}. \tag{II.38}$$

Multiply by P_2 on the left:

$$P_2P_1P_2 + P_2P_1 = \mathrm{O}. \tag{II.39}$$

Now multiply by P_2 on the right:

$$P_1P_2 + P_2P_1P_2 = \mathrm{O}. \tag{II.40}$$

Equations (II.38)–(II.40) together imply that $P_2P_1P_2 = \mathrm{O}$, and therefore also $P_1P_2 = \mathrm{O}$.

Conversely if P_1 and P_2 are projections and $P_1P_2 = \mathrm{O}$, then $(P_1 + P_2)^2 = P_1 + P_2$, so $P_1 + P_2$ is a projection.

The reader should be able to prove the following theorems:

(1) If $\mathbf{M}_1 \subset \mathbf{M}_2$, then the following four operators are equal: P_1, P_2P_1,

P_1P_2, $P_2P_1P_2$. Furthermore $P_2 - P_1$ is a projection, $\|P_2f\| \geqq \|P_1f\|$ for every $f \in \mathfrak{H}$.

(2) $P_2 - P_1$ is a projection if and only if $\mathbf{M}_1 \subset \mathbf{M}_2$.

(3) The equation $P_2P_1 = P_1$ implies $\mathbf{M}_1 \subset \mathbf{M}_2$.

(4) If the inequality $\|P_2f\| \geqq \|P_1f\|$ holds for every f, then $\mathbf{M}_1 \subset \mathbf{M}_2$.

(5) Given an increasing sequence of closed linear manifolds $\mathbf{M}_1 \subset \mathbf{M}_2 \subset \mathbf{M}_3 \subset \ldots$, the following inequalities hold $\|P_1f\| \leqq \|P_2f\| \leqq \cdots \leqq \|f\|$.

(6) If the sequence $P_1 \leqq P_2 \leqq P_3 \ldots$ is infinite, the sequence P_nf tends to a limit as $n \to \infty$ for every $f \in \mathfrak{H}$.

(7) If $\mathbf{M}$ is spanned by the orthonormal elements $\varphi_1, \ldots, \varphi_n$ and $\mathbf{M}^\perp$ by the elements $\varphi_{n+1}, \varphi_{n+2}, \ldots$, then the matrix representation of P is $P_{ik} = \delta_{ik}$ for $k \leqq n$ and $P_{ik} = 0$ for $k > n$.

Interesting examples of projection operators can be constructed in the space $\mathfrak{L}_1[-\infty, +\infty]$. Let $f(x)$ be an element of this space. A family of projection operators dependent on a real parameter λ may be constructed in the following manner: Let $P(\lambda)f(x) = f(x)$ for $x \leqq \lambda$ and 0 for $x > \lambda$. The following propositions may then be verified:

(a) $P(\lambda)$ is a projection operator for any real λ.

(b) $P(\lambda) - P(\mu)$ is a projection operator when $\lambda \geqq \mu$.

(c) The norm $\|P(\lambda)f\|$ is a monotone increasing function of λ for any fixed $f \in \mathfrak{L}_2$.

Such projection operators play an important role in the theory of self-adjoint operators.

III. Spectral Theory of Bounded Self-Adjoint Operators

A. Initial Formulation of the Spectral Problem

The discussion of bounded operators is considerably simpler than that of the unbounded ones because the former can be readily extended so that they are defined over the entire Hilbert space. We assume therefore in this part that every operator is linear and defined over the entire space.

A bounded linear operator is said to be *self-adjoint* when it coincides with its adjoint. Such operators are frequently called *Hermitean-symmetric*, or briefly *Hermitean* operators and are usually denoted by the letter H. Characteristic for such an operator is that the equation

$$(Hf, g) = (f, gH) \tag{III.1}$$

holds for every f and g in $\mathfrak{H}$. Let the matrix representation of such an operator possess the elements h_{ik}, then (III.1) is equivalent to $h_{ik} = h^*_{ki}$, no matter what o.n. system is used to obtain the matrix representation.

Bounded, self-adjoint operators possess a number of interesting properties. We shall establish a few of these.

(1) If $(Hf, f) = 0$ for every f, then $H = \mathrm{O}$.

Proof. From the relation

$$(H(f \pm g), (f \pm g)) = (Hf, f) \pm (Hf, g) \pm (Hg, f) + (Hg, g)$$

and $(Hg, f) = (g, Hf) = (Hf, g)^*$ it follows that

$$4\,\mathrm{Re}(Hf, g) = (H(f+g), (f+g)) - (H(f-g), (f-g)). \qquad \text{(III.2)}$$

On replacing g by ig, we get

$$4\,\mathrm{Im}(Hf, g) = (H(f+ig), (f+ig)) - (H(f-ig), (f-ig)). \qquad \text{(III.3)}$$

The condition of the theorem requires that the right-hand sides of (III.2) and (III.3) vanish for any f and g. Consequently $(Hf, g) = 0$, again for every f and g. On letting $g = Hf$, we obtain $(Hf, Hf) = 0$ which is equivalent to $Hf = \mathrm{O}$ valid for every f.

(2) The eigenvalues of H are all real; i.e., the equation $Hf = zf$ requires that z is a real number, or else $f = \mathbf{O}$.

Proof. From $Hf = zf$ it follows that $(Hf, f) = (zf, f) = z(f, f)$ and also that $(Hf, f) = (f, Hf) = (f, zf) = z^*(f, f)$. Consequently $z\|f\|^2 = z^*\|f\|^2$, which in turn requires that either $z = z^*$, or that $f = \mathbf{O}$.

(3) If λ and μ are two different eigenvalues of H and $Hf = \lambda f$, $Hg = \mu g$, then $(f, g) = 0$.

Proof. $(Hf, g) = \lambda(f, g)$ and $(Hf, g) = (f, Hg) = (f, \mu g) = \mu^*(f, g)$. But according to the preceding theorem, λ and μ must be real, therefore $\mu^* = \mu$ and hence $(\lambda - \mu)(f, g) = 0$. For $\lambda \neq \mu$, we get $(f, g) = 0$.

We turn our attention to the finite-dimensional analogies of bounded, self-adjoint operators; the finite Hermitean matrices. These permit a very simple representation. An orthogonal basis may be introduced in the space in such manner that the given Hermitean matrix becomes a diagonal matrix, i.e., a matrix whose elements are all zero except for the elements which lie in the principal diagonal. The theorem of algebra which assures the existence of the proper orthogonal basis is called the theorem of principal axes, or the *spectral theorem*. We formulate it (without proof) as follows:

Given an $n \times n$ Hermitean matrix h_{ik}, the system of equations

$$\sum_{k=1}^{n} h_{ik} x_k = \lambda x_i \qquad (i = 1, 2, \ldots, n) \tag{III.4}$$

has nontrivial solutions for certain specific values of the variable λ. These values $\lambda_1, \lambda_2, \ldots$ are called the *eigenvalues* of the matrix. The solutions of (III.4) are called *eigenvectors*. An eigenvector $\mathbf{X}^j = \{x_i^j, x_2^j, \ldots, x_n^j\}$ satisfies the equations

$$\sum_{k=1}^{n} h_{ik} x_k = \lambda_j x_i \qquad (i = 1, 2, \ldots, n), \tag{III.5}$$

which is written in the compact form $H\mathbf{X}^j = \lambda_j \mathbf{X}^j$.

The solutions of the Eq. (III.3) contain a complete orthonormal system of vectors. When these vectors are introduced to define the axes of a coordinate system in the n-dimensioned space, the Hermitean matrix assumes the following diagonal form:

$$\begin{pmatrix} \lambda_1 & 0 & 0 & \ldots \\ 0 & \lambda_2 & 0 & \ldots \\ 0 & 0 & \lambda_3 & \ldots \\ . & . & . & \ldots \\ 0 & 0 & 0 & \lambda_n \end{pmatrix}.$$

The numbers λ_1, λ_2, etc., are all real, but not necessarily different. A number occurring more than once is said to be a *multiple*, or *degenerate eigenvalue*.

At first one might think that it ought to be possible to generalize the spectral theorem to the infinite-dimensional case by simply permitting an infinite number of eigenvalues and eigenfunctions, and that one ought to obtain a diagonal matrix with infinitely many rows and columns. If this were possible, the solutions of the infinitely many equations which take the place of (III.5) would always contain a complete o.n. system in Hilbert space. It has been known since about the turn of the century that such is not always the case.

Before proceeding further it is well to remember that the vectors in (III.5) are not uniquely determined by the matrix (operator), although the eigenvalues are. When an eigenvalue is multiple the corresponding eigenvectors determine a subspace $\mathbf{M}_j$, but within that subspace the choice of eigenvectors is arbitrary. Let us introduce the projection operators P_j associated with the subspaces $\mathbf{M}_j$ and restate the spectral theorem for finite, Hermitean matrices: To every such matrix there exists a finite sequence of eigenvalues λ_1, λ_2, etc., with the corresponding projection operators P_1, P_2, etc., so that

$$\Sigma P_j = I, \tag{III.6a}$$

$$P_i P_j = \delta_{ij} P_i, \tag{III.6b}$$

$$HP_j = \lambda_j P_j. \tag{III.6c}$$

From the operator (matrix) relations (III.6) we can obtain the vector relation

$$HY = H\sum_j P_j Y = \sum_j \lambda_j P_j Y \tag{III.7}$$

valid for all vectors Y, or a numerical relation

$$(HY, Y) = \sum_j \lambda_j (P_j Y, Y). \tag{III.8}$$

It is still not possible to obtain a representation of the type (III.8) for a bounded, self-adjoint operator in Hilbert space. We shall see that the corresponding representation requires in some instances not only a finite or an infinite sum, but also an integral over the region known as the continuous spectrum. Nevertheless (III.8) contains a valid suggestion: At least some bounded self-adjoint operators will permit a representation of this type. The reader will have no difficulty in showing that if there is given a finite or infinite sequence of mutually orthogonal projection operators $P_1, P_2, \ldots$, and a bounded sequence of real numbers $\lambda_1, \lambda_2, \ldots$, then the series $A = \Sigma_i \lambda_i P_i$ defines a bounded, self-adjoint operator.

B. Resolution of the Identity

Given a subspace $\mathbf{M}$ in $\mathfrak{H}$ and the corresponding projection operator E, we say that $\mathbf{M}$ reduces the bounded, self-adjoint operator H if $EH = HE$. When $\mathbf{M}$ reduces H, then $\mathbf{M}^\perp$ also reduces H because the projection operator of $\mathbf{M}^\perp$ is $I - E$, and this commutes with H whenever E does.

Let f be an element of $\mathbf{M}$ which reduces H. Then $Ef = f$,

$$Hf = HEf = EHf,$$

therefore $Hf \in \mathbf{M}$. Similarly, if $g \in \mathbf{M}^\perp$, then $Hg \in \mathbf{M}^\perp$. Therefore, if we introduce an orthogonal system in $\mathbf{M}$ and another in $\mathbf{M}^\perp$ and form the matrix representation of H in the combined complete o.n. system, the matrix will be of the form

$$\left(\begin{array}{ccc|ccc} h_{11} & h_{12} & \cdots & & & \\ h_{21} & h_{22} & \cdots & & 0 & \\ \cdot & \cdot & \cdots & & & \\ \hline & & & & & \\ & 0 & & h_{nn} & h_{nn+1} & \cdots \\ & & & \cdot & \cdot & \cdots \end{array}\right)$$

The zeros indicate that all elements in the corresponding block vanish. Thus the discovery of a subspace which reduces H already brings us one step toward the diagonal representation. The important matter is to find an entire sequence of reducing subspaces ordered in a very special way.

We return temporarily to the finite, Hermitean matrices, but we will discuss them in terms of the Hilbert space formalism. For these matrices we are assured of the existence of the projection operators exhibited in (III.6). Let us now define

$$E_0 = \sum_{\lambda_i \leqq 0} P_i. \tag{III.9}$$

The operator E_0 is a projection by virtue of the relations (III.6b). It commutes with H, therefore the range of E_0 reduces H. Moreover, if $f = E_0 f$, then,

$$(Hf, f) = \sum_{\lambda_i \leqq 0} \lambda_i (P_i f, f) \leqq 0. \tag{III.10}$$

If, on the other hand, $g = (I - E_0)g \neq 0$, then

$$(Hg, g) = \sum_{\lambda_i > 0} \lambda_i (P_i g, g) > 0. \tag{III.11}$$

Thus the matrix H has been split into a positive and a negative part; $H(I - E_0)$ and HE_0. This splitting can be carried out not only at $\lambda = 0$, but at any real number λ by setting

$$E_\lambda = \sum_{\lambda_i \leqq \lambda} P_i. \tag{III.12}$$

With this definition we have $(Hf, f) \leqq \lambda(f, f)$ when $f \in \mathbf{M}$; and $(Hg, g) > (g, g)$ when $g \in \mathbf{M}^\perp$ $(g \neq 0)$. Thus the spectral theorem assures the existence of a one-parameter family of projection operators E_λ. This family is a monotone-increasing function of λ in the following sense: $E_\lambda - E_\mu$ is a projection operator when $\lambda > \mu$, each $\mathbf{M}_\lambda$ is contained in all others with a larger index. For any given f, the function $(E_\lambda f, f)$ is a monotone-increasing function of λ, because $(E_\lambda f, f) - (E_\mu f, f) = ((E_\lambda - E_\mu)f, f) \geqq 0$ for $\lambda > \mu$. Given a real interval $\Delta = [a, b]$, we associate with it a projection

$$E(\Delta) = E(b) - E(a) = \sum_{a<\lambda_i \leqq b} P_i. \qquad \text{(III.13)}$$

The spectral theorem may then be expressed in the form:

$$(Hf, f) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, f), \qquad \text{(III.14)}$$

where the Stieltjes integral in (III.14) is merely a fancy form for the expression encountered in (III.8), since under the circumstances described, the function $(E_\lambda f, f)$ is constant except at the eigenvalues of the matrix H. The form of the spectral theorem as shown in (III.14) is, however, valid for self-adjoint operators in Hilbert space. In the general case the above Stieltjes integral no longer represents a finite or infinite sum, one encounters regions where the function $(E_\lambda f, f)$ varies continuously.

We shall be concerned with the proof of the spectral theorem for bounded self-adjoint operators and we shall no longer use the properties of finite matrices. As a preparation we define resolution of the identity and show how a self-adjoint operator may be constructed from a given resolution of the identity.

A one-parameter family of projection operators E_λ is called a *resolution of the identity* if it has the following properties:

(a) $E_\lambda E_\mu = E_\mu E_\lambda = E_\lambda$ for $\lambda \leqq \mu$,
(b) $E_{\lambda+\varepsilon} \to E_\lambda$ as $\varepsilon \to 0$ over positive numbers,
(c) $E_\lambda \to I$ as $\lambda \to \infty$; $E \to 0$ as $\lambda \to -\infty$.

The limiting processes for operators are understood in the following sense: $T(\varepsilon) \to T$ means that $\|T(\varepsilon)f - Tf\| \to 0$ as $\varepsilon \to 0$, for every $f \in \mathfrak{H}$. Condition (a) means that $E_\mu - E_\lambda$ is a projection for $\mu \geqq \lambda_e$, condition (b) means that E_λ is continuous to the right, and condition (c) determines the behavior of the E_λ's for large values of λ. We call a resolution of the identity *finite* if condition (c) may be replaced by the following one:

(c) There is a positive number K such that $E_{-K} = 0$ and $E_K = I$.

The family of projections defined by (III.12) is a finite resolution of the identity. Another example of a resolution of the identity is the following family of operators in $\mathfrak{L}_2$:

$$E_\lambda f(x) = f(x) \quad \text{for} \quad x \leqq \lambda \qquad \text{and} \qquad E_\lambda f(x) = 0 \quad \text{for} \quad x > \lambda.$$

This family has already been introduced in Section II,E. It represents a resolution of the identity with continuous variation, since

$$(E(\Delta)f, f) = \int_a^b |f(x)|^2 \, dx, \tag{III.15}$$

and

$$d(E_\lambda f, f) = |f(\lambda)|^2 \, d\lambda. \tag{III.16}$$

The following properties of a general resolution of the identity are evident:

(i) $(E_\lambda f, f) = \|E_\lambda f\|^2$ is a monotone-increasing function of λ.
(ii) $\lim\limits_{\lambda \to -\infty} \|E_\lambda f\| = 0, \qquad \lim\limits_{\lambda \to \infty} \|E_\lambda f\| = \|f\|.$

Since the functions $\psi(\lambda) = \|E_\lambda f\|^2$ are monotone-increasing functions of λ with bounded variation, we can define the Stieltjes integral

$$\int_{-\infty}^{+\infty} \lambda^k \, d\psi(\lambda) = \int_{-\infty}^{+\infty} \lambda^k \, d\|E_\lambda f\|^2 \tag{III.17}$$

in the customary manner. Such integrals are not always convergent. However, if E is a *finite* resolution of the identity, the integrals extend only over the finite interval $-K$ to $+K$, because ψ does not vary outside these limits. Then all integrals of the type (III.17) are convergent for $k > 0$.

We can now prove that every finite resolution of the identity generates a bounded, self-adjoint operator. The formal expression for this operator is

$$H = \int \lambda \, dE_\lambda, \tag{III.18}$$

but this relationship is a purely formal one because we have not defined integration over operators. In place of (III.18) we must justify the equation

$$(Hf, g) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, g) \tag{III.19}$$

for every f and g in $\mathfrak{H}$. This last equation is an equation between numbers. Unfortunately, it involves Stieltjes integration according to a complex function; it can, however, be reduced to integrations according to bounded monotone-increasing, real functions. The reduction is based on the observation that if we know (Hf, f) for every f then we can calculate (Hf, g) for every f and g by means of equations (III.2) and (III.3). These equations are applicable to any self-adjoint operator, in particular to the operator E_λ, therefore $(E_\lambda f, g)$ is calculable as the sum of four functions of the type $(E_\lambda h, h)$. Thus the integral on the right of (III.19) is the sum of four integrals according to bounded, monotone-increasing functions. For any fixed f this integral is a bounded linear functional of g because $(E_\lambda f, g)$ is such a functional and, E_λ being a finite resolution of the identity, the integration is confined to a finite interval. According to the theorem of F. Riesz, there is an element f^*, such that

$$(f^*, g) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, g). \tag{III.20}$$

We define the operator A by setting $Af = f^*$ for every $f \in \mathfrak{H}$. This operator is linear because $(E_\lambda f, g)$ is linear in f. The self-adjoint character of A follows from

$$(E_\lambda f, g) = (f, E_\lambda g) = (E_\lambda g, f)^*, \tag{III.21}$$

because

$$(f, Ag) = (Ag, f)^* = \left[\int_{-\infty}^{+\infty} \lambda \, d(E_\lambda g, f)\right]^* = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, g) = (Af, g). \tag{III.22}$$

For $g = f$ we have

$$(Af, f) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, f). \tag{III.23}$$

We have thus shown that every finite resolution of the identity generates a bounded, self-adjoint transformation in Hilbert space. If the region of variability of E_λ is confined to the interval $-K$ to $+K$, then

$$|(Af, f)| \leqq K(f, f). \tag{III.24}$$

Having proved the self-adjoint character of A, we adopt for this operator the symbol H which is customary for self-adjoint operators.

The operator H is permutable with every element of the family which forms the resolution of the identity. We demonstrate $E_\mu H = HE_\mu$ for a fixed μ. Since $E_\lambda E_\mu = E_\lambda$ when $\lambda \leqq \mu$, and E_μ when $\lambda \geqq \mu$, it follows that

$$(HE_\mu f, g) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda E_\mu f, g) = \int_{-\infty}^{\mu} \lambda \, d(E_\lambda f, g). \tag{III.25}$$

But

$$(E_\mu Hf, g) = (Hf, E_\mu g) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, E_\mu g) = \int_{-\infty}^{\mu} \lambda \, d(E_\lambda f, g), \tag{III.26}$$

therefore

$$(E_\mu Hf, g) = (HE_\mu f, g) \tag{III.27}$$

for every f and g, which we were to prove. In fact, H is permutable not only with every E_λ but with every bounded operator A which is permutable with every E_λ. This follows from the equations:

$$\begin{aligned}(HAf, g) &= \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda Af, g) = \int_{-\infty}^{+\infty} \lambda \, d(AE_\lambda f, g) \\ &= \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, A^\dagger g) = (Hf, A^\dagger g) = (AHf, g).\end{aligned} \tag{III.28}$$

In the light of what has been said before, we may concentrate on the calculation of expressions of the type (Hf, f) in place of those of the type (Hf, g). Let H be the self-adjoint operator generated by the finite resolution of the identity E_λ, and let us calculate

$$\|Hf\|^2 = (Hf, Hf) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, Hf) = \int_{-\infty}^{+\infty} \lambda \, d(HE_\lambda f, f). \tag{III.29}$$

The differential in the last integral is calculated from (III.25) which gives after the substitution of the proper letters $d(HE_\lambda f, f) = \lambda \, d(E_\lambda f, f)$. Therefore

$$\|Hf\|^2 = (H^2 f, f) = \int_{-\infty}^{+\infty} \lambda^2 \, d(E_\lambda f, f). \tag{III.30}$$

We have now obtained a new proof of the fact that $\|Hf\|^2 \leqq K^2 \|f\|^2$, or $\|Hf\| \leqq K \|f\|$.

An obvious generalization of (III.30) is

$$(H^n f, f) = \int_{-\infty}^{+\infty} \lambda^n \, d(E_\lambda f, f), \tag{III.31}$$

valid for any positive integer n. It may be proven by mathematical induction. This last formula enables one to write polynomials of a bounded self-adjoint operator in the following form

$$P_n(H) = \int_{-\infty}^{+\infty} P_n(\lambda)\, dE_\lambda, \tag{III.32}$$

which is a symbolic form for the equations

$$(P_n(H)f, f) = \int_{-\infty}^{+\infty} P_n(\lambda)\, d(E_\lambda f, f), \tag{III.33}$$

valid for every f. When the polynomial $P_n(\lambda) = a_0 + a_1\lambda + \cdots + a_n\lambda^n$ has real coefficients, the operator $P(H)$ is self-adjoint. Its bound does not exceed the maximum of $|P_n(\lambda)|$ in the interval $-K$ to $+K$.

C. Auxiliary Theorems of F. Riesz

We have shown that every finite resolution of the identity generates a bounded, self-adjoint operator. Our next major objective is to show that to every bounded, self-adjoint operator belongs a uniquely determined resolution of the identity.

There are many essentially different methods of proving this theorem (Riesz and Sz.-Nagy, 1955; Cook, 1953). We shall follow an approach based on the ideas of Riesz (1930) and Wecken (1935). The essential step in this proof is that one demonstrates that every bounded self-adjoint operator H can be decomposed into a negative and a positive definite part. In other words, the Hilbert space may be split into two complementary orthogonal subspaces, each reduced by H and such that H is positive definite in one subspace and negative in the other. As we shall see, the splitting is accomplished once we have found the positive square root of the operator H^2; i.e., an operator T which is positive and such that $T^2 = H^2$. That such an operator should exist is easily inferred from the spectral representation, since T must be equal to $\int |\lambda|\, dE_\lambda$. But we cannot yet rely on the spectral representation which is to be proven.

We recall that A is called positive when $(Af, f) \geqq 0$ for every f. An operator A is called greater than the operator B when $A - B$ is a positive operator. In symbols: $A > B$.

The following statements are easily verified:

When $A > O$ and $B > O$ then $A + B > O$. When $A > B$ then $-A < -B$.

When A and B are permutable positive operators, the products AB^2 and A^2B are easily seen to be positive operators because

$$(AB^2f, f) = (BABf, f) = (ABf, Bf) \geqq 0. \tag{III.34}$$

It takes a little work to show that AB is also positive. We have to represent one of the operators, say A, as the sum of the squares of positive operators all permutable with B and then apply what we have just learned about operators of the form A^2B. Let us assume that the bound of A does not exceed one, otherwise we divide by a positive number to achieve this. Then, starting with $A_1 = A$, we define A_{n+1} by means of the recursion formula

$$A_{n+1} = A_n - A_n^2. \tag{III.35}$$

Now $A_1 > O$ and $I - A_1 > O$. If we assume $A_n > O$ and $I - A_n > O$, then the relations $A_{n+1} > O$ and $I - A_{n+1} > O$ follow from the equations

$$A_{n+1} = A_n^2(I - A_n) + A_n(I - A_n)^2, \tag{III.36}$$

$$I - A_{n+1} = I - A_n + A_n^2. \tag{III.37}$$

Therefore, the inequality $O < A_n < I$ must be true for every index n. By summation we obtain from (III.36) that

$$A = A_1^2 + A_2^2 + \cdots + A_n^2 + A_{n+1}, \tag{III.38}$$

and since $A_{n+1} > O$, this implies

$$(A_1^2f, f) + (A_2^2f, f) + \cdots + (A_n^2f, f) \leqq (Af, f) \tag{III.39}$$

for every f. Hence the positive series $\sum_{i=1}^{\infty} (A_i^2f, f)$ is convergent for every f and therefore $(A_n^2f, f) = \|A_nf\|^2 \to 0$ as $n \to \infty$. So we may write

$$A = \sum_{i=1}^{\infty} A_i^2, \tag{III.40}$$

where each A_i is permutable with every operator permutable with A. Consequently BA is a positive operator because it is the sum of positive operators of the type BA_i^2.

As an interesting special case let us consider a positive operator B whose bound does not exceed one, and let $A = I - B$. Then A is again positive and the theorem we have proven asserts that $B(I - B)$ is also positive, therefore

$$(Bf, f) \geqq (B^2f, f) = \|Bf\|^2. \tag{III.41}$$

The partial sums of the series (III.40) form a monotone-increasing sequence of positive operators which are all bounded from above by the fixed operator A. We can now show that every operator sequence of this type converges. The exact theorem is the following:

Given an infinite sequence $H_1, H_2, \ldots$ of positive, self-adjoint operators such that

$$O < H_1 < H_2 < \cdots < H_n < \cdots < A,$$

the sequence converges to a limiting operator H in the sense that $\lim\|(H_n - H)f\| = 0$ for all f. Moreover $O < H < A$.

Without losing generality we assume that $A \leqq I$. We note that for $n > m$ the following order relation holds

$$O < H_n - H_m < I - H_m < I. \tag{III.42}$$

therefore the operator $H_n - H_m$ is positive and its bound does not exceed one. Given any element f, the sequence of numbers (H_nf, f) is a positive, monotone-increasing sequence which remains below $\|f\|^2$, therefore the sequence is convergent. We substitute $B = H_n - H_m$ in (III.41) and obtain

$$\|H_nf - H_mf\|^2 \leqq (H_nf - H_mf, f) = (H_nf, f) - (H_mf, f). \tag{III.43}$$

The right-hand side of (III.43) tends to zero, therefore the sequence H_nf tends to a limit as asserted. We designate its limit by Hf. The sequence (H_nf, f) is monotone increasing and such that

$$0 \leqq (H_nf, f) \leqq (Af, f).$$

Therefore $0 \leqq \lim(H_nf, f) = (Hf, f) \leqq (Af, f)$.

Now we come to the main theorem of this section, known as Wecken's lemma:

For every bounded, self-adjoint operator H there is a positive operator T such that $T^2 = H^2$ and this T is permutable with every bounded operator permutable with H.

Without restricting generality we may assume that the bound of H does not exceed one, then

$$O < H^2 < I. \tag{III.44}$$

We introduce the operator $C = I - H^2$, thus $O < C < I$. Now let $Y_0 = O$, $Y_1 = \frac{1}{2}C$, and

$$Y_{n+1} = \tfrac{1}{2}(C + Y_n^2). \tag{III.45}$$

By mathematical induction we prove readily that

$$O < Y_n < I \tag{III.46}$$

for all n. The fact that the operators Y_n form a monotone increasing sequence of the type (III.42) also follows by induction with the aid of the equation

$$Y_{n+1} - Y_n = \tfrac{1}{2}[Y_n^2 - Y_{n-1}^2] = \tfrac{1}{2}(Y_n - Y_{n-1})(Y_n + Y_{n-1}). \tag{III.47}$$

Here we make use of the fact that the product of positive operators is positive. By virtue of their construction the Y's are permutable with every bounded operator permutable with H. The existence of a limiting operator $Y = \lim Y_n$ is now assured. Moreover $O < Y < I$. We rewrite (III.45) in the following form:

$$H^2 = I - 2Y_{n+1} + Y_n^2. \tag{III.48}$$

Then as n tends to ∞, we obtain $H^2 = I - 2Y + Y^2 = (I - Y)^2$, where $T = I - Y$ is a positive operator. Thus we have shown

$$H^2 = T^2. \tag{III.49}$$

The permutability of T with every bounded operator permutable with H follows from the permutability of all Y's with such operators.

D. Reduction of a Bounded Self-Adjoint Operator

We shall prove the following theorem: Given a bounded, self-adjoint operator H there exists a projection operator P permutable with H and such that

(a) When $Hf = \mathbf{O}$ then $Pf = f$,
(b) HP is a negative operator; $(HPf, f) \leqq 0$,
(c) $H(I - P)$ is a positive operator, $(H(I - P)f, f) \geqq 0$.
(d) P is permutable with every bounded operator permutable with H.

Wecken's lemma assures the existence of a *positive* operator T, permutable with H, such that $T^2 = H^2$. We define the operators

$$H^+ = \tfrac{1}{2}(T + H), \qquad H^- = \tfrac{1}{2}(T - H). \tag{III.50}$$

Clearly

$$T = H^+ + H^-, \tag{III.51}$$

$$H = H^+ - H^-, \tag{III.52}$$

Let $\mathbf{M}$ be the subspace for which $H^+f = \mathbf{O}$, and let P be the projection operator of $\mathbf{M}$. From $Hf = \mathbf{O}$ follows $H^2f = T^2f = \mathbf{O}$, therefore $\|Tf\|^2 = (T^2f, f) = 0$, finally $Tf = \mathbf{O}$. Consequently $Hf = \mathbf{O}$ implies that $H^+f = \mathbf{O}$, or that $Pf = f$.

By definition $H^+P = O$, taking the adjoint of both sides gives $PH^+ = O$. Furthermore

$$H^+H^- = \tfrac{1}{4}(T^2 - H^2) = O, \tag{III.53}$$

Therefore $H^{-}f$ always belongs to **M**; $H^{-} = PH^{-}$. The adjoint relation is $H^{-}P = H^{-}$. So P is permutable with H^{+} and H^{-}. Multiplying (III.52) by P and $I - P$, respectively, we get

$$HP = -H^{-}, \tag{III.54}$$

$$H(I - P) = H^{+}. \tag{III.55}$$

Multiplication of (3.51) by P and $I - P$ gives

$$TP = H^{-}, \tag{III.56}$$

$$T(I - P) = H^{+}. \tag{III.57}$$

Thus H^{-} and H^{+} are positive operators.

Let U be a bounded operator permutable with H. Then $U^{\dagger}$, the adjoint of U, is also permutable with H and, as a consequence of Wecken's lemma, U and $U^{\dagger}$ are permutable with T as well as with H^{+} and H^{-}. Permutability with H^{+} implies that

$$H^{+}UP = UH^{+}P = 0,$$

therefore UPf is always in **M**, hence $UP = PUP$. Similarly $U^{\dagger}P = PU^{\dagger}P$, and from the latter $PU = PUP$, hence

$$UP = PU, \tag{III.58}$$

which completes the proof.

The reduction can be applied not only to the operator H, but also to the equally self-adjoint operator $H_{\lambda} = H - \lambda I$, where λ is any real number. From the reduction of H_{λ} we obtain a one-parameter family of projections $E_{\lambda} = P_{\lambda}$. It follows then that every projection E_{λ} is permutable with every bounded operator permutable with H. In particular, the E_{λ}'s are permutable among each other, moreover

(a) $Hf = \lambda f$ implies $E_{\lambda}f = f$,
(b) $HE_{\lambda} < \lambda E_{\lambda}$; i.e., $(HE_{\lambda}f, f) \leqq \lambda(E_{\lambda}f, f)$
(c) $H(I - E_{\lambda}) > \lambda(I - E_{\lambda})$; i.e., $(H[I - E_{\lambda}]f, f) \geqq \lambda([I - E_{\lambda}]f, f)$.

In order to prove that E_{λ} is a finite resolution of the identity one must show that

(d) $E_{\lambda}E_{\mu} = E_{\mu}E_{\lambda} = E_{\lambda}$ for $\mu > \lambda$.

(e) E_{λ} is continuous to the right; i.e., $\|E_{\lambda+\varepsilon}f - E_{\lambda}f\| \to 0$ as ε tends to zero over positive numbers.

(f) There is a positive number K such that $E_{\lambda} = O$ for $\lambda < -K$, and $E_{\lambda} = I$ for $\lambda \geqq K$.

We restrict ourselves to the proof of property (d). The permutability of all E's being assured, it is sufficient to prove $E_\mu E_\lambda = E_\lambda$ for $\mu > \lambda$. The operator $(H - \lambda I)E_\lambda$ is negative, therefore

$$HE_\lambda < \lambda E. \tag{III.59}$$

The operator $(H - \mu I)(I - E_\mu)$ is positive, therefore

$$\mu(I - E_\mu) < H(I - E_\mu). \tag{III.60}$$

On multiplying (III.59) by $(I - E_\mu)$ and (III.60) by E_λ we obtain

$$\mu(I - E_\mu)E_\lambda < H(I - E_\mu)E_\lambda < \lambda E_\lambda(I - E_\mu). \tag{III.61}$$

Hence

$$\mu([I - E_\mu]E_\lambda f, f) \leqq \lambda(E_\lambda[I - E_\mu]f, f) \tag{III.62}$$

for every $f \in \mathfrak{H}$. The operator $(I - E_\mu)E_\lambda = E_\lambda(I - E_\mu)$ is a projection, because it is the product of permutable projections. Therefore

$$(\lambda - \mu)\|E_\lambda(I - E_\mu)f\|^2 \geqq 0, \tag{III.63}$$

and since our assumption requires that $\lambda - \mu < 0$, it follows that $E_\lambda(I - E_\mu) = O$, or

$$E_\lambda = E_\lambda E_\mu. \tag{III.64}$$

The proof of property (e) may be found in any textbook, while the proof of property (f) is an easy exercise.

Exercises

1. If H is a finite matrix which may be written in the diagonal form, what are the matrices T, H^- amd H^+?
2. Show that if $Hf = \lambda_0 f$ then $E_\lambda f = \mathbf{O}$ for $\lambda < \lambda_0$, and the expression $\|E_\lambda f\|^2 = (E_\lambda f, f)$ has a discontinuity at $\lambda = \lambda_0$.
3. Show that if $mI < H < MI$, then $E_M = I$. Is $E_m = O$?

E. Integral Representation

Given a bounded, self-adjoint operator H for which we have

$$m(f, f) \leqq (Hf, f) \leqq M(f, f), \tag{III.65}$$

we subdivide the interval m to M by the number λ_1, λ_2, etc., in the following manner:

$$m < \lambda_1 < \lambda_2 < \cdots < \lambda_n = M. \tag{III.66}$$

Finally, we add a number $\lambda_0 < m$. According to the results of the preceding section, we are assured of the existence of a resolution of the identity E_λ which satisfies conditions (a)–(f) and for which $E_{\lambda_0} = O$, $E_{\lambda_n} = I$. We introduce projections associated with real intervals by defining

$$E(\Delta_k) = E_{\lambda_k} - E_{\lambda_{k-1}}, \tag{III.67}$$

for $k = 1, 2, \ldots, n$. Thus we construct n projection operators which are mutually orthogonal and which add up to the identity operator I. In fact, if $i < k$,

$$E_{\lambda_i} E(\Delta_k) = E_{\lambda_i} E_{\lambda_k} - E_{\lambda_i} E_{\lambda_{k-1}} = E_{\lambda_i} - E_{\lambda_i} = O, \tag{III.68}$$

and

$$\sum_{k=1}^{n} E(\Delta_k) = E_{\lambda_n} - E_{\lambda_0} = I. \tag{III.69}$$

In the range of $E(\Delta_k)$ the operator H is so restricted that the numbers m and M in (III.65) are replaced by λ_{k-1} and λ_k respectively. In fact, for $f = E(\Delta_k)g$, we have $E_{\lambda_k} f = E_{\lambda_k}(E_{\lambda_k} - E_{\lambda_{k-1}})g = (E_{\lambda_k} - E_{\lambda_{k-1}})g = f$, therefore

$$(Hf, f) \leqq \lambda_k (f, f). \tag{III.70}$$

Moreover $E_{\lambda_{k-1}} f = E_{\lambda_{k-1}}(E_{\lambda_k} - E_{\lambda_{k-1}})f = \mathbf{O}$, therefore

$$\lambda_{k-1}(f, f) \leqq (Hf, f) \tag{III.71}$$

and equality in (II.71) holds for $f = \mathbf{O}$ only. Consequently

$$\lambda_{k-1} \|E(\Delta_k)f\|^2 \leqq (HE(\Delta_k)f, f) \leqq \lambda_k \|E(\Delta_k)f\|^2 \tag{III.72}$$

holds for every $f \in \mathfrak{H}$ and for every integer k. A double inequality such as shown in (III.72), enables one to define a Riemann-Stieltjes integral, because one may sum over k, noting that

$$\sum_{k=1}^{n} E(\Delta_k) f = f,$$

and obtain

$$\sum_{k=1}^{n} \lambda_{k-1} \|E(\Delta_k)f\|^2 \leqq (Hf, f) \leqq \sum_{k=1}^{n} \lambda_k \|E(\Delta_k)f\|^2. \tag{III.73}$$

If the net of subdivision is continually refined in such a manner that the length of the longest subdivision tends to zero, both sums in the inequality (III.73) tend to the same limit which is by definition

$$\int_{m-\varepsilon}^{M} \lambda \, d\|E_\lambda f\|^2.$$

The ε in the lower limit of integration is necessary, otherwise one might lose elements for which $Hf = mf$. It is certainly correct to write

$$(Hf, f) = \int_{-\infty}^{+\infty} \lambda \, d\|E_\lambda f\|^2 \tag{III.74}$$

noting, however, that all variation of E_λ is confined to the point m and to the interval $[m, M]$.

It is interesting to examine closely what happens when μ is an eigenvalue and $Hf = \mu f$. According to the definition of the resolution of the identity (Property A), we have $E_\mu f = f$. On the other hand, let $\lambda = \mu - \varepsilon$, where $\varepsilon > 0$. Then

$$(H_\lambda f, f) = (Hf - \mu f + \varepsilon f, f) = \varepsilon\|f\|^2 > 0,$$

therefore f is in the range of $I - E_\lambda$ consequently $E_\lambda f = \mathbf{O}$. So

$$(E_\mu f, f) - (E_{\mu-\varepsilon} f, f) = \|f\|^2 \tag{III.75}$$

for every $\varepsilon > 0$. The function $(E_\lambda f, f)$ has a discontinuity at $\lambda = \mu$; it changes from 0 to $\|f\|^2$. The integral in (III.74) reduces to a single term, namely $\mu\|f\|^2$. Conversely, every discontinuity in $\|E_\lambda f\|^2$ gives rise to an eigenvalue of H.

IV. Spectral Theory of Unbounded Linear Operators

A. General Definition of the Adjoint Operator

Unbounded linear operators are not defined or definable over the entire Hilbert space. It is conceivable, however, that they were too narrowly defined originally and that they are capable of natural extensions beyond their original domains. We shall discuss later what the vague term, "natural extension," really means. Let us first consider an example.

In the space $\mathfrak{L}_2$ over a finite interval let us define an operator A_1 so that its domain consists of even polynomials and let A_1 transform the even polynomial into its derivative. This is clearly a very restricted operator. We are inclined to replace it first with an operator A_2 applicable to *all* polynomials. If we do this, we get an operator A_2 which can be applied more than once, although the square of the original operator can only be applied to $f =$

const. A further extension could be made in several ways, one could define $A_3f = 0$ whenever f is not a polynomial. Such an extension would exhibit great irregularities, because if a sequence of polynomials $p_n(x)$ is chosen to approximate a differentiable function $f(x)$ that is not a polynomial, then A_3p_n will approximate $f'(x)$, while $A_3f(x) = 0$. It seems more natural to extend the operator A_2 to every differentiable function by assigning to A_3f the value $f'(x)$.

In the case of bounded, and therefore continuous, operators we used continuity as a guide to make the proper extension. Here we have to be satisfied with a weaker property which we shall soon define.

We prove the following theorem: The adjoint operator $A^\dagger$ is uniquely defined if the domain $\mathbf{D}$ of the operator A is everywhere dense.

The product (Af, g) is defined for every $f \in \mathbf{D}$ and every $g \in \mathfrak{H}$. It is a linear functional of f, and *for some g's* it is a *bounded linear functional.* If g is such an element, then according to the theorem of F. Riesz there is an element g^*, such that

$$(Af, g) = (f, g^*) \tag{IV.1}$$

for every $f \in \mathbf{D}$. The adjoint operator $A^\dagger$ is then defined by the equation

$$Ag = g^*. \tag{IV.2}$$

Uniqueness of g^* follows from the assumption that $\mathbf{D}$ is everywhere dense. In fact, if another element h^* could take the place of g^* in (IV.1), then we would get by subtraction

$$(f, g^* - h^*) = 0 \tag{IV.3}$$

for every f in $\mathbf{D}$, therefore $g^* = h^*$. When $\mathbf{D}$ is not everywhere dense, g^* is not uniquely defined, because every element orthogonal to D could be added to g^* without affecting (IV.1).

If the domain $\mathbf{D}^\dagger$ of $A^\dagger$ is again everywhere dense, then the operator $A^{\dagger\dagger} = (A^\dagger)^\dagger$ can be defined. It is easy to see that, whenever $f \in \mathbf{D}$, then $f \in \mathbf{D}^{\dagger\dagger}$ and $A^{\dagger\dagger}f = Af$. Therefore, if $A^{\dagger\dagger}$ exists, it is an extension of A.

A linear operator is called self-adjoint if $A^\dagger = A$. In the case of an operator that is not defined everywhere, this requires more than

$$(Af, g) = (f, Ag) \tag{IV.4}$$

for every f and g in $\mathbf{D}$. An operator that satisfies (IV.4) is called *symmetric.* An operator is symmetric when $Af = A^\dagger f$ for every $f \in \mathbf{D}$, and $\mathbf{D} \subset \mathbf{D}^\dagger$. For a self-adjoint operator $\mathbf{D} = \mathbf{D}^\dagger$.

When the domain of an operator is enlarged, the domain of its adjoint is either decreased or it remains the same. In symbols: $A \supset B$ implies $B^\dagger \supset A^\dagger$. The question immediately arises, what symmetric operators can be extended so that they become self-adjoint? In order to discuss this question and related other questions we have to digress and introduce the concept of closure. The next section is devoted to this topic.

Exercises

1. Starting with an o.n. set $\{\varphi_n\}$in $\mathfrak{H}$, define a linear operator H formally by the equations $H\varphi_n = n\varphi_n$, $n = 1, 2, 3, \ldots$. Now specify the domain of H first so that H is symmetric, but not self-adjoint; then extend the domain of it so as to obtain a self-adjoint operator.

2. Show that if the operators A, B, and AB have adjoints then $(AB)^\dagger = B^\dagger A^\dagger$.

B. The Property of Closure

When an operator is continuous it transforms every convergent sequence in its domain into a convergent sequence. An unbounded operator is not continuous, from the convergence of a sequence in its domain it does not follow that the transformed sequence is convergent.

An operator A is called *closed* (German: abgeschlossen) when the convergence of the sequence $\{f_n\}$ in $\mathbf{D}$ and that of the sequence $\{Af_n\}$ together imply that the element $f = \lim f_n$ is in $\mathbf{D}$ and $Af = \lim Af_n$.

The essential difference between continuity and closure is that continuity implies the convergence of the sequence $\{Af_n\}$, while closure does not. It implies, however, that if $\{Af_n\}$ converges for *some sequence* that tends to an element f, then *every sequence* tending to the same limit f produces a convergent sequence $\{Af_n\}$, and that all these tend to the same limit.

We now introduce the graph of the operator, a concept helpful in giving a simple illustration of the meaning of closure. Graphs are most useful in the exploration of the properties of self-adjoint operators.

Consider pairs of elements in Hilbert space in the same manner as one considers a pair of real numbers as coordinates of a point in the plane. Thus a point in the pair space, or double space, is of the form $\{f, g\}$. The basic operations in the pair space are defined by the equations:

$$\{f_1, g_1\} + \{f_2, g_2\} = \{f_1 + f_2, g_1 + g_2\}, \tag{IV.5}$$

$$\alpha\{f, g\} = \{\alpha f, \alpha g\}, \tag{IV.6}$$

$$(\{f_1, g_1\}, \{f_2, g_2\}) = (f_1, f_2) + (g_1, g_2). \tag{IV.7}$$

It is easy to prove that the pair space is again a Hilbert space. Certain simple transformations in this space are measure preserving; i.e., they do not change the norm of an element. Such are, for example, $S\{f, g\} = \{g, f\}$ and $U\{f, g\} = \{f, -g\}$. Clearly

$$\|\{f, g\}\|^2 = \|f\|^2 + \|g\|^2 = \|S\{f, g\}\|^2 = \|U\{f, g\}\|^2.$$

The graph of the function $y = f(x)$ is the set of points with coordinates $\{x, f(x)\}$. We define the graph of an operator A as the set of points $\{f, Af\}$ in the pair space while f varies over $\mathbf{D}$. The graph of a linear operator is a linear manifold which does not contain pairs of the type $\{\mathbf{O}, h\}$ where $h \neq \mathbf{O}$. Conversely, every linear manifold of this type is the graph of a linear operator. If $A \supset B$ then the graph of A contains the graph of B.

An operator is closed if and only if its graph is a closed linear manifold. Every linear manifold can be made closed by adding all its limit points, but a given operator can be extended to a closed operator only if the closure of its graph does not contain pairs of the type $\{\mathbf{O}, h\}$ with $h \neq \mathbf{O}$.

The definition of the operator $A^\dagger$ as the adjoint of operator A is then equivalent to saying that

$$(f, A^\dagger g) - (Af, g) = (\{f, Af\}, \{A^\dagger g, -g\}) = 0 \qquad \text{(IV.8)}$$

for every $f \in \mathbf{D}$, and every $g \in \mathbf{D}^\dagger$. Whether the graph of A is closed, or not, the linear manifold orthogonal to $\{f, Af\}$ is closed, therefore the set $\{A^\dagger g, -g\}$ is a closed set. Consequently the set $\{g, A^\dagger g\}$ obtained by the application of the norm-preserving operators S and U is also closed. *Whenever the adjoint operator $A^\dagger$ exists, it is a closed operator.*

When the operator A has closed extensions, the least of these is determined by adding the limit points to the linear manifold $\{f, Af\}$. This process is equivalent to determining the orthogonal complement of the closed linear manifold formed by the pairs $\{A^\dagger g, -g\}$. When the closed linear manifold so formed contains no pairs of the type $\{\mathbf{O}, h\}$, it is the graph of the operator $A^{\dagger\dagger}$ which is the least closed extension of the operator A.

By examining the graphs it is easy to see that the following propositions are true:

(1) If A has an inverse A^{-1}, then the closure of A implies that of A^{-1}.

(2) If $A^\dagger$ has an inverse, then $(A^\dagger)^{-1} = (A^{-1})^\dagger$.

(3) If the operator $A^{\dagger\dagger}$ exists, its adjoint is $A^\dagger$.

(4) If A is a closed operator with domain everywhere dense, the operator $A^\dagger$ has the same properties.

C. Symmetric and Self-Adjoint Operators

A linear operator A is called symmetric if its domain is everywhere dense and if the equation

$$(Af, g) = (f, Ag) \tag{IV.9}$$

holds for every f and g in $\mathbf{D}$. This definition implies that the adjoint operator $A^\dagger$ exists and is an extension of A. Thus $\mathbf{D}^\dagger \supset \mathbf{D}$ is everywhere dense and the existence of $A^{\dagger\dagger}$ is also assured. Since $A^{\dagger\dagger}$ is a closed extension of A whose adjoint is again $A^\dagger$, it is sufficient to consider closed symmetric operators only. A closed symmetric operator that has no further symmetric extensions is called a maximal symmetric operator. A maximal symmetric operator for which $A = A^\dagger$ (that is $\mathbf{D} = \mathbf{D}^\dagger$) is called self-adjoint.

We shall now state a series of theorems concerning symmetric and self-adjoint operators.

Theorem 1. Let α be any real number, the operator $A + \alpha I$ is symmetric whenever A is symmetric, and self-adjoint whenever A is self-adjoint.

The proof is an easy exercise.

Theorem 2. If the range of a symmetric operator A is the entire space $\mathfrak{H}$, then A is self-adjoint.

It is necessary to show that every element of $\mathbf{D}^\dagger$ is in $\mathbf{D}$. Let $g_0 \in \mathbf{D}^\dagger$. Then $(Af, g_0) = (f, A^\dagger g_0)$ for every $f \in \mathbf{D}$. According to our assumption, $A^\dagger g_0$ is in the range of A, therefore there is an element $u \in \mathbf{D}$ such that $Au = A^\dagger g_0$. Then $(Af, g_0) = (f, Au) = (Af, u)$ holds for every f in $\mathbf{D}$, and hence $g_0 - u$ is orthogonal to the entire range of A. Consequently $g_0 = u$, an element of $\mathbf{D}$.

Theorem 3. Let A be a closed operator whose domain is everywhere dense, the operators $I + AA^\dagger$ and $I + A^\dagger A$ are symmetric operators whose range is the entire space.

We prove the theorem for $I + A^\dagger A$, whose symmetric character follows from $(A^\dagger Af, g) = (Af, Ag) = (f, A^\dagger Ag)$ and Theorem 1 above. That the range of $I + A^\dagger A$ is the entire space is shown as follows. The linear manifolds $\{f, Af\}$ with $f \in \mathbf{D}$, and $\{A^\dagger g, -g\}$ with $g \in \mathbf{D}^\dagger$ are not only orthogonal to each other, *they are orthogonal complements.* This is assured by the fact that A is closed and therefore the adjoint of $A^\dagger$. An arbitrary element in the pair space may then be resolved in components in these complementary subspaces. For an arbitrary element h we can find an f and a g such that

$$\{h, \mathbf{O}\} = \{f, Af\} + \{A^{+}g, -g\}, \tag{IV.10}$$

or in detail

$$h = f + A^{\dagger}g, \tag{IV.11}$$

$$\mathbf{O} = Af - g. \tag{IV.12}$$

On eliminating g, we get

$$h = f + A^{\dagger}Af = (I + A^{\dagger}A)f. \tag{IV.13}$$

Since (IV.13) has a solution for every h, we conclude that the range of the operator $I + A^{\dagger}A$ is $\mathfrak{H}$. Thus by means of elementary theorems concerning complementary subspaces, we have demonstrated that the operator $I + A^{\dagger}A$ has an inverse whose domain is $\mathfrak{H}$. The result applies to $I + AA^{\dagger}$ as well.

Combining Theorems 1, 2, and 3, we get:

Theorem 4. The operators $AA^{\dagger}$ and $A^{\dagger}A$ are self-adjoint whenever A is a closed operator with domain everywhere dense. We note that $AA^{\dagger}$ and $A^{\dagger}A$ are positive operators because $(AA^{\dagger}f, f) = (A^{\dagger}f, A^{\dagger}f) \geqq 0$, etc.

This result is rather surprising, because it is not at all evident that the domain of the product of two unbounded operators is large enough to make this product self-adjoint. In fact, without this theorem one might wonder if the square of a self-adjoint operator is self-adjoint. Fortunately Theorem 4 assures this. The success of the preceding development depends on the discovery that although the operators A and $A^{\dagger}$ may be unbounded, and therefore difficult to manage, the inverses of $I + A^{\dagger}A$ and of $I + AA^{\dagger}$ are *bounded* symmetric operators which must therefore be self-adjoint. The use of these inverses was implicit so far, now we state their properties explicitly.

The representation (IV.10) assures that the linear equations (IV.11) and (IV.12) may be solved for any given h. The solutions f and g are linear functions of h, therefore Eqs. (IV.11) and (IV.12) define the linear operators $f = Bh$ and $g = Ch$.

Theorem 5. The operators B and C are bounded, their bounds do not exceed one. B is a positive self-adjoint operator, $C = AB$, and

$$(I + A^{\dagger}A)B = I. \tag{IV.14}$$

The fact that (IV.13) can be solved for any h ensures that the operator $I + A^\dagger A$ has an inverse. For an arbitrary $h \in \mathfrak{H}$ we have $f = Bh$ and $(I + A^\dagger A)f = (I + A^\dagger A)Bh = h$. This establishes (IV.14).

The representation (IV.10) splits the element $\{h, \mathbf{O}\}$ in two orthogonal parts, therefore

$$\|h\|^2 = \|\{h, \mathbf{O}\}\|^2 = \|f\|^2 + \|Af\|^2 + \|A^\dagger g\|^2 + \|g\|^2. \qquad \text{(IV.15)}$$

Hence

$$\|Bh\|^2 + \|Ch\|^2 = \|f\|^2 + \|g\|^2 \leqq \|h\|^2, \qquad \text{(IV.16)}$$

therefore the bounds of B and C cannot exceed one. The operator B is the inverse of a symmetric operator $I + A^\dagger A$, therefore symmetric; as a consequence of its boundedness it is also self-adjoint. Moreover, $(Bu, u) = (Bu, (I + A^\dagger A)Bu) = (Bu, Bu) + (ABu, ABu) \geqq 0$ for every u.

We now specialize on the case where the operator A is self-adjoint and we denote such an operator by H. Then, in place of (IV.14), we have

$$B = (I + H^2)^{-1} \quad \text{and} \quad C = H(I + H^2)^{-1}. \qquad \text{(IV.17)}$$

We shall now prove that

$$(H - iI)(C + iB) = 1. \qquad \text{(IV.18)}$$

From Theorem 5 it follows that every element of the form Bf is in the domains of H and $I + H^2$, therefore also in the domain of H^2. Consequently $Cf = HBf$ is in the domain of H, therefore the operator on the left-hand side of (IV.18) has $\mathfrak{H}$ as its domain. Then

$$(H - iI)(C + iB) = (H - iI)(H + iI)(I + H^2)^{-1} = I,$$

as we were to prove.

The operator $C + iB = (H - iI)^{-1}$ is a special case of the *resolvent operator* R_z which is defined as follows

$$R_z = (H - zI)^{-1};$$

an operator which is bounded for every nonreal value of z.

Theorem 6. The bounded operators B and C defined by a self-adjoint operator H are permutable with H in the following sense:

The elements Bh and Ch are always in the domain $\mathbf{D}_H$ of H. Whenever h is in $\mathbf{D}_H$ then

$$HBh = BHh, \qquad \text{(IV.19)}$$

$$HCh = CHh. \qquad \text{(IV.20)}$$

The permutability is suggested by Eqs. (IV.17) which indicate that B and C are functions of H. Its proof is obtained from the basic equations (IV.11) and (IV.12) which in the case of a self-adjoint operator take the form:

$$h = f + Hg, \tag{IV.21}$$

$$\mathbf{O} = Hf - g. \tag{IV.22}$$

The definition of the operators B and C gives $f = Bh$, $g = Ch$. Therefore, we have

$$Hf = HBh, \qquad Hg = HCh \tag{IV.23}$$

for every h. When h is in $\mathbf{D}_H$ we may apply H to Eqs. (IV.21) and (IV.22) obtaining

$$Hh = hf + H^2 g, \tag{IV.24}$$

$$\mathbf{O} = H^2 f - Hg. \tag{IV.25}$$

Thus Hf and Hg are related to Hh as f and g are related to h. Hence

$$Hf = BHh, \qquad Hg = CHh. \tag{IV.26}$$

Equations (IV.23) and (IV.26) demonstrate the asserted permutability of H with B and C. The permutability of B with C follows from

$$CB = HBB = BHB = BC.$$

Note that (IV.21) may be written in the form

$$HCh = h - Bh,$$

valid for every h in $\mathfrak{H}$. Therefore

$$HC = I - B.$$

Now multiply $C = HB$ by C. Then

$$C^2 = CHB = HCB = (I - B)B = B - B^2.$$

Hence

$$B = B^2 + C^2. \tag{IV.27}$$

The operator B is seen to be positive. If $h = \mathbf{O}$ then from (IV.15) it follows $f = Bh = \mathbf{O}$, therefore, B is positive definite, and, moreover (IV.16) ensures that the bound of B does not exceed 1. Hence

$$0 \leqq (Bh, h) \leqq (h, h) \tag{IV.28}$$

holds for every h in $\mathfrak{H}$.

The relations derived for the bounded, self-adjoint operators B and C will be used for the spectral resolution of general self-adjoint operators.

D. Examples of Unbounded, Symmetric Operators

In this section we examine certain concrete operators in order to illustrate the concepts of the preceding section and to prepare ourselves for the spectral theory of unbounded, self-adjoint operators. As we found, an operator must have a domain everywhere dense in space to ensure the existence of a unique adjoint operator. Nevertheless the domain of an unbounded operator cannot be the entire space. This conclusion is the consequence of a theorem of Hellinger and Toeplitz which we did not prove (Akhiezer and Glazman, 1961, p. 48). Thus the domain of an unbounded operator will not be a closed set, but we shall arrange matters so that the operator will be a closed operator in the sense of the definition of Section IVB; i.e., the graph of the operator in double space will be a closed set. We recall that if $A^\dagger$, the adjoint of A, has a domain $\mathbf{D}_{A^\dagger}$ which is everywhere dense, then $A^{\dagger\dagger}$ exists. It is a closed operator and an extension of A. In symbols $A^{\dagger\dagger} \supset A$. Thus whenever $\mathbf{D}_{A^\dagger}$ is everywhere dense, the existence of a closed extension of A is assured. This extension, $A^{\dagger\dagger}$, may coincide with A.

Now to the examples:

(a) Let $\{\phi_n\}$ be a complete orthonormal sequence and let

$$A\phi_n = n\phi_n, \qquad n = 1, 2, 3, \ldots. \tag{IV.29}$$

By requiring A to be linear it becomes defined for every element of the form $f = \sum_{n=1}^{N} x_n\phi_n$, and then $Af = \sum_{n=1}^{N} x_n n\phi_n$. For elements of the general type,

$$f = \sum_{n=1}^{\infty} x_n\phi_n, \tag{IV.30}$$

where $\sum_{n=1}^{\infty} |x_n|^2$ is finite; we may define

$$Af = \sum_{n=1}^{\infty} x_n n\phi_n, \tag{IV.31}$$

provided the sum

$$\sum_{n=1}^{\infty} |x_n|^2 n^2 \tag{IV.32}$$

is convergent. We therefore include in $\mathbf{D}_A$ those and only those elements f for which the sums $\Sigma\, |x_n|^2$ and $\Sigma\, n^2|x_n|^2$ are convergent. This domain is clearly everywhere dense in $\mathfrak{H}$, therefore $A^\dagger$ is uniquely defined. Let now

$$g = \sum_{n=1}^{\infty} y_n \phi_n. \tag{IV.33}$$

The equation

$$(Af, g) = \sum_{n=1}^{\infty} x_n n y_n{}^* = (f, A^\dagger g) \tag{IV.34}$$

shows that $A^\dagger$ must be of the form

$$A^\dagger g = \sum_{n=1}^{\infty} y_n n \phi_n, \tag{IV.35}$$

and that $\mathbf{D}_{A^\dagger}$ consists of all elements of the form (IV.33) for which $\Sigma\,|y_n|^2$ and $\Sigma\,|y_n n|^2$ converge. Thus $\mathbf{D}_{A^\dagger} = \mathbf{D}_A$ and $A = A^\dagger$; the operator is self-adjoint.

The eigenvalues of this operator are the positive integers, and its eigenfunctions are the elements of the orthonormal set $\phi_1, \phi_2, \ldots$.

(b) Consider for the moment the multiplication operator in the space $\mathfrak{L}_2$ over a finite interval, say $\mathfrak{L}_2[0, 1]$. The elements of this space are the functions $f(x)$ for which

$$\int_0^1 |f(x)|^2\,dx$$

is finite. The multiplication operator B_F transforms $f(x)$ into $xf(x)$. But, since

$$\|B_F f\|^2 = \int_0^1 |xf(x)|^2\,dx \leqq \int_0^1 |f(x)|^2\,dx = \|f\|^2,$$

the operator B_F is bounded and defined over $\mathfrak{L}_2[0, 1]$. Since it is clearly a symmetric operator, it is also self-adjoint.

The multiplication operator B in the space $\mathfrak{L}_2$ over an infinite interval is no longer bounded. Its domain $\mathbf{D}_B$ must be restricted to such functions $f(x)$ in $\mathfrak{L}_2[-\infty, +\infty]$ for which $xf(x)$ again belongs to $\mathfrak{L}_2$. Whenever f and g are such elements, we have

$$(Bf, g) = \int_{-\infty}^{+\infty} xf(x)g(x)^*\,dx = (f, B^\dagger g). \tag{IV.36}$$

Therefore $\mathbf{D}_{B^\dagger} \supset \mathbf{D}_B$ and $B^\dagger g = xg = Bg$. The operator B is symmetric. To prove that B is self-adjoint we must show that $\mathbf{D}_{B^\dagger} = \mathbf{D}_B$.

Let $f \in \mathfrak{L}_2$, and let f be so restricted that $f(x) = 0$ when $|x|$ exceeds some large number N. Then $f \in \mathbf{D}_B$, and we may write for every g in $\mathbf{D}_{B^\dagger}$ and $h = B^\dagger g$ that

$$\int_{-\infty}^{+\infty} f(x)xg(x)^* \, dx - \int_{-\infty}^{+\infty} f(x)h^*(x) \, dx = \int_{-N}^{N} f(x)[xg(x) - h(x)]^* \, dx = 0. \tag{IV.37}$$

Since this equation holds for any truncated function $f(x)$, it follows that whenever $|x| < N$, then

$$h(x) = xg(x). \tag{IV.38}$$

The number N is arbitrary, therefore $xg(x)$ belongs to $\mathfrak{L}_2$, since h is in $\mathfrak{L}_2$. Thus g, which was an arbitrary element of $\mathbf{D}_{B^\dagger}$, belongs to $\mathbf{D}_B$. The conclusion is $\mathbf{D}_{B^\dagger} = \mathbf{D}_B$ and $B^\dagger = B$.

(c) An important differential operator in $\mathfrak{L}_2$ is defined formally by the equation

$$Df = i\frac{df}{dx}. \tag{IV.39}$$

This formal definition leads to a number of different operators depending on the nature of the interval of $\mathfrak{L}_2$ and on the specifications for the domain of the operator. In any case, in order that the operator equation (IV.39) be meaningful, every element of $\mathfrak{L}_2$ in the domain of D must satisfy the following condition:

(A) The function $f(x)$ must be absolutely continuous; i.e., equal to the integral of its derivative $f'(x)$, moreover the function $f'(x)$ must also belong to $\mathfrak{L}_2$.

We shall examine the operator D separately for the case of a finite interval typified by $\mathfrak{L}_2[0, 1]$, the infinite interval $\mathfrak{L}_2[-\infty, +\infty]$, and the semi-infinite interval $\mathfrak{L}_2[0, \infty]$.

In the first case, we may write, for any pair of functions which satisfy condition (A),

$$\int_0^1 if'(x)g(x)^* \, dx - \int_0^1 f(x)[ig'(x)]^* \, dx = i[f(1)g(1)^* - f(0)g(0)^*]. \tag{IV.40}$$

If we define $\mathbf{D}_D$ by specifying that this set consists of all functions which vanish at 0 and 1 in addition to satisfying condition (A) then the right side of (IV.40) vanishes for *any* function g satisfying condition (A). We then have an operator D_0 which is symmetric but not self-adjoint because $\mathbf{D}_{D_0} \subset \mathbf{D}_{D_0^\dagger}$; $D_0^\dagger$ is a proper extension of D_0. It is possible to prove that $D_0 = D_0^{\dagger\dagger}$, therefore D_0 is a closed, symmetric operator.

Let us now construct an operator D_1 which is an extension of D_0. The domain $\mathbf{D}_1$ of D_1 must be so chosen that

$$f(1)g(1)^* - f(0)g(0)^* = 0 \tag{IV.41}$$

for every $f \in \mathbf{D}_1$ and every g in the domain $\mathbf{D}_1^\dagger$ of the operator $D_1^\dagger$. If the earlier boundary condition $f(0) = f(1) = 0$ is replaced by the following more general condition:

$$f(1) = f(0)e^{i\theta}, \tag{IV.42}$$

where θ is an arbitrary real number, we obtain an extension D_1 of D_0 which is not only symmetric but also self-adjoint. In fact, Eqs. (IV.41) and (IV.42) together require that

$$g(1) = g(0)e^{i\theta}, \tag{IV.43}$$

i.e., $g \in \mathbf{D}_1$. Thus $\mathbf{D}_1 = \mathbf{D}_1^\dagger$. For every real value of θ in the interval 0 to 2π, we obtain a different extension of D_0. *All these extensions are self-adjoint.*

We shall now prove that D_0 has no other symmetric extension than the family described above. Let f_0 be an element in $\mathbf{D}'$, the domain of a symmetric extension D' of D_0, but let f_0 *not* be in $\mathbf{D}_{D_0}$. Then $f_0(0) \neq 0$. Let $\alpha = f_0(1)/f_0(0)$. The operator D' is symmetric, therefore (IV.41) must be satisfied for $f = f_0$ and for any g in $\mathbf{D}'^\dagger$, the domain of $D'^\dagger$. Thus if $g \in \mathbf{D}'^\dagger$,

$$[\alpha g(1)^* - g(0)^*]f_0(0) = 0, \tag{IV.44}$$

therefore

$$g(1)^* = \frac{1}{\alpha} g(0)^*, \tag{IV.45}$$

and

$$g(1) = \frac{1}{\alpha^*} g(0). \tag{IV.46}$$

For the special case $g = f_0$, it follows from (IV.46) and the definition of α that

$$f_0(1) = \frac{1}{\alpha^*} f_0(0) = \alpha f_0(0), \tag{IV.47}$$

and therefore, since $f_0(0) \neq 0$,

$$\alpha\alpha^* = 1. \tag{IV.48}$$

Thus α may be represented in the form $e^{i\theta}$ with a real θ, and condition (IV.46) reduces to (IV.42). But in this case, (IV.42) must hold for every f in $\mathbf{D}'$, not only for $f = f_0$. Thus we have arrived at one of the self-adjoint extensions of D_0 which we encountered earlier.

Having completed the analysis of operator D for the finite interval, we turn to the same problem in the space $\mathfrak{L}_2[-\infty, +\infty]$ which we denote for brevity by $\mathfrak{L}_{2\infty}$. This problem is much simplified by the fact that no boundary conditions are necessary, because for all functions which satisfy condition (A) in $\mathfrak{L}_{2\infty}$, $\lim_{x\to\infty} f(x) = \lim_{x=-\infty} f(x) = 0$. Taking this statement for granted, it is clear that

$$\int_{-\infty}^{+\infty} if'(x)g(x)^*\,dx - \int_{\infty}^{\infty} f(x)[ig'(x)]^*\,dx = 0 \tag{IV.49}$$

for all pairs of functions f and g which satisfy condition (A). Therefore $\mathbf{D}$ is defined by the single requirement of condition (A), moreover $\mathbf{D}^\dagger = \mathbf{D}$, the operator is self-adjoint.

It remains to prove the statement that the functions satisfying condition (A) vanish at both ends. For the general elements of $\mathfrak{L}_{2\infty}$ one cannot assert the existence of these limits. It is true, however, that if $\lim_{x=\infty} |f(x)|$ exists, then the convergence of the integral

$$\int_{-\infty}^{+\infty} |f(x)|^2\,dx$$

ensures that this limit is zero. In the case of a function f subject to condition (A), the function $f(x)f'(x)^*$ is also integrable and we have by elementary integration

$$\int_0^N f(x)f'(x)^*\,dx + \int_0^N f'(x)f(x)^*\,dx = |f(N)|^2 - |f(0)|^2. \tag{IV.50}$$

As N tends to infinity, the integrals on the left-hand side of (IV.50) tend to a definite limit because ff'^* is integrable. Therefore the right-hand side also tends to a limit, ensuring the existence of $\lim_{N\to\infty} |f(N)|$, and this limit must be zero.

In the case of the differential operator over the semi-infinite interval, it follows as above that $\lim_{N\to\infty} f(x) = 0$ for any f subject to condition (A). However $f(0)$ need not be 0. Let $\mathbf{D}$ be the set in $\mathfrak{L}_2[0, \infty]$ which satisfies condition (A) and the boundary condition $f(0) = 0$. Then for any g which satisfies condition (A) alone

$$\int_0^\infty if'(x)g(x)^*\,dx - \int_0^\infty f(x)[ig'(x)]^*\,dx = -if(0)g(0)^* = 0. \quad \text{(IV.51)}$$

Hence D is a symmetric operator and $\mathbf{D}^\dagger$ is the set which satisfies condition (A); in other words a set larger than $\mathbf{D}$. Thus this operator is not self-adjoint. It does not even have a symmetric extension because if the domain $\mathbf{D}$ were extended to contain a new element h such that $h(0) \neq 0$, then

$$(Dh, h) - (h, Dh) = \int_0^\infty ih'h^*\,dx - \int_0^\infty h(ih')^*\,dx = -i|h(0)|^2 \neq 0, \quad \text{(IV.52)}$$

therefore h could not be in the domain of the adjoint operator. We have thus encountered a maximal symmetric operator which is not self-adjoint.

Note: We have tacitly assumed that functions which satisfy condition (A) in any of the $\mathfrak{L}_2$ spaces form a dense set in the space in question. This is a true theorem, and is proven in many treatises. Its proof can be constructed by demonstrating that an element of $\mathfrak{L}_2$ which is orthogonal to every function satisfying condition (A) is identically 0. The demonstration proceeds by choosing judiciously a convenient subset of the functions satisfying this condition and proving that orthogonality to this subset already requires an element to be identically 0.

Exercises

(A, B and C refer to the operators defined in this section.)

1. What is the domain of the operator A^2? Is this operator self-adjoint?
2. What is the domain of the operator B^2 over $\mathfrak{L}_{2\infty}$? Is this operator self-adjoint?
3. Prove that the operator D on $\mathfrak{L}_2[0, \infty]$ is a closed symmetric operator.
4. Show that the operator d^2/dx^2 with a proper definition of its domain is self-adjoint in all three types of $\mathfrak{L}_2$ spaces discussed.

E. An Auxiliary Theorem about Bounded Self-Adjoint Operators

In the proof of the spectral theorem for *general* self-adjoint operators we shall need a theorem concerning *bounded* self-adjoint operators. This theorem asserts that if such an operator is bounded away from zero then it can be inverted and the inverse is again a bounded self-adjoint operator. It is usually proven by making use of the spectral theorem for bounded operators and the concept of the continuous function of such an operator. Here we shall give a direct proof. The precise statement of the theorem is as follows:

If the self-adjoint operator H is such that

$$0 < a(f,f) \leqq (Hf,f) \leqq b(f,f) \tag{IV.53}$$

for every $f \neq 0$, then it has an inverse H^{-1} defined over the entire space; i.e., there is a unique, bounded, self-adjoint operator H^{-1} such that

$$HH^{-1} = H^{-1}H = I. \tag{IV.54}$$

Clearly, it is sufficient to prove the theorem for $b = 1$ and $a < b$. We carry out the proof by constructing the required operator. The operator

$$Q = H - I \tag{IV.55}$$

is again self-adjoint and bounded because from

$$a(f,f) \leqq (Hf,f) \leqq (f,f) \tag{IV.56}$$

it follows for $0 < a < 1$ that

$$-(1 - a)(f,f) \leqq (Qf,f) \leqq 0, \tag{IV.57}$$

therefore the bound of Q does not exceed $1 - a$. [See relations (II.19) and (II.20).] Then the series

$$Uf = f + Qf + Q^2f + \cdots + Q^nf + \cdots \tag{IV.58}$$

is convergent for every f in $\mathfrak{H}$ because

$$\|Q^nf\| < (1 - a)^n \, \|f\|, \tag{IV.59}$$

and thus the norms of the terms of (IV.58) are majorized by a convergent geometrical progression. Thus the operator U has the entire space as its domain, it is permutable with Q and therefore with H, it is symmetric because it is the sum of such operators. Finally, we apply Q to (IV.58) and obtain

$$QUf = Uf - f, \tag{IV.60}$$

valid for every f, and therefore with the aid of (IV.55) it follows that

$$(I - Q)U = HU = I. \tag{IV.61}$$

Since U is permutable, with H it is equal to H^{-1}.

The bound of $U = H^{-1}$ cannot exceed a^{-1}. In fact, from $f = Ug$ it follows that

$$\|Ug\|^2 \leqq \frac{1}{a}\,\|HUg\|\;\|Ug\| = \frac{1}{a}\,\|g\|\;\|Ug\|, \tag{IV.62}$$

and therefore

$$\|Ug\| \leqq \frac{1}{a}\,\|g\|,$$

for every g in $\mathfrak{H}$.

Note: It is instructive to construct the inverse of the operator H by making use of the spectral theorem for bounded self-adjoint operators. The reader may be able to verify that for an operator H as we have specified in the auxiliary theorem

$$\int_0^b \frac{1}{\lambda}\, d(E_\lambda f, Hf) = (f, f)$$

for every f. Therefore H^{-1} may be represented in the form

$$\int_0^b \frac{1}{\lambda}\, dE_\lambda .$$

F. Proof of the Spectral Theorem

This section is devoted entirely to the proof of the central theorem in the theory of self-adjoint operators. It represents a climax toward which we have been striving gradually.

The Spectral Theorem. For every self-adjoint operator H there corresponds one and only one resolution of the identity E_λ such that the following propositions are true:

(*a*) *E_λ is permutable with H and with every bounded operator permutable with H.*

(*b*) *The domain of H is the set of elements f for which the integral*

$$\int_{-\infty}^{+\infty} \lambda^2\, d(E_\lambda f, f)$$

exists.

(*c*) *When f is in the domain of H, then*

$$(Hf, f) = \int_{-\infty}^{+\infty} \lambda\, d(E_\lambda f, f). \tag{IV.63}$$

Three essentially different proofs of this theorem were published nearly simultaneously by von Neumann (1929), Stone (1929), and Riesz (1930). They all reduce the problem in one form or the other to the study of bounded operators. The common point in all these proofs is the exploitation of the fact that the inverse of the operator $H - iI$ is a bounded operator, even though H is unbounded. The operator $R = (H - iI)^{-1}$ is comparatively easy to deal with; even though it is not self-adjoint.

We reproduce here a simplified proof due to Riesz and Lorch (1936). Since this simplified proof is still quite long, we first take a birds-eye view of it before delving into technical details. The object of this work is to find a sequence of mutually orthogonal subspaces $\{\mathbf{M}_n\}$, each of which is entirely in the domain of the operator H, each of which reduces H, and finally such that all the $\mathbf{M}_n$'s together span the entire space $\mathfrak{H}$. In each of these subspaces H is a bounded, self-adjoint operator, the bound varying from subspace to subspace. On account of its boundedness, H has a resolution of the identity $E_{\lambda n}$ in every subspace $\mathbf{M}_n$. Adding the $E_{\lambda n}$'s we obtain the desired E_λ.

The construction of the sequence $\mathbf{M}_n$ is accomplished with the aid of the operator $R = iB + C$ introduced in Section IV, C. The sequence of mutually orthogonal subspaces that leads to the spectral resolution of the unbounded self-adjoint operator H is determined in terms of the resolution of the identity which belongs to the bounded self-adjoint operator B.

We begin the proof by contemplating a sequence of mutually orthogonal subspaces $\{\mathbf{M}_n\}$ which together span the entire Hilbert space.

Let P_i be the projection operator of $\mathbf{M}_i$, then $P_i P_j = 0$ for $i \neq j$, and $\sum_{i=1}^{\infty} P_i = I$. Let there be given a bounded self-adjoint operator H_i in each of the subspaces. It is understood that H_i is defined for the elements of $\mathbf{M}_i$, it transforms these again into elements of $\mathbf{M}_i$. Then the following lemma is true:

Lemma. Given the decomposition of $\mathfrak{H}$ in a sum of orthogonal subspaces as described, there exists a unique, self-adjoint operator H in $\mathfrak{H}$ which is identical with H_i in $\mathbf{M}_i$. The domain $\mathbf{D}_H$ of H consists of such elements f for which the sum $\sum_{i=1}^{\infty} \|H_i P_i f\|^2$ converges. If $f \in \mathbf{D}_H$, then $Hf = \sum_{i=1}^{\infty} H_i P_i f_i$.

We first show that an operator defined in the lemma is self-adjoint. Its domain is everywhere dense, because the orthogonal sum of a finite number of subspaces is dense in $\mathfrak{H}$. If $f \in \mathbf{D}_H$, then $f_i = P_i f$ and $f - f_i$ are both in $\mathbf{D}_H$. Moreover, $H(f - f_i)$ is in $\mathbf{M}_i^{\perp}$. Thus $H^\dagger$ is defined in $\mathbf{M}_i$ and is equal to H in $\mathbf{M}_i$, because the following equation holds for every f in $\mathbf{D}_H$ and every g in $\mathbf{M}_i$:

$$(Hf, g) = (H(f - f_i), g) + (Hf_i, g) = (f_i, Hg) = (f, Hg). \tag{IV.64}$$

Since $H^\dagger$ is a closed operator which coincides with H in every $\mathbf{M}_i$, the domain of $H^\dagger$ includes that of H. To prove that H is self-adjoint we have to show that $\mathbf{D}_{H^\dagger} \subset \mathbf{D}_H$. In fact, let $h \in \mathbf{D}_{H^\dagger}$, and let $h_i = P_i h$, then

$$(H^\dagger(h - h_i), Hh_i) = ((h - h_i), H^2 h_i) = 0, \tag{IV.65}$$

and hence

$$\|H^\dagger h\|^2 = \|H^\dagger(h - h_i)\|^2 + \|Hh_i\|^2. \tag{IV.66}$$

We can extend (IV.66) by noting that $H^2 h_i$, being an element of $\mathbf{M}_i$, is orthogonal not only to $h - h_i$, which was used in (IV.65), but to $h - \Sigma h_j$ as well, provided the summation includes the index i. Hence (IV.66) may be replaced by

$$\|H^\dagger h\|^2 = \left\| H^\dagger\left(h - \sum_{i=1}^{n} h_i\right)\right\|^2 + \sum_{i=1}^{n} \|Hh_i\|^2. \tag{IV.67}$$

This last equation is valid for any n, therefore

$$\|H^\dagger h\|^2 \geqq \sum_{i=1}^{\infty} \|Hh_i\|^2. \tag{IV.68}$$

Thus $\sum_{i=1}^{\infty} \|HP_i h\|^2$ converges and $h \in \mathbf{D}_H$, as we were to show.

Finally, to show that the operator H is unique, we assume that there is a self-adjoint operator X which coincides with H_i in $\mathbf{M}_i$. Then X is an extension of H, and this implies $X \equiv H$ because a self-adjoint operator cannot have a proper extension.

Now we may show that, given a resolution of the identity E_λ, we can construct a unique, self-adjoint operator H as announced in the spectral theorem. For a finite resolution E_λ, this was already demonstrated in Section III, B. In the case of a general resolution of the identity, we introduce the projection operators

$$P_n = E_n - E_{n-1}$$

for $n = 0, \pm 1, \pm 2, \ldots$. The ranges of these projections are the subspaces $\mathbf{M}_0, \mathbf{M}_1, \mathbf{M}_{-1}, \mathbf{M}_2, \mathbf{M}_{-2}, \ldots$ which are mutually orthogonal and together span the entire space $\mathfrak{H}$. In the range of P_n the resolution of the identity defines a bounded, self-adjoint operator given by the relations

$$H_n = \int_{n-1}^{n} \lambda \, dE_\lambda, \qquad \|H_n f\|^2 = \int_{n-1}^{n} \lambda^2 \, d(E_\lambda f, f), \tag{IV.69}$$

and $\mathbf{M}_n$ reduces to H_n. The lemma is then applicable and assures the existence of a unique self-adjoint operator H whose domain is the set for which

$$\sum_{i=0}^{\pm\infty} \|H_i P_i f\|^2 = \int_{-\infty}^{+\infty} \lambda^2 \, d(E_\lambda f, f) \tag{IV.70}$$

converges.

If $f \in \mathbf{D}_H$, then

$$(Hf, g) = \sum_{i=0}^{\pm\infty} (H_i f, g) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, g), \tag{IV.71}$$

for every g in $\mathfrak{H}$.

To prove that a resolution of the identity may be found for any given self-adjoint operator H, we turn to the bounded self-adjoint operators B and C generated by H. These were introduced in Section II, C and are formally the operators $(I + H^2)^{-1}$ and $H(I + H^2)^{-1}$. We found that $Bh = \mathbf{O}$ implies $h = \mathbf{O}$, and that for $h \neq \mathbf{O}$,

$$0 < (Bh, h) \leqq (h, h).$$

According to the results of Section III, D, there is a finite resolution of the identity $E_\lambda(B)$ associated with B. For convenience, and in order to distinguish this resolution from that of the operator H, we write $E(\lambda)$ to designate $E_\lambda(B)$. The properties of B assure that $E(0) = 0$ and $E(1) = I$. Let $\mathbf{M}_n$ be the range of the projection $E(1/n) - E(1/n + 1)$. Then the subspaces $\mathbf{M}_n$ are mutually orthogonal and span the entire space as required by (IV.64), because the sum of their projections is $E(1) = I$. We now proceed to show that the operator H is defined throughout $\mathbf{M}_n$ and that $\mathbf{M}_n$ reduces H. The crucial point of the proof is that B has a *bounded* inverse in $\mathbf{M}_n$.

Since $\mathbf{M}_n$ reduces B, as assured by the spectral theorem for bounded self-adjoint operators, we may disregard for a moment the behavior of B outside $\mathbf{M}_n$ and regard B as an operator in the subspace $\mathbf{M}_n$. In this subspace

$$\frac{1}{n+1}(h, h) < (Bh, h) \leqq \frac{1}{n}(h, h) \tag{IV.72}$$

for every $h \neq 0$. According to the auxiliary theorem of Section II, E, the operator B restricted to $\mathbf{M}_n$ has a bounded inverse; i.e., there exists an operator $R(B)$ defined for every element $h \in \mathbf{M}_n$, such that

$$BR(B)h = R(B)Bh = h. \tag{IV.73}$$

We noted in Section IV, C that Bh is always in the domain of H. Equation (IV.73) ensures that every element $g \in \mathbf{M}_n$ may be written in the form $g = Bh = BR(B)g$. Therefore every such g is in the domain of the original operator H.

Any bounded operator permutable with B is permutable with every operator $E(\lambda)$, hence it transforms each $\mathbf{M}_n$ into itself. In particular, the operator C is permutable with B, therefore it is reduced by $\mathbf{M}_n$. Then, if $g \in \mathbf{M}_n$,

$$Hg = HBR(B)g = CR(B)g \tag{IV.74}$$

is again in $\mathbf{M}_n$, the subspace reduces H as well. In $\mathbf{M}_n$, the operator H is bounded because C and $R(B)$ are bounded. The spectral theory of bounded operators assures us that a resolution of the identity $E_{\lambda n}$ may be found which is the resolution of the operator H in the subspace $\mathbf{M}_n$. Let E_λ represent the family of projections in $\mathfrak{H}$ which are identical with $E_{\lambda n}$ in $\mathbf{M}_n$ for every n. It is easy to show that E_λ is a resolution of the identity. The integral

$$\int_{-\infty}^{+\infty} \lambda \, dE_\lambda$$

represents a self-adjoint operator G whose domain is the set for which

$$\int_{-\infty}^{+\infty} \lambda^2 \, d(E_\lambda f, f)$$

is finite and for which

$$(Gf, g) = \int_{-\infty}^{+\infty} \lambda \, d(E_\lambda f, g)$$

for every f in $\mathbf{D}_G$ and every g in $\mathfrak{H}$. This operator is identical with H in every subspace $\mathbf{M}_n$, therefore the uniqueness asserted by our lemma ensures that $G = H$. This concludes the proof of the spectral theorem.

Note: It is instructive to examine in detail the multiplication operator in the space $\mathfrak{L}_2[-\infty, \infty]$ already introduced in Section IV, D. The reader may show that the resolution of the identity associated with this operator may be defined as follows: $E_\lambda f(x) = f(x)$ for $x \leqq \lambda$, and 0 for $x > \lambda$. The operator is unbounded and has no eigenvalues.

V. Unitary Operators. Equivalence of Operators

A. Definition of Unitary and Isometric Operators

The geometrical properties of Hilbert space are invariants of the operators which map the space onto itself without changing the fundamental inner product (f, g). Such operators are generalizations of the coordinate rotations and symmetry operations in ordinary space. They form a group. Frequently they are called transformations instead of operators because, when studying and using them, one's attention is focused on their mapping properties rather than on their properties as functions.

An operator U *whose domain and range coincide with* $\mathfrak{H}$ *is called unitary if*

$$(Uf, Ug) = (f, g) \tag{V.1}$$

holds for every pair f, g.

We note that the definition does not require U to be linear. This fact follows, however, as we shall see. First we show that every unitary operator has an inverse U^{-1} which is also unitary. From (V.1) we can show by elementary algebra that

$$\|Uf - Ug\| = \|f - g\| \tag{V.2}$$

for every pair of elements. Thus $Uf = Ug$ implies $f = g$, so that the inverse of U exists. Its domain and range coincide with the range and the domain of U respectively. Thus U^{-1} also has $\mathfrak{H}$ as its domain and range. Moreover, it leaves (f, g) unchanged, hence it is a unitary operator. Both U and U^{-1} are bounded operators with bounds equal to 1.

Let us now replace g in (V.1) by $U^{-1}h$. Then $Ug = h$, and

$$(Uf, h) = (f, U^{-1}h) \tag{V.3}$$

for every pair f, h. We have thus proved that

$$U^{\dagger} = U^{-1}. \tag{V.4}$$

The adjoint operator is always a linear operator, therefore U^{-1}, and hence also $U = (U^{-1})^{\dagger}$ are linear operators.

The class of unitary operators is a group. It contains the identity, the inverse of every unitary operator, and the product of any two unitary operators U_1 and U_2. This last statement is true by virtue of the fact that $U_1 U_2$ is an operator that maps $\mathfrak{H}$ onto itself and satisfies the relation $(U_1 U_2 f, U_1 U_2 g) = (U_2 f, U_2 g) = (f, g)$.

A linear operator V is called isometric if the equation

$$(Vf, Vg)) = (f, g) \tag{V.5}$$

is satisfied for every pair f, g in the domain of V.

A unitary operator is a special isometric operator whose domain and range coinciae with $\mathfrak{H}$. It is easy to verify the following propositions:

(a) An isometric operator is bounded; in fact $\|Vf\| = \|f\|$ for every $f \in \mathbf{D}_V$.

(b) An isometric operator may be extended over the subspace $\bar{\mathbf{D}}_V$ determined by $\mathbf{D}_V$. The extended operator V is closed and isometric.

(c) A necessary and sufficient condition that the linear operator V be isometric is that it preserves distances (norms); i.e.,

$$\|Vf - Vg\| = \|f - g\| \tag{V.6}$$

for every pair $f, g \in \mathbf{D}_V$.

It is of interest to contemplate a few examples.

(i) Let $\phi_1, \phi_2, \ldots$ be a complete orthonormal system and let $\psi_1, \psi_2, \ldots$ be another such system. The linear operator $U\phi_k = \psi_k$, $k = 1, 2, 3, \ldots$ is bounded and defined for every f of the form $f = \sum_{k=1}^N a_k\phi_k$, and $Uf = \sum_{k=1}^N a_k\psi_k$. It can be extended over the entire space and it then becomes a unitary operator.

(ii) The linear operator V_1 defined by the equations $V_1\phi_k = \phi_{k+1}$, $k = 1, 2, \ldots$ is bounded and preserves the norm of any element in its domain because if $f = \sum_{k=1}^N a_k\phi_k$, then

$$\|V_1 f\|^2 = \left\|\sum_{k=1}^N a_k\phi_{k+1}\right\|^2 = \sum_{k=1}^N |a_k|^2 = \|f\|^2.$$

Consequently, V_1 may be extended so that its domain is $\mathfrak{H}$. It is an isometric operator which is not unitary because its range is orthogonal to ϕ_1.

(iii) Let the next operator V_2 be defined over the subspace spanned by $\phi_2, \phi_3, \ldots$. The linear operator defined by the equations $V_2\phi_{k+1} = \phi_k$, $k = 1, 2, 3, \ldots$ is again isometric, but not unitary, because its domain is orthogonal to ϕ_1. We have $V_2V_1 = I$, but $V_1V_2 \neq I$, because ϕ_1 is not in the domain of V_1V_2.

Exercises

1. Prove that (V.2) follows from (V.1) without assuming the linearity of the operator.

2. Let $\phi_1, \phi_2, \ldots$ be a complete, orthonormal sequence, and $\theta_1, \theta_2, \ldots$ a sequence of real numbers. Form a linear operator starting with $U\phi_k = e^{i\theta_k}\phi_k$, $k = 1, 2, \ldots$. Show that it can be extended so that its domain becomes $\mathfrak{H}$, and that the operator U is then unitary.

3. Show that if α is the eigenvalue of a unitary operator, then $|\alpha| = 1$.

4. Generate the unitary operators U_1, U_2, and U_3 using the defining equations: $U_1\phi_k = i^k\phi_k$, $U_2\phi_k = (-1)^k\phi_k$, $U_3\phi_k = (-i)^k\phi_k$ for $k = 1, 2, \ldots$. These operators together with $U_4 = I$ form a group of order 4. Try now to construct a group of unitary operators of order 5.

B. The Fourier-Plancherel Theorem

One learns that if $f(x)$ is a "good" function, one may form its Fourier transform

$$F(t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} f(x)e^{-ixt}\, dx, \tag{V.7}$$

which has the property that

$$\int_{-\infty}^{+\infty} |F(t)|^2\, dt = \int_{-\infty}^{+\infty} |f(x)|^2\, dx. \tag{V.8}$$

Moreover, $f(x)$ may be regained by the formula

$$f(x) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} F(t)e^{ixt}\, dt. \tag{V.9}$$

Equation (V.8) suggests that the Fourier transformation is a unitary transformation in the space $\mathfrak{L}_2[-\infty, \infty]$. Unfortunately, the integral (V.7) does not converge for every f in $\mathfrak{L}_2$. Nevertheless, the integrations may be carried out over a set which is everywhere dense in $\mathfrak{L}_2$ and they lead to the definition of a unitary operator by extension of the original linear operator. In fact, it is possible to replace Eqs. (V.7) and (V.9) by analytical formulas valid over the entire space $\mathfrak{L}_2$, and these formulas reduce to (V.7) and (V.9) when the latter are applicable. To demonstrate that the Fourier transform defines a unitary operator, we introduce a complete orthonormal sequence $\{\phi_n(x)\}$ in $\mathfrak{L}_2$, such that the transformation

$$\Phi_n(t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} e^{-ixt}\phi_n(x)\, dx \tag{V.10}$$

is defined for every $\phi_n(x)$. Moreover

$$\|\Phi_n\|^2 = \|\phi_n\|^2 = 1, \tag{V.11}$$

and the set spans the entire space. Then the linear operator defined by the equations

$$\Phi_n = U\phi_n, \qquad n = 0, 1, 2, \ldots, \tag{V.12}$$

is an isometric operator whose domain and range are everywhere dense. It may be extended to a closed operator whose domain and range is $\mathfrak{H}$ and which is therefore a unitary operator.

The Hermite polynomials, $H_n(x)$, are defined in terms of their generating function:

$$\psi(x, s) = \exp[-s^2 + 2sx] = \sum_{n=0}^{\infty} \frac{H_n(x)\, s_n}{n!}. \tag{V.13}$$

(Akhiezer and Glazman, 1961, p. 24; Courant and Hilbert, 1953).
It is shown in standard treatises that these functions are orthogonal over the interval $[-\infty, \infty]$ with a weight function $\exp[-x^2]$, and that they form a complete set. Therefore the functions

$$\phi_n(x) = C_n \exp[-x^2/2]\, H_n(x) \tag{V.14}$$

form a complete orthogonal set of functions in $\mathfrak{L}_2[-\infty, \infty]$ which is normalized for proper choice of the C_n's. We introduce the generating function

$$\psi_1(x, s) = \exp[-x^2/2]\, \psi(x, s) = \sum_{n=0}^{\infty} \frac{\phi_n(x)}{C_n n!} s^n. \tag{V.15}$$

We apply the Fourier transformation to the function ψ_1 and to the $\phi_n(x)$'s. These operations are permissible because of the convergence-producing $\exp[-x^2/2]$ factors. Then

$$\begin{aligned} \Psi_1(t, s) &= \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} \exp[-ixt]\, \psi(x, s)\, ds \\ &= \frac{\exp[-s^2]}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} \exp[-x^2/2 + 2sx - ixt]\, dx. \end{aligned} \tag{V.16}$$

It is easily calculated that

$$\int_{-\infty}^{+\infty} \exp[-x^2/2 + ax]\, dx = (2\pi)^{1/2} \exp[a^2/2],$$

therefore

$$\Psi_1(t, s) = \exp[-t^2/2]\exp[s^2 - 2its] = \psi_1(t, -is). \tag{V.17}$$

Since

$$\Psi_1(t, s) = \sum_{n=0}^{\infty} \frac{\Phi_n(t)}{C_n n!} s^n = \sum_{n=0}^{\infty} \frac{\phi_n(t)}{C_n n!} (-is)^n, \tag{V.18}$$

we obtain

$$\Phi_n(t) = (-i)^n \phi_n(t), \tag{V.19}$$

valid for every integer n. Let f be an element in the linear manifold determined by ϕ_n, i.e.,

$$f = \sum_{n=0}^{N} a_n \phi_n . \tag{V.20}$$

Then, denoting the linear transformation defined by (V.19) by U, we have

$$Uf = \sum_{n=0}^{N} a_n (-i)^n \phi_n , \tag{V.21}$$

and therefore

$$\|Uf\|^2 = \sum_{n=0}^{N} |a_n|^2 = \|f\|^2 .$$

The transformation U is isometric; its domain and range are everywhere dense. The inverse transformation U^{-1} is obtained by replacing i by $-i$. This fact follows from (V.19). Thus we have shown not only that the closed extension of U is a unitary operator, but also that the inverse operator is the one obtained by replacing i by $-i$. This result establishes Eq. (V.9).

The analytical form of the transformations U and $U^\dagger$ applicable to any element of $\mathfrak{L}_2[-\infty, \infty]$ is given by the equations

$$F(t) = \frac{1}{(2\pi)^{1/2}} \frac{d}{dt} \int_{-\infty}^{+\infty} \frac{e^{-ixt} - 1}{-ix} f(x)\, dx, \tag{V.22}$$

$$f(x) = \frac{1}{(2\pi)^{1/2}} \frac{d}{dx} \int_{-\infty}^{+\infty} \frac{e^{ixt} - 1}{it} F(t)\, dt. \tag{V.23}$$

The content of the Fourier–Plancherel theorem is that to every f in $\mathfrak{L}_2$ the transformation (V.22) *orders an element F which is also in $\mathfrak{L}_2$ and has the same norm as f. Moreover, the inverse transformation is given by* (V.23).

Since the function $(e^{ixt} - 1)/ix$ belongs to $\mathfrak{L}_2$, the integral in (V.22) exists and is finite for every value of t and for every f in $\mathfrak{L}_2$. When in addition $f(x)$ is absolutely integrable, then a theorem of Lebesgue assures us that the differentiation with respect to t and integration with respect to x may be interchanged.[2] Then, because

$$\frac{d}{dt}\left(\frac{e^{-ixt}-1}{-ix}\right) = e^{-ixt}, \tag{V.24}$$

Eq. (V.22) reduces to (V.7). We have established here already that (V.7) is meaningful on a linear manifold everywhere dense in $\mathfrak{L}_2$, namely, in the manifold determined by (V.20). It represents an isometric operator which, for absolutely integrable element of $\mathfrak{L}_2$, coincides with the unitary operators defined by (V.22). Since absolutely integrable functions are also everywhere dense in $\mathfrak{L}_2$, the closed extension of the operator defined by (V.7) is identical with the unitary operator defined by (V.22).

Exercises

1. Show that the operators U, U^2, U^3, and $U^4 = I$ form a group, where U is the operator defined in the Fourier–Plancherel theorem.
2. Show that i, -1, $-i$ and 1 are eigenvalues of U.
3. Show that the operators $P_0 = \frac{1}{4}(I + U + U^2 + U^3)$, $P_1 = \frac{1}{4}(I - U + U^2 - U^3)$, $P_3 = \frac{1}{4}(I - iU - U^2 + iU^3)$, and $P_4 = \frac{1}{4}(I + iU - U^2 - iU^3)$ are pairwise orthogonal projections whose sum is I.
4. Show that every element in the range of P_i $(i = 0, 1, 2, 3)$ is an eigenfunction of U.

C. Unitary Equivalence

Let us consider a unitary operator U as a transformation or mapping of the Hilbert space upon itself. Together with an operator A defined on $\mathbf{D}_A$ we shall consider another operator A' related to A as follows: the domain $\mathbf{D}_{A'}$ is $U\mathbf{D}_A$; and if $f = Ag$, then $A'Ug = UAg$. Thus

$$UA = A'U \tag{V.25}$$

valid for every g in $\mathbf{D}_A$. The operators A and A' must represent very similar relationships. They are called *equivalent* to each other.

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[2] This matter involves rather basic properties of Lebesgue integration (see, for example, Riesz and Sz.-Nagy, 1955, pp. 37–38 and 294–295).

It is easy to see that if f is an eigenfunction of A then Uf is an eigenfunction of A' with the same eigenvalue. In fact, from $Af = \lambda f$ it follows that

$$A'Uf = UAf = U\lambda f = \lambda Uf. \tag{V.26}$$

Equivalence among self-adjoint operators is reflected by the equivalence among their respective resolutions of the identity. We shall prove that if the self-adjoint operator H has the resolution E_λ, then $E_\lambda' = UE_\lambda U^{-1}$ is also a resolution of the identity. It determines the self-adjoint operator

$$H' = UHU^{-1}. \tag{V.27}$$

The fact that E_λ' is a resolution of the identity is verified by the use of relations of the type

$$E_\lambda' E_\mu' = UE_\lambda U^{-1} UE_\mu U^{-1} = UE_\lambda E_\mu U^{-1}, \tag{V.28}$$

and

$$(E')^\dagger = (UEU^{-1})^\dagger = UEU^{-1} = E'. \tag{V.29}$$

The resolution E_λ' generates a self-adjoint operator H', whose domain is characterized by the finiteness of the integral $\int_{-\infty}^{+\infty} \lambda^2\, d(E_\lambda' f, f)$. But $(E_\lambda' f, f) = (UE_\lambda U^{-1} f, f) = (E_\lambda U^{-1} f, U^{-1} f)$. Therefore

$$\int_{-\infty}^{+\infty} \lambda^2\, d(E_\lambda' f, f) = \int_{-\infty}^{+\infty} \lambda^2\, d(E_\lambda U^{-1} f, U^{-1} f). \tag{V.30}$$

Hence $f = Uh$ is in the domain $\mathbf{D}_{H'}$ of H' if and only if $h = U^{-1} f$ is in $\mathbf{D}_H$. Thus $\mathbf{D}_{H'} = U\mathbf{D}_H$. Then, for every $f \in \mathbf{D}_{H'}$ and every $g \in \mathfrak{H}$,

$$\begin{aligned}(H'f, g) &= \int_{-\infty}^{+\infty} \lambda\, d(E_\lambda' f, g)\\ &= \int_{-\infty}^{+\infty} \lambda\, d(UE_\lambda U^{-1} f, g)\\ &= \int_{-\infty}^{+\infty} \lambda\, d(E_\lambda U^{-1} f, U^{-1} g)\\ &= (HU^{-1} f, U^{-1} g)\\ &= (UHU^{-1} f, g),\end{aligned} \tag{V.31}$$

and (V.27) is proved.

The Fourier–Plancherel theorem enables us now to prove the unitary equivalence of two important operators. These are the multiplication and the differentiation operators in $\mathfrak{L}_2[-\infty, +\infty]$ introduced in Section D. They are associated with position and momentum in quantum mechanics.

One discovers heuristically the equivalence of these operators as follows: Assuming that all integrals converge and the differentiation may be carried out, it follows from

$$F(t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} f(x) e^{-ixt}\, dt \tag{V.7}$$

that

$$iF'(t) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} x f(x) e^{-ixt}\, dt. \tag{V.32}$$

Therefore, designating the Fourier transformation by U, the multiplication by x by B, and $i\, d/dx$ by D, we have:

$F = Uf$; $xf(x) = Bf$, and $i\, dF/dt = DF$. Therefore, according to (V.32) $DF = UBf = DUf$, hence

$$D = UBU^{-1}. \tag{V.33}$$

We have to be careful in the actual proof of (V.33) because none of the formulas used in this heuristic argument are valid for every f in $\mathfrak{L}_2$. We have to show first that $h \in \mathbf{D}_B$ implies that $Uh \in \mathbf{D}_D$ and $DUh = UBh$. Second, we must prove that $g \in \mathbf{D}_D$ implies that $U^{-1}g \in \mathbf{D}_B$ and $BU^{-1}g = U^{-1}Dg$.

An essential element of our proof is the proposition that $h \in \mathbf{D}_B$ implies that $h(x)$ is absolutely integrable in $\mathfrak{L}_2[-\infty, +\infty]$. We shall prove this proposition first. It may be rephrased in the following form:

The relations $h(x) \in \mathfrak{L}_2$ and $xh(x) \in \mathfrak{L}_2$ together imply that

$$\int_{-N}^{+N} |h(x)|\, dx$$

is bounded as N tends to ∞.

Given h as specified, it is convenient to introduce a function of unit modulus $\theta(x) = h(x)/|h(x)|$. (When x is such that $h(x) = 0$, we let $\theta = 1$.) In addition to θ, we introduce the auxiliary function $u(x)$ defined as follows: For $|x| \leqq 1$ let $u(x) = 0$; for $|x| > 1$ let $u(x) = \theta(x)/x$. The function $u(x)$ clearly belongs to $\mathfrak{L}_2$, therefore

$$\left| \int_{-N}^{+N} xh(x) u^*(x)\, dx \right| \leqq \left[\int_{-\infty}^{+\infty} |xh(x)|^2\, dx \int_{-\infty}^{+\infty} |u(x)|^2\, dx \right]^{1/2}.$$

Hence

$$\int_{-N}^{+N} |h(x)|\, dx = \int_{-1}^{+1} |h(x)|\, dx + \int_{-N}^{+N} xh(x)u^*(x)\, dx$$

is bounded, as we were required to show.

Now we return to our main theorem. Given an arbitrary element h in $\mathbf{D}_B$, we apply (V.22) to the function $Bh = xh(x)$ obtaining

$$\begin{aligned} UBh &= \frac{1}{(2\pi)^{1/2}} \frac{d}{dt} \int_{-\infty}^{+\infty} \frac{e^{-ixt} - 1}{-ix}\, xh(x)\, dx \\ &= \frac{i}{(2\pi)^{1/2}} \frac{d}{dt} \int_{-\infty}^{+\infty} (e^{-ixt} - 1) h(x)\, dx. \end{aligned} \tag{V.34}$$

As we noted, h is absolutely integrable and this fact has two consequences. First, the differentiation with respect to t may be carried out under the improper integral (V.34) yielding

$$UBh = i \frac{d}{dt} \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} e^{-ixt} h(x)\, dx. \tag{V.35}$$

Second, the original Fourier transformation formula (V.7) becomes directly applicable to $h(x)$, and therefore

$$Uh = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{+\infty} e^{-ixt} h(x)\, dx. \tag{V.36}$$

Combining (V.35) and (V.36), we have the desired relation

$$DUh = UBh,$$

for every h in $\mathbf{D}_B$.

Let us assume now that g is in $\mathbf{D}_D$ and let us write down the inverse Fourier transformation (V.23) for $ig'(t)$

$$U^{-1} ig'(t) = \frac{1}{(2\pi)^{1/2}} \frac{d}{dt} \int_{-\infty}^{+\infty} \frac{e^{ist} - 1}{is}\, ig'(s)\, ds. \tag{V.37}$$

Integrating by parts, we obtain

$$\int_{-\infty}^{+\infty} \frac{e^{ist} - 1}{s} g'(s)\, ds = - \int_{-\infty}^{+\infty} \frac{d}{ds} \frac{e^{ist} - 1}{s} g(s)\, ds, \tag{V.38}$$

because $g(x)$ tends to 0 as x tends to ∞ (see p. 56). Then

$$\frac{d}{ds} \frac{e^{ist} - 1}{s} = \frac{e^{ist} ist - e^{ist} + 1}{s^2} = -t \frac{e^{ist} - 1}{is} - \frac{e^{ist} - 1 - is}{s^2}. \tag{V.39}$$

From (V.37)–(V.39) it follows that

$$U^{-1}g(t) = \frac{1}{(2\pi)^{1/2}}\frac{d}{dt}t\int_{-\infty}^{+\infty}\frac{e^{ist}-1}{is}g(s)\,ds$$
$$+\frac{1}{(2\pi)^{1/2}}\frac{d}{dt}\int_{-\infty}^{+\infty}\frac{e^{ist}-1-ist}{s^2}g(s)\,ds. \qquad \text{(V.40)}$$

Both integrals in (V.40) exist for all g in $\mathfrak{L}_2$, and the differentiations with respect to t may be carried out. But

$$\frac{d}{dt}t\int_{-\infty}^{+\infty}\frac{e^{ist}-1}{is}g(s)\,ds = t\frac{d}{dt}\int_{-\infty}^{+\infty}\frac{e^{ist}-1}{is}g(s)\,ds + \int_{-\infty}^{+\infty}\frac{e^{ist}-1}{is}g(s)\,ds, \qquad \text{(V.41)}$$

and

$$\frac{d}{dt}\frac{e^{ist}-1-ist}{s^2} = -\frac{e^{ist}-1}{is}.$$

Hence

$$U^{-1}Dg = t\frac{d}{dt}\frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{+\infty}\frac{e^{ist}-1}{is}g(s)\,ds = tU^{-1}g(t),$$

and finally

$$U^{-1}D = BU^{-1}. \qquad \text{(V.42)}$$

This completes the proof of the equivalence of the position and momentum operators.

D. Cayley Transformation. Von Neumann's Theory of Symmetric Operators

Let A be a closed symmetric operator. Then, for every f in $\mathbf{D}_A$, we have

$$\|(A+iI)f\|^2 = \|Af\|^2 + (Af, if) + (if, Af) + \|f\|^2 = \|Af\|^2 + \|f\|^2. \qquad \text{(V.43)}$$

Similarly

$$\|(A-iI)f\|^2 = \|Af\|^2 + \|f\|^2. \qquad \text{(V.44)}$$

Let us regard the set of elements

$$g = Af + if \qquad \text{(V.45)}$$

while f runs through $\mathbf{D}_A$ as the domain $\mathbf{D}_V$ of a new operator V, and let

$$Vg = Af - if. \qquad \text{(V.46)}$$

This operator is clearly linear. It is an isometric operator, because

$$\|Vg\|^2 = \|Af\|^2 + \|f\|^2 = \|g\|^2, \tag{V.47}$$

for every g in $\mathbf{D}_V$. The operator V is called the Cayley transform of the operator A. The relations (V.45) and (V.46) are written symbolically as

$$V = \frac{A - iI}{A + iI}. \tag{V.48}$$

It is easily shown that the closure property of A implies the closure of V, moreover that the Cayley transform of an extension of A is an extension of the Cayley transform of A.

The definition of self-adjointness is relatively straightforward. An operator is self-adjoint if it coincides with its adjoint. When a symmetric but not self-adjoint operator H is given it is not so easy to determine directly whether or not this operator can be extended to a self-adjoint operator. The characterization of such operators is accomplished in terms of their Cayley transforms. The basic results pertaining to this characterization are due to von Neumann (1932). They are stated below without proof:

(1) The operator H is self-adjoint if and only if its Cayley transform V is a unitary operator.

(2) H is a maximal symmetric operator if and only if V is a maximal isometric operator. (An operator without proper isometric extensions.)

(3) The symmetric operator H has a self-adjoint extension if and only if its Cayley transform has a unitary extension.

It is instructive to solve (V.48) formally for the operator A. We obtain

$$A = i(I + V)(I - V)^{-1}. \tag{V.49}$$

As long as V is unitary and one is not an eigenvalue of V, Eq. (V.49) defines a self-adjoint operator, but the equation is meaningless if one is an eigenvalue of V. If we start with an isometric V, we get a symmetric A as long as the eigenvalue one is absent.

VI. Resolvent and Spectrum

A. Definitions

Let us attempt to solve an equation of the type

$$Tf - zf = g, \tag{VI.1}$$

where T is an operator, z is a complex number, and g is a given element in

Hilbert space. The solution of this equation requires the construction of the inverse of the transformation $T_z = T - zI$. In order to avoid pathological situations, we shall only consider here closed operators with domains everywhere dense in $\mathfrak{H}$. Therefore the existence of $T^\dagger$ is assured, and $T^{\dagger\dagger} = T$.

We recall that in the finite-dimensional case the corresponding problem requires the solution of n equations of the form

$$\sum_{k=1}^{n} (t_{ik} - z\delta_{ik})x_k = y_i, \qquad i = 1, 2, \ldots, n. \tag{VI.2}$$

In this case Cramer's rules assure us that one of the following alternatives takes place: Either the system (VI.2) has a unique solution $\{x_1, x_2, \ldots, x_n\}$ for every given vector $\{y_1, y_2, \ldots, y_n\}$, or the homogeneous system

$$\sum_{k=1}^{n} (t_{ik} - z\delta_{ik})x_k = 0, \qquad i = 1, 2, \ldots, n \tag{VI.3}$$

has a solution other than $x_1 = x_2 = \cdots x_n = 0$. In the latter case the transposed system

$$\sum_{k=1}^{n} (t_{ki} - z\delta_{ik})x_k = 0 \tag{VI.4}$$

has exactly the same number of independent solutions as (VI.3) has, and the system (VI.2) is solvable only for such vectors $\{y_1, y_2, \ldots, y_n\}$ which are orthogonal to all solutions of (VI.4). The two alternatives are distinguished from one another by the value of the determinant $D(z) = \det(t_{ik} - z\delta_{ik})$. When $D(z) \neq 0$ the first alternative takes place; when $D(z) = 0$, the second.

In the infinite-dimensional Hilbert space the alternatives are not so simple. Not even when the operator T is required to be bounded. It is necessary to attack the problem of solving (VI.1) from a new point of view. In the finite-dimensional case the value of $D(z)$ leads to a classification of the points in the complex plane, a point may be called regular when $D(z) \neq 0$. There is no corresponding determinant in the infinite-dimensional case. We shall classify the points of the complex plane with respect to the operator T as follows:

A point z is called a regular point of the operator T if the operator $T_z = T - zI$ has a bounded inverse whose domain is $\mathfrak{H}$. The set of regular points of T is called the resolvent set of T.

A point z which is not a regular point of T is said to belong to the spectrum of T.

When z is a regular point of T the operator

$$R_z = (T - zT)^{-1} \tag{VI.5}$$

is a bounded operator whose domain is $\mathfrak{H}$. The inverse is to be interpreted as follows: For any element f of $\mathfrak{H}$, the element $g = R_z f$ is in the domain of T and

$$(T - zI)R_z f = f. \tag{VI.6}$$

The operator R_z is called the *resolvent* of T.

When a complex number z is such that there exists an element f other than $\mathbf{O}$, such that $Tf = zf$, z is called an eigenvalue of T and f an eigenvector. (The terms "characteristic value" and "characteristic element" are frequently used.)

An eigenvalue is clearly not a regular point because $T_z f = \mathbf{O}$ without f being equal to $\mathbf{O}$, therefore T_z does not have an inverse. It is said to belong to the point spectrum of T. When z is not an eigenvalue the inverse of T_z will exist.

A point may belong to the spectrum even if it is not an eigenvalue. It may occur that the inverse of T_z is (a) an unbounded operator defined everywhere dense in $\mathfrak{H}$, or (b) an operator not defined everywhere dense in $\mathfrak{H}$. In the first instance we say that z belongs to the *continuous spectrum* of T, in the second instance that it belongs to its *residual spectrum.*

The following two examples illustrate how the continuous and residual spectra—absent in n-dimensional space—arise in Hilbert space:

Let $\{\phi_n\}$ be a complete, orthonormal system, and let the linear operators T_1 and T_2 be defined by the equations:

$$T_1 \phi_k = \phi_k / k, \tag{VI.7}$$

$$T_2 \phi_k = \phi_{k+1}, \tag{VI.8}$$

for every value of k. Both operators are bounded; they may be extended so that their domain covers the entire space $\mathfrak{H}$. The point $z = 0$ belongs to the continuous spectrum of T_1 and to the residual spectrum of T_2.

The rôle of the residual spectrum is further clarified by the following theorem: If z is in the residual spectrum of T, then z^* is an eigenvalue of $T^\dagger$.

Proof. If z is in the residual spectrum of T then T_z^{-1} has a domain which is not everywhere dense. Hence the range of T_z is not everywhere dense. Therefore there is an element $g \neq \mathbf{O}$, such that

$$(T_z f, g) = 0 \tag{VI.9}$$

for every f in $\mathbf{D}_T$. Thus $(Tf, g) = zf, (g)$ and

$$(f, T^\dagger g - z^* g) = 0 \tag{VI.10}$$

for every f in $\mathbf{D}_T$. Since $\mathbf{D}_T$ is everywhere dense, it follows that

$$T^\dagger g = z^* g. \tag{VI.11}$$

Note that from (VI.11) it does not always follow that z is in the residual spectrum of T, because z may belong to the point spectrum of T.

Exercises

1. Show that for the operator T_2 of this section the equation $T_2 f = \mathbf{O}$ implies $f = \mathbf{O}$, but $Tf = g$ is not solvable for every g.

2. Let T be an operator with domain $\mathfrak{H}$. Prove that if 0 is an eigenvalue of T^k for some integer k, then 0 is also an eigenvalue of T.

3. Let the bounded linear operator A be defined by the equations

$$A\phi_k = \phi_{k+1}/(k+1)$$

for $k = 1, 2, 3, \ldots$, and let A be extended so that $\mathbf{D}_A = \mathfrak{H}$.

(a) Show that A has an inverse A^{-1} and determine the domain of A^{-1}.
(b) Show that $I - A$ has an inverse $B = (I - A)^{-1}$.
(c) Prove that $S_n = I + A + A^2 + \cdots + A^{n-1}$ tends to a limit S as $n \to \infty$ in the sense that $\lim_{n\to\infty} S_n f$ exists for every f.
(d) Prove that $Sf = \lim S_n f = Bf$.

B. Analytical Properties of the Resolvent

We shall examine now the dependence of $R_z = (T - zI)^{-1}$ on the complex number z. In so doing we shall restrict ourselves to complex numbers lying in the resolvent set $\mathbf{R}$ of the closed linear operator T. Let z and w be two numbers in $\mathbf{R}$, then there is a functional relation between the operators R_z and R_w. This is the subject of our first theorem:

Theorem 1. If T is a closed linear operator with resolvent R_z then

$$(z - w)R_z R_w = R_z - R_w \tag{VI.12}$$

for every pair of points (z, w) in the resolvent set of T. Moreover if $R_z f = \mathbf{O}$ then $f = \mathbf{O}$.

We know from the preceding section that R_z and R_w are bounded operators defined over $\mathfrak{H}$. From the obvious relations $R_z T_w R_w = R_z$, $R_z T_z R_w = R_w$, and $T_w - T_z = (z - w)I$, we find immediately

$$R_z(T_w - T_z)R_w = (z - w)R_zR_w = R_z - R_w.$$

As to the second property of R_z, we observe that it follows from the fact that R_z is the inverse of a linear operator. From Eq. (VI.12) we can conclude that the operators R_z and R_w are permutable. This follows by interchanging the letters z and w and thus obtaining the equation $(w - z)R_wR_z = R_w - R_z$, which together with (VI.42) gives $R_wR_z = R_zR_w$.

The functional equation (VI.12) satisfied by the resolvent suggests that the resolvent must depend analytically on the complex variable z. That this is indeed the case, we shall demonstrate immediately. We rewrite Eq. (VI.12) and we make use of the observation that R_z and R_w are permutable operators:

$$R_z = R_w + (z - w)R_wR_z, \tag{VI.13}$$

for every pair of numbers (z, w) in the resolvent set.

We substitute for R_z in the last term and obtain

$$R_z = R_w + (z - w)R_w\,[R_w + (z - w)R_wR_z]. \tag{VI.14}$$

Repeated application of this step leads us to

$$\begin{aligned} R_z = R_w &+ (z - w)R_w{}^2 + (z - w)^2R_w{}^3 + \cdots \\ &+ (z - w)^{n-1}R_w{}^n + (z - w)^nR_w{}^nR_z. \end{aligned} \tag{VI.15}$$

When the last term on the right-hand side tends to zero as n tends to infinity, the series $\sum_{k=1}^{\infty}(z - w)^{k-1}R_w{}^k$ is convergent and its sum is R_z.

We regard w as a fixed point in the resolvent set and designate the bound of R_w by C. Then $\|(z - w)^nR_w{}^nR_zf\| \leqq |z - w|^nC^n\|R_zf\|$. This will tend to zero whenever $|z - w| < 1/C$. Therefore we have shown that if w and z are points in the resolvent set and $|z - w| < 1/C$, then R_z can be written in terms of the convergent power series

$$R_z = \sum_{k=1}^{\infty} (z - w)^{k-1}R_w{}^k, \tag{VI.16}$$

or in terms of complex numbers the equation

$$(R_zf, g) = \sum_{k=1}^{\infty} (z - w)^{k-1}(R_w^kf, g) \tag{VI.17}$$

holds for every f and g in $\mathfrak{H}$.

We can show now that if the distance between z and w is less than $1/C$, then z *must* be in the resolvent set, consequently the series expansions

(VI.16) and (VI.17) truly represent the resolvent in the circle of radius $1/C$ around w. In fact, the convergence of the series is assured as is readily seen by comparison with a geometric progression. Hence the series on the right-hand side of (VI.16) defines an operator S whose domain is $\mathfrak{H}$ and we only have to show that S is the inverse of T_z.

Let $S_n = \sum_{k=1}^{n}(z-w)^{k-1}R_w{}^k$. The identity

$$(T - zI)R_w = I - (z-w)R_w \tag{VI.18}$$

implies

$$T_zS_n = \sum_{k=1}^{n} (z-w)^{k-1}\{R_w^{k-1} - (z-w)R_w{}^k\} = I - (z-w)^nR_w{}^n. \tag{IV.19}$$

The last term on the right-hand side tends to zero as n tends to infinity. Therefore $\lim_{n\to\infty}T_zS_n = I$, consequently $T_zS = I$. We formalize our results as follows:

Theorem 2. If the resolvent set of a closed linear operator T contains the point w, then there exists a positive constant C, dependent on w, such that the bound of R_w is C. Every point z within distance of $1/C$ of the point w belongs to the resolvent set of T, and $R_z = \sum_{k=1}^{\infty}(z-w)^{k-1}R_w{}^k$.

An obvious consequence of this theorem is that if the resolvent set of T is not empty then it is an open set and the function (R_zf, g) is an analytic function of z in the resolvent set for every f and g in $\mathfrak{H}$.

It is useful to know, when possible, an expression for R_z in terms of the given operator T. We will show now how an expression of this type can be found for a *bounded* operator. The expression to be derived is valid on the outside of a circle in the complex plane specified by $|z| = K$, where K is the bound of T. It is possible to show that every point z in that region is a regular point of T.

The resolvent R_z is permutable with T, since it is permutable with $T_z = T - zI$. Therefore

$$R_zT = R_z(T_z + zI) = I + zR_z. \tag{VI.20}$$

Hence, for $z \neq 0$,

$$R_z = -\frac{I}{z} + \frac{T}{z}R_z. \tag{VI.21}$$

We repeat the process of replacing R_z by the entire right-hand side of (VI.21) and arrive at the equation

$$R_z = -\frac{1}{z}\left\{I + \frac{T}{z} + \frac{T^2}{z^2} + \cdots + \frac{T^n}{z^n}\right\} + \frac{T^{n+1}}{z^{n+1}}R_z. \tag{VI.22}$$

Whenever $|z|$ is greater than K, the bound of the transformation T/z is less than one, the last term on the right of (VI.22) tends to zero and we have

$$R_z = -\frac{1}{z}\sum_{k=0}^{\infty}\frac{T^k}{z^k}. \tag{VI.23}$$

Exercises

1. Prove that the spectrum of any projection operator consists of the two numbers 0 and 1.

2. Show that every complex number of absolute value less than one is in the resolvent set of every unitary operator. (Hint: First show that 0 is a regular point, then apply Theorem 2.)

C. Resolvents and Spectrum of Symmetric and Self-Adjoint Operators

Spectral sets and resolvents of symmetric operators possess a number of interesting properties not shared by other linear operators. We recall that a linear operator H whose domain is everywhere dense in $\mathfrak{H}$ is defined to be symmetric when the equation $(Hf, g) = (f, Hg)$ holds for every f and g in its domain, or what is the same, when $H^\dagger$ is an extension of H. The operator H is self-adjoint when $H = H^\dagger$.

A symmetric operator has real eigenvalues only. In fact, from $f \neq \mathbf{O}$ and $Hf = zf$ it follows that

$$(zf, f) = (Hf, f) = (f, Hf) = (f, zf).$$

Hence

$$z\,\|f\|^2 = z^*\,\|f\|^2,$$

and finally, $z = z^*$.

Now let x_1 and x_2 be eigenvalues of H and let f_1 and f_2 be the corresponding eigenvectors. Then $(Hf_1, f_2) = x_1(f_1, f_2) = (f_1, Hf_2) = x_2(f_1, f_2)$. Hence $(x_1 - x_2)(f_1, f_2) = 0$, showing that when $x_1 \neq x_2$ the eigenvectors f_1 and f_2 are orthogonal.

The continuous spectrum of a symmetric operator is also restricted to the real axis. This can be shown by proving the boundedness of $H_z^{-1} = (H - zI)^{-1}$ for every nonreal z. Let $z = x + iy$ and $y \neq 0$, then, as we have just seen, H_z^{-1} exists. If g is in the domain of H_z^{-1} then $f = H_z^{-1}g$ is in the domain of H and we may estimate $\|f\|$ as follows: From the definition of H_z^{-1} we get

$$HH_z^{-1} = I + zH_z^{-1}, \tag{VI.24}$$

and therefore

$$Hf = g + zf. \tag{VI.25}$$

Hence

$$(Hf, f) - (f, Hf) = (g, f) - (f, g) + z(f, f) - z^*(f, f), \tag{VI.26}$$

and this is zero because H is a symmetric operator. Thus

$$(z - z^*)(f, f) = 2\,\mathrm{Im}(f, g) = 2\,\mathrm{Im}(H^{-1}g, g). \tag{VI.27}$$

Hence

$$2y\,\|f\|^2 = 2y\,\|H_z^{-1}g\|^2 = 2\,\mathrm{Im}(H_z^{-1}g, g), \tag{VI.28}$$

and the absolute value of the right-hand side does not exceed $2\|H_z^{-1}g\|\;\|g\|$. Therefore

$$\|H_z^{-1}g\| \leqq \frac{1}{|y|}\,\|g\| \tag{VI.29}$$

for any g in the domain of H_z^{-1}. We have shown that, when y, the imaginary part of z, is not 0, the operator has $1/|y|$ as its bound. The boundedness of H_z^{-1} means that z is either a regular point, or that it is in the residual spectrum of H.

If a nonreal number z is in the residual spectrum of H then z^* is an eigenvalue of $H^\dagger$. When the operator is not only symmetric but self-adjoint then all eigenvalues are real. In this case, the residual spectrum must be empty and every nonreal point z is a regular point.

It is shown in standard treatises that functions of a self-adjoint operator are expressible in terms of the resolution of the identity of the operator. Thus, for example, a polynomial operator

$$p_n(H) = a_0 I + a_1 H + \cdots + a_n H^n$$

with complex coefficients $a_0, \ldots, a_n$ is representable in the form

$$p_n(H) = \int_{-\infty}^{+\infty} p_n(\lambda)\, dE_\lambda, \tag{VI.30}$$

where

$$p_n(\lambda) = a_0 = a_1\lambda + \cdots + a_n\lambda^n.$$

Since the resolvent is the inverse of $H - zI$, it is not surprising that in the case of self-adjoint operators it is representable in the form

$$R_z = \int_{-\infty}^{+\infty} \frac{1}{\lambda - z}\, dE_\lambda. \tag{VI.31}$$

Conversely the resolution of the identity may be constructed by contour integrals over R_z in the z plane.

REFERENCES

AKHIEZER, N. I., and GLAZMAN, I. M. (1961, 1963). "Theory of Linear Operators in Hilbert Space (translated from Russian), 2 vols. Ungar, New York.

COOK, R. G. (1953). "Linear Operators." Macmillan, New York.

COURANT, R., and HILBERT, D. (1953). "Methods of Mathematical Physics" (translated from German), Vol. 1, p. 91. Wiley (Interscience), New York.

HALMOS, P. R. (1951). "Introduction to Hilbert Space." Chelsea, New York.

Riesz, F. (1930). *Acta Sci. Math. Szeged.* **5**, 23–54.

RIESZ, F., and LORCH, E. R. (1936). *Trans. Am. Math. Soc.* **39**, 331–340.

RIESZ, F., and SZ.-NAGY, B. (1955). "Functional Analysis" (translated from French). Ungar, New York.

STONE, M. H. (1929). *Proc. Natl. Acad. Sci. U.S.* **15**, 198–200.

STONE, M. H. (1932). "Linear Transformations in Hilbert Space." Am. Math. Soc., New York.

VON NEUMANN, J. (1929). *Math. Ann.* **102**, 49–131.

VON NEUMANN, J. (1932). "Mathematische Grundlagen der Quantenmechanik." Springer, Berlin. (English translation, Princeton Univ. Press, Princeton, New Jersey, 1955.)

WECKEN, F. J. (1935). *Math. Ann.* **110**, 722–725.

The Symmetric Group Made Easy

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I. Introduction

According to my, possibly inadequate, understanding of history, President Theodore Roosevelt while enumerating the most urgent problems facing the United States declaimed, "What this country needs is a good ten-cent cigar."

In a similar vein, a Dutch mathematician remarked to the author that what the *world* urgently needs is a summary and proof of all useful properties of the symmetric group in ten easy pages! Anyone who has struggled with the eighty formidable pages which Hamermesh devotes to the symmetric group in his admirable book on Group Theory, will doubt the feasibility of this desideratum.

In the present article, a few simple results concerning irreducible representations of the symmetric group which appear to be unfamiliar to or unappreciated by most chemists and physicists are set forth without proof. These results are closely associated with the familiar methods expounded by Kotani for constructing symmetry-adapted spin functions. Also a new method and two new formulas for calculating the irreducible characters of the symmetric group are announced.

Our chief tools were forged by Alfred Young between 1900 and 1925. Much of the following can be found scattered in the literature, in particular in the books by Boerner (1963), Robinson (1961), and Hamermesh (1962). We shall assume that the reader is familiar with the definition of *representation* and with the *orthogonality relations* for the irreducible characters.

II. Young Diagram

We use cyclic notation to denote permutations. Thus (12) denotes the transposition which interchanges 1 and 2 and leaves objects $3, 4, \ldots, n$ fixed, in a set of objects named by natural numbers $1, 2, \ldots, n$. Similarly (123), replaces 1 by 2, 2 by 3, and 3 by 1. Thus if (12) acts on the expression $A \equiv x_1{}^2x_2x_3 + 2x_2{}^2x_3{}^4$ we obtain

$$(12)A = x_2{}^2x_1x_3 + 2x_1{}^2x_3{}^4.$$

If (23) acts on $(12)A$, we obtain

$$(23)(12)A = (23)[(12)A] = x_3{}^2x_1x_2 + 2x_1{}^2x_2{}^4.$$

The reader should verify that $(23)(12)A = (132)A$. Indeed, this will be true for all A, so we write

$$(23)(12) = (132).$$

In actual calculations of such products of permutations, one can obtain the effect of the product on any object by reading from right to left. Thus (12) changes 1 to 2 and (23) changes 2 to 3. Therefore the net effect of (23)(12) on 1 is to change it to 3. One then finds the effect of the product on 3 and so on until a cycle is closed. The reader may verify in this way that

$$(12)(23)(12) = (13), \tag{1}$$

$$(145)(135) = (13)(45). \tag{2}$$

It is clear that two *disjoint cycles* (i.e., ones which contain no common object) *commute* and also that any permutation can be expressed as a product of mutually disjoint cycles.

We denote by n the *neuter* or *neutral element*, which leaves every object fixed. Verify that

$$(12)(12) = n, \qquad (123)(321) = n, \qquad (1234)(4321) = n,$$

and, in general, that the inverse of a cycle is obtained by reversing the order of the elements in the cycle.

In abstract group theory the concept of *conjugate* elements plays an important role. Two group elements p and q are *conjugate* if and only if there is a group element t, say such that $q = tpt^{-1}$. We shall say that *q is conjugate to p under t*. A group may be partitioned into disjoint exhaustive classes—so-called *conjugate classes*—such that *any* two elements of the same class are mutually conjugate. (It is clear that $q = tpt^{-1}$ implies $p = t^{-1}qt$ so that if q is conjugate to p under t, then p is conjugate to q under t^{-1}).

For the *symmetric group* $\mathscr{S}_m$, that is the group of *all* permutations on m objects, the conjugate classes may be described quite *explicitly*. Equation (1) together with

$$(123)(24516)(321) = (34526) \tag{3}$$

illustrate the fact that if p is a cycle then tpt^{-1} is a cycle of the same length but with objects permuted according to the action of t. Since $\mathscr{S}_m$ contains all possible permuations, any two cycles of the same length are conjugate in $\mathscr{S}_m$. If $p = p_1 p_2 \cdots p_m$, where p_i is a cycle, then $q = tpt^{-1} = tp_1t^{-1}tp_2t^{-1}tp_3t^{-1}tp_mt^{-1}$ so that q is a permutation with *cycle structure* identical to that of p. Thus, from the mere fact that (12)(345)(6789) and (123)(78)(4569) are each products of a 2-cycle, a 3-cycle, and a 4-cycle, we know that they are conjugate.

Thus the *conjugate* classes of $\mathscr{S}_m$ can be put into one-to-one correspondence with the distinct partitions of m into positive integers. For example, since $3 = 2 + 1 = 1 + 1 + 1$, there are *three* conjugate classes of $\mathscr{S}_3$ of which (123), (12)(3), and (1)(2)(3) are typical elements. We shall denote a conjugate class by *the corresponding partition in round brackets*. Thus

$$\begin{array}{lll} (3) & = \{(123), (132)\} & \text{even,} \\ (2, 1) & = \{(12), (13), (23)\} & \text{odd,} \\ (1, 1, 1) = (1^3) & = \{(1),(2),(3)\} & \text{even.} \end{array}$$

Notice, that by (12) we mean (12)(3), i.e., the group element which interchanges 1 and 2 and leaves 3 fixed; that we abbreviate repetitions of the same integer by index notation, so that $(3, 3, 2, 2,) = (3^2, 2^2)$; that $(1)(2)(3) = n$, the neuter of the group; that an element and its inverse are in the same conjugate class; and that there are the same number of odd as even permutations. Following common practice, we use parentheses to indicate both group elements and conjugate classes. That which is intended in a particular case should be clear from context. Also, in the symbol for a conjugate class the digits are usually separated by commas, while in a cycle the order can be arbitrary and normally commas are omitted. In the case of $\mathscr{S}_3$, there are $3! = 6$ group elements, and we observe that each occurs in one conjugate class. The reader should verify that $\mathscr{S}_4$ and $\mathscr{S}_5$ have respectively 5 and 7 conjugate classes and he should evaluate the number of elements in each class. He can check his conclusions by the formula

$$\frac{m!}{1^a a!\, 2^b b!\, 3^c c! \cdots},$$

which gives the number of elements in the class $(1^a, 2^b, 3^c \cdots)$ where $1 \cdot a + 2 \cdot b + 3 \cdot c + \cdots = m$. This formula can be proved by a simple combinatorial argument if one notes that (123) = (231) = (312), and similarly for other cycles.

It is an obvious step to associate a diagram to a conjugate class as follows:

$$(3) \to \cdots, \qquad (2, 1) \to \begin{array}{l} \cdot\;\cdot \\ \cdot \end{array}, \qquad (1^3) \to \begin{array}{l} \cdot \\ \cdot \\ \cdot \end{array} \quad ,$$

i.e., to each number of the partition we associate a row of an equal number of dots. In order to be systematic and avoid counting the same class twice, we arrange the rows in nonincreasing order. Thus for $\mathscr{S}_4$ we have the diagrams

$$\begin{array}{l} \cdot\;\cdot\;\cdot\;\cdot \end{array} \qquad \begin{array}{l} \cdot\;\cdot\;\cdot \\ \cdot \end{array} \qquad \begin{array}{l} \cdot\;\cdot \\ \cdot\;\cdot \end{array} \qquad \begin{array}{l} \cdot\;\cdot \\ \cdot \\ \cdot \end{array} \qquad \begin{array}{l} \cdot \\ \cdot \\ \cdot \\ \cdot \end{array}$$

corresponding to the five conjugate classes. Such diagrams were used for the study of partitions by Ferrers, an English mathematician of the latter part of the nineteenth century, so are called *Ferrers graphs* by MacMahon (1915). However, Young employed them in a most ingenious way in the representation theory of $\mathscr{S}_m$ so we follow the widespread practice of calling such an ordered arrangement of m nodes a *Young diagram.*

It is a well-known theorem that over the complex numbers (or any algebraically closed field of characteristic zero) there are exactly as many classes of equivalent irreducible representations of a finite group as there are conjugate classes. Recall that a representation A of a group G associates to each group element g a matrix, or linear transformation $A(g)$, such that $A(g_1 g_2) = A(g_1)A(g_2)$. A representation by linear transformations $A(g)$ on a vector space V is *reducible* if there is a proper nontrivial sub-space V_1 of V, such that $A(g)V_1$ is contained in V_1 for *all* $g \in G$. If no such invariant subspace exists, we say that A is *irreducible.* Two representations A and B are *equivalent* or *similar* if there is a mapping T such that $B(g) = TA(g)T^{-1}$ for all g *with* T *independent* of g. The set of all representations similar to a fixed representation forms an equivalence class. If we collect the irreducible representations of a *finite* group G into equivalence classes, there are exactly as many such classes as there are conjugate classes in G.

It follows that there are *precisely* enough Young diagrams to provide names for the inequivalent irreducibles of the symmetric group. It required the genious of Young to associate the diagrams to the irreducible representations in a manner which enables many properties of the representations to be inferred directly from the corresponding diagram. We shall attempt later in this article to justify Young's *choice of names* for the representations, but we first concentrate on describing this choice.

All groups possess a one-dimensional irreducible representation, called the *identity representation* which we denote by J, which maps each group element onto the identity transformation of a one-dimensional space, or onto the 1×1 unit matrix. Clearly if $J(g)v = v$ for all g, then $J(g_1 g_2)v = v$ and $J(g_1)J(g_2)v = J(g_1)v = v$, so that $J(g_1 g_2) = J(g_1)J(g_2)$. In the case of any *permutation* group, there is another one-dimensional representation, the *alternating representation*, $\tilde{J}$, such that

$$\tilde{J}(g)v = \begin{cases} v & \text{if } g \text{ is an even permutation} \\ -v & \text{if } g \text{ is an odd permutation.} \end{cases}$$

Of course, if G has only even permutations, then $J = \tilde{J}$, so that the identity and alternating representations coincide. However, for the symmetric group $\mathcal{S}_m$ $(m > 1)$ there are always odd permutations so that in this case J and $\tilde{J}$ are distinct.

If $g \to A(g)$ is an irreducible representation of G, then we easily see that $\tilde{A} : g \to \tilde{J}(g)A(g)$ is also an irreducible representation of G. If χ is the character of A, then the character $\tilde{\chi}$ of this new representation $\tilde{A}$ is defined by $\tilde{\chi}(g) = \varepsilon(g)\chi(g)$ where $\varepsilon(g)$ is $+1$ or -1 according to whether g is even or odd. If we denote the order of G by $|G|$, then from the orthogonality relations and using the fact that g and g^{-1} are in the same conjugate class, the frequency of A in $\tilde{A}$ is given by

$$|G|^{-1} \sum_{g \in G} \tilde{\chi}(g)\chi(g^{-1}) = |G|^{-1} \sum_{g \in G} \varepsilon(g)\chi^2(g)$$

But this is less than or equal to 1, since A being irreducible, $|G|^{-1} \sum \chi^2(g) = 1$, by the orthogonality relations. Since frequency is a nonnegative integer, the above sum will be less than 1, and therefore 0, if $\chi(g) \neq 0$ for any g for which $\varepsilon(g) = -1$. Thus A and $\tilde{A}$ are distinct irreducible representations *unless* $\chi(g) = 0$ *for all odd permutations* in which case A and $\tilde{A}$ have the same character and are therefore equivalent.

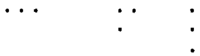
The representations $g \to A(g)$ and $g \to \tilde{A}(g) = \varepsilon(g)A(g)$ are called *conjugate* representations. Conjugate representations have the same dimension. The values of their characters are equal for even permutations and differ only in sign for odd permutations. If A and $\tilde{A}$ are similar then A is called *self-conjugate*.

Young's association between diagrams and irreducible representations of $\mathcal{S}_m$ is such that a pair of conjugate representations corresponds to diagrams obtained from one another by interchanging rows and columns.

Thus . . and : correspond to conjugate representations; so do :˙ and :˙˙. We infer that :˙ must be a self-conjugate representation.

Young associates the partition [m], corresponding to a single row of m nodes, to the identity representation J. Hence, $\tilde{J}$ corresponds to a column of m nodes or to the partition [1^m]. Note that we put the partition of m in *square* brackets when we use it to name an irreducible *representation*. This contrasts with the round brackets which denote a conjugate class. It is common to use the symbols λ_i, $i = 0, 1, \ldots, p$, to denote the number of nodes in rows of a Young diagram. The corresponding irreducible representation is denoted by $[\lambda_0, \lambda_1, \ldots, \lambda_p]$, by $[\lambda]$ or, sometimes, simply by λ.

It follows from Burnside's completeness theorem for a finite group, that the *sum of the squares* of the dimensions of a complete set of irreducible representations of G is equal to $|G|$, the order of the group. For $\mathcal{S}_3$, this is 6. But $\mathcal{S}_3$ has only three irreducibles:



[3] [2, 1] [1^3].

Since [3] and [1^3] each have dimension 1, it follows that [2, 1] has dimension 2. Similarly $\mathcal{S}_2$ has the two irreducibles [2] and [1^2], each of dimension 1.

Since [2, 1] is self-conjugate its character for the class (2, 1) of odd permutations must equal zero. Using the fact that the characters of [2, 1] and [3] are orthogonal enables us to obtain the following character tables:

$\mathcal{S}_2$

	(1^2)	(2)
[2]	1	1
[1^2]	1	−1

$\mathcal{S}_3$

	(1^3)	(2, 1)	(3)
[3]	1	1	1
[2, 1]	2	0	−1
[1^3]	1	−1	1

Since the first column of these tables gives the character of the neuter of the group, the entries are the dimensions of the corresponding irreducibles. We now explain a "magic" method of obtaining the dimensions which, by itself, almost justifies Young's choice of names for the irreducibles.

To *each node* of the diagram we associate a positive integer equal to the number of nodes to the right of the designated node *plus* the number of nodes below the designated node *plus* one. Thus

$$\begin{array}{ccc} \cdot\ \cdot\ \cdot & \rightarrow & \begin{matrix} 3 & 2 & 1 \end{matrix} \\[1em] \begin{matrix} \cdot & \cdot \\ \cdot & \end{matrix} & \rightarrow & \begin{matrix} 3 & 1 \\ 1 & \end{matrix} \\[1em] \begin{matrix} \cdot & \cdot \\ \cdot & \cdot \end{matrix} & \rightarrow & \begin{matrix} 3 & 2 \\ 2 & 1 \end{matrix} \end{array}$$

These numbers are called *hook lengths* because they are the number of nodes in a hook of which the corresponding node is the head node.

$$\begin{array}{lllll} \text{Head node.} \rightarrow & \bullet & \cdot & \cdot & \cdot \\ & \cdot & & & \\ & \cdot & & \text{A hook!} & \end{array}$$

Hook length = 3 + 2 + 1 = 7.

These *hooks* and the corresponding hook lengths are quite important in the representation theory for $\mathscr{S}_m$. This is particularly so for the *principal hook lengths* which occur in the first *column* of the diagram.

The startling truth is that *the dimension of an irreducible representation of* $\mathscr{S}_m$ *equals* $m!$ *divided by the product of the hook lengths.*

Let us test this rule. It certainly works for $[m]$ and $[1^m]$ for which the hook lengths are 1, 2, 3, ..., m. But for [2, 1], the rule also gives $3! \div 3 \times 1 \times 1 = 2$, which is correct. Let us try the rule on $\mathscr{S}_4$.

Diagram	Hook graph	Dimension of [λ]
. . . .	4 3 2 1	4!/4! = 1
. . . .	4 2 1 1	4!/8 = 3
. . . .	3 2 2 1	4!/12 = 2
. . . .	3 1 2 1	4!/8 = 3
. . . .	4 3 2 1	4!/24 = 1

Notice that [3, 1] and [2, 1^2] are conjugate representations and our rule assigns them the same dimensions. Also $1^2 + 3^2 + 2^2 + 3^2 + 1^2 = 24$, which agrees with Burnside's theorem.

We summarize the simple but basic facts of this section! An irreducible representation of $\mathscr{S}_m$ is given an unambiguous name, $[\lambda]$, by a Young diagram consisting of m nodes arranged in nonincreasing rows. The dimension of the representation can be obtained immediately from the diagram by the simple rule given. Conjugate representations A and $\tilde{A}$ such that $\tilde{A}(g) = \varepsilon(g)A(g)$ correspond to diagrams with rows and columns interchanged. For a self-conjugate representation, the value of the character for an odd permutation is zero.

III. Young Tableaux

Possibly the reader is now convinced that Young diagrams are useful. However, he will so far have only a slight foretaste of the crowning achievement of Young's work which was to use the diagrams to provide an explicit rule for obtaining the matrices of the irreducible representations. This now follows.

In order that a representation be described, names are needed for a set of basis vectors. Suppose a Young diagram corresponds to the partition of m, $[\lambda_0, \lambda_1, \lambda_2, \ldots.\ \lambda_p] = [\lambda]$, and therefore has $p + 1$ rows of which the first has λ_0 nodes, the second, λ_1 nodes, and so on, where $\lambda_0 \geqq \lambda_1 \geqq \lambda_2 \cdots$. We speak of the representation $[\lambda]$, or simply λ, when no confusion can arise. By f_λ, we denote the dimension of $[\lambda]$, obtained by the previous rule. The immediate problem is to find names for f_λ vectors which are to span the carrier space of $[\lambda]$. As with the Young diagrams, we would like to find names which ease the path as much as possible!

In how many ways can one arrange the first m natural numbers on the nodes of a Young diagram in such a way that these numbers always increase to the right and increase vertically downwards? For example, in the accompanying figure, (a), (b), and (d) satisfy the conditions but (c) and (e) do not.

$$\begin{array}{ccccc}
\begin{array}{ll}1 & 2\\ 3 & \end{array} &
\begin{array}{ll}1 & 3\\ 2 & 4\end{array} &
\begin{array}{ll}1 & 3\\ 4 & 2\end{array} &
\begin{array}{lll}1 & 2 & 3\\ 4 & 5 & 7\\ 6 & & \end{array} &
\begin{array}{lll}1 & 3 & 5\\ 2 & 6 & 4\\ 7 & & \end{array} \\
\text{(a)} & \text{(b)} & \text{(c)} & \text{(d)} & \text{(e)}
\end{array}$$

It is clear that $[m]$ or $[1^m]$ admit only *one* arrangement satisfying the given restrictions, namely

$$1\ \ 2\ \ 3 \cdots m \qquad\qquad \text{and} \qquad\qquad \begin{array}{c}1\\ 2\\ \cdot\\ \cdot\\ \cdot\\ m\end{array}$$

respectively. Recall that $[m] = J$, and $[1^m] = \tilde{J}$ are each of dimension *one*. For [2, 1] we have only *two* possibilities

$$\begin{array}{cc}1 & 2\\ 3 & \end{array} \qquad \begin{array}{cc}1 & 3\\ 2 & \end{array}$$

Recall that $f_{[2,1]} = 2$. For [3, 1], there are exactly *three* possibilities.

$$\begin{array}{ccc}1 & 2 & 3\\ 4 & & \end{array} \qquad \begin{array}{ccc}1 & 2 & 4\\ 3 & & \end{array} \qquad \begin{array}{ccc}1 & 3 & 4\\ 2 & & \end{array}$$

Again, $f_{[3,1]} = 3$. An arrangement of the first m natural numbers in a Young diagram (YD) satisfying the above ordering restriction is a *Young tableau* (YT). Doubtless, the intelligent reader has already guessed the remarkable truth: *for a Young diagram* $[\lambda]$ *there are precisely* f_λ *Young tableaux*. Possibly the suspicion has even darkened his mind that the Young tableaux associated with a fixed Young diagram will be used to name a set of basis vectors for the corresponding representation.

There are two other equivalent sets of symbols which could be used for the same purpose and which are explained, in passing, since they are quite useful: *lattice permutations* and *Yamanouchi symbols*.

The topic of lattice permutations is treated by MacMahon in Section III, Chapter V of his "Combinatory Analysis." If a Young tableaux has $p + 1$ rows, both the corresponding lattice permutations and Yamanouchi symbols are sequences of the natural numbers 1, 2, ..., $p + 1$ with repetitions. We begin with examples.

Young tableau	Lattice permutation	Yamanouchi symbol
1 2	1 1	1 1
1 2 3 4	1 1 2 2	2 2 1 1
1 3 2 4	1 2 1 2	2 1 2 1
1 3 2 4 5	1 2 1 3 4	4 3 1 2 1

Note that Yamanouchi symbol is the lattice permutation written backwards. The digits in the lattice permutation correspond in succession to the digits 1, 2, 3, ..., m in the YT and denote the row in which the latter digit occurs. The rule restricting the digits of the YT is equivalent to the following condition on a lattice permutation: at each stage as the lattice permutation is read from left to right, the number of 1's which have occurred is not less than the number of 2's, the number of 2's is not less than the number of 3's, and so on. Since in 122 there are more 2's than 1's, 1221 is not a lattice permutation. It would correspond to the pattern

$$\begin{matrix} 1 & 4 \\ 2 & 3 \end{matrix}$$

which is not a YT, since 4 is above 3. Notice that if the YT corresponding to a particular YD are ordered lexicographically, the resulting order corresponds precisely to that obtained by regarding the lattice permutations as numerals for real numbers and ordering them according to increasing magnitude, or ordering the Yamanouchi symbols according to decreasing magnitude. Note also, that if the digit m is removed from a Young tableau the resulting pattern is still a proper Young tableau for the first $m - 1$ digits. This process corresponds to removing the last digit from a lattice permutation and the first digit from a Yamanouchi symbol.

We now turn to the problem of describing explicitly a set of matrices which realizes the irreducible representation of $\mathscr{S}_m$ corresponding to a given YD. Since such a representation is determined only to within a similarity transformation, if there is one, there will be an infinity of such sets of matrices. Alfred Young gave three distinct rules for displaying such representations of $\mathscr{S}_m$. They are described by Rutherford (1948) who names them the *natural*, *seminormal* and *orthogonal* representations. Here, only the latter are described.

First, note that any permutation in $\mathscr{S}_m$ can be obtained as a product of the $m - 1$ transpositions (12), (23), (34), (45) $\cdots$ $(m-2, m-1), (m-1, m)$. For example $\mathscr{S}_3$ is generated by (12) and (23) since $(12)(23)(12) = (13)$, $(12)(23) = (123)$, $(23)(12) = (132)$, $(12)(12) = n$. Thus, if the matrices $A((12))$ and $A((23))$ corresponding to (12) and (23) in a given representation are known, all the other matrices of the representation can be obtained as their products. For example, $A((123)) = A((12))A((23))$. The above remark generalizes immediately from $\mathscr{S}_3$ to $\mathscr{S}_m$.

We now exhibit two examples, namely [2, 1] and [3, 1] and then state the general rule for Young's orthogonal representation.

From the hook diagram

$$\begin{matrix} 3 & 1 \\ 1 & \end{matrix}$$

for the representation [2, 1] of $\mathscr{S}_3$ we deduce that the dimension of [2, 1] is $3!/3 = 2$. There are two YT:

$$\begin{matrix} 1 & 2 \\ 3 & \end{matrix} \qquad \begin{matrix} 1 & 3 \\ 2 & \end{matrix}$$

with Yamanouchi symbols

$$2\ 1\ 1 \qquad 1\ 2\ 1.$$

If $g \rightarrow A(g)$ is Young's orthogonal form of the irreducible representation [2, 1], then

$$A((12)) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad A((23)) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}.$$

The reader should verify the following properties where I is the 2×2 identity matrix:

(1) $A^2((12)) = A^2((23)) = I$.
(2) $A((12))$ and $A((23))$ are orthogonal matrices. That is (i) the scalar product of any two rows or columns is zero, and (ii) the scalar product of each row, or column, with itself is 1.
(3) $\det A((12)) = \det A((23)) = -1$.
(4) If $B = A((12))A((23))$ then $B^3 = I$.
(5) The multiplicative group generated by the above two matrices contains 6 elements and is not commutative.

The truth of these properties should convince the reader that the *six* matrices generated from the two just given explicitly constitute an irreducible two-dimensional representation of $\mathscr{S}_3$. Since, to within similarity, there is only one such irreducible, it must be [2, 1].

As a second example, matrices which generate the representation [3, 1] of $\mathscr{S}_4$ are exhibited. From the hook diagram $\begin{matrix} 4 & 2 & 1 \\ 1 & & \end{matrix}$ it follows that the dimension is 3. The corresponding YT are

$$\begin{array}{lll} 1\ 2\ 3 & \quad 1\ 2\ 4 & \quad 1\ 3\ 4 \\ 4 & \quad 3 & \quad 2 \end{array}$$

with Yamanouchi symbols

$$2\ 1\ 1\ 1 \qquad 1\ 2\ 1\ 1 \qquad 1\ 1\ 2\ 1.$$

In this case,

$$A((12)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$A((23)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \qquad A((34)) = \begin{pmatrix} -\frac{1}{3} & \frac{\sqrt{8}}{3} & 0 \\ \frac{\sqrt{8}}{3} & \frac{1}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The reader should again verify

(1) The square of each of these matrices is the identity matrix.
(2) Each is an orthogonal matrix.
(3) The determinant of each matrix is -1.
(4) The product of the three matrices is a matrix, whose fourth power is the identity.
(5) (Rather tedious!) The three matrices given above generate a multiplicative group of order 24.

Notice that in the above two cases the YT are displayed in lexicographical order, that is such that the corresponding Yamanouchi symbols are in order of decreasing magnitude. This practice is followed in the general case.

Young provides a simple rule for obtaining the matrices correspondng to the $m-1$ transpositions (ij) *where* $j = i + 1$. As noted above, these transpositions suffice to generate $\mathcal{S}_m$ and hence their matrices, in *any* representation of $\mathcal{S}_m$, generate the whole representation. The digits i and j $(j = i + 1)$ occur in each of the YT associated with a fixed diagram. There are three mutually exclusive possibilities:

(a) i and j occur in the same row of the YT;
(b) i and j occur in the same column of the YT;
(c) i and j are neither in the same row or column.

In case (c), since j is the successor of i, interchanging i and j in the given YT changes it into a different YT associated with the same diagram.

We use the YT to label the rows and columns of the matrices of the representation. The matrix corresponding to the transposition (ij), where $j = i + 1$, is obtained as follows.

(i) For a YT of type (a) put 1 in the diagonal position and zeros in the other positions of the corresponding row and column.

(ii) For a YT of type (b) put -1 in the diagonal position and zeros in the other positions of the corresponding row and column.

(iii) For the four positions covered by the two YT's of type (c), put the matrix

$$\begin{pmatrix} -\rho & (1-\rho^2)^{1/2} \\ (1-\rho^2)^{1/2} & \rho \end{pmatrix}$$

and zeros elsewhere in the corresponding rows and columns. Here ρ^{-1} is the number of "steps" along the hook from i to j.

Thus for (23) in

$$\begin{array}{l} 1 \leftarrow 2 \\ \downarrow \\ 3 \end{array}$$

$\rho = \frac{1}{2}$.

For (45) in

$$\begin{array}{l} 1 \leftarrow 2 \leftarrow 3 \leftarrow 4 \\ \downarrow \\ 5 \end{array}$$

$\rho = \frac{1}{4}$.

The reader should verify that the particular matrices given above are all special cases of this general rule. He should note that the rule does *not* give the matrix corresponding to a transposition, such as (25), between *non-consecutive* integers. It applies only to transpositions involving consecutive integers but these suffice to generate $\mathscr{S}_m$.

An important immediate consequence of the above recipe for irreducible representations is the famous Branching rule for the *subduced* representation of $\mathscr{S}_{m-1}$ obtained by restricting an irreducible representation $[\lambda]$ of $\mathscr{S}_m$ to the subgroup $\mathscr{S}_{m-1}$ of all permutations of $1, 2, \ldots, m-1$. The latter group is generated by the consecutive transpositions *excluding* $(m\ m-1)$. These transpositions all leave the object m fixed.

Notice that if the numeral 3 is removed from the two YT for [2, 1] we are left with YT

$$\begin{matrix} 1 & 2 \end{matrix} \quad \text{and} \quad \begin{matrix} 1 \\ 2 \end{matrix}$$

which are proper YT for the irreducible representations [2] and $[1^2]$ of $\mathscr{S}_2$. Thus, when $\mathscr{S}_3$ is restricted to $\mathscr{S}_2$ the irreducible representation [2, 1] of $\mathscr{S}_3$ *reduces* to the direct sum of the two irreducible representations [2] and $[1^2]$ of $\mathscr{S}_2$. This situation is symbolized by

$$[2, 1] \downarrow \mathscr{S}_2 = [2] + [1^2]$$

and we refer to $[2, 1] \downarrow \mathscr{S}_2$ as the *representation of* $\mathscr{S}_2$ *subduced from*, or *by* [2, 1]. The reader should verify that

$$[3, 1] \downarrow \mathscr{S}_3 = [3] + [2, 1].$$

Indeed, the matrices given above for $A((12))$ and $A((23))$ each have the form

$$\begin{pmatrix} D_1 & T \\ S & D_2 \end{pmatrix},$$

where D_1 is a 1×1 matrix, D_2 is a 2×2 matrix, T is the 1×2 zero matrix, and S is the 2×1 zero matrix. Further, $g \to D_1(g)$ is the representation [3] and $g \to D_2(g)$ is the representation [2, 1] of $\mathscr{S}_3$.

Removing the digit m from a YT is equivalent to removing the first digit from the Yamanouchi symbol. One easily sees that when this is done *the set of* YT *corresponding to a fixed* YD *can be collected into sets of* YT *corresponding to precisely those* YD's *obtainable from the original* YD *by removing one node*. Thus,

$$\begin{aligned}
\begin{smallmatrix} \cdot & \cdot \\ \cdot & \end{smallmatrix} \downarrow \mathscr{S}_2 &= \begin{smallmatrix} \cdot & \cdot \end{smallmatrix} + \begin{smallmatrix} \cdot \\ \cdot \end{smallmatrix} = [2] + [1^2], \\
\begin{smallmatrix} \cdot & \cdot \\ \cdot & \cdot \end{smallmatrix} \downarrow \mathscr{S}_3 &= \begin{smallmatrix} \cdot & \cdot \\ \cdot & \end{smallmatrix} = [2, 1], \\
\begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & & \end{smallmatrix} \downarrow \mathscr{S}_3 &= \begin{smallmatrix} \cdot & \cdot & \cdot \end{smallmatrix} + \begin{smallmatrix} \cdot & \cdot \\ \cdot & \end{smallmatrix} \\
&= [3] + [2,1], \\
\begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \\ \cdot & & \end{smallmatrix} \downarrow \mathscr{S}_5 &= \begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \end{smallmatrix} + \begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & & \\ \cdot & & \end{smallmatrix} + \begin{smallmatrix} \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \end{smallmatrix} \\
&= [3, 2] + [3, 1^2] + [2^2, 1].
\end{aligned}$$

This last equation symbolizes the fact that the subduced representation

$$[321] \downarrow \mathscr{S}_5 = [3, 2] + [3, 1^2] + [2^2, 1].$$

The reader should verify that the sum of the dimensions of the irreducible representations of $\mathscr{S}_5$ on the right-hand side equals the dimension of the representation [321] of $\mathscr{S}_6$.

The above italicized statement is the *branching rule* for the symmetric group. Its simplicity amply justifies Young's choice of names for the irreducible representations.

IV. Characters

As is well known, the character, $\chi\colon g \to \chi(g) = \operatorname{tr} A(g)$ of a representation A of a finite group determines the representation to within a similarity transformation. Indeed if χ_λ is the character of an irreducible representation then

$$\sum_g \chi(g)\chi_\lambda(g^{-1}) = |G|n_\lambda,$$

where $|G|$ is the order of G and n_λ is a nonnegative integer giving the frequency of occurrence of the irreducible representation λ in the direct decomposition of A. The characters frequently have physical importance. For example, in Eq. (8.18) of the last chapter of "The Theory of Groups and Quantum Mechanics," Weyl obtains the sums of various powers of the first order perturbed energy levels in the case of equivalence degeneracy for m electrons, expressed by means of the exchange energies and the character of the appropriate irreducible representation of $\mathscr{S}_m$. Thus, if one is interested only in energy levels and not wave functions, one need only calculate characters and not the matrices of the relevant irreducible representations.

In the case of the symmetric group, in contrast to most other groups, there are powerful straight-forward methods of calculating characters. The first method discussed here was discovered by the author about ten years ago. It was inspired by T. Nakayama's version of a determinantal method due to Murnaghan (1937).

To find the character of the class (2^3) in [4, 2] of $\mathscr{S}_6$, proceed as follows.

(1) In the hook diagram
$$\begin{matrix} 5 & 4 & 2 & 1 \\ 2 & 1 & & \end{matrix}$$

note that the *principal hook lengths*, i.e., the numbers in the first column, are 5, 2.

(2) The calculation of $\chi_{[4,2]}((2^3))$ is then effected as follows:

$$\begin{aligned}
2^3 &: |5 \quad 2| \\
2^2 &: |3 \quad 2| + |5 \quad 0| \\
2 \; &: |1 \quad 2| + |3 \quad 0| + |3 \quad 0| = |1 \quad 2| + 2|3 \quad 0| \\
\phi \; &: |1 \quad 0| + 2|1 \quad 0| = 3|1 \quad 0|,
\end{aligned}$$

therefore

$$\chi_{[4,2]}((2^3)) = 3.$$

Explanation. The vertical bars are not essential. They derive from the determinant of Murnaghan's original approach and help keep track of sign which is the most troublesome part of Nakayama's approach.

At each stage we "subtract" one cycle length from each side, so that on the left, by the last line, the conjugate class has evaporated leaving the empty set ϕ. On the right, the subtraction corresponds to differentiating the determinant, by subtracting the cycle lengths from *each* digit of the determinant in succession, and adding the resulting determinants.

A determinant vanishes if (i) it contains a negative digit, or (ii) if two digits are equal. So if any such occur in the above process they may simply be omitted.

There is a Leibnitzian preestablished harmony such that, if the YD had $p+1$ rows and if no arithmetical mistakes are made, the only determinants remaining in the final row contain the $p+1$ distinct digits 0, 1, 2, ..., p. The determinant $|p, p-1, \ldots, 2, 1, 0| = 1$. Others are $+1$ or -1 according to whether they are obtained by an even or an odd permutation from the preceding determinant.

The cycles can be removed in any order. Usually it is most economical to begin with the larger cycle lengths, since they are more likely to give rise to negative digits in the determinants, thus causing them to vanish.

As a second example of the method, we find the character of the class $(5^2, 3^2, 2^2)$ in the representation $[10, 8, 2]$ of $\mathcal{S}_{20}$. The principal hook lengths $\lambda_0 + 2$, $\lambda_1 + 1$, λ_2 are 12, 9, 2.

$$\begin{array}{llll}
5^2 & 3^2 & 2^2: & |12 \quad 9 \quad 2| \\
5 & 3^2 & 2^2: & |7 \quad 9 \quad 2| + |12 \quad 4 \quad 2| \\
 & 3^2 & 2^2: & 2|7 \quad 4 \quad 2| \\
 & 3 & 2^2: & 2|7 \quad 1 \quad 2| \\
 & & 2^2: & 2|4 \quad 1 \quad 2| \\
 & & 2\ : & 2|4 \quad 1 \quad 0| \\
 & & \phi\ : & 2|2 \quad 1 \quad 0|
\end{array}$$

therefore

$$\chi_{[10,8,2]}((5^2 \quad 3^2 \quad 2^2)) = 2.$$

If one is interested in the character of a particular conjugate class for a specific $[\lambda]$, the preceding method is the most efficient known to the author However, if one is interested in obtaining *complete* character tables, some recursive procedure might be more economical.

The Murnaghan–Nakayama procedure is essentially a method involving recursion on the *cycle* structure. For our purposes, it is convenient to introduce a new notation for conjugate classes. We speak of the conjugate class α, if α is the m-component vector $(\alpha_1, \alpha_2, \ldots, \alpha_m)$, such that the corresponding class has cycle structure $(1^{\alpha_1}, 2^{\alpha_2}, 3^{\alpha_3}, \ldots, m^{\alpha_m})$. In other words, α_i is the number of cycles of length i, so that $\Sigma i\alpha_i = m$. Suppose that α' is the class obtained from α by deleting *one* cycle of length i, then the character of α for the irreducible representation λ is given by

$$\chi_\lambda{}^\alpha = \sum_\mu \pm \chi_\mu{}^{\alpha'} \tag{4}$$

where the μ and the signs occurring in the sum on the right-hand side are determined as follows. Suppose $l_0, l_1, l_2, \ldots, l_p$ are the principal hook lengths for the YD $[\lambda]$. The l_p are necessarily distinct. Form the determinantal sum

$$|l_0 - i, l_1 l_2 \cdots l_p| + |l_0, l_1 - i, l_2 \cdots l_p| + \cdots + |l_0 l_1 \cdots l_{p-1} l_p - i|.$$

If two digits in a determinantal symbol are equal or any digit is negative discard the corresponding term. If the digits are distinct they are principal hook lengths of a unique YD, $[\mu]$ and the corresponding μ occurs in (4) with positive or negative sign, depending on whether an even or odd permutation is needed to bring the digits of the determinant into *decreasing* order. The formula (4), which is due to Murnaghan, is explained in Section 7–5 of Hamermesh (1962).

For example, if $\alpha_5 > 0$, and we take $i = 5$, the first step in the last worked example is a particular case of the general formula

$$\chi^{\alpha}_{[10,8,2]} = -\chi^{\alpha'}_{[7,6,2]} + \chi^{\alpha'}_{[10,3,2]}. \tag{5}$$

However, there is still another approach involving recursion on *the number of rows in the* YD. As far as the author is aware, the two formulas we shall now give are new, although particular cases of them were known to G. Frobenius and to F. Murnaghan. We shall express $\chi_\lambda{}^\alpha$ in terms of binomial coefficients involving the integers α_i and characters of the symmetric group on $m - \lambda_0$, or less, objects. Suppose that $\beta_i \leqq \alpha_i$, then, by definition,

$$\binom{\alpha}{\beta} = \prod_i \binom{\alpha_i}{\beta_i} \tag{6}$$

where $\binom{\alpha_i}{\beta_i}$ is the binomial coefficient $\alpha_i!/\beta_i!(\alpha_i - \beta_i)!$ It was shown by Coleman (1965), that

$$\chi_\lambda{}^\alpha = \sum_r \sum_\mu \sum_\beta (-1)^r \chi_\mu{}^\beta \tbinom{\alpha}{\beta}, \tag{7}$$

where

(i) $[\lambda] = [\lambda_0, \lambda_1, \ldots, \lambda_p]$, $0 \leqq r \leqq p$,
(ii) for each r, the summation on μ is on all $[\mu_1, \mu_2, \ldots, \mu_p]$ satisfying $\lambda_i - 1 \leqq \mu_i \leqq \lambda_i$, $\Sigma \mu_i = m - \lambda_0 - r$,
(iii) the summation on β is on all β_j satisfying $\Sigma j\beta_j = m - \lambda_0 - r$ and $\beta_j \leqq \alpha_j$.

In case the YD has only two rows, i.e., $p = 1$, $[\lambda] = [\lambda_0, \lambda_1]$, (7) is very simple to apply and gives rise to an explicit formula for the character of an arbitrary conjugate class as a polynomial in the α_i. In this case, $r = 0$ or 1, $\mu = [\mu_1]$, and $\mu_1 = \lambda_1 - r$. Whence

$$\chi_\lambda{}^\alpha = \sum_\beta \binom{\alpha}{\beta} - \sum_\gamma \binom{\alpha}{\gamma}, \tag{8}$$

where $\Sigma i\beta_i = \lambda_1$, $\Sigma i\gamma_i = \lambda_1 - 1$. The summations are on all β and γ consistent with these restrictions and satisfying $\beta_i \leqq \alpha_i$, $\gamma_i \leqq \alpha_i$. For example, if $\lambda_1 = 3$, β corresponds to the classes (1^3), $(1, 2)$, or (3) for which β is $(3, 0, 0, \ldots)$, $(1, 1, 0, 0, \ldots)$ and $(0, 0, 1, 0, 0, \ldots)$ respectively, whereas γ can be $(2, 0, 0, \ldots)$ or $(0, 1, 0, 0, \ldots)$. Thus

$$\chi_{[m-3,3]}^\alpha = \binom{\alpha_1}{3} + \binom{\alpha_1}{1}\binom{\alpha_2}{1} + \binom{\alpha_3}{1} - \binom{\alpha_1}{2} - \binom{\alpha_2}{1} \tag{9}$$

$$= \tfrac{1}{6}\alpha_1(\alpha_1 - 1)(\alpha_1 - 5) + \alpha_2(\alpha_1 - 1) + \alpha_3. \tag{10}$$

In particular, setting $\alpha_1 = m$, $\alpha_j = 0$ for $j > 1$, gives the character of the neutral element which is equal to the dimension, so that we have the formula

$$f_{[m-3,3]} = \tfrac{1}{6}\, m(m - 1)(m - 5). \tag{11}$$

Sometimes the summation over μ in (7) can be tedious, in which case it may be simpler to employ the following alternative formula

$$\chi_\lambda{}^\alpha = \sum_r \sum_\beta \sum_\gamma \frac{(-1)^a}{\gamma!\,\Pi(j^{\gamma_j})} \chi_{\bar\lambda}^{\gamma\beta} \binom{\alpha}{\beta} \tag{12}$$

In this equation, $\bar\lambda = [\lambda_1, \lambda_2, \ldots, \lambda_p]$, γ_j are the indices of a partition of r, $\gamma\beta$ is a partition of $m - \lambda_0$ such that $\gamma_j + \beta_j \leqq \alpha_j$, $\gamma! = \Pi_j(\gamma_j!)$, and $a = \Sigma\gamma_j$. As before, the r-summation is on all r such that $0 \leqq r \leqq p$. Thus, we have replaced the μ summation on representations by a summation on subconjugate classes, γ. Thus (12) has the advantage of requiring, as known, only the characters of $\bar{\lambda}$. Note that the $r = 0$ terms in (7) and (12) are identical. Usually, it is most efficient to use a combination of the two formulas (7) and (12).

For example, to suggest the power of the preceding two formulas, we note that with the aid of tables of characters for the representation [3, 2, 1] of $\mathscr{S}_6$ and [2, 1] of $\mathscr{S}_3$ we can immediately write the formula

$$\begin{aligned}\chi^{\alpha}_{[m-6,3,2,1]} = {} & 16\binom{\alpha_1}{6} - 2\binom{\alpha_1}{3}\binom{\alpha_3}{1} + \binom{\alpha_1}{1}\binom{\alpha_5}{1} - 2\binom{\alpha_3}{2} - 16\binom{\alpha_1}{5} \\ & + 2\binom{\alpha_1}{2}\binom{\alpha_3}{1} - \binom{\alpha_5}{1} + 8\binom{\alpha_1}{4} - \binom{\alpha_1}{1}\binom{\alpha_3}{1} \\ & - 2\binom{\alpha_1}{3} + \binom{\alpha_3}{1}. \qquad (13)\end{aligned}$$

In this we used (12) for $r = 0, 1, 2$ and (7) for $r = 3$. In particular, setting $\alpha_1 = m$ and $\alpha_j = 0$ for $j > 1$, the following dimension is obtained:

$$\begin{aligned}f_{[m-6,3,2,1]} &= 16\binom{m}{6} - 16\binom{m}{5} + 8\binom{m}{4} - 2\binom{m}{3} \\ &= \frac{1}{45} m(m-1)(m-2)(m-4)(m-6)(m-8). \qquad (14)\end{aligned}$$

It is clear that the methods of this section for calculating the characters of $\mathscr{S}_m$ may be easily programmed for electronic computer. This has already been done at Uppsala for our first method.

V. Schur's Theorem and Spin Functions

Young diagrams and tableaux are not only useful for studying representations of the symmetric group but also those of the *full linear groups*, *GL*(n, C). The full linear group on a complex n-dimensional vector space contains the set of all regular linear transformations on the space and is therefore isomorphic to the multiplicative group of all $n \times n$ matrices with nonzero determinant. We denote this group by $\mathscr{L}_n$. The capital facts of the representation theory of $\mathscr{L}_n$, first stated clearly by Issai Schur in his Berlin Dissertation in 1901, are that (i) any irreducible integral rational representation of $\mathscr{L}_n$ is equivalent to a tensor representation, and (ii) the algebra of all linear operators which commute with a tensor representation of order m is generated by $\mathscr{S}_m$. We refer to these two results as *Schur's theorem.* To the uninitiated, statement (ii) may not sound very impressive. However, if he recalls that a *good* quantum number is an eigenvalue of an operator which commutes with the Hamiltonian, then he may be persuaded, by analogy, to accept the assertion that (ii) implies that the knowledge of the representation of $\mathscr{S}_m$ which we have assembled in the preceding sections *immediately* gives us access to the irreducible representations of $\mathscr{L}_n$. Since the two-dimensional spinor group $SU(2)$ is a subgroup of $\mathscr{L}_2$, and since products of spin functions span tensor representations of $SU(2)$, the two concepts in the title of the present section are closely related.

The relation of the representations of the full linear group and those of the symmetric group have been discussed by Weyl (1946), Boerner (1963), Ludwig (1954), and many other authors. It is too extensive a subject to be given a systematic exposition here. However, we hope that our outline of the key ideas will be useful for some readers.

Suppose that $c = (c_{ij})$ is an element of $\mathscr{L}_n$, i.e., a $n \times n$ matrix with determinant $|c| \neq 0$. In the two most important cases for physical application, c_{ij} are either *real* or *complex numbers.* In either case, $\mathscr{L}_n$ depends on the n^2 parameters, c_{ij}, *real* in the first instance, *complex* in the other. The c_{ij} are restricted only by the one condition, that $|c| \neq 0$. *Topologically,* the real and complex full linear groups are quite different—the latter is connected while the former is not. (If c_{ij} are real, it is impossible to join an element of the set of c, for which $|c| > 0$, to an element of the set for which $|c| < 0$, by means of a continuous curve which does not intersect the set for which $|c| = 0$.) Half of the much-discussed T.C.P. symmetry group arises because the extended Lorentz group is real and therefore disconnected, so the reader should not feel that by mentioning *topology* the author is dragging in mathematical abstractions which have no physical significance!

In order to please the typesetter and to explain the idea of *tensor representation,* we replace c_{ij} by $c(i,j)$ which will enable us to avoid second-order subscripts. Recall that a representation Γ of $\mathscr{L}_n$ is a mapping Γ: $c \rightarrow \Gamma(c)$, where $\Gamma(c)$ is a linear transformation on an appropriate linear space, V. Equivalently, we may regard $\Gamma(c)$ as a matrix. Further $\Gamma(c'c'') = \Gamma(c')\Gamma(c'')$ for all $c', c'' \in \mathscr{L}_n$. Suppose the linear space V_m is spanned by n^m objects $X(i_1, i_2, \ldots, i_m)$, where $i_j \in \{1, 2, \ldots, n\}$. These "objects" are linearly independent if V_m has dimension n^m, othrewise they are linearly dependent. As elements of V_m, $X(i_1, i_2, \ldots, i_m)$ are necessarily "vectors" in the sense that they can be added and can be multiplied by scalars. We used the word "object" in order not to prejudge the intrinsic nature of tensors.

To $c \in \mathscr{L}_n$ we associate the map $\Gamma(c)$ which sends $X(i_1, i_2, \ldots, i_m)$ into

$$\Gamma(c)X(i_1, i_2, \ldots, i_m) = \sum_{j_1 \cdots j_m} c(j_1 i_1)c(j_2 i_2) \cdots c(j_m i_m)X(j_1, j_2, \ldots, j_m). \quad (15)$$

The mapping $\Gamma(c)$ is certainly linear for all c if $X(i_1 \cdots i_m)$ are linearly independent, but otherwise it is by no means obvious that $\Gamma(c)$ is a linear map.

Indeed, in general it will not be. We make the further *assumption* about the $X(i_1 \cdots i_m)$: $\Gamma(c)$ is *linear* for all $c \in \mathscr{L}_n$. Thus for $b = (b(i, j)) \in \mathscr{L}_n$, since $\Gamma(b)$ is linear

$$\begin{aligned}\Gamma(b)[\Gamma(c)X(i_1, i_2, \ldots, i_m)] &= \sum_{j_1 \ldots j_m} c(j_1 i_1) \cdots c(j_n i_m)\Gamma(b)X(j_1, \ldots, j_m) \\ &= \sum_{j_1 \cdots j_m} \sum_{k_1 \ldots k_m} b(k_1 j_1) \cdots b(k_m j_m)c(j_1 i_1) \\ &\qquad \cdots c(j_m i_m)X(k_1, \ldots, k_m) \\ &= \sum_{k_1 \ldots k_m} bc(k_1 i_1) \cdots bc(k_m i_m)X(k_1, \ldots, k_m) \\ &= \Gamma(bc)X(i_1, \ldots, i_m),\end{aligned}$$

therefore

$$\Gamma(bc) = \Gamma(b)\Gamma(c).$$

In the course of this calculation, we assumed the following rule for matrix multiplication: $bc(ki) = \sum_j b(kj)c(ji)$.

It follows that *if* it is possible to define Γ: $c \to \Gamma(c)$, as above, then Γ is a representation of $\mathscr{L}_n$ on the space V_m. The elements of V_m are called *tensors of order m* and Γ is said to be a representation of $\mathscr{L}_n$ by means of *m*th-order tensors. A reader familiar with classical tensor algebra should recognize our tensors as tensors of order m. Whether he will call them contravariant or covariant will depend on whether he chooses to think of the group $\mathscr{L}_n$ as acting on *coordinates* or on an *ordered basis* of a vector space.

We illustrate the main ideas involved by the simple case $m = 2$. Suppose $X(i_1, i_2)$, $1 \leqq i_1, i_2 \leqq n$, are n^2 linearly independent elements of a real vector space, and that $c \in \mathscr{L}_n$, where $\mathscr{L}_n$ is the full linear group of dimension n over the reals. Then

$$\Gamma(c)X(i_1, i_2) = \sum_{j_1, j_2} c(j_1 i_1)c(j_2 i_2)X(j_1, j_2).$$

Associated with (12), the transposition acting on the subscripts of i_1 and i_2, we define an operator τ which acts on the $X(i_1, i_2)$ so that $\tau X(i_1, i_2) =$

$X(i_2, i_1)$. Hence τ^2 is the identity operator. It follows that

$$\begin{aligned}\tau\Gamma(c)X(i_1, i_2) &= \Gamma(c)X(i_2, i_1)\\ &= \sum_{j_1 j_2} c(j_1 i_2)c(j_2 i_1)X(j_1, j_2)\\ &= \sum_{j_1 j_2} c(j_2 i_2)c(j_1 i_1)X(j_2, j_1)\\ &= \Gamma(c)\tau X(i_1, i_2).\end{aligned}$$

Thus

$$\tau\Gamma(c) = \Gamma(c)\tau \qquad \text{for all} \quad c \in \mathscr{L}_n.$$

If we set

$$\begin{aligned}X_s(i_1 \quad i_2) &= \tfrac{1}{2}(X(i_1, i_2) + X(i_2, i_1)),\\ X_a(i_1 \quad i_2) &= \tfrac{1}{2}(X(i_1, i_2) - X(i_2, i_1)),\end{aligned}$$

then

$$\tau X_s(i_1, i_2) = X_s(i_1, i_2), \qquad \tau X_a(i_1, i_2) = -X_a(i_1, i_2).$$

One also easily verifies that

$$\begin{aligned}\Gamma(c)X_s(i_1, i_2) &= \sum_{j_1 j_2} c(j_1 i_1)c(j_2 i_2)X_s(j_1, j_2),\\ \Gamma(c)X_a(i_1, i_2) &= \sum_{j_1 j_2} c(j_1 i_1)c(j_2 i_2)X_a(j_1, j_2).\end{aligned}$$

If $X(i_1, i_2)$ are linearly independent then the $X_s(i_1, i_2)$ span a space $V_2{}^s$ of dimension $\frac{1}{2}n(n+1)$, and the restriction of Γ to $V_2{}^s$ can be shown to be an irreducible representation of $\mathscr{L}_n$. Similarly, the $X_a(i_1, i_2)$ span a space $V_2{}^a$ of dimension $\frac{1}{2}n(n-1)$ which carries an irreducible representation of $\mathscr{L}_n$. We can infer that our assumption about Γ, namely that it is a representation of $\mathscr{L}_n$ by means of *linear* transformations of second order tensors, is so restrictive as to force the dimension of V_2 to be 0, $\frac{1}{2}n(n-1)$, $\frac{1}{2}n(n+1)$, or n^2.

The fact that the operator τ commutes with all $\Gamma(c)$ implies that it is possible to choose a basis of V_2 whose elements transform *simultaneously* as would a basis for an irreducible representation of $\mathscr{L}_n$ *and* a basis for an irreducible representation of $\mathscr{S}_2$. Since $\mathscr{S}_2$ has only two irreducible representations [2] and [1^2] each of dimension 1, the elements of a basis such as that just described must be either symmetric or antisymmetric under the action of τ. This is precisely the basis we have obtained. *Each* $X_s(i_1, i_2)$ gives a representation [2] of $\mathscr{S}_2$. All the $X_s(i_1, i_2)$ together span the unique subspace $V_2{}^s$ containing the elements of V_2 which are *fixed* under τ. As mentioned, this subspace $V_2{}^s$, uniquely determined as the carrier space of the representation [2] of $\mathcal{S}_2$ with multiplicity $\frac{1}{2}n(n+1)$, simultaneously carries an irreducible representation of $\mathcal{L}_n$, which we denote by $\langle 2\rangle$. Thus, $V_2{}^s$ carries the irreducible representation $\langle 2\rangle$ of $\mathcal{L}_n$ with *multiplicity* equal to the *dimension* of [2], and simultaneously carries the irreducible representation of [2] of $\mathcal{S}_2$ with *multiplicity* equal to the *dimension* of $\langle 2\rangle$. This is the simplest instance of Schur's theorem (apart from the trivial case $m = 1$). Formulated in this way, it generalizes immediately in an obvious manner.

The general result is as follows. Suppose V_m is the linear space of mth order tensors over $\mathcal{L}_n$, of dimension n^m. As for $\mathcal{S}_2$ in the case V_2, we regard $\mathcal{S}_m$ as acting on the subscripts of the indices $i_1, i_2, \ldots, i_m$ in (15). If $\tau\colon X(i_1 \quad i_2 \cdots i_m) \to \tau X(i_1 \cdots i_m)$ is the mapping of V_m corresponding to any particular element of $\mathcal{S}_m$, then by the same argument as above we can show that

$$\tau\Gamma(c) = \Gamma(c)\tau$$

for all $\Gamma(c)$ and all τ. The space V_m can be reduced into a direct sum of spaces $V_m{}^\lambda$, such that $V_m{}^\lambda$ either carries the irreducible representation $[\lambda]$ of $\mathcal{S}_m$ or reduces into a number of irreducible representations of $\mathcal{S}_m$, *all* equivalent to $[\lambda]$. On the other hand, $V_m{}^\lambda$ carries a representation of $\mathcal{L}_n$ which is either irreducible or reduces into a number of irreducible representations, *all* of which are equivalent to one another. We denote this irreducible representation of $\mathcal{L}_n$ occurring in the reduction of $V_m{}^\lambda$ by $\langle\lambda\rangle$. Schur's theorem then states that in the reduction of $V_m{}^\lambda$ with respect to the action of $\mathcal{L}_n$ and $\mathcal{S}_m$, *the frequency of* $[\lambda]$ *is equal to the dimension of* $\langle\lambda\rangle$ *and the frequency of* $\langle\lambda\rangle$ *is equal to the dimension of* $[\lambda]$. Further, V_m is the direct sum of the $V_m{}^\lambda$, i.e.,

$$V_m = \sum_\lambda V_m{}^\lambda, \tag{16}$$

where the sum is *direct* and λ runs over all inequivalent irreducible representations of $\mathcal{S}_m$.

As a final elegant application of Young diagrams, we give a rule for obtaining the dimensions of $\langle\lambda\rangle$. [cf. Eq. (3.282) Robinson (1961)]. Associate to the YD both the hook graph and the n-graph. For [2 1] and [2 2] these are respectively

$$\begin{array}{ll} 3 & 1 \\ 1 & \end{array} \qquad \begin{array}{ll} n & n+1 \\ n-1 & \end{array} \tag{17}$$

$$\begin{array}{ll} 3 & 2 \\ 2 & 1 \end{array} \qquad \begin{array}{ll} n & n+1 \\ n-1 & n \end{array} \tag{18}$$

In the *n-graph*, the diagonal nodes are replaced by n. The numerals increase in unit steps to the right and decrease downwards. *For the partition λ, the product of the numbers in the n-graph divided by the product of the hook lengths is the dimension of $\langle\lambda\rangle$.* Thus the dimensions of $\langle 2\quad 1\rangle$ and $\langle 2\quad 2\rangle$ are $\frac{1}{3}n(n^2-1)$ and $\frac{1}{12}n^2(n^2-1)$ respectively.

The following examples may convince the reader of the validity of this rule. For [2] we have

$$2\quad 1 \qquad n\quad n+1$$

giving the dimension of $\langle 2\rangle$ as $\frac{1}{2}n(n+1)$; whereas for $[1^2]$ we have

$$\begin{matrix} 2 & \quad & n \\ 1 & \quad & n-1 \end{matrix}$$

giving the dimension of $\langle 1^2\rangle$ as $\frac{1}{2}n(n-1)$. These are the dimensions just obtained.

In the case $m = 3$, there are three partitions $3 = 2 + 1 = 1 + 1 + 1$, and the following dimensions for the corresponding $\langle\lambda\rangle$ are obtained.

Representation	Hook graph	n-graph	Dimension
$\langle 3\rangle$	3 2 1	$n \quad n+1 \quad n+2$	$\frac{1}{6}n(n+1)(n+2)$
$\langle 2, 1\rangle$	3 1 1	$n \quad n+1$ $n-1$	$\frac{1}{3}n(n^2-1)$
$\langle 1^3\rangle$	3 2 1	n $n-1$ $n-2$	$\frac{1}{6}n(n-1)(n-2)$

Since [3], [2, 1], and $[1^3]$ are of dimension 1, 2, and 1 respectively, it follows that $\langle 3\rangle$, $\langle 2, 1\rangle$, and $\langle 1^3\rangle$ occur in the reduction of V_3 with frequency 1, 2, and 1 respectively. Indeed,

$$\frac{1}{6}n(n+1)(n+2) + 2 \times \frac{1}{3}n(n^2-1) + \frac{1}{6}n(n-1)(n-2) = n^3. \qquad (19)$$

This equality illustrates the truth of Schur's theorem and of the rule for the dimension of the representation $\langle\lambda\rangle$. From the latter it follows that if the number of rows in the partition λ is greater than n, then the dimension of $\langle\lambda\rangle$ is zero.

For example, if $n = 2$ and $m = 3$ though there are, formally, the three irreducible tensor representations $\langle 3\rangle$, $\langle 2\quad 1\rangle$, and $\langle 1^3\rangle$ described above, the last has dimension 0. Thus, for $n = 2$, the tensor space V_3 is completely spanned by $V_3^{[3]}$ and $V_3^{[2\quad 1]}$ each of dimensions 4. $V_3^{[3]}$ carries the one-dimensional irreducible representation [3] of $\mathcal{S}_3$ with frequency *four* and the four-dimensional irreducible representation $\langle 3 \rangle$ of L_2 with frequency *one*.

The fundamental representation for the theory of spin is $\mathcal{D}_{1/2}$ which gives rise to the so-called "double-valued" representation of the orthogonal group in three dimensions. We may think of it as the group $SU(2)$ acting on a space of two dimensions spanned by $\alpha(1)$ and $\beta(1)$, the familiar spin wave functions. Now by a famous argument due to H. Weyl and called the "unitarian trick," it follows that a representation is irreducible with respect to $\mathcal{L}_n(C)$ if and only if it is irreducible with respect to $SU(n, C)$. The proof follows rather easily from the fact that over the complex numbers, C, *all* operators are linear combinations of *Hermitian* operators.

For tensors of order 1, only the symmetric group on one object, $\mathcal{S}_1$, comes into play. Thus the space spanning the irreducible representation $\mathcal{D}_{1/2}$ of $SU(2)$ may also be regarded as carrying the representation $\langle 1 \rangle$ of $\mathcal{L}_2(C)$. The spin wavefunction of a pair of electrons is a linear combination of $\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)$, $\alpha(2)\beta(1)$, and $\beta(1)\beta(2)$. The set of *all* linear combinations of these can be regarded as V_2. Under $\mathcal{L}_2$ it reduces to give the representations [2] and $[1^2]$ of $\mathcal{S}_2$, and the corresponding representations $\langle 2 \rangle$ of dimensions 3 and $\langle 1^2 \rangle$ of dimension 1, of $\mathcal{L}_2$. When we restrict $\mathcal{L}_2$ to $SU(2)$, these two representations are still irreducible according to the unitarian trick. They constitute the triplet and singlet pair states.

Similarly, the spin functions for three electrons span a space V_3 of dimension 8, which, as remarked, reduces under $\mathcal{S}_3$ into a direct sum

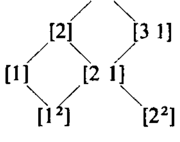
$$V_3 = V_3^{[3]} + V_3^{[2\ \ 1]}.$$

Here $V_3^{[3]}$ has dimension 4, carries [4] with frequency 4 and $\langle 4 \rangle$ with frequency 1. Also $V_3^{[2\ \ 1]}$ has dimension 4, carrying [2 1] with frequency 2 and $\langle 2\ \ 1 \rangle$ with frequency 2.

Notice that

$$[3] \downarrow \mathcal{S}_2 = [2],$$
$$[2\ \ 1] \downarrow \mathcal{S}_2 = [2] + [1^2],$$

so that we can construct a genealogical chart



which is immediately recognizable as the same as that familiar pattern used by Kotani and others (1955) for the genealogical formation of spin functions.

Since $n = 2$, the YD's which enter this chart have either one or two rows. If we set $2s = \lambda_0 - \lambda_1$, then s is the total spin of the representation subduced by $\langle\lambda_0 \quad \lambda_1\rangle$ when $\mathscr{L}_2$ is restricted to $SU(2)$. The corresponding representation $\langle\lambda_0 \quad \lambda_1\rangle$ has dimension $2s + 1$, and frequency equal to the dimension of $[\lambda_0 \quad \lambda_1]$, namely

$$f_{[\lambda_0\lambda_1]} = \binom{m}{\lambda_0} - \binom{m}{\lambda_1 - 1}. \tag{20}$$

If $\lambda_1 = 0$, the second binomial coefficient is to be interpreted as 0. The reader should check the validity of formula (20) in a few simple cases.

REFERENCES

BOERNER, H. (1963). "Representations of Groups." North-Holland Publ., Amsterdam. (German edition, Springer, Berlin, 1955.)

COLEMAN, A. J. (1965). "Induced Representations," Queen's Papers in *Pure Appl. Math.* No. 6. Queen's University.

HAMERMESH, M. (1962). "Group Theory and Its Applications to Physical Problems." Addison-Wesley, Reading, Massachusetts.

KOTANI, M., *et al.* (1955). "Table of Molecular Integrals." Maruzen, Tokyo.

LUDWIG, G. (1954). "Grundlagen der Quantenmechanik." Springer, Berlin.

MACMAHON, P. A. (1915). "Combinatory Analysis." Cambridge Univ. Press, London and New York. (Reprinted by Dover, New York, 1960.)

MURNAGHAN, F. D. (1937). *Am. J. Math.* **59**, 739–739.

ROBINSON, G. DE B. (1961). "Representation Theory of Symmetric Groups." Univ. of Toronto Press, Toronto.

RUTHERFORD, D. E. (1948). "Substitutional Analysis." Edinburgh Univ. Press.

WEYL, H. (1946). "The Classical Groups." Princeton Univ. Press, Princeton, New Jersey.

Field Theoretic Approach to Atomic Helium

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I. Introduction

During the past ten years, the methods of quantum field theory have been used with much success in the many-body problem.[1] The main advantages of using quantum field theoretic Green's functions are:

(1) They provide a way of discussing complicated terms in a perturbation expansion with a semiphysical language by using Feynman diagrams.

(2) They provide a way of summing infinite sets of diagrams which goes beyond ordinary perturbation theory.

(3) The energy spectrum can be obtained directly by investigating the poles of the Green's functions.

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[1] See, e.g., the following books and the references contained therein: Bonch-Bruevich and Tyablikov (1962), Morrison (1962), Nozières (1964), Pines (1961), and Schultz (1964).

(4) The self-consistent field problem can be connected smoothly onto the perturbation series.

(5) Unlinked clusters do not occur.[2]

(6) The coordinates of the particles do not enter and the Pauli exclusion principle is automatically satisfied by using second quantization.[3]

These advantages are extremely important in the many-body problem, where the configuration space approach soon becomes unwieldy.[4] However, in the few-body problem these advantages are not so important, and the traditional methods of configuration space are adequate. On the other hand, the few-body systems are in general simpler and have been well studied,[4a] so it would be interesting to apply the methods of many-body theory to them to obtain some insight into the relation between the configuration space approach and the field theoretic approach. Approximations that are made for many-body systems can be investigated in the few-body problem to see what the corresponding approximations are in configuration space, and thus more understanding of their validity can be gained.

The simplest few-body problem is the hydrogen atom for which the Green's function method gives the Schrödinger equation, and is thus trivial. However the problem will be discussed to illustrate the Green's function formalism, since the ideas used will be the same for more complicated systems.

The helium isoelectronic series is the first nontrivial few-body problem, which will be the main subject of this paper. The investigation illustrates the application of rather formal field theoretic methods and diagrams to a simple system which is familiar. The singlet and triplet states behave like boson and fermion systems respectively, since the spin will be separated out from the beginning. The Green's functions are taken with respect to the ground state of a one-particle system, and the poles thus occur for a two-particle and a no-particle system. Since the two-particle Green's function is involved in the equation of motion for the single-particle Green's function,

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[2] Kobe (1966a) has shown that if the Green's function equations of motion are used, the unlinked diagrams do not appear.

[3] See, e.g., Kobe (1966b), and references contained therein.

[4] Density matrices can of course be used to simplify the configuration space approach [see, e.g., Löwdin (1955)]. The Green's function method is a generalization of the density matrix method to include the time.

[4a] See, e.g., the following articles and the references contained therein: Holøien (1958); Hylleraas and Midtdal (1956), Löwdin and Redei (1959), Löwdin and Shull (1956), Nesbet and Watson (1958), Ritter and Pauncz (1960), and Shull and Löwdin (1955, 1956, 1959).

some insight is obtained in the case where the number of creation of annihilation operators exceeds the number of particles in the ground state. The Green's functions are simplified in this case, but are not zero.

The investigation also shows the connection between the usual configuration space approach and the field theoretic approach. The concepts of dressed and bare particles can be discussed in terms of a familiar system and configuration space. The field theoretic approach leads naturally to a quasi-particle model in which one of the electrons is bare and the other is dressed. The equations for this model are the same as the Hartree–Fock (HF) equations with one of the electrons fixed in a hydrogenic 1s orbital. Since the equation is linear, it might be a good starting point for a subsequent perturbation treatment.

The next section deals with the application of the many-body Green's function method to atomic hydrogen in order to illustrate the technique. In Section III, the Hamiltonian and state vectors for the helium atom are written in second quantization. The Green's function and its spectral representation are introduced in Section IV. The single-particle Green's function equation of motion is obtained in Section V. In Section VI the two-particle Green's function for the triplet state is discussed. The perturbation expansion for the single-particle Green's function is obtained in Section VII for the triplet state. In Section VIII the factorization of the two-particle Green's function is investigated. A comparison of the Green's function method with Hartree–Fock theory is made in Section IX. The triplet state energy for the $1s\,2s\,^3S$ is obtained in Section X. In Section XI the two-particle Green's function is factorized for the singlet state. The approximate equation for the single-particle propagator is obtained in Section XII for the singlet state. In Section XIII the singlet ground state and $1s\,2s\,^1S$ are investigated by the $1/Z$ expansion method. Section XIV contains a summary of the results of the paper and conclusions.

II. Application to Atomic Hydrogen

In order to obtain some insight into the Green's function method in the few-body problem, it will be applied to the trivial case of the hydrogen atom. This problem is trivial, since there is only one electron and hence no interelectronic interaction. The formulation will reduce to solving the Schrödinger equation, but the basic features of the Green's function method will be illustrated.

The Hamiltonian for the hydrogen atom in atomic units is

$$H = h(1) = -\tfrac{1}{2}\nabla_1{}^2 - Z/r_1, \tag{II.1}$$

where the coordinates are represented by $(1) = (\mathbf{r}_1)$. There is no simplification obtained by expressing the Hamiltonian in terms of second quantization, since the system contains only one particle. However the single-particle operator in Eq. (II.1) can be written as (Kobe, 1966c)

$$H = \int d1\, \psi^+(1)\, h(1)\, \psi(1). \tag{II.2}$$

When Eq. (II.2) is applied to a one-particle state, the Hamiltonian of Eq. (II.1) will be recovered. The field creation operator $\psi^+(1)$ creates a particle with a delta function wave function at the point $\mathbf{r}_1$. The field annihilation operator $\psi(1)$ annihilates a particle with a delta function wave function at the point $\mathbf{r}_1$. Together they satisfy the fermion anticommutation relations[3]

$$\begin{aligned} &[\psi(1), \psi^+(2)]_+ \equiv \psi(1)\psi^+(2) + \psi^+(2)\psi(1) = \delta(1-2), \\ &[\psi(1), \psi(2)]_+ = 0 = [\psi^+(2), \psi^+(1)]_+ . \end{aligned} \tag{II.3}$$

Boson commutation relations could also be used, since the statistics are irrelevant for a one-particle system. A single-particle function $\varphi(\mathbf{r})$ can be expressed as a state vector by using the field creation operator[3]

$$|\varphi\rangle = \int d1\, \varphi(1)\, \psi^+(1)\, |\text{vac}\rangle, \tag{II.4}$$

where $|\text{vac}\rangle$ is the state of no particles, or vacuum state.

In order to find the energy eigenvalues of the system, the Green's function or propagator can be used. Its Fourier transform will be shown to have poles at the exact eigenvalues of the system. The Green's function is defined field theoretically as[5]

$$G(\mathbf{x}, t; \mathbf{y}, 0) \equiv -i\langle \text{vac}|\, \psi(\mathbf{x}, t)\, \psi^+(\mathbf{y}, 0)\, |\text{vac}\rangle\, \theta(t). \tag{II.5}$$

The annihilation operator $\psi(\mathbf{x}, t)$ is in the Heisenberg representation

$$\psi(\mathbf{x}, t) = e^{iHt}\psi(\mathbf{x})e^{-iHt}. \tag{II.6}$$

The function $\theta(t)$ is the Heaviside step function which is zero for negative arguments and unity for positive

$$\theta(t) = \begin{cases} 1 & \text{if } t > 0, \\ 0 & \text{if } t < 0. \end{cases} \tag{II.7}$$

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[5] The usual definition of the causal Green's function involves a time-ordered product. Since the ground state here is the vacuum state, the annihilation operator acting on it will give zero. Thus the causal Green's function reduces to the retarded Green's function.

The Green's function defined above will later be shown to be the same as the Green's function defined in the theory of differential equations.

The spectral representation of the Green's function can be obtained by introducing the eigenfunctions of the Hamiltonian H,[6]

$$H|\varphi_n\rangle = E_n|\varphi_n\rangle, \tag{II.8}$$

which form a complete orthonormal set[7]

$$\sum_n |\varphi_n\rangle\langle\varphi_n| = 1. \tag{II.9}$$

If the complete set of states is inserted into Eq. (II.5) and the Hamiltonian in the exponent acts on them, the result is

$$G(\mathbf{x}, t; \mathbf{y}, 0) = -i\sum_n \varphi_n(\mathbf{x})\varphi_n^*(\mathbf{y})e^{-iE_nt}\theta(t), \tag{II.10}$$

since the inner product is

$$\langle\mathrm{vac}|\,\psi(\mathbf{x})\,|\varphi_n\rangle = \varphi_n(\mathbf{x}), \tag{II.11}$$

which can be obtained from Eqs. (II.3) and (II.4). If the Fourier transform of Eq. (II.8) is taken the spectral representation is obtained[8]

$$G(\mathbf{x}, \omega; \mathbf{y}, 0) = \sum_n \frac{\varphi_n(\mathbf{x})\varphi_n^*(\mathbf{y})}{\omega - E_n + i0}, \tag{II.12}$$

where the $+0$ is an infinitesimal positive quantity used to insure convergence of the integral.[9] The problem now is to obtain the Green's function and examine its poles.

The Green's function can be obtained from its equation of motion.[10] If Eq. (II.5) is differentiated with respect to the time, the result is

$$\{i\partial/\partial t - h(\mathbf{x})\}G(\mathbf{x}, t; \mathbf{y}, 0) = \delta(\mathbf{x} - \mathbf{y})\,\delta(t). \tag{II.13}$$

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[6] The Schrödinger equation is being introduced here, and later it will be seen necessary to solve it explicitly to obtain the Green's function.

[7] The sum is of course a sum over the discrete states and an integral over the continuum.

[8] See, e.g., Kobe (1962) and the references given there to spectral representations.

[9] If the Fourier transform

$$G(\omega) = \int_{-\infty}^{\infty} dt\; e^{i\omega t}G(t)$$

is defined in the generalized function sense, then the $+i0$ occurs naturally.

[10] The equation of motion method was first used by Galitskii and Migdal (1958). It was further developed by Martin and Schwinger (1959).

In order to obtain Eq. (II.13), use was made of the fact that the derivative of $\theta(t)$ is a delta function, and the anticommutation relations. The equation of motion for an operator in the Heisenberg picture was also used, and is

$$\begin{aligned} i\,\partial\psi(\mathbf{x}, t)/\partial t &= [\psi(\mathbf{x}, t), H] \\ &= h(\mathbf{x})\psi(\mathbf{x}, t) \end{aligned} \tag{II.14}$$

if Eqs. (II.2) and (II.3) are used. Eq. (II.13) shows that $G(\mathbf{x}, t; \mathbf{y}, 0)$ is the usual Green's function associated with the differential operator $i\,\partial/\partial t - h(\mathbf{x})$.

Equation (II.13) is the equation satisfied by the single-particle Green's function or propagator which describes the creation of a particle at the point $\mathbf{y}$ at time zero, its propagation to the point $\mathbf{x}$ during the time interval zero to t, and its annihilation there. Equation (II.13) can be represented graphically as shown in Fig. 1, where the box represents G, the reciprocal of the arrow represents the operator $[i\,\partial/\partial t - h(\mathbf{x})]$, and the circle represents the delta function.[11]

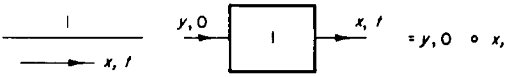

Fig. 1. The equation of motion for the single-particle propagator for atomic hydrogen in graphical form.

If Eq. (II.10) is substituted into Eq. (II.13) the equation will be satisfied if

$$h(\mathbf{x})\varphi_n(\mathbf{x}) = E_n\varphi_n(\mathbf{x}) \tag{II.15}$$

by using the completeness of the eigenfunctions.

Equation (II.15) is just the Schrödinger equation for the hydrogen atom, so the apparatus of quantum field theory and second quantization has not helped to solve the hydrogen atom problem. However, the approach here has illustrated the methods used in the many-body problem by applying them to the most trivial few-body problem available. The next simplest system is the two-body problem, i.e., the helium isoelectronic series. The application of the Green's function method to this system is not trivial, and gives some more insight into the nature of the Green's function method.

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[11] The graphical representation here is in terms of the coordinates and time, whereas the usual diagrams are in terms of the states and the frequency. The latter can be obtained from the former by calculating the matrix elements with respect to the single-particle orbitals and taking the Fourier transform with respect to the time.

III. The Second Quantized Helium System

In this section, the helium problem will be formulated in terms of second quantization, which must be done before the field theoretic Green's functions can be applied. The helium atom contains two electrons which can be either in a singlet or a triplet spin state.[12] For the singlet state, the wave function can be written as

$$\Psi^{(s)}(x_1, x_2) = \Psi_s(\mathbf{r}_1, \mathbf{r}_2)(1/\sqrt{2})[\alpha(\mathscr{S}_1)\beta(\mathscr{S}_2) - \beta(\mathscr{S}_1)\alpha(\mathscr{S}_2)], \qquad \text{(III.1)}$$

where $x = (\mathbf{r}, \mathscr{S})$ is the combined space and spin coordinate. The function $\Psi_s(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric since the function $\Psi^{(s)}(x_1, x_2)$ is antisymmetric under exchange of all of the coordinates. For the triplet state the wave function can be written as

$$\Psi^{(t)}(x_1, x_2) = \Psi_t(\mathbf{r}_1, \mathbf{r}_2)\begin{cases}\alpha(\mathscr{S}_1)\alpha(\mathscr{S}_2), \\ (2^{-1/2})[\alpha(\mathscr{S}_1)\beta(\mathscr{S}_2) + \alpha(\mathscr{S}_2)\beta(\mathscr{S}_2)], \\ \beta(\mathscr{S}_1)\beta(\mathscr{S}_2).\end{cases} \qquad \text{(III.2)}$$

where $\Psi_t(\mathbf{r}_1, \mathbf{r}_2)$ is an antisymmetric function of its variables. In the following discussion the spin will be factored out, and only the spatial part of the wave function will be considered.

The Hamiltonian for the nonrelativistic helium isoelectronic series is spin independent and in reduced and modified Hartree atomic units is

$$H = h(1) + h(2) + V(1, 2), \qquad \text{(III.3)}$$

where $(1) = (\mathbf{r}_1)$, $(2) = (\mathbf{r}_2)$. The hydrogenic Hamiltonian h is defined as

$$h(1) = -\tfrac{1}{2}\nabla_1{}^2 - 1/r_1 \qquad \text{(III.4)}$$

and the interaction term V is the mutual Coulomb repulsion

$$V(1, 2) = 1/Zr_{12}. \qquad \text{(III.5)}$$

The Hamiltonian in Eq. (III.3) can be written in second quantized form as (Kobe, 1966c)

$$H = \int d1\,\psi^+(1)h(1)\psi(1) + \tfrac{1}{2}\iint d1\, d2\, \psi^+(1)\psi^+(2)V(1, 2)\psi(2)\psi(1), \qquad \text{(III.6)}$$

where $\psi^+(1)$ and $\psi(1)$ are the field creation and annihilation operators

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[12] For a good review of the helium problem see Bethe and Salpeter (1957) and Hylleraas (1964).

respectively. They satisfy the (anti)commutation relations[3]

$$\begin{aligned}[\psi(1), \psi^+(2)]_\pm &\equiv \psi(1)\psi^+(2) \pm \psi^+(2)\psi(1) = \delta(1-2),\\ [\psi(1), \psi(2)]_\pm &= 0 = [\psi^+(2), \psi^+(1)]_\pm .\end{aligned} \tag{III.7}$$

For singlet states the commutator (−sign) is used, since the spatial part of the wave function in Eq. (III.1) is symmetric with respect to interchange of the coordinates and is therefore like a boson function. For the triplet state the anticommutator (+ sign) is used, since the spatial part of the wave function in Eq. (III.2) is antisymmetric with respect to interchange of the coordinates and is therefore like a fermion function. The second quantized Hamiltonian does not explicitly involve the number of particles, which is not so important for the few-body problem but is in the many-body problem.

The wave function for a two-particle system can be conveniently converted into a state vector by using the field operators. If the two-particle spatial wave function is $\Psi(1, 2)$ the state vector corresponding to it is[3]

$$|\Psi\rangle = 2^{-1/2} \iint d1\, d2\, \Psi(1, 2)\psi^+(2)\psi^+(1)\,|\text{vac}\rangle \tag{III.8}$$

where $|\text{vac}\rangle$ denotes the state of no particles. If the wave function is normalized, then the state vector is also.

IV. Green's Function

The method used to obtain the energy spectrum in quantum field theory is to investigate the poles of the Green's function or propagator.[13] These functions are convenient also because they can be represented by diagrams. The one-particle Green's function for an N particle system has poles related to the eigenvalues of an $N+1$ particle system and an $N-1$ particle system. Therefore the one-particle Green's function for a one-particle system will be studied here to give the energies of a two-particle system.

The one-particle causal Green's function of interest here is defined as

$$G(\mathbf{x}, t; \mathbf{y}, 0) \equiv -i\langle 1s|\, T\{\psi(\mathbf{x}, t)\psi^+(\mathbf{y}, 0)\}\,|1s\rangle, \tag{IV.1}$$

where the annihilation operator $\psi(\mathbf{x}, t)$ in the Heisenberg representation is

$$\psi(\mathbf{x}, t) = e^{iHt}\psi(\mathbf{x})e^{-iHt}. \tag{IV.2}$$

The expectation value in Eq. (IV.1) is taken with respect to the exact

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[13] See, e.g., Layzer (1963) and Kobe (1964).

ground state of a one-particle system. In this case it is the hydrogenic-like $1s$ state, which is of course well known.

The time-ordering operator T in Eq. (IV.1) is the operator which puts the largest time to the left and the smallest to the right with a plus (minus) sign for an even (odd) permutation of the original order for the triplet state, and plus for the singlet. Therefore, Eq. (IV.1) can be written as a sum of a retarded part and an advanced part

$$G = G^r \mp G^a \qquad \begin{pmatrix}\text{triplet}\\ \text{singlet}\end{pmatrix}. \tag{IV.3}$$

The retarded part G^r is defined as

$$G^r(\mathbf{x}, t; \mathbf{y}, 0) = -i\langle 1s|\psi(\mathbf{x}, t)\psi^+(\mathbf{y}, 0)|1s\rangle\theta(t), \tag{IV.4}$$

where $\theta(t)$ is the Heaviside step function defined in Eq. (II.7). The function G^r describes the creation of a particle at a point $\mathbf{y}$ at the time zero, and the annihilation of a particle at the point $\mathbf{x}$ at some positive time t. Since this process corresponds to our concept of causality, the function is called retarded in analogy with the retarded potential in electromagnetic theory.

The advanced part G^a of the causal Green's function in Eq. (III.3) is defined as

$$G^a(\mathbf{x}, t; \mathbf{y}, 0) = -i\langle 1s|\psi^+(\mathbf{y}, 0)\psi(\mathbf{x}, t)|1s\rangle\theta(-t), \tag{IV.5}$$

which describes the annihilation of a particle at a point $\mathbf{x}$ at a time $t < 0$, and a creation of a particle at point $\mathbf{y}$ at time zero. Therefore this process violates our concept of causality and is called the advanced Green's function in analogy with the advanced potential in electromagnetic theory. The causal function G is convenient to use however, since it satisfies a simpler equation which has a one-to-one correspondence with diagrams.

A complete set of two-particle states $|\Psi_n\rangle$ can be inserted in the retarded Green's function. These states must be eigenstates of the Hamiltonian, so

$$H|\Psi_n\rangle = E_n|\Psi_n\rangle, \tag{IV.6}$$

where E_n is the two-particle energy eigenvalue. They are also assumed to be orthonormal and complete, so that[7]

$$\sum_n |\Psi_n\rangle\langle\Psi_n| = 1. \tag{IV.7}$$

If Eq. (IV.7) is substituted into Eq. (IV.4) and Eq. (IV.6) is used, the result is

$$G^r(\mathbf{x}, t; \mathbf{y}, 0) = -i\sum_n f_n(\mathbf{x})f_n^*(\mathbf{y})\exp\{-i(E_n - E_{1s})t\}, \tag{IV.8}$$

where the energy E_{1s} is the energy of the hydrogenic 1*s* state. The function $f_n(\mathbf{x})$ is defined as

$$f_n(\mathbf{x}) = \langle 1s|\,\psi(\mathbf{x})\,|\Psi_n\rangle \tag{IV.9}$$

and in configuration space has the form[3]

$$f_n(\mathbf{x}) = \sqrt{2}\int d\mathbf{z}\, u_{1s}^*(\mathbf{z})\Psi_n(\mathbf{x}, \mathbf{z}). \tag{IV.10}$$

If the Fourier transform which is defined as

$$G(\mathbf{x}, \omega; \mathbf{y}, 0) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} G(\mathbf{x}, t; \mathbf{y}, 0) \tag{IV.11}$$

is taken in Eq. (IV.8), the result is the spectral representation of the retarded part of the Green's function[8]

$$G^r(\mathbf{x}, \omega; \mathbf{y}, 0) = \sum_n \frac{f_n(\mathbf{x}) f_n^*(\mathbf{y})}{\omega - \xi_n + i0}. \tag{IV.12}$$

The energy ξ_n in Eq. (IV.12) is defined by

$$\xi_n = E_n - E_{1s}, \tag{IV.13}$$

which is the difference between the true two-particle energy and the energy of the ground state of the one-particle system. Therefore it is only necessary to determine the poles of G^r to determine E_n since the energy E_{1s} is known.

For the advanced part of the Green's function in Eq. (IV.5), a similar procedure can be followed. In this case, however, there is an annihilation operator acting on a one-particle state which gives a zero-particle state, or the vacuum in field theoretical language. The vacuum has zero energy and thus Eq. (IV.5) becomes

$$G^a(\mathbf{x}, t; \mathbf{y}, 0) = -i\langle 1s|\,\psi^+(\mathbf{y})\,|\text{vac}\rangle\langle\text{vac}|\,\psi(\mathbf{x})\,|1s\rangle \exp[-iE_{1s}t]\,\theta(-t) \tag{IV.14}$$

If the Fourier transform of Eq. (IV.14) is taken, the spectral representation of the advanced part of the Green's function is obtained

$$G^a(\mathbf{x}, \omega; \mathbf{y}, 0) = -\frac{u_{1s}(\mathbf{x})u_{1s}^*(\mathbf{y})}{\omega - E_{1s} - i0}, \tag{IV.15}$$

since the inner product in Eq. (IV.14) is just

$$\langle\text{vac}|\,\psi(\mathbf{x})\,|1s\rangle = u_{1s}(\mathbf{x}). \tag{IV.16}$$

The advanced part of the function does not provide any information that is not already known, but it is needed since the equation of motion for the causal Green's function is simpler than for the retarded function alone. It is now necessary to have some method for calculating the Green's function, and in the next section its equations of motion will be discussed.

V. Single-Particle Green's Function Equation of Motion

The traditional method for calculating the Green's function is to express it in terms of the interaction representation. Then Wick's theorem is used to obtain an expansion in terms of linked and unlinked diagrams. Finally the unlinked diagrams are shown to cancel and a linked perturbation expansion is obtained.[14]

An alternative method, which has been shown to be equivalent to the traditional method,[2] is the equation of motion method.[10] The Green's function $G(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2)$ in Eq. (IV.1) can be differentiated with respect to the time to give

$$i\frac{\partial}{\partial t_1} G(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2) = -i\left\langle 1s \left| T\left\{ i\frac{\partial}{\partial t_1}\psi(\mathbf{x}_1, t_1)\psi^+(\mathbf{x}_2, t_2)\right\}\right| 1s\right\rangle + \delta(\mathbf{x}_1 - \mathbf{x}_2)\,\delta(t_1 - t_2), \qquad \text{(V.1)}$$

if use is made of the (anti)commutation relations in Eq. (III.7). The field operator $\psi(\mathbf{x}, t)$ satisfies the Heisenberg equation of motion which gives

$$\begin{aligned} i\frac{\partial}{\partial t}\psi(\mathbf{x}, t) &= [\psi(\mathbf{x}, t), H] \\ &= h(\mathbf{x})\psi(\mathbf{x}, t) + \int d\tau \int d\xi\, \psi^+(\xi, \tau_+)V(\mathbf{x}, \xi)\,\delta(t-\tau)\,\psi(\xi, \tau)\psi(\mathbf{x}, t), \end{aligned} \qquad \text{(V.2)}$$

when use is made of Eqs. (III.6) and (III.7). The time τ_+ is slightly greater than the time τ.

If Eq. (V.2) is substituted into Eq. (V.1) the result is

$$\left\{ i\frac{\partial}{\partial t_1} - h(1)\right\} G(1, 2) = \delta(1, 2) \mp \int d1'\, V(11')G_2(1'1, 21'_+) \qquad \begin{pmatrix}\text{triplet}\\ \text{singlet}\end{pmatrix}, \qquad \text{(V.3)}$$

---

[14] See, e.g., Nozières (1964, Chap. 5).

where

$$(1) = (\mathbf{x}_1, t_1), \qquad (2) = (\mathbf{x}_2, t_2), \qquad \text{etc.},$$

$$\delta(1,2) = \delta(\mathbf{x}_1 - \mathbf{x}_2)\, \delta(t_1 - t_2),$$

and

$$V(1,2) = V(\mathbf{x}_1, \mathbf{x}_2)\, \delta(t_1 - t_2)$$

The coordinate 1_+ means $(\mathbf{x}_1, t_1 + 0)$ where the time $t_1 + 0$ is infinitesimally greater than t_1. Equation (V.3) couples the single-particle Green's function to the two-particle Green's function. The two-particle Green's function is defined as

$$G_2(1234) = -i\langle 1s|\, T\{\psi(1)\psi(2)\psi^+(3)\psi^+(4)\}\, |1s\rangle, \tag{V.4}$$

where the field operators are again in the Heisenberg representation shown in Eq. (IV.2). The time ordering operator T is defined in the same way as it is for Eq. (IV.1) by putting the largest times on the left and the smallest on the right with a plus (minus) sign for an even (odd) permutation of the original order for the triplet state, and pluses for the singlet state.

Equation (V.3) can conveniently be represented by diagrams as shown in Fig. 2. The diagrams in Fig. 2 are in one-to-one correspondence with the mathematical quantities in Eq. (V.3) as shown in Fig. 3. The graphical equation in Fig. 2 has the advantage that it shows the basic structure of the mathematical equation. If Fig. 2 is multiplied through by the arrow, i.e., the differential operator in Eq. (V.3) is inverted, then the equation can easily be interpreted. It says that the propagation of a particle from point 2 to point 1 is equal to free propagation without any interaction, minus (plus) for the triplet (singlet) state an interaction term. The interaction term describes the entrance of two particles into a "black box" where they interact in all possible ways. When they emerge they scatter with each other and one of the particles enters the box while the other propagates freely.

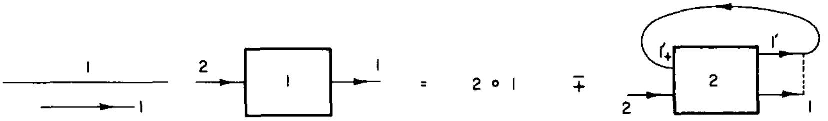

Fig. 2. The equation of motion for the single-particle propagator for the helium atom in graphical form.

In order to solve Eq. (V.3) it is necessary to know the two-particle Green's function or at least to approximate it by a perturbation expansion, which will be done in the next section.

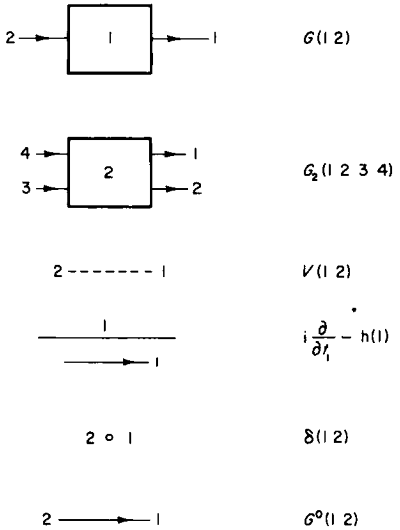

Fig. 3. Correspondence between the diagrams and the mathematical quantities for the single-particle Green's function equation of motion.

VI. Two-Particle Green's Function Equation for the Triplet State

The two-particle Green's function defined in Eq. (V.4) also satisfies an equation of motion. If a perturbation expansion is obtained for it, then it can be substituted into Eq. (V.3) and a perturbation expansion for the single-particle Green's function can be obtained, from which a perturbation expansion for the energy can be obtained by using the Dyson equation (Dyson, 1949). The discussion here will begin generally, but then will be specialized to the triplet state.

If Eq. (V.4) for the two-particle Green's function is differentiated with respect to the time, and Eq. (V.2) is substituted into it, the result is

$$\left\{i\frac{\partial}{\partial t_1} - h(1)\right\}G_2(1234) = i\{\delta(1,4)G(2,3) \mp \delta(1,3)G(2,4)\}$$

$$\mp \int d1'\, V(1,1')G_3(1'\,12;\,341'_+) \qquad \begin{pmatrix}\text{triplet}\\ \text{singlet}\end{pmatrix} \qquad \text{(VI.1)}$$

The three-particle Green's function is defined in a manner similar to the two-particle Green's function in Eq. (V.4) as

$$G_3(123456) = -i\langle 1s|\,T\{\psi(1)\psi(2)\psi(3)\psi^+(4)\psi^+(5)\psi^+(6)\}\,|1s\rangle, \qquad \text{(VI.2)}$$

and is represented by a box with three lines in and three out. Equation (VI.1) can be represented graphically as shown in Fig. 4. The three-particle Green's function is of course unknown, so it is necessary to make some approximation for it. Equation (VI.1) is completely general, but the approximation which will be made now is valid only for the triplet state.[15]

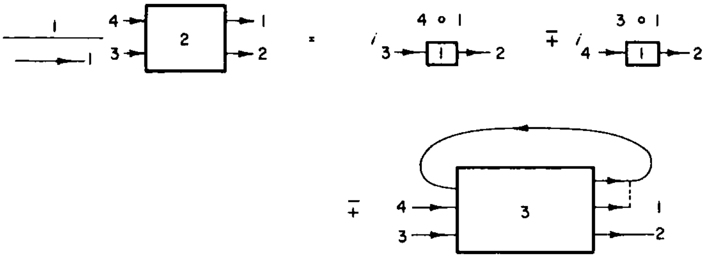

Fig. 4. The graphical equation of motion for the two-particle Green's function.

It will be assumed that for the triplet state the three-particle Green's function can be factored as shown in Fig. 5. One of the particles is assumed to propagate without interaction with the others. Since the single-particle orbitals for the triplet state can be made orthogonal it is not necessary to consider overlap here. There are of course only two particles in the system, but the three-particle Green's function is still needed in order to describe interactions of one particle with, for example, virtual particle-hole pairs.

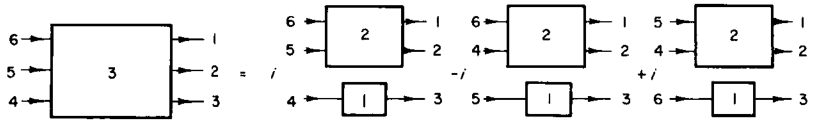

Fig. 5. Factorization of the three-particle Green's function.

If Fig. 5 is substituted into Fig. 4, the result in Fig. 6 is obtained. Figure 6 can be rewritten by using Fig. 2 for the single-particle propagator to give Fig. 7. If the right-hand side of Fig. 7 is neglected, then it is seen that the

---

[15] The reasons for this statement will be clear after reading Sections VIII and XI on the factorization of the two-particle Green's function.

two-particle Green's function can be factored into a product of a one-particle Green's functions, which will be justified further in Section VIII.

The equation in Fig. 7 can be solved approximately to give the expansion shown in Fig. 8. The equation in Fig. 7 has the mathematical form

$$\left\{i\frac{\partial}{\partial t_1} - h(1)\right\}\{G_2(1234) - i[G(14)G(23) - G(13)G(24)]\}$$
$$= -i\iint d1'\,d2'\;V(1'2')G_2(1'2'34)G(21'_+)\,\delta(12'). \qquad \text{(VI.3)}$$

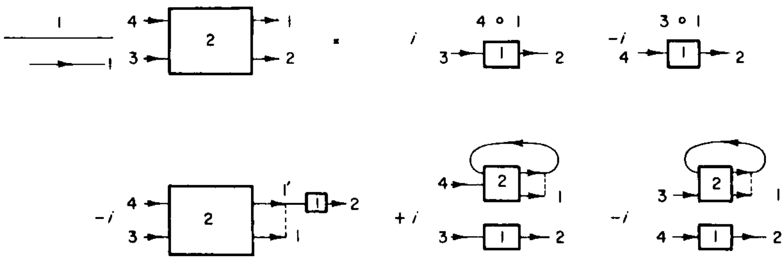

Fig. 6. The approximate graphical equation of motion for the two-particle Green's function.

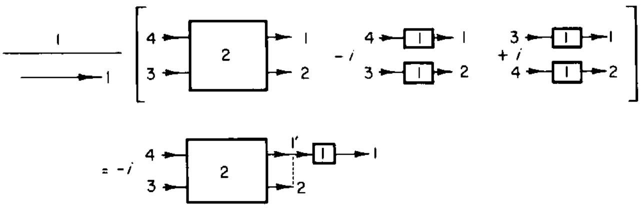

Fig. 7. The approximate graphical equation for the two-particle Green's function after simplification using the equation for the single-particle propagator.

The expansion in Fig. 8 is obtained by factorizing the two-particle Green's function on the right-hand side of Eq. (VI.3) and inverting the differential operator

$$G_2(1234) = iG(14)G(23) - iG(13)G(24)$$
$$- \iint d1'\,d2'\;G(21'_+)G^0(12')V(1'2')G(2'4)G(1'3)$$
$$+ \iint d1'\,d2'\;G(21'_+)G^0(12')V(1'2')G(2'3)G(1'4) + \cdots. \qquad \text{(VI.4)}$$

The function $G^0(12)$ in Eq. (VI.4) is the function $G(12)$ in Eq. (V.3) or Fig. 2 in the absence of interaction. The perturbation expansion in Eq. (VI.4) or Fig. 8 can be substituted into Eq. (V.3) or Fig. 2 for the single-particle Green's function to obtain an equation involving only the single-particle Green's function and the interaction, which can in principle be solved.

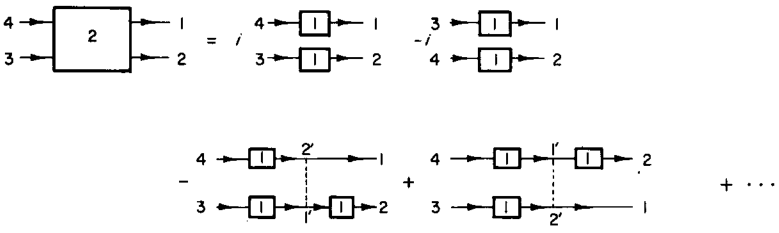

Fig. 8. The perturbation expansion for the two-particle Green's function.

VII. The Approximate Equation for the One-Particle Green's Function for the Triplet State

A perturbation expansion of the single-particle Green's function can be obtained by substituting Fig. 8 into Fig. 2, which gives the graphical equation shown in Fig. 9. The corresponding equation can be obtained by substituting Eq. (VI.4) into Eq. (V.3) which gives

$$
\begin{aligned}
\left\{i\frac{\partial}{\partial t_1} - h(1)\right\}G(1,2) &= \delta(1,2) \\
&+ \Big\{-i\int d1'\; G(1'1'_+)V(11')G(12) \\
&+ i\int d1'\; G(11'_+)V(11')G(1'2) \\
&+ \iiint d1'\,d2'\,d3'\;\; G(11'_+)V(13')G^0(3'2')G(2'3'_+)V(1'2')G(1'2) \\
&- \iiint d1'\,d2'\,d3'\; G(11'_+)V(13')G^0(3'2')G(1'3'_+)\; V(1'2')G(2'2) \\
&+ \cdots\Big\}\theta(t_1 - t_2). \qquad \text{(VII.1)}
\end{aligned}
$$

because the interaction term in Eq. (V.3) vanishes if $t < 0$, the restriction that $t_1 > t_2$ must be imposed on the interaction terms on the right-hand side of Eq. (VII.1). Equation (VII.1) is a complicated nonlinear equation which should be solved for the Green's function in a self-consistent way. It is however too complicated to solve in practice. Only the first-order terms will be considered here, and the higher-order terms can be treated by perturbation theory.

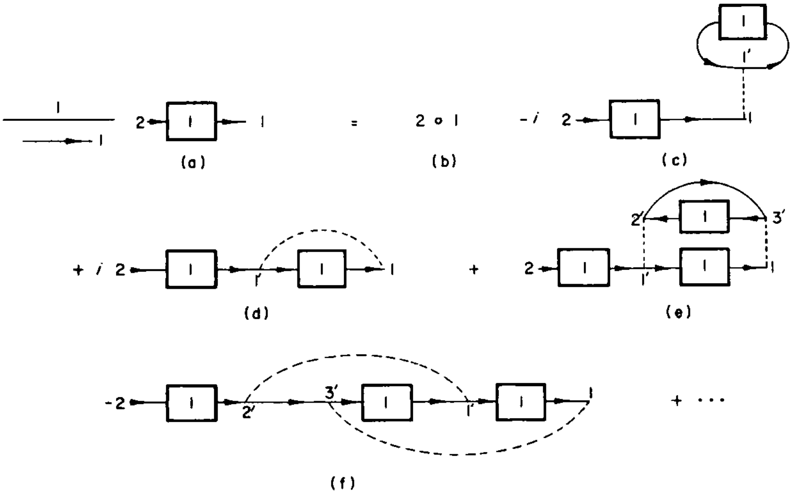

Fig. 9. The perturbation expansion for the single-particle propagator.

Equation (VII.1) has the general form given by the Dyson equation (Dyson, 1949)

$$\left\{ i\frac{\partial}{\partial t_1} - h(1) \right\} G(1, 2) = \delta(1, 2) + \int d1'\, M(11')G(1'2), \qquad \text{(VII.2)}$$

where $M(1, 2)$ is the mass operator or the self-energy function. Equation (VII.2) is shown graphically in Fig. 10 where the self-energy is represented

Fig. 10. The Dyson equation in graphical form.

by a circle. By equating Eq. (VII.2) with Eq. (VII.1) a perturbation expansion for the mass operator M can be obtained. The energies ξ_n can be obtained by substituting the spectral representation of $G(1, 2)$ in Eqs.

(IV.12) and (IV.15) into Eq. (VII.2) and solving the resulting equation. The best method to solve the equation is to take matrix elements with respect to the single-particle states and solve the resulting matrix equation. In this way the self-consistent field problem can be joined smoothly onto a perturbation treatment.

The perturbation problem will not be considered here however, but only the lowest order self-consistent field problem which can be used as a starting point for the perturbation treatment. If the second-order terms in Eq. (VII.1) are neglected, the equation can be written in a much simpler form as

$$\left\{i\frac{\partial}{\partial t_1} - H_{\mathrm{eff}}(1)\right\}G^r(1, 2) - \left\{i\frac{\partial}{\partial t_1} - h(1)\right\}G^a(12) = \delta(12). \qquad \text{(VII.3)}$$

The effective Hamiltonian $H_{\mathrm{eff}}(1)$ is defined as

$$H_{\mathrm{eff}}(1) = h(1) - i\int d1'\ V(11')G(1'1'_+) + i\int d1'\ V(11')G(11'_+)P(11'), \qquad \text{(VII.4)}$$

where the operator $P(11')$ exchanges the coordinates 1 and 1′. If Eq. (IV.15) is substituted into Eq. (VII.4) the effective Hamiltonian becomes

$$H_{\mathrm{eff}}(\mathbf{x}) = h(\mathbf{x}) + \int d\mathbf{z}\ V(\mathbf{x}, \mathbf{z})[1 - P(\mathbf{x}, \mathbf{z}')]\rho(\mathbf{z}', \mathbf{z}), \qquad \text{(VII.5)}$$

where the one-particle density matrix $\rho(\mathbf{x}, \mathbf{y})$ is defined as

$$\rho(\mathbf{x}, \mathbf{y}) = u_{1s}^*(\mathbf{x})u_{1s}(\mathbf{y}) \qquad \text{(VII.6)}$$

and the operator $P(\mathbf{x}, \mathbf{z}')$ interchanges $\mathbf{x}$ with $\mathbf{z}'$ and the primes are removed before integration.

If the spectral resolution of the Green's function in Eq. (IV.12) is substituted into Eq. (VII.3), it can be seen that the equation is satisfied if the functions $f_n(\mathbf{x})$ are eigenfunctions of the effective Hamiltonian with the eigenvalue ξ_n,

$$H_{\mathrm{eff}}(\mathbf{x})f_n(\mathbf{x}) = \xi_n f_n(\mathbf{x}). \qquad \text{(VII.7)}$$

Since the function $u_{1s}(\mathbf{x})$ is an eigenfunction of $h(\mathbf{x})$ with eigenvalue E_{1s} the advanced part of the Green's function merely enables the anticommutation relations in Eq. (III.7) to be used. The connection between Eq. (VII.7) and the Hartree–Fock equations will be discussed in Section IX, but first the factorization of the Green's function will be justified.

VIII. Factorization of the Two-Particle Green's Function

In Section VI, it was assumed that the factorization of the three-particle Green's function was valid for the triplet state. The approximation used at the end of the last section was the same as assuming the two-particle Green's function could be factorized. In the many-body problem the factorization is made on the physical grounds of neglecting correlation between one particle and the others, and is ultimately justified by the results. In the helium problem, the two-particle Green's function has a simpler form than usual, and the factorization assumption can be examined in more detail.

The two-particle Green's function in Eq. (V.3) can be written as

$$\mp iG_2(\mathbf{z}, t; \mathbf{x}, t; \mathbf{y}, 0; \mathbf{z}, t_+)$$

$$= \langle 1s|\, \psi^+(\mathbf{z}, t_+)\psi(\mathbf{z}, t)\psi(\mathbf{x}, t)\psi^+(\mathbf{y}, 0)\,|1s\rangle\theta(t). \quad \text{(VIII.1)}$$

If the time is negative there would be two annihilation operators acting on a one particle state, which would of course give zero. If the complete set of two-particle states in Eq. (IV.7) is inserted into Eq. (VIII.1), and the vacuum state is also inserted, the equation becomes

$$\mp iG_2 = \sum_n \langle 1s|\, \psi^+(\mathbf{z}, t_+)\,|\text{vac}\rangle\langle\text{vac}|\, \psi(\mathbf{z})\psi(\mathbf{x})\,|\Psi_n\rangle$$

$$\cdot \langle\Psi_n|\, e^{-iHt}\psi^+(\mathbf{y})\,|1s\rangle\theta(t) \quad \text{(VIII.2)}$$

By using Eqs. (III.7), (III.8), and (IV.16), Eq. (VIII.2) can be simplified to give

$$\mp iG_2 = \sum_n u_{1s}^*(\mathbf{z})e^{iE_{1s}t}\sqrt{2}\,\Psi_n(\mathbf{x}, \mathbf{z})\langle\Psi_n|\, e^{-iHt}\psi^+(\mathbf{y})\,|1s\rangle\theta(t). \quad \text{(VIII.3)}$$

Eq. (VIII.3) is completely general and exact, but some approximations will now be made.

In order to factor the Green's function it is necessary to express the two-particle wave function as a product of single-particle functions

$$\Psi_n(\mathbf{x}, \mathbf{z}) = 2^{-1/2}[v_n(\mathbf{x})u_{1s}(\mathbf{z}) - u_{1s}(\mathbf{x})v_n(\mathbf{z})], \quad \text{(VIII.4)}$$

or in second quantization

$$|\Psi_n\rangle = \int d\xi\, v_n(\xi)\psi^+(\xi)\,|1s\rangle \quad \text{(VIII.5)}$$

for the triplet state. For the singlet state, the ground state must be given special treatment, and this will be done in Section XI. The set of functions $\{v_n\}$ is assumed to be a complete orthonormal set. If Eqs. (VIII.4) and (VIII.5) are substituted into Eq. (VIII.3) the result is

$$\begin{aligned} -iG_2 &= u_{1s}^*(\mathbf{z})u_{1s}(\mathbf{z})\langle 1s|\,\psi(\mathbf{x}, t)\psi^+(\mathbf{y}, 0)\,|1s\rangle\theta(t) \\ &\quad - u_{1s}^*(\mathbf{z})u_{1s}(\mathbf{x})\langle 1s|\,\psi(\mathbf{z}, t)\psi^+(\mathbf{y}, 0)\,|1s\rangle\theta(t). \end{aligned} \qquad \text{(VIII.6)}$$

Equation (VIII.6) can be rewritten in more conventional form by using Eq. (IV.14) and gives

$$\begin{aligned} &G_2(\mathbf{z}, t; \mathbf{x}, t; \mathbf{y}, 0; \mathbf{z}, t_+) \\ &\quad = iG(\mathbf{z}, t; \mathbf{z}, t_+)G^r(\mathbf{x}, t; \mathbf{y}, 0) - iG(\mathbf{x}, t; \mathbf{z}, t_+)G^r(\mathbf{z}, t; \mathbf{y}, 0), \end{aligned} \qquad \text{(VIII.7)}$$

which is the usual factorization of the Green's function shown in the zeroth order part of Fig. 8.

The treatment here shows that the use of the antisymmetrized product wave function for the two-particle wave functions is equivalent to the factorization procedure. It is essential that the functions in Eq. (VIII.4) are orthonormal, but of course they are only approximately complete. Since the Hamiltonian does not act on the states it is not necessary that they be even approximate eigenstates to the Hamiltonian. Only the orthonormality and approximate completeness were used. Thus the functions $\{v_n\}$ can be hydrogenic functions or functions including interelectronic interaction. The modifications required for the singlet state will be discussed in Section XI.

IX. Comparison with Hartree-Fock Theory

In Hartree–Fock (HF) theory, the wave function for the triplet state of the helium atom is assumed to be of the form

$$\Psi(\mathbf{x}, \mathbf{y}) = 2^{-1/2}[u(\mathbf{x})v(\mathbf{y}) - v(\mathbf{x})u(\mathbf{y})]. \qquad \text{(IX.1)}$$

The expectation value of the Hamiltonian is calculated using the above wave function, and then is minimized to obtain equations for the functions u and v. In this way a set of two coupled nonlinear integro-differential equations is obtained, which have been studied by a number of investigators.[16]

If the u function in Eq. (IX.1) is chosen to be a hydrogenic $1s$ function,

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[16] See, e.g., Bethe and Salpeter (1957, p. 140).

and the v chosen to be orthogonal to it, the function $f(\mathbf{x})$ in Eq. (IV.10) is equal to v. The effective Hamiltonian in Eq. (VII.5) is just the HF Hamiltonian with one of the electrons fixed in the $1s$ hydrogenic orbital. The eigenvalue problem in Eq. (VII.7) would be obtained by just varying the v in Eq. (IX.1) and keeping the u fixed in a hydrogenic $1s$ state.

The energy obtained by this method is of course not as low as that obtained by varying both u and v. However, in this approach only a single linear integro-differential equation is obtained instead of two coupled nonlinear ones, so the calculations are much simpler. The functions obtained from this approach can then be used as a basis for a perturbation calculation of the other terms in Eq. (VII.1).

The Green's function describes the addition of a second electron to a system with one electron present in a hydrogenic $1s$ orbital. In the language of field theory the electron in the hydrogenic ground state is a "bare" electron. The added electron would also go into a hydrogenic orbital if there were no interaction with the other electron, and would also be "bare." However, due to the interelectronic interaction the added electron is "dressed," i.e., its wave function and energy are modified from the hydrogenic ones. In this model the original electron remains bare and the second electron is dressed. The dressed electron can be called a "quasi-particle" or an "elementary excitation" in the language of many-body theory, since all the excited states of the system are described by exciting it. The second electron can be further dressed by calculating the higher-order diagrams for the single-particle propagator. For example the term (e) in Fig. 9 describes the interaction of the electron with a virtual particle-hole pair, which goes beyond HF theory. However, the phrase "quasi-particle model" (QPM) will be used here to describe the dressing of the second electron by interaction with the charge density of the first electron only, as shown in Fig. 9 (c) and (d).

In HF theory both the electrons are dressed to a certain extent by the interelectronic interaction, and thus both are quasi-particles. The HF orbitals can be used as the basis for a perturbation expansion, but the calculations would be much more complicated. The HF theory is better than the simple QPM described above, but the extent to which it is better will be investigated in the next section.

X. Triplet State Energies

In this section the equation for the QPM given in Eq. (VII.7) will be solved by the $1/Z$ expansion method (Linderberg, 1961) for the $1s\,ns\;{}^3S$

states. For these states Eq. (VII.7) can be written as (Sharma and Coulson, 1962)

$$Lv + (1/Z)v\,|\,uu\rangle - (1/Z)u\,|\,uv\rangle = \xi v, \tag{X.1}$$

where the function u denotes the hydrogenic $1s$ state, and the operator L is defined as

$$L = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} - \frac{1}{r}. \tag{X.2}$$

The ket $|uv\rangle$ is defined as

$$|uv\rangle = r^{-1}\int_0^r u(s)v(s)s^2\,ds + \int_r^\infty u(s)v(s)s\,ds. \tag{X.3}$$

In Eq. (X.1) reduced and modified Hartree atomic units are used, i.e., the unit of length is Z^{-1} a.u. and the unit of energy is Z^2 a.u. The orthonormality conditions are

$$\langle u\,|\,u\rangle = 1, \qquad \langle u\,|\,v\rangle = 0, \qquad \langle v\,|\,v\rangle = 1. \tag{X.4}$$

In the following, it will be convenient to use the notations below, which are the same as Sharma and Coulson (1962). The inner products are defined as

$$\langle u\,|\,v\rangle = \int_0^\infty u(s)v(s)s^2\,ds \tag{X.5}$$

and

$$\langle uv\,|\,pq\rangle = \int_0^\infty u(r)v(r)\,|pq\rangle r^2\,dr. \tag{X.6}$$

The matrix element of an arbitrary operator A is

$$\langle u\,|\,A\,|\,v\rangle = \int_0^\infty u(s)Av(s)s^2\,ds. \tag{X.7}$$

In Eq. (X.1) the function u is understood to be the hydrogenic $1s$ function given by

$$u(r) = 2e^{-r}, \tag{X.8}$$

which has an energy eigenvalue $-\frac{1}{2}$ when L in Eq. (X.2) acts on it.

Equation (X.1) can be solved by the $1/Z$ expansion method used by

Linderberg (1961) and Sharma and Coulson (1962). The eigenfunction v and eigenvalue ξ are both expanded in powers of $1/Z$

$$v = \sum_{n=0}^{\infty} v_n Z^{-n} \tag{X.9}$$

and

$$\xi = \sum_{n=0}^{\infty} \xi_n Z^{-n}. \tag{X.10}$$

When these expansions are substituted into Eq. (X.1) and the resulting perturbation equations solved for the energy, the result for the zeroth-order term in the energy expansion is

$$\xi_0 = v_0^{-1} L v_0. \tag{X.11}$$

The first-order term is given by

$$\xi_1 = \langle v_0 v_0 \,|\, uu \rangle - \langle v_0 u \,|\, u v_0 \rangle, \tag{X.12}$$

while the second-order term is

$$\xi_2 = \langle v_0 v_1 \,|\, uu \rangle - \langle v_0 u \,|\, u v_1 \rangle. \tag{X.13}$$

The third-order term is

$$\xi_3 = \langle v_1 v_1 \,|\, uu \rangle - \langle v_1 u \,|\, u v_1 \rangle - \xi_1 \langle v_1 \,|\, v_1 \rangle, \tag{X.14}$$

while the fourth-order term would of course involve v_2 which would be more difficult to compute.

For the $1s\,2s\ {}^3S$ state Sharma and Coulson (1962) used an expansion in terms of first-order Laguerre polynomials first used by Linderberg (1961) to solve the HF equations to third order. The corresponding energy coefficients for the QPM were calculated from Eqs. (X.11)–(X.14), using the matrix elements of Sharma and Coulson (1962). Table I gives the coefficients in the expansion of the total energy calculated by the QPM, the HF equations, and the exact ones (Sharma and Coulson, 1962).

In the QPM the total energy is just the sum of the quasi-particle energy ξ and the hydrogenic $1s$ state energy $E_{1s} = -\frac{1}{2}$. However, in HF theory the total energy must be calculated from the orbital energies, and is not just their sum. Thus the QPM is simpler than the HF theory in the calculation of the total energy.

Table I shows that the coefficient of Z^{-3} for the QPM is actually closer to the exact coefficient than the HF coefficient. The coefficient of Z^{-2}

is of course larger for the QPM. In order to see how much difference there is between the QPM and the HF theory, the actual energies were calculated for different values of Z, and are listed in Table II.

TABLE I

COEFFICIENTS IN THE $1/Z$ EXPANSION OF THE ENERGY OF THE $1s\,2s\;{}^3S$ STATE[a]

Method	Z^0	Z^{-1}	Z^{-2}	Z^{-3}
Quasi-particle	−5/8	137/729	−0.045231	−0.007300
Hartree–Fock[b]	−5/8	137/729	−0.045278	−0.007619
Exact[b]	−5/8	137/729	−0.047330	−0.005040

[a] All energies in H_{RM}.
[b] See Sharma and Coulson (1962).

TABLE II

ENERGIES OF THE HELIUM ISOELECTRONIC SERIES[a]
FOR THE $1s\,2s\;{}^3S$ STATE[b]

Z	Quasi-particle	Hartree–Fock[c]	Exact[c]
1[d]	−0.489602	−0.489968	−0.489441
2	−1.797167	−1.797373	−1.798136
3	−5.108878	−5.109032	−5.110224
4	−9.295342	−9.295468	−9.296876
5	−14.732048	−14.732159	−14.733767
6	−21.418876	−21.418976	−21.420598
7	−29.355774	−29.355866	−29.357550
8	−38.542715	−38.542802	−38.544531
9	−48.979685	−48.979767	−48.981533
10	−60.666675	−60.666754	−60.668548

[a] Energies are in H_R.
[b] Calculated from the $1/Z$ expansion given in Table I.
[c] See Sharma and Coulson (1962).
[d] The "exact" energy is higher which indicates that the expansion is poorly convergent for $Z = 1$.

XI. Factorization of the Two-Particle Green's Function for the Singlet State

The singlet state must be treated more carefully since the Green's function cannot be factorized as simply as in the triplet state. The singlet state behaves as if the particles were bosons, and it is well known in the theory of boson systems that the ground state must be given special treatment (see, e.g., Belyaev, 1958). In this section it will be shown why the ground state must be given special treatment for the singlet state of helium and some insight will be obtained into boson systems in general.

The two-particle Green's function that enters the equation for the single-particle propagator for the singlet state is also given by Eq. (VIII.1), since the equation of motion in Eq. (V.3) is valid for both the singlet and triplet states. The two-particle Green's function can also be reduced to the form of Eq. (VIII.3), since no approximations have been made up to that point. However, when an approximation is used for the complete orthonormal set of functions $\{\Psi_n\}$ it is necessary to use for the excited states

$$\Psi_n(\mathbf{x}, \mathbf{z}) = 2^{-1/2}[u_{1s}(\mathbf{x})u_n(\mathbf{z}) + u_n(\mathbf{x})u_{1s}(\mathbf{z})] \qquad \text{(XI.1)}$$

where the u_n are hydrogenic orbitals that are orthogonal to u_{1s} for $n \neq 1s$. However, for the ground state the function

$$\Psi_0(\mathbf{x}, \mathbf{z}) = u_{1s}(\mathbf{x})u_{1s}(\mathbf{z}) \qquad \text{(XI.2)}$$

must be used if Ψ_0 is to be normalized. Since these functions occur in an intermediate step of the calculation it is not necessary to use the best single-particle orbitals for u_n but hydrogenic orbitals are sufficient and have the necessary orthonormality properties.

In second quantization the state vector corresponding to Eq. (XI.1) is given by Eq. (VIII.5). On the other hand the state vector corresponding to the ground state in Eq. (XI.2) is given by

$$|\Psi_0\rangle = 2^{-1/2} \int d\xi \, u_{1s}(\xi)\psi^+(\xi)\,|1s\rangle \qquad \text{(XI.3)}$$

because there are two particles in the same state.

If Eqs. (XI.1)–(XI.3) are substituted into Eq. (VIII.3) and the completeness of the set $\{u_n\}$ is used, the result is

$$\begin{aligned} iG_2 = {} & u_{1s}^*(\mathbf{z})u_{1s}(\mathbf{z})\langle 1s|\,\psi(\mathbf{x}, t)\psi^+(\mathbf{y}, 0)\,|1s\rangle\theta(t) \\ & + u_{1s}^*(\mathbf{z})u_{1s}(\mathbf{x})\langle 1s|\,\psi(\mathbf{z}, t)\psi^+(\mathbf{y}, 0)\,|1s\rangle\theta(t) \\ & - u_{1s}^*(\mathbf{z})u_{1s}(\mathbf{z})u_{1s}(\mathbf{x}) \int d\xi \, u_{1s}^*(\xi)\langle 1s|\,\psi(\xi, t)\psi^+(\mathbf{y}, 0)\,|1s\rangle\theta(t), \end{aligned} \qquad \text{(XI.4)}$$

where the last term arises from the different form of the ground state. Therefore the two-particle Green's function can be factorized as

$$\begin{aligned} G_2(\mathbf{z}, t; \mathbf{x}, t; \mathbf{y}, 0; \mathbf{z}, t_+) = {} & \Big[1 + P(\mathbf{z}', \mathbf{x}) \\ & - u_{1s}(\mathbf{x}) \int d\xi \, u_{1s}^*(\xi)P(\xi, \mathbf{x})\Big] iG(\mathbf{z}', t; \mathbf{z}, t_+)G^r(\mathbf{x}, t; \mathbf{y}, 0), \end{aligned} \qquad \text{(XI.5)}$$

where the prime on the $\mathbf{z}$ is removed before the integration is performed. Equation (XI.5) gives the modification of the factorization method that is necessary to deal with the peculiarities of the ground state for boson systems.

In order to represent Eq. (XI.5) in a way that is more familiar for large boson systems, the last term can be rewritten making use of the pair propagator

$$G_{02}(1,2) \equiv -i\langle\Psi_0|\,\psi^+(2)\psi^+(1)\,|\text{vac}\rangle\theta(t_1 - t_2) \qquad \text{(XI.6)}$$

and its complex conjugate

$$G_{20}(12) = G^*_{02}(12), \qquad \text{(XI.7)}$$

where Ψ_0 is the true two-particle ground state. Then Eq. (XI.5) can be written approximately as

$$\begin{aligned} &G_2(\mathbf{z}, t; \mathbf{x}, t; \mathbf{y}, 0; \mathbf{z}, t_+) \\ &\quad = iG(\mathbf{z}, t; \mathbf{z}, t_+)G^r(\mathbf{x}, t; \mathbf{y}, 0) + iG(\mathbf{x}, t; \mathbf{z}, t_+)G^r(\mathbf{z}, t; \mathbf{y}, 0) \\ &\quad -\tfrac{1}{2}G(\mathbf{z}, t; \mathbf{z}, t_+)\int d\xi\, G_{20}(\mathbf{x}, t_+; \xi, t)G_{02}(\xi, t; \mathbf{y}, 0) \\ &\quad -\tfrac{1}{2}G(\mathbf{x}, t; \mathbf{z}, t_+)\int d\xi\, G_{20}(\mathbf{z}, t_+; \xi, t)G_{02}(\xi, t; \mathbf{y}, 0). \qquad \text{(XI.8)} \end{aligned}$$

Equation (XI.8) can be represented graphically as shown in Fig. 11, which explicitly shows the last terms in Eq. (XI.8) which are needed for boson systems.

XII. The Approximate Equation for the Single-Particle Propagator for the Singlet State

In this section, the approximate equation of motion for the single-particle Green's function will be obtained by substituting Eq. (XI.5) into Eq. (V.3). Graphically this is the same as substituting Fig. 11 into Fig. 2 which gives Fig. 12. Figure 12 resembles the equation for large boson systems since the pair propagators enter the equation (see, e.g., Hugenholtz and Pines, 1959). However, for large boson systems it is necessary to have another equation for the pair propagator. Here Eq. (XI.5) can be used and an equation can be obtained involving only the single-particle

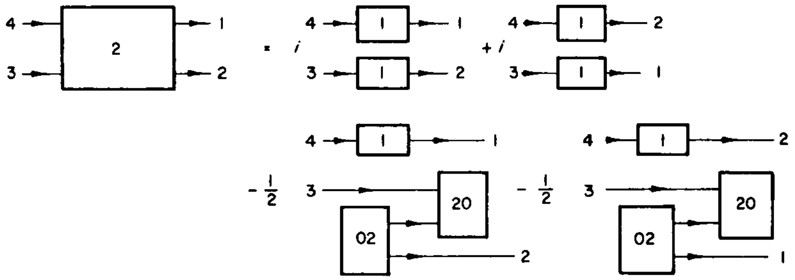

Fig. 11. Factorization of the two-particle Green's function for the singlet state.

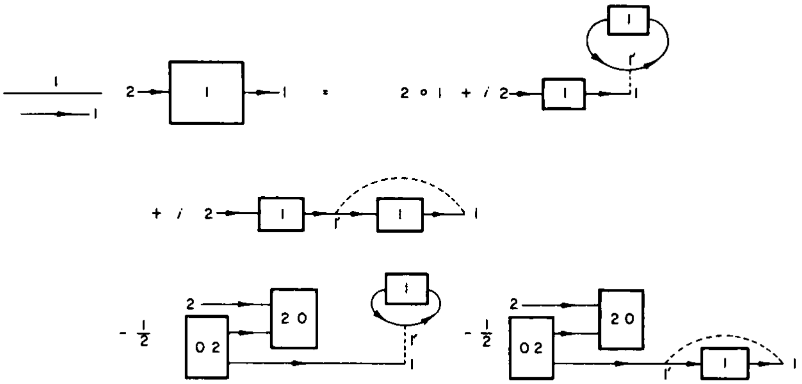

Fig. 12. The equation of motion for the single-particle propagator for the singlet state in graphical form.

propagators. When Eq. (XI.5) is substituted into Eq. (V.3) and the result simplified, an equation similar to Eq. (VII.3) is obtained:

$$\left\{i\frac{\partial}{\partial t_1} - H_{\text{eff}}(1)\right\}G^r(12) + \left\{i\frac{\partial}{\partial t_1} - h(1)\right\}G^a(12) = \delta(12). \tag{XII.1}$$

However, now the effective Hamiltonian is given by

$$H'_{\text{eff}}(\mathbf{x}) = h(\mathbf{x}) + \int d\mathbf{z}\, V(\mathbf{x}, \mathbf{z})\Big[1 + P(\mathbf{x}, \mathbf{z}') - u_{1s}(\mathbf{x})\int d\xi\, u^*_{1s}(\xi)P(\xi, \mathbf{x})\Big]\,\rho(\mathbf{z}, \mathbf{z}'). \tag{XII.2}$$

Therefore Eq. (XII.1) can be seen from Eqs. (III.7), (IV.8), and (IV.14) to be satisfied if

$$H'_{\text{eff}}(\mathbf{x})f_n(\mathbf{x}) = \xi_n f_n(\mathbf{x}). \tag{XII.3}$$

If $\Psi_n(\mathbf{x}, \mathbf{z})$ is expressed as a linear combination

$$\Psi_n(\mathbf{x}, \mathbf{z}) = 2^{-1/2}[u_{1s}(\mathbf{x})v_n(\mathbf{z}) + v_n(\mathbf{x})u_{1s}(\mathbf{z})], \qquad \text{(XII.4)}$$

where v_n is an orbital to be determined and the expression is substituted into Eq. (IV.10), the result for the function $f_n(\mathbf{x})$ is

$$f_n(\mathbf{x}) = v_n(\mathbf{x}) + u_{1s}(\mathbf{x})\langle 1s \mid v_n\rangle \qquad \text{(XII.5)}$$

When Eq. (XII.5) is substituted into Eq. (XII.3) an equation is obtained for the single-particle orbital v_n :

$$H_{\text{eff}}(\mathbf{x})v_n(\mathbf{x}) = \xi_n v_n(\mathbf{x}) + \langle 1s \mid v_n\rangle(\xi_n - E_{1s})u_{1s}(\mathbf{x}). \qquad \text{(XII.6)}$$

The effective Hamiltonian here is given by

$$H_{\text{eff}}(\mathbf{x}) = h(\mathbf{x}) + \int d\mathbf{z}\, V(\mathbf{x}, \mathbf{z})[1 + P(\mathbf{x}, \mathbf{z}')]\rho(\mathbf{z}, \mathbf{z}'), \qquad \text{(XII.7)}$$

and differs from Eq. (VII.5) only in that the exchange term has a positive sign. Equation (XII.6) is the same as would be obtained by using the extended HF scheme to calculate the orbitals if one of the electrons were fixed in a hydrogenic $1s$ orbital (Sharma and Coulson, 1962).

XIII. Singlet State Energies

Equation (XII.6) of the last section is the same as given by the extended Hartree–Fock scheme for singlet states, except that one of the electrons is fixed in a hydrogenic $1s$ orbital. If u denotes the hydrogenic $1s$ orbital, Eq. (XII.6) can be written as

$$Lv + (1/Z)v\,|uu\rangle + (1/Z)u\,|uv\rangle = \xi v + (\xi - E_{1s})\langle u\,|v\rangle u \qquad \text{(XIII.1)}$$

for $1s\ ns\ {}^1S$ states. The quantities in Eq. (XIII.1) are defined in Section X.

Equation (XIII.1) can now be solved by the $1/Z$ expansion method to obtain the coefficients for the expansion of the total energy. Sharma and Coulson (1962) have investigated the extended HF equations for the $1s\ 2s\ {}^1S$ state and their matrix elements were used to calculate the coefficients for the quasi-particle model. The coefficients in the $1/Z$ expansion of the total energy for the $1s\ 2s\ {}^1S$ state are shown in Table III. It can be seen that the QPM is not as good for the excited singlet state as it was for the excited triplet state. Nevertheless it might be a good starting point for a treatment of the higher-order terms in perturbation theory. The more highly excited states would be expected to be described better than the low lying states.

TABLE III

COEFFICIENTS IN THE $1/Z$ EXPANSION OF THE $1s\ 2s\ ^1S$ STATE[a]

Method	Z^0	Z^{-1}	Z^{-2}	Z^{-3}
Quasi-particle	$-5/8$	169/729	-0.101509	-0.020854
Hartree–Fock[b]	$-5/8$	169/729	-0.103634	-0.014683
Exact[b]	$-5/8$	169/729	-0.112990	-0.004094

[a] All energies in H_{RM}.
[b] See Sharma and Coulson (1962).

The ground state of the helium isoelectronic series was calculated by Linderberg (1961) using the usual product function

$$\Psi_0(\mathrm{x}, \mathrm{y}) = \mathrm{U}(\mathrm{x})\mathrm{U}(\mathrm{y}) \tag{XIII.2}$$

and solving the resulting HF equation, which is nonlinear, by the $1/Z$ expansion method. If the QP idea is used, the ground state is given by

$$\Psi_0(\mathrm{x}, \mathrm{y}) = 2^{-1/2}[u_{1s}(\mathrm{x})v(\mathrm{y}) + v(\mathrm{x})u_{1s}(\mathrm{y})], \tag{XIII.3}$$

which also has only one unknown function v. The function v satisfies Eq. (XIII.1) which is a linear equation. Table IV shows a comparison of Linderberg's coefficients in a $1/Z$ expansion of the total ground state energy with the coefficients obtained by the QPM. It can be seen that they are identical up to Z^{-2}. The exact expansion (Scherr and Knight, 1963) has a smaller coefficient of Z^{-2} but larger coefficient of Z^{-3}.

TABLE IV

COEFFICIENTS IN THE $1/Z$ EXPANSION OF THE GROUND STATE ENERGY[a]

Method	Z^0	Z^{-1}	Z^{-2}	Z^{-3}
Quasi-particle	-1	5/8	-0.11100317	<-0.00105525
Hartree–Fock[b]	-1	5/8	-0.11100317	-0.00105525
Exact[c]	-1	5/8	-0.157666405	$+0.008698991$

[a] All energies in H_{RM}.
[b] See Linderberg (1961).
[c] Scherr and Knight (1963).

The expression obtained by Linderberg for the coefficient of Z^{-3} in the total energy is

$$E_3 = 4\langle uv_1 \,|\, uv_1\rangle + 2\langle uu \,|\, v_1v_1\rangle - 2\langle uu \,|\, uu\rangle\langle v_1 \,|\, v_1\rangle. \tag{XIII.4}$$

In the QPM the same coefficient is given by

$$\xi_3 = 2\langle uv_1 \,|\, uv_1\rangle + 2\langle uu \,|\, v_1 v_1\rangle - 2\langle uu \,|\, uu\rangle\langle v_1 \,|\, v_1\rangle. \qquad \text{(XIII.5)}$$

Therefore the energy E_3 is larger by a term $2\langle uv_1 \,|\, uv_1\rangle$ which is positive. Thus the QPM gives a more negative coefficient of Z^{-3} and thus better agreement with the true energy. This result is not surprising since the split shell calculation using hydrogenic-like is orbitals gives effective charges of about 2.18 and 1.18 (Shull and Löwdin, 1956). Therefore, keeping one of the electrons in a hydrogenic 1*s* orbital with charge 2 and allowing the other to be dressed is not a bad approximation.

XIV. Conclusion

The purpose of this paper has been to apply the method of Green's functions used in the many-body problem to simple atomic systems so that a comparison could be made with the usual configuration space approach. The application of the Green's function method to the hydrogen atom was trivial, but served to illustrate the method used. The application to the helium atom gave some general insights into the advantages and disadvantages of the Green's function method applied to small systems.

The quasi-particle model arose naturally from the Green's function method, and corresponds to keeping one of the electrons fixed in the hydrogenic ground state while the other one is dressed. This model could perhaps be applied more naturally to the alkali metals where the core would be fixed and only the outer valence electron would be dressed.[17] The dressing was done only in first order, which corresponded to minimizing the energy with respect to only one orbital. However, by calculating the higher-order terms in the perturbation expansion the dressing could take into account the interaction of the electron with, for example, a virtual particle-hole pair. In this sense, it would be possible to go beyond HF theory, but it must be remembered that one of the electrons is always kept in the hydrogenic 1*s* state.

The usual technique of factorizing the two-particle Green's function could be used in the triplet state in which the spatial part of the electron wave function is that for two spinless fermions. Thus, the many-body methods used in fermi systems were directly applicable in this case. It was shown that the factorization of the two-particle Green's function corresponded to expressing the two-particle wave functions as antisymmetrized

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[17] Öhrn and McWeeny (1966). L. Hedin (private communication) is applying these methods to alkali metal atoms.

products of orbitals, which clarifies the relation between the approximations made in the Green's function method and the configuration space approach.

The singlet state of helium behaves as a pair of bosons, and it is well known that the ground state of large boson systems gives difficulties, since it must be a vacuum for the annihilation operators if Wick's theorem is to be used (see, e.g., Belyaev, 1958). In the usual treatment of boson systems, the ground state is separated out at the beginning and then Wick's theorem can be used to obtain a perturbation expansion. In this paper, on the other hand, the equation of motion method was used. The special treatment of the ground state arose in the factorization of the two-particle Green's function due to the different type of normalization that was necessary. Thus the equation of motion method is also valid for boson systems, and the perturbation expansions obtained must allow for the different normalization of the ground state. This method could also be applied to large boson systems.

The approach investigated here gives a method of uniting self-consistent theories with perturbation expansions in one formalism. In order to obtain part of the correlation energy it would be necessary to calculate the second-order terms in the perturbation expansion which would require solving the quasi-particle model equations for all the excited states. This procedure would be much simpler than, for example, solving the HF equations for all the excited states and then basing perturbation theory on these functions and energies (Kelly, 1964).

Other types of Green's functions, as for example the density-density fluctuation propagator, could be investigated to see if other lines of attack might be possible within the Green's function framework. On the other hand, the configuration space approach seems to offer greater flexibility, since the variation method with different trial functions can be used as well as perturbation theory. However, the method investigated here certainly warrants further development.

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REFERENCES

BELYAEV, S. T. (1958). *Zh. Eksperim. i Teor. Fiz.* **34**, 417 [*English Transl.*: *Soviet Phys.-JETP* **7**, 289 (1958)].

BETHE, H. A., and SALPETER, E. E. (1957). "Quantum Mechanics of One- and Two-Electron Systems." Springer-Verlag, Berlin.

BONCH-BRUEVICH, V. L., and TYABLIKOV, S. V. (1962). "The Green Function Method in Statistical Mechanics." North-Holland, Amsterdam.

DYSON, F. J. (1949). *Phys. Rev.* **75**, 1736.

GALITSKII, V. M., and MIGDAL, A. B. (1958). *Zh. Eksperim. i Teor. Fiz.* **34**, 139 [*English Transl.*: *Soviet Phys.-JETP* **7**, 96 (1958)].

HOLØIEN, E. (1958). *Proc. Phys. Soc.* (*London*) **LXXI**, 357.

HUGENHOLTZ, N. M., and PINES, D. (1959). *Phys. Rev.* **116**, 489.

HYLLERAAS, E. A. (1964). *Advan. Quan. Chem.* **1**, 1.

HYLLERAAS, E. A., and MIDTDAL, J. (1956). *Phys. Rev.* **103**, 829.

KELLY, H. P. (1964). *Phys. Rev.* **136**, B896.

KOBE, D. H. (1962). *Ann. Phys.* (*N.Y.*) **19**, 448.

KOBE, D. H. (1964). *Ann. Phys.* (*N.Y.*) **28**, 400.

KOBE, D. H. (1966a). *J. Math. Phys.* **7**, 1806.

KOBE, D. H. (1966b). *Am. J. Phys.* **34**, 1150.

KOBE, D. H. (1966c). *Proc. Phys. Soc.* (*London*) **88**, 9.

LAYZER, A. J. (1963). *Phys. Rev.* **129**, 897.

LINDERBERG, J. (1961). *Phys. Rev.* **121**, 816.

LÖWDIN, P.-O. (1955). *Phys. Rev.* **97**, 1474, 1490, 1509.

LÖWDIN, P.-O., and REDEI, L. (1959). *Phys. Rev.* **114**, 752.

LÖWDIN, P.-O., and SHULL, H. (1956). *Phys. Rev.* **101**, 1730.

MARTIN, P. C., and SCHWINGER, J. (1959). *Phys. Rev.* **115**, 1342.

MORRISON, K. L., Ed. (1962). "The Quantum Theory of Many-Particle Systems." Gordon and Breach, New York.

NESBET, R. K., and WATSON, R. E. (1958). *Phys. Rev.* **110**, 1073.

NOZIÈRES, P. (1964). "Theory of Interacting Fermi Systems." Benjamin, New York.

ÖHRN, Y., and MCWEENY, R. (1966). *Arkiv Fysik* **31**, 461.

PINES, D. (1961). "The Many-Body Problem." Benjamin, New York.

RITTER, Z., and PAUNCZ, R. (1960). *J. Chem. Phys.* **32**, 1820.

SCHERR, C. W., and KNIGHT, R. E. (1963). *Rev. Mod. Phys.* **35**, 436.

SCHULTZ, T. D. (1964). "Quantum Field Theory and the Many-Body Problem." Gordon and Breach, New York.

SHARMA, C. S., and COULSON, C. A. (1962). *Proc. Phys. Soc.* (*London*) **80**, 81.

SHULL, H., and LÖWDIN, P.-O. (1955). *J. Chem. Phys.* **23**, 1362 and 1565.

SHULL, H., and LÖWDIN, P.-O. (1956). *J. Chem. Phys.* **25**, 1035.

SHULL, H., and LÖWDIN, P.-O. (1959). *J. Chem. Phys.* **30**, 617.

Atomic Intensities: A Comparison of Theoretical and Experimental *f*-Values for Zn I, Cd I and Hg I

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I. Introduction

In the past, spectroscopy has concerned itself primarily with the analysis of atomic spectra and the subsequent assignment of atomic levels, but it is only within the last ten years that certain parameters important to the analysis of atomic processes have been seriously investigated. This may be partly attributed to the great interest developed in plasmas as well as to the availability of large computers. Certainly these two items have been very instrumental in the resurgence of the experimental and theoretical investigations in atomic physics. This is not to imply that this area of physics was completely dormant until fairly recently, since astrophysicists have always had a strong interest in this area, especially insofar as oscillator strengths or *f*-values, transition probabilities, and collision cross sections are concerned, because these parameters are of utmost importance in the determination of the abundances of the elements in stars and nebulae as well as the temperatures and densities of free electrons. Since the interest was confined mostly to astrophysicists, the effort was small. However, from the late 1950's to the present time, the interest in atomic spectroscopy has risen sharply in both experimental and theoretical work. In this paper the results of an experimental and theoretical investigation of three atoms, namely Zn I, Cd I, and Hg I are presented. All three of these involve *f*-values for transitions from an ns^2 to an $nsnp$ configuration.

II. Apparatus and Experimental Procedures

The oscillator strengths reported here were measured by the method of total absorption in which a metallic sample is sealed in an evacuated cell and then heated to produce a usable vapor pressure. From a measurement of the temperature of the cell, the atomic density can be calculated using vapor pressure data (Hultgren *et al.*, 1963) for the element. A continuum of radiation irradiates the cell, and the resulting absorption spectrum is photographed in a high-dispersion spectrograph. Standard techniques of photographic photometry are then employed to reduce the data from the plates to obtain the equivalent widths W_λ.

A convenient expression for the equivalent width W_λ can be obtained by considering the attenuation of the incident intensity I_0 (ergs cm^{-2} sec^{-1} cm^{-1}) as it passes through the absorbing vapor. Within the absorption line, the transmitted intensity will be I_λ. When expressed in terms of these quantities, the equivalent width W_λ becomes

$$W_\lambda = \int_0^\infty \frac{I_0 - I_\lambda}{I_0}\, d\lambda \tag{1}$$

From Eq. (1), the equivalent width is seen to be the area measured under the line contour divided by the continuum intensity near the line. Generally both quantities are readily accessible to measurement.

For a spectral line on the linear or lower Doppler part of the curve of growth, which gives the relationship between W_λ and Nf, the oscillator strength f is related to the equivalent width W_λ by the relation (Unsold, 1948):

$$W_\lambda = \pi^{1/2}\, \Delta\lambda_D \sum_{n=1}^{\infty} \frac{(-1)^{n-1}\, C^n}{n!\, \sqrt{n}}, \tag{2}$$

where $\Delta\lambda_D = (\lambda/c)\,(2RT/M)^{1/2}$ is the Doppler width in wavelength units, λ is the wavelength, c is the velocity of light, R is the universal gas constant, T is the temperature in °K, and M is the atomic weight. The dimensionless parameter C is defined by

$$C = \left(\frac{\pi^{1/2} e^2 \lambda^2}{mc^2\, \Delta\lambda_D}\right) Nfl \tag{3}$$

where N is the density of atoms contributing to the line, f is the absolute oscillator strength of the transition, and l is the length of the absorbing column of vapor. The quantity in parentheses is the absorption cross section per oscillator, while Nfl is the number of equivalent classical oscillators per unit area normal to l. Once W_λ and N are known, the oscillator strength f can be conveniently found from Eqs. (2) and (3).

In the investigation of zinc and cadmium, an absorbing column of vapor was obtained by inserting the metallic sample into a 2.5-cm diameter quartz cell with plane parallel windows approximately 4 cm apart. After being fused to an all-glass vacuum system, the cell was evacuated and at the same time baked in an electric oven to release adsorbed gases from the cell walls. Pressures obtained by this technique were of the order of 10^{-8} mm Hg (as read by an ionization gauge). After evacuation, the cell was fused shut and then inserted into a muffle furnace to vaporize the metallic charge.

The core of the furnace consisted of two concentric alumina muffles wound with either nickel or molybdenum wire. The inner muffle was wound along its entire length and provided the main portion of the heat required to vaporize the metallic sample. On the other hand, the outer muffle was only wound one-third of the way from each end. By heating both ends of the outer muffle, the temperature gradient inside the inner muffle could be kept uniform over a distance 6.25 cm about the center. This arrangement also permitted regulating the temperature gradient at the center of the furnace independently of the current heating the inner muffle. Before an experiment, the absorption cell was inserted into the center of the furnace, inside the inner muffle. Two alumina disks with 1.6-cm diameter apertures were placed on either side of the cell, and two more such disks were used to cap the ends of the inner heating muffle. Figure 1 shows the arrangement of

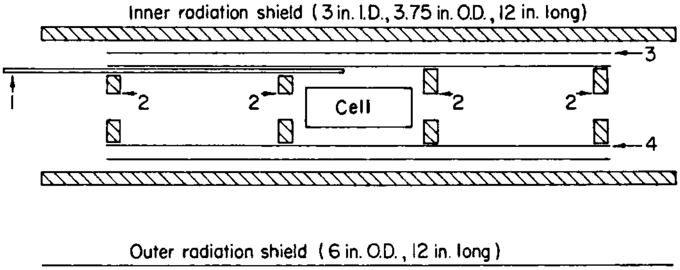

Fig. 1. Schematic view of furnace. 1: Thermocouple tube; 2: furnace aperture; 3: outer heating coil (2 in. I.D., 10 in. long); 4: inner heating coil (1.75 in. I.D., 10 in. long).

furnace elements, furnace apertures and absorption cell relative to one another. Also shown in Fig. 1, is a typical arrangement of radiation shields used in the furnaces to prevent excessive heat losses. With the cell in position, the furnace was heated by passing current through the resistance heating wire. Power for the furnaces was taken either directly from a 3 KVA Sola constant voltage transformer or from a temperature regulator backed by a 220-V Variac. In operation, the furnace could attain steady state temperatures as high as 1350°C with a temperature gradient across the cell of less than 1°C.

Of the measurements taken in this investigation, the temperature measurement was the most critical because of the steep exponential dependence of the vapor pressure of metals on temperature. All temperatures were measured with platinum, platinum and 10% rhodium thermocouples with calibration certified by the U.S. National Bureau of Standards or with chromel-alumel thermocouples calibrated against a certified thermocouple. With the certified platinum, platinum and 10% rhodium thermocouples, an accuracy of 1°C was attained, while the calibrated chromel-alumel thermocouples gave an accuracy of about 2°C. Altogether three thermocouples were used. One measured the temperature at the center of the cell, and the other two thermocouples measured the temperatures at both ends of the cell. An ice bath provided the 0°C reference junction. The output of the thermocouples was read on a potentiometer capable of resolving 0.1 μV. A certified Weston standard cell provided the standardizing voltage for the potentiometer.

Figure 2 gives the essential features of the optical system. All lenses shown are quartz-lithium fluoride achromats. The source of continuous radiation was either a 1.2-kVA high-pressure mercury arc lamp operated directly from a dc generator through a ballast resistor or a high-pressure xenon arc lamp. It can be seen from Fig. 2 that the furnace apertures allow only the light passing through the absorption cell to enter the spectrograph. The spectrographs used in these measurements were either a 6.6-meter Rowland mount instrument giving a dispersion of 1.252 Å/mm in the second order or a 2-meter Czerny-Turner mount instrument giving a dispersion of 0.855 Å/mm. In all experiments the band pass admitted into either spectrograph was limited by a suitable array of filters.

All the data for the experiments with cadmium and zinc were photographed on Ilford N. 50 halftone plates, which have very fine grain, but only moderate speed. Typical exposures ranged from 8 sec to 6 min. All the plates were developed in fresh D-19 developer for 4 min at 20°C. Standard techniques of photographic photometry were employed to calibrate the plates and reduce the lines to equivalent widths. Any procedure that varied from normal photometric techniques was carefully checked with test plates to insure its accuracy.

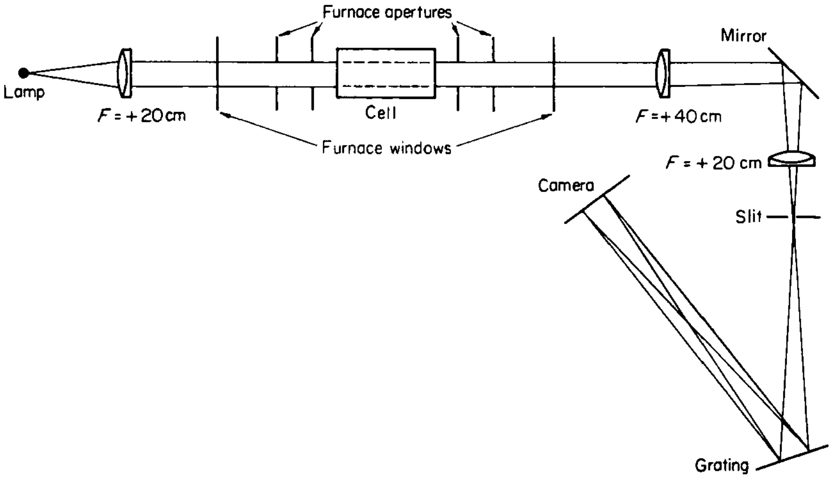

Fig. 2. The optical system.

Since mercury has a high vapor pressure at room temperature, a somewhat different experimental procedure was adopted to measure the equivalent width. A stainless steel cell with quartz windows and a long glass cold finger was prepared. After placing a droplet of mercury at the bottom of the cold finger, the cell was evacuated and sealed. The cold finger was then immersed in an ice bath at 0°C while the cell remained at room temperature. In this manner the vapor pressure in the cell was adjusted exactly to the value 1.85×10^{-4} mm Hg. The continuum radiation from an argon arc operating at atmospheric pressure was then passed through the cell to form the absorption signal. After passing through the cell, the radiation was dispersed in a 2-meter Czerny-Turner spectrograph, and the resulting absorption line was scanned with an EMI 9558 QB photomultiplier. The photomultiplier output, after amplification, was then transferred to a recorder, and the recorder tracings were planimetered to find the equivalent width.

In an alternate method a sample of mercury was sealed in an evacuated quartz cell with plane parallel windows 2.0 mm apart. During the experiment, the entire cell was maintained at a temperature of 24.4°C, which was measured by a precision laboratory thermometer with an uncertainty of less than ±0.3°C. To obtain the absorption signal, the continuum radiation from a carbon arc, operating in a stream of flowing argon, was passed through the cell and then dispersed in a 2-meter Czerny-Turner spectrograph. Kodak Spectrum Analysis Type I plates were used to photograph the resulting absorption line. Standard techniques of photographic photometry were then employed to calibrate the plates and to reduce the absorption lines to equivalent widths.

III. Theoretical Considerations

In order to calculate the f-values, accurate atomic wave functions are a necessary prerequisite. Atomic wave functions used in present-day calculations are usually obtained by the Hartree-Fock self-consistent field method (HFSCF) with exchange. The methods and procedures for these calculations have been thoroughly described in the literature (Hartree, 1957). For the heavier atoms such as those used in this investigation the methods of Froese (1963) and Mayers and Hirsh (1965) are the best; either method gives good results. In these methods, the second-order differential equation for the radial wave functions of the electrons under certain boundary conditions are solved. The program for solving the Hartree-Fock equations was written in Fortran II for the IBM 7090 computer and the equation which the program solves is:

$$\frac{d^2P_\alpha}{dr^2} + \left[\frac{2}{r}\,Y_\alpha(r) - \varepsilon_{\alpha\alpha} - \frac{\lambda_\alpha(\lambda_\alpha + 1)}{r^2}\right]P_\alpha(r) = X_\alpha(r) \tag{4}$$

where

$$\begin{aligned} Y_\alpha(r) = Z - \sum_{\beta} q_\beta Y_0(\beta\beta, r) + Y_0(\alpha\alpha, r) \\ + \frac{1}{q_\alpha}\sum_{k} B_{\alpha\alpha k} Y_k(\alpha\alpha, r) + \frac{1}{q_\alpha}\sum_{\substack{\beta \\ k>0}} C_{\beta\alpha k} Y_k(\beta\beta, r), \end{aligned} \tag{5}$$

$$X_\alpha(r) = -\frac{2}{q_\alpha r}\sum_{\substack{\beta\neq\alpha \\ k>0}} B_{\beta\alpha k} Y_k(\beta\alpha, r)P_\beta(r) + \frac{1}{q_\alpha}\sum_{\beta\neq\alpha} \varepsilon_{\beta\alpha}P_\beta(r), \tag{6}$$

and

$$Y_k(\beta\alpha, r) = r\int_0^\infty U_k(rt)P_\beta(t)P_\alpha(t)\,dt, \tag{7}$$

with

$$U_k = r^k/t^{k+1}, \quad r < t,$$
$$= t^k/r^{k+1}, \quad t < r.$$

The equations are solved subject to the following restrictions:

$$\int_0^\infty P_\alpha^{\,2}(r)\,dr = 1$$

and

$$\int_0^\infty P_\alpha(r)P_\beta(r)\,dr = 0 \qquad \text{if} \quad \lambda_\alpha = \lambda_\beta, \quad \alpha \neq \beta.$$

The aggregate of the two numbers representing the principal quantum number and the orbital angular momentum is denoted by α or β; $\varepsilon_{\alpha\alpha}$ is the one electron energy parameter; λ_α is the orbital angular momentum; Z is the atomic number; q_α is number of electrons in shell α; and $\varepsilon_{\beta\alpha}$ is the off-diagonal energy parameter. The quantities $B_{\beta\beta k}$, $C_{\beta\alpha k}$ and $B_{\beta\alpha k}$ are the coefficients of the Slater integrals in the expression for the energy, E, of the ion or atom, i.e.,

$$\begin{aligned} E = {} & \sum_\alpha q_\alpha I_\alpha + \sum_\alpha \tfrac{1}{2} q_\alpha(q_\alpha - 1)F_0(\alpha, \alpha) + \sum_{\beta \neq \alpha} q_\alpha q_\beta F_0(\beta, \alpha) \\ & - \sum_{\alpha, k} \tfrac{1}{2} B_{\alpha\alpha k} F_k(\alpha, \alpha) - \sum_{\substack{\beta \neq \alpha \\ k > 0}} B_{\beta\alpha k} G_k(\beta, \alpha) - \sum_{\substack{\beta \neq \alpha \\ k > 0}} C_{\beta\alpha k} F_k(\beta, \alpha). \end{aligned} \tag{8}$$

The respective wave functions of Zn I, Cd I and Hg I were calculated by the method of Mayers and Hirsh for the following configuration of electrons outside the closed shells: $4s^2$, $4s4p$; $5s^2$, $5s5p$; and $6s^2$, $6s6p$. These are the configurations involved in the transitions.

With these wave functions, the necessary parameter, i.e., the dipole length, required for the determination of the f-values was calculated as

$$\sigma^2(nl, n'l') = \frac{1}{4l_>^{\,2} - 1}\left[\int_0^\infty rP(nl; r)\,P(n'l'; r)\,dr\right]^2 \tag{9}$$

where $l_> = 1$ for the above mentioned transitions. The f-values can be obtained from the expression

$$S(\beta J, \beta' J') = \left[\sum_{\alpha\alpha'} (\beta J \mid \alpha J)\{S(\alpha J, \alpha' J')\}^{1/2}(\alpha' J' \mid \beta' J')\right]^2, \tag{10}$$

where $S(\beta J, \beta' J')$ is the line strength in the intermediate coupling caused by the spin-orbit (ζ) interaction, $S(\alpha J, \alpha' J')$ is the line strength in LS coupling, and $(\beta J \mid \alpha J)$ and $(\alpha' J' \mid \beta' J')$ are the coefficients of the transformation matrix connecting the two coupling schemes. $S(\alpha J, \alpha' J')$ is given by

$$S(\alpha J, \alpha' J') = (\pm)^2 \mathscr{S}(\mathscr{L}) \mathscr{S}(\mathscr{M}) \sigma^2 \tag{11}$$

where $\mathscr{S}(\mathscr{L})$ and $\mathscr{S}(\mathscr{M})$ are the coefficients involved in the transition and depend on the particular line of the multiplet and particular multiplet of the transition array respectively. The f-value for absorption can be then obtained by employing the following relation

$$f(J, J') = \frac{3.336 \times 10^{-1}}{2J + 1} \bar{\nu}\, S(\beta J, \beta' J'), \tag{12}$$

where $\bar{\nu}$ is the wave number of the transition in rydbergs, and J and J' refer to the ground and excited states respectively.

The spin-orbit parameter ζ can be calculated from the atomic wave functions, but a somewhat better value for it may be obtained from the observed energy levels. Under the assumption that the spin-orbit interaction is the only one causing the splitting of the energy levels, it can be shown for *nsnp* configurations that

$$\zeta = \tfrac{2}{3}[{}^3P_2 - {}^3P_0]. \tag{13}$$

where ${}^3P_2$ and ${}^3P_0$ are the respective energy levels involved in the transition.

IV. Discussion

In Tables I and II the results of the theoretical calculations and experimental determinations are shown. In order to calculate the experimental f-value, one must consider the hyperfine structure of the spectral lines. The unresolved line recorded on the photographic plate contains all the components of the hyperfine structure. If the separation between the components is greater than the Doppler width $\Delta\lambda_D$, the observed equivalent width should be treated as the sum of the equivalent widths of each unresolved hyperfine component. For zinc and cadmium, the intensity distribution of the hyperfine structure components spans a wavelength interval less than one Doppler width. Therefore, the equivalent widths of the zinc and cadmium lines were treated as if there were no hyperfine splitting (Brix and Steudel, 1950; Brix and Kopfermann, 1952). For the mercury line, the hyperfine splitting separates the single line into seven distinct groups of components, each group being separated by a wavelength span greater than

TABLE I

DATA AND RESULTS OF THE THEORETICAL CALCULATION

Element	Zn I	Cd I	Hg I
Transition	$4s^{2}\,{}^{1}S_0 - 4s4p\,{}^{3}P_1$	$5s^{2}\,{}^{1}S_0 - 5s5p\,{}^{3}P_1$	$6s^{2}\,{}^{1}S_0 - 6s6p\,{}^{3}P_1$
ζ_{obs} (cm^{-1})	386	1142	4265
$\sigma^2(a_0{}^2e^2)$	14.67	3.09	3.24
$\mathcal{S}(\mathcal{L})$	1	1	1
$\mathcal{S}(\mathcal{M})$	6	6	6
$S(J, J')(a_0{}^2e^2)$	5.39×10^{-3}	7.11×10^{-2}	8.23×10^{-1}
f_{th}	5.32×10^{-3}	6.63×10^{-3}	9.86×10^{-2}

TABLE II

EXPERIMENTAL DATA AND RESULTS

Element		Zn I		Cd I	Hg I	
λ (Å)		3075.90		3261.06	2536.52	
$W_\lambda \times 10^{11}$ (cm)	8.24	8.77	8.63	4.24	5.18	12.29
T (°K)	640.5	643.1	641.1	475.8	273.2	297.6
N (atoms/cm^3)	3.60×10^{14}	3.95×10^{14}	3.68×10^{14}	7.93×10^{12}	6.54×10^{12}	5.69×10^{13}
l (cm)	3.66	3.66	3.66	4.30	0.50	0.20
$\Delta\lambda_D \times 10^{11}$ (cm)	4.14	4.15	4.14	2.89	1.32	1.33
f_{exp}	1.35×10^{-4}	1.40×10^{-4}	1.45×10^{-4}	1.94×10^{-3}	3.31×10^{-2}	3.65×10^{-2}

one Doppler width (Brix and Kopfermann, 1952). Therefore, the equivalent width in Table II was divided into seven equivalent widths according to the weight of each group. Each of these equivalent widths was then inserted into Eq. (2) to get C. Finally all seven values of C obtained in this manner were added together, and the resulting value of C was used in Eq. (3) to obtain f.

Table II presents all the data needed to calculate the f-value from the measurements taken in this investigation. The equivalent widths W_λ in Table II are the averages of a number of trials all taken at the same temperature. There were 17, 23, and 14 trials respectively for the three zinc experiments; 50 trials for the cadmium experiment; and 28 and 37 trials respectively for the two mercury experiments. In Table II, Hultgren's thermodynamic tables were used to compute the atomic densities N at the temperatures shown. These tables represent probably the most reliable vapor pressure data presently available, and their use to calculate the atomic density N would not introduce an uncertainty exceeding 10% in any of the experimental f-values reported in this investigation.

To check the photographic photometry used in all the experiments, the f-value for mercury was measured in two separate experiments as shown in Table II. Both experiments used the same method of total absorption, but in the first experiment, the results were recorded photoelectrically, and in the second experiment by photography. The agreement between both experiments shown in Table II thus confirms the reliability of the photographic photometry and would indicate that any systematic errors in the photometry do not exceed 10%. All the f-values reported here agree within 30% with those published in the literature (see Glennon and Wiese, 1966).

Reference to Table II also permits a useful observation concerning the applicability of the method of total absorption to the measurement of atomic f-values. Due to the markedly nonlinear nature of Eq. (2) for large values of C, reliable results can normally be obtained only for equivalent widths W_λ, not exceeding three times the Doppler width $\Delta\lambda_D$. For elements with large Doppler widths such as cadmium and zinc, this restriction, while inconvenient, is not unduly severe. For elements with small Doppler widths, such as mercury, this restriction could be very severe were it not for the mitigating influence of a well-resolved hyperfine structure splitting. Since the restriction on the magnitude of the equivalent width applies separately to each resolved component of the hyperfine structure pattern, the total equivalent width can still have an easily measurable magnitude. This latter point would, therefore, suggest that for spectral lines with small Doppler widths and unresolved hyperfine structure, the permissible magnitude of the equivalent width could be increased by splitting the spectral line by some means such as the Zeeman Effect.

TABLE III

COMPARISON OF EXPERIMENTAL AND THEORETICAL f-VALUES

Element	Zn I	Cd I	Hg I
f_{th}	5.32×10^{-4}	6.63×10^{-3}	9.86×10^{-2}
f_{exp} (average)[a]	$1.40 \pm 0.08 \times 10^{-4}$	$1.94 \pm 0.11 \times 10^{-3}$	$3.48 \pm 0.43 \times 10^{-2}$

[a] Experimental uncertainty shown is one standard deviation.

In Table III a comparison between the experimental and theoretical f-values is shown. The present theoretical calculations do not include configuration interaction. Had configuration interaction been included the theoretical f-values would have been considerably reduced, i.e., anywhere from approximately one-half to one-third of the reported values. Our estimate of the reduction in f-values is based on the earlier work of Garstang (1962a,b) and Steele and Trefftz (1966) who employed a semi-empirical method to take into account configuration interaction in which they showed that configuration interaction will reduce the f-values by a factor of as much as 2 or 3. However, the methods which they used are not applicable to the configurations investigated here. At present theoretical calculations of atomic wave functions for heavy atoms have not as yet been developed to include configuration interaction that involve excited levels of this type, i.e., interactions between *nsnp* and *nsn'p* configurations. This problem is being investigated in order to improve the existing method for calculating atomic wave functions.

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REFERENCES

BRIX, P., and KOPFERMANN, H. (1952). *In* "Landolt-Bornstein Zahlenwerte und Funktionen" (A. Eucken, ed.), Vol. 1, No. 5, pp. 1–63. Springer, Berlin.

BRIX, P., and STEUDEL, A. (1950). *Z. Physik* **128**, 260.

FROESE, C. (1963). *Can. J. Phys.* **41**, 1895.

GARSTANG, R. H. (1962a). *Monthly Notices Roy. Astron. Soc.* **124**, 321.

GARSTANG, R. H. (1962b). *Ann. Astrophys.* **25**, 109.

GLENNON, B. M., and WIESE, W. L. (1966). National Bureau of Standards Miscellaneous Publication 278, U.S. Government Printing Office, Washington, D.C.
HARTREE, D. R. (1957). "The Calculation of Atomic Structures." Wiley, New York.
HULTGREN, R., ORR, R. L., ANDERSON, P. D., and KELLEY, K. K. (1963). "Selected Values of Thermodynamic Properties of Metals and Alloys." Wiley, New York.
MAYERS, D., and HIRSH, A. (1965). "The Calculation of Atomic Wave Functions by Solution of the Hartree-Fock Equations," ARL 65–62, Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio.
STEELE, R., and TREFFTZ, E. (1966). *J. Quant. Spectrosc. Radiat. Transfer* **6**, 833.
UNSOLD, A. (1948). "Physik der Sterneatmospharen." Springer, Berlin.

Probability of Singlet-Triplet Transitions*†

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Introduction

Since Kowalski's (1911) observation of phosphorescence and Sklar's (1937) assignment of the singlet-triplet bands in benzene, followed by Lewis and Kasha's (1944) and Terenin's (1943, 1944) identification of phosphorescence as $T \rightarrow S_0$ emission, the study of singlet-triplet transitions has developed a large niche in molecular spectroscopy. A recent selective review of the triplet state by Lower and El-Sayed (1966) lists over 400 papers on organic molecules alone. Despite this activity, some fundamental aspects concerning the probability of singlet-triplet transitions—even at the most basic level—remain unresolved. There has been concern over the validity of carrying over the spin-free fundamental optical transition

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probability expressions to S–T transitions, for example. A proper quantum-mechanical treatment of spin-forbidden transitions must then be relativistic. In this way the basic probability expressions evolve unambiguously. In Sections I–III of this chapter we develop a rigorous derivation of the basic probability expressions for S–T transitions. In Sections IV and V, sources of intensity are discussed. Since the theory for polyatomic molecules becomes perforce approximate at this level, experiments are analyzed which lead to a choice among the alternatives.

Historical perspective and the literature can be obtained from the excellent reviews by Lower and El-Sayed (1966), and by Kasha and McGlynn (1956). Also see texts by Hameka (1965) and Hochstrasser (1966).

I. Transition Probabilities

As is well known the probability of an optical transition occurring between an initial stationary state n and the state s is (Merzbacher, 1960)

$$\mathscr{P}_{n\to s} = |\langle\psi_s{}^0|P\exp\left(-i/\hbar\int_0^t V'\,dt\right)|\psi_n{}^0\rangle|^2, \tag{I.1}$$

where P is the time-ordering operator and V' is the operator $\exp[(i/\hbar)\cdot H^0t]$ $V\exp[-(i/\hbar)H^0t]$. V is the time-dependent part of the Hamiltonian. The stationary state eigenfunctions $\psi_s{}^0$ and their eigenvalues E_s are generated by the time-independent operator H^0, i.e., $H^0\psi_s{}^0 = E_s\psi_s{}^0$. A discussion of the relativistic Hamiltonian for a system of N electrons is given in the following section in order to define in more definite terms the stationary states $\psi_s{}^0$ and the form of the particle-radiation interaction V.

II. Relativistic N-Particle Equation

A. One Particle

The Dirac equation for a single particle of mass m and charge e in an electromagnetic field described by the potentials ϕ and $\mathbf{A}$ (Dirac, 1958; Bethe and Salpeter, 1957) is

$$i\hbar\frac{\partial\Psi}{\partial t} = \{e\varphi + \beta mc^2 + \boldsymbol{\alpha}\cdot(c\mathbf{p} - e\mathbf{A})\}\Psi. \tag{II.1}$$

The quantity $\mathbf{p}$ is the particle momentum operator and the Dirac operators β and $\boldsymbol{\alpha}$ are a set of quantities which anticommute with each other and whose squares are unity. Because of the form of the Dirac operators the wave function Ψ can no longer be looked upon as a single function but instead it must be represented as a bispinor, i.e., a column matrix with 4 components. Each component is a function of the space and time coordinates, i.e.,

$$\Psi = \begin{pmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \\ \Phi_4 \end{pmatrix}. \tag{II.2}$$

When stationary state solutions of the time-independent part of the Hamiltonian in Eq. (II.1), i.e.,

$$\{e\varphi + \beta mc^2 + c\boldsymbol{\alpha} \cdot \mathbf{p}\}\psi^0 = E\psi^0, \tag{II.3}$$

are examined it is found that both positive- and negative-energy solutions occur. The former are interpreted as electron states and the latter as positron states. It is easily shown that, if the particle is moving slowly compared to the speed of light, two of the four components in the wave function (II.2) become small. In the case of the electron the lower two components are small compared to the upper two. That is, in the nonrelativistic limit the Dirac electron becomes describable by a Pauli two-component wave function. An elegant and systematic method of reducing the wave function from the four- to the two-component form is due to Foldy and Wouthuysen (1950). It is based upon the observation that the operator $\boldsymbol{\alpha}$ mixes the upper two components with the lower two but β does not. They have called operators like $\boldsymbol{\alpha}$ "odd" and those like β "even." By a series of unitary transformations they are able to transform the wave function and operator to a new representation in which the Hamiltonian is free of odd operators. Then the upper two components can be interpreted as describing electron states whereas the lower two describe the positron. Later (in Section III) the Foldy-Wouthuysen reduction is used to develop a rigorous transition probability expression between a singlet and a triplet state.

In order to make the discussion more concrete we consider first the free particle case in detail. The results will be useful in what follows.

In the case of the free particle ($\varphi = 0$), Eq. (II.3) can be subjected to a single unitary transformation which allows the wave function to be expressed in terms of two-component wave functions, that is,

$$\exp(iS)\{\beta mc^2 + c\boldsymbol{\alpha} \cdot \mathbf{p}\}\exp(-iS)\psi = E\psi, \tag{II.4}$$

where $\psi = \exp(iS)\psi^0$ with $S = \frac{1}{2}\tanh(\boldsymbol{\gamma} \cdot \mathbf{p}/mc)$ and $\boldsymbol{\gamma} = \beta\boldsymbol{\alpha}$. The quantity $\exp(iS)$ is the Foldy-Wouthuysen (F-W) transform. Working out the transformation one obtains the even Hamiltonian

$$\beta(m^2c^4 + c^2p^2)^{1/2}\psi = E\psi. \tag{II.5}$$

By writing $\psi = (\Phi^+ + \Phi^-)$, with

$$\begin{aligned}\Phi^+ &= \tfrac{1}{2}(1+\beta)\psi,\\ \Phi^- &= \tfrac{1}{2}(1-\beta)\psi,\end{aligned} \tag{II.6}$$

(i.e., the sum of a bispinor Φ^+ with lower two components zero and a bispinor Φ^- with upper two components zero) these functions satisfy the equations

$$\begin{aligned}(m^2c^4 + c^2p^2)^{1/2}\Phi^+ &= E\Phi^+,\\ -(m^2c^4 + c^2p^2)^{1/2}\Phi^- &= E\Phi^-.\end{aligned} \tag{II.7}$$

The first of Eqs. (II.7) describes an electron, the second a positron.

In the case of a particle in an electromagnetic field, it is also possible to describe electrons in terms of two-component functions. However, no single unitary operator will do this. Instead, an infinite sequence of unitary operators are needed to free the Hamiltonian of odd operators. The F–W reduction is complicated in this case: however, Kursunoğlu (1956) noted that if the F–W free particle transformation is applied once, one can obtain a Hamiltonian equation that is free of odd operators to order (c^{-2}). Our interest in this method lies in its capability of generalization to the many-particle case.

B. Two or More Particles

An approximate relativistic equation for two particles is the Breit (1929) equation. It is correct to order (c^{-2}) and reads

$$i\hbar\frac{\partial\Psi}{\partial t} = \left\{H_1 + H_2 + \frac{e^2}{r}\left[1 - \frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{2} - \frac{(\boldsymbol{\alpha}_1\cdot\mathbf{r})(\boldsymbol{\alpha}_2\cdot\mathbf{r})}{2r^2}\right]\right\}\Psi, \tag{II.8}$$

where H_1 and H_2 are Dirac Hamiltonians [cf. Eq. (II.1)] and r is the interparticle distance.

Since the Dirac operators of one particle commute with those of another particle, the wave function for the two-particle system can be written as the "product" of two four-component wave functions, i.e., $\Psi = \Psi_1\Psi_2$ that is a tensor product of two bispinors. Therefore, Dirac operators for particle 1 acting upon Ψ will operate only on Ψ_1. It is clear that the momentum operators do not commute with r, so that each component in this product depends on both electron coordinates.

The Foldy-Wouthuysen-Kursunoğlu method begins with the time-independent equation

$$H^0\psi^0 = \left\{H_1{}^0 + H_2{}^0 + \frac{e^2}{r}\left[1 - \frac{\alpha_1 \cdot \alpha_2}{2} - \frac{(\alpha_1 \cdot \mathbf{r})(\alpha_2 \cdot \mathbf{r})}{2r^2}\right]\right\}\psi^0 = E\psi^0, \tag{II.9}$$

where $H_1{}^0$ is the Dirac Hamiltonian for particle 1 [cf. Eq. (II.3)] and $\psi^0 = \psi_1{}^0\psi_2{}^0$. In analogy to Eqs. (II.4) and (II.5) we have

$$\mathscr{H}^0\psi = \exp(iS)\,H^0\exp(-iS)\,\psi = E\psi, \tag{II.10}$$

where S is the sum of the two single-particle F–W transforms and $\psi = \psi_1\psi_2$. This transformation reduces only part of H^0 to an even operator. More explicitly

$$\left\{\sum_{k=1}^{2} \beta_k(m^2c^4 + c^2p_k{}^2)^{1/2} + \mathscr{E}\mathscr{E} + \mathscr{E}\mathscr{O} + \mathscr{O}\mathscr{E} + \mathscr{O}\mathscr{O}\right\}\psi = E\psi \tag{II.11}$$

contains terms which may be even in the first particle but odd in the second, e.g., $\mathscr{E}\mathscr{O}$. As in Eq. (II.6) wave functions can be projected out of the transformed functions ψ, which have only two components. However, here there are four possible functions

$$\Phi^{\pm\pm} = \tfrac{1}{4}(1 \pm \beta_1)(1 \pm \beta_2)\psi = \Phi_1{}^{\pm}\Phi_2{}^{\pm}, \tag{II.12}$$

ψ being the sum of all four functions. The wave function which describes *two electrons is* Φ^{++}. It is an eigenfunction of a Hamiltonian which can be obtained in the following way. Writing Eq. (II.11) as

$$(\mathscr{M} - \mathscr{E}\mathscr{E} - \mathscr{E}\mathscr{O} - \mathscr{O}\mathscr{E} - \mathscr{O}\mathscr{O})\psi = 0 \tag{II.13}$$

with $\mathscr{M} = E - \sum_k (m^2c^4 + c^2p_k{}^2)^{1/2}$ and operating with all four possible products of the projectors $(1 \pm \beta_1)$ and $(1 \pm \beta_2)$, the four equations

$$\begin{aligned}
&(\mathscr{M} - \mathscr{E}\mathscr{E})\Phi^{++} - \mathscr{E}\mathscr{O}\Phi^{+-} - \mathscr{O}\mathscr{E}\Phi^{-+} - \mathscr{O}\mathscr{O}\Phi^{--} = 0,\\
&(\mathscr{M} - \mathscr{E}\mathscr{E})\Phi^{+-} - \mathscr{E}\mathscr{O}\Phi^{++} - \mathscr{O}\mathscr{E}\Phi^{--} - \mathscr{O}\mathscr{O}\Phi^{-+} = 0,\\
&(\mathscr{M} - \mathscr{E}\mathscr{E})\Phi^{-+} - \mathscr{E}\mathscr{O}\Phi^{--} - \mathscr{O}\mathscr{E}\Phi^{++} - \mathscr{O}\mathscr{O}\Phi^{+-} = 0,\\
&(\mathscr{M} - \mathscr{E}\mathscr{E})\Phi^{--} - \mathscr{E}\mathscr{O}\Phi^{-+} - \mathscr{O}\mathscr{E}\Phi^{+-} - \mathscr{O}\mathscr{O}\Phi^{++} = 0,
\end{aligned} \tag{II.14}$$

are obtained. A solution of this system of homogeneous equations for Φ^{++} (hereafter simply Φ) is

$$\{(u + v) - (u - v)(u + v)^{-1}(u - v)\}\Phi = 0, \tag{II.15}$$

where

$$u = (\mathscr{M} - \mathscr{E}\mathscr{E} - \mathscr{O}\mathscr{O}) - (\mathscr{E}\mathscr{O} + \mathscr{O}\mathscr{E})(\mathscr{M} - \mathscr{E}\mathscr{E} - \mathscr{O}\mathscr{O})^{-1}(\mathscr{E}\mathscr{O} + \mathscr{O}\mathscr{E}),$$

$$v = (\mathscr{M} - \mathscr{E}\mathscr{E} + \mathscr{O}\mathscr{O}) - (\mathscr{E}\mathscr{O} - \mathscr{O}\mathscr{E})(\mathscr{M} - \mathscr{E}\mathscr{E} + \mathscr{O}\mathscr{O})^{-1}(\mathscr{E}\mathscr{O} - \mathscr{O}\mathscr{E}).$$

It can be verified that the operator acting on Φ is even. Further, to order (c^{-2}), which is all that the Breit equation allows, Eq. (II.15) may be approximated as

$$(\mathscr{M} - \mathscr{E}\mathscr{E})\Phi = 0. \tag{II.16}$$

When this result is expanded and terms to order (c^{-2}) are kept, the nonrelativistic equation

$$\mathscr{H}^0\Phi = (\mathscr{H}_0 + \mathscr{H}^1)\Phi = E\Phi \tag{II.17}$$

is obtained, where $\mathscr{H}_0 = \sum_k (p_k{}^2/2m - p_k{}^4/8m^3c^2 + e\varphi_k) + e^2/r$, and $\mathscr{H}^1$ is the sum of a term linear in the spin operators $\mathscr{H}_\mu{}^1$ and a term $\mathscr{H}_\sigma{}^1$ which contains spin-independent and spin-spin parts, i.e.,

$$\begin{aligned}\mathscr{H}_\mu{}^1 &= \frac{\hbar}{4m^2c^2}\sum_k (\mathbf{E}_k \times \mathbf{p}_k)\cdot\boldsymbol{\sigma}_k - \left(\frac{e}{2mc}\right)^2\frac{1}{r^3}\{[\mathbf{r}\times(\mathbf{p}_1 - 2\mathbf{p}_2)]\cdot\boldsymbol{\sigma}_1 \\ &\qquad\qquad - [\mathbf{r}\times(\mathbf{p}_2 - 2\mathbf{p}_1)]\cdot\boldsymbol{\sigma}_2\}, \\ \mathscr{H}_\sigma{}^1 &= -2\left(\frac{e}{2mc}\right)^2\left\{2\pi\hbar^2\delta(\mathbf{r}) + \frac{\mathbf{p}_1\cdot\mathbf{p}_2}{r} + \frac{\mathbf{r}\cdot(\mathbf{r}\cdot\mathbf{p}_1)\mathbf{p}_2}{r^3}\right\} \\ &\quad + \left(\frac{\pi e\hbar^2}{2m^2c^2}\right)\sum_k \rho(\mathbf{r}_k) + \left(\frac{e}{2mc}\right)^2\left\{\frac{\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2}{r^3} - 3\frac{(\boldsymbol{\sigma}_1\cdot\mathbf{r})(\boldsymbol{\sigma}_2\cdot\mathbf{r})}{r^5} - \frac{8\pi}{3}\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2\delta(\mathbf{r})\right\}\end{aligned} \tag{II.18}$$

The definitions $\nabla_k{}^2\phi(\mathbf{r}_k) = -4\pi\rho(\mathbf{r}_k)$ and $\mathbf{E}_k = -\nabla_k\phi(\mathbf{r}_k)$ have been used. The vectors $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ are the Pauli spin vectors for each particle. Equation (II.17) has been derived by other approaches (e.g., Slater, 1960; Bethe and Salpeter, 1957; Chraplyvy, 1953; Baker and Glover, 1955; Itoh, 1965). A discussion of many of the terms in Eq. (II.17) may be found in Bethe and Salpeter (1957) and Hameka (1965). The problem is readily generalized to the N-electron system (Kramers, 1958; Itoh, 1965). In this case the relativistic wave function is a 4^N-component function with 2^N components in the nonrelativistic limit.

III. Nonrelativistic Transition Probabilities

We join the results of Section II with Eq. (I.1) to obtain a nonrelativistic transition probability expression with the help of the F–W transformation:

$$\mathscr{P}_{n\to s} = |\langle\Phi_s|P\exp\left(-\frac{i}{\hbar}\int_0^t \mathscr{V}'\,dt\right)|\Phi_n\rangle|^2, \tag{III.1}$$

where $\mathscr{V}'$ is the operator $\exp(i/\hbar\mathscr{H}^0 t)\mathscr{V}\exp(-i/\hbar\mathscr{H}^0 t)$ and $\mathscr{V}$ is the F–W transform of V, i.e., $\exp(iS)\,V\exp(-iS)$. Because the interaction between the radiation field and the electrons is weak, the exponential in Eq. (III.1) can be expanded in a power series where the first term contributes nothing and the next term is a major source of probability. This second term is responsible for single-photon processes whereas the third is responsible for the simultaneous absorption or emission of two photons, etc. We consider single photon processes only. In this case the probability becomes

$$\begin{aligned}\mathscr{P}_{n\to s} = (2\pi t\rho/3\hbar^3)\{&|\langle\Phi_s|\sum_k e\mathsf{r}_k|\Phi_n\rangle|^2\\ &+|\langle\Phi_s|\sum_k(e/2)(\mathsf{r}_k\times\boldsymbol{a}_k)|\Phi_n\rangle|^2\\ &+(3\pi/40)(\omega_{sn}/c)^2\langle\Phi_s|\sum_k e\mathsf{r}_k\mathsf{r}_k|\Phi_n\rangle|^2\},\end{aligned} \tag{III.2}$$

formally similar to the probability expression for a system of electrons without spin. Here, however, we are dealing with spinor wave functions and transformed operators (the Sans Serif symbols r and $\boldsymbol{a}$ indicate the F–W transforms of $\mathbf{r}$ and $\boldsymbol{\alpha}$, respectively). Fortunately these transforms have already been calculated in closed form by Foldy and Wouthuysen. To the appropriate order in (c^{-2}) the probability expression becomes

$$\begin{aligned}\mathscr{P}_{n\to s} = (2\pi t\rho/3\hbar^2)\{&|\langle\Phi_s|\mathbf{u}|\Phi_n\rangle|^2+(e/2mc)^2|\langle\Phi_s|(\mathbf{J}+\mathbf{S})|\Phi_n\rangle|^2\\ &+(3\pi/40)(\omega_{sn}/c)^2|\langle\Phi_s|e\mathbf{rr}|\Phi_n\rangle|^2\},\end{aligned} \tag{III.3}$$

where ρ is the radiation density and the operators appearing in Eq. (III.3) are electric dipole, magnetic dipole, and electric quadrupole, respectively, i.e. $\mathbf{u} = -\sum_k e\mathbf{r}_k$, $\mathbf{J}+\mathbf{S} = \sum_k(\mathbf{L}_k+2\mathbf{S}_k)$, $e\mathbf{rr} = -\sum_k e\mathbf{r}_k\mathbf{r}_k$.

It is clear that the dipole moment operator still appears as the leading term in the probability expression even though the wave functions satisfy Eq. (II.17) which contains spin-orbit and other operators. This result is not a trivial one. Recently there has been concern (Hameka and Goodman, 1965) over the validity of Eq. (III.3) for singlet-triplet transitions. Lohr

(1966) partially resolved this problem for the special case of a Hamiltonian containing one-electron spin-orbit coupling as the only spin-dependent term, showing that dipole moment matrix elements are obtained by a commutator relation from the more fundamental matrix elements of an operator which is the sum of the ordinary linear momentum and a spin-dependent momentum. [*Added in proof:* Englman (1966) also has recently treated the one-election problem.] The derivation given here is general.

As is well known the wave functions Φ_s are mixtures of singlets and triplets (Araki, 1937; Pluvinage, 1952), and one speaks of a "singlet-triplet" transition only in the sense that the system has gone from a state Φ_n which is primarily a singlet $\Phi_n{}^0$ to a state $\Phi_{s\alpha}$ which is primarily a triplet $\Phi_{s\alpha}^0$.[1] To the first order Eq. (III.3) contains the dipole and magnetic moments to order (c^{-4}) as

$$|\langle\Phi_n|\mathbf{u}|\hat{\Phi}_{s\alpha}\rangle \equiv \mathbf{M}(n, s\,\alpha) = \left(\frac{1}{c^2}\right)\left\{\sum_{i\neq s}\frac{\langle\Phi_n{}^0|\mathbf{u}|\Phi_i{}^0\rangle\langle\Phi_i{}^0|\mathscr{H}_\mu{}^1|\hat{\Phi}_{s\alpha}^0\rangle}{E_s{}^0 - E_i{}^0}\right.$$

$$\left.+\sum_{j\neq n}\frac{\langle\hat{\Phi}_{s\alpha}|\mathbf{u}|\Phi_j{}^0\rangle\langle\Phi_j{}^0|\mathscr{H}_\mu{}^1|\Phi_n{}^0\rangle}{E_n{}^0 - E_j{}^0}\right\}.$$

$$\langle\Phi_n|(\mathbf{J}+\mathbf{S})|\hat{\Phi}_{s\alpha}\rangle = \langle\Phi_n|\mathbf{S}|\hat{\Phi}_{s\alpha}\rangle$$

$$= \langle\hat{\Phi}_n{}^0|\mathbf{S}|\hat{\Phi}_{s\alpha}^0\rangle + \left(\frac{1}{c^2}\right)\left\{\sum_{i\neq s}\frac{\langle\hat{\Phi}_n{}^0|\mathbf{S}|\Phi_i{}^0\rangle\langle\Phi_i{}^0|\mathscr{H}_\sigma{}^1|\hat{\Phi}_{s\alpha}^0\rangle}{E_s{}^0 - E_i{}^0}\right.$$

$$\left.+\sum_{j\neq n}\frac{\langle\hat{\Phi}_{s\alpha}^0|\mathbf{S}|\Phi_j{}^0\rangle\langle\Phi_j{}^0|\mathscr{H}_\sigma{}^1|\Phi_n{}^0\rangle}{E_n{}^0 - E_j{}^0}\right\}. \qquad \text{(III.4)}$$

Since the transition probability is expressed in terms of eigenfunctions of L^2, L_z, S^2, and S_z for which selection rules are well known (Condon and Shortley 1935) the first sum in Eq. (III.4) involves singlet-singlet transition moments only and the second sum contains triplet-triplet transition moments only. [The magnetic dipole terms in the second of Eqs. (III.4) are not considered further here.]

IV. Sources of Intensity in S–*T* Transitions

Partition of the first of Eqs. (III.4) shows that an electric dipole transition from a singlet ground state S_0 to a lowest triplet state T_1 obtains

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[1] Treating the part of $\mathscr{H}$ (i.e., $\mathscr{H}^1$) which does not commute with L^2, L_z, S^2 and S_z as a small perturbation. $\hat{\Phi}_{s\alpha}^0$ is the proper combination of triplet functions.

intensity through the following terms

$$\begin{aligned}\mathbf{M}(S_0, T_{1\alpha}) = \sum_{j\neq 0} \lambda_{1j}\mathbf{M}(S_0, S_j) + \sum_{k\neq 1} \Lambda_{0k}\mathbf{M}(T_1, T_k) \\ + \lambda_{10}\mathbf{M}(S_0, S_0) + \Lambda_{01}\mathbf{M}(T_1, T_1).\end{aligned} \qquad \text{(IV.1)}$$

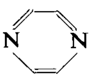
where

$$\lambda_{1j} = \frac{\langle \Phi_j{}^0 | \mathscr{H}_\mu{}^1 | \hat{\Phi}^0_{T_{1\alpha}} \rangle}{E^0_{T_1} - E^0_{S_j}} \quad \text{and} \quad \Lambda_{0i} = \frac{\langle \Phi_i{}^0 | \mathscr{H}_\mu{}^1 | \Phi^0_{s_0} \rangle}{E^0_{s_0} - - E^0_{T_i}}.$$

Equation (IV.1) shows that there are four electronic sources of intensity in $S_0 \rightarrow T_1$: (i) Spin-orbit interaction between the excited triplet and those excited singlet states to which an electronic promotion is allowed. Intensity is "stolen" in this process from allowed singlet-singlet transitions with transition moments $\mathbf{M}(S_0, S_j)$. (ii) Spin-orbit interaction between the ground state and those excited triplet states to which an electronic transition from T_1 is allowed. Intensity is stolen here from triplet-triplet transitions [transition moments $\mathbf{M}(T_1, T_k)$]. (iii) A contribution is obtained from the ground state dipole moment [$\mathbf{M}(S_0, S_0)$] through mixing of S_0 into T_1. (iv) Mixing of T_1 into S_0 produces a term containing $\mathbf{M}(T_1, T_1)$, the triplet state dipole moment.

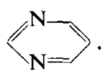
While the physical significance of a breakdown of intensity sources arising from a basis set of pure singlets and triplets is questionable, such an analysis provides a bridge between the spectroscopist and the theorist. The usefulness lies in its expression in terms of either known or understood transitions.

For atoms and nonpolar molecules, (iii) and (iv) vanish. For the $^1S_0$ atomic ground state, (ii) also vanishes. We concern ourselves with the importance of the four paths in molecular *S–T* transitions. To do this we consider the direction (polarization) of $\mathbf{M}(S_0, T_1)$ in two organic molecules with key symmetry properties:



pyrazine

and



pyrimidine

According to Eq. (IV.1) the polarization of $S_0 \rightarrow T_1$ is determined by the weighted average of the $S_0 \rightarrow S_j$ and $T_1 \rightarrow T_k$ transition moments and the dipole moments in the ground and triplet states. In pyrazine both dipole moment terms vanish. The $S_0 \rightarrow T_1$ transition has been rigorously assigned [see Lower and El-Sayed (1966) for references on assignments] as $^1A_g \rightarrow {}^3B_{2u}$ ($n\pi^*$) axes: (y out of plane, z parallel to *N–N*). The spin-orbital symmetry

(Weissman, 1950) of the T_1 components are then B_{1u}, A_u, and B_{3u}. An electric dipole transition from A_u to the A_g ground state is forbidden apart from any spin forbiddenness and the ${}^1A_g \rightarrow {}^1B_{1u}$ and ${}^1A_g \rightarrow {}^1B_{3u}$ path (i) moments are, respectively, z and x polarized. Similarly the ${}^3B_{2u} \rightarrow {}^3B_{3g}$ and ${}^3B_{2u} \rightarrow {}^3B_{1g}$ path (ii) moments are, respectively, z and x polarized.

Further insight can be gained by considering the local symmetry only. $\langle \Phi_i{}^0 | \mathscr{H}_\mu{}^1 | \hat{\Phi}^0_{T\alpha} \rangle$ will be zero unless $\Gamma(T) \cdot \Gamma(R_k) \cdot \Gamma(i) = A_g \, (k = x, y, z)$. Two types of matrix elements will be encountered: (1) between $S_j(\pi, \pi^*)$ and $T_1(n\pi^*)$ and (2) between $T(\sigma, \pi^*)$ or $T(\pi, \sigma^*)$ and S_0. These reduce over the three triplet components to $(\pi | \mathscr{H}^1_{x\mu} | n)$, $(\pi | \mathscr{H}^1_{y\mu} | n)$, and $(\pi | \mathscr{H}^1_{z\mu} | n)$. Since the operation of $\mathscr{H}^1_{x\mu}$ on n orbitals corresponds to rotating n around the x-axis and some other transformations which do not change the symmetry further the first term gives a nonvanishing contribution. Terms involving $\mathscr{H}_y{}^1$ and $\mathscr{H}_z{}^1$ vanish. We have then $B_{2u} \cdot B_{3g} \cdot \Gamma(S) = A_g$ requiring the path (i) perturbing singlets to have B_{1u} symmetry. The path

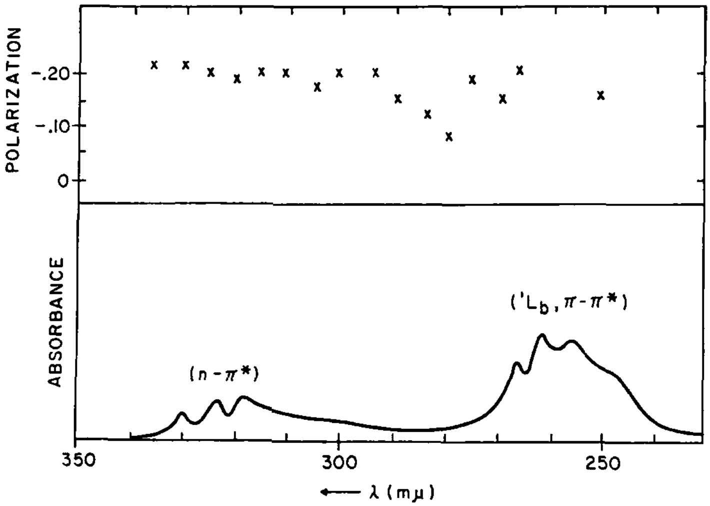


Fig. 1. Polarization[2] of the O—O band of T_1 ${}^3B_{2u}(n\pi^*) \rightarrow S_0$ emission of pyrazine in EPA at 77°K versus the exciting wavelength. The $n \rightarrow \pi^*$ absorption band is y polarized, the $\pi \rightarrow \pi^*$ (L_b) band is x polarized (y is out of plane and z is parallel to the N—N bond). The highly negative polarization to both absorption bands requires M(S_0, T_1) to be perpendicular to both, and thus z polarized.

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[2] Polarization is defined by $(I_\parallel - I_\perp)/I_\parallel + I_\perp$ where $\perp$ and $\parallel$ subscripts refer to emission intensity with perpendicular and parallel electric vectors to exciting electric vector.

(ii) condition $\Gamma(T) \cdot \Gamma(R_x) \cdot \Gamma(S_0) = \Gamma(T) \cdot B_{3g} \cdot A_g = A_g$ requires the perturbing triplet states to have B_{3g} symmetry. Hence $S_0 \rightarrow T_1$ is predicted to be z polarized, i.e., along the N–N axis.

Figure 1 shows the observed polarization spectrum for the pyrazine $T_1 \rightarrow S_0$ emission (Krishna and Goodman, 1961) verifying the predicted z-axis polarization. This experiment does not order the importance of path (ii) *vs.* path (i). However the polarization experiment is a powerful one and when applied to pyrimidine $T_1 \rightarrow S_0$ allows an elucidation. T_1 is quite definitely ${}^3B_1(n\pi^*)$ in this molecule (Krishna and Goodman, 1962) and the two perturbable components have A_1 and B_2 spin-orbital symmetries. The dominant term in the spin-orbit matrix elements should for pyrimidine (and pyrazine) T_1 be controlled by the residual atomic spin-orbit coupling at the nitrogen atoms (see Section V). Since the matrix elements between S_j and the two perturbable components of T_1 will differ only by the projection coefficients of n along x and z axes, the not very different II densities at the nitrogen atom in various $S_j(\pi, \pi^*)$ states, and the similar energy gaps between S_j and T_1 (Goodman and Krishna, 1962); the z polarized ${}^1A \rightarrow {}^1A$ and the x-polarized ${}^1A \rightarrow {}^1B$ path (i)

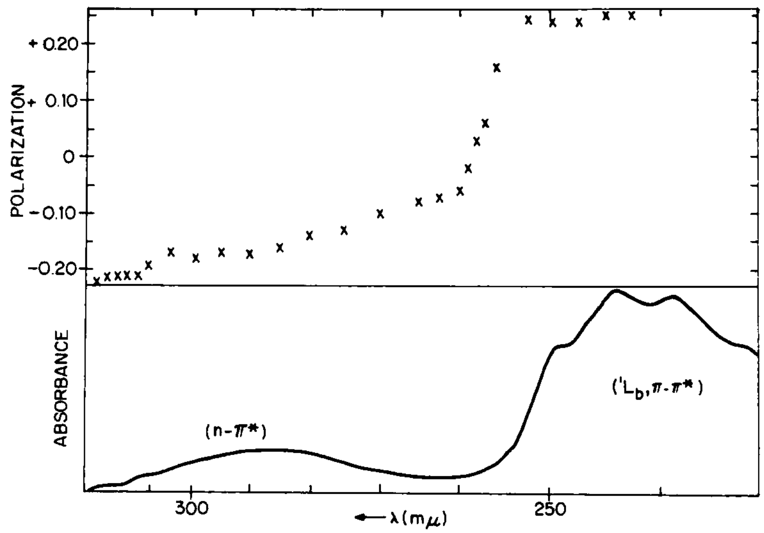
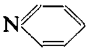


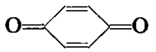
Fig. 2. Polarization[2] of the O—O band of T_1 ${}^3B_1(n\pi^*) \rightarrow S_0$ emission of pyrimidine in EPA at 77°K versus the exciting wavelength. The absorption bands are polarized as in Fig. 1. (z along the C_2 axis). The highly positive polarization to the L_b band requires $\mathrm{M}(S_0, T_1)$ to be x polarized.

transitions are expected to have approximately equal importance. The observed well-defined x-axis polarization shown in Fig. 2 indicates that other paths are dominant. The observed dipole moments in both the ground states and the excited states (Baba *et al.*, 1966, and references therein) are too small for paths (iii) and (iv) to be important. This leaves path (ii). The energy gap between S_0 and T_k is so great that this path can be dominant only if $\mathbf{M}(T_1, T_k)$ is large. In pyrimidine such opportunity exists. The n-electron excited to form T_1 has its origin in the antibonding (out-of-phase) combination of N lone pair orbitals. There is a T_k, probably T_2, which arises from promotion of an electron in the bonding (in-phase) combination to the same π^* orbital yielding a ${}^3B_2$ state [of correct symmetry to perturb $S_0({}^1A_1)$]. $\mathbf{M}(T_1, T_2)$ is similar to the strong $N \rightarrow V$ transitions found in homonuclear diatomic molecules (e.g., $\Sigma_g{}^+ \rightarrow \Sigma_u{}^-$ in $H_2{}^+$). Path (ii) should also be important in pyrazine. $\mathbf{M}(T_1, T_2)$ is estimated as ~ 6 debyes and the intensity of $S_0 \rightarrow T_1$ is predicted to be at least 10 times greater than for the analogous transition in pyridine



where path (ii) should be minor because of the lack of large $\mathbf{M}(T_1, T_k)$.

The unusually high intensity of $S_0 \rightarrow T_1$ (${}^3A_u(n\pi^*)$) in p-benzoquinone.



($f = 6.3 \times 10^{-7}$)

provides further corroboration for the importance of path (ii) (Hollas and Goodman, 1965). There is no particular reason to conclude that path (i) transition moments are unusually large for aromatic carbonyl compounds [e.g., $f(S_0, T_1) = 1.8 \times 10^{-7}$ for benzaldehyde $S_0 \rightarrow T_1$ (${}^3A'(n\pi^*)$) (Kanda *et al.*, 1964)]. The prominent O–O band demonstrates that intensification does not proceed through vibronic processes. However, the ${}^3A_u \rightarrow {}^3B_{1g}(T_1 \rightarrow T_2)$ (path ii) transition should be unusually strong for the same reasons given for pyrazine and pyrimidine.

It is feasible for paths (iii) and (iv) to be important for $S_0 \rightarrow T_1$ in polar molecules having dipole moments in the 3–5 debye range. A simple test of the importance of these paths could be provided by lowering the overall dipole moment of the molecule through polar group substitution, but still retaining the essential electronic and symmetry features. Pyridazine may provide an example where path (iii) provides the major source of intensity. In Section V paths (iii) and (iv) are calculated to be important in the case of formaldehyde.

V. Two-Electron Spin-Orbit Coupling

Partitioning $\mathscr{H}_\mu{}^1$ gives

$$\mathscr{H}_\mu{}^1 = \alpha^2 \sum_i \mathbf{F}_i \times \mathbf{p}_i \cdot \mathbf{S}_i - \alpha^2 \sum_{i \neq j} \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \cdot \mathbf{S}_i - 2\alpha^2 \sum_{i \neq j} \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \cdot \mathbf{S}_j. \qquad \text{(V.1)}$$

The first term represents the interaction of the nuclear field on the electron i, the second the spin-same orbit interaction, the third the spin-other orbit interaction. The fine structure constant $\alpha = e^2/4\pi\varepsilon_0 c$.

The importance of the atomic number on the probability of S–T transitions in atoms is well established (Condon and Shortley, 1935). In the atomic case $\mathbf{F}_i = Z\mathbf{r}_i/r_i{}^3$, and the matrix elements of Eq. (III.4) involving the nuclear field term become proportional to Z^4 for hydrogen-like atoms and still strongly Z-dependent for many-electron atoms. McClure's experiments on $S_0 \rightarrow T_1(\pi, \pi^*)$ intensities and $T_1(\pi, \pi^*) \rightarrow S_0$ lifetimes of halogen substituted hydrocarbons during 1949–1954 clearly established that molecular S–T transition probability also increases rapidly with an increase in halogen atomic number (see McClure, 1949, 1952; McClure *et al.*, 1954). These effects are so pronounced that little doubt remains that the increasingly large nuclear field term breaks the $\Delta S = 0$ selection rule. (Since McClure's work, the effect of either halogen substitution, or the parallel effect of intensity enhancement brought about by solvents containing a halogen atom of high atomic number, has frequently been used to identify $S \rightarrow T$ absorption bands.) Although the effect of the two-electron terms on atomic S–T transition probability has been explored by Breit and Teller (1940), Yilmaz (1955), Pluvinage (1952), Araki (1937), and others (particularly in the case of the ${}^1D - {}^3P$ and ${}^1P - {}^3D$ helium transitions), little has been done in the case of molecular S–T transitions. An exception is $T_1(\pi, \pi^*)$ in aromatic hydrocarbons. McClure (1952) showed that the nuclear field terms vanish between (π, π^*) states and Hameka and Oosterhoff (1958) calculated approximate two-electron matrix elements.

The usual procedure in calculating the spin-orbit matrix elements is to disregard the spin-other orbit interaction and to handle the spin-same orbit interaction by assuming that the electric field set up by both the nuclei and the electrons is spherically symmetric about each nucleus. With these assumptions $\mathbf{F}_i = \sum_u Z_u \mathbf{r}_{iu}/r_{iu}^3$ as in atoms, and the spin-same orbit interaction can be included in the nuclear field term if Z_u is replaced at each nucleus, u by an effective screened charge Z_u^{eff}. The spin-orbit Hamiltonian is then $\mathscr{H}_u' = \alpha^2 \sum_i \sum_u Z_u^{\text{eff}} (\mathbf{r}_{iu}/r_{iu}^3)\mathbf{P}_i \cdot \mathbf{S}_i$, and the calculation becomes much more tractable than it would be if the two electron terms were explicitly included.

Aside from the possibility that the above assumptions may be quantitatively unfounded (Blume and Watson, 1962; Hameka, 1965), they fundamentally alter the nature of the interaction Hamiltonian in that the two electron terms are eliminated. As a consequence, singlets doubly orthogonal to the triplet in question and triplets doubly orthogonal to the singlet in question are artificially excluded from contributing to $\mathrm{M}(S_0, T_1)$.

TABLE I

FORMALDEHYDE SPIN-ORBIT COUPLING MATRIX ELEMENTS[a,b]

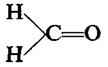
	Nuclear field	Spin-same orbit	Spin-other orbit	Total
Singlet configurations				
Interacting with T_1 $^3A_2(n\pi^*)$[c]				
Singly orthogonal A_1 configurations:				
S_0	9.64	0.03	0.09	9.75
$\frac{1}{2}n^2n'^2(\pi\bar{\pi}^* - \bar{\pi}\pi^*)$	6.63	0.03	0.04	6.68
Singly orthogonal B_1 configurations:				
$\frac{1}{2}\pi^2n^2(n'\bar{\pi}^* - \bar{n}'\pi^*)$	−7.65	−0.09	−0.21	−7.96
Doubly orthogonal B_1 configurations:				
$\frac{1}{2}n^2n'^2(\bar{\pi}\sigma^* - \pi\bar{\sigma}^*)$	− .0	0.01	−0.02	−0.01
Triplet configurations				
Interacting with ground state				
Singly orthogonal B_1 configurations:				
$\pi^2n'^2n\pi^*$	−9.64	−0.03	−0.09	9.75
$\pi^2n'^2n\sigma^*$	2.52	−0.01	0.03	2.54
Singly orthogonal A_2 configurations:	10.27	0.14	0.14	10.55
$\pi^2n^2n'\pi^*$				
Doubly orthogonal A_2 configurations:	0	−0.01	0.03	0.01
$n^2\pi n'\pi^{*2}$				

[a] In units of $a^2\xi^3 i \times 10^{-3}$ a.u., α is the fine structure constant. In atomic units $\alpha = e^2/4\pi\varepsilon_0 c \approx 1/137$, $i = \sqrt{-1}$. See Table II, Footnote *b*, for ξ.

[b] Pople *et al.* (1965) CNDO wave functions have been utilized. The results are not particularly sensitive to the wave function choice.

[c] n contains $O(2p_x)$, n' contains $O(2p_y - 2s)$ hybrids. See Footnote *c*, Table II, for axis orientation.

Spin-orbit coupling matrix elements for $T_1\ {}^3A_2(n\pi^*)$ in formaldehyde



are given in Table I (Ginsburg, 1967). Formaldeyde is chosen because the matrix elements are illustrative of those in a large class of molecules. Ginsburg used the methods developed by Blume and Watson (1962, 1963) to exactly calculate two-electron integrals over Slater $2p$ AO (Table II) for the formaldehyde ground state (c_{2v}) conformation. Pople *et al.* (1965) CNDO molecular orbitals have been utilized. They have explicitly treated all electrons except the $1s$ carbon and oxygen cores. The two molecular orbitals significantly more localized on the oxygen are designated $n(b_2)$ and

TABLE II

FORMALDEHYDE SPIN-ORBIT COUPLING INTEGRALS[a,b]

Integrals[c,d,e]	Value	Integrals[c,d,e]	Value
$\langle p_xp_z(V_{12})_yp_zp_z\rangle$	-1.219	$\langle sp_x(V_{12})_yp_zs\rangle$	1.836
$\langle p_yp_x(V_{12})_yp_yp_z\rangle$	1.830	$\langle p_yp_x(V_{12})_yp_zp_y\rangle$	-1.832
$\langle p_xp_x(V_{12})_yp_zp_x\rangle$	-1.223	$\langle p_xp_y(V_{12})_yp_zp_y\rangle$	2.442
$\langle p_xs(V_{12})_ysp_z\rangle$	$+1.851$	$\langle ss(V_{12})_xp_yp_z\rangle$	1.836
$\langle p_xp_z(V_{12})_zp_yp_z\rangle$	-2.442	$\langle p_ys(V_{12})_xsp_z\rangle$	-1.851
$\langle p_zp_x(V_{12})_zp_yp_z\rangle$	1.832	$\langle p_xp_y(V_{12})_xp_zp_x\rangle$	1.832
$\langle p_xp_z(V_{12})_zp_zp_y\rangle$	1.830	$\langle p_yp_x(V_{12})_xp_xp_z\rangle$	1.830
$\langle p_yp_x(V_{12})_zss\rangle$	$+1.836$	$\langle p_ys(V_{12})_xsp_z\rangle$	-1.851
$\langle sp_x(V_{12})_zp_ys\rangle$	-1.836	$\langle p_yp_z(V_{12})_xp_zp_z\rangle$	1.219
$\langle p_zp_y(V_{12})_xss\rangle$	$+1.836$	$\langle p_xs(V_{12})_zsp_y\rangle$	-1.851
$\langle sp_y(V_{12})_xp_zs\rangle$	-1.836	$\langle p_xp_y(V_{12})_zss\rangle$	-1.8512
$\langle p_yp_x(V_{12})_xp_zp_x\rangle$	-2.442	$\langle p_xp_y(V_{12})_zp_yp_y\rangle$	1.223
$\langle p_yp_y(V_{12})_xp_zp_y\rangle$	1.223	$\langle p_xp_x(V_{12})_zp_yp_x\rangle$	1.219
$\langle p_y(V_1)_xp_z\rangle$	$-44.605Z_{\text{eff}}$		

[a] In units of $\alpha^2\xi^3 i \times 10^{-3}$ a.u., α is the fine structure constant. In atomic units $\alpha = e^2/4\pi\varepsilon_0,c \approx 1/137$: $i = \sqrt{-1}$.

[b] The 0(2s) and 2p orbital exponents (ξ) were taken equal to 2.275. $Z^{\text{eff}} = 5.60$.

[c] $P_z = 0(2p_z)\cdot p_x = 0(2p_x)$, $s = 0(2s)$, y is parallel to the C=O bond, z is out of plane.

[d] Calculated by the Blume-Watson (1962, 1963) expansion procedure where $(V_{12})_x = \alpha^2[(\mathbf{r}_{12}/r_{12}^3) \times \mathbf{p}_1]_x$, $(V_1)_x = \alpha^2[(\mathbf{r}_1 \times p_1)/r_1{}^3]_x$, etc.

[e] The following integrals vanish: $\langle p_zp_x(V_{12})_yp_zp_z\rangle$, $\langle p_yp_x(V_{12})_yp_yp_z\rangle$, $\langle p_xp_x(V_{12})_yp_xp_z\rangle$, $\langle p_yp_y(V_{12})_xp_yp_z\rangle$, $\langle p_xp_x(V_{12})_zp_xp_y\rangle$, $\langle p_zp_x(V_{12})_zp_zp_y\rangle$, $\langle p_zp_y(V_{12})_xp_zp_z\rangle$, $\langle p_xp_y(V_{12})_xp_xp_z\rangle$, $\langle p_yp_y(V_{12})_zp_yp_y\rangle$.

$n'(a_1)$. Only one-center integrals are considered to effectively contribute to the spin-orbit coupling. The $1s$ electrons are not explicitly included in the Hamiltonian but are considered to act as a spherically symmetric charge distribution which modifies the nuclear field term by replacing Z with Z^{eff}. The summations in Eq. (V.1) then go over all n, σ, and π electrons. For formaldehyde there are no $B_2(n\pi^*)$ or $(\pi\pi^*)$ configurations, hence only B_1 and A_1 singlets can perturb T_1, and only B_1 or A_2 triplets can perturb S_0.

It is apparent that the two electron interactions are overwhelmed by the nuclear field term and that mixing of doubly-orthogonal configurations is unimportant. The first surprise is that the absolute magnitude of the spin-other orbit interaction is in some cases comparable or even larger than spin-same orbit interaction. It is interesting that the total effect of the two electron interactions is not always that of screening, i.e., the sign is the same as that of the nuclear field term.

The calculated path (i) contributions to the transition moment $\mathbf{M}(S_0, T_1)$ are (in a.u.)—1.00 for $n\sigma^*$, 0.01 for $\pi\sigma^*$, -0.14 for $n'\pi^*$, and -1.17 for $\pi\pi^*$. The path (ii) contributions are calculated to be 0.02 for $n'\pi^*$ and -0.12 for $n\sigma^*$, the path (iii) contribution to be 0.91, and path (iv) 0.62. Considering the present degree of accuracy attainable in molecular calculations, neglect of two electron interactions are justifiable when the nuclear field terms are sizeable as is exemplified by formaldehyde.

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REFERENCES

ARAKI, G. (1937). *Proc. Math. Soc. Japan* **19**, 128.

BABA, H., *et al.* (1966). *J. Am. Chem. Soc.* **88**, 5044.

BAKER, W. A., and GLOVER, F. N. (1955). *Phys. Rev.* **99**, 317.

BETHE, H. A., and SALPETER, E. E. (1957). Quantum Mechanics of One-and Two-Electron Systems. Springer-Verlag, Berlin.

BLUME, M., and WATSON, R. E. (1962). *Proc. Roy. Soc.* (*London*) **A270**, 127.

BLUME, M., and WATSON, R. E. (1963). *Proc. Roy. Soc.* (*London*) **A271**, 565.

BREIT, G. (1929). *Phys. Rev.* **34**, 553.

BREIT, G., and TELLER, E. (1940) *Astrophys. J.* **91**, 215.

CHRAPLYVY, Z. V. (1953). *Phys. Rev.* **91**, 388; **92**, 1310.

Condon, E. V., and Shortley, G. H. (1935). "The Theory of Atomic Spectra." Cambridge Univ. Press, London and New York.

Dirac, P. A. M. (1958). "The Principles of Quantum Mechanics." Oxford Univ. Press, London and New York.

Englman, R. (1966). *J. Chem. Phys.* **45**, 2669.

Foldy. L. L., and Wouthuysen, S. A. (1950). *Phys. Rev.* **78**, 29.

Ginsburg, J. L. (1967). Thesis, Rutgers University.

Goodman, L., and Krishna V. G. (1962). *J. Chem. Phys.* **37**, 2721.

Hameka, H. F. (1965). "Advanced Quantum Chemistry." Addison-Wesley, Reading, Massachusetts.

Hameka, H. F., and Goodman. L. (1965). *J. Chem. Phys.* **42**, 2305.

Hameka, H. F., and Oosterhoff, L. (1958). *Mol. Phys.* **1**, 358.

Hochstrasser, R. M. (1966). "Molecular Aspects of Symmetry." Benjamin, New York.

Hollas, J. M., and Goodman, L. (1965). *J. Chem. Phys.* **43**, 760.

Itoh, T. (1965). *Rev. Mod. Phys.* **37**, 159.

Kanda *et al.* (1964). *Spectrochim. Acta* **20**, 1387.

Kasha, M., and McGlynn, S. P. (1956). *Ann. Rev. Phys. Chem.* **7**, 403.

Kowalski, I. von (1911). *Physik Z.* **12**, 956.

Kramers, H. A. (1958). "Quantum Mechanics." North-Holland, Amsterdam.

Krishna, V. G., and Goodman, L. (1961). *Nature* **191**, 800.

Krishna, V. G., and Goodman L. (1962). *J. Chem. Phys.* **36**, 2217.

Kursunoğlu, B. (1956). *Phys. Rev.* **101**, 1419.

Lewis, G. N., and Kasha, M. (1944). *J. Am. Chem. Soc.* **66**, 2100.

Lohr, L. L. (1966). *J. Chem. Phys.* **45**, 1362.

Lower, S. K., and El-Sayed, M. A. (1966). *Chem. Rev.* **66**, 199.

McClure, D. S. (1949). *J. Chem. Phys.* **17**, 905.

McClure, D. S. (1952). *J. Chem. Phys.* **20**, 682.

McClure, D. S., *et al.* (1954). *J. Chem. Phys.* **22**, 255.

Merzbacher, E. (1960). "Quantum Mechanics." Wiley, New York.

Pluvinage, P. (1952). *J. Phys. Radium* **13**, 405.

Pople, J. A., Santry and Segal, G. A. (1965). *J. Chem. Phys.* **43**, S129.

Sklar, A. L. (1937). *J. Chem. Phys.* **5**, 699.

Slater, J. C. (1960). "Quantum Theory of Atomic Structure," Vol. II. McGraw-Hill, New York.

Terenin, A. (1943). *Acta Physiochim. URSS* **18**, 210.

Terenin, A. (1944). *Zh. Fiz. Khim.* **18**, 1.

Weissman, S. (1950). *J. Chem. Phys.* **18**, 232.

Yilmaz, H. (1955). *Phys. Rev.* **100**, 1148.

Molecular Orbital Theories of Inorganic Complexes

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I. Introduction

The crystal field theory, as formulated by Bethe and Van Vleck in the early thirties, has in the last years enjoyed considerable attention. As a result, the nature of nearly all the low lying electronic levels in complexes containing an unfilled *d* shell is by now pretty well understood. However, the characterization of the higher lying states of such complexes, the so-called charge transfer states, not to speak of the excited states of complexes with no *d* electrons as MnO_4^- etc., remains uncertain.

It is believed that molecular orbital (MO) theories are able to extend our knowledge about transition metal complexes considerably, and there has accordingly also been great interest in developing such theories. Now, molecular orbital theories are presented on various levels of sophistication; a natural division is into empirical, semi-empirical, semiquantitative, and quantitative theories. The present report concerns itself mainly with the development of semi-empirical and semiquantitative theories.

The semi-empirical theories can, after their very nature, only give a very rough picture of a certain complex, but they are nevertheless of great utility. They parallel the Hückel methods of organic chemistry, and like these, they are particularly useful when special trends in a homolog series of compounds are to be reflected. The semiquantitative theories have as their counterparts in organic chemistry the methods of Pariser, Parr, and Pople. They are not yet as developed as the latter, essentially because the higher quantum numbers of the orbitals involved makes the evaluation of integrals considerably more difficult in the treatment of inorganic complexes.

Much effort has gone into constructing MO theories which will reproduce the value of the well-known crystal field parameter 10 *Dq*, or Δ. However, we do not think that this should be the primary goal for a MO theory. The crystal field parameter is of penultimate importance in accounting for the *d*-*d* transitions, but the nature of these is, as already said, well understood. No MO theory can hope to do better than the "complete crystal field theory," i.e., operations solely with 10*Dq*, the atomic integrals F_2 and F_4, and the spin-orbit coupling parameter λ. As is well known, the energy diagrams resulting from this theory can reproduce the crystal field bands to within a few hundred wavenumbers (Tanabe and Sugano, 1954; Liehr and Ballhausen, 1959; Liehr, 1963).

Apart from a characterization of the electronic ground state of a complex, it is in the elucidation of charge transfer states that MO theories have one of their great missions. For this purpose, the value of 10*Dq* is of little importance. We can, of course, check whether the quantity is reasonable when calculated, but we have no guarantee that a good value of 10 *Dq* also means that the calculated charge transfer states will be placed correctly.

Our aim, then, in this report is to try to make some progress towards the understanding of the "charge transfer states" in inorganic complexes. As is to be expected, electron-electron interaction terms are of great importance in the description of such states, and we shall discuss these terms at considerable length, since, frequently, insufficient attention is paid to this aspect.

II. General Considerations

Consider some inorganic complex made up of a central metal ion and a number of ligand ions. For simplicity, we assume the metal ion to belong to the first transition series, and the ligand ions are assumed to belong to the second period in the periodic table. These restrictions are trivial and can be removed without any change of the formalism. We define a core consisting of the metal and ligand nuclei, the 1*s* electrons of the ligands, and the 18 electrons in the "argon core" of the metal. The core electrons are assumed to reside in the same atomic orbitals as in the free ions; thus we assume the core to be unpolarized by molecular formation. This assumption may have to be modified for very special applications, but such modifications are far beyond the scope of the present report.

The remaining electrons in the complex are considered as "valence electrons." They are assigned, not more than two at a time, to molecular orbitals (MO's), extending over all ions in the complex. In all applications these MO's, φ_i, are represented as linear combinations of atomic orbitals (LCAO's), χ_r. Thus

$$\varphi_i = \sum_r C_{ri}\chi_r. \tag{II.1}$$

The atomic orbitals χ_r are usually chosen as free ion orbitals, viz. 3*d*, 4*s*, and 4*p* for the metal ion, and 2*s* and 2*p* for the ligands. The quantities to be determined are the coefficients C_{ri}.

Ideally, the molecular orbitals should satisfy the Hartree-Fock equations

$$\hat{H}(1)\varphi_i(1) = \varepsilon_i\varphi_i(1), \tag{II.2}$$

with the effective Hamiltonian $\hat{H}$ defined as

$$\hat{H}(1) = \hat{H}^{\text{core}}(1) + \hat{G}(1). \tag{II.3}$$

Here $\hat{H}^{\text{core}}(1)$ includes the kinetic energy operator ($-\nabla_1{}^2/2$ in atomic units) as well as the interaction between a valence electron and the core. $\hat{G}(1)$ accounts for the interaction between the valence electron considered and all the other valence electrons in the complex. In the case of a closed-shell configuration we have the expression

$$\hat{G}(1) = \sum_{j=1}^{n} (2\hat{J}_j - \hat{K}_j), \tag{II.4}$$

if there are n doubly-occupied valence orbitals. $\hat{J}_j$ and $\hat{K}_j$ are the usual Coulomb and exchange operators. By definition,

$$\hat{J}_j\varphi_i(1) = \int \varphi_j^*(2)\varphi_j(2)\frac{1}{r_{12}}\,d\tau_2 \cdot \varphi_i(1), \tag{II.5}$$

$$\hat{K}_j\varphi_i(1) = \int \varphi_j^*(2)\varphi_i(2)\frac{1}{r_{12}}\,d\tau_2 \cdot \varphi_j(1). \tag{II.6}$$

In the LCAO approximation, (II.2) is replaced by the matrix equations

$$\sum_s H_{rs}C_{si} = \varepsilon_i \sum_s S_{rs}\,C_{si}, \tag{II.7}$$

$$\mathbf{H}\mathbf{C}_i = \varepsilon_i\mathbf{S}\mathbf{C}_i, \tag{II.8}$$

where $\mathbf{C}_i$ is a column vector representing the ith MO:

$$\mathbf{C}_i = \begin{bmatrix} C_{1i} \\ C_{2i} \\ \cdot \\ \cdot \\ \cdot \end{bmatrix}, \tag{II.9}$$

and

$$H_{rs} = \int \chi_r^*(1)\hat{H}(1)\chi_s(1)\,d\tau_1, \tag{II.10}$$

$$S_{rs} = \int \chi_r^*(1)\chi_s(1)\,d\tau_1. \tag{II.11}$$

The orbital energies ε_i are found as the roots of the secular equation

$$|\mathbf{H} - \varepsilon\mathbf{S}| = 0, \tag{II.12}$$

and, assuming the molecular orbitals to be normalized, we have

$$\varepsilon_i = \int \varphi_i^*(1)\hat{H}\varphi_i(1)\,d\tau_1 = \sum_{r,s} C_{ri}^*H_{rs}C_{si}. \tag{II.13}$$

According to Koopmans' theorem, $-\varepsilon_i$ represents an ionization energy, namely, the energy required to remove an electron from the orbital φ_i.

It is well known that the secular problem (II.12) is considerably reduced by using symmetry adapted functions, i.e., functions which span the irreducible representations of the point group characterizing the complex under consideration. The construction of these "basis functions" is described in

TABLE I

BASIS FUNCTIONS FOR T_d MOLECULES[a]

Irreducible representation	Row	Metal orbitals	Ligand orbitals
a_1	1	s	$\frac{1}{2}(s_1+s_2+s_3+s_4)$, $\frac{1}{2}(p_{z1}+p_{z2}+p_{z3}+p_{z4})$
e	1	d_{z^2}	$\frac{1}{2}(p_{x1}-p_{x2}-p_{x3}+p_{x4})$
	2	$d_{x^2-y^2}$	$\frac{1}{2}(p_{y1}-p_{y2}-p_{y3}+p_{y4})$
t_2	1	p_x, d_{yz}	$\frac{1}{2}(p_{z1}-p_{z2}+p_{z3}-p_{z4})$, $\frac{1}{2}(s_1-s_2+s_3-s_4)$, $\frac{1}{4}[p_{x1}+p_{x2}-p_{x3}-p_{x4}+\sqrt{3}(-p_{y1}-p_{y2}+p_{y3}+p_{y4})]$
	2	p_y, d_{xz}	$\frac{1}{2}(p_{z1}+p_{z2}-p_{z3}-p_{z4})$, $\frac{1}{2}(s_1+s_2-s_3-s_4)$, $\frac{1}{4}[p_{x1}-p_{x2}+p_{x3}-p_{x4}+\sqrt{3}(p_{y1}-p_{y2}+p_{y3}-p_{y4})]$
	3	p_z, d_{xy}	$\frac{1}{2}(p_{z1}-p_{z2}-p_{z3}+p_{z4})$, $\frac{1}{2}(s_1-s_2-s_3+s_4)$, $-\frac{1}{2}(p_{x1}+p_{x2}+p_{x3}+p_{x4})$
t_1	1		$\frac{1}{4}[\sqrt{3}(p_{x1}+p_{x2}-p_{x3}-p_{x4})+p_{y1}+p_{y2}-p_{y3}-p_{y4}]$
	2		$-\frac{1}{4}[\sqrt{3}(p_{x1}-p_{x2}+p_{x3}-p_{x4})-p_{y1}+p_{y2}-p_{y3}+p_{y4}]$
	3		$-\frac{1}{2}(p_{y1}+p_{y2}+p_{y3}+p_{y4})$

[a] Referred to the coordinate system shown in Fig. 1.

most elementary textbooks (see e.g., Ballhausen and Gray, 1964). As an example, we list in Table I the basis functions for a tetrahedral complex, using the coordinate system of Fig. 1. In the following we shall often assume

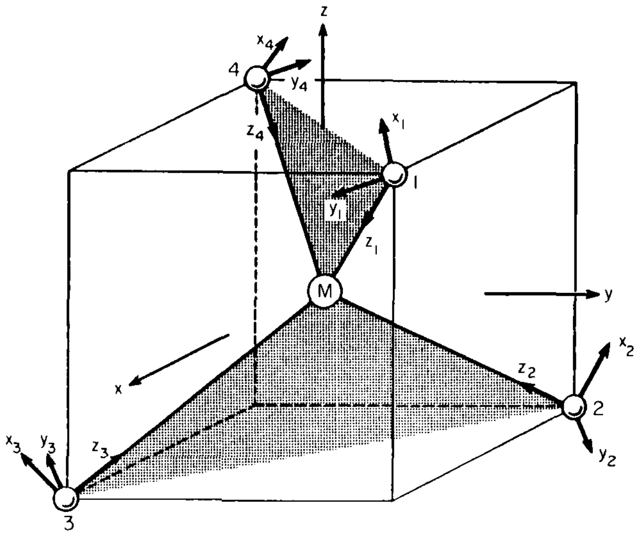

Fig. 1. Coordinate system for a tetrahedral complex.

that the functions χ_r of Eq. (II.1) are symmetry-adapted. Only functions transforming in exactly the same way can combine to form molecular orbitals; hence (II.12) is replaced by a set of secular equations, one for each irreducible representation. In our tetrahedral example, the secular equation for the a_1 orbitals will be of order 3, the equation for the e orbitals of order 2. When symmetry-adapted functions are used we often refer to the integrals (II.10) and (II.11) as group integrals, and distinguish them by means of a tilde.

The determination of the matrix elements H_{rs} of the effective Hamiltonian is of course the crucial point in any MO theory. Once the matrices **H** and **S** are known, the solution of (II.12) and (II.8) is rather trivial.

In Table II we represent the results from a MO calculation for the MnO_4^- ion (Viste and Gray, 1964), and Fig. 2 shows the corresponding energy level diagram. The calculation was performed using the extended Wolfsberg-Helmholz method. However, the actual mode of calculation is not an important point at the present time; rather, we are interested in some general features.

TABLE II

MOLECULAR ORBITALS FOR MnO_4^- (EIGENVALUES IN UNITS OF 10^3 CM^{-1})

	Eigenvalues	Eigenvectors				
		s	σ_s	σ_p		
a_1	128.75	1.37	−0.98	−0.25		
	−112.11	−0.03	0.13	−1.00		
	−276.54	0.12	0.92	0.01		
		d	π			
e	−72.98	−0.72	0.90			
	−136.56	0.74	0.51			
		p	σ_p	d	σ_s	π
t_2	−18.83	1.08	0.06	0.24	−0.42	0.27
	−49.29	−0.14	−0.67	0.80	−0.30	−0.58
	−105.65	0.02	0.69	0.13	−0.07	−0.67
	−126.26	−0.17	0.35	0.63	−0.17	0.49
	−260.45	0.03	0.02	−0.16	−0.96	0.03
		π				
t_1	−96.40	1.00				

First we notice that the MO's which correspond to the e and t_2 orbitals of crystal field theory are the orbitals $2e$ and $4t_2$. These orbitals are empty in MnO_4^-, but may hold electrons in other tetrahedral complexes. From Tables I and II it is clear that the $2e$ orbitals are linear combinations of the $3d$ metal orbitals and the ligand π orbitals, whereas the $4t_2$ orbitals are of a more complex nature. Not only do they include σ as well as π ligand orbitals, but the metal character is not pure d type, as $4p$ orbitals are involved. This dissimilarity makes it clear that the energy difference

$$\varepsilon(4t_2) - \varepsilon(2e)$$

is very sensitive to the choice of matrix elements in (II.12). Since this energy difference is closely related to the crystal field parameter $10Dq$ (but in general not equal to it, as discussed later), *a priori* calculations of the latter quantity is an extremely difficult matter.

A point of great interest is the distribution of the metal $4s$ and $4p$ orbitals among the molecular orbitals. The trends of Table II are common to all MO calculations performed; the $4s$ and $4p$ orbitals have high energies as compared to the other basis orbitals, and as a consequence, they enter with small coefficients in all MO's except the highest ones, $\varphi(5t_2)$ and $\varphi(3a_1)$. These latter orbitals can, on the other hand, to a first approxima-

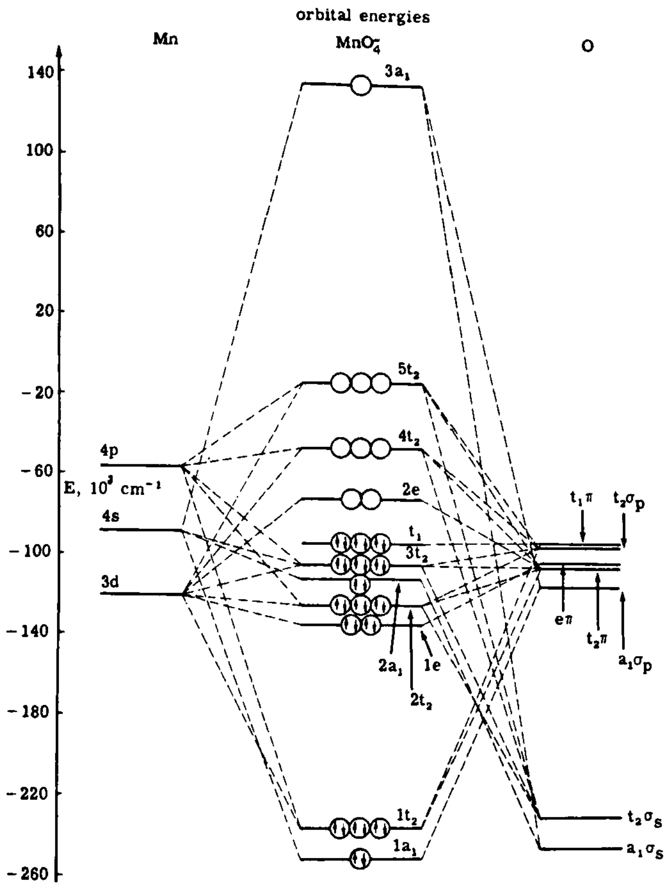

Fig. 2. Molecular orbital energy level diagram for MnO_4^-.

tion, be considered as $4s$ and $4p$ orbitals which have been orthogonalized to the ligand basis functions. By the Schmidt procedure we find, for instance, that an orthogonalized $4s$ orbital has the form

$$\chi'(4s) = N[\chi(4s) - S(4s, \sigma_s)\chi(\sigma_s) - S(4s, \sigma_p)\chi(\sigma_p)], \qquad \text{(II.14)}$$

where N is a normalizing factor. Using the overlap integrals appropriate to the calculation in Table II, we find

$$\chi'(4s) = 1.37\chi(4s) - 0.91\chi(\sigma_s) - 0.30\chi(\sigma_p). \qquad \text{(II.15)}$$

The similarity with $\varphi(3a_1)$ is striking.

This observation suggests the use of Schmidt orthogonalized $4s$ and $4p$ orbitals as basis functions in MO calculations, instead of pure $4s$ and $4p$ orbitals. The distinction is really only a formal one, but it gives a better understanding of the functioning of the $4s$ and $4p$ orbitals. Notice that they play much the same role as plane waves in energy band calculations on crystals, and that the MO's $5t_2$ and $3a_1$ are parallel to the crystal conduction bands. As long as an isolated complex unit is considered, the analogy is purely formal, but when the unit is embedded in a crystal, the $4s$ and $4p$ orbitals on neighboring sites may overlap quite strongly, and the $3a_1$ and $5t_2$ levels will broaden into conduction bands of the crystal. It is clear that this fact makes the proper choice of $4s$ and $4p$ basis orbitals quite difficult in MO calculations.

After these general considerations we shall now pass on to a discussion of the actual methods used in setting up and solving the secular equation (II.12).

III. Semiempirical MO Theories

A. The Wolfsberg–Helmholz (W–H) Method

The first attempt to solve the secular equation (II.12) for an inorganic complex was due to Wolfsberg and Helmholz (1952). The following simplifications were introduced.

(1) The values of H_{rr}, the energy of an electron in the rth atomic orbital in the field of the core and the remaining valence electrons, were estimated close to the valence state ionization potentials for the central metal and for the ligands. The chosen values were varied by trial and error until the first and second excitation energies were qualitatively correct and until the resulting charge distribution approximated the assumed one.

(2) H_{rs} were approximated as

$$H_{rs} = F_x \tilde{S}_{rs} \tfrac{1}{2}(H_{rr} + H_{ss}), \qquad \text{(III.1)}$$

where $\tilde{S}_{rs}$ is the group overlap. The values of F_x were taken as $F_\sigma = 1.67$ for σ overlaps and $F_\pi = 2.00$ for π overlaps. These values of F were taken from energy calculations of homonuclear diatomic molecules.

(3) The wave functions occurring in the LCAO were taken as analytical atomic wave-functions which approximated the existing SCF functions.

Using these simplifications, the ground and excited states energies of the MnO_4^- and $CrO_4^=$ ions were calculated. The result was certainly promising, but a number of curious features emerged.

Most important, Wolfsberg and Helmholz found a remarkable stabilization of the non-σ bonding metal orbital of symmetry e due to π bonding. As a consequence of this, the empty e_π is placed at a very high energy. From crystal field theory one would expect the e_π orbital to be the lowest empty orbital, consequently a slightly altered semi-empirical level scheme which took these features into account was proposed (Ballhausen and Liehr, 1958).

B. The Extended W–H Method

The available tables of atomic states show clearly that the d, s, and p valence state ionization energies (VSIE's) are strong functions of the charge and orbital configuration of the metal atom. With the off-diagonal elements approximated as in the W–H method, everything depends critically on the evaluation of H_{rr} and S_{rs}. In the extended W–H method (Ballhausen and Gray, 1962), it is assumed that a metal VSIE for a particular configuration (say d^n) can be represented by

$$\text{VSIE} = Aq^2 + Bq + C,$$

where q is the charge on the metal. Such functions can be calculated from, e.g., Moore's Tables of Atomic States (C. E. Moore, 1958).

The ligand VSIE's are given fixed, chemically "reasonable" values, close to the ionization potentials of the neutral atoms or values for an appropriate hydride (H_2O). The group overlaps are calculated using the best available SCF orbitals, from known bond distances.

For the solution of the secular equations, one assumes an input electronic configuration and charge on the metal. The H_{rr}'s for the metal are then computed, and put into the secular equation together with S_{rs}. For each of the MO's calculated, a Mulliken population analysis (Mulliken, 1955) is performed, in which each overlap population is divided equally between the metal— and combined ligand—orbital. In subsequent cycles the input configuration is altered until a self-consistent charge distribution is obtained.

The calculations performed in this way upon MnO_4^- (Viste and Gray, 1964), yielded a level scheme consistent with the proposed semi-empirical molecular orbital energy diagram. Furthermore, a great many other metal complexes have been treated in an analogous way, seemingly with reasonable results (Lohr and Lipscomb, 1963; Bedon *et al.*, 1964, 1965; Hatfield *et al.*, 1965; Wirth, 1965; Basch *et al.*, 1966; Johansen and Ballhausen, 1966; Ingraham, 1966; J. W. Moore, 1966; Valenti and Dahl, 1966; Yeranos, 1966).

C. Critique of the W–H Method

As the method has been developed (see, e.g., Ballhausen and Gray, 1964), Cotton and Haas (1964), and Fenske (1965) have leveled some critique against the procedure. It was pointed out that the use of constant F factors in the off-diagonal elements (see Eq. (III.1)) and the neglect of variation of the VSIE for the ligands, lead to minor variations of the calculated levels. This critique is certainly valid, but it is hardly the most serious criticism which can be raised.

Fenske (1965) points out further that the "hybrid mixing parameter" occurring when the $2s_\sigma$ and $2p_\sigma$ ligand orbitals are hybridized is an all-dominating factor. This point is well taken; it transpires that it is better not to hybridize the ligand σ orbitals, but to use a double σ basis set ($2s$, $2p$) in tetrahedral complexes.

Apart from the question of the values of F_σ and F_π, Fenske also comments that the placement of the antibonding orbitals is very sensitive to the chosen values of the Coulomb terms H_{rr}. This is particularly the case if $H_{rr} \gg H_{ss}$; with $H_{rs} = F\tilde{S}_{rs}(H_{rr}H_{ss})^{1/2}$ (Ballhausen and Gray, 1962) very little happens to the bonding level, but the antibonding level is pushed way up. This effect is, however, entirely natural since it simply shows the large polarization effects. This point can thus not be used against the method.

Cotton and Haas (1964) and Fenske (1965) approached the problem of the "goodness of the method" from the experimental side, wanting to have the theory fit the spectral data "exactly." In doing so, they apparently did not realize two very important features of the theory. The first is that the form (III.1) of the W–H off-diagonal element makes the electron "interact with itself." This can easily introduce an error of about 5 eV into the off-diagonal element. This feature is an inherent serious source of error in any W–H-like method of estimating the off-diagonal matrix element. Their second mistake lies in not realizing that $10Dq$ for octahedral complexes in the crystal field method is defined as $\varepsilon^{\text{core}}(e) - \varepsilon^{\text{core}}(t_2)$, while the single orbital energies obtained from the W–H method are more like ε^{SCF}'s. The difference between the calculated W–H energies of the t_2 and e electrons is therefore not equal to $10Dq$. The argumentation is that since H_{rr}'s are estimated as ionization energies, these quantities correspond to the ε^{SCF} in Roothaan's theory (Roothaan, 1951a). It is true that the W–H approximation used for the off-diagonal element is not consistent with this approach. Nevertheless one expects certainly the found molecular orbitals energies to be "closer" to the ε^{SCF}'s than to the $\varepsilon^{\text{core}}$'s. The appropriateness of Cotton and Fenske's argumentation is therefore questionable. As an example of the correct way of using the W–H method we refer to the work of Zerner and Gouterman (1966).

The use of atomic valence state ionization energies to estimate the diagonal terms H_{ii} in the secular equation has been criticized by Ros and Schuit (1966). These authors proposed instead the use of the full molecular Hamiltonian for the evaluation of H_{ii}. However, in the potential function the energy of an electron in the field of the surrounding nuclei were taken together with the Coulomb and exchange interactions of the electron with the electrons centered on these nuclei and estimated using a screened Coulomb potential. The H_{ij} terms were again approximated as in the W–H method.

In the calculation of H_{ij} and S_{ij}, a "variation" atomic configuration $M(d^{10-A}, s^B, p^C)L^{-D}$ was used and A, B, C, and D varied until the initial and final charge distribution was identical. It is, however, seen that the calculation of the off-diagonal element still suffers from the same inherent errors we have discussed above, and it is therefore highly doubtful whether a possible refinement of the diagonal terms only, will lead to an improvement over the W–H scheme.

The extended Wolfsberg-Helmholz methods can in many ways be paralleled with the ω-techniques developed by Wheland, Mann, and Streitwieser in π-electron theory (see, e.g., Streitwieser, 1961). One must abandon a great deal of rigor in order to get fast results. Nevertheless, the non realization of the scope and validity of semiempirical MO theories is very common in the current literature. A result obtained by such a theory indicates that one possibility is perhaps more likely than others. The consequences of exploring in that direction should then be tested by experiments. One cannot and must not demand more than a prediction or perhaps a rationalization from such a theory.

In the following sections we shall outline some more general MO theories than that of Wolfsberg and Helmholz. It is, however, clear that many of the attractive, simple features of this theory thereby have to be abandoned.

IV. Semiquantitative MO Theories

A. Introductory Remarks

A semiquantitative theory arises when certain approximations are made in a quantitative theory, and its success is highly dependent on the nature of these approximations. A theory of this kind cannot be expected to give an elaborated picture of the true affairs, but merely a rough outline. Many details are swept away by the approximations, and the resulting picture is more or less distorted; it must be expected, indeed, that it is misleading, unless the approximations are very well balanced.

Molecular orbital calculations on complex compounds can at present only be carried through along the semiquantitative lines, and even then they tend to become rather involved. Unfortunately, there is a tendency to demand that such calculations give exact results, and this has led to the introduction of scale factors at certain stages of the calculations. The values of these factors are determined so that one or two experimental numbers can be reproduced by the theory and the role of the scale factors is believed to be to compensate for the approximations made on the way. The unfortunate thing is that this brings with it a tendency not to be particular enough about the nature of the approximations made, because it is felt that the scale factors will re-establish everything. For this reason, there exists in the literature several approximations which are inconsistent, from either a physical or a mathematical point of view.

In the following analysis of semiquantitative MO theories, we start from the Hartree–Fock equations in Roothaan's matrix form and discuss the nature of various approximations. A new semiquantitative theory is also suggested, and applied to the permanganate ion. This theory deals with the metal *s*- and *p*-orbitals in a more detailed way than is usually the case in such calculations, and it demonstrates that it is possible to carry through semiquantitative calculations without excessive use of empirical parameters.

B. The Hartree–Fock Equations

The present section contains some definitions, equations, and remarks which will be referred to in the following discussion. Some characteristics of the Hartree–Fock equations are discussed, and expressions for excitation energies derived. The form of the core operator is also touched on.

Consider a system of N valence electrons. Following the general outlines of Section II, we assume an N-electron Hamiltonian of the form

$$\hat{\mathscr{H}} = \sum_{i=1}^{N} \hat{H}^{\text{core}}(i) + \frac{1}{2} \sum_{i,j=1}^{N}{}' \frac{e^2}{r_{ij}}, \tag{IV.1}$$

where the prime on the summation sign for the double sum indicates that terms for which $i = j$ are to be omitted. The N-electron wave function for a particular state of the electronic system may be represented as a linear combination of Slater determinants, a single determinant being of the form

$$\Phi = |\psi_1\psi_2 \cdots \psi_N| = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix}, \qquad \text{(IV.2)}$$

where $\psi_i(j)$ stands for the *i*th spin orbital as a function of the space and spin coordinates of the *j*th electron. The spin orbitals are assumed to be simple products of α- or β-spin functions and pure space orbitals (molecular orbitals) φ_i, thus:

$$\psi_i(1) = \varphi_i(x_1, y_1, z_1)\alpha(\sigma_1) = \overset{+}{\varphi}_i(1), \qquad \text{(IV.3a)}$$

or

$$\psi_i(1) = \varphi_i(x_1, y_1, z_1)\beta(\sigma_1) = \overset{-}{\varphi}_i(1). \qquad \text{(IV.3b)}$$

In what follows we assume, for simplicity, that the complex under consideration has a totally symmetric ground state, so that we are dealing with a "closed shell" of electrons.

We approximate the ground state wave function with a single determinant:

$$\Psi_0 = |\overset{+}{\varphi}_1\overset{-}{\varphi}_1\overset{+}{\varphi}_2\overset{-}{\varphi}_2 \cdots \overset{+}{\varphi}_n\overset{-}{\varphi}_n|, \qquad \text{(IV.4)}$$

letting $2n = N$ denote the number of valence electrons.

For the ground state energy we obtain, by combining Eqs. (IV.1) and (IV.4):

$$E_0 = 2\sum_{i=1}^{n} (\varphi_i|H^{\text{core}}|\varphi_i) + \sum_{i,j=1}^{n} (2J_{ij} - K_{ij}), \qquad \text{(IV.5)}$$

where

$$(\varphi_i|H^{\text{core}}|\varphi_i) = \int \varphi_i^*(1)\hat{H}^{\text{core}}(1)\varphi_i(1)\, d\tau_1, \qquad \text{(IV.6)}$$

$$J_{ij} = [\varphi_i\varphi_i \mid \varphi_j\varphi_j] = \iint \varphi_i^*(1)\varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_i(1)\varphi_j(2)\, d\tau_1\, d\tau_2, \qquad \text{(IV.7)}$$

$$K_{ij} = [\varphi_i\varphi_j \mid \varphi_j\varphi_i] = \iint \varphi_i^*(1)\varphi_j^*(2)\frac{e^2}{r_{12}}\varphi_j(1)\varphi_i(2)\, d\tau_1\, d\tau_2. \qquad \text{(IV.8)}$$

The Coulomb integral J_{ij} can be interpreted as the electrostatic interaction between an electron with the charge distribution $\varphi_i^*(1)\varphi_i(1)$ and an electron with the charge distribution $\varphi_j^*(2)\varphi_j(2)$. Similarly, K_{ij} measures the interaction between the charge distributions $\varphi_i^*(1)\varphi_j(1)$ and $\varphi_j^*(2)\varphi_i(2)$. We note that

$$J_{ii} = K_{ii}. \tag{IV.9}$$

So far, no procedure has been devised for obtaining the molecular orbitals $\varphi_1, \varphi_2, \ldots, \varphi_n$ themselves. According to the variation principle, they should be determined in such a way that the energy E_0 be minimized. This criterion leads to the Hartree–Fock equations for the orbitals φ_i (see, e.g., Roothaan, 1951a):

$$\left\{\hat{H}^{\mathrm{core}}(1) + \sum_{j=1}^{n} (2\hat{J}_j - \hat{K}_j)\right\}\varphi_i(1) = \varepsilon_i\varphi_i(1), \tag{IV.10}$$

with the Coulomb and exchange operators $\hat{J}_j$ and $\hat{K}_j$ as defined in Eqs. (II.5 and II.6). $\hat{J}_j$ may be considered as the electrostatic potential from an electron in φ_j, whereas $\hat{K}_j$ has no classical interpretation. From the definitions it follows that

$$\hat{J}_i\varphi_i(1) = \hat{K}_i\varphi_i(1). \tag{IV.11}$$

As in Section II, we interpret (IV.10) as a one-electron Schrödinger equation. $\hat{H}^{\mathrm{core}}(1)$ gives the kinetic energy and the interaction with the core, and will be discussed in more detail in the following. To interpret the terms in the sum we imagine that the electron in φ_i is in a certain spin state (α or β). The jth orbital is doubly occupied, and $\hat{J}_j - \hat{K}_j$ gives the interaction with the electron in φ_j which has its spin parallel to the considered electron in φ_i. With the other electron in φ_j, of antiparallel spin, there is the interaction $\hat{J}_j$.

Since there are n terms in the sum in (IV.10), an interaction with $2n$ electrons is apparently encountered. Consider, however, the term for which $j = i$. Because of Eq. (IV.11) we have:

$$\begin{aligned}(2\hat{J}_i - \hat{K}_i)\varphi_i(1) &= (\hat{J}_i - \hat{K}_i)\varphi_i(1) + \hat{J}_i\varphi_i(1)\\ &= \hat{J}_i\varphi_i(1).\end{aligned} \tag{IV.12}$$

Thus, the electron considered does not interact with itself, but of course with the other electron in φ_i. Consequently the electron in φ_i only "sees" $2n - 1$ electrons, as it should.

The result, that an electron in φ_i only interacts with $2n - 1$ electrons, was derived under the assumption, that the sum in (IV.10) includes a term for which $j = i$, i.e., φ_i was assumed to be a doubly occupied orbital, present in the determinant defining Ψ_0 (see (IV.4)). However, (IV.10) has not only the n solutions

$$\varphi_1, \varphi_2, \ldots, \varphi_n$$

but, indeed, an infinity of solutions. Let φ_k be a solution different from $\varphi_1, \varphi_2, \ldots, \varphi_n$. Then there is no term in the sum of Eq. (IV.10) for which $j = k$, so that an electron in φ_k sees, not $2n - 1$, but $2n$ electrons. We refer to φ_k as a virtual, or an excited orbital, as opposed to an occupied orbital i.e., one of the orbitals $\varphi_1, \varphi_2, \ldots, \varphi_n$.

The difference between the two types of orbitals also manifests itself through the orbital energies ε_i and ε_k. Multiplying (IV.10) from the left with $\varphi_i^*(1)$ and integrating, gives

$$\varepsilon_i = (\varphi_i|H^{\text{core}}|\varphi_i) + \sum_{j=1}^{n} (2J_{ij} - K_{ij}), \qquad i = 1, 2, \ldots, n. \tag{IV.13}$$

Similarly we get for ε_k :

$$\varepsilon_k = (\varphi_k|H^{\text{core}}|\varphi_k) + \sum_{j=1}^{n} (2J_{kj} - K_{kj}), \qquad k > n. \tag{IV.14}$$

In (IV.13) the term $J_{ii} - K_{ii}$ vanishes because of (IV.9), whereas no cancellation occurs in (IV.14).

Consider now the excitation of an electron from an occupied orbital φ_i to a virtual orbital φ_k. This gives rise to a singlet state and a triplet state, with the wave functions

$${}^1\Psi_{i\to k} = \frac{1}{\sqrt{2}}\{|\overset{+}{\varphi}_1\overset{-}{\varphi}_1 \cdots \overset{+}{\varphi}_i\overset{-}{\varphi}_k \cdots \overset{+}{\varphi}_n\overset{-}{\varphi}_n| - |\overset{+}{\varphi}_1\overset{-}{\varphi}_1 \cdots \overset{-}{\varphi}_i\overset{+}{\varphi}_k \cdots \overset{+}{\varphi}_n\overset{-}{\varphi}_n|\} \tag{IV.15}$$

$${}^3\Psi_{i\to k} = \begin{cases} |\overset{+}{\varphi}_1\overset{-}{\varphi}_1 \cdots \overset{+}{\varphi}_i\overset{+}{\varphi}_k \cdots \overset{+}{\varphi}_n\overset{-}{\varphi}_n| \\ \dfrac{1}{\sqrt{2}}\{|\overset{+}{\varphi}_1\overset{-}{\varphi}_1 \cdots \overset{+}{\varphi}_i\overset{-}{\varphi}_k \cdots \overset{+}{\varphi}_n\overset{-}{\varphi}_n| + |\overset{+}{\varphi}_1\overset{-}{\varphi}_1 \cdots \overset{-}{\varphi}_i\overset{+}{\varphi}_k \cdots \overset{+}{\varphi}_n\overset{-}{\varphi}_n|\} \\ |\overset{+}{\varphi}_1\overset{-}{\varphi}_1 \cdots \overset{-}{\varphi}_i\overset{-}{\varphi}_k \cdots \overset{+}{\varphi}_n\overset{-}{\varphi}_n| \end{cases} \tag{IV.16}$$

It is easily verified that the associated energies may be written

$$E({}^1\Psi_{i\to k}) = E_0 + \varepsilon_k - \varepsilon_i - J_{ik} + 2K_{ik}, \tag{IV.17}$$

$$E({}^3\Psi_{i\to k}) = E_0 + \varepsilon_k - \varepsilon_i - J_{ik}, \tag{IV.18}$$

with E_0 being the ground state energy. The excitation energies are thus

$$E({}^1\Psi_{i\to k}) - E_0 = \varepsilon_k - \varepsilon_i - J_{ik} + 2K_{ik}, \tag{IV.19}$$

$$E({}^3\Psi_{i\to k}) - E_0 = \varepsilon_k - \varepsilon_i - J_{ik}. \tag{IV.20}$$

Equations (IV.19) and (IV.20) express the well-known, but often overlooked, fact that the excitation energies differ from the orbital energy difference $\varepsilon_k - \varepsilon_i$. J_{ik} usually lies between 5 and 10 Ev for transition metal complexes, and thus cannot be neglected. The presence of the electron interaction terms in (IV.19) and (IV.20) is, of course, connected with the fact that ε_i includes interactions with $2n - 1$ electrons, ε_k with $2n$ electrons.

It is stressed that the validity of Eqs. (IV.19) and (IV.20) rests on a strict fulfilment of Eq. (IV.12). This equation is trivial, but if the molecular orbitals are expanded on atomic orbitals, it becomes a more complex equation between two-electron integrals over atomic orbitals. In semiquantitative theories, some of these two-electron integrals are neglected, some are approximated by simpler integrals. Then Eq. (IV.12) may no longer be fulfilled, and so it is no longer clear how to correct for electron-electron interaction during excitation. We shall see later that the requirement that "an electron may not interact with itself," puts very severe restrictions on the form of approximations which may be introduced.

Finally, we shall discuss the influence which the core, as described in Section II, has upon the form of the valence orbitals. The investigation of Lykos and Parr (1956), concerning the $\sigma - \pi$ separability in conjugate systems, also applies to the present case. We assume that the $2q$ electrons of the core can be described by a closed-shell wave function

$$\Psi^{\text{core}} = |\overset{+}{\varphi}_1{}^{\text{core}}\overset{-}{\varphi}_1{}^{\text{core}} \cdots \overset{+}{\varphi}_q{}^{\text{core}}\overset{-}{\varphi}_q{}^{\text{core}}|, \tag{IV.21}$$

so that the total wave function for core + valence electrons is

$$\Psi^{\text{total}} = \mathscr{A}(\Psi^{\text{core}}\Psi^{\text{val}}), \tag{IV.22}$$

Ψ^{val} being the wave function for the valence electrons. $\mathscr{A}$ is an antisymmetrization operator which interchanges electrons between the core and the valence shell.

Ψ^{val} is, as in Eqs. (IV.4), (IV.15), and (IV.16), expressed through the valence orbitals

$$\varphi_1, \varphi_2, \ldots, \varphi_n, \ldots, \varphi_k, \ldots.$$

However, as shown by Lykos and Parr, such a description is only parctical if all valence orbitals are kept orthogonal to all core orbitals, i.e.,

$$\int \varphi_i^*(1)\varphi_j^{\text{core}}(1)\, d\tau_1 = 0. \tag{IV.23}$$

If this condition is fulfilled, the following expression holds for $\hat{H}^{\text{core}}$

$$\hat{H}^{\text{core}}(1) = \hat{T}(1) - \sum_g \frac{Z_g e^2}{r_{1g}} + \sum_{j=1}^{q} (2\hat{J}_j^{\text{core}} - \hat{K}_j^{\text{core}}), \tag{IV.24}$$

where $\hat{T}$ is the kinetic energy operator, and the second term gives the nuclear attraction energy (summation over the nuclei g). The third term contains Coulomb as well as exchange potentials from the core electrons.

The core thus influences the form of the valence orbitals through the core operator (IV.24) and through the strong orthogonality requirement (IV.23). The division into core and valence orbitals may be somewhat arbitrary, but (IV.23) must be obeyed for any choice. The 2*s*-electrons on the ligands (see Section II) have often been included in the core in MO calculations on complexes without paying due regard to (IV.23); this implies neglect of overlap integrals greater than 0.5, which have a profound influence on the form and energies of the valence orbitals. An orthogonalization to the core orbitals may be performed by the Schmidt procedure, and Eq. (II.15) gives an example of its effect.

As mentioned in Section II, one always assumes that the core electrons reside in the same orbitals as in the free ions. Assuming core orbitals on different centers to be nonoverlapping, this implies that the core operator (IV.24) may be written

$$\hat{H}^{\text{core}}(1) = \hat{T}(1) + \sum_g V_g(1), \tag{IV.25}$$

with

$$V_g(1) = -\frac{Z_g e^2}{r_{1g}} + \sum_{j \text{ on } g} (2\hat{J}_j^{\text{core}} - \hat{K}_j^{\text{core}}). \tag{IV.26}$$

Evidently V_g only depends on the core around nucleus g. The approximation (IV.25) is similar to an approximation in the theory of conjugated hydrocarbons, introduced by Goeppert-Mayer and Sklar (1938).

C. The Ionic Model

We shall now pass on to a description of some of the more important semiquantitative works on transition metal complexes, and as a natural starting point we give a brief summary of work carried out in the ionic model, i.e., the model on which crystal field theory is founded. It is illustrating to carry the discussion through in the light of the preceding section.

No attempt is made to solve the Hartree–Fock equations in the ionic model. Rather, one assumes these equations to be solved, and then proceeds to calculate orbital energies and electron interaction integrals. Common to all calculations performed is that all ligand orbitals are included in the core, and that the valence orbitals $4s$ and $4p$ are neglected (assuming, as in Section II, the metal ion to belong to the first transition series). Thus the only valence orbitals are the metal $3d$ orbitals.

In octahedral complexes the $3d$ orbitals span the irreducible representations t_2 and e, and the aim of calculations in the ionic model is to calculate the quantity $10Dq$, which is defined as

$$10Dq = (e|H^{\text{core}}|e) - (t_2|H^{\text{core}}|t_2), \tag{IV.27}$$

with e and t_2 denoting basis functions in the e and t_2 representations respectively. In applying this definition it must be remembered that all occupied ligand orbitals are included in the core. The core potential is further broken up according to Eqs. (IV.25) and (IV.26).

In the early calculations by Van Vleck (1939) and Polder (1942) the core potentials V_g of Eq. (IV.26) were approximated as potentials from point charges or point dipoles centered at the ligands. The d orbitals on metal were chosen as hydrogen-like functions, and reasonably good estimates for $10Dq$ were obtained. It was remarked by Van Vleck (1939) that the good agreement with experiment probably was accidental—and this was later confirmed by Freeman and Watson (1960), who used more accurate d functions in Eq. (IV.27).

Kleiner (1952) used a more realistic core potential, since he actually calculated the integrals resulting from $\hat{J}_j^{\text{core}}$ in Eq. (IV.26), whereas the exchange integrals resulting from $\hat{K}_j^{\text{core}}$ were neglected. The d orbitals were constructed on the basis of Slater's rules (Slater, 1930), and the result was a value for $10Dq$ of the wrong sign. However, as shown by Freeman and Watson (1960), the more contracted self-consistent field orbitals for the free ion reverse the sign for $10Dq$ again, but a far too small value is obtained.

The final step in the ionic model was taken by Tanabe and Sugano (1956). These authors not only included the exchange contributions from the operators $\hat{K}_j^{\text{core}}$ of Eq. (IV.26), but also payed due attention to the strong orthogonality requirement (IV.23), by Schmidt-orthogonalizing the metal d orbitals to the ligand orbitals. They obtained in this way a value for $10Dq$ which was of the proper sign, but much too large. Several approximations were introduced by Tanabe and Sugano, and the atomic wave functions used were fairly crude; but their work certainly showed the necessity of a molecular orbital approach, in which the $2s$ and $2p$ orbitals on the ligands were to be treated as valence orbitals. With the molecular orbital methods appearing on the scene, therefore, extensive calculations in the ionic model are no longer performed.

D. Roothaan's Equations

When the molecular orbitals are represented as linear combinations of atomic orbitals,

$$\varphi_i = \sum_{r=1}^{m} C_{ri}\chi_r, \tag{IV.28}$$

the variation principle leads to Roothaan's equation (II.7) and (II.8) for the coefficients C_{ri} (Roothaan, 1951a). Formally, one obtains these equations by substituting (IV.28) into the Hartree-Fock equations (IV.10), and such a procedure can also be justified theoretically; it is the more appropriate one in the present context.

The following notation for some integrals and operators will be used extensively:

$$(r|H^{\text{core}}|s) = \int \chi_r^*(1)\hat{H}^{\text{core}}(1)\chi_s(1)\,d\tau_1 \tag{IV.29}$$

$$[rs \mid tu] = \iint \chi_t^*(1)\chi_t^*(2)\frac{e^2}{r_{12}}\chi_s(1)\chi_u(2)\,d\tau_1\,d\tau_2 \tag{IV.30}$$

$$[\quad \mid tu]\varphi(1) = \int \chi_t^*(2)\chi_u(2)\frac{e^2}{r_{12}}\,d\tau_2 \cdot \varphi(1) \tag{IV.31}$$

$$[\;u \mid t\;]\varphi(1) = \int \chi_t^*(2)\varphi(2)\frac{e^2}{r_{12}}\,d\tau_2 \cdot \chi_u(1) \tag{IV.32}$$

and we consider $[\quad \mid tu]$ and $[\;u \mid t\;]$ as Coulomb and exchange operators respectively, associated with the orbitals χ_t and χ_u. If χ_t and χ_u are different, we refer to $\chi_t\chi_u$ as an overlap charge distribution.

When (IV.28) is substituted into the Hartree–Fock equations (IV.10) we obtain:

$$\left\{\hat{H}^{\text{core}}(1) + \sum_{t,u} P_{t,u}([\quad \mid tu] - \tfrac{1}{2}[\;u \mid t\;])\right\}\varphi_i(1) = \varepsilon_i\varphi_i(1), \tag{IV.33}$$

where the elements $P_{t,u}$ of the charge and bond-order matrix **P** are defined thus

$$P_{t,u} = 2 \sum_{j=1}^{n} C_{tj}^{*} C_{uj}. \tag{IV.34}$$

Only the occupied orbitals contribute to this matrix.

Equation (IV.33) forms the natural basis for parts of the subsequent discussion, in other parts the integrated form (II.7) is more appropriate, and to obtain it, (IV.28) is substituted into (IV.33). Multiplication from the left with $\chi_r^*(1)$ and integration then gives

$$\sum_{s} \left\{ (r|H^{\text{core}}|s) + \sum_{t,u} P_{t,u}([rs \mid tu] - \tfrac{1}{2}[ru \mid ts]) \right\} C_{si} = \varepsilon_i \sum_{s} S_{rs} C_{si}, \tag{IV.35}$$

which is Eq. (II.7) written out in full.

Like the Hartree–Fock equations themselves, Eqs. (IV.33) and (IV.35) are solved by an iterative technique: a set of coefficients for the occupied orbitals are guessed, and hence a charge and bond-order matrix follows. This matrix is used to solve for a new set of MO coefficients, and the first step in the iteration has then been carried through. In subsequent iterations, one obtains better and better approximations to the true solution (actually, a special technique is often required for the process to converge).

Historically, the first attempts to solve Roothaan's equations for transition metal compounds applied the zero differential overlap approximation. This mode of attack will be treated later; it is expedient first to discuss some calculations which take Eq. (IV.33) as their starting point.

E. The Sugano–Shulman Treatment

The calculation of Sugano and Shulman (1963) on the octahedral $[\text{NiF}_6]^{4-}$ ion stands half-way between the ionic model and a self-consistent field model, since only the first step in the iterative procedure mentioned above was carried through. The starting orbitals were those corresponding to the ionic model without overlap; overlap was not, however, neglected when solving for the molecular orbitals.

When overlap is neglected in setting up Eq. (IV.33), the Hartree–Fock operator becomes a sum of atomic operators associated with the various ions in the complex. With the set of valence orbitals described in Section II, there are no bond-orders between different metal orbitals, since no two metal orbitals transform in the same way in an octahedral complex. The ligand s orbitals may, however, mix with the p_σ orbitals; neglecting this mixing in setting up the Hartree–Fock operator (as was done by Sugano and Shulman), one obtains:

$$\left\{\hat{H}^{\text{core}}(1) + \sum_t P_{tt}([\quad | \, tt] - \tfrac{1}{2}[\; t \,|\, t \;])\right\}\varphi_i(1) = \varepsilon_i\varphi_i(1). \tag{IV.36}$$

In this equation only simple Coulomb and exchange operators occur.

P_{tt} measures the number of electrons in the atomic orbital χ_t and is an integer in the ionic approach. However, the $[\text{NiF}_6]^{4-}$ ion does not have a closed-shell structure, and consequently Sugano and Shulman replaced (IV.36) with the equation

$$\left\{\hat{H}^{\text{core}}(1) + \sum_t Q_t([\quad | \, tt] - \delta(m_{st}, m_{si})[\; t \,|\, t \;])\right\}\varphi_i(1) = \varepsilon_i\varphi_i(1). \tag{IV.37}$$

In this equation, we sum over spin orbitals, each atomic orbital occurring once or twice according to whether it is singly or doubly occupied; m_{st} and m_{si} are the spin quantum numbers associated with χ_t and φ_i respectively. Q_t is, of course, zero or one.

The highest occupied orbitals in $[\text{NiF}_6]^{4-}$ are the antibonding t_2 orbitals (ξ, η, ζ transforming like d_{yz}, d_{zx}, d_{xy}) and the antibonding e orbitals (u, v transforming like d_{z^2}, $d_{x^2-y^2}$). They consist mainly of metal d orbitals. The ground state is of symmetry ${}^3A_{2g}$ and the lowest excited state of symmetry ${}^3T_{2g}$. The associated wave functions (with $M_S = 1$) are, neglecting the lower lying, doubly occupied orbitals:

$$\begin{aligned}\Psi({}^3A_2) &= |\overset{+}{\xi}\,\overset{-}{\xi}\,\overset{+}{\eta}\,\overset{-}{\eta}\,\overset{+}{\zeta}\,\overset{-}{\zeta}\,\overset{+}{u}\,\overset{+}{v}|,\\ \Psi({}^3T_2, \zeta) &= |\overset{+}{\xi}\,\overset{-}{\xi}\,\overset{+}{\eta}\,\overset{-}{\eta}\,\overset{+}{\zeta}\,\overset{-}{v}\,\overset{+}{u}\,\overset{+}{v}|.\end{aligned} \tag{IV.38}$$

In the ionic (crystal field) model, all lower lying orbitals would be included in the core, and the antibonding t_2 and e orbitals would be pure d orbitals. The determinants in (IV.38) differ in the orbitals ζ and v, i.e., d_{xy} and $d_{x^2-y^2}$ in crystal field theory. d_{xy} and $d_{x^2-y^2}$ interact in similar ways with the remaining electrons, and consequently

$$E({}^3T_2) - E({}^3A_2) = (v|H_0^{\text{core}}|v) - (\zeta|H_0^{\text{core}}|\zeta), \tag{IV.39}$$

where $\hat{H}_0^{\text{core}}$ has been supplied with the subscript 0 to indicate that the lower valence orbitals are included in the core.

According to Eq. (IV.27), the right-hand side of Eq. (IV.39) is just $10Dq$, so that crystal field theory identifies the energy associated with the ${}^3A_2 \rightarrow {}^3T_2$ transition with this quantity. In molecular orbital theory, however, the orbitals ζ and v will interact differently with the remaining electrons, and hence Eq. (IV.39) ceases to be strictly fulfilled. The question then arises, which side of Eq. (IV.39) should be compared to $10Dq$ when an MO calculation is performed.

In answering this question it must be remembered, that it is only in naïve crystal field theory that (IV.39) holds. The complete theory, referred to in Section I, calculates $E(^3T_2) - E(^3A_2)$ with configuration interaction included, and then it is the right-hand side of (IV.39) which is $10Dq$. In order to obtain a one-to-one correspondence between crystal field theory and MO theory, we must then also identify $10Dq$ with the right-hand side of (IV.39) in the latter. This does not, however, imply that MO theory should lead to exactly the same value for $10Dq$ as crystal field theory, because the latter—as it was seen above—allows certain relations between two-electron integrals to be fulfilled, that follow from spherical symmetry rather than from octahedral symmetry.

Sugano and Shulman (and later authors) identified the left-hand side of (IV.39) with $10Dq$, but we prefer to see their efforts as an attempt to calculate the energy associated with the transition $^3A_2 \rightarrow {}^3T_2$. It is in agreement with this point of view that Eq. (IV.39) was not used by Sugano and Shulman at all. Instead they used the equation

$$E(^3T_2) - E(^3A_2) = \varepsilon'(v) - \varepsilon'(\zeta), \tag{IV.40}$$

where

$$\begin{aligned} \varepsilon'(v) = (v|H_0^{\text{core}}|v) &+ 2J(\xi, v) - K(\xi, v) + 2J(\eta, v) - K(\eta, v) \\ &+ J(\zeta, v) + J(u, v) + J(v, v), \end{aligned} \tag{IV.41}$$

and

$$\begin{aligned} \varepsilon'(\zeta) = (\zeta|H_0^{\text{core}}|\zeta) &+ 2J(\xi, \zeta) - K(\xi, \zeta) + 2J(\eta, \zeta) - K(\eta, \zeta) \\ &+ J(\zeta, \zeta) + J(u, \zeta) + J(v, \zeta). \end{aligned} \tag{IV.42}$$

Equation (IV.40) is, of course, the proper one to use in an MO calculation.

The primed orbital energies $\varepsilon'(v)$ and $\varepsilon'(\zeta)$ were determined by solving (IV.37) *for two different states* $^3T_2$ and $^3A_2$ respectively, a valid approach when the remaining valence orbitals are restricted to be the same in the two states. This restriction implies, for instance, that the bonding e and t_2 orbitals are unchanged during the excitation, while the corresponding antibonding orbitals refer to different states, a restriction which was later lifted by Watson and Freeman (1964).

If we (reluctantly) identify the left-hand side of Eq. (IV.39) with $10Dq$, Eq. (IV.40) can be written

$$10Dq = \varepsilon'(v) - \varepsilon'(\zeta), \tag{IV.43}$$

but it must then be remembered that the two orbital energies involved refer to different states. We might imagine using the ground state ($^3A_2$) form of (IV.37) to obtain as well ζ as v; this would be more in keeping with the discussion of Section IV, B. Calling the pertinent orbital energies $\varepsilon(v)$ and $\varepsilon(\zeta)$ and requiring the same space orbital in v^+ and v^-, we would then find:

$$\varepsilon(v) = (v|H_0^{\text{core}}|v) + 2J(\xi, v) - K(\xi, v) + 2J(\eta, v) - K(\eta, v)$$
$$+ 2J(\zeta, v) - K(\zeta, v) + J(u, v) - K(u, v)$$

or

$$\varepsilon(v) = \varepsilon'(v) + J(\zeta, v) - K(\zeta, v) - J(v, v) - K(u, v).$$

On the other hand $\varepsilon(\zeta) = \varepsilon'(\zeta)$ so that (IV.43) becomes:

$$10Dq = \varepsilon(v) - \varepsilon(\zeta) - J(\zeta, v) + J(v, v) + K(\zeta, v) + K(u, v). \quad \text{(IV.44)}$$

The distinction between the primed and unprimed orbital energies is an important one to which we shall later have opportunity to refer.

Sugano and Shulman obtained a value of 6350 cm^{-1} for the $^3A_{2g} \rightarrow {}^3T_{2g}$ excitation energy, which compares favorably with the experimental value of 7250 cm^{-1}. The agreement with experiment, however, vanished in the somewhat refined treatment of Watson and Freeman (1964). These authors allowed bonding as well as antibonding orbitals to change during excitation, and obtained in this way an excitation energy of about 2800 cm^{-1}. The theoretical expression for the excitation energy is, of course, considerably more complex than (IV.43) in such an approach. One may say that these authors allowed for different crystal fields in the two states, and it is interesting to note that this does not improve the numerical result. Thus qualitative arguments concerning the change of the crystalline field must be viewed with care.

As was pointed out by Šimánek and Šroubek (1964) and by Sugano and Tanabe (1965) correlation effects have been neglected in the above treatment. These effects have recently been examined by Hubbard *et al.* (1966) in a configuration interaction approach (such a method was also discussed by Keffer *et al.* (1959)), and the agreement with experiment was re-established, a value of 5400 cm^{-1} being obtained for the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition energy.

It should be mentioned, as realized by Sugano and Tanabe (1965), that the Hartree–Fock equations in the form (IV.37) are incomplete, off-diagonal multipliers having been neglected.

The calculation which we have just discussed belongs to the most extensive ones made in the theory of transition metal complexes. Reasonable approximations were made for three-center integrals, and all one- and two-center integrals were calculated exactly, using the DIATOM programs by Corbató and Switendick (1963). These programs have been of inestimable importance for the development in the theory of inorganic complexes, and have been used in almost all numerical work to be reported later.

The $[NiF_6]^{4-}$ ion can be considered "almost ionic," and it is for this reason that very extensive calculations have been possible for this ion. The calculations to be reported in the following sections deal with compounds in which overlap effects often are considerably larger, and hence it is a bad approximation to start from an ionic Hamiltonian. This implies that reiterations are required in order to get reliable results, and quite drastic approximations must be made in evaluating matrix elements.

F. Radial Functions, Population Analysis, and Integral Approximations

The reliability of the results from an MO calculation depends highly on the nature of the approximations made during the calculation, but also on the radial functions used in the atomic orbitals from which the molecular orbitals are constructed as LCAO's (linear combinations of atomic orbitals). So far, no general criterion is known which can be used to find the best radial functions, but it is generally assumed that they should be referred to the atoms *in situ*. Attempts are therefore made to convert the charge density from an MO calculation to a sum of atomic charge densities, so that it becomes possible to define a configuration for each atom. Fractional charges will occur in such an analysis, but since radial functions always are determined for atoms or ions with integer charges, one picks the atom or ion which comes closest to the configuration suggested by the population analysis, and for which radial functions have been determined.

It is clear that the choice of radial functions is somewhat ambigious, so although one picks the best Hartree–Fock atomic orbitals from the literature, it is permissible to simplify these somewhat, for instance by reducing them to a sum of a few Slater orbitals. This is, on the other hand, also necessary in order to make the problem of evaluating the integrals tractable. For the metal orbitals $3d$, $4s$, $4p$ the functions of Richardson *et al.* (1962, 1963) are in general use, and the functions by Clementi (1964), or by Clementi and Raimondi (1963) seem appropriate for the ligand orbitals. For atoms belonging to the higher transition series, no analytical functions are available, but numerical functions have been computed by Herman and Skillman (1963).

We can illustrate the choices which are present in performing a population analysis by limiting ourselves to consider the diatomic problem, in which the *i*th MO is represented as

$$\varphi_i = C_{ai}\chi_a + C_{bi}\chi_b . \tag{IV.45}$$

The charge density associated with this doubly-occupied orbital is

$$\begin{aligned} 2\varphi_i(1)\varphi_i(1) = 2C_{ai}^2\chi_a(1)\chi_a(1) + 4C_{ai}C_{bi}\chi_a(1)\chi_b(1) \\ + 2C_{bi}^2\chi_b(1)\chi_b(1), \end{aligned} \tag{IV.46}$$

and by integration we get

$$2 = 2C_{ai}^2 + 4C_{ai}C_{bi}S_{ab} + 2C_{bi}^2 . \tag{IV.47}$$

We interpret this equation, following Mulliken (1955), by saying that out of the two electrons the fractions $2C_{ai}^2$ and $2C_{bi}^2$ are associated with the atoms *a* and *b* respectively, and the fraction $4C_{ai}C_{bi}S_{ab}$ is associated with the overlap charge.

The problem now arises how to divide the overlap charge between the atoms *a* and *b*. In the well-known scheme suggested by Mulliken (1955), the overlap charge was equally divided between the two atoms, and this seems the natural choice when the center of gravity for the charge distribution $\chi_a(1)\chi_b(1)$ is located roughly halfway between the centers *a* and *b*. This is the case if χ_a and χ_b are two ligand orbitals or if χ_b is a ligand orbital and χ_a a metal 3*d* orbital. We shall use the expression that the orbital set (χ_a, χ_b) belongs to class I.

If, however, χ_b is a ligand orbital and χ_a is a metal orbital of type 4*s* or 4*p*, the charge distribution $\chi_a\chi_b$ looks different. This is illustrated in Figs. 3–6, using the atomic orbitals from the MnO_4^- calculation to be reported later. It is seen from Figs. 3 and 5 that the 4*s* orbital is very diffuse, and almost constant in the region where the ligand orbital is most intense (and the same holds for the 4*p* orbital). Consequently, as Figs. 4 and 6 show, the overlap charge distribution $\chi_a(1)\chi_b(1)$ looks quite similar to the functions $\chi_b(1)$. (It should be noted that the functions in Figs. 3 and 5 are the radial functions multiplied by the value of the proper angular function along the bond axis.)

When 4*s* or 4*p* orbitals are involved in the orbital set (χ_a, χ_b), which we say belongs to class II in this case, it seems more appropriate, therefore, to assign the whole overlap charge to the ligand atom. This has also been suggested by other authors, e.g., Nieuwpoort (1965) and Fenske *et al.* (1966a), but the Mulliken method has often been used for orbital sets in class II also.

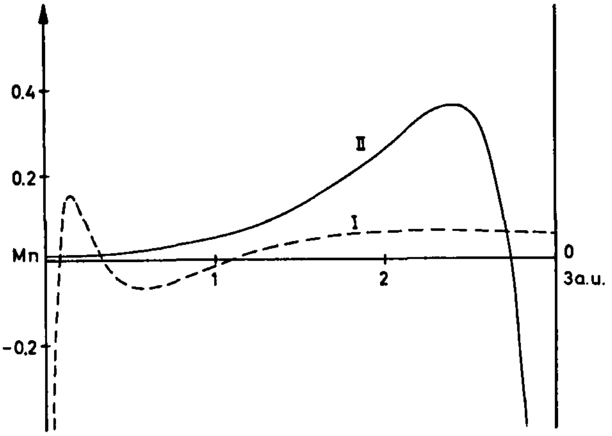

Fig. 3. Manganese 4s orbital (I) and oxygen 2s orbital (II) plotted along the Mn—O bond axis.

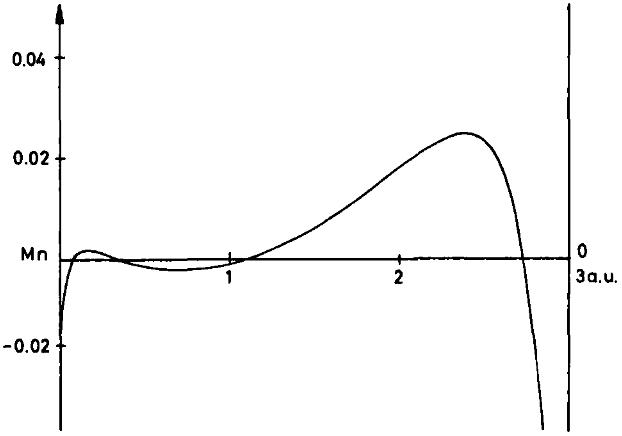

Fig. 4. Product of the functions in Fig. 3 along the Mn—O bond axis.

The division of the orbital sets into the classes I and II was made using plausibility considerations. It might well be asked whether a more mathematical procedure can be devised. Oleari *et al.* (1966b) have suggested that one expand the molecular orbital φ_i on the complete set of atomic orbitals for a given center, a say, and use the sum of squared expansion coefficients for the lower orbitals as a measure for the amount of charge on center a. It is claimed then, that this should uniquely define the atomic configuration

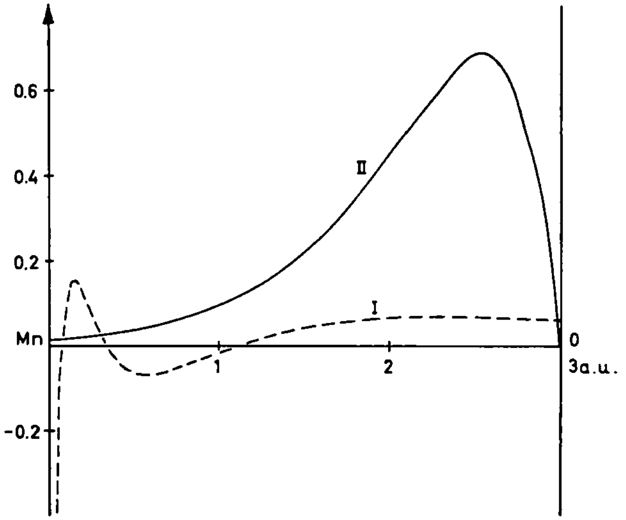

Fig. 5. Manganese 4s orbital (I) and oxygen 2p_σ orbital (II) plotted along the Mn—O bond axis.

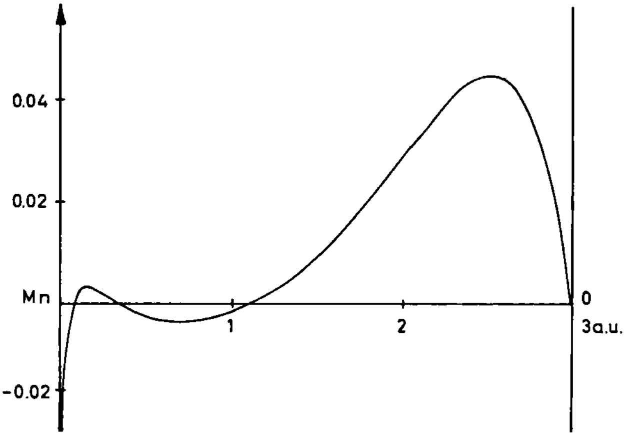

Fig. 6. Product of the functions in Fig. 5 along the Mn—O bond axis.

from which the atomic orbitals entering the LCAO should be taken. If, however, one consults an early paper by Coulson (1937) dealing with the screening constants of the hydrogen molecule, it is easy to convince oneself that this method only considers one of the factors determining the atomic orbitals in a molecule. In the case of the hydrogen molecule the method would suggest misleading screening constants. It is doubtful, therefore, whether it makes much sense to use very refined arguments in connection with a population analysis.

Although somewhat arbitrary, it would seem that the picture of an atom in a molecule, given by a population analysis, would be the natural thing to start from when choosing atomic orbitals for the LCAO's. However, there are still severe difficulties, especially with the 4*s* and 4*p* orbitals. The complex considered will usually be imbedded either in a crystal or in a solution. As it is indicated by Figs. 3 and 5, the 4*s* and 4*p* orbitals extend beyond the ligand ions and into the surrounding medium. But this means, in fact, that to a large extent it is the surroundings that determine which orbital should be used. To see this we consider Fig. 7, showing the manganese 3*s* and 4*s* orbitals. The 3*s* orbital has been multiplied by 0.2154 to demonstrate that the actual form of the two orbitals is the same until the maximum of the 3*s* orbital is reached. As discussed by Slater (1960, p. 230), this behavior stems from the fact that the difference between the energy eigenvalues for the functions is small compared to the values of the potential energy in the region of the inner shells. Consequently, it is the conditions for larger values of *r* (the distance from the nucleus), that fix the form of the 4*s* and 4*p* orbitals; in other words, it is the potential energy fields

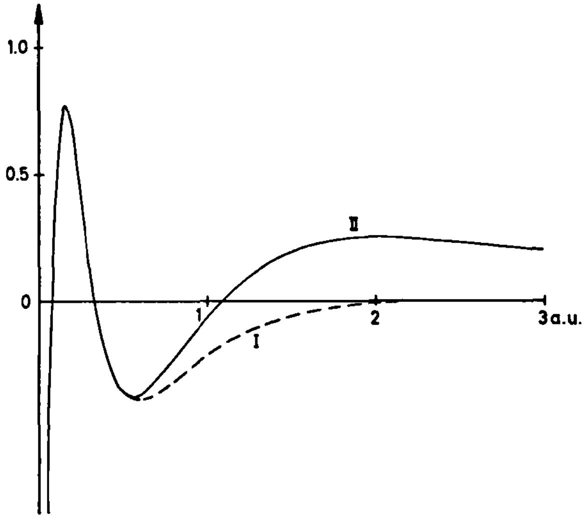

Fig. 7. Manganese 4*s* orbital (II) compared with the 3*s* orbital (I) multiplied by 0.2154.

around the ligands and in the external medium, made up of other ions and neutral molecules.

It would seem that there is no simple way to estimate the best orbitals to use in MO calculations. But it is important that no matter how the orbitals are chosen they should be orthogonal to the core orbitals, and in particular to the core orbitals on the metal (strong orthogonality condition Eq. (IV.23)). This condition is exactly fulfilled for the metal core if free atom orbitals are chosen and it is quite well fulfilled for the $1s$-ligand cores.

We shall now comment on the problem of evaluating integrals in MO calculations. As mentioned in Section IV,E all one- and two-center integrals can be calculated exactly using the DIATOM programs, although it is still necessary to use radial functions built of as few Slater orbitals as possible to save computer time. The three- and four-center integrals, however, remain a problem, and approximation methods are required. Usually one replaces the charge distribution $\chi_a(1)\chi_b(1)$ with a simpler one, say

$$\chi_a(1)\chi_b(1) \approx \alpha\chi_a(1)\chi_a(1) + \beta\chi_b(1)\chi_b(1), \tag{IV.48}$$

where, in order to preserve the amount of charge, we must demand that

$$\alpha + \beta = S_{ab}. \tag{IV.49}$$

The approximation (IV.48) has been discussed by Löwdin (1953). For $\alpha = \beta = \frac{1}{2}S_{ab}$ it reduces to the familiar Mulliken approximation (Mulliken, 1949), originally expressed on integral form.

Nieuwpoort (1965) used (IV.48) with α and β variable; otherwise, the Mulliken form has been most widely used. Three- and four-center integrals, and also many two-center integrals can be estimated in this way to an accuracy of a few percent. It is, in general, not a very good approximation for two-center nuclear attraction integrals or for integrals containing the kinetic energy operator.

We shall later show that we can obtain a great simplification of Roothaan's equations if we adopt the following approximations for the overlap charge distribution

$$\chi_a(1)\chi_b(1) = \begin{cases} \frac{1}{2}S_{ab}[\chi_a(1)\chi_a(1) + \chi_b(1)\chi_b(1)] & \text{with } \chi_a\chi_b \text{ in class I,} \\ S_{ab}\chi_b\chi_b & \text{with } \chi_a\chi_b \text{ in class II.} \end{cases} \tag{IV.50}$$

These approximations are, of course, in harmony with the proposed form of the population analysis.

G. The Molecular Orbital Theory of Fenske *et al.*

In the light of the preceding sections, we shall now discuss the recent MO method suggested by Fenske *et al.* (1966a), which has been applied to some metal hexafluorides $[MF_6]^{3-}$ (M = Ti, V, Cr, Fe, Co) (Fenske *et al.*, 1966b). This work may be regarded as an attempt to apply some of the methods by Sugano and Shulman without neglecting overlap terms in the effective one-electron Hamiltonian.

The theory is a self-consistent one, and for each iteration a population analysis was performed along the lines described in the previous section. A distinction was made between class I and class II orbital sets; the sets belonging to class I were treated as suggested above, but the whole charge associated with orbital sets of class II was attributed to the ligands. For $[TiF_6]^{3-}$, calculations were also made using both the original Mulliken analysis throughout, and associating the charge $2C_{ai}^2/(C_{ai}^2 + C_{bi}^2)$ with atom a and the charge $2C_{bi}^2/(C_{ai}^2 + C_{bi}^2)$ with atom b (See Eq. (IV.47)). The results were found to be rather insensitive to the kind of population analysis chosen.

Approximations were introduced in the Hamiltonian of Eq. (IV.33), in order to throw the Hartree–Fock equations into a form similar to (IV.36), in which the Hamiltonian is a sum of ionic terms (plus the kinetic energy operator). The two-center terms in Eq. (IV.33) are of the form

$$[\quad | \, ab] - \tfrac{1}{2}[\ b \, | \, a\ ].$$

$[\quad | \, ab]$ is the potential from the overlap distribution $\chi_a(1)\chi_b(1)$, and Fenske *et al.* approximated this distribution according to Eq. (IV.50). For orbital sets in class I, this implies that

$$[\quad | \, ab] = \tfrac{1}{2}S_{ab}([\quad | \, aa] + [\quad | \, bb]), \qquad \text{(IV.51)}$$

and, as mentioned in the preceding section, this is a quite accurate approximation.

An approximation similar to (IV.51) was applied to the exchange operator $[\ b \, | \, a\ ]$, *viz.*

$$[\ b \, | \, a\ ] = \tfrac{1}{2}S_{ab}([\ a \, | \, a\ ] + [\ b \, | \, b\ ]), \qquad \text{(IV.52)}$$

and it is clear that this leads to a Hamiltonian of the desired form (IV.36). The approximation (IV.52) is, however, quite *ad hoc*, which is rather unfortunate for two reasons.

First, it is an inaccurate approximation, leading for instance to equations like

$$[ab \, | \, aa] = \tfrac{1}{2}S_{ab}([aa \, | \, aa] + [ab \, | \, ba]). \qquad \text{(IV.53)}$$

This equation is obtained by taking matrix elements on both sides of Eq. (IV.52) of χ_a with itself. On the other hand, we may also take matrix elements of χ_a with itself using the operators of Eq. (IV.51). This leads to the equation

$$[aa \mid ab] = \tfrac{1}{2}S_{ab}([aa \mid aa] + [aa \mid bb]). \tag{IV.54}$$

Comparing Eqs. (IV.53) and (IV.54) gives the relation

$$[ab \mid ba] = [aa \mid bb] \tag{IV.55}$$

which is far from being fulfilled, since the integrals $[ab \mid ba]$ and $[aa \mid bb]$ are of different orders of magnitude. The approximations (IV.51) and (IV.52) are hence not compatible from a numerical point of view.

Second, theoretical objections may be raised against Eq. (IV.52). As stressed in Section IV,B a valance electron does not interact with itself in the Hartree-Fock scheme. It is important that this feature be retained in semiquantitative theories, not only from a purely formal point of view, but also because electrons interact with very strong forces, and unless Eq. (IV.12) is fulfilled, one is actually calculating the electronic structure of an ion with a total charge different from the one assumed.

When incompatible approximations are used in the Coulomb and exchange part of the Hartree–Fock operator as above, the requirement that an electron may not interact with itself cannot be fulfilled, and hence such approximations should be avoided.

Except for a calculation on $[TiF_6]^{3-}$, the calculations on the metal hexafluorides treated the 2*s* orbitals of the ligands as belonging to the core. No attempt was made, however, to meet the strong orthogonality requirement (IV.23), although overlap integrals as large as $S(4s, 2s) = 0.5891$ occurred. Observation of Eq. (IV.23) should drastically change the orbital energies of those valence MO's which overlap strongly with the ligand 2*s* orbital, but leave the energies of the lower lying 2*s* orbitals themselves, almost unchanged. In this way one should obtain an orbital level scheme similar to the scheme from a calculation, in which the 2*s* orbitals were considered as valence orbitals.

As just mentioned, a calculation was actually performed for $[TiF_6]^{3-}$ with the 2*s* orbitals included among the valence orbitals. This calculation was, however, rejected by the authors because it resulted in an orbital energy difference

$$\varepsilon(2e_g) - \varepsilon(2t_{2g}) = 7.48 \quad \text{eV}. \tag{IV.56}$$

$2e_g$ is here an empty orbital, and $2t_{2g}$ holds a single electron, i.e., we are dealing with a d^1 system in the language of crystal field theory. Excluding the $2s$ orbitals resulted instead in the value

$$\varepsilon(2e_g) - \varepsilon(2t_{2g}) = 2.73 \quad \text{eV}. \tag{IV.57}$$

The energy differences quoted are those of Table IV in the paper of Fenske *et al.* (1966a).

The reason for considering the result in (IV.57) as superior to that in (IV.56) was that $\varepsilon(2e_g) - \varepsilon(2t_{2g})$ should be identified with $10Dq$, or the energy of the first "ligand field" transition $2t_{2g} \rightarrow 2e_g$ found at 1.98 eV. However, $2e_g$ is a virtual orbital, $2t_{2g}$ an occupied orbital, and consequently formulas similar to those of Eqs. (IV.19) and (IV.20) ought to be considered. Thus (IV.57) predicts, in fact, a negative excitation energy, whereas (IV.56) probably predicts an excitation energy close to zero. In other words, it is (IV.56) which should be preferred.

It might finally be mentioned that several integral approximations not touched on so far were introduced in taking matrix elements of the Hartree–Fock operator; these approximations were probably not serious, but it should be noted that certain three-center integrals were actually evaluated. This appears a meaningless refinement, in so far as other three-center integrals were neglected through the approximations (IV.52) and (IV.53) in the Hartree–Fock operator. It should also be mentioned that certain scaling factors R_σ and R_π were introduced in the off-diagonal elements of the operator in order to reproduce the experimental Dq value through (IV.57).

In conclusion, the MO theory of Fenske *et al.* contains so many inconsistencies that it is difficult to see which advantages it has above, say, the extended Wolfsberg–Helmholz method described in Section III,B.

H. Nieuwpoort's Treatment of Some Metal Carbonyls

In the sections which follow, we shall consider some MO calculations which take the Roothaan equations in their integrated form (IV.35) as a starting point, rather than Eq. (IV.33). It is doubtful whether (IV.33) has any advantages at all if a consistent theory is wanted; for instance the previous section showed the difficulties associated with the reduction to a Sugano–Shulman form like (IV.36).

The extensive calculation of Nieuwpoort (1965) is the only existing investigation in which all integrals in (IV.35) have been considered. All tractable integrals were evaluated exactly, and Eq. (IV.48) was used for the remaining ones, as mentioned in Section IV,F. The compounds studied by Nieuwpoort were the metal carbonyls $Ni(CO)_4$, $Co(CO)_4{}^-$, and $Fe(CO)_4^{2-}$

which he treated as a 50 electron problem, i.e., the core contained the orbitals suggested in Section II, namely the 1*s* orbitals on carbon and oxygen and the orbitals of the argon core on the metal.

The highest filled orbital in $Ni(CO)_4$ was found to be of *e* symmetry. This orbital, which represents the important metal-carbon π bond, was found to have an orbital energy of -7.9 eV. The first ionization potential of $Ni(CO)_4$ is given as 8.28 eV, showing quite good agreement. The first empty orbital occurred at about 7.1 eV and was found to be strongly antibonding in nature, being the π antibonding orbital located on CO. The average energy required to excite an electron to this virtual orbital was calculated to be about 9 eV. One would then expect the near uv spectrum to show typical charge-transfer bands with large absorption over a wide range. It is furthermore highly probable that excitation into these will lead to photoionization.

V. Zero Differential Overlap Approximations

A. The ZDO and CNDO Schemes

The zero differential overlap (ZDO) approximation was originally introduced in the theory of conjugated hydrocarbons by Pariser and Parr (1953) and Pople (1953), and it has since been applied to a great number of organic compounds. In the theory of transition metal complexes it was first applied to the so-called sandwich compounds by Yamazaki (1956), Shustorovich and Dyatkina (1959), and the present authors (Dahl and Ballhausen, 1961). Recently it has also been used by Oleari *et al.* (1966a,b) in calculations on the chromate and permanganate ions, and by Roos (1966) in a study of the copper complexes $Cu(NH_3)_6^{2+}$ and $Cu(H_2O)_6^{2+}$. A calculation on the permanganate ion has also been performed by the present authors and will be reported at the end of this paper.

In the ZDO approximation, the full Roothaan equation (IV.35) is taken as the starting point, but this equation is simplified by a set of approximations, *viz.*

(1) All overlap integrals are neglected.

(2) $(r|H^{\text{core}}|s) = 0$ unless χ_r and χ_s belong to the same center or are nearest neighbors.

(3) $\chi_r(1)\chi_s(1)$ is neglected in evaluating two-electron integrals if χ_r and χ_s belong to different centers.

The first of these approximations implies that S_{rs} does not occur on the right-hand side of Eq. (IV.35), and the third approximation reduces all two-center, two-electron integrals to the form $[r_a s_a \mid t_b u_b]$ with a and b referring to the centers involved. The approximations mentioned lead to a great simplification of Roothaan's equations, because they eliminate the problem of evaluating the difficult three- and four-center integrals. However, such a drastic set of approximations needs justification, and these will be discussed in the next section.

The approximations (1)–(3) as stated here are somewhat more general than in the original formulation by Pariser, Parr, and Pople. The generalization consists in an extension to systems in which each atom may contribute more than one atomic orbital to the set of valence orbitals. Since no one-center integrals are neglected in the formulation above, this seems a straightforward extension which includes no further assumptions. This is, however, not entirely so; it will be shown below that a complete theoretical justification for the scheme in the suggested form is difficult to give, if there are LCAO's present which include more than one atomic orbital on the same center.

In an attempt to include the σ orbitals in calculations on organic molecules, Pople *et al.* (1965) also suggested the use of the ZDO approximation given above. However, an additional scheme was also devised (Pople and Segal, 1965), based on a CNDO (complete neglect of differential overlap) approximation. This scheme neglects the charge distribution $\chi_r(1)\chi_s(1)$ in the evaluation of two-electron integrals whenever χ_r is different from χ_s, and also if the two orbitals belong to the same center. With these approximations (IV.35) reduces to the following equation

$$\sum_s H_{rs} C_{si} = \varepsilon_i C_{ri}, \tag{V.1}$$

where

$$H_{rr} = (r|H^{\text{core}}|r) + \sum_t P_{tt}[rr \mid tt] - \tfrac{1}{2}P_{rr}[rr \mid rr], \tag{V.2}$$

$$H_{rs} = (r|H^{\text{core}}|s) - \tfrac{1}{2}P_{rs}[rr \mid ss], \quad r \neq s. \tag{V.3}$$

These equations are of the same functional form as the original equations of Pariser, Parr, and Pople. When symmetry adapted functions are used in a calculation, it should be noted that (V.2) and (V.3) refer to the original atomic orbitals.

Whenever the ZDO and CNDO schemes are used on organic compounds, semi-empirical features are introduced. The two-electron integrals are often evaluated numerically using simple Slater orbitals, but more often they are obtained from an analysis of spectral data for the various atoms in the molecule. Such a procedure gives only one-center integrals; two-center, two-electron integrals are obtained by interpolation techniques which utilize the known values for these integrals at large interatomic distances as well as the one-center values. Two-electron integrals obtained in this way have considerably smaller values than the corresponding ones obtained using Slater orbitals.

The diagonal elements $(r|H^{\text{core}}|r)$ can, in a semi-empirical approach, be assigned values with reference to atomic spectral data also, although there are some ambiguities at this point. On the other hand, the values for $(r|H^{\text{core}}|s)$ with $r \neq s$ must be obtained from the spectral data of the molecule itself.

The semi-empirical approach seems quite adequate when only one atomic orbital per atom is considered. With each atom supplying more than one orbital it becomes a very cumbersome and much less well-defined method of approach. In particular, the number of different $(r|H^{\text{core}}|s)$ elements exceeds the number of spectral constants available for the molecule to be treated. In such cases it is customary to introduce additional assumptions, say

$$(r|H^{\text{core}}|s) = aS_{rs}, \quad r \neq s, \tag{V.4}$$

where a is a constant to be determined empirically, with reference to the electronic spectrum of the molecule considered. Whereas (V.4) probably is a reasonable approximation if all orbitals involved are quite similar (as in organic molecules), it is less valid in inorganic complexes where there are large variations as to the shapes of the atomic orbitals involved.

The evaluation of two-electron integrals by semi-empirical methods also becomes much more involved for such systems, as for instance exemplified by Oleari *et al.* (1966a) in their MnO_4^- calculation. It is necessary here to use rather unsatisfactory interpolation techniques to obtain the values of the two-center, two-electron integrals. All in all, one encounters so many ambiguities in an attempt to apply the semi-empirical approach just outlined to inorganic complexes, that one's faith in the reliability of the results is badly shaken.

A different approach is, however, possible. This approach utilizes a reinterpretation of the ZDO and CNDO approximations to obtain numerical values for the matrix elements by computation alone. These computations can all be carried out using the DIATOM programs, and there is no reason to believe that such a method should be inferior to the semi-empirical methods. In fact, it has earlier been used by the authors (Dahl and Ballhausen, 1961), seemingly with meaningful results.

This alternative approach will be described in the next section which deals with the problem of justifying zero differential overlap approximations.

B. Orthogonalization Procedures

As originally shown by Löwdin (1955), it is possible to justify the ZDO approximation in the case of a single orbital per atom by assuming that the original atomic orbitals $\chi_1, \chi_2, \ldots, \chi_m$ have been replaced by a new set of orbitals $\lambda_1, \lambda_2, \ldots, \lambda_m$, defined through the equation

$$\boldsymbol{\lambda} = \boldsymbol{\chi}\mathbf{S}^{-1/2}. \tag{V.5}$$

$\boldsymbol{\lambda}$ and $\boldsymbol{\chi}$ are row matrices with elements λ_r and χ_r respectively, and S is the overlap matrix corresponding to the functions χ_r. Only real orbitals are considered in this and the following sections.

The λ_r orbitals defined through Eq. (V.5) form an orthonormal set

$$\int \lambda_r(1)\lambda_s(1)\, d\tau_1 = \delta_{rs}, \tag{V.6}$$

and they are referred to as symmetrically orthogonalized orbitals. A very general analysis of (V.5) and its implications has been given by Fischer-Hjalmars (1965a,b), to which the reader is referred for details. For the present purposes it is important that the right-hand side of Eq. (V.5) can be written as a power series in the overlap integrals. Confining ourselves to the diatomic case for simplicity we have, when only first-order terms in the overlap integrals are retained (S_{ab} small),

$$\lambda_a = \chi_a - \tfrac{1}{2}S_{ab}\chi_b, \qquad \lambda_b = \chi_b - \tfrac{1}{2}S_{ab}\chi_a. \tag{V.7}$$

From (V.7) we get expressions for the charge distributions $\lambda_a\lambda_a$, $\lambda_b\lambda_b$, and $\lambda_a\lambda_b$ in terms of the normalized distributions $\chi_a\chi_a$, $\chi_b\chi_b$, and $\chi_a\chi_b/S_{ab}$. Retaining only first-order terms in S_{ab} we obtain:

$$\begin{aligned} \lambda_a\lambda_a &= \chi_a\chi_a, \\ \lambda_b\lambda_b &= \chi_b\chi_b, \\ \lambda_a\lambda_b &= \chi_a\chi_b - \tfrac{1}{2}S_{ab}(\chi_a\chi_a + \chi_b\chi_b). \end{aligned} \tag{V.8}$$

This gives immediately for the matrix elements of $\hat{H}^{\text{core}}$:

$$\begin{aligned} (\lambda_a|H^{\text{core}}|\lambda_a) &= (\chi_a|H^{\text{core}}|\chi_a), \\ (\lambda_b|H^{\text{core}}|\lambda_b) &= (\chi_b|H^{\text{core}}|\chi_b), \\ (\lambda_a|H^{\text{core}}|\lambda_b) &= (\chi_a|H^{\text{core}}|\chi_b) \\ &\quad - \tfrac{1}{2}S_{ab}[(\chi_a|H^{\text{core}}|\chi_a) + (\chi_b|H^{\text{core}}|\chi_b)]. \end{aligned} \tag{V.9}$$

If the (χ_a, χ_b) set can be assigned to class I (see Section IV,F), the Mulliken approximation of Eq. (IV.50) may be appropriate for the evaluation of two-electron integrals. For this purpose we may thus replace (V.8) by

$$\lambda_a\lambda_a = \chi_a\chi_a, \qquad \lambda_b\lambda_b = \chi_b\chi_b, \qquad \lambda_a\lambda_b = 0. \tag{V.10}$$

If the Roothaan equations (IV.35) are formulated with the symmetrically orthogonalized orbitals λ_r instead of the orbitals χ_r, we obtain immediately the ZDO form of Eqs. (V.1)–(V.3) by observing Eq. (V.10). In this way the ZDO approximation has been justified in the case of only one valence orbital per atom, assuming small overlap integrals. According to Eqs. (V.9) and (V.10), it is only in evaluating $(\lambda_a|H^{\text{core}}|\lambda_b)$ that it is necessary to observe that the orbitals λ_r are being used instead of the orbitals χ_r.

The results which we have just stated are well known (see Fischer-Hjalmars, 1965a,b). Consider now the case where there is more than one orbital per atom which can contribute to the same LCAO MO. For simplicity, we consider again the diatomic case and assume that there is one orbital, χ_a, on center a and two orbitals, χ_b and χ_b' on center b. Equation (V.5) gives in this case, for small overlaps,

$$\begin{aligned} \lambda_a &= \chi_a - \tfrac{1}{2}S_{ab}\chi_b - \tfrac{1}{2}S'_{ab}\chi_b', \\ \lambda_b &= \chi_b - \tfrac{1}{2}S_{ab}\chi_a, \\ \lambda_b' &= \chi_b' - \tfrac{1}{2}S'_{ab}\chi_a. \end{aligned} \tag{V.11}$$

We have assumed that χ_b and χ_b' are orthogonal, since this is usually the case.

From (V.11) we get, through application of the Mulliken approximation,

$$\lambda_a\lambda_b = -\tfrac{1}{2}S'_{ab}\chi_b\chi_b', \qquad \lambda_a\lambda_b' = -\tfrac{1}{2}S_{ab}\chi_b\chi_b'. \tag{V.12}$$

The right-hand sides of these equations can not, in general, be neglected, and consequently we cannot give a theoretical justification for the ZDO approximation, when there is more than one valence orbital on each atom. The approximations (1)–(3) of Section V,A are not quite consistent, since $\chi_b\chi_b'$ is retained in some integrals, neglected in others, namely those which originate from $\lambda_a\lambda_b$ and $\lambda_a\lambda_b'$.

It is clear, however, that if the assumption is made that $\chi_b\chi_b'$ can be neglected in the calculation, then $\lambda_a\lambda_b = \lambda_a\lambda_b' = 0$. In this way we obtain the CNDO approximation as a consistent basis for calculations. Although it is, in general, a bad approximation to neglect $\chi_b\chi_b'$ in evaluating integrals, we shall in the next section give reasons to neglect it in the Roothaan equations.

We have so far assumed that all overlap integrals are small, and that it is feasible to use the Mulliken approximation. For orbital sets in class II (Section IV,F), none of these assumptions may be valid. In this case we suggest using the Schmidt procedure rather than (V.5) to obtain a new set of atomic orbitals. Let χ_a be a metal 4*s* or 4*p* orbital, and χ_b a ligand orbital. Two new orbitals are then defined as

$$\mu_a = (1 - S_{ab}^2)^{-1/2}(\chi_a - S_{ab}\chi_b), \qquad \mu_b = \chi_b . \tag{V.13}$$

These two orbitals are orthogonal for all values of S_{ab}, and we find

$$\mu_a\mu_b = (1 - S_{ab}^2)^{-1/2}(\chi_a\chi_b - S_{ab}\chi_b\chi_b). \tag{V.14}$$

If, in the evaluation of two-electron integrals, we make the assumption that

$$\chi_a\chi_b \approx S_{ab}\chi_b\chi_b \tag{V.15}$$

(see Eq. (IV.50)), then $\mu_a\mu_b$ vanishes, and a ZDO approximation has been obtained.

For the purpose of evaluating two-electron integrals we have then the following expressions:

$$\begin{aligned} \mu_a\mu_a &= (1 - S_{ab}^2)^{-1}(\chi_a\chi_a - S_{ab}^2\chi_b\chi_b), \\ \mu_b\mu_b &= \chi_b\chi_b , \\ \mu_a\mu_b &= 0. \end{aligned} \tag{V.16}$$

We note that $\mu_a\mu_a$ cannot simply be replaced by $\chi_a\chi_a$, but also that (V.16) only gives rise to simple Coulomb integrals.

Corresponding to Eq. (V.9), we get for the matrix elements of $\hat{H}^{\text{core}}$

$$\begin{aligned} (\mu_a|H^{\text{core}}|\mu_a) &= (1 - S_{ab}^2)^{-1}[(\chi_a|H^{\text{core}}|\chi_a) + S_{ab}^2(\chi_b|H^{\text{core}}|\chi_b) \\ &\quad - 2S_{ab}(\chi_a|H^{\text{core}}|\chi_b)], \\ (\mu_b|H^{\text{core}}|\mu_b) &= (\chi_b|H^{\text{core}}|\chi_b), \\ (\mu_a|H^{\text{core}}|\mu_b) &= (1 - S_{ab}^2)^{-1/2}[(\chi_a|H^{\text{core}}|\chi_b) - S_{ab}(\chi_b|H^{\text{core}}|\chi_b)]. \end{aligned} \tag{V.17}$$

These expressions are somewhat more complicated than those of Eq. (V.9), but they are not much harder to work with.

In using Eqs. (V.9) and (V.17) it is advantageous to write (IV.25) in the form

$$\hat{H}^{\text{core}}(1) = \hat{T}(1) + V_a(1) + V_b(1) + \sum_c V_c(1), \tag{V.18}$$

where the sum over *c* includes all centers different from *a* and *b*. If the approximations (IV.50) are used in evaluating the matrix elements involving the V_c terms, then these terms do not contribute to $(\lambda_a|H^{\text{core}}|\lambda_b)$ and

$(\mu_a|H^{\text{core}}|\mu_b)$. In other words, the off-diagonal elements of the operator $\hat{H}^{\text{core}}$ are to a good approximation quantities that only depend on the two centers involved (a and b). This is an important conclusion because it allows one to transfer these quantities from one molecule to another and to interpolate in homologue series.

In the case of more than one orbital per atom the Schmidt orthogonalization scheme gives, instead of (V.11),

$$\begin{aligned} \mu_a &= (1 - S_{ab}^2 - S_{ab}'^2)^{-1/2}(\chi_a - S_{ab}\chi_b - S_{ab}'\chi_b'), \\ \mu_b &= \chi_b, \\ \mu_b' &= \chi_b', \end{aligned} \qquad \text{(V.19)}$$

and we see that for instance

$$\mu_a\mu_b = -(1 - S_{ab}^2 - S_{ab}'^2)^{-1/2}\, S_{ab}'\chi_b\chi_b', \qquad \text{(V.20)}$$

so that the discussion following Eq. (V.12) also holds in this case: the only zero differential overlap approximation which can be justified is the CNDO approximation, and that presupposes the extra assumption that $\chi_b\chi_b' = 0$.

The extension of the formulas given in this section to two or more orbitals per atom is straightforward and will not be given here. But it is stressed that all matrix elements of $\hat{H}^{\text{core}}$ can be evaluated using the DIATOM programs, and this procedure seems to us to be preferable as compared, for instance, to Eq. (V.4). This does not mean that we want to exlude semi-empirical parameters in the evaluation of $\hat{H}^{\text{core}}$ matrix elements; they have not been necessary so far, but a natural procedure would be to scale the calculated matrix elements, rather than the overlap integrals of Eq. (V.4).

In closing this section, it should be mentioned that none of the approximations introduced here allow an electron to interact with itself. This follows from the fact that wherever a charge distribution like $\chi_a\chi_b$ occurs in the evaluation of two-electron integrals, it is always treated in the same way, and this is sufficient to ensure the proper cancellation of matrix elements.

C. Interpretation of the CNDO Approximation

In the present section, we discuss the physical content of the CNDO method, and arrive at the conclusion that this method should form a good basis for MO calculations on transition metal complexes. This conclusion is supported by the results of a calculation on the permanganate ion, to be reported in the next section.

One of the results of the previous section was that there are certain internal inconsistencies in the ZDO approximation when an atom can contribute more than one atomic orbital to an LCAO MO. Table I shows that this is usually the case in tetrahedral complexes, and the situation is not altered much in a case of octahedral symmetry. It might well be that the objections raised are not too serious from a practical point of view, but then it is a matter of doubt whether the ZDO method can give any reliable information exceeding that supplied by the CNDO method.

One feature of the CNDO method has not been touched on so far. It was shown by Pople *et al.* (1965) that this method will only give results independent of the orientation of coordinate systems if all atomic orbitals are considered to be s-like in the evaluation of two-electron integrals. Thus it is only through the radial functions that one can distinguish s, p, d orbitals etc., on the same center in such integrals. The angular dependence of atomic orbitals highly complicates the evaluation of two-electron integrals, so the requirement of Pople *et al.* leads to a welcome simplification. The physical content of this requirement as well as the CNDO approximation itself will now be discussed.

We take our starting point in Eq. (IV.33), which gives the expression for the Hartree–Fock operator in the LCAO MO method. The exchange part of the operator is neglected for the moment; it will be introduced again later, using the requirement that an electron may not interact with itself. The part of the operator to be considered at present is then

$$\hat{H}_0 = \hat{H}^{\text{core}} + \sum_{t,u} P_{t,u}[\quad | t'u'], \tag{V.21}$$

and we assume that the atomic orbitals defining $[\quad | tu]$ have been orthogonalized using the procedures of the preceding section. This is indicated with primes in Eq. (V.21).

Using equations like (V.10), (V.12), (V.16), and (V.20), it is possible to reduce the sum in (V.21) to a sum over the various atoms in the system. We shall not carry the reduction through, but the result must emerge on the form

$$\hat{H}_0 = \hat{H}^{\text{core}} + \sum_a \sum_{t_a,u_a} B_{t_a,u_a}[\quad | t_a u_a], \tag{V.22}$$

with the operator $[\quad | t_a u_a]$ defined in terms of the original, nonorthogonalized orbitals; a refers to the atoms over which we sum. Introducing the Goeppert-Mayer, Sklar approximation of Eq. (IV.25) we get:

$$\hat{H}_0 = \hat{T} + \sum_a \left(V_a + \sum_{t_a,u_a} B_{t_a,u_a}[\quad | t_a u_a] \right). \tag{V.23}$$

The expression in brackets in (V.23) can be interpreted as the Coulomb potential from the atom *a in situ*. This potential is not spherically symmetric around a, but we shall consider it to be so. Three reasons may be given for this consideration:

(1) The spherically symmetric part of the potential from the atom a is likely to be the predominant part. It includes a point charge potential due to the fact that the atom is not neutral in the molecule, and a penetration part.

(2) The deviations from spherical symmetry are probably not well represented by (V.23). This is because this equation is dependent on the approximations of Eq. (IV.50). We may consider the potential from the charge distribution $\chi_a\chi_b$ as being made up of monopole, dipole, quadrupole terms, etc. Through (IV.49) we have assured a correct representation of the monopole term, and we may consider the distinction between two forms in Eq. (IV.50) as an attempt to reproduce the dipole term correctly, but this attempt is probably not a very successful one (see also Löwdin, 1953). No attempt is made in (IV.50) to reproduce quadrupole and higher order terms correctly. Hence, by only retaining the spherical terms of the potential from the atom a we take the consequences of our approximations at an earlier stage.

(3). Deviation from spherical symmetry has for a long time been neglected in energy band calculations on solids, using the augmented plane wave method, and very accurate and detailed results have been obtained in this way (see e.g., a recent review article by Slater, 1964). Energy band calculations use large basis sets and the success of the augmented plane wave method indicates that it might be more important to introduce a larger number of atomic orbitals on each center in MO calculations than to consider deviations from spherical symmetry.

The spherical average around a of the potential

$$V_a + \sum_{t_a, u_a} B_{t_a, u_a} [\quad | \, t_a u_a]$$

can be obtained by taking the spherical average of each term separately. Since V_a is already spherically symmetric we are left with the problem of finding the spherical average of the potential $[\quad | \, t_a u_a]$. To find this potential, we imagine an expansion of the charge distribution $\chi_{t_a}\chi_{u_a}$ in spherical harmonics $Y_l^m(\theta, \varphi)$ times radial functions around a. We then note that the potential from a charge distribution $R(r)\,Y_l^m(\theta, \varphi)$ can be written as $U(r)\,Y_l^m(\theta, \varphi)$, where U is some function of r (see e.g. Roothaan, 1951b)., Since the spherical average of $Y_l^m(\theta, \varphi)$ is zero unless $m = l = 0$, we conclude that it is only the first term in the expansion of $\chi_{t_a}\chi_{u_a}$ which contributes to the spherical average looked for. It is thus a correct procedure to replace $[\quad | t_a u_a]$ by the potential from the spherical average of $\chi_{t_a}\chi_{u_a}$.

The spherical average of $\chi_{t_a}\chi_{u_a}$ is zero unless χ_{t_a} and χ_{u_a} have the same angular dependence, and this is usually not the case in MO calculations on transition metal complexes. The extension to more than one atomic orbital per atom of given l, m values should not be difficult, but it is not considered here.

We finally note that the spherical average of $\chi_{t_a}\chi_{t_a}$ results, when χ_{t_a} is replaced by an s orbital with the same radial dependence as χ_{t_a} itself. Denoting such an orbital $\bar{\chi}_{t_a}$ we get for the averaged part of (V.23):

$$\hat{\bar{H}}_0 = \hat{T} + \sum_a \left(V_a + \sum_{t_a} B_{t_a,t_a}[\quad | \bar{t}_a \bar{t}_a] \right). \tag{V.24}$$

Consider now the matrix element of an original atomic orbital χ_{r_a} with itself, using the operator (V.24). From $\hat{T}$ and the atom a we get the contribution

$$(r_a|T|r_a) + (r_a|V_a|r_a) + \sum_{t_a} B_{t_a,t_a}[\bar{r}_a \bar{r}_a | \bar{t}_a \bar{t}_a].$$

We have here replaced χ_{r_a} with an s-like orbital in the sum over t_a, because only the spherically symmetric part of the charge distribution $\chi_{r_a}\chi_{r_a}$ contributes, when the potential itself is spherically symmetric. Such a replacement is, however, not allowed in the integrals $(r_a|T|r_a)$ and $(r_a|V_a|r_a)$, because $\hat{T}$ is a differential operator, and because V_a according to (IV.26) contains exchange terms.

The contribution from atoms other than a to the matrix element considered is evaluated under the assumption that the other atoms supply a potential which is spherically symmetric around a. The reasons which support this approximation are similar to the previous reasons (1)–(3):

(1) The spherically symmetric part is the predominant part.

(2) Deviations from spherical symmetry are difficult to calculate exactly, and are probably not well represented in our scheme because of the approximations of Eq. (IV.50). It should be noted here that we are neglecting—by the assumption above—the electrostatic contribution to the splitting parameter $10Dq$. But then it is known, from the investigations of Kleiner (1952) and Freeman and Watson (1960), that this contribution is

small, and further that even the sign of the contribution cannot be reproduced correctly unless very accurate calculations are performed (see Section IV,C). Again, we are taking the consequences of our approximations at an earlier stage.

(3) The same approximation is made in successful calculations on solids.

Instead of explicitly evaluating the spherical average of the potential from atoms other than a, we take advantage of the fact that we can take the spherical average of $\chi_{r_a}\chi_{r_a}$ instead, i.e., we consider χ_{r_a} as an s orbital. Thus the contribution to the matrix element considered is

$$\sum_{b\neq a}\left((\bar{r}_a|V_b|\bar{r}_a)+\sum_{t_b}B_{t_b,t_b}[\bar{r}_a\bar{r}_a \mid \bar{t}_b\bar{t}_b]\right),$$

so that

$$\begin{aligned}(r_a|\bar{H}_0|r_a) &= (r_a|T+V_a|r_a)+\sum_{t_a}B_{t_a,t_a}[\bar{r}_a\bar{r}_a \mid \bar{t}_a\bar{t}_a]\\ &\quad +\sum_{b\neq a}\left((\bar{r}_a|V_b|\bar{r}_a)+\sum_{t_b}B_{t_b,t_b}[\bar{r}_a\bar{r}_a \mid \bar{t}_b\bar{t}_b]\right).\end{aligned} \tag{V.25}$$

Strictly, this equation is only true when the exchange part of V_b is neglected, but this is an excellent approximation.

If, instead of evaluating the matrix element between χ_{r_a} and itself, we had taken the matrix element between two different orbitals on center a we should get zero by carrying through the same set of approximations, because there is no matrix element between such orbitals with respect to a spherically symmetric potential.

It is now easy to see that the approximations carried through lead to the CNDO approximation. Equation (V.24) follows from (V.21), if we neglect all terms in the latter for which $t \neq u$ and perform a spherical averaging in the original basis set. The coefficients B_{t_a,t_a} would equal P_{t_a,t_a} if we had used symmetrical orthogonalization throughout, but since Schmidt orthogonalization has been used for some of the orbitals, equations like (V.16) must be observed.

Next, the matrix element between an orthogonalized orbital and itself can be expressed in terms of elements like (V.25), and if the matrix element is taken between two different orbitals, we get zero if the two orbitals refer to the same center, and a core contribution only if the two orbitals belong to different centers (due to Eqs. (V.12) and (V.19), which are used for the two-electron terms).

We can in this way verify that the spherical average approximation discussed above is equivalent to the CNDO approximation so far as the core and Coulomb parts of (IV.35) are concerned. With respect to the exchange terms (the terms with negative sign in (IV.35)) such approximations should be made that prevent an electron from interacting with itself, i.e., all integrals should be treated exactly as in the Coulomb terms, and this leads immediately to the CNDO equations (V.1–3).

It appears that the CNDO scheme in the form outlined above should be a reasonably accurate scheme situated between semi-empirical schemes like the extended Wolfsberg–Helmholz scheme and the quantitative approach based on an exact solution of Roothaan's equations. The CNDO scheme seems to be the only semiquantitative scheme which is free of internal inconsistencies, although there are reasons to believe that the inconsistencies involved in the ZDO method are not very serious.

VI. The Permanganate Ion

A. An MO Calculation in the CNDO Approximation

A molecular orbital calculation has been performed for the MnO_4^- ion, using the procedure discussed in the preceding section. The division into core orbitals and valence orbitals was the one suggested in Section II, and we refer to Table I and Fig. 1 of that section with regard to the construction of symmetry-adapted functions.

The orthogonalization procedures described in Section V,B were applied, and generalizations of the formulas given in that section were used in the evaluation of matrix elements. All integrals were evaluated exactly by means of the DIATOM programs. The radial functions were those of Clementi and Raimondi (1963) for the ligands, whereas the functions of Richardson *et al.* (1962, 1963) were used for the metal orbitals $3d$, $4s$, $4p$. The orbitals used were those corresponding to the configurations $(3d)^7$, $(3d)^5(4s)^2$, and $(3d)^5\,(4p)^2$, respectively.

The radial functions chosen are all orthogonal to the core orbitals on the center to which they belong, but there are small overlap integrals with core orbitals on different centers. These overlap integrals were neglected in the present investigation (as in all other MO calculations performed hitherto), but since some of them have a value close to 0.10 (metal $3p$, oxygen $2p$ overlaps), it would be desirable to reconsider this approximation in later calculations. In the same token ligand-ligand overlaps between valence orbitals were neglected in the calculation, since these are considerably smaller (less than 0.02). Matrix elements of $\hat{H}^{\text{core}}$ between ligand orbitals on different centers were likewise discarded.

TABLE III

GROUP OVERLAP INTEGRALS

a_1	$\tilde{S}(s, \sigma_s) =$	0.6542
	$\tilde{S}(s, \sigma_p) =$	0.1661
e	$\tilde{S}(d, \pi) =$	0.2809
t_2	$\tilde{S}(p, \sigma_p) =$	−0.0123
	$\tilde{S}(p, \sigma_s) =$	0.4816
	$\tilde{S}(p, \pi) =$	−0.2458
	$\tilde{S}(d, \sigma_p) =$	0.1920
	$\tilde{S}(d, \sigma_s) =$	0.3050
	$\tilde{S}(d, \pi) =$	0.1622

TABLE IV

MATRIX ELEMENTS OF $\hat{H}^{\text{core}}$ BETWEEN SYMMETRY-ADAPTED, ORTHOGONALIZED FUNCTIONS. ATOMIC UNITS (1 a.u. = 27.21 eV)

a_1	s	σ_s	σ_p
s	−8.2329	0.3785	−0.2797
σ_s	0.3785	−10.7969	0
σ_p	−0.2797	0	−10.2379

e	d	π
d	−11.9436	−0.0854
π	−0.0854	−10.2379

t_2	p	σ_p	d	σ_s	π
p	−6.8679	−0.2914	0	0.3086	−0.2627
σ_p	−0.2914	−10.2379	−0.3666	0	0
d	0	−0.3666	−11.9436	−0.3659	−0.0493
σ_s	0.3086	0	−0.3659	−10.7969	0
π	−0.2627	0	−0.0493	0	−10.2379

The group overlap integrals and the matrix elements of $\hat{H}^{\text{core}}$ between symmetry adapted, orthogonalized orbitals are listed in Tables III and IV. By comparing the two tables it is noted that there are exceptions to the rule that a positive overlap integral implies a negative matrix element of $\hat{H}^{\text{core}}$ and vice versa. The exceptions occur in connection with the 4*s* and 4*p* orbitals and are due to the fact that these orbitals have been Schmidt orthogonalized to the ligand 2*s* and 2*p* orbitals with which they overlap strongly.

This effect is illustrated in Fig. 8 where the 4*s* orbital, orthogonalized to a ligand 2*s* orbital, is plotted along the metal-ligand bond axis. The 2*s* orbital contributes so much to this orbital that the latter becomes negative in the region of the 2*s* orbital. The bonding combination between the 2*s* orbital and the orthogonalized 4*s* orbital will consequently correspond to different signs for the two orbitals in an LCAO MO, and this is effected through a positive ratio between overlap integral and core matrix element. Figure 9 shows that the 2*p* orbital has a smaller effect on the 4*s* orbital and hence the ratio is negative for these two orbitals.

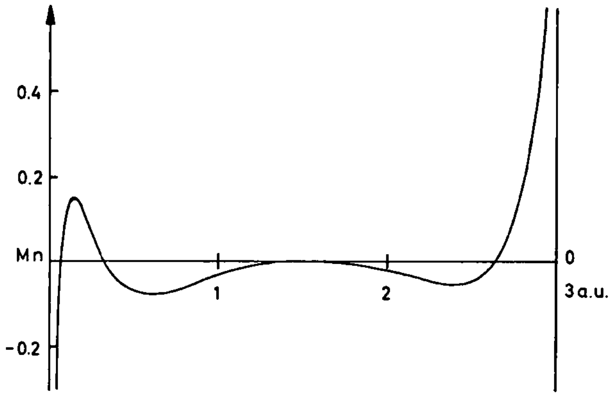

Fig. 8. The function $\chi(4s)-0.3271\chi(\sigma_s)$ plotted along the Mn—O bond axis.

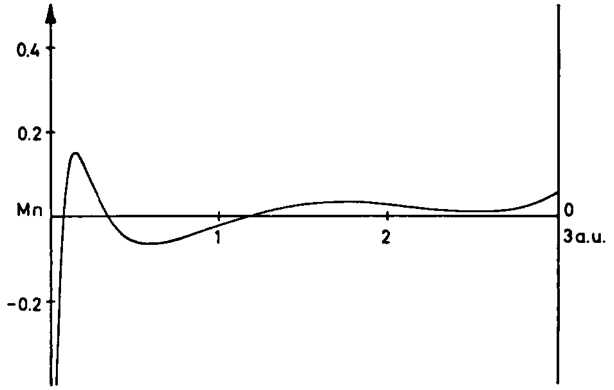

Fig. 9. The function $\chi(4s)-0.0831\chi(\sigma_p)$ plotted along the Mn—O bond axis.

A comparison between Tables III and IV does not reveal any simple relation as for instance (V.4), since even the sign of the ratio $(r|H^{\text{core}}|s)/S_{rs}$ is not constant in going from one orbital pair to another. This fact supports the assertion stated in Section V,A, that the various atomic orbitals differ too much in shape for simple relations like (V.4) to be even approximately valid.

In Table V we present the self-consistent LCAO MO's and the corresponding orbital energies from our calculation. All orbitals with energies less than −10 eV are fully occupied, the remaining ones are empty. Table V shows some important features:

TABLE V

MOLECULAR ORBITALS FOR MnO_4^-; CALCULATION A

Eigenvalues (eV)		Eigenvectors				
		s	σ_s	σ_p		
a_1	3.17	0.3887	0.1318	−0.9119		
	−18.75	0.6793	0.6276	0.3803		
	−38.59	0.6225	−0.7673	0.1544		
		d	π			
e	−2.91	0.6850	−0.7286			
	−16.46	0.7286	0.6850			
		p	σ_p	d	σ_s	π
t_2	11.21	−0.3012	0.7635	−0.5390	0.0956	0.1632
	1.57	−0.6189	0.0039	0.4393	−0.3920	0.5199
	−14.05	−0.1840	0.3923	0.3743	−0.2987	−0.7635
	−25.53	0.6263	0.5107	0.4787	0.0076	0.3431
	−37.89	−0.3164	0.0484	0.3838	0.8648	−0.0491
		π				
t_1	−12.21	1.0000				

The 4s and 4p orbitals are distributed among all the molecular orbitals, a result which is at variance with all earlier MO calculations (cf. the discussion at the end of Section II). We do not think that this feature is a result of the approximations made in our calculation, but rather that it occurs because the overlap problem has been treated in a more detailed way than is usually the case. The conclusion is then that the 4s and 4p orbitals are actively involved in the chemical bonding. This point of view is in qualitative agreement with Pauling's hybridization idea, that the metal-ligand bonding is arranged through sp^3 hybrids on the metal.

TABLE VI

MOLECULAR ORBITALS FOR MnO_4^-; CALCULATION B

Eigenvalues (eV)		Eigenvectors				
		s	σ_s	σ_p		
a_1	1.70	0.4816	0.1621	−0.8613		
	−18.55	0.6888	0.5377	0.4863		
	−39.01	0.5419	−0.8274	0.1473		
		d	π			
e	−4.88	0.7656	−0.6433			
	−18.49	0.6433	0.7656			
		p	σ_p	d	σ_s	π
t_2	9.15	−0.3780	0.7522	−0.5031	0.0684	0.1828
	0.56	−0.6529	−0.0791	0.4741	−0.3982	0.4293
	−16.53	−0.1565	0.3709	0.3430	−0.2746	−0.8031
	−26.75	0.5781	0.5345	0.4885	−0.0752	0.3686
	−39.70	−0.2687	0.0679	0.4073	0.8693	−0.0396
		π				
t_1	−15.16	1.0000				

It should not, however, be believed that σ bonding alone is responsible for the chemical bonding. Table V shows that π bonding plays a role as well; essentially through the orbitals $3t_2$ and $1e$.

The nonoccupied orbitals of Table V may be used in the construction of excited-state wave functions, according to Eqs. (IV.15) and (IV.16). The energies of these singly excited states have been given in Eqs. (IV.17) and (IV.18). Since the ground state wave function transforms as $^1A_1$, transitions are only allowed to states of symmetry $^1T_2$. In order to approximate the energies of the true excited states of $^1T_2$ symmetry, we must set up a configuration interaction between singly excited states of this symmetry, and in order to approximate the true ground state energy a configuration interaction calculation must be performed which includes the wave function (IV.2) and wave functions for doubly excited states.

From calculations on simple molecules we know that both types of configuration interaction are very important in calculating transition energies. This means that extremely extensive calculations are required to place states of different symmetry in the correct order, and also to evaluate energy differences between states of the same symmetry correctly.

In Table VII we have attempted to obtain a very qualitative picture of the first excited states by calculating transition energies by means of Eq. (IV.20). The proper expressions to use for singly excited states differ from (IV.20) through exchange integrals and other two-electron integrals of a similar magnitude. We can, however, not calculate those even approximately in the CNDO scheme, because important one-center integrals are neglected. Hence, we use only the simple expression (IV.20).

TABLE VII

CALCULATED TRANSITION ENERGIES IN MnO_4^-

Transition	Transition energy (eV[a])		
	A	B	C
$t_1 \rightarrow 2e$	0.00	1.06	2.27
$3t_2 \rightarrow 2e$	1.41	1.92	3.13
$t_1 \rightarrow 4t_2$	5.95	8.11	9.32
$3t_2 \rightarrow 4t_1$	7.61	9.27	10.48

[a] See explanation in text.

The calculated transition energies appear in column A of Table VII. The $t_1 \rightarrow 2e$ transition energy is found to be zero. Thus we lose no energy by allowing the π electrons on the ligands to spread onto the metal ion. We assume that this result is due to a neglect of the surroundings. The negative ligands of the MnO_4^- ion must coordinate with positive ions in the solution or the crystal, and in this way electrons are stabilized on the ligands. It is a part of future investigations to estimate the magnitude of this stabilization. We have arbitrarily introduced a stabilization of 0.2 a.u. = 5.44 eV and redone the self-consistent field calculation with this number subtracted from all core integrals for the ligands.

The results from this calculation are presented in Table VI, and the corresponding transition energies are listed in column B of Table VII. These energies are now all positive, but according to Eq. (IV.20), they represent transitions to the triplet states. In order to represent the singlet states, the quantity $2K_{ik}$ must be added. If we assume that $2K_{ik} = 1.21$ eV, which is not unreasonable, the first band maximum in the spectrum of MnO_4^- is reproduced. Hence we have added 1.21 eV to all energies in column B to obtain the results of column C. These results will be discussed in the next section.

In concluding this section we remark that the calculations in Tables V and VI predict the $3d$ orbital populations 5.22 and 4.79 respectively. Since the Mn atom has five d electrons in its ground state, this finding is very reasonable.

Note added in proof: Since the completion of the present report, a series of calculations have been performed in which the radial functions of the problem have been varied systematically (Dahl and Johansen, 1968). From these calculations conclusions have been drawn with respect to the proper choice of atomic orbitals in such calculations, and a whole series of tetrahedral ions have been treated (Johansen and Dahl, 1968).

B. Interpretation of the Electronic Spectrum

The electronic structure of MnO_4^- has been under discussion for about 15 years, but there are still differences in opinion regarding the interpretation of the visible and near spectrum of this ion. In this section, we discuss the results of earlier calculations on MnO_4^-, and add the extra information obtained through the CNDO calculations of the previous section.

The absorption spectrum of MnO_4^- consists of three bands with maxima at 2.27 eV, 3.99 eV, 5.45 eV, and a shoulder at 3.47 eV. Viste and Gray (1964) report an additional, weak band at 1.80 eV, but measurements in this laboratory (Holt and Ballhausen, 1967) on MnO_4^- dissolved in $KClO_4$ do not show any sign of this absorption. Through an analysis of the vibrational fine structure of the absorption bands it has been concluded that there is only one electronic transition associated with each of the maxima at 2.27 eV, 3.99 eV, and 5.45 eV, and that the shoulder at 3.47 eV probably represents a separate transition (Wolfsberg and Helmholz, 1952; Ballhausen, 1963; Holt and Ballhausen, 1967).

The early calculation of Wolfsberg and Helmholz (1952) and the investigation by Ballhausen and Liehr (1958) have already been mentioned in Section III,A. The orbital energies found by Wolfsberg and Helmholz are shown in column I of Fig. 10, and it was the finding that $3t_2$ has lower energy than $2e$ that was challenged by Ballhausen and Liehr. The following assignments of the bands at 2.27 eV and 3.99 eV were proposed.

Assignment 1: $t_1 \rightarrow 3t_2$ (2.27) eV) (Wolfsberg and Helmholz,
$2t_2 \rightarrow 3t_2$ (3.99 eV) 1952)

Assignment 2: $t_1 \rightarrow 2e$ (2.27 eV) (Ballhausen and Liehr, 1958)
$t_1 \rightarrow 3t_2$ (3.99 eV)

Later, Fenske and Sweeney (1964) concluded that the extended Wolfsberg–Helmholz method was unable to settle the question which orbital has higher energy, $2e$ or $3t_2$. However, these authors did not allow the ligand $2s$ and $2p$ orbital coefficients to vary independently. When this was done (Viste and Gray, 1964) the t_2 orbital was found to have the higher energy. This result is in accordance with simple crystal field theory and Ballhausen and Liehr's suggestion.

The level scheme obtained by Viste and Gray is shown in Fig. 2 and in column II of Fig. 10. The numbering of the t_2 orbitals is different from that of column I, because Viste and Gray included the $2s$ orbitals on the ligands in the basis set. This was not done by Wolfsberg and Helmholz; neither was the strong orthogonality condition (IV.23) observed, and this is probably the reason for their reversal of the $3t_2$ and $2e$ orbitals, since a larger spread of the t_2 orbitals should occur, when (IV.23) is taken into account (as shown in column II of Fig. 10). Viste and Gray suggested the following interpretation of the electronic spectrum:

Assignment 3:	$t_1 \rightarrow 2e$	$(^1A_1 \rightarrow {}^1T_1)$	1.80 eV	
	$t_1 \rightarrow 2e$	$(^1A_1 \rightarrow {}^1T_2)$	2.27 eV	
	$3t_2 \rightarrow 2e$	$(^1A_1 \rightarrow {}^1T_1)$	3.47 eV	(Viste and Gray, 1964)
	$3t_2 \rightarrow 2e$	$(^1A_1 \rightarrow {}^1T_2)$	3.99 eV	
	$t_1 \rightarrow 4t_2$	$(^1A_1 \rightarrow {}^1T_2)$	5.45 eV	

Only $^1A_1 \rightarrow {}^1T_2$ transitions are allowed in tetrahedral symmetry, so that two of the transitions listed $(^1A_1 \rightarrow {}^1T_1)$ are orbitally forbidden.

Quite recently Oleari *et al.* (1966a,b) have performed a calculation on MnO_4^- and CrO_4^{2-} using the ZDO method described in Section V,A. All one-center integrals were evaluated from atomic spectra and two-electron integrals referring to two centers were treated by an interpolation technique (see Section V,A). The matrix elements of $\hat{H}^{\text{core}}$ were estimated from an equation similar to Eq. (III.1) with $F_x = 1$. A semi-empirical factor was also introduced in connection with the calculation of penetration integrals. The self-consistent field calculation was followed by a configuration interaction calculation between singly excited states.

Oleari *et al.* did not include the ligand $2s$ orbitals in their calculation, and they did not observe Eq. (IV.23). For this reason, they found too small a spread in the orbital energies and they concluded that essentially two electronic transitions should be associated with each band maximum. As mentioned at the beginning of this section this finding is at variance with the results from a vibrational analysis.

The level scheme of Oleari *et al.* is shown in column III of Fig. 10. It is noted that $2e$ is lower than $3t_2$, but Oleari *et al.* were also able to obtain the reverse order by choosing different radial functions for the atomic orbitals.

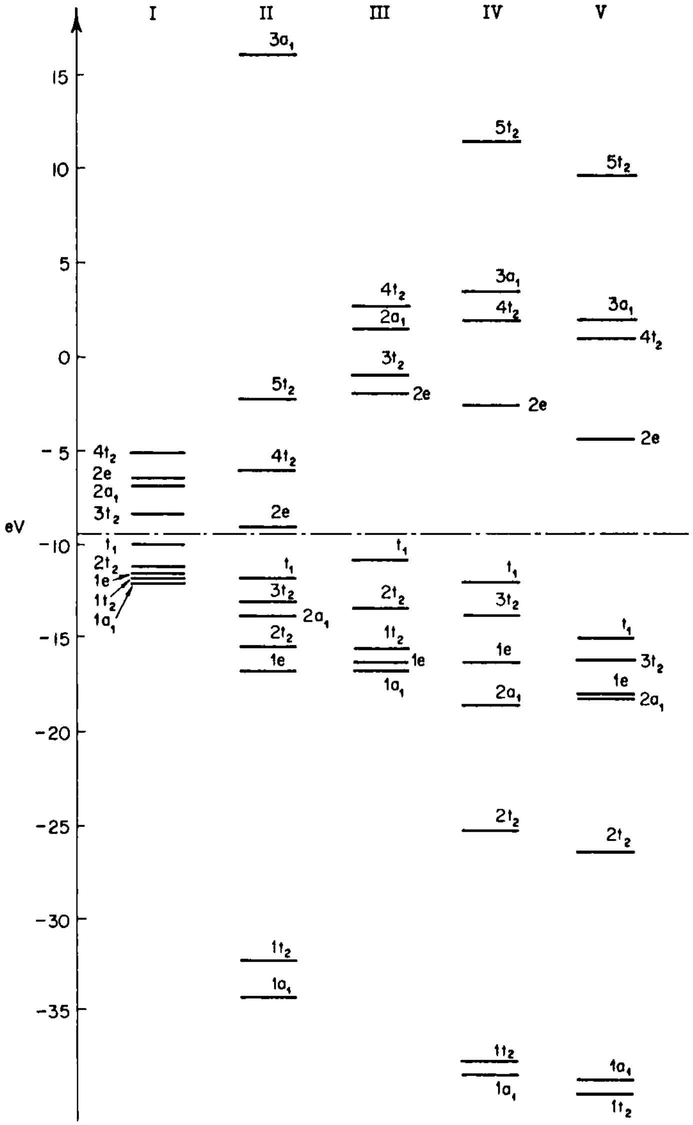

Fig. 10. Molecular orbital energy level diagrams for MnO_4^- according to various calculations described in the text. Orbitals below the broken line are fully occupied, orbitals above it empty.

Column IV of Fig. 10 shows the results from the CNDO calculation of Table V. In contrast to the other calculations mentioned in this section, this investigation does not use semi-empirical parameters at all. The calculation places $2e$ below $4t_2$, but the energy of the $3a_1$ orbital is now also rather low. This is surprising if we compare to Viste and Gray's results in column II, whereas it is more in accordance with the other calculations presented in Fig. 10.

The results in column V refer to the CNDO calculation of Table VI in which atomic orbitals on oxygen were stabilized by 0.2 a.u. = 5.44 eV, in order to simulate the field from neighboring cations. The relative ordering of the levels is not changed in going from column IV to V.

The two CNDO calculations just mentioned lead to the following assignment (See Table VII):

Assignment 4:	$t_1 \rightarrow 2e$	2.27 eV	
	$3t_2 \rightarrow 2e$	3.99 eV	(this work)
	$t_1 \rightarrow 4t_2$	5.45 eV	

The weak band at 3.47 eV is difficult to assign. As discussed in the previous section, it is very difficult to place transitions of different symmetry relative to each other.

The conclusion of the present section is that the two most consistent calculations, namely the calculation of Viste and Gray (1964) and the calculation in this paper, agree on the assignment of the bands at 2.27 eV and 3.99 eV. It is thus safe to state that the transitions involved are $t_1 \rightarrow 2e$ and $3t_2 \rightarrow 2e$ respectively. With respect to the band at 5.45 eV, we favor assignment 4 on the basis of Table VII. It must, however, be remembered that higher one-electron transitions contribute to this band through configuration interaction.

VII. Summary

In the present review we have discussed the semi-empirical and semiquantitative methods which have been used in molecular orbital calculations on transition metal complexes. We have contended that the extended Wolfsberg–Helmholz method forms a rational basis for semi-empirical calculations, but like semi-empirical methods in other fields, it should be used with care, and only the gross features of the results should be considered to be meaningful.

An analysis of semiquantitative methods led to the conclusion that the only completely consistent method uses the CNDO (complete neglect of differential overlap) approximation, and we are of the opinion that it is necessary to go to a completely quantitative scheme in order to get answers which are more detailed than those supplied by the CNDO method.

Finally, we have applied the CNDO method to the permanganate ion and arrived at important conclusions concerning the bonding and the electronic spectrum for this ion, without introducing semi-empirical factors which are so abundant in calculations on transition metal complexes.

Acknowledgments

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REFERENCES

BALLHAUSEN, C. J. (1963). *Theoret. Chim. Acta* **1**, 285.

BALLHAUSEN, C. J., and GRAY, H. B. (1962). *Inorg. Chem.* **1**, 111.

BALLHAUSEN, C. J., and GRAY, H. B. (1964). "Molecular Orbital Theory." Benjamin, New York.

BALLHAUSEN, C. J., and LIEHR, A. D. (1958). *J. Mol. Spectr.* **2**, 342.

BASCH, H., Viste, A., and GRAY, H. B. (1966). *J. Chem. Phys.* **44**, 10.

BEDON, H. D., HORNER, S. M., and TYREE, S. Y., Jr. (1964). *Inorg. Chem.* **3**, 647.

BEDON, H. D., HATFIELD, W. E., HORNER, S. M., and TYREE, S. Y., Jr. (1965). *Inorg. Chem.* **4**, 743.

CLEMENTI, E. (1964). *J. Chem. Phys.* **40**, 1944.

CLEMENTI, E., and RAIMONDI, D. L. (1963). *J. Chem. Phys.* **38**, 2686.

CORBATO, F. J., and SWITENDICK, A. C. (1963). *In* "Methods in Computational Physics" (B. Alder, S. Fernbach, and M. Rotenberg, eds.), Vol. 2, p. 155. Academic Press, New York.

COTTON, F. A., and HAAS, T. E. (1964). *Inorg Chem.* **3**, 1004.

COULSON, C. A. (1937). *Trans. Faraday Soc.* **33**, 1479.

DAHL, J. P., and BALLHAUSEN, C. J. (1961). *Kgl. Dansk. Videnskab. Selskab, Mat. Fys. Medd.* **33**, No. 5.

DAHL, J. P., and JOHANSEN, H. (1968). *Theoret. Chim. Acta,* in press.

FENSKE, R. F. (1965). *Inorg. Chem.* **4**, 33.

FENSKE, R. F., and SWEENEY, C. C. (1964). *Inorg. Chem.* **3**, 1105.

FENSKE, R. F., CAULTON, K. G., RADTKE, D. D., and SWEENEY C. C. (1966a). *Inorg. Chem.* **5**, 951.

FENSKE, R. F., CAULTON, K. G., RADTKE, D. D., and SWEENEY, C. C. (1966b). *Inorg. Chem.* **5**, 960.

FISCHER-HJALMARS, J. (1965a). *Advan. Quantum Chem.* **2**, 25.

FISCHER-HJALMARS, J. (1965b). *J. Chem. Phys.* **42**, 1962.

FREEMAN, A. J., and WATSON, R. E. (1960). *Phys. Rev.* **120**, 1254.

GEOPPERT-MAYER, M., and SKLAR, A. L. (1938). *J. Chem. Phys.* **6**, 645.

HATFIELD, W. E., BEDON, H. D., and HORNER, S. M. (1965). *Inorg. Chem.* **4**, 1181.

HERMAN, F., and SKILLMAN, S. (1963). "Atomic Structure Calculations." Prentice-Hall, Englewood Cliffs, New Jersey.

HOLT, S., and BALLHAUSEN, C. J. (1967). *Theoret. Chim. Acta* **7**, 313.

HUBBARD, J., RIMMER, D. E., and HOPGOOD, F. R. A. (1966). *Proc. Phys. Soc.* (*London*) **88**, 13.

INGRAHAM, L. L. (1966). *Acta Chem. Scand.* **20**, 283.

JOHANSEN, H., and BALLHAUSEN, C. J. (1966). *Mol. Phys.* **10**, 175.

JOHANSEN, H., and DAHL, J. P. (1968). *Theoret. Chim. Acta*, in press.

KEFFER, F., OGUCHI, T., O'SULLIVAN, W., and YAMASHITA, J. (1959). *Phys. Rev.* **115**, 1553.

Kleiner, W. H. (1952). *J. Chem. Phys.* **20**, 1784.

LIEHR, A. D. (1963). *J. Phys. Chem.* **67**, 1314.

LIEHR, A. D., and BALLHAUSEN, C. J. (1959). *Ann. Physik* [7] **6**, 134.

LOHR, L. L., Jr., and LIPSCOMB, W. W. (1963). *J. Chem. Phys.* **38**, 1607.

LÖWDIN, P. O. (1953). *J. Chem. Phys.* **21**, 374.

LÖWDIN, P. O. (1955). *Svensk Kem. Tidskr.* **67**, 380.

LYKOS, P. G., and PARR, R. G. (1956). *J. Chem. Phys.* **24**, 1166.

MOORE, C. E. (1958). "Atomic Energy Levels." Nat. Bur. St., Washington, D.C.

Moore, J. W. (1966). *Acta Chem. Scand.* **20**, 1154.

MULLIKEN, R. S. (1949). *J. Chim. Phys.* **46**, 497, 675.

MULLIKEN, R. S. (1955). *J. Chem. Phys.* **23**, 1833.

NIEUWPOORT, W. C. (1965). *Philips Res. Rep. Suppl.* **6**.

OLEARI, L., DI SIPIO, L., and DE MICHELIS, G. (1966a). *Mol. Phys.* **10**, 97.

OLEARI, L., DE MICHELIS, G., and DI SIPIO, L. (1966b). *Mol. Phys.* **10**, 111.

PARISER, R., and PARR, R. G. (1953). *J. Chem. Phys.* **21**, 466 and 767.

POLDER, D. (1942). *Physica* **9**, 709.

POPLE, J. A. (1953), *Trans. Faraday Soc.* **49**, 1375.

POPLE, J. A., and SEGAL, G. A. (1965). *J. Chem. Phys.* **43**, S136.

POPLE, J. A., SANTRY, D. P., and SEGAL, G. A. (1965). *J. Chem. Phys.* **43**, S129.

RICHARDSON, J. W., NIEUWPOORT, W. C., and POWELL, R. R. (1962). *J. Chem. Phys.* **36**, 1057.

RICHARDSON, J. W., POWELL, R. R., and NIEUWPOORT, W. C. (1963). *J. Chem. Phys.* **38**, 796.

ROOS, B. (1966). *Acta Chem. Scand.* **20**, 1673.

ROOTHAAN, C. C. J. (1951a). *Rev. Mod. Phys.* **23**, 69.

ROOTHAAN, C. C. J. (1951b). *J. Chem. Phys.* **19**, 1445.

ROS, P., and SCHUIT, G. C. A. (1966). *Theoret. Chim. Acta* **4**, 1.

SHUSTOROVICH, E. M., and DYATKINA, M. E. (1959). *Dokl. Akad. Nauk SSSR* **128**, 1234.

ŠIMÁNEK, E., and ŠROUBEK, Z. (1964). *Phys. Status Solidi* **4**, 251.

SLATER, J. C. (1930). *Phys. Rev.* **36**, 57.

SLATER, J. C. (1960). "Quantum Theory of Atomic Structure," Vol. I. McGraw-Hill, New York.

SLATER, J. C. (1964). *Advan. Quantum Chem.* **1**, 35.

STREITWIESER, A. (1961). "Molecular Orbital Theory for Organic Chemists." Wiley, New York.

SUGANO, S., and SHULMAN, R. G. (1963). *Phys. Rev.* **130**, 517.

SUGANO. S., and TANABE, Y. (1965). *J. Phys. Soc. Japan* **20**, 1155.
TANABE, Y., and SUGANO, S. (1954). *J. Phys. Soc. Japan* **9**, 753, 766.
TANABE, Y., and SUGANO, S. (1956). *J. Phys. Soc. Japan* **11**, 864.
VALENTI, V., and DAHL, J. P. (1966). *Acta Chem. Scand.* **20**, 2387.
VAN VLECK, J. H. (1939). *J. Chem. Phys.* **7**, 72.
VISTE, A., and GRAY, H. B. (1964). *Inorg. Chem.* **3**, 1113.
WATSON, R. E., and FREEMAN, A. J. (1964). *Phys. Rev.* **134**, A1526.
WIRTH, T. H. (1965). *Acta Chem. Scand.* **19**, 2261.
WOLFSBERG, M., and HELMHOLZ, L. (1952). *J. Chem. Phys.* **20**, 837.
YAMAZAKI, M. (1956). *J. Chem. Phys.* **24**, 1260.
YERANOS, W. A. (1966). *Mol. Phys.* **11**, 85.
ZERNER, M., and GOUTERMAN, M. (1966). *Theoret. Chim. Acta* **4**, 44.

Paramagnetic Properties and Electronic Structure of Iron in Heme Proteins

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I. Introduction and Early Measurements

A. Heme Proteins and Hemes

Among the proteins, there exists a particular class called heme proteins. Molecules of these proteins have small groups of atoms called heme, attached to thin main skeletons of polypeptide chains. Familiar examples of heme proteins are: hemoglobin, which is found at a high concentration in red blood cells (erythrocytes) and carries oxygen from the lung to tissues of vertebrates; myoglobin, which exists in muscles and preserves oxygen, and various kinds of cytochromes, which are found mainly in mitochondria of cells and play important roles in the so-called electron transport systems. Peroxydase and catalase provide further examples.

As is well known, protein molecules are linear polymers consisting of amino acid residues, called polypeptides, and each protein is characterized by a definite sequence of amino acids along the polypeptide chain(s). This sequence is usually slightly different even for the same protein from one species to another of animals. Myoglobin molecule is a single polypeptide chain. In the case of human myoglobin, the chain consists of 153 amino acid residues, and a heme is attached to the 64th amino acid histidine (amino acid residues are numbered from the NH_2 terminal to the COOH terminal). However, one molecule of hemoglobin consists of four polypeptide chains of two kinds. There are two identical α-chains and two identical β-chains. In the case of human hemoglobin α- and β-chains have 141 and 146 amino acid residues respectively. Each chain carries one heme, so that a molecule of hemoglobin contains four hemes. Amino acid sequences in myoglobins and α- and β-chains of hemoglobins of several species, have been determined by chemical methods, and it has been found that the sequences in these chains are closely related.[1]

The spatial conformations of polypeptide chains in myoglobin and hemoglobin in crystalline states have been revealed through laborious X-ray studies by Kendrew, Perutz, and their collaborators (Kendrew *et al.*, 1960; Perutz, 1965). In the case of sperm whale myoglobin, even the approximate coordinates of individual atoms have been determined, complementing structural data in small molecules to the electron density pattern derived from X-ray diffraction. It has been found that these polypeptide chains consist of about eight rather straight, helical portions, and a smaller number of residues which connect these portions and give rather sharp bends. Consequently, polypeptide chains wind in complicated ways, and distant parts of a single chain may come near to each other in the real space. Table I gives partial amino acid sequences in sperm-whale myoglobin and α- and β-chains of human and horse hemoglobins for the parts which are in the neighborhood of heme in three-dimensional structures of these molecules.

Hemes in myoglobin, hemoglobin, peroxydase, and catalase have a common structure, which is obtained by substituting two central hydrogen atoms of protoporphyrin by an iron (Fe) atom. Protoporphyrin has a structure shown in Fig. 1. Its main part, called porphin, consists of four pyrrole rings connected circularly by methine bridges. To the peripheral carbon atoms of these pyrrole rings are attached methyl, propionic acid, and vinyl residues, as shown in the diagram. These "tails" reduce the tetragonal symmetry of the heme.

Heme is normally attached to a histidine, its Fe atom forming a bond with a N atom of imidazole ring in the side chain of histidine. Figure 2 shows heme and its surroundings with several amino acids, for sperm-whale myoglobin and horse hemoglobin (See Table I). Figure 3 shows (a)

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[1] For the amino acid sequence of sperm-whale myoglobin and horse hemoglobin, see, e.g., Perutz (1965).

TABLE I. Partial Sequences of Amino Acids in Myoglobin and Hemoglobin

Common numbering according to segments	Myoglobin[a]		Hemoglobin[b]			
			α-chain		β-chain	
	No.	Amino acid	No.	Amino acid	No.	Amino acid
C 1	36	His	36	Phe, Pro	35	Tyr
2	37	Pro	37	Pro	36	Pro
3	38	Glu	38	Thr	37	Try
4	39	Thr	39	Thr	38	Thr
5	40	Leu	40	Lys	39	Gln
6	41	Glu	41	Thr	40	Arg
7	42	Lys	42	Tyr, Thr	41	Phe
CD 1	43	Phe	43	Phe	42	Phe
E 6	63	Lys	57	Gly, Ala	62	Ala
7	64	His	58	His	63	His
8	65	Gly	59	Gly	64	Gly
9	66	Val	60	Lys	65	Lys
10	67	Thr	61	Lys	66	Lys
11	68	Val	62	Val	67	Val
12	69	Leu	63	Ala	68	Leu
13	70	Thr	64	Asp	69	Gly, His
14	71	Ala	65	Ala, Gly	70	Ala, Ser
15	72	Leu	66	Leu	71	Phe
F 3	88	Pro	82	Ala, Asp	87	Thr, Ala
4	89	Leu	83	Leu	88	Leu
5	90	Ala	84	Ser	89	Ser
6	91	Gln	85	Asp	90	Glu
7	92	Ser	86	Leu	91	Leu
8	93	His	87	His	92	His
9	94	Ala	88	Ala	93	Cys
FG 1	95	Thr	89	His	94	Asp
2	96	Lys	90	Lys	95	Lys
3	97	His	91	Leu	96	Leu
4	98	Lys	92	Arg	97	His
5	99	Ile	93	Val	98	Val
G 5	104	Leu	98	Phe	103	Phe
6	105	Glu	99	Lys	104	Arg
7	106	Phe	100	Leu	105	Leu
8	107	Gln, Ile	101	Leu	106	Leu
H 15	138	Phe	132	Val	137	Val

[a] The amino acids shown are those common to human and sperm-whale myoglobins, except when two names (the first for human, the second for sperm whale) are given.

[b] The amino acids shown are those common to human and horse hemoglobins, except when the two names (the first for human, the second for horse) are given.

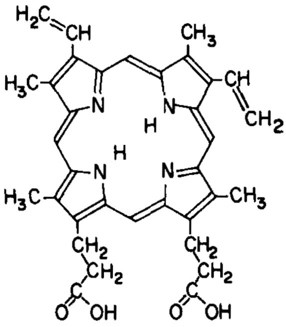


Fig. 1. Protoporphyrin.

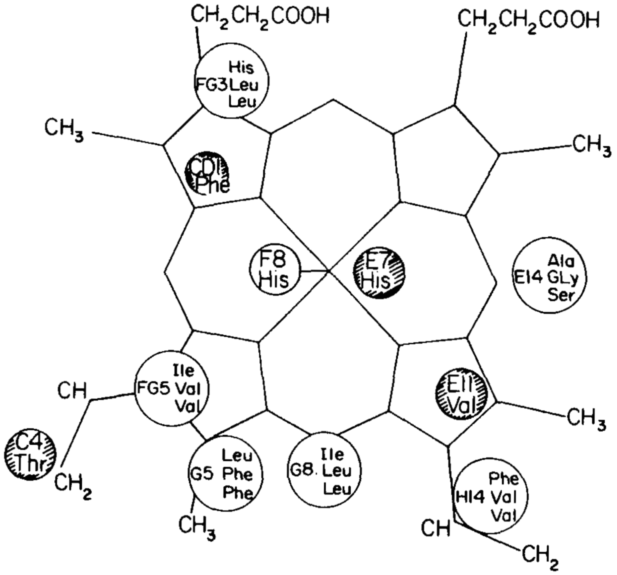


Fig. 2. Surroundings of the heme group. Circles show the positions of amino acids in the immediate neighborhood of the heme, as determined by X-ray diffraction on sperm-whale myoglobin and α- and β-chains of horse hemoglobin. Blank and shaded circles indicate, respectively, amino acids below and above the plane of the heme group, looking from the side which combines with oxygen. Where three amino acids are given in a circle, the first stands for sperm-whale myoglobin, the second for the α-chain and the third for the β-chain of horse hemoglobin. Reproduced from the paper by Perutz (1965).

the electron density distribution and (b) the corresponding atomic arrangement in the neighborhood of heme of sperm-whale myoglobin. Heme is viewed parallel to lines of sight in this diagram.

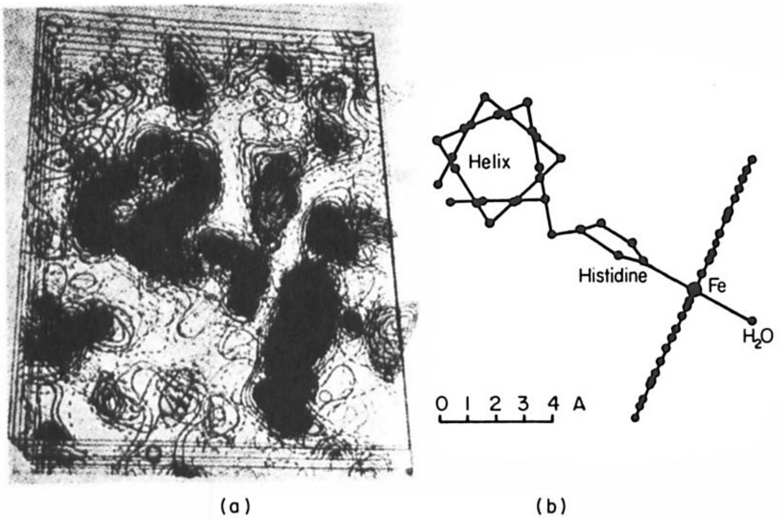


Fig. 3. Electron density (a) and atomic positions (b) showing combination of heme with polypeptide chain through histidine. Reproduced from the paper by Kendrew *et al.* (1960).

In normal physiological conditions, Fe in hemes of hemoglobin is divalent, i.e., it exists in ferrous form; but, if hemoglobins are taken out of cells and are kept in O_2 atmosphere, Fe is gradually oxydized into ferric form. In this paper, hemoglobin and myoglobin are denoted by Hb and Mb respectively, and if the valency of Fe is to be indicated, prefix ferro- (Fe^{++}) or ferri- (Fe^{+++}) is added to these symbols. Thus ferro-Hb denotes normal hemoglobin in which Fe is in the ferrous state (ferrohemoglobin), while ferri-Mb denotes myoglobin with ferric Fe in its heme (ferrimyoglobin). Heme in which Fe is ferric is sometimes called hemin.

Heme may be easily separated from globin by chemical treatments and also may be synthesized chemically. Hemin chloride, in which a chlorine anion Cl^- is attached to Fe from one side of hemin, has been crystallized and its structure was studied by X-ray analysis (Koenig, 1965). From this study it has been found that Fe nucleus does not lie in the plane of porphysin, but is displaced normally from this plane by about $\frac{1}{2}$Å. Displacements of this order of Fe nuclei from porphyrin planes seem to exist also in hemes incorporated in myoglobin. In these cases, the local symmetry in the neighborhood of heme is not D_4, but is approximately C_{4v}.

Since the displacement just discussed is small if not zero, Fe atom in the heme may be regarded as coordinated by four N atoms of porphyrin forming a square. Using the terminology of coordination chemistry, we call these four N sites as the 1st, 2nd, 3rd and 4th coordination sites. If we take the porphyrin plane as horizontal, another N atom of the imidazole ring of histidine is ligated to Fe from the lower side. This N atom occupies the 5th coordination site. The 6th coordination site above the plane may be occupied by different atoms and small molecules.

Physiological functions of hemoglobin and myoglobin, i.e., the transport and preservation of oxygen, are based on the capabilities of attaching O_2 reversibly at the 6th position. This reversible combination of O_2 to hemes is called oxygenation; by an increase of partial pressure of oxygen, hemoglobin is converted from deoxy-Hb to oxy-Hb, as manifested by the change of blood color from dark red to bright red. In ferro-Hb and ferro-Mb, CO can be combined more easily and firmly to Fe than O_2, so that the presence of CO above a threshold damages the function of hemoglobin and makes the supply of oxygen to cells in tissues difficult.

In the cases of ferrihemoglobin and ferrimyoglobin, a large number of derivatives can be prepared by attaching different molecules as the 6th ligand to hemes. H_2O, F^-, CN^-, OH^-, OCN^-, $N_3{}^-$, SH^- are examples of possible 6th ligands.

B. Spin States of Heme

As mentioned in Section A, hemes can be either in reduced (ferrous) or in oxydized (ferric) state. In the former case the total number of electrons of the system is even, while in the latter it is odd. Consequently, the resultant spin quantum number S is integral in reduced hemes, but is half-integral in oxydized ones.

Historically, the first assignment of S to different states of heme and its derivatives were made from the results of magnetic susceptibility measurements. Reduced hemes can be paramagnetic or diamagnetic depending on the kind of the 6th ligand. Deoxy-Hb and deoxy-Mb are paramagnetic, but they become diamagnetic on being oxygenated or carboxygenated. It is true that at room temperature paramagnetism due to hemes are overcompensated by diamagnetism due to bulky polypeptide chains, globins, but it is possible to separate paramagnetic part from diamagnetic one, because the paramagnetic susceptibility is roughly inversely proportional to the absolute temperature T while the diamagnetic susceptibility is almost independent of temperature.

From the magnitude of this term inversely proportional to T, one can estimate the magnetic moment. According to Curie's law the paramagnetic susceptibility is represented by

$$\chi = N\frac{\mu^2}{3kT} \tag{I.1}$$

where N is the number of magnetic ions in the quantity of the sample for which χ is defined, μ is the magnetic moment of the ion, and k is the Boltzmann constant. It is convenient to express μ in terms of Bohr magneton

$$\mu_B = \frac{e\hbar}{2mc} = 0.9273 \times 10^{-10} \quad \text{erg} \cdot \text{G}^{-1}, \tag{I.2}$$

which is the natural unit of magnetic moment due to electrons in atomic systems. Thus one defines the Bohr magneton number n by

$$\mu = n\mu_B. \tag{I.3}$$

Assuming that the magnetic moment comes solely from spins of electrons, and that spins of f electrons are aligned parallel in each magnetic ion, we have

$$n = (f(f+2))^{1/2},$$

or, introducing resultant spin quantum number $S = f/2$, we can write

$$n = 2(S(S+1))^{1/2}.$$

These figures are as follows:

f	0	1	2	3	4	5
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$
n	0	1.73	2.83	3.87	4.90	5.92

According to measurements made by L. Pauling and Coryell as early as 1936, the Bohr magneton number for deoxy-Hb is 5.4 (Pauling and Coryell, 1936). This falls somewhere between values corresponding to $S = 2$ and $S = \frac{5}{2}$, but it is natural to adopt $S = 2$ for deoxy-Hb which should have an even number of unpaired electrons. The deviation from the "spin-only value" 4.90 may be accounted for by taking into account contribution from orbital magnetic moment, as will be discussed in Section III. On the other hand, oxy-Hb and carboxy-Hb are diamagnetic. Thus, there are two cases concerning spin values of hemes in the normal state: in one case $S = 2$, and in the other $S = 0$. These cases are called the high-spin case and the low-spin case respectively.

Similarly, there are two cases in which oxydized hemes take different spin values in their normal states. For instance, myoglobin fluoride (MbF) gives $n = 5.9$ corresponding to $S = \frac{5}{2}$, while hemoglobin hydrosulphide (HbSH) and hemoglobin cyanide (HbCN) give $n = 2.26$ and 2.50 respectively. These latter derivatives are regarded as having $S = \frac{1}{2}$, taking into account the situations that orbital magnetic moment may give considerable contribution in the case $S = \frac{1}{2}$, but not in the case $S = \frac{5}{2}$, as will be discussed in Section III.

In summary, there are four cases corresponding to the different spin values in the normal states of heme and its derivatives, as shown in Table II.

TABLE II

FOUR CASES OF HEME

	Reduced (ferro-)	Oxydized (ferri-)
High-spin	$S = 2$ Ex. (deoxy-)Hb	$S = \frac{5}{2}$ Ex. ferri-Hb·F^-
Low-spin	$S = 0$ Ex. oxy-Hb Hb-CO	$S = \frac{1}{2}$ Ex. ferri-Hb·CN^- ferri-Hb·N_3^-

Some of the derivatives of ferri-Hb and ferri-Mb have, however, effective Bohr magneton numbers which are intermediate between the high-spin value and the low-spin value, and are rather far from either of these extremes. By effective Bohr magneton number we mean n, which is defined by

$$\chi = \chi_{\text{dia}} + N\frac{n^2\mu_B{}^2}{3kT}; \tag{I.4}$$

n may be temperature dependent if the Curie law does not hold. Examples of derivatives with intermediate n values are ferri-HbOH and ferri-MbOH, which give $n = 4.47$ and 5.10 respectively at room temperatures.

As pointed out by Griffith, it is difficult on theoretical grounds to believe that the normal states of these compounds belong to $S = \frac{3}{2}$. George, Beetlestone, and Griffith have proposed an interpretation according to which hemes in these compounds are mixtures of hemes in high-spin states and those in low spin states (George *et al.*, 1964). On the assumption of thermal equilibrium between these two species they have shown that both the magnetic susceptibility and the optical spectra can be explained consistently as follows.

Denoting the fraction of hemes with low spin and of those with high spin by α and $1 - \alpha$ respectively, and the Bohr magneton numbers in the low-spin state and in the high-spin state by n_l and n_h respectively, the effective Bohr magneton number of, say, ferri-MbOH, n_{Mb}, is determined by the equation

$$n_{Mb}^2 = n_l^{\,2}\alpha_{Mb} + n_h^{\,2}(1 - \alpha_{Mb}), \tag{I.5}$$

and the similar equation for ferri-HbOH is

$$n_{Hb}^2 = n_l^{\,2}\alpha_{Hb} + n_h^{\,2}(1 - \alpha_{Hb}). \tag{I.6}$$

n_h is $=\sqrt{35}$, but n_l may be larger than the spin-only value $\sqrt{3}$. Taking $n_l = \sqrt{5}$, a value not far from the one measured for ferri-MbCN, and putting $n_{Mb}^2 = 26$ and $n_{Hb}^2 = 20$, one gets

$$\alpha_{Mb} = 0.30, \qquad \text{and} \qquad \alpha_{Hb} = 0.50.$$

Then, in the absorption spectra of these derivatives, the extinction coefficient ε at a given wave length will be given by

$$\varepsilon_{Mb} = \varepsilon_l\alpha_{Mb} + \varepsilon_h(1 - \alpha_{Mb}), \tag{I.7}$$

$$\varepsilon_{Hb} = \varepsilon_l\alpha_{Hb} + \varepsilon_h(1 - \alpha_{Hb}), \tag{I.8}$$

where ε_l and ε_h denote extinction coefficients in the low-spin and high-spin states. Determining ε_l and ε_h from spectra of cyanides, George *et al.* have shown that the absorption spectra of ferri-MbOH and ferri-HbOH can be reasonably well reproduced by Eq. (I.7) and (I.8).

From the knowledge of α, one can determine the equilibrium constant $K = \alpha/(1 - \alpha)$ for the reaction high-spin $\rightleftharpoons$ low-spin. Analysis of temperature dependence of K gives changes in energy and entropy associated with this spin change. Their results for ferri-MbOH shows that the energy of the high-spin state is higher than that of the low-spin state by about 1200 cal/mol ($\sim$420 cm^{-1}), and the entropy difference is about 5.8 cal/mol/deg, which is more than twice the entropy change expected from the difference of weights due to spin R log 3 = 2.4 cal/mol/deg.

C. Application of Electron Paramagnetic Resonance Absorption (EPR). Determination of Heme Orientations in Crystals

Besides susceptibility measurements, the electron paramagnetic resonance absorption provides an effective means of study on paramagnetic substances. In this section we review the experimental results obtained by applying the EPR method to hemoglobins and myoglobins.

As is well known, EPR method is usually applicable to molecular systems with an odd number of unpaired electrons; in such systems all energy levels are at least doubly degenerate in the absence of magnetic field. These "Kramers' doublets" are split into two levels on applying magnetic field H, and this splitting is measured by the absorption of microwaves. The splitting is usually written as $g\mu_B H$, with the introduction of a dimensionless "g factor." The g factor and shape of the absorption line are obtained from experiments. To examine possible dependence of these quantities on H, experiments with the use of microwaves at different wave lengths are required. Further, combining these results with saturation measurements, one can estimate relaxation times T_1 and T_2.

EPR studies have been made both on single crystal specimen and on amorphous samples in paste-like form or in concentrated solutions. Detailed information relating to the orientation of hemes can be obtained from experiments on single crystal specimens only, so that the use of these specimens is preferable as far as crystals can be prepared.

Now, out of the four cases discussed in Section B, the reduced, low-spin case, giving $S = 0$, falls outside the applicability of EPR method. Hemoproteins in the reduced, high-spin case are also difficult to study by EPR experiments, because in this case hemes have an even number of unpaired electrons and every energy level is single already in the absence of the magnetic field, if the local symmetry around the Fe atom is not particularly high. Application of the magnetic field does not give rise to new splitting of levels, but only shifts these levels in the second order of H. The success of finding EPR signals depends on a rather accidental situation in which two magnetically combining levels are separated by a distance consistent with the frequency of microwave used. No success has been reported in EPR measurements on hemoglobins and myoglobins in reduced form.

In the case of ferri-Hb and ferri-Mb derivatives, EPR studies have been made both in the high-spin state (Bennett, Gibson, and Ingram, 1957) and in the low-spin state. At first the main results of EPR studies on single crystals of ferri-Mb carried out by these authors will be described as typical example of high-spin ferric case.

The crystal of ferri-Mb is monoclinic; its b axis is perpendicular to the *a* and *c* axes, but the *a* axis and *c* axis are not mutually perpendicular. If we take c^* in the direction of normal to the *ab*-plane, abc^* forms a rectangular system, and the *c* axis lies in the ac^* plane. Furthermore, each unit cell of ferri-Mb contains two molecules, and consequently two hemes. This fact suggests that there are two groups of hemes, and hemes of each group are oriented parallel throughout the whole crystal.

Now, applying a magnetic field in a definite direction relative to the crystalline axes and varying its intensity, one gets in general two signals corresponding to two different g values. As the direction of the magnetic field is changed, two g values will also show variations.

Consequently, if one plots g values as lengths of vectors in the direction of the magnetic field from a fixed origin O, one obtains two g surfaces with O as the centre of symmetry. Figure 4 gives a stereoprojection of these two surfaces on a plane parallel to the *ab* plane. This shows that the two surfaces are symmetrically located with respect to the *ac* plane, each being concident with the mirror image of the other. For each surface, the minimum $g = 2$ occurs at a single point H, but g keeps its maximum value 6 along the equatorial circle perpendicular to OH.

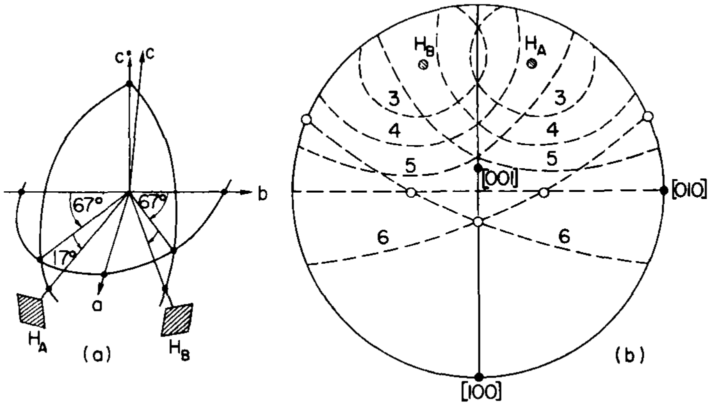


Fig. 4. (a) Orientation of heme normals in the single crystal of myoglobin. (b) Contour map of g values in stereographic projection, from which directions of heme normals were determined. Figures 4 and 5 have been reproduced from the paper by Bennett *et al.* (1957).

The obvious interpretation of these results is as follows: each g surface is given by a group of hemes mutually parallel, and OH gives the direction of common normal to the hemes. Thus, hemes give $g = 2$ when the magnetic field is parallel to the normal, and $g = 6$ when it is perpendicular to the latter.

These g values can be explained in the following way. In a hemin of ferri-Mb, the normal state belongs to $S = \frac{5}{2}$, and consists of $2S + 1 = 6$ independent spin states. Taking the z axis normal to the porphin plane, these 6 states are represented by $S_z = \pm\frac{1}{2}$, $\pm\frac{3}{2}$ and $\pm\frac{5}{2}$. Now, it is natural to assume that, for some reason, these spin states have slightly different energies depending on $|S_z|$, in the absence of magnetic fields, and $S_z = \pm\frac{1}{2}$ form the lowest doublet. If the magnetic field $\mathbf{H}$ is applied, the Hamiltonian gets a Zeeman term

$$+\frac{eh}{mc}\mathbf{S}\cdot\mathbf{H} = 2\mu_s\mathbf{S}\cdot\mathbf{H}. \tag{I.9}$$

If $\mathbf{H}$ is in the z direction, (I.9) reduces to $2\mu_s S_z H = \pm\mu_s H$, so that the splitting is $2\mu_s H$. This gives $g = 2$.

If $\mathbf{H}$ is perpendicular to z (parallel to the heme plane), the Zeeman term is

$$2\mu_\beta(S_x \cos\varphi + S_y \sin\varphi)H.$$

Now, in the two-dimensional space spanned by $S_z = \pm\frac{1}{2}$, S_x and S_y are represented by matrices

$$S_x = \begin{pmatrix} 0 & \frac{1}{2}(S+\frac{1}{2}) \\ \frac{1}{2}(S+\frac{1}{2}) & 0 \end{pmatrix}, \qquad S_y = \begin{pmatrix} 0 & -\frac{1}{2}i(S+\frac{1}{2}) \\ \frac{1}{2}i(S+\frac{1}{2}) & 0 \end{pmatrix},$$

where S is the resultant spin quantum number. Hence the splitting of the ground doublet is given by diagonalizing

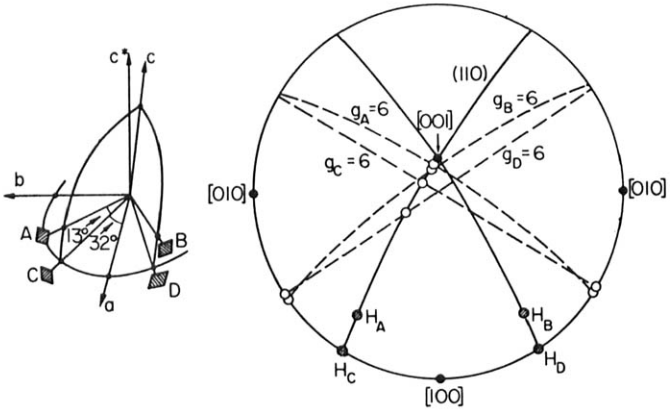
$$\begin{pmatrix} 0 & (S+\frac{1}{2}e^{-i\varphi}\mu_B H \\ (S+\frac{1}{2})e^{i\varphi}\mu_B H & 0 \end{pmatrix}$$

The eigenvalues are $\pm(S+\frac{1}{2})\mu_B H$, and the level splitting is given by $(2S+1)\mu_B H$. This gives $g = 2S + 1$, independent of φ, the azimuth of the magnetic field. We can identify this to observed value $g = 6$, and get $S = \frac{5}{2}$. This may be regarded as a conclusive proof for the fact that the normal state belongs to to the spin sextet.

Among three Kramers' doublets of the normal state $S = \frac{5}{2}$, the other two doublets $S_z = \pm\frac{3}{2}$ and $S_z = \pm\frac{5}{2}$ will also be split by the magnetic field, but transition between split sublevels are highly forbidden on account of large differences of S_z values ($\Delta S_z = 3$ and 5 respectively). Consequently, the splitting of doublet can be directly observed for the ground doublet only.

If the second doublet, $S_z = \pm\frac{3}{2}$, is sufficiently low, the transition between $S_z = -\frac{1}{2}$ and $-\frac{3}{2}$ should be observable, but this transition has not been observed within the range of available magnetic field intensity. This has led to the estimate that the second doublet must be separated from the ground one by more than $10\,\mathrm{cm}^{-1}$.

EPR method has been applied also to single crystals of ferri-HbF and ferri-$HbOH_2$. In crystals of hemoglobin, two molecules contained in each unit cell have the parallel orientation. Since a single molecule consists of four polypeptide chains and each polypeptide chain has one heme, there are four different orientations of heme in the crystal. One group of hemes in parallel orientation gives $g = 2$ for $H \| z$, and $g = 6$ for $H \perp z$ just like the hemes in myoglobin, where z denotes the common direction normal to the heme plane. From the analysis of EPR spectra, directions of heme normals have been determined as shown in Fig. 5. The mutual distances between these hemes, as determined by X-ray analysis by Perutz *et al.* are shown in Fig. 6.



(a) (b)

Fig. 5. Diagrams similar to those of Fig. 4 for hemoglobin.

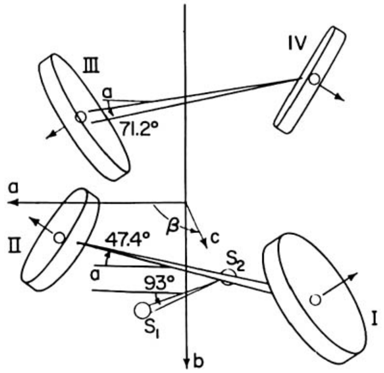


Fig. 6. Mutual distances and orientations of hemes in hemoglobin. Reproduced from the paper by Perutz et al. (1965).

II. Electronic Structure of Ferric and Ferrous Ions. Ligand Field Theory

A. Free Ferric and Ferrous Ions

In Section III experimental results of EPR and susceptibility experiments will be discussed on electronic theory of hemes, and some further experimental studies will be presented. Since the discussions will be made mainly on the basis of ligand field theory, it will be appropriate to give here expositions of elements of this theory and its application to ferric and ferrous complexes. In the present section, electronic structures of free ferric and ferrous ions will be discussed, in order to pave the road to ligand field theory.

Ferric and ferrous ions have 23 and 24 electrons respectively, and their normal electron configurations are

$$(1S)^2(2S)^2(2p)^6(35)^2(3p)^6(3d)^n,$$

where n is 5 for Fe^{+++} and 6 for Fe^{++}. The incomplete shell $(3d)^n$ is responsible for paramagnetic properties of these ions, as the rest of the electrons are accommodated in closed shells which are paramagnetically inactive. Therefore, our attention will be focused on the properties of these electrons in d orbitals.

Referring to a Cartesian coordinate system with its origin at the nucleus of Fe atom, five d orbitals are represented as follows:

$$\begin{gathered} \rho = \tfrac{1}{2}CR(r)(x^2 - y^2), \qquad \tau = (1/\sqrt{12})CR(r)(2z^2 - x^2 - y^2), \\ \xi = CR(r)yz, \qquad \eta = CR(r)zx, \qquad \zeta = CR(r)xy. \end{gathered} \tag{II.1}$$

These orbitals constitute an orthonormal set if $R(r)$ is normalized by

$$\int_0^\infty R(r)^2 r^6\, dr = 1, \tag{II.2}$$

and

$$C = \left(\frac{15}{4\pi}\right)^{1/2}.$$

These five orbitals have the same energy if the ion is in a free space. Now we proceed to discuss electronic structure of free ferric and ferrous ions which have five and six d electrons respectively. The problem we have to find out here is the lower energy levels arising from electron configurations d^5 and d^6, taking interelectronic Coulomb repulsion into account. On the neglect of spin-orbit interaction, each energy level (term) of an atomic ion is characterized by a set of quantum numbers γSL, where S and L determine the magnitudes of spin angular momentum $\mathbf{S}$ and orbital angular momentum $\mathbf{L}$ respectively. γ distinguishes different terms with the same (S, L). In fact, $\mathbf{S}^2$ is $=\hbar^2 S(S+1)$ and $\mathbf{L}^2$ is $=\hbar^2 L(L+1)$. With the conventional notation in spectroscopy, terms with $L = 0, 1, 2, 3, \ldots$ are denoted by $S, P, D, F, \ldots$ and the "multiplicity" $2S + 1$ is written as the left superscript. Thus, for instance, ^4P means a term with $S = \frac{3}{2}, L = 1$.

It is easy to show that the electronic configuration d^5 gives rise to the following 16 terms:

$$^6S,$$

$$^4P, {}^4D, {}^4F, {}^4G,$$

$$^2S, {}^2P, {}^2D(3 \text{ times}), {}^2F(\text{twice}), {}^2G(\text{twice}), {}^2H, {}^2I.$$

Since each (S, L) term has $(2S+1)(2L+1)$ linearly independent wavefunctions, these 16 terms give in total $\Sigma(2S+1)(2L+1) = 252$ independent functions. This number coincides with the number of ways in which 5 out of 10 spin orbitals of the d shell can be chosen.

Among these 16 terms, the term with the highest multiplicity ^6S constitutes the ground state, in accordance with the Hund rule. Some of the lower terms are shown in Table III, together with their excitation energies determined from spectroscopic observations. It is to be noted that the lowest doublet ($S = \frac{1}{2}$) term ^2I is higher than ^6S by about 6 eV.

Energy separations between these (S, L) terms arising from a single configuration are due to the difference in effectiveness of interelectronic Coulomb repulsions $\sum_{i<j} e^2/r_{ij}$ for different terms (Condon and Shortley,

TABLE III

LOWER EXCITED STATES OF FREE FERRIC ION, Fe^{+++}

State	Excitation energy	
	Observed (cm^{-1})	Formula
^6S	0	0
^4G	32000	$10B + 5C$
^4P	35100	$7B + 7C$
^4D	38500	$17B + 5C$
^4F	52100	$22B + 7C$
^2I		$11B + 8C$

1935). Slater has shown that all elements of full matrix of $\sum_{i<j} e^2/r_{ij}$ are expressible as linear combinations of two parameters F_2, F_4, where

$$F_k = c_k e^2 \int_0^\infty R(r_2)^2 r_2^{k+2}\, dr_2 \int_{r_2}^\infty R(r_1)^2 r_1^{1-k}\, dr_1. \tag{II.3}$$

$$c_2 = \frac{2}{49}, \qquad c_4 = \frac{18}{441},$$

except for a constant common to all diagonal elements. Therefore, energy separations between different terms can be expressed in terms of F_2 and F_4. According to Racah, it is more convenient to use B and C defined by

$$B = F_2 - 5F_4, \qquad C = 35F_4, \tag{II.4}$$

instead of F_2 and F_4. In Table III, theoretical expressions in terms of Racah parameters are given for some excitation energies.

For our purposes it is preferable to determine numerical values of Racah parameters B, C empirically so as to obtain the best fit to empirical excitation energies rather than to calculate by Eqs. (II.3) and (II.4) *ab initio*. In this way the following values are obtained:

$$B = 1015 \quad \mathrm{cm}^{-1}, \qquad C = 4800 \quad \mathrm{cm}^{-1} \tag{II.5}$$

for the free ferric ion.

Similar analysis can be applied to free ferrous ion with configuration d^6, which gives the following variety of terms:

^5D,

^3P (twice), ^3D, ^3F (twice), ^3G, ^3H,

^1S (twice), ^1D (twice), ^1F, ^1G (twice), ^1I.

The total number of independent wavefunctions is

$$\sum (2S+1)(2L+1) = 210 = \binom{10}{6}.$$

In this case the ground term is ^5D, and the lowest singlet term, ^1I, is located above the ground term by about 30000 cm^{-1}. Empirical values of Racah parameters are

$$B = 917 \quad \mathrm{cm}^{-1}, \qquad C = 4040 \quad \mathrm{cm}^{-1}. \tag{II.6}$$

B. Ligand Field Theory

1. Introduction

Heme and its derivatives are polyatomic molecules, and the standard method used for describing the electronic structure of such polyatomic molecules is the molecular orbital method, in various versions. For the interpretation of optical spectra of these molecules, this approach is almost inevitable, and many studies have been done along this line in recent years.[2] However, the magnetic properties of hemes, in which we are mainly interested, are primarily due to behaviors of electrons in $3d$ orbitals of iron, which are primarily atomic in character. It is true that these $3d$ orbitals enter into linear combination with π and σ orbitals of the porphyrin ring in the molecular orbital picture, but the coefficients of $3d$ atomic orbitals are fairly large $(0.7 \sim 1.0)$. Hence it may be a reasonable first approximation to neglect delocalization, i.e., the overflow of these orbitals to porphyrin ring and to treat them as atomic. We start in this approximation, and modifications made necessary by delocalization of these orbitals will be discussed in later stages.

The main reason for adopting this approach lies in the fact that in this picture we can avail ourselves of powerful theoretical methods of the ligand field theory. It enables us to have an overall and clear view of various energy levels and of their magnetic properties, at least semiquantitatively, with minimum number of empirical parameters. On the other hand, discussions on the basis of MO picture are rather difficult without the knowledge of the quantitative shape of orbitals, which could be obtained only after elaborate calculations. Thus, in our approach we consider Fe ion with five or six $3d$ electrons, and investigate the effect of a ligand field of a definite symmetry exerted on this ion. The ligand field V_{lf} is essentially an electrostatic field due to charge distributions in ligands, but may be an operator which can include the effect of exchange interaction with electrons on ligands. The detailed functional form of V_{lf} is unnecessary, however; the important characteristic of V_{lf} is its symmetry, represented by one of the point groups.[3]

2. Orbitals

In the following we take the Cartesian coordinate system with its center at the Fe nucleus in such a way that the z axis is normal to the heme plane,

---

[2] Concerning MO studies of Fe-porphin system, see, e.g., Zerner and Gouterman (1966).

[3] Concerning details of ligand field theory, see, e.g., Griffith (1961) and Ballhausen (1962).

and four pyrrole N atoms lie in xz and yz planes. If Fe is in the porphin plane, x and y axes pass through pyrrole nitrogens, but if Fe is elevated above this plane, the xy plane is parallel to, but not coincident with, the porphin plane.

Coordinates x, y, z used in the definition (II.1) of five d orbitals ρ, τ, ξ, η, ζ should henceforth be understood as those in the coordinate system defined above.

In the case of the free ion, i.e., in the absence of ligand field, orbital energies of these five orbitals are equal, but under a ligand field they may have partly different energies. For instance, if the ligand field has the cubic symmetry, the d level is split into two sublevels $d\varepsilon$ and $d\gamma$.

$$d\varepsilon \supset \xi, \eta, \zeta. \qquad d\gamma \supset \rho, \tau.$$

If the orbital energy of any orbital σ is denoted by ε_σ, we have

$$\varepsilon_\xi = \varepsilon_\eta = \varepsilon_\zeta, \qquad \varepsilon_\rho = \varepsilon_\tau.$$

Lowering the symmetry to tetragonal, for instance to C_{4v}, splits $d\varepsilon$ and $d\gamma$ into two further sublevels:

$$\varepsilon_\xi = \varepsilon_\eta \neq \varepsilon_\zeta, \qquad \varepsilon_\rho \neq \varepsilon_\tau \quad \text{(tetragonal)}.$$

In ligand fields of rhombic and lower symmetries, all five orbitals have different energies.

Orbital ρ is obtained from orbital ζ by a rotation around the z axis. However, charge distribution of ρ extends much nearer to electronic charges of pyrrole nitrogens than that of ζ. Hence ε_ρ must be ε_ζ. This gives

$$\varepsilon(d\varepsilon) < \varepsilon(d\gamma) \quad \text{(cubic)}.$$

In this paper $\varepsilon(d\gamma) - \varepsilon(d\varepsilon)$ is denoted by Δ.

In the ligand field theory, these orbital energies are treated as parameters which characterize given ligand fields. If all orbital energies are equal, the theory should reproduce the situation of the free Fe ion, in the approximation inherent in the orbital theory.

3. (*S*, Γ) *States*

As explained in Section A, energy terms of free atoms and ions are classified into $S, P, D, F, \ldots$ terms, according to different values of L. Wavefunctions of these terms have different spatial symmetrics. Disregarding spins, the S term has only one wavefunction which is spherically symmetric. Hence the S term wavefunction is invariant against rotation around any axis passing through the origin. The P term has three spatial wavefunctions, and these three functions are transformed just like coordinates x, y, z against rotation. In general, each L has its own characteristic linear transformations, by which $2L + 1$ wavefunctions are transformed against rotation of space. These $2L + 1$ wavefunctions have a common energy, and this degeneracy cannot be removed as long as the atom is in the free space.

For atoms (and ions) in a ligand field a similar qualitative classification, which reflects symmetry types of wavefunctions, is possible. The classification must be done, however, for each symmetry of ligand field separately. Firstly, for the field of cubic symmetry there are five kinds of symmetry types A_1, A_2, E, T_1, T_2, as shown in Table IV. In technical language of group theory, these symmetry types correspond to different irreducible representations of the cubic group O.

TABLE IV

SYMMETRY TYPES OF WAVEFUNCTIONS IN LIGAND FIELD OF OCTAHEDRAL SYMMETRY (IRREDUCIBLE REPRESENTATIONS OF O_h)[a]

Symbol	No. of independent wavefunctions, deg. of degeneracy	Examples of functions
A_{1g}	1	1
A_{2g}	1	$(y^2 - z^2)(z^2 - x^2)(x^2 - y^2)$
E_g	2	$x^2 - y^2$, $2z^2 - x^2 - y^2$
T_{1g}	3	$yz(y^2 - z^2)$, $zx(z^2 - x^2)$, $xy(x^2 - y^2)$
T_{2g}	3	yz, zx, xy

[a] Odd representations are omitted.

Each energy term is, therefore, characterized by one of these five symbols and spin multiplicity. For example, ${}^4T_1$ is a term which has four independent spin functions and three spatial wavefunctions, so that it has $4 \times 3 = 12$ independent functions which are degenerate.

Similarly, for tetragonal symmetry C_{4v} we have Table V. Primes (′) are attached to representation symbols to avoid confusion with similar symbols for the cubic case.

Similar tables can be given for other thirty point groups.

When a general symbol for symmetry type is needed we write Γ. Then Γ corresponds to L used for the free ion case. Energy terms are characterized by (S, Γ).

TABLE V

SYMMETRY TYPES OF WAVEFUNCTIONS IN LIGAND FIELD OF TETRAGONAL SYMMETRY (IRREDUCIBLE REPRESENTATIONS OF C_{4v})

Symbol	No. of independent wavefunctions, deg. of degeneracy	Examples of functions
A_1'	1	1
A_2'	1	$xy(x^2 - y^2)$
B_1'	1	$x^2 - y^2$
B_2'	1	xy
E'	2	x, y

4. *Coulomb Interaction*

If a ferric or ferrous ion is introduced into a ligand field $v(x, y, z)$, the Hamiltonian for the system of d electrons is

$$\mathscr{H} = \sum f(i) + V_C + V_{LF}, \tag{II.7}$$

where

$$V_C = \sum_{i<j} \frac{e^2}{r_{ij}}, \qquad V_{LF} = \sum_i v(x_i, y_i, z_i),$$

and $f(i)$ stands for kinetic energy and core field acting on the ith d electron. The essential feature of the ligand field theory is found in the presence of the ligand field term V_{LF} in the Hamiltonian, which is simply added to the Hamiltonian of the same ion in free space. Our problem is then to construct the matrix for $V_C + V_{LF}$ and to find its eigenvalues and eigenfunctions. Each eigenvalue has definite S and Γ, and it has $(2S + 1)n_\Gamma$ independent wavefunctions where n_Γ is the degree of degeneracy of Γ.

In order to have an insight to energy term structures of ions in ligand fields, let us examine ferric and ferrous ions from two extremes: $V_C \gg V_{LF}$ and $V_C \ll V_{LF}$, assuming cubic symmetry of V_{LF}. These are called the weak field case and the strong field case, respectively.

(*a*) *Weak Field Case.* In this case V_{LF} is treated as a perturbation term. the unperturbed system is the ion in free space. S terms which have no spatial degeneracy will be shifted, but not split by the perturbation. For instance, ^6S of ferric ion changes to $^6A_1$ in a cubic field, but its six-fold degeneracy due to spin persists. The three-fold degeneracy of the P term cannot be removed in the cubic field, because it belongs to T_1 or T_2 in cubic symmetry. However, the D term is split into two terms, E and T_2, doubly and triply degenerate respectively. Consider, as an example, the ground state ^5D of ferrous ion. Taking wavefunctions with maximum spin component for convenience, we see that five spin-orbitals with α spin are occupied, and one electron must have β spin. There are five choices of orbitals for the last electron, which correspond to five-fold degeneracy of D. Now, in a cubic ligand field, d is split into $d\varepsilon$ and $d\gamma$ as mentioned in Section 3, and consequently D is plit into E and T_2, with electron configurations $(d\varepsilon)^3(d\gamma)^3$ and $(d\varepsilon)^4(d\gamma)^2$ respectively. Since $d\gamma$ is higher than $d\varepsilon$ in the case of nearly octahedral coordination as that of heme, T_2 must be lower. Therefore, the ground term of a ferrous ion in the cubic field must be $^5T_2$.

(*b*) *Strong Field Case.* When the ligand field is sufficiently strong, V_{LF} is more important than V_{C}, so that difference in orbital energies must be considered before taking V_{C} into account. For instance, ligand field of cubic symmetry gives difference between $\varepsilon(d\varepsilon)$ and $\varepsilon(d\gamma)$, and the single configuration d^5 in the free ion case is divided into five configurations

$$(d\varepsilon)^5, \quad (d\varepsilon)^4(d\gamma), \quad (d\varepsilon)^3(d\gamma)^2, \quad (d\varepsilon)^2(d\gamma)^3, \quad (d\varepsilon)(d\gamma)^4. \qquad \text{(II.8)}$$

Hence we have to distinguish these configurations from the beginning. As long as we neglect V_{C}, each configuration of (II.8) has a definite energy, and differences of energies of successive configurations are Δ.

If V_{C} is taken into account, each configuration gives in general several levels of different energies, each of which is characterized by (S, Γ). The lowest configuration $(d\varepsilon)^5$ gives only one level $^2T_2$, but, for instance, $(d\varepsilon)^3(d\gamma)^2$ gives the following 15 levels:

$$^6A_1, \quad ^4A_1, \quad ^4A_2, \quad ^4E, \quad ^4T_1, \quad ^4T_2, \quad ^2A_2, \quad ^2T_1\ \text{(4 times)}, \quad ^2T_2\ \text{(4 times)}.$$

To obtain theoretical estimate for energies of these levels in the first approximation, one constructs matrix of V_{C} within each configuration and calculates its eigenvalues. Reduction of secular equations will result if appropriate linear combinations of wavefunctions corresponding to various symmetry types A_1, A_2, E, ... are used to construct matrices of V_{C}.

(*c*) *Intermediate Situations.* So far we have discussed energy levels in the neighborhoods of a weak field limit and a strong field limit. Our real interest lies in the intermediate situations, because the properties of ferric and ferrous ions in heme seem to correspond to just the intermediate case. In order to find theoretical picture of energy levels throughout the whole range of ligand field strength, one has to diagonalize the complete matrix of $V_C + V_{LF}$ for d^5 and d^6, or in other words, one has to take interactions between configurations such as those given in (II.8). Before carrying out detailed calculations, however, the following important feature can be pointed out.

As far as the crystallographic symmetry of the ligand field does not change, (S, Γ) are good quantum numbers, and (S, Γ) of each level does not change with ligand field strength. Now, in cubic field, the ground state of a ferric ion was shown to be $^6A_1$ when the field is weak, whereas it was found to be $^2T_2$ when it is strong. Therefore, crossing of these two levels must occur at a certain point if the ligand field strength is varied throughout the whole range. This critical field strength corresponds to a particular value of Δ, the separation between $d\gamma$ and $d\varepsilon$, which shall be denoted by Δ_c. Then the ground state is $^6A_1$ in the range $\Delta < \Delta_c$, while it is $^2T_2$ in the range $\Delta > \Delta_c$. This phenomenon is basically important for the interpretation of high spin and low spin cases of hemes, as will be discussed in Section III.

Our consideration described here gives a qualitative picture of low energy levels of a ferric ion in a cubic ligand field as shown in Fig. 7. It is to be

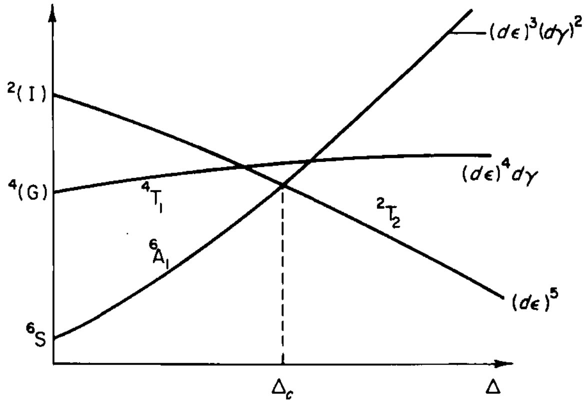


Fig. 7. Crossing of sextet, quartet, and doublet levels of ferric ion in cubic ligand field, shown semiqualitatively.

noted that excitation energy to the lowest quartet level $^4T_1$ is probably fairly low in the neighborhood of the critical region $\Delta \sim \Delta_c$.

Calculation of complete matrix of $V_C + V_{LF}$ and its eigenvalues was made by Tanabe and Sugano (1954), and the results for d^n $(2 \leqq n \leqq 8)$ were given in diagrams known by their names. Here are shown their diagrams for d^5 and d^6 (Fig. 8 and Fig. 9, respectively), in which the abscissa give

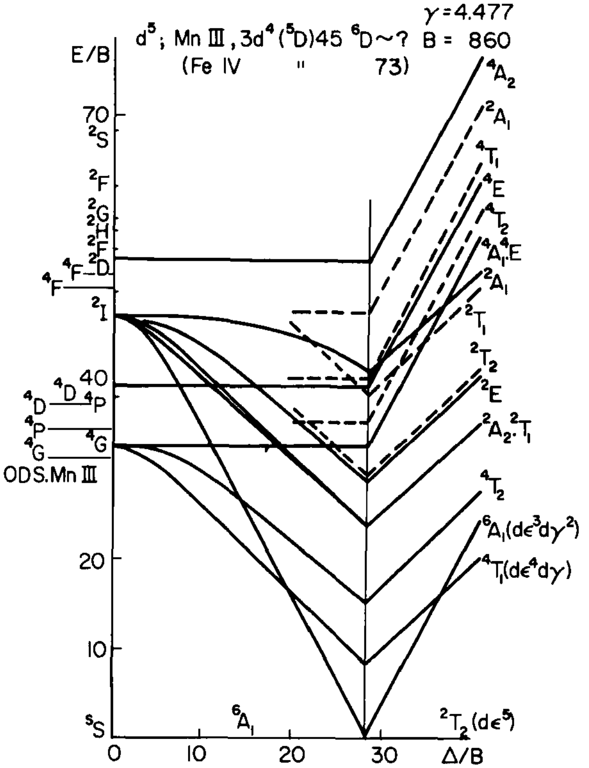


Fig. 8. Energy levels of d^5 configuration in cubic ligand field. Reproduced from the paper by Tanabe and Sugano (1954).

Δ/B, a measure of relative strength of V_{LF} and V_C, and the ordinates give energies above the ground state for different excited levels, in units of B. Values of C/B adopted in constructing these diagrams are those taken from spectra of Mn^{++} and Co^{+++}, but they are not much different from the corresponding values for Fe^{+++} and Fe^{++}. Characteristic features shown

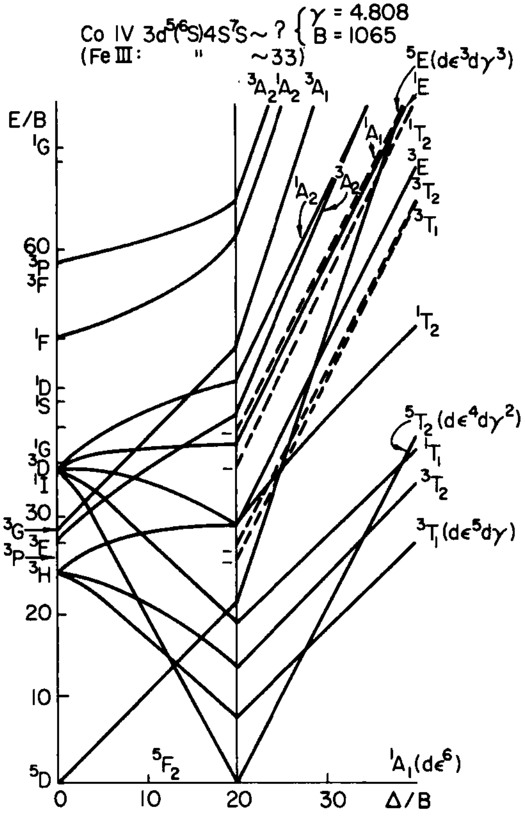


Fig. 9. Energy levels of d^6 configuration in cubic ligand field. Reproduced from the paper by Tanabe and Sugano (1954).

in Fig. 7 may easily be read from Fig. 8. Figure 9 shows that a similar alternation of the ground state takes place also in the case of a ferrous ion. In the range of weaker field the ground state is $^5T_2$, but at higher field strength it is $^1A_1$, arising from the configuration $(d\varepsilon)^6$.

(*d*) *Case of Tetragonal Field.* The actual symmetry around Fe in hemes is lower than cubic, although cubic symmetry may be used in a first approximation (see Section III). A better approximation will be tetragonal, corresponding to C_{4v}. If a small tetragonality is added to the cubic field, orbitally degenerate levels in cubic field will split into two levels with different types in C_{4v}. The correspondences are as follows:

Cubic, O_h		Tetragonal, C_{4v}
A_{1g}	→	A_1'
A_{2g}	→	B_1'
E_g	→	$A_1' + B_1'$
T_{1g}	→	$A_2' + E'$
T_{2g}	→	$B_2' + E'$

(*e*) *Spin-Orbit Interaction.* Spin-orbit interaction gives further splitting of energy levels given by (S, Γ). This is very important for the following discussions but explanation will be given where it is needed.

C. Molecular Orbital Formation and Delocalization

It was mentioned in Section B,1 that the molecular orbital theory is more general than the ligand field theory. In the former picture *d* orbitals of Fe are linearly combined with various orbitals of ligands, subject to restrictions arising from symmetry requirement. Thus we have, instead of a purely atomic orbital ψ_i, a molecular orbital (MO) ϕ_i of the form

$$\phi_i = c_i\psi_i + \text{(linear combination of ligand orbitals)}.$$

Accordingly, the orbital is delocalized, and unpaired electrons may travel through the whole porphin, and the probabilities of finding unpaired electrons at the positions of other nuclei may be detected by hyperfine structure of EPR and other methods.

For these orbitals occupied by unpaired electrons, however, the coefficients c_i are fairly large, as remarked in Section B,1, so that the ligand field theoretic approach is a reasonable working approximation. Furthermore, some of the important effects of MO formation can be implicitly taken into account in the frame of ligand field theory, by modifying parameters in appropriate ways. In fact, Sugano and Shulman (1963) have shown that the origin of Δ is to be attributed to this delocalization of *d* orbitals, i.e., to covalency, rather than to direct effect of the ligand electrostatic field. This is one of the reasons why honest numerical calculations of parameters are generally discouraged in the ligand field theory.

First, MO formation affects orbital energy. Most of the MO's which are important in magnetic problems are so-called antibonding orbitals, and MO formation raises orbital energy, depending on the degree of delocalization. Secondly, MO formation will decrease the effective values of Racah parameters and of spin-orbit interaction coefficients, although these modifications cannot cover all effects of MO formation. Tanabe and Sugano found, in their analysis of absorption spectra of complex salts based on the ligand field theory, that good agreement with observation can be obtained for trivalent ions of transition metals only when the values of Racah parameters are reduced by about 20%. Electric field gradient at the position of nucleus, which is responsible for quadrupole interaction, is also sensitive to MO formation, or delocalization of essentially atomic orbitals.

III. Theoretical Studies and Some Recent Experiments

In this section electronic structure of ferric and ferrous ions in hemes is discussed in detail, with attention paid to those features of electronic structure which are related to magnetic properties of heme proteins. Spin-orbit interaction, which was neglected in the last section, here plays an important role. To arrive at a satisfactory picture of electronic structure for each case described in Section I, theory with full use of information obtained by experimental studies must be developed. Therefore, in this section, not only theoretical considerations (Kotani, 1961) but also recent experimental results, particularly those obtained in our laboratory, will be presented and discussed.

The basic assumption is that the iron in the heme is in a rather singular condition in which high-spin and low-spin states are energetically very near to each other. In the approximation of cubic ligand field this assumption is expressed by the condition: $\Delta \sim \Delta_c$. This is very plausible because there are among derivatives of hemoglobin and myoglobin both high-spin species and low-spin species, and further there are intermediate ones, which may indicate thermal coexistence of high-spin and low-spin hemes, as mentioned in Section I. One of the results of our assumption is the fact that heme has a large number of lower excited electronic states. In other words, heme iron has a particularly flexible, "soft" electronic structure, which is seldom realized in the inorganic world. There is good reason to speculate that this particular feature of heme iron is closely related to the effectiveness of biological activity of heme proteins.

A. Ferric High-Spin Case

1. *Theory of Splitting*

In this case, the electronic ground state is sextet corresponding to $S = \frac{5}{2}$, but EPR experiments show that the six-fold degeneracy is partly lifted (see Section I,C). Probably the sextet is already split into three Kramers' doublets, and the lowest doublet corresponds to $S = \pm\frac{1}{2}$. How can we account for this splitting?

It seems reasonable to assume that the local symmetry at the iron is lower than cubic, and the deviation of the ligand field from cubic gives rise to the splitting of ${}^6A_1$. However, the ground sextet is orbitally nondegenerate, and the spin cannot "feel" the ligand field directly. Spin-orbit interaction $a \sum_i \mathbf{l}_i \mathbf{s}_i$ relates spin to orbitals, but, since the expectation value of $\mathbf{l}$ is zero for any nondegenerate orbital, matrix elements of spin-orbit interaction vanish within the sextet ${}^6A_1$.

It can be shown, however, that spin-orbit interaction gives the splitting of the sextet in the second order, via the excited quartet states. It was found in Section II,B that there is one quartet state ${}^4T_1$, whose excitation energy is very low. There are nonvanishing matrix elements between ${}^4T_1$ and ${}^6A_1$. In cubic symmetry, the second-order perturbation gives only a common shift of all six substates. But if the symmetry of the ligand field is lowered to, say, tetragonal, ${}^4T_1$ is split into two levels ${}^4A_2{}'$ and ${}^4E'$, and then the shift due to the second-order perturbation may be different for different subtrates of ${}^6A_1$. This gives splitting of ${}^6A_1$ (Kotani, 1963).

By straightforward calculation along this line, it is found that the splitting is given by the expression

$$DS_z^{\,2} \tag{III.1}$$

where

$$D = c^2 \frac{a^2}{2} \left\{ \frac{1}{E({}^4A_2{}') - E({}^6A_1)} - \frac{1}{E({}^4E') - E({}^6A_1)} \right\}. \tag{III.2}$$

In this formula, a is the coefficient of spin-orbit interaction appearing in $a \sum_i \mathbf{l}_i \mathbf{s}_i$, and c^2 is the relative amount of ${}^4P$ of free ion contained in ${}^4T_1$. c depends on configuration interaction, but in the strong field approximation, in which ${}^4T_1$ comes from single configuration $(d\varepsilon)^4(d\gamma)$, we have

$$c^2 = \tfrac{4}{5}. \tag{III.3}$$

A more complete formula for D has been worked out, by taking all combining excited states and using coefficients of mixing of configurations for these states. But (III.2) is found to be a good approximation.

Equation (III.1) gives three Kramers' doublets corresponding to $S = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$. Since $S_z = \pm\frac{1}{2}$ is known to be the lowest from EPR studies (see Section I,C), D must be positive. Doublets $S_z = \pm\frac{3}{2}$ and $S_z = \pm\frac{5}{2}$ are higher in energy by $2D$ and $6D$ respectively, above the ground doublet $S_z = \pm\frac{1}{2}$.

According to formula (III.2), the sign of D depends on the relative positions of ${}^4A_2'$ and ${}^4E'$; D is >0 if ${}^4A_2'$ is lower. Now, in the strong field approximation, ${}^4A_2'$ and ${}^4E'$ belong to configurations $\xi\eta\zeta^2\tau$ and $(\xi, \eta)^3\zeta\tau$ respectively, so that

$$E({}^4E') - E({}^4A_2') = \varepsilon_{\xi,\eta} - \varepsilon_\zeta . \tag{III.4}$$

Accordingly, $D > 0$ requires that among three $d\varepsilon$ orbitals ξ, η, and ζ, ζ is the lowest. This order agrees with the result of analysis of EPR spectra observed for low-spin ferri-Mb.N_3^-(see Section III,B), although the latter represents the situation in the state ${}^2T_2$.

As to the magnitude of D, only a tentative estimate can be made, since no direct experimental information is available concerning the excitation energies to quartets. From theoretical calculation along the line of Tanabe-Sugano's method (Section II,B), $E({}^4T_1) - E({}^6A_1)$ is obtained as $\sim$6000 cm^{-1} at $\Delta = \Delta_c$. On the other hand, EPR study about low-spin ferri-Mb.N_3^- gives

$$\tfrac{1}{2}(\varepsilon_\xi + \varepsilon_\eta) - \varepsilon_\zeta = 1900 \quad \mathrm{cm}^{-1}. \tag{III.5}$$

Assuming that the centre of gravity of ${}^4A_2'$ and ${}^4E'$ is at $E({}^4T_1)$, and the separation between ${}^4E'$ amd ${}^4A_2'$ (III.4) is given by (III.5), and taking 400 cm^{-1} for a, a value somewhat smaller than that of the free ion, we get

$$D \fallingdotseq 1.9 \quad \mathrm{cm}^{-1}. \tag{III.6}$$

This is roughly the right order of magnitude, but is smaller than the value expected from magnetic measurements by a factor $3 \sim 5$ (see Section III,A,3). According to (III.2), excitation energy to ${}^4A_2'$ must be $\lesssim$3000 cm if the formula is to give the value of D in agreement with experiments.

If the local symmetry is lower than tetragonal and there is an anisotropy in the heme plane (xy plane), orbital energies ε_ξ and ε_η may be different. For this case, the second-order perturbation gives such splitting of ${}^6A_1$ as described by spin Hamiltonian

$$DS_z^2 + E(S_x^2 - S_y^2). \tag{III.7}$$

The formula for D is the same as (III.2) except that $\{({}^4E') - E({}^6A_1)\}^{-1}$ is replaced by the mean of $\{E_x - E({}^6A_1)\}^{-1}$ and $\{E_y - E({}^6A_1)\}^{-1}$, where E_x and E_y denote energies of two levels arising from E' by splitting, and the formula for E is given by

$$E = c^2 \frac{a^2}{4}\left\{\frac{1}{E_x - E({}^6A_1)} - \frac{1}{E_y - E({}^6A_1)}\right\}. \tag{III.8}$$

Evidence for the presence of small but finite E has been recently given by EPR experiments, which will be described in the following.

2. *EPR Studies*

Small periodic variations of g values depending on the azimuth of magnetic field in the heme plane have been observed by Morimoto (1967), using single crystal specimens of ferri-MbOH$_2$ and ferri-MbF$^-$. The mounting holder, on which single crystal specimen is fired, can be rotated around a vertical and a horizontal axis. For each fixed setting of rotation around the horizontal axis, the crystal is rotated around the vertical axis, and the maximum g value is recorded. Results can be represented by the following equations:

$$\begin{aligned} g &= 5.92 + 0.06\cos(2\varphi - 2\alpha), && \text{for ferri-Mb.OH}_2, \\ g &= 5.97 + 0.09\cos(2\varphi - 2\alpha'), && \text{for ferri-Mb.F}^-, \end{aligned} \qquad \text{(III.9)}$$

where φ denotes the azimuth of the magnetic field **H** in the heme plane, measured from the x direction. α, α' cannot be determined, as the directions of pyrrole nitrogens in the porphin plane for hemes in crystals are not known.

On the other hand, spin Hamiltonian (III.7) gives the following formula for g values expected when **H** is applied parallel to the heme plane, in the direction φ:

$$g = 6 + 24\frac{E}{D}\cos 2\varphi \qquad \text{(III.10)}$$

in the first order of E/D.

Comparison of (III.9) with (III.10) gives

$$\begin{aligned} \frac{E}{D} &= \pm 0.0025, && \text{for ferri-Mb.OH}_2 \\ &= \pm 0.0038, && \text{for ferri-Mb.F}^-. \end{aligned} \qquad \text{(III.11)}$$

If we substitute values of D determined by paramagnetic anisotropy (Section III,A,3), we find

$$\begin{aligned} |E| &= 0.025 \ \text{cm}^{-1}, && \text{for ferri-Mb.OH}_2 \\ &= 0.023 \ \text{cm}^{-1}, && \text{for ferri-Mb.F}^-. \end{aligned} \qquad \text{(III.12)}$$

It is to be noted that $|E|$ for these two molecules are almost the same. Values of $|E|/D$ larger than those given in (III.11) has been obtained by Watari for some of the human abnormal hemoglobins (Watari *et al.*, 1965). His observation was made on condensed solutions of $\mathrm{HbM}_{\mathrm{Boston}}$, which gave split peaks in the neighborhood of $g \sim 6$. This gives

$$\frac{E}{D} = \pm 0.011 \qquad (\text{ferri-HbM}_{\mathrm{Boston}}).$$

Summarizing these observations, it may be said that E is much smaller than D in the case of ferri-Hb, ferri-Mb and their derivatives in the high-spin state. According to formula (III.8), $E = 0.1\ \mathrm{cm}^{-1}$ gives $E_x - E_y = \pm 220\ \mathrm{cm}^{-1}$, on the same assumption $E(^4T_1) - E(^6A_1) = 6000\ \mathrm{cm}^{-1}$. Thus splitting of $^4E'$ seems to be smaller than the distance between A_2' and E', at least by a factor of 10.

There are several factors which may contribute to the asymmetry in the xy plane of this order of magnitude. Firstly, the imidazole is coordinated to iron with its plane almost normal to the heme plane, and the orientation of its plane at a fixed azimuth gives asymmetry. A rough estimate of asymmetry due to this cause gives $|\varepsilon_\xi - \varepsilon_\eta| \sim 60\ \mathrm{cm}^{-1}$ (Kotani, 1964). Vinyl groups will also give a certain asymmetry through conjugated system of π electrons. In the case of $\mathrm{HbM}_{\mathrm{Boston}}$, OH_2 molecule coordinated at the 6th site may form a hydrogen bridge with oxygen atom of tyrosine, and the molecular plane of OH_2 will be fixed. This may be another cause for asymmetry. After all, the presence of a small asymmetry, such as found by EPR measurements, seems to be reasonable.

3. Paramagnetic Susceptibility

Measurement and analysis of paramagnetic susceptibility provide us, in some sense, with information complementary to that obtained by EPR technique, although of course two are closely related. The latter gives us precise and detailed knowledge concerning magnetic behavior of the lowest state, while the former shows us interplay of several low lying energy levels. For the study through paramagnetic susceptibilities, temperature is an important parameter; study of temperature dependence of any physical quantity may be regarded as the study of Laplace transforms of the same quantity as function of energy.

Theory of paramagnetic susceptibility is well established (Van Vleck, 1932). Consider an atom or a molecule in quantum state n, subject to an applied magnetic field $\mathbf{H}$, and denote its energy by $\varepsilon_n(H_x, H_y, H_z)$. Then the magnetic moment of this system $\boldsymbol{\mu}_n$ is given by

$$\mu_{np} = -\frac{\partial \varepsilon_n}{\partial H_p}, \qquad p = x, y, z. \tag{III.13}$$

The macroscopic magnetization of an assembly of N such systems is therefore given by

$$M_p = \frac{\sum_n \mu_{np} e^{-\varepsilon_n/kT},}{\sum_r e^{-\varepsilon_n/kT}}, \qquad p = x, y, z. \tag{III.14}$$

Expanding the numerator in powers of H_q, and noting that $\mathbf{M}$ vanishes for $\mathbf{H} = 0$, we have

$$M_p = \frac{N}{\sum_n e^{-\varepsilon_n(0)/kT}} \sum_n \left\{ \frac{1}{KT} \left(\frac{\partial \varepsilon_n}{\partial H_p} \right)_0 \left(\frac{\partial \varepsilon_n}{\partial H_q} \right)_0 - \left(\frac{\partial^2 \varepsilon_n}{\partial H_p \partial H_q} \right)_0 \right\} e^{-\varepsilon_n(0)/kT} H_q \tag{III.15}$$

to the first order of $\mathbf{H}$. Coefficient of $\mathbf{H}_q$ in this formula is the (p, q) component of the susceptibility: χ_{pq}. In (III.15), suffix 0 denotes values of derivatives at $\mathbf{H} = 0$. It is always possible to take the coordinate system in such a way that $\chi_{pq} = 0$ for $p \neq q$, for each temperature. Then the principal susceptibilities are expressed by the formula:

$$\chi_{pp} = \frac{N}{\sum_n e^{-\varepsilon_n(0)/kT}} \sum_n \left\{ \frac{1}{kT} \left(\frac{\partial \varepsilon_n}{\partial H_p} \right)_0^2 - \left(\frac{\partial^2 \varepsilon_n}{\partial H_p^2} \right)_0 \right\} e^{-\varepsilon_n(0)/kT}. \tag{III.16}$$

First we apply this formula to a (fictitious) assembly of hemes all of which are oriented parallel. From the structure of the system, the z direction, which is the common normal to all hemes, will be one of the directions of principal susceptibilities, and χ_{xx} and χ_{yy} will be equal if small anisotropy in the heme plane is neglected.

In order to evaluate χ_{zz} and $\chi_{xx} - \chi_{yy}$, it is necessary to know the energies of lower excited levels up to the second order of magnetic field intensity. For this purpose we take Hamiltonian in the form

$$DS_z^2 - \tfrac{1}{4}D + 2\mu_{\mathrm{B}}\mathbf{S} \cdot \mathbf{H}, \tag{III.17}$$

neglecting the E term, and assuming other electronic states such as ${}^2T_2$ too high to be populated sensibly. It is easy to find six eigenvalues of (III.17) for $\mathbf{H} \| z$ and $\mathbf{H} \perp z$. For $\mathbf{H} \| z$, we have exactly

$$\begin{gathered} 6D \pm 5\mu_{\mathrm{B}}H, \\ 2D \pm 3\mu_{\mathrm{B}}H, \\ \pm \mu_{\mathrm{B}}H. \end{gathered} \tag{III.18}$$

For $\mathbf{H} \perp z$, we use matrix of S_x, and calculate eigenvalues up to the second order in H. The result is

$$\begin{aligned} &6D + \frac{5}{4}\frac{\mu_B^2}{D}H^2, \\ &2D + \frac{11}{4}\frac{\mu_B^2}{D}H^2, \\ \pm\, &3\mu_B H - 4\frac{\mu_B^2}{D}H^2. \end{aligned} \tag{III.19}$$

Then χ_{zz} and χ_{xx} can be calculated by (III.16) in a straightforward manner.

Now, in the case of assembly of noninteracting rigid magnets with magnetic moment $\mu = n\mu_B$ the paramagnetic susceptibility is given by the well-known formula

$$\chi = N\frac{n^2\mu_B^2}{3kT}, \tag{III.20}$$

which represents Curie's law. We write χ_{zz} and χ_{xx} in expressions similar to (III.20),

$$\chi_{zz} = N\frac{n_\parallel^2\mu_B^2}{3kT}, \qquad \chi_{xx} = N\frac{n_\perp^2\mu_B^2}{3kT}. \tag{III.21}$$

These expressions define $n_\parallel$ and $n_\perp$, which are temperature-dependent, since Curie's law does not hold in our case. $n_\parallel$ and $n_\perp$ are called effective Bohr magneton numbers.

Formulas for $n_\parallel$ and $n_\perp$, obtained from (III.16), (III.18), (III.19) are (see Kotani, 1961)

$$n_\parallel^2 = \frac{3}{1 + e^{-2x} + e^{-6x}}(1 + 9e^{-2x} + 25e^{-6x}), \tag{III.22}$$

$$n_\perp^2 = \frac{3}{1 + e^{-2x} + e^{-6x}}\left(9 + \frac{8}{x} - \frac{11}{2x}e^{-2x} - \frac{5}{2x}e^{-6x}\right), \tag{III.23}$$

where $x = D/kT$.

Limiting values of $n_\parallel$ and $n_\perp$ for $x \to 0$ and $x \to \infty$ are easy to interpret. In the high temperature limit $x \to 0$, $n_\parallel$, and $n_\perp$ reduce to a common value $\sqrt{35} = 5.92$, which is the magnitude of spin magnetic moment for $S = \frac{5}{2}$ in units of μ_B (see Section I,B). This is what we expect, because at temperatures much higher than D/k the splitting of sextet should be of no importance.

In the opposite limit $T \rightarrow 0$, or $x \rightarrow \infty$, $n_{\parallel}$ and $n_{\perp}$ tend to $\sqrt{3}$ and $3\sqrt{3}$ respectively. In this limit only the lowest Kramers' doublet $S_z = \pm\frac{1}{2}$ is populated, and when **H** is $\parallel z$ its behavior is similar to that of a free spin with $S = \frac{1}{2}$, giving $n_{\parallel} = \sqrt{3}$. If **H** is applied in the heme plane the splitting in the first order of H is 3 times larger, so that $n_{\perp}$ will become equal to $3n_{\parallel} = 3\sqrt{3}$.

$n_{\parallel}$ and $n_{\perp}$ are shown in Fig. 10 in dependence on x.

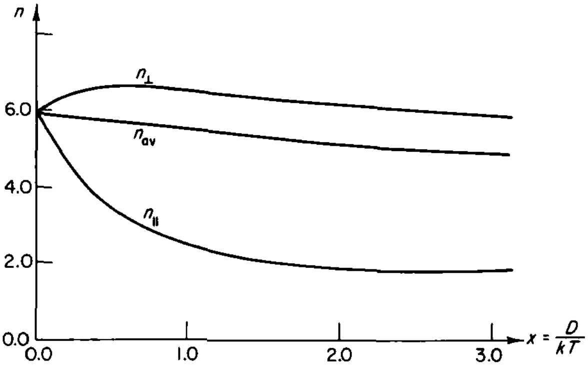


Fig. 10. Effective Bohr magneton numbers. For explanation see text.

4. *Measurement of Mean Susceptibility*

For isotropic specimen of heme proteins, such as concentrated solution, in which orientations of hemes are at random, only the mean susceptibility

$$\chi = \tfrac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}) \tag{III.24}$$

is measurable. Correspondingly, the effective Bohr magneton number to be derived from experiments is the average value

$$n_{\text{av}}^2 = \tfrac{1}{3}n_{\parallel}{}^2 + \tfrac{2}{3}n_{\perp}{}^2 \tag{III.25}$$

which depends on x as follows:

$$n_{\text{av}}^2 = \frac{1}{1 + e^{-2x} + e^{-6x}}\left\{19 + \frac{16}{x} + \left(9 - \frac{11}{x}\right)e^{-2x} + \left(25 - \frac{5}{x}\right)e^{-6x}\right\}. \tag{III.26}$$

n_{av} is also shown in Fig. 10. n_{av} decreases from its high temperature value $\sqrt{35}$ to its low temperature limit $\sqrt{19}$ as the temperature decreases.

Such temperature dependence of n_{av} has been observed by Tasaki *et al.*

(1965), who measured the susceptibilities of various heme protein samples from room temperature down to temperature range of liquid helium. Results obtained by them for ferri-Mb are most easy to interpret. Figure 11 shows the temperature dependence of observed n_{av} for sample of sperm-whale myoglobin in paste form. They tried to fit the observed curve by the theoretical formula (III.26) by adjusting the parameter D. Best fit is obtained by taking $D = 10\ \mathrm{cm}^{-1}$; the theoretical function for this choice of D is shown in Fig. 11 by the broken curve.

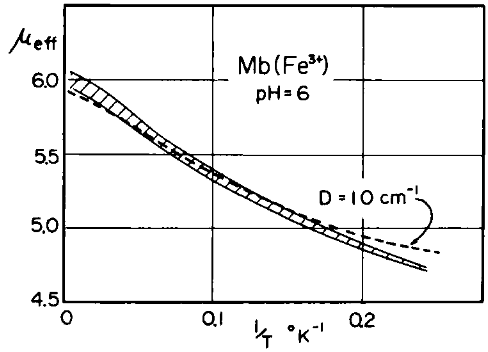


Fig. 11. Temperature dependence of the effective Bohr magneton number in ferri-Mb. The shaded strip shows observed values, the breadth indicating the range of probable error. Dotted curve shows theoretical values, calculated with the value $D = 10\ \mathrm{cm}^{-1}$.

In this way the magnitude of D has been determined, which is not easy to estimate by EPR alone.

Heme proteins other than ferric Mb seem to give n_{av} curves which deviate more or less from simple theoretical expectations. Even for ferri-Mb, comparison of two curves in Fig. 11 seem to suggest that the actual ratio of two intervals between Kramers' doublets is somewhat different from 2 : 1. If this is real, a term such as FS_z^4 might not be negligible in the spin Hamiltonian. In the case of ferri-Hb n_{av} seems to be lower than the values given by (III.26), including high temperature limit, which may suggest coexistence of hemes in low-spin states. There remains much to be clarified, before overall satisfactory interpretation is established.

5. *Measurement of Anisotropy of the Susceptibility Tensor*

Observation of torque exerted on a paramagnetic single crystal suspended in a static magnetic field makes it possible to measure directly differences between principal susceptibilities. McKim (1961) carried out this type of experiment by observing period of torsional oscillation of a suspended Mb crystal in a horizontal magnetic field. Recently the measurement of torque has been successfully carried out for myoglobin and hemoglobin crystals by Morimoto *et al.* (1965) covering a wide temperature range.

Consider a single crystal of heme protein suspended vertically in a horizontal magnetic field **H**. There may be hemes with different orientations in the sample crystal. The direction of normal to the ith heme in a unit cell is denoted by (θ_i, φ_i), where θ_i is the angle between the heme normal and the vertical direction and φ_i is the azimuth of this heme normal measured from a fixed horizontal direction. Let the azimuth of horizontally applied magnetic field be φ. Then the angle γ_i between the ith heme normal and the magnetic field is determined by

$$\cos \gamma_i = \sin \theta_i \cos(\varphi_i - \varphi). \tag{III.27}$$

Now the partial susceptibility χ_i, per heme due to the family of the ith hemes, with respect to the magnetic field applied in the direction described above, is given by

$$\begin{aligned} \chi_i &= \chi_{\parallel} \cos^2 \gamma_i + \chi_{\perp} \sin^2 \gamma_i \\ &= \chi_{\perp} + (\chi_{\parallel} - \chi_{\perp}) \cos^2 \gamma_i . \end{aligned} \tag{III.28}$$

Averaging over hemes in different orientations, the susceptibility of the crystal can be written as

$$\chi = \tfrac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) + (\chi_{\parallel} - \chi_{\perp})(A + B\cos 2\varphi + C \sin 2\varphi), \tag{III.29}$$

where

$$\begin{gathered} A = \tfrac{1}{2}\langle \sin^2 \theta_i - \tfrac{2}{3} \rangle, \qquad B = \tfrac{1}{2}\langle \sin^2 \theta_i \cos 2\varphi_i \rangle, \\ C = \tfrac{1}{2}\langle \sin^2 \theta_i \sin 2\varphi_i \rangle, \end{gathered} \tag{III.30}$$

where $\langle\ \rangle$ means averaging over i.

Now, the crystal will be exerted by a torque if χ depends on φ. Since the magnetic energy is $-\tfrac{1}{2}N\chi H^2$, the torque L is given by

$$\begin{aligned} L &= -\frac{\partial}{\partial \varphi}(-\tfrac{1}{2}N\chi H^2) \\ &= N(B^2 + C^2)^{1/2}(\chi_{\parallel} - \chi_{\perp}) \sin(2\varphi - 2\alpha) H^2, \end{aligned} \tag{III.31}$$

where N is the number of hemes in the crystal, and

$$\tan 2\alpha = C/B. \tag{III.32}$$

In terms of effective Bohr magneton numbers, L is written as

$$L = N\frac{\mu_B^2}{3kT}(B^2 + C^2)^{1/2}(n_\parallel^2 - n_\perp^2)\sin(2\varphi - 2\alpha)\, H^2. \qquad \text{(III.33)}$$

It is interesting to observe that from torque measurement products of $(B^2 + C^2)^{1/2}$ and $n_\parallel^2 - n_\perp^2$ can be determined, of which the latter factor is expected to vary according to the theoretical formula. The factor $(B^2 + C^2)^{1/2}$ and α give information about the distribution of directions of heme normals. Dependence of B and C on the choice of axis of suspension will increase the amount of information of the latter nature.

From the viewpoint of electronic theory we are interested in the factor $n_\parallel^2 - n_\perp^2$, which is temperature dependent. Combination of (III.22) and (III.23) gives

$$n_\parallel^2 - n_\perp^2 = \frac{3}{1 + e^{-2x} + e^{-6x}}\left\{8\left(1 + \frac{1}{x}\right) - \left(\frac{11}{2x} + 9\right)e^{-2x} - 5\left(\frac{1}{2x} + 5\right)e^{-6x}\right\}, \qquad \text{(III.34)}$$

It is expected that D can be determined by fitting observed $n_\parallel^2 - n_\perp^2$ to this function, similarly to the case of $n_{\rm av}^2$.

Figure 12 shows the theoretical curve (III.34) and results of fitting of experimental data for ferri-Mb.F$^-$ and ferri-MbOH$_2$. The nice fit shown

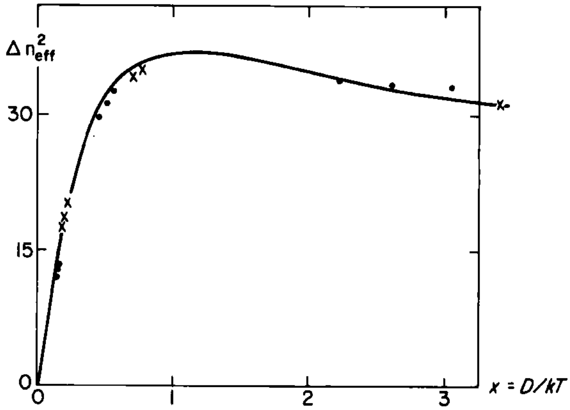


Fig. 12. $\Delta n_{\rm eff}^2 = n_\perp^2 - n_\parallel^2$ determined from torque experiments on single crystals of ferri-Mb derivatives. Solid line, theoretical curve; dots, observed ferri-Mb.F$^-$, $D = 6.49 \pm 0.18$; crosses, observed ferri-MbH$_2$O, $D = 9.96 \pm 0.34$.

in the figure was obtained by adopting the following for D

$$\begin{aligned} D &= 6.5 \quad \mathrm{cm}^{-1}, \qquad \text{for ferri-Mb.F}^{-} \\ &= 10.0 \ \mathrm{cm}^{-1}, \qquad \text{for ferri-Mb.OH}_2. \end{aligned} \tag{III.35}$$

Large difference between D values for such similar molecules is very remarkable.

Provided that single crystals can be prepared, this torque method is suitable for determining accurate values of D, because ${n_{\|}}^2 - {n_{\top}}^2$ is far more sensitive to the change of D than the average n_{av}^2.

B. Ferric Low-Spin Case

If the ligand field has the cubic symmetry, the ground state in this case is ${}^2T_2$, which corresponds to the configuration $(d\varepsilon)^5$ in the strong field picture. This means that there is one hole in $d\varepsilon$ shell; the triple degeneracy of T_2 arises from the freedom of this hole to take any one of the three orbitals ξ, η, and ζ. Of course, the real symmetry around Fe in low-spin hemes is lower, and there is good reason to believe that orbital energies ε_ξ, ε_η, and ε_ζ are different by 1000–2000 cm^{-1}.

The most detailed information concerning orbital energies ε_ξ, ε_η, and ε_ζ can be derived for EPR spectra. Gibson and Ingram has shown that, for instance, ferri-$\mathrm{MbN_3}^-$ (ferri-myoglobin azide) gives three principal g values (Gibson *et al.*, 1958)

$$g_x = 1.72, \qquad g_y = 2.22, \qquad g_z = 2.80. \tag{III.36}$$

It is remarkable that the difference between g_x and g_y is almost equal to the difference between g_y and g_z. This already suggests that the local symmetry is very low, and tetragonal symmetry is not a good approximation. Large deviation of these g values from 2.00 is due to a partial contribution of orbital magnetic moment. Although diagonal matrix elements of spin-orbit interaction V_{so} are zero for $\xi\eta^2\zeta^2$, $\xi^2\eta\zeta^2$, and $\xi^2\eta^2\zeta$, mixing of these three configurations takes place through the intermediation of V_{so}, so that the orbital magnetic moments become active to some extent. If $\varepsilon_\xi - \varepsilon_\zeta$, $\varepsilon_\eta - \varepsilon_\zeta$, and the spin-orbit interaction coefficient a were known, the matrix of $V_{\mathrm{LF}} + V_{\mathrm{so}}$ can be numerically constructed among six wave functions of $(d\varepsilon)^5$. By taking the lowest eigenvalue of this matrix, a pair of eigenfunctions for this eigenvalue can be determined. These functions constitute the lowest Kramers' doublet, i.e., the ground doublet. Computing magnetic energy $\mu_{\mathrm{B}} \sum_i (2\mathbf{s}_i + \mathbf{l}_i) \cdot \mathbf{H}$ with these functions, magnetic splitting of the ground doublet is obtained. This gives g_x, g_y, and g_z.

It is possible to proceed these steps in the reverse order. From experiments g_x, g_y, g_z are known. Starting from this end, we can determine wavefunctions for the ground doublet, and construct the matrix $V_{\mathrm{LF}} + V_{\mathrm{so}}$ which have these wavefunctions as the lowest eigenfunctions. Then, ratios of differences of diagonal elements to off-diagonal elements of this matrix give $\varepsilon_\xi - \varepsilon_\zeta$, $\varepsilon_\eta - \varepsilon_\zeta$ as definite numerical multiples of a.

The calculation has been carried out by Griffith (1957) and Kotani (1961); results obtained by Kotani for ferri-MbN$_3^-$ are

$$\varepsilon_\xi - \varepsilon_\zeta = 5.94\, a, \qquad \varepsilon_\eta - \varepsilon_\zeta = 3.54a. \tag{III.37}$$

This shows that among three $d\varepsilon$ orbitals, ζ is the lowest. Since a is ~400 cm^{-1}, ε_ξ and ε_η are higher than ε_ζ by about 2400 cm^{-1} and 1500 cm^{-1} respectively.

The reason for the fact that ζ is the lowest orbital may be found in stronger participation of ξ and η in antibonding molecular orbitals (see Section II,C).

The fairly large energy separation, ~1000 cm^{-1}, between ξ and η is remarkable. This is much larger than the corresponding value in the high-spin case, which was estimated from the small but finite E values of high-spin ferri-Mb derivatives. One reason for the large in-plane anisotropy of ferri-Mb.N$_3^-$ may be found in the simple electrostatic effect of the azide ion N$_3^-$ on orbitals ξ and η. N$_3^-$ has a straight form, and it is known from X-ray analysis that N$_3^-$ is attached to Fe very obliquely, the line of N$_3^-$ making a rather small angle with the heme plane. However, this explanation does not seem to solve the whole problem of large anisotropy in low-spin derivatives. Other low-spin derivatives such as ferri-Mb.CN$^-$, ferri-Mb.OH$^-$ (alkaline), give similar EPR signals, with large difference between g_x and g_y.

Some time ago, Kamimura suggested that Jahn-Teller effect may be the answer. The ferric ion in the high-spin case is in an orbitally symmetric and nondegenerate state, but the situation is different for the ion in the low-spin case. If the in-plane asymmetry imposed from outside is small, $\xi\eta^2\zeta^2$ and $\xi^2\eta\zeta^2$ will have a nearly same energy, and a spontaneous distortion of the porphyrin, which reduces the tetragonal symmetry, may stabilize the ferric ion in $\xi\eta^2\zeta^2$, or in $\xi^2\eta\zeta^2$, or in a certain linear combination of these two. Thus the heme may deform itself spontaneously to reach the most stable state. This phenomenon is known as static Jahn-Teller effect. Some quantitative investigation has been made by Kamimura and Mizuhashi, but the realization of this effect seems to depend very much on possible existence of low frequency deformation mode of porphyrin which couples with the electronic states of the ferric ion.

We have discussed in-plane magnetic anisotropy of heme, both in the high-spin state and in the low-spin state. If the magnetic field is applied parallel to the heme plane and is rotated in the same plane, g values of EPR signal vary sinusoidally between maximum and minimum values. The absolute directions of these principal axes of in-plane anisotropy, in reference to the geometrical structure of heme, are not certainly known. Recently Morimoto (1967) has shown that for ferri-MbF$^-$ (high-spin) and ferri-Mb.N$_3{}^-$ (low spin) these principal axes do not coincide, but those for fluoride and those for azide make an angle of about 45°. To show this, he prepared a single crystal of ferri-Mb and added hydrogen fluoride and sodium azide simultaneously to this crystal. Then some of the hemes catch F$^-$ and some N$_3{}^-$, and signals from high-spin hemes and those from low-spin hemes could be observed on the same crystal. On the assumption that the attachment of F$^-$ and N$_3{}^-$ does not affect the geometry of hemes, it was possible to compare the directions of principal axes of anisotropy of two derivatives. By constructing a Lissajous-like plot, it has been shown that the principal axes of high-spin heme and those of low-spin hemes make an angle of about $\pi/4$.

C. Ferrous Cases

There are high-spin and low-spin cases. Paramagnetic studies can be applied only to the former case, although Mössbauer effect can be observed on heme proteins of both cases. No EPR spectra has been observed on ferrous high-spin hemes, so that the only magnetic methods applicable to them are mean susceptibility measurement and anisotropy measurement by the torque method. Experimental work using these methods is going on in our laboratory, but it is premature to discuss the results in a systematic way. Theoretical studies of the electronic structure on ferrous ions in hemes have been made, but detailed quantitative considerations would be profitable only when theory can make full use of experimental results. On these grounds discussions of ferrous cases are omitted in the present paper, and readers are referred to a few review papers (see Kotani, 1961, 1965; Weissbluth, 1966).

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REFERENCES

BALLHAUSEN, C. J. (1962). "Introduction to Ligand Field Theory." McGraw-Hill, New York.

BENNETT, J. E., GIBSON, J. F., and INGRAM, D. J. E. (1957). *Proc. Roy. Soc.* (*London*) **A240**, 67.

CONDON, E. U., and SHORTLEY, G. J. (1935). "Theory of Atomic Spectra." Cambridge Univ. Press, London and New York.

GEORGE, P., BEETLESTONE, J., and GRIFFITH, J. S. (1964) *Rev. Mod. Phys.* **36**, 441.

GIBSON, J. F., INGRAM, D. J. E., and SCHONLAND, D. (1958) *Discussions Faraday Soc.* **26**, 72.

GRIFFITH, J. S. (1957). *Nature* **180**, 30.

GRIFFITH, J. S. (1961). "Theory of Transition Metal Ions." Cambridge Univ. Press, London and New York.

KENDREW, J. C., DICKERSON, R. E., STRANDBERG, B. E., HART, R. G., DAVIES, D. R., PHILLIPS, D. C. and SHORE, V. C. (1960). *Nature* **185**, 422.

KOENIG, D. F. (1965). *Acta Cryst.* **18**, 663.

KOTANI, M. (1961). *Progr. Theoret. Phys., Suppl.* No. 17, 4.

KOTANI, M. (1963). *Rev. Mod. Phys.* **35**, 717.

KOTANI, M. (1964). Biopolymers, Symposia No. 1, 67.

KOTANI, M. (1965). *Advan. Chem. Phys.* **7**, 159.

MCKIM, F, R. (1961). *Proc. Roy. Soc.* (*London*) **A262**, 287.

MORIMOTO, H. (1967). Private communication.

MORIMOTO, H., IIZUKA, T., OTSUKA, J., and KOTANI, M. (1965). *Biochim. Biophys. Acta* **102**, 624.

PAULING, L., and CORYELL, C. D. (1936). *Proc. Natl. Acad. Sci. U.S.* **22**, 210.

PERUTZ, M. F. (1965). *J. Mol. Biol.* **13**, 646.

SUGANO, S., and SHULMAN, R. G. (1963). *Phys. Rev.* **130**, 517.

TANABE, Y., and SUGANO, S. (1954). *J. Phys. Soc. Japan* **9**, 87.

TASAKI, A., OTSUKA, J., and KOTANI, M. (1965). *Ann. Repts. Res. Group on Biophys. Japan* **5**, 7.

VAN VLECK, J. H. (1932). "Theory of Electric and Magnetic Susceptibilities." Oxford Univ. Press, London and New York.

WATARI, H., SHIMIZU, A., HAYASHI, A., and YAMAMURA, Y. (1965). *Biochim. Biophys. Acta* **102**, 626.

WEISSBLUTH, M. (1966). Biophys. Lab. Rept. No. 162.

ZERNER, M., and GOUTERMAN, M. (1966). *Theoret. Chim. Acta* **4**, 44,

Aspects of the Electronic Structure of the Purine and Pyrimidine Bases of the Nucleic Acids and of Their Interactions

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I. Introduction

The determination of the *molecular structure* of the nucleic acids, i.e., of the nature and the spatial arrangement of the chemical species which make up these giant polymers, stands out as one of the greatest achievements of modern biochemistry. It is also one of its most important successes, because, among the principal chemical constituents of the living matter, the nucleic acids occupy a predominant place. These biological macromolecules have, in particular, the major functions of being the determinants of heredity and of directing the synthesis of specific proteins.

After the establishment of these fundamental data, a natural step in the development of this field of research is a deeper analysis of the underlying physical reality which essentially consists of the determination of the characteristics of the *electronic structure* of the nucleic acids. This implies primarily the determination of the electronic structure of their constituents. in particular of their purine and pyrimidine bases, and of the nature, at the electronic level, of the interactions which take place between these constituents and of the manifestations of these interactions at the macromolecular level. Our general knowledge of modern chemistry and physics does not leave any doubt about the fact that a great part of the observable properties of these acids must depend to a large extent on their electronic constitution.

The definite establishment of the main features of the molecular structure of the nucleic acids, due to Watson and Crick, dates back to 1953. Important refinements of the proposed pattern, due mostly to Wilkins and his collaborators, were presented in a series of papers extending over the period 1953–1957. The first theoretical calculation on the fundamental purine and pyrimidine bases of the nucleic acids was carried out in 1956 (A. Pullman *et al.*, 1956) and developed appreciably in the following years (A. Pullman and Pullman, 1958a, 1959; Nakajima and Pullman, 1958b, 1959). The first theoretical calculations on the purine-pyrimidine complementary base pairs were published in 1959 (B. Pullman and Pullman, 1959). All these and a large number of subsequent calculations have been carried out in the Hückel approximation of the molecular orbital method In spite of the well-known shortcomings of the Hückel approximation, they yielded a great mass of extremely useful information concerning the structure and the properties of these molecules which enabled a general interpretation of a large body of experimental data concerning the chemical, physicochemical, and biochemical properties of these molecules and of the nucleic acids themselves. This led to a number of predictions which have since been largely substantiated by subsequent experimentation. The success of the procedure was due mainly to the careful manipulation of the method, which was used essentially for the *comparative* study of the electronic characteristics of the compounds investigated, in other words for the classification on a *relative scale* of compounds or molecular regions or their constituent atoms with respect to the electronic properties under investigation. The results of this work are summarized in B. Pullman and Pullman (1963).

This preliminary work accomplished and although Hückel-type molecular orbital calculations are still frequently being carrried out nowadays in connection with different problems concerning the nucleic acids or their constituents, recent years have, naturally, witnessed the advent of more refined calculations relating to these molecules. There more refined studies are generally based on the self-consistent field molecular orbital procedures. The first calculation utilizing the Pariser–Parr–Pople approxima-

TABLE I. ESSENTIAL QUANTUM-MECHANICAL CALCULATIONS ON THE ELECTRONIC STRUCTURE OF THE PURINE AND PYRIMIDINE COMPONENTS OF THE NUCLEIC ACIDS

Subject and method	Reference
Huckel-type calculations on the purine and pyrimidine bases	A. Pullman and Pullman (1958a, 1959); Nakajima and Pullman (1958b, 1959); B. Pullman and Pullman (1963); Fernandez-Alonso (1964); De Voe and Tinoco (1962); Ladik (1964).
Hückel-type calculations on the π and σ electrons of purines and pyrimidines	Berthod and Pullman (1965); Bradley *et al.* (1964).
Self-consistent field calculations, generally in the Pariser–Parr–Pople approximation, with (b) or without (a) configuration interaction on the purines and pyrimidines	(a) Veillard and Pullman (1963); Nagata *et al.* (1965); Berthod *et al.* (1966a). (b) Nesbet (1964); Ladik and Appel (1966); Berthod *et al.* (1966b, 1967); Kwiatkowski (1966).
Calculations on purine-pyrimidine base-pairs	B. Pullman and Pullman (1959); A. Pullman (1963); B. Pullman (1965); Ladik (1964).
SCF studies on the electronic structure of the hydrogen bonds in the base pairs	Löwdin (1964, 1965); Rein and Harris (1964, 1965).
Van der Waals–London interactions between hydrogen-bonded or (and) stacked purines and pyrimidines.	De Voe and Tinoco (1962); Bradley *et al.* (1964); Nash and Bradley (1965); B. Pullman *et al.* (1966, 1967a,b); Sinanoğlu and Abdulnur (1964, 1965).
Van der Waals–London interactions between purines and pyrimidines (or the nucleic acids) and conjugated aromatics (hydrocarbons, aminoacridines).	B. Pullman *et al.* (1965); Gersch and Jordan (1965).
Spin densities in purine and pyrimidine free radicals	Baudet *et al.* (1962); A. Pullman (1964b); B. Pullman and Mantione (1964, 1965b).
Ring currents in purines and pyriamidines	Giessner-Prettre and Pullman (1965).
SCF and Hückel-type calculations on pyrimidines saturated at the 5–6 double bond	B. Pullman and Dupuy (1966, 1967).
Charge-transfer complexes involving purines and pyrimidines	Mantione and Pullman (1966a); A. Pullman and Pullman (1967).
Hückel type calculations on base analogs	B. Pullman and Pullman (1958b); A. Pullman and Pullman (1958b); Berthod and Pullman (1966)
Rare tautomeric forms of the bases. Problems of mutation	A. Pullman (1964a,c)
Interaction of carcinogens with nucleic acids and their constituents	B. Pullman (1964); B. Pullman *et. al.* (1965)

tion of the self-consistent method (PPP–SCF–MO) is due to Veillard and Pullman (1963). As it is well known, the self-consistent field methods yield, in principle, more reliable *absolute* values for a number of indices of electronic structure and should therefore be suitable for a *direct* comparison of theoretical and experimental results. *In practice*, although the whole scheme of these procedures is more satisfactory than that of the semi-empirical methods, they nevertheless suffer in calculations concerning heteromolecules from many of the drawbacks of the semi-empirical methods. Generally, they do introduce in one way or another some semi-empirical parameters into their scheme, in particular in connection with the different integrals related to heteroatoms. As a consequence of this situation, the absolute values of the quantities which they evaluate may be appreciably in error. That such really is the situation may be observed from the comparison *vide infra* of the results obtained by the different calculations available now in the PPP–SCF–MO approximation for purines and pyrimidines. A very careful scrutinization of the choice of the integrals appearing in the method, their optimization on reference compounds are indispensable for a successful calculation. This has been accomplished recently (Berthod *et al.*, 1966a,b, 1967), leading to results which may be considered very satisfactory.

Simultaneously with these technical developments, the number of problems investigated has increased and their scope broadened. A partial account covering the work carried in this field in the early nineteen sixties has been given in A. Pullman (1964a) and B. Pullman (1965). Work is, however, progressing rapidly in this field. The present review covers the more recent achievements.

Table I summarizes the essential references related to the quantum mechanical calculations on the nucleic acids and their constituents, as available at present.

II. Refined Molecular Orbital Calculations on the Purine and Pyrimidine Components of the Nucleic Acids

A. Parametrization of the Pariser–Parr–Pople Approximation

As stated before, and as is evident from Table I, a number of self-consistent field molecular orbital method calculations have been carried out in recent years for the purine and pyrimidine components of the nucleic acids, generally within the limits of the Pariser–Pople–Parr approximation. All these calculations have adopted the usual hypothesis of $\sigma - \pi$ separation and dealt essentially with the system of π electrons in the field of the

σ core. The most elaborate of these calculations and which has also been used the most extensively in relation with the physicochemical and biochemical properties of these compounds, are those due to Berthod *et al.* (1966a, 1967). We shall therefore essentially present in this chapter the results of this work, pointing out occasionally, however, its relation to other similar calculations and to the previous results obtained within the Hückel scheme. The more satisfactory character of this work resides in the very careful optimization of the integrals carried out by its authors and generally absent in the other publications. Important also is the fact that an approximate representation of the σ framework has been attempted by a procedure described in Section II,B.

The molecular orbitals of the π electrons are written as a linear combination of atomic orbitals

$$\varphi_i = \sum_r c_{ri} \lambda_r, \tag{1}$$

and the best orbitals of this form compatible with a single Slater determinant representing the closed-shell ground state can be found by the classical SCF Roothaan equations (Roothaan, 1951). If a set of orthogonal atomic orbitals λ obtained from the usual AO's by a Löwdin transformation (Löwdin, 1950) is used to build the MO's, a first-order approximation to the transformed Roothaan equations is given by (see e.g., Parr, 1963)

$$\sum_q (F_{pq} - \delta_{pq} \varepsilon_{qi}) c_{qi} = 0, \tag{2}$$

with

$$F_{pq} = I_{pq} + G_{pq'} \tag{3}$$

$$I_{pq} = \int \lambda_p \, H^{\text{core}} \, \lambda_q \, d\tau \tag{4}$$

$$G_{pp} = \sum_j \left\{ c_{jp}^2 (pp \mid pp) + \sum_{r \neq p} 2 c_{jr}^2 (pp \mid rr) \right\}, \tag{5}$$

$$G_{pq} = - \sum_j c_{jp} c_{jq} (pp \mid qq). \tag{6}$$

This set of equations is the same as the Pariser–Parr–Pople SCF equations obtained upon inserting into the Roothaan equations the zero-differential-overlap hypothesis of Pariser and Parr.

In principle, it should be possible to calculate all the integrals using the orthogonal basis λ; in practice, however, on account of the "built-in" approximations of the method (correlation error, frozen σ core, valence-state σ core, truncated basis set of AO's, poor approximation of atoms-in-molecules AO's etc; for a discussion, see A. Pullman, 1965a), satisfactory results can be obtained only if a series of empirical corrections are introduced, namely:

(a) a strong reduction of the one-center coulomb integrals $(pp \mid pp)$;
(b) a reduction of the two-center $(pp \mid qq)$ integrals, at least for nearest-neighbors;
(c) an empirical choice of I_{pq} values so as to fit spectral data for reference compounds.

These are the main features of the Pariser–Parr approximation. There remains the choice of the I_{pp} integrals, the classical expression of which is

$$\alpha_p = I_p - \sum_A (A/pp) - \sum_{q \neq p} (qq \mid pp). \qquad (7)$$

This expression is generally used as such with or without neglect of the second term and using as I_p the negative of the valence-state ionization potential of atom P. Although such a simplification may be of little importance in hydrocarbons, where it seems to influence merely the absolute values of the molecular ionization potentials and where the atomic π electron-populations are close to unity, this is no more the case in heteromolecules. There, an empirical choice of U_p values in place of the first two terms of Eq. (7) is strongly required (A. Pullman and Rossi, 1964).[1]

---

[1] An argument for the lowering of the valence-state ionization potential of an atom in a molecule can be found in the idea that the potential of the A core seen by a π electron is not that of a A^+ ion in the appropriate valence state but merely that of such an ion carrying a net σ charge due to σ bond polarization. Thus the corresponding part of the core integral should be written accordingly:

$$-I_p - \sum_\sigma Q_\sigma (J_{\sigma\pi} - \tfrac{1}{2}K_{\sigma\pi}). \qquad (8)$$

The summation bearing over all the σ orbitals on atom A, Q_σ being the charge on each σ orbital. For instance in the CH_3 radical, calculation of the σ distribution by the procedure described below yields a net excess of charge of approximately 0.05 e on each carbon σ orbital. An estimate of $J_{\sigma\pi} - \frac{1}{2}K_{\sigma\pi}$ of about 8 eV can be made using integral values calculated from spectroscopic data by Berthier *et al.* (1965). The lowering of I_p by this σ bond polarization effect is thus as large as 1.2 eV even though the polarity of the CH bonds is small.

Although it may be tempting to evaluate the U_p values in using an appropriate σ core, there are so many approximations involved that it is probably more secure to treat them as empirical parameters.

One of the main concerns of Berthod, Giessner and Pullman was to determine an appropriate set of empirical U_p values together with the remaining empirical integrals.

This was done by trial and error so as to obtain a set of integral values which reproduce as many observable properties as possible for a number of reference molecules. Details of this procedure can be found in Berthod *et al.* (1966a). We summarize below only the main points:

(a) The one-center coulomb integrals for carbon, nitrogen, and oxygen were given the values

$$\gamma_p{}^0 = (pp \mid pp) = I_p - A_p \qquad (9)$$

according to the Pariser (1953) relation, where I_p and A_p are the valence-state ionization potential and electron affinity of atom p. The authors used the values tabulated by Hinze and Jaffé (1962) for the appropriate valence states. For π lone-pairs like those of the pyrolic nitrogen, relation (8) was also adopted according to Julg's (1958) argument.

(b) Concerning the two-center coulomb integrals $\gamma_{pq} = (pp \mid qq)$, the authors tentatively adopted the theoretical values calculated with the usual Slater orbitals for all pairs p, q of nondirectly bonded atoms, since this does not seem to strongly affect the results (Lykos, 1961). Concerning the coulomb integrals for pairs of bonded atoms, it has been emphasized (Lykos, 1961; Ruedenberg, 1961) that they affect the results essentially through their difference with respect to the one-center value adopted. The best fit for this difference in carbon compounds (Pariser, 1956; Simmons, 1964) yields a value of 6.9 eV for γ_{CC} (1.39 Å) when $\gamma_C{}^0$ is put equal to the value of Table II. This value would be obtained through the theoretical formulas in using Slater orbitals with an effective quantum number ζ' equal to 0.83 (instead of the Slater value 1.625). For adjacent atoms, all the γ_{CC} values have been calculated with this value of ζ'. A similar procedure has been used for heteronuclear integrals (for details, see Berthod *et al.*, 1967).

It must be pointed out that this choice of Coulomb integrals does not correspond to a smooth interpolation curve from the γ_{13} values to the empirical γ^0 values, as in the original Pariser–Parr (1953) quadratic expression. Although this discontinuous character of the reduced Coulomb integrals seems to be a necessity for obtaining good transitions in carbon compounds, the authors have assessed its effect in a series of heterocycles by comparison with the use of the original Pariser–Parr (1953) interpolation formula. The transitions obtained with a smooth curve were 0.1–0.6 eV higher than the ones calculated with the discontinuous curve. In addition the agreement of the calculated dipole moments with the experimental values is much better when the broken γ_{pq} curve is used instead of the smooth curve.

The discontinuous character of the γ_{pq} can perhaps be found in the fact that some justification for the integrals calculated with the orthogonalized basis λ (Löwdin, 1950) leads to a larger difference $\gamma_{11} - \gamma_{12}$ than the integrals calculated with the usual Slater atomic orbital basis, whereas the difference $\gamma_{11} - \gamma_{1p}$ (for $p \neq 2$) is practically the same in the two basis. Moreover, the exchange integrals are indeed very small in the λ basis, with the exception of those involving nearest neighbors [McWeeny (1955)]. Since all the exchange integrals are neglected in the method, the fitting of the γ_{pq} must make up for the error so introduced.

(c) The remaining parameters concern the one-center and two-center core integrals α_p and β_{pq}. The authors have adopted as a starting point the β_{CC} value, -2.39 eV, determined for benzene (C—C = 1.39 Å) and the β_{CN} value of -2.576 eV adjusted for *s*-triazine (Pariser and Parr, 1953) (C—N = 1.34 Å) and have evaluated β_{CO}, β_{C-NH}, and β_{C-NH_2} by trial and error on formaldehyde, pyrrole, and aniline. The R dependence of β_{pq} adopted has been $\beta = -K/R^6$, following a suggestion by Kon (1955).

There remains the choice of the U_p values. As a starting point, the authors adopted $U_C = -9.5$ eV, which is known to give satisfactory values of the ionization potentials in hydrocarbons (Pople, 1953) and determined U_O, U_N, U_{NH}, and U_{NH_2} so as to reproduce the ionization potentials of formaldehyde, pyridine, pyrimidine, pyrrole, and aniline. Moreover, in this trial-and-error procedure, they have attempted to reproduce at the same time the values of the dipole moments of the reference compounds, obtained by adding to the calculated π component, the σ component (obtained in a way described in the next section).

The set of integral values which gave the best overall agreement with as many properties as possible in a series of reference compounds without

TABLE II

INTEGRAL VALUES FOR THE π SYSTEM

p	$\gamma_p{}^0$ (eV)	ζ'	$K_{(C-p)}$	U_p (eV)
C	11.13	0.83	17.238	-9.5
N	12.34	0.92	14.913	-11.8
NH	12.34	0.92	15.195	-9.9
NH_2	12.34	0.92	11.579	-8.9
O	15.23	1.135	8.573	-14.5

configuration mixing is listed in Table II (see Berthod *et al.*, 1967, for details on the reference molecules). Configuration mixing with all the singly excited configurations was introduced afterwards (Berthod *et al.*, 1966b, 1967).

B. The Representation of the σ Bonds

A simple procedure has been formerly proposed by Del Re (1958) for representing the σ bonds in saturated compounds. Its essential features were as follows:

(a) treat each bond as a two-electron problem;

(b) describe each electron in the bond by a molecular orbital

$$\varphi = a\chi_a + b\chi_b \tag{10}$$

linear combination of two atomic orbitals;

(c) use an effective one-electron Hückel-type Hamiltonian yielding the secular equation of 2^d order

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{bb} - E \end{vmatrix} = 0, \tag{11}$$

with

$$H_{aa} = \int \chi_a H\chi_a \, d\tau, \tag{12}$$

$$H_{ab} = \int \chi_b H\chi_b \, d\tau; \tag{13}$$

(d) neglect overlap, put

$$H_{aa} = \alpha_a = \alpha + \delta_a\beta, \tag{14}$$

$$H_{ab} = \varepsilon_{ab}\beta, \tag{15}$$

as usual, in terms of units α and β. (These units are α_H and ε_{CH} respectively.)

(e) As an original feature of the procedure, one defines

$$\delta_a = \delta_a{}^0 + \sum_c \gamma_a(c)\delta_c{}^0 \tag{16}$$

where $\delta_a{}^0$ is a characteristic of atom a, c stands for all the atoms bound to atom a, and $\gamma_a(c)$ is a proportionality factor which introduces what Del Re calls the inductive effect of atom c on atom a.

(f) The set of δ^0, γ, and ε values were chosen by Del Re by trial and error for reproducing as many properties as possible for a number of saturated molecules, imposing a few logical conditions to the parameters. In particular the initial set of δ^0 values obeyed a linear law in the *global* atomic electronegativities x:

$$\delta_a{}^0 = k\,\frac{x_a - x_H}{x_H}\,. \tag{17}$$

(g) The preceding technique was adapted by Berthod and Pullman (1965) so as to make allowance for the possible differences in valence state or hybridization ratio of the same atom. Thus, orbital electronegativities must be used as a guide for the choice of δ^0 values. This leads in particular to the use of different σ-parameter values for saturated and conjugated molecules, a logical step in a procedure which uses linear combinations of valence orbitals.

One can justify both the choice of δ^0 values according to electronegativity values and the introduction of the inductive effect as follows:

(1) In the Hückel method, each electron of the system is subjected to a molecular effective field that one may write as:

$$T + V_A + \sum_{R \neq A} V_R\,. \tag{18}$$

It has been recently recalled (Del Re and Parr, 1963) that V_A is not simply the potential of an $A^{\pm}$ core, but the potential of an $A^{\pm}$ core carrying a fraction of electron equal to $(n-1)/N$ in a system of $n\pi$ electrons contributed by N atoms. Thus, the accurate expression of the corresponding coulomb integral is (A. Pullman, 1965a)

$$\alpha_A = -I_A + \frac{n-1}{2\,n} J_{aa} - \sum_{R \neq A} \left\{ \left(p_R - \frac{n-1}{N} \right) (J_{ra} - \tfrac{1}{2} K_{ra}) + (R/aa) \right. \tag{19}$$

where p_R is the number of electrons contributed by atom R.

Applying these ideas to the present two-electron case along a bond AB, one has

$$\alpha_A = -I_A + \tfrac{1}{4} J_{aa} - \tfrac{1}{2}(J_{ab} - \tfrac{1}{2} K_{ab}) - (B/aa), \tag{20}$$

$$\alpha_B = -I_B + \tfrac{1}{4} J_{bb} - \tfrac{1}{2}(J_{ab} - \tfrac{1}{2} K_{ab}) - (A/bb). \tag{21}$$

Using the Pariser relation for J_{aa}, one readily obtains the main term in the difference $\alpha_A - \alpha_B$:

$$-\tfrac{3}{4}(x_B - x_A) + \tfrac{1}{2}(A_B - A_A), \tag{22}$$

where $x = -\tfrac{1}{2}(I + A)$ is Mulliken's electronegativity.

(2) In fact, if atom *A* is adjacent to another atom *C* which is itself more electronegative than *A*, the σ orbital forming the bond *AC* will be polarized so as to leave a positive net charge on *A*. Thus the effective potential seen by the σ electrons of the bond *AB* is in fact larger than the potential used in (1) by an amount:

$$Q_{a'}(J_{a'} - \tfrac{1}{2}K_{a'}), \tag{23}$$

where a' corresponds to the orbital of atom *A* used in forming the molecular orbital with *C*, while *J* and *K* are the Coulomb and exchange operators. Thus, the term $-I_A$ in α_A must be replaced by

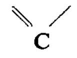
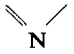
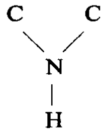
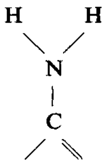
$$-I_A + Q_{a'}(J_{aa'} - \tfrac{1}{2}K_{aa'}). \tag{24}$$

But $Q_{A'}$ is directly proportional to the electronegativity parameter used on atom *C*, i.e., to $\delta_C{}^0$. There is the justification of the second term in Eq. (16).

Table III gives the values used for the σ parameters. Figure 1 shows the dependence of δ^0 on the electronegativity values.

TABLE III

σ-PARAMETER VALUES

μ	$\delta_\mu{}^0$	$\mu\nu$	$\varepsilon_{\mu\nu}$
C: 	0.12	C—H	1
N: 	0.38	C=N	0.7
N: 	0.30	C—N N—H	0.7 0.6
N: 	0.24	C—N N—H	1 0.45
O: O=	0.28	C=O	0.7
O: —OH	0.40	C—OH O—H	0.95 0.45

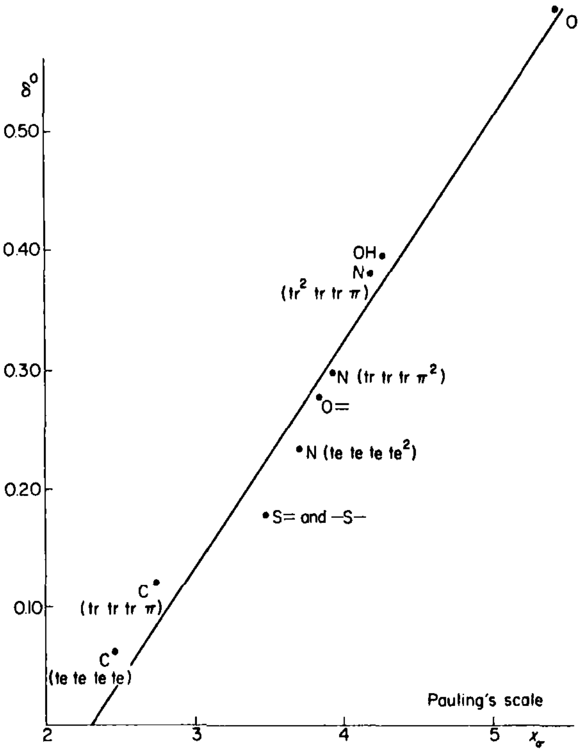


Fig. 1. Dependence of δ^0 values on electronegativities.

C. The Electronic Properties of the Purines and Pyrimidines

We shall describe the results of the application of the foregoing procedure to the nucleic bases and to some of their close analogs. Since configuration mixing, involving only singly excited configurations, does not alter the ground state, we can use the SCF results for studying the ground state properties.

The following abbreviated notations will frequently be used: P(purine) A(adenine), G(guanine), X(xanthine), HX(hypoxanthine), UA(uric acid), U(uracil), C(cytosine), T(thymine).

1. Ionization Potentials and Electron-Donor Properties

According to Koopman's theorem, the negative of the energy of the highest filled molecular orbital (HOMO) obtained in the SCF calculation gives an approximation to the first molecular ionization potential. The values of the HOMO for the four nucleic bases and some analogs are given in the second column of Table IV. The numerical values obtained are definitely smaller than the previous values of Veillard–Pullman (1963), Nesbet (1964) or the Japanese workers, Nagata *et al.* (1965). This was to be expected as a result of the more appropriate choice of U_p values. As concerns the order of magnitude obtained for the ionization potentials, it seems to be in a reasonable region: no direct experimental data are available concerning these compounds but an indirect evaluation of the ionization potentials of guanine, adenine and cytosine has been made (Mantione and Pullman, 1966a) from data on the wave-length of the charge-transfer absorption band in the complexes of these compounds with chloranil, no band being visible in the interaction of thymine or uracil (Machmer and Duchesne, 1965). Column III of Table IV indicates the values obtained in this way either (first value) by using Briegleb's (1964) empirical formula

TABLE IV

IONIZATION POTENTIALS AND ELECTRON AFFINITIES

Compound	HOMO (eV)	I_D (eV)	LEMO (eV)
Guanine	−7.59	7.8–8	+1.47
Adenine	−7.92	8.0–8.2	+1.52
Hypoxanthine	−8.00		+1.01
Cytosine	−8.16	8.1–8.4	+0.87
Purine	−8.87		+1.09
Uric acid	−8.66		+0.17
Xanthine	−8.82		+0.65
Uracil	−9.15		+0.38

$$h\nu = I_D - 5.70 + \frac{0.44}{I_D - 5.70}$$

or (second value) by a more direct evaluation of the involved quantities. Both the numerical values and their relative order compare favorably with the SCF results.

The order of decreasing ionization potentials shown by the present calculations for the nucleic bases is:

$$U > C > A > G.$$

This order is the same as that previously obtained by Veillard and Pullman and also by Nesbet, and in fact is also the same as that predicted initially by the Hückel approximation. In particular, in conformity with early predictions by B. Pullman and Pullman (1958a, 1963) guanine should be the best π-electron donor among the four nucleic bases. This is in complete agreement with the charge-transfer data just quoted.

Another apparent confirmation of this ordering may be found in the results of recent measurements of the oxidation potentials (anodic waves) at the stationary graphite electrode which show that the two pyrimidines U and C are not oxidizable, whereas the two purines A and G are, and indicate moreover, that guanine is oxidized more easily than adenine (Elving *et al.*, 1965). Also fitting with the calculated electron-donor abilities are the facts that purine is not oxidizable in the same conditions whereas hypoxanthine is oxidized. The same experiments, however, report oxidizability of xanthine and uric acid whereas their calculated ionization potentials locate them above cytosine, thus among the nonoxidizable compounds. The situation regarding uric acid is particularly troubling because the Hückel-type calculations (B. Pullman and Pullman, 1963) predict particularly great electron donor properties for this compound. We are investigating further this point in connection with the possible mechanism of the polarographic oxidation (Struck and Elving, 1965).

2. *Electron Affinities and Electron-Acceptor Properties*

The values of the energies of the lowest empty molecular orbital (LEMO) give a measure of the electron affinities of the bases or at least of their electron-acceptor capacities.

It can be seen from the energies of the molecular orbitals listed in the last column of Table IV, that the LEMO's appear, in the four nucleic bases, with a positive sign in the present calculation as opposed to the negative sign obtained in all previous calculations. This is due to the general rising of the orbital energy values due to the U_p adjustment.

The relative order of the LEMO energies indicates that the pyrimidines should be better electron-acceptors than the purines, in agreement with Veillard–Pullman and the other SCF calculations, but in contradiction with the previous Hückel prediction, according to which adenine and cytosine should be better acceptors than guanine and uracil (B. Pullman and Pullman, 1963).

It is practically impossible to have a direct check of the exactness of the absolute values of these energies, since the measurements of molecular electron affinities are practically non-existent and, moreover, their exact relation to the LEMO energies is not entirely clear. However, some information on the relative electron-acceptor properties of the molecules are available, through the measurements of the polarographic reduction potentials at the dropping mercury electrode. For the nucleic acid bases, it is found that adenine and cytosine are reducible whereas guanine and uracil are not (Struck and Elving, 1964; Elving *et al.*, 1965). Following Kotelnikova and Solomatina (1966), uracil may be reduced although with more difficulty and to a lesser extent than adenine or cytosine. These authors confirm the nonreducibility of guanine. Thus, it appears that in this respect the results of the Hückel calculations are more in agreement with the experimental data than the self-consistent results. It is, however, difficult to draw definite conclusions on this point, on account of the highly complex character of the reactions which may be determinant in the reduction processes.

3. Dipole Moments

The calculated values of the dipole moments obtained for the four nucleic bases and some oxygenated derivatives are given in Table V. The

TABLE V

DIPOLE MOMENTS (DEBYE UNITS)

Compound	μ_π	μ_{total}	μ_{exp}
Purine	3.0_5	3.7	4.3
Adenine	2.0	2.3	3.0
Guanine	6.1	7.2	—
Hypoxanthine	5.0	5.6	—
Xanthine	3.5	3.9	3.4
Uric acid	2.4	2.2	—
Uracil	3.3	4.0	3.9
Cytosine	5.4	7.1	—

agreement with the known experimental values is satisfactory. In accordance with previous calculations (De Voe and Tinoco, 1962; Berthod and Pullman, 1965) relatively high values of the moments are predicted for guanine and cytosine.

4. Electronic Charges and Bond Orders

The distribution of the π-electron charges and mobile bond orders may be used for the study of a number of properties of the purine and pyrimidine

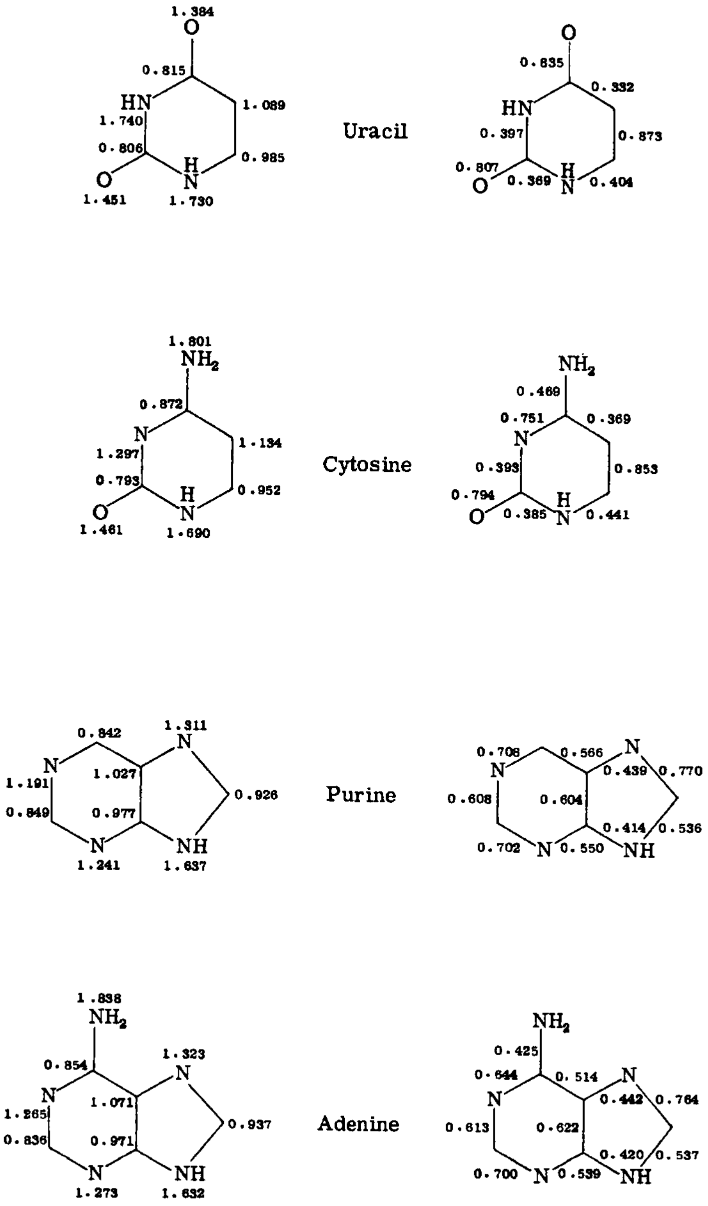
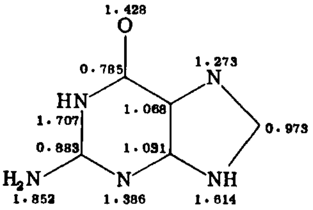
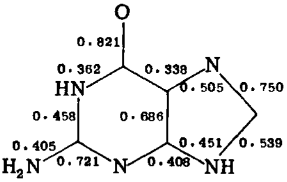
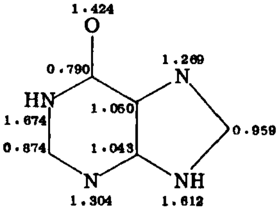


Fig. 2. Distribution of π charges

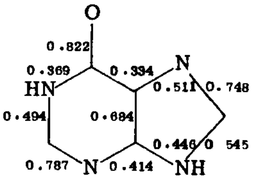


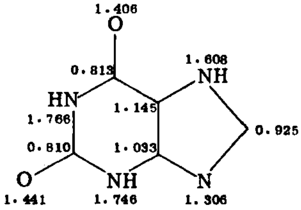
Guanine



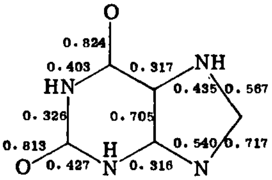


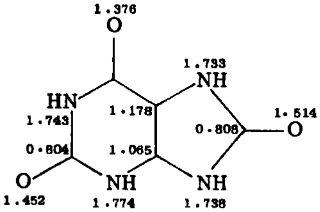
Hypoxanthine



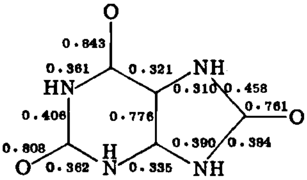


Xanthine





Uric acid



and mobile bond orders.

bases. We shall not discuss this problem in any detail because the overall distribution obtained here (Fig. 2) is similar to that obtained previously in our laboratory and so the discussion would follow closely the previous ones (B. Pullman and Pullman, 1963; B. Pullman, 1965). We feel, however, the need of considering more closely one point.

In agreement with Veillard and Pullman (1963) we find now for the relative order of the electron densities on the nitrogens $N_7 > N_3 > N_1$ in adenine and $N_3 > N_7$ in guanine, Nagata *et al.* (1965) obtain a different order for adenine, namely $N_1 > N_3 > N_7$ and they invoke, in favor of the correctness of their results, the fact that protonation occurs at the N_1 position of this molecule. The argument may, however, be easily returned against its authors. Thus, protonation of guanine is well known to occur at N_7 (Lawley and Brookes, 1963) in agreement with an early theoretical prediction (Nakajima and Pullman, 1958b), while the electron density of Nagata *et al.* is much larger at N_3 than at N_7 for this molecule.

As a matter of fact, it has been shown a number of years ago (Nakajima and Pullman, 1958a) that the basicities in heterocycles containing more than one nitrogen atom cannot be considered as being a function of the charge densities only, but vary rather like

$$\sum_p Q_p(dd\,|\,pp),$$

where Q_p is the net charge of atom p, and d is the lone-pair orbital of the nitrogen considered. The values of this quantity for adenine and guanine

TABLE VI

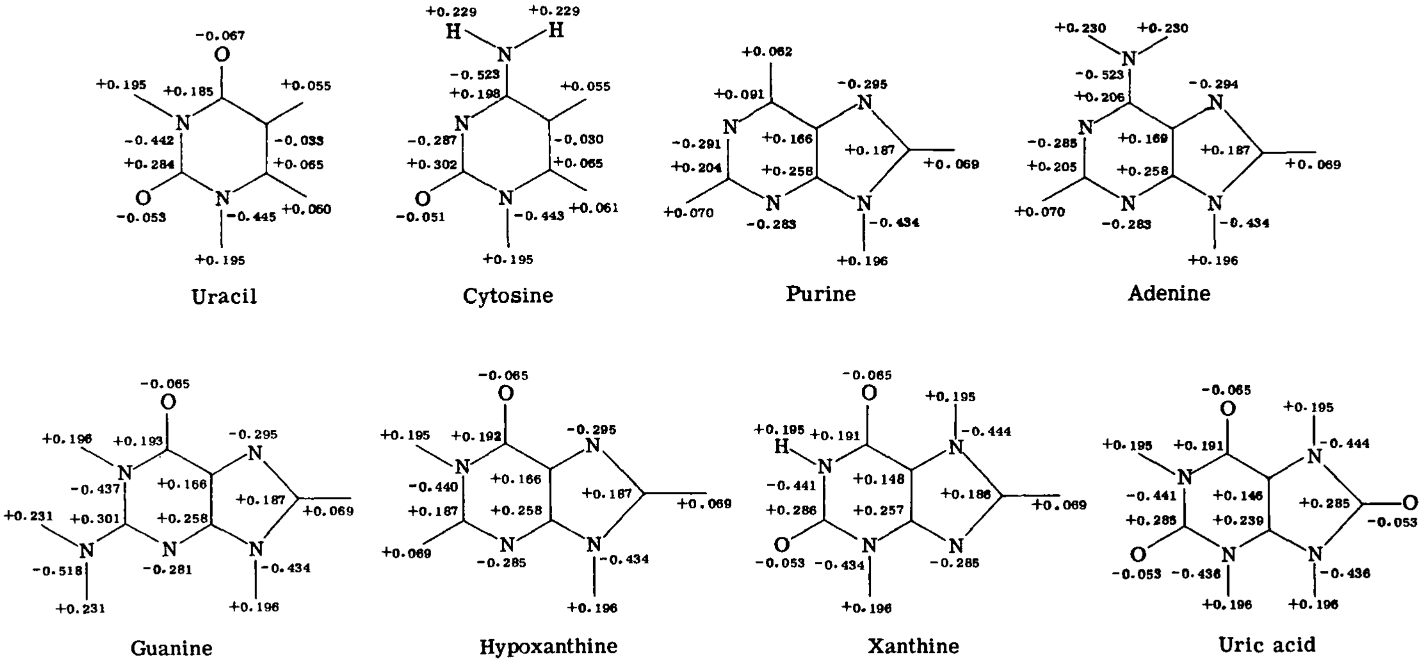
THEORETICAL BASICITIES

Compound	N_1	N_3	N_7[a]
A	−1.68	−1.60	−1.20
G	—	−1.14	−1.60

[a] With the appropriate correction related to a pentacyclic nitrogen (Nakajima and Pullman, 1958a).

are given in Table VI. They give the order $N_1 \approx N_3 > N_7$ for the basicities of the nitrogens in adenine, and $N_7 > N_3$ for guanine and are thus in general agreement with experiment.

For completion we reproduce here also (Fig. 3) the distribution of the net σ charges.



Uracil

Cytosine

Purine

Adenine

Guanine

Hypoxanthine

Xanthine

Uric acid

Fig. 3. Distribution of net σ charges.

5. *The Absorption Spectra*

The near ultraviolet absorption spectra of the purine and pyrimidine bases have been studied by different authors (Mason, 1954; Beaven *et al.*, 1955; De Voe and Tinoco, 1962). Voet *et al.* (1963) extended the spectra down to 180 mμ in aqueous solutions, and more recently a systematic study of the various spectra has been performed with an attempt of classification (Clark and Tinoco, 1965). This has been lately completed by measurements in the vapor phase for some of the bases by Clark *et al.* (1965). Mention must also be made of a recent very detailed study of both the absorption and emission of purine and of some of its derivatives in different solvents (Drobnik and Augenstein, 1966a,b).

Clark and Tinoco (1965) classify the observed transitions in the nucleic bases into three groups which they name B_{2u}, B_{1u} and E_{1u} by analogy to the corresponding nomenclature of the benzene transitions. This corresponds to the L_b, L_a and B bands of Platt's nomenclatures. In order to avoid discussions on terminology, we shall simply refer to the three corresponding domains of absorption as the first, second and third regions respectively.

The following systematization is possible after a careful examination of the spectra of the purines and pyrimidines listed by Clark and Tinoco, namely: P, A, G (data are for 9-ethyl guanine), HX (data for the 9-methyl derivative), U, and C (Table VII).

TABLE VII

EXPERIMENTAL SPECTRA (mμ–eV)

	Regions of absorption							
Compound	First[a]		Second		Third			
	mμ	eV	mμ	eV	mμ	eV	mμ	eV
U	258 (244)	4.8 (5.1)	230	5.4	203	6.1	181	6.8
A	260 (252)	4.8 (4.9)	—	—	208	5.9_5	185	6.7
P	265	4.7	240	5.15	200	6.1	188	6.6
C	277 (290)	4.5 (4.3)	237	5.2	204	6.1	185	6.7
G	275 (293)	4.5 (4.2)	256	4.8	203	6.1	190	6.5
HX	278 (281)	4.4_5 (4.4)	247	5.0	198	6.2_5	185	6.7
UA	286	4.3_5	—	—	—	—	—	—
X	267	4.6	—	—	—	—	—	—

[a] Vapor phase data are in parentheses.

(a) In all six molecules, the first band corresponding to the longest wavelength of absorption is situated between 260 and 278 mμ (4.76–4.4 eV) with HX, G, and C absorbing towards the longer wavelength limit. In the vapor phase, the distinction between HX, G, C on the one hand, and P, A, U, on the other, is still more marked since the first band of hypoxanthine, guanine, and cytosine is shifted to 290, 293, and 281 mμ respectively (4.2–4.4 eV) while the corresponding absorption in uracil and adenine occurs at 244 and 252 mμ respectively (5.1 and 4.9 eV). From the data available (Bergmann and Dikstein, 1955), uric acid seems to belong to the group HX, G, and C. We shall classify xanthine separately for reasons which will appear later.

(b) Towards the short wavelength end of the spectrum (the third region) all these molecules exhibit two strong maxima, one around 200–208 mμ (6–6.2 eV) and another towards 180–188 mμ (6.8–6.6 eV).

(c) In between these extremes is located the second transition which, however, does not appear in all molecules: present in HX about 247 mμ (5eV), it is seen as a shoulder in the spectrum of C (237 mμ or 5.2 eV), of G (256 mμ or 4.8 eV), and of P (240 mμ or 5.2 eV), whereas it is not visible in the spectrum of U or A. However in the case of U, the existence of a weak hidden band around 230 mμ (5.4 eV) has been suggested on the basis of experiments in optical rotatory dispersion (Yolles, unpublished, quoted by Clark and Tinoco, 1965). On the other hand, the first band in adenine has been suggested to be a composite one (Mason, 1954) formed by the superposition of two transitions, a suggestion supported by dichroïsm measurements (Stewart and Davidson, 1963, 1964) and studies of polarized fluorescence (Callis *et al.*, 1964).

As can be seen clearly from Table VIII, the SCF results even without configurational mixing (CM) correlate already in a very satisfactory way with the previous classification. As concerns the transition of longest wavelength, the calculations distinguish obviously two groups among the bases: guanine, cytosine, hypoxanthine, and uric acid absorbing towards longer wavelengths and adenine, uracil, and purine absorbing towards shorter wavelength. On the other end of the spectrum, all molecules exhibit a calculated band in the region 5.9–6.1 eV, corresponding clearly to the first band of the third region. Then comes a group of maxima which may reasonably be correlated with the second band in this region. As to the intermediate region, all compounds exhibit a calculated absorption in the range 5.3–5.5 eV, except purine, in which the corresponding maximum is shifted to 6 eV so as to be accidentally degenerated with the next transition. Interestingly enough, the calculated intensity of this theoretical band in uracil is exceptionally low, in accordance with the absence of an observable maximum in the intermediate region in this compound. As to the case of adenine, it seems tempting to consider the 5.5 eV transition, which is very close to the first (at 5.3 eV), as representing the second component of the composite band system.

TABLE VIII

Calculated Transitions (eV)

Compound	First region	Second region	Third region
SCF (intensities in parentheses)			
U	5.1(0.7)	5.5(0.02)	5.9(0.2)–6.3(0.5)–7.2(0.01)
A	5.2(0.4)–5.5(0.3)	—	6.1(0.5)–6.3(0.01)–6.4(0.2)–6.9(0.2)
P	5.5(0.65)	6.0(0.4)	6.0(0.7)–6.7(0.03)
C	4.2(0.1)	5.3(0.4)	6.0(0.5)–6.5(0.05)–6.8(0.3)
G	4.4(0.4)	5.4(0.6)	6.0(0.1)–6.3(0.1)–6.6(0.2)–6.8(0.1)
HX	4.4(0.3)	5.5(0.7)	6.1(0.1)–6.3(0.1)–6.7(0.4)–6.7(0.04)
AU	4.6(0.3)	5.5(0.1)	6.0(0.4)–6.1(0.3)–6.2(0.2)–6.5(0.4)–7.0(0.2)
$X(N_7H)$	5.0(0.4)	5.9(0.3)	6.1(0.3)–6.2(0.1)–6.4(0.2)–7.2(0.01)
SCF CM (intensities in parentheses)			
U	4.8(0.3)	5.4(0.06)	5.8(0.2)–6.2(0.6)–7.2(0.04)
A	4.8(0.1)–5.0(0.1)	—	5.8(0.2)–6.3(0.1)–6.5(0.5)–6.9(0.2)
P	4.9(0.1)	5.5(0.2)	6.3(0.3)–6.7(0.3)
C	4.1(0.1)	5.1(0.1)	5.8(0.4)–6.3(0.3)–6.9(0.2)
G	4.3(0.3)	5.1(0.3)	5.7(0.1)–5.9(0.1)–6.2(0.3)–6.6(0.03)
HX	4.2(0.2)	5.1(0.2)	5.8(0.1)–5.9(0.2)–6.6(0.2)–6.8(0.5)
AU	4.3(0.2)	5.4(0.3)–5.5(0.4)	5.8(0.1)–6.0(0.2)–6.2(0.4)–6.8(0.2)
$X(N_7H)$	4.7(0.5)	5.4(0.1)–5.6(0.3)	6.0(0.2)–6.3(0.1)–6.8(0.01)

The calculated intensities are reasonable without being particularly good, a feature to be expected from such a calculation.

The results after configuration mixing (Table VIII) confirm entirely the previous assignments with the following characteristics:

(a) As concerns the absorption band of longest wavelength, the calculations continue to distinguish two groups among the compounds: one group absorbing farther towards the red, comprising G, C, HX, and UA, and another group absorbing towards shorter wavelength, composed of P, A, and U. This distinction is slightly emphasized after configuration mixing where the respective ranges are 4.1–4.3 eV for the first group, and 4.8–4.9

eV for the second, in very satisfactory agreement with the observed values. The location of this band was in fact already fairly satisfactory without configuration mixing with the notable exception, however, of purine, which shows now a very strong lowering of the energy of this transition (and a parallel improvement of the results) through the mixing of essentially the first *three* excited configurations.

As a rule, the calculated intensities of the first band are closer to the experimental values after configuration mixing in these compounds. In particular, the anomalously high value obtained for uracil before mixing is appreciably lowered and brought much closer to the observed one.

(b) Leaving aside, for the moment, the second calculated transition, we observe in all compounds a series of maxima ranging from 5.7 to 7.2 eV (6.0 to 7.2 eV before mixing) which clearly correspond to the third region.

(c) In the intermediate region, we calculate a transition between 5.1 and 5.5 eV in all compounds after configuration mixing. Obviously, this transition can be correlated with the second band. Its position is improved with respect to the SCF results and compares very favorably with the experimental wavelength in the compounds in which it can be seen. In uracil, the low value of its calculated intensity is in agreement with the fact that it seems to exist as a hidden transition. On the other hand, in adenine, it appears very close to the first transition (much closer than in any of the other compounds), thus confirming the interpretation of the observed farthest absorption of this molecule as being composite. This phenomenon, already visible in the SCF results, becomes much clearer after configuration mixing. In contrast, no such phenomenon appears in purine, where the second band is appreciably separated from the first one.

Thus, on the whole, the classification and the interrelations of the observed spectra are reproduced in a very satisfactory way by the calculations. The main features of this agreement are already present in the SCF results. Configuration interaction does not bring about any drastic modification although it yields a general improvement of the results, particularly as concerns the position of the second transition and the intensities of the bands. Purine is the only compound for which the SCF results are relatively poor and for which configuration mixing has a rather strong improving effect. This is obviously related to the accidental degeneracy of the $5 \rightarrow 7$ and $4 \rightarrow 6$ configurations and to their strong mixing with the $5 \rightarrow 6$ configuration yielding a first excited state in which the three of them are equally weighted.

In general the discrepancy between the theoretical and the experimental energies of the electronic transitions, in particular as concerns the first and the second transitions, does not exceed 0.2 eV in the present calculations, in any of the compounds studied. This satisfactory result may be opposed to that of the calculation by Ladik and Appel (1966) with partial configuration mixing in which this discrepancy is sometimes as large as 1 eV. The present results seem also more satisfactory than those given by the SCF calculations of Nagata *et al.* (1965) of the first three singlets of A, C, G, U, and T. Their agreement with experiment is satisfactory for the first bands of adenine and cytosine only. No detailed systematic comparison with the other bands has been carried out, but the values reported seem less satisfactory than those of the present calculation. Moreover the value obtained for the first transition in uracil is far too low in energy (4.2 eV). This is not surprising since the calculations of these authors have been made erroneously for a rare tautomeric form of uracil. In fact, the calculated value which should be taken for uracil is the value 6.4 eV (198 mμ), reported by the authors for what they call "demethylated thymine." This is not satisfactory either.

6. *The Directions of Polarization*

The directions of polarization of the transitions have been studied experimentally in some detail for 9-methyladenine and 1-methylthymine (Stewart and Davidson, 1963, 1964; Stewart and Jensen, 1964). The results supplemented by a study of the A–T dimer indicate that the first band of 1-methylthymine is polarized at 19° with respect to the N_1C_4 axis (Fig. 4), the polarization of the second absorption below 240 mμ being qualified as "reversed." For 9-methyladenine, the major component of the first long wavelength transition is at 3° with respect to the C_4C_5 line (transverse axis) and the second weaker component is suggested to be polarized at right angles to the first one (Fig. 4).

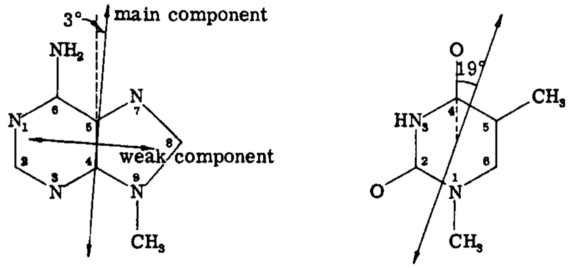
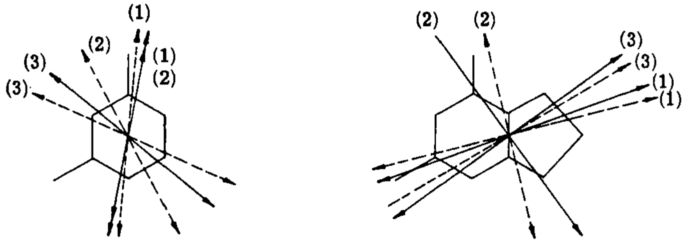


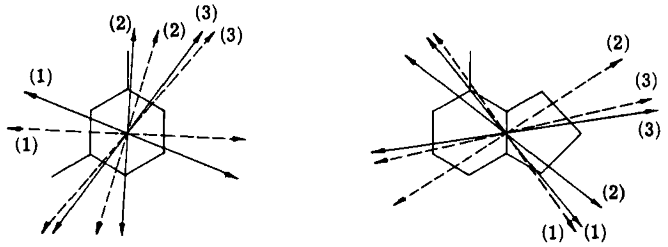
Fig. 4. Polarization of the first transition in 9-methyladenine and 1-methylthymine (after Stewart and Davidson, 1963, 1964; Stewart and Jensen, 1964).

Moreover, the absorption band below 240 mμ for 9-methyladenine is assigned a longitudinal polarization. These results for 9-methyladenine are in partial disagreement with the previous assignments of Mason (1954), who advocated a strong longitudinal component in the first band of adenine with a small contribution of a transversely polarized band. As to the other compounds, the only available experimental result indicates that the first two bands (at 275 and 230 mμ) in 9-ethylguanine are polarized at right angles to each other (Callis, *et al.*, 1964).

Figures 5 and 6 give the calculated directions of the polarization for the



Uracil Guanine



Cytosine Adenine

Fig. 5. Calculated polarizations in A, C, G, and U. (1), (2), and (3) correspond to the first three calculated transitions starting with $\lambda_{\max}$. ···, SCF; —, CM.

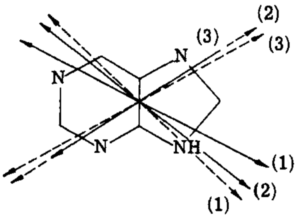


Fig. 6. Calculated polarizations in purine. (1), (2), and (3) correspond to the first three calculated transitions starting with $\lambda_{\max}$. ···, SCF; —, CM.

first three transitions in the nucleic bases and in purine. Both the SCF and SCF CM results are given for comparison. Examination of these figures shows the following features:

(a) With the exception of the second maximum of purine and adenine, configuration mixing changes very little the directions of polarization.

(b) In cytosine and uracil the polarization directions for the first two (*visible*) bands are reversed. In uracil, the first band is polarized close to the N_1C_4 axis, and the second close to the N_3C_6 axis. Insofar as the experiments on 1-methyl thymine are representative of the situation in uracil, the theoretical result is very satisfactory.

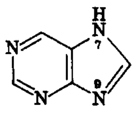
(c) In guanine the polarization of the first band appears as closer to the "long axis" with the second band closer to the transverse direction.

(d) In adenine, the first calculated maximum is closer to the transverse than to the longitudinal axis. In fact, it is roughly parallel to the N_1N_3 direction of the pyrimidine ring, indicating a very weak perturbation of the polarization that occurs in pyrimidine. Now, the SCF results indicated the second absorption (which we attribute to the second component of the first band) to be polarized perpendicularly to the first component, but configuration mixing reverses the situation so as to bring it close to the first transition in direction. The next transition appears as roughly longitudinal.

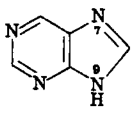
It can be seen that a very similar situation occurs in purine, where, however, the "transverse" or "longitudinal" character of the directions is more distorted.[2]

It may be mentioned that these results closely parallel those that can be deduced from the calculations of Nesbet (1964).

A particular remark needs to be made in connection with xanthine. We have not classified this molecule among the other bases since it seems highly probable (Sukhorukov and Poltev, 1963) that the measured spectrum corresponds to the unusual tautomeric form of the purine skeleton I,



(I)



(II)

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[2] It is interesting to mention that the early Hückel calculations of De Voe and Tinoco (1962) indicated the same opposed behavior of cytosine and uracil as concerns the directions of polarization of the first two bands, and also as concerns the longitudinal character of the first transition in guanine. Their result for adenine (first band longitudinal)

whereas the purines usually occur at least in their biological compounds in the form II. Calculations have been performed for both forms and also for different assumed geometries. In all cases, the first calculated band for the form N_9H lies at 5 eV or higher, while the N_7H form has a first band appreciably below this value and much closer to the experimental maximum of 4.6 eV (270 mμ) (Cavalieri *et al.*, 1954; Bergmann and Dikstein, 1955).

7. *The Energies of the Triplet States*

From the experimental viewpoint, precise results concerning the triplet states in these molecules are still rather scarce. The phosphorescence of the purine bases, their nucleosides and nucleotides, and of DNA has been studied and characterized by different authors (Longworth, 1962; Bersohn and Isenberg, 1964; Douzou *et al.*, 1961; Rahn *et al.*, 1964). The most recent and most precise measurements concern the first triplet state of adenine and purine (Cohen and Goodman, 1965) (see Table IX). The comparison of guanine with adenine is difficult on account of the closeness of the emitting regions (Bersohn and Isenberg, 1964); Longworth (1962) locates the phosphorescence maximum of guanine at a lower energy than the corresponding maximum of adenine, while determinations by Hélène (1966) indicate practically no difference between the two molecules from that point of view. On the other hand, phosphorescence studies (Hélène *et al.*, 1966) in dinucleotides containing guanine and adenine, seem to indicate triplet-triplet energy transfer from guanine to adenine thus suggesting the location of the adenine triplet below that of guanine one, at least in this experimental context. The pyrimidine bases do not phosphoresce under normal conditions (Bersohn and Isenberg, 1964; Longworth *et al.*, 1967).

The calculated positions of the triplet states (T_{CM}) and of the singlet-triplet splittings (ΔE_{ST}) with configuration mixing are given in Table IX. The positions before configuration mixing (T_{SCF}) are also indicated for comparison. The positions of the triplet states are, on the whole, more sensitive to configuration mixing than those of the corresponding singlets.

The last line in Table IX gives the value of $K = (1/\Delta E_{ST}^2)(\nu_3/\nu_1)^3$ a factor which plays an important role in the expression of the emission probability from a triplet state in the first order perturbation theory of

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which fitted Mason's conception is, however, not in accord with the present calculation which seems more compatible with the more recent measurements on the crystal spectrum.

TABLE IX

DATA RELATED TO THE LOWEST TRIPLET (eV)

Molecule	AU	U	C	X	HX	G	A	P
T_{SCF} (eV)	3.1	2.7	3.1	3.8	3.1	3.2	3.7[a]	3.7[a]
T_{CM} (eV)	2.1	2.1	2.3	2.4	2.5	2.6	3.0[a] 3.05[b]	3.1[a] 3.1[b]
ΔE_{ST} (eV)	2.2	2.7	1.8	2.3	1.7	1.7	1.8[a] 1.7[b]	1.8[a] 1.6[b]
K	0.024	0.012	0.054	0.025	0.074	0.071	0.069[a]	0.077[a]

[a] Calculated values.
[b] Experimental values.

spin-orbit coupling [McClure (1949)]. The examination of the results after configuration mixing shows the following points:

(a) The agreement of the calculated values with the experimental ones when these are known is quite remarkable.

(b) The triplets of the pyrimidine bases are lower than the triplets of the nucleic purines and of purine itself, the triplet of uracil being the lowest of all.

(c) The first triplets of the oxygenated bases are lower than the first triplets of adenine and purine.

(d) The three molecules AU, U, and X exhibit a relatively large singlet-triplet splitting (2.2 to 2.7 eV), whereas the corresponding quantity for the other bases is only of the order of 1.6 to 1.8 eV.

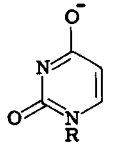
(e) The smallest *K* value is that of U followed by UA and X, then by C. Mono (lactam) or nonhydroxylated purines have a *K* factor much higher.

In agreement with these results are the facts that:

(a) The purines P, G, and A phosphoresce readily whereas the pyrimidines C and U do not.

(b] Xanthosine does not phosphoresce (Hélène *et al.*, 1966).

(c) Phosphorescence appears in uracil and uridine at alkaline *pH* (Longworth *et al.*, 1967). In such conditions, the molecule has lost a proton and is probably essentially in a form of type III.



(III)

Calculations done for the lactim form of uracil corresponding to III, have shown (Berthod *et al.*, 1966a) that lactimization of the group —C═O—N_3H of U raises the first triplet to 3.1 eV and reduces the S-T separation to 1.3 eV yielding a *K* value much higher than for the doubly lactam form.[3]

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[3] It must be stressed that the *K* values considered here represent only the contribution to the probability of emission of the spin-orbit coupling term involving the lowest π-π^* singlet. This is of course not the only factor involved in particular in cases like that of adenine and purine where the intensity of the phosphorescence seems to be, at least partly, borrowed from the lowest $n \rightarrow \pi^*$ singlet (Cohen and Goodman, 1965). A detailed study of the inter-system crossing terms is under investigation.

8. Spin Densities in the First Triplet State

Figure 7 shows the distribution of the spin densities in the first triplet state of purine and of the nucleic bases before and after configuration mixing (SCF and SCF CM respectively) (Berthod *et al.*, 1967).

It must be kept in mind that the SCF representation, using the virtual orbitals of the ground state for the building up of the excited states, does not distinguish between a singlet and the corresponding triplet as far as electron distribution is concerned. Intrinsically the corresponding representation of the triplet is thus not quite satisfactory. From that point of view, the SCF CM representation is an improvement over the SCF data. However, concerning the spin densities in the triplet states, the SCF CM representation has its shortcomings as long as singly excited configurations only (with respect to the ground state) have been introduced, a restriction which precludes the possibility of obtaining negative spin densities in triplets. Such negative spin densities in triplets can be obtained only upon inclusion of configurations which involve at least four uncoupled electrons.

In the present state of the available results the diagrams of Fig. 7 call for the following remarks:

(a) In both approximations the C_5—C_6 bond in uracil appears as bearing the highest concentration of odd electrons, whereas the corresponding densities in cytosine are much smaller. Moreover, the bond order of the C_5—C_6 bond is strongly decreased in the excited state with respect to its value in the ground state (0.449 in the triplet, 0.413 in the singlet, 0.873 in the ground state) after CM while such a situation does not occur in cytosine (triplet: 0.826; singlet: 0.665; ground state: 0.853). Similar conclusions were reached on the basis of the Hückel approximation and have been related to the ability of thymine and some analogs to undergo photodimerization (Mantione and Pullman, 1966; B. Pullman and Mantione, 1965a).

(b) In the purine bases, the distribution of the unpaired electrons cannot be considered to involve preferentially any particular bond. The configuration mixing has no large effect in adenine where the highest densities appear on NH_2 and on the C_8 carbon as before mixing. In purine the mixing brings about an inversion in the order of the positions C_6—C_2. In guanine, rather different distributions appear before and after configuration mixing: examination of the details of the mixing shows that the first two triplets (without CM) are rather close in energy and interact strongly in such a fashion that, after mixing, the weight of the *second* triplet is the largest in the *first* state. The second triplet state after CM is

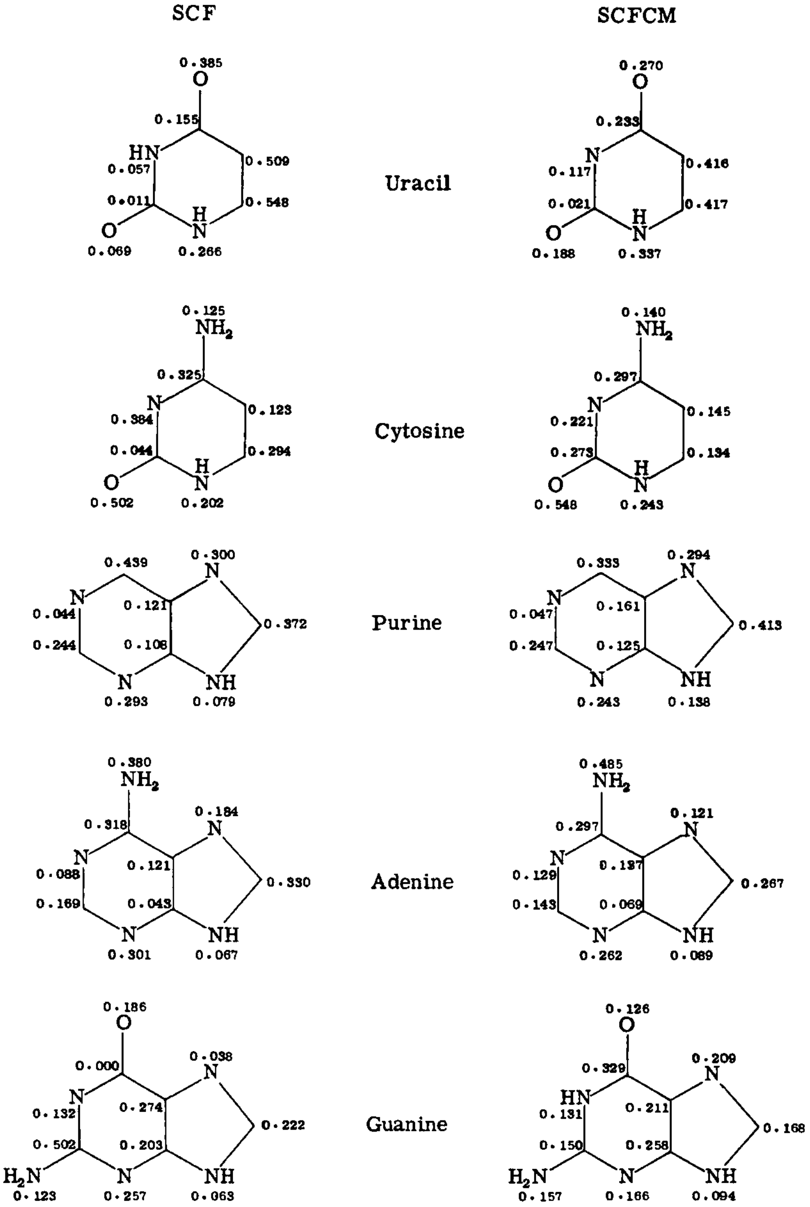


Fig. 7. Spin densities in the first triplet state.

very close to the first one. In such a case it is very difficult to assess the validity of the results until the effect of doubly excited configurations has been considered.

III. Purine-Pyrimidine Interactions

A. The Forces Involved

The essential features of the electronic structure of the purine and pyrimidine bases described, the next important problem that we wish to discuss here concerns the interactions between such bases, in particular those leading to the type of associations which occur in the nucleic acids. These interactions are obviously of two types: *in-plane interactions* related to hydrogen-bonding and *vertical interactions* between stacked bases.

In recent years it has become more and more evident that the most important forces contributing to these interactions are of the van der Waals–London type (De Voe and Tinoco, 1962; B. Pullman, 1965). The possible contributions of resonance energy stabilization through electronic delocalization across the hydrogen bond for the horizontal interactions (B. Pullman and Pullman, 1959) and of the overlapping of their π-electronic cloud (Ladik, 1964) or of charge-transfer complexations (Mantione and Pullman, 1966a), for the vertical interactions appear to be of much smaller order of magnitude than the stabilization increments due to the van der Waals–London forces. For this reason we shall deal here essentially only with this last type of interaction.

The van der Waals–London forces are usually evaluated and have been so initially for the interactions between the nucleic acid bases (De Voe and Tinoco, 1962) in the "dipole" approximation which considers these interactions (E_D) as the sum of three principal contributions:

$$E_D = E_{\mu\mu} + E_{\mu\alpha} + E_L,$$

where $E_{\mu\mu}$ are the dipole-dipole, $E_{\mu\alpha}$ the dipole-induced dipole, and E_L the London or dispersion interaction energies. These are defined respectively as follows:

$$E_{\mu\mu} = \frac{1}{R_{AB}^3}\left[\boldsymbol{\mu}_A\boldsymbol{\mu}_B - \frac{3}{R_{AB}^2}(\boldsymbol{\mu}_A\mathbf{R}_{AB})(\boldsymbol{\mu}_B\mathbf{R}_{AB})\right],$$

$$E_{\mu\alpha} = -\frac{1}{2}\frac{1}{R_{AB}^6}\left\{\alpha_A\left[3\left(\frac{\boldsymbol{\mu}_B\mathbf{R}_{AB}}{R_{AB}}\right) + 1\right] + \alpha_B\left[3\left(\frac{\boldsymbol{\mu}_A\mathbf{R}_{AB}}{R_{AB}}\right) + 1\right]\right\},$$

$$E_L = -\frac{3}{2}\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A\alpha_B}{R_{AB}^6},$$

where $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$ are the respective dipole moments of molecules A and B (with R_{AB} the distance between the points of location of these dipoles), α_A and α_B their polarizabilities, and I_A and I_B their ionization potentials.

It may, however, be observed (Bradley *et al.*, 1964) that because of the shortage of the intermolecular distances with respect to the molecular dimensions, this "dipole" approximation may be rather inaccurate in the particular case of the interactions between the purine and pyrimidine bases and that it may be preferable to treat the problem in the "monopole" approximation, by means of considering all the negative and positive charges in the system as interacting in a simple coulombic fashion. In this "monopole" approximation the total energy (E_M) may then be considered as the sum of three main contributions:

$$E_M = E_{\rho\rho} + E_{\rho\alpha} + E_L,$$

where $E_{\rho\rho}$ are the monopole-monopole, $E_{\rho\alpha}$ the monopole-induced dipole, and E_L the dispersion interaction energies. The first two are defined by:

$$E_{\rho\rho} = \sum_{i\in A} \sum_{j\in B} \frac{\rho_i \rho_j}{R_{ij}},$$

$$\begin{aligned} E_{\rho\alpha} &= -\tfrac{1}{2}[\boldsymbol{\mu}_{A\to B}\mathbf{E}_{A\to B} + \boldsymbol{\mu}_{B\to A}\mathbf{E}_{B\to A}])^2] \\ &= -\tfrac{1}{2}[\alpha_B(\mathbf{E}_{A\to B})^2 + \alpha_A(\mathbf{E}_{B\to A})^2], \end{aligned}$$

since

$$\boldsymbol{\mu}_{A\to B} = \alpha_B \mathbf{E}_{A\to B} \qquad \text{and} \qquad \boldsymbol{\mu}_{B\to A} = \alpha_A \mathbf{E}_{B\to A},$$

with

$$\mathbf{E}_{A\to B} = \sum_{i\in A} \frac{\rho_i}{(R_{iB})^3} \mathbf{R}_{iB} \qquad \text{and} \qquad \mathbf{E}_{B\to A} = \sum_{j\in B} \frac{\rho_j}{(R_{jA})^3} \mathbf{R}_{jA},$$

where index i designates the atoms of molecule A and j those of molecule B, the ρ's are the net charges of the corresponding atoms, $\boldsymbol{\mu}_{A\to B}$ represents the dipole moment induced in B by the distribution of charges in A and $\mathbf{E}_{A\to B}$ the field induced in B by the charges in A at the point of location of the induced dipole. ($\mathbf{R}_{iB}$ designates the vector from atom i in A to this point), etc.

For calculations concerning $E_{\mu\alpha}$, $E_{\rho\alpha}$, and E_L anisotropic polarizabilities may naturally be used instead of the isotropic ones.

The corresponding formulas become then:

$$E_{\mu\alpha} = -\frac{1}{2}\frac{1}{R_{AB}^6}\boldsymbol{\mu}_A(\mathbf{T}\mathbf{A}_B\mathbf{T})\boldsymbol{\mu}_A - \frac{1}{2}\frac{1}{R^6}\boldsymbol{\mu}_B(\mathbf{T}\mathbf{A}_A\mathbf{T})\boldsymbol{\mu}_B,$$

where $\mathbf{A}_A$ and $\mathbf{A}_B$ are the respective polarizability tensors of the molecules represented in a basis $0x$, $0y$, $0z$ by symmetric matrices such as:

$$[\mathbf{A}] = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix},$$

where α_{xy}, for instance, gives the α component of the dipole induced by a unit electric field along the y axis.

$$\alpha\mathbf{1} = \begin{bmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{bmatrix}$$

represents the isotropic polarizability α. $\mathbf{1}$ designs the unit tensor, which is represented by the unit matrix in any basis. $\mathbf{T}$ designates the tensor which appears in the expression of the field $\mathbf{E}$ created by a dipole $\boldsymbol{\mu}$ at a point $\mathbf{R}$:

$$\mathbf{E} = \frac{1}{\mathbf{R}^3}\left[3\frac{\mathbf{R}}{R}\left(\frac{\mathbf{R}}{R}\boldsymbol{\mu}\right) - \boldsymbol{\mu}\right] = \frac{1}{R^3}\left[3\frac{R}{R}\otimes\frac{R}{R} - \mathbf{1}\right]\boldsymbol{\mu},$$

which leads to the definition $\mathbf{T} = 3(\mathbf{R}/R \otimes \mathbf{R}/R) - \mathbf{1}$.

The action of $\mathbf{R}/R \otimes \mathbf{R}/R$ on any vector $\mathbf{V}$ is defined by:

$$\left(\frac{\mathbf{R}}{R}\otimes\frac{\mathbf{R}}{R}\right)\mathbf{V} = \frac{\mathbf{R}}{R}\left(\frac{\mathbf{R}}{R}\mathbf{V}\right),$$

which signifies that $\dfrac{\mathbf{R}}{R}\otimes\dfrac{\mathbf{R}}{R}$ is the projection operator on the axis spanned by the unit vector $\mathbf{R}/R$; in an orthogonal basis $0xyz$, the matrix representing $\mathbf{R}/R \otimes \mathbf{R}/R$ is extremely easy to obtain:

$$\left[\frac{\mathbf{R}}{R}\otimes\frac{\mathbf{R}}{R}\right]_{xy} = \frac{Rx}{R}\frac{Ry}{R}, \quad \text{etc.}$$

That is,

$$\left[\frac{\mathbf{R}}{R}\otimes\frac{\mathbf{R}}{R}\right] = \frac{1}{R^2}\,[\mathbf{R}\otimes\mathbf{R}] = \frac{1}{R^2}\begin{bmatrix} R_x{}^2 & R_xR_y & R_xR_z \\ R_yR_x & R_y{}^2 & R_yR_z \\ R_zR_x & R_zR_y & R_z{}^2 \end{bmatrix},$$

and hence the matrix representing $\mathbf{T}$ can be immediately constructed. Similarly

$$E_{\rho_\alpha} = -\tfrac{1}{2}\mathbf{E}_{A\to B}\mathbf{A}_B\mathbf{E}_{A\to B} - \tfrac{1}{2}\mathbf{E}_{B\to A}\mathbf{A}_A\mathbf{E}_{B\to A}$$

and

$$E_L = -\frac{1}{4}\frac{I_AI_B}{I_A + I_B}\frac{1}{R^6}\,\mathrm{Tr}(\mathbf{T}\mathbf{A}_A\mathbf{T}\mathbf{A}_B),$$

where Tr designates the trace (sum of the diagonal elements). It can be easily verified that the usual formulas are obtained by putting the isotropic polarizability tensors $\mathbf{A}_A = \alpha_A \mathbf{1}$ and $\mathbf{A}_B = \alpha_B \mathbf{1}$ in the general formulas and using (for E_L): $\mathrm{Tr}(\mathbf{R}/R \otimes \mathbf{R}/R) = (R_x^2 + R_y^2 + R_z^2)/R^2 = 1$ and $\mathrm{Tr}\,\mathbf{1} = 3$. (Of course, all the formulas for $E_{\mu\mu}$, $E_{\mu\alpha}$, E_L, $E_{\rho\rho}$, and $E_{\rho\alpha}$ involve a numerical factor, not written here, and depending on the chosen units. In a given system of units there are only two different factors: one for $E_{\mu\mu}$, $E_{\mu\alpha}$, $E_{\rho\rho}$, $E_{\rho\alpha}$ and another for E_L. For instance, if the charges are expressed in electron units, the lengths in angstroms, the polarizabilities in cubic angstroms, the ionization potentials in electron volts and the resulting energies in kilocalories per mole, the constant for $E_{\mu\mu}$, $E_{\mu\alpha}$, $E_{\rho\rho}$, and $E_{\rho\alpha}$ is 331.934, the constant for E_L is 23.055 (conversion of electron volts into kilocalories per mole); if dipole moments are expressed in Debye units ($1e \times 1$ Å $= 4.802962$ D), the constant for $E_{\mu\mu}$ and $E_{\mu\alpha}$ becomes $331.934/(4.80296)^2 = 14.391876$.)

The comparison of the results of the calculations carried out in the two approximations (isotropic or anisotropic polarizabilities), indicates that the differences between them are always very small and will therefore not be considered here.

The situation is different as concerns the comparison of the "dipole" and the "monopole" approximation. In this case quite different absolute values of interaction energies may be obtained (Bradley *et al.*, 1964; B. Pullman *et al.*, 1966) although frequently the order of the *relative* values of such interactions in a series of complexes is the same. In the few cases where a disagreement appears between the two procedures as to the relative strength of two interactions, the predictions based on the "monopole" approximation are, as might have been expected, in better agreement with experimental facts than those based on the "dipole" approximation (B. Pullman *et al.*, 1966). For this reason, only the results obtained in the "monopole" approximation are being presented.

It may be useful to indicate that, for simple reasons of overlapping in time, the practical basis for the evaluation of the electrostatic interactions described in the following section of this review, has not been the SCF calculations described above but Hückel-type calculations specifically calibrated for the good reproduction of experimental dipole moments (Berthod and Pullman, 1965) which, in fact, reproduce them even better than the SCF ones. The results are, however, as far as the π-electronic distribution is concerned, in so good an agreement with the SCF calculation that it may be safely stated that both bases are equivalent. Similarly the values of the ionization potentials utilized have been those deduced from a reference curve, connecting these values with the coefficient of the highest filled molecular orbital in a series of simple reference compounds. It has been shown (Mantione and Pullman, 1966a) that insofar as the nucleic bases are concerned they are in sufficiently satisfactory agreement both with the SCF calculations and with the empirical values deduced from charge transfer spectra to warrant that no serious error may result from their utilization. Finally, the polarizabilities are obtained with the help of the usual additivity rules (Le Fèvre, 1965). With the z axis along the bond, the polarizability tensor for this bond is represented by the matrix

$$\alpha = \begin{bmatrix} \alpha_\perp & 0 & 0 \\ 0 & \alpha_\perp & 0 \\ 0 & 0 & \alpha_\parallel \end{bmatrix},$$

where $\alpha_\perp$ is the polarizability perpendicular to the bond, and $\alpha_\parallel$ is the polarizability parallel to the bond. It is easy then to obtain the new matrix in the coordinate system chosen for the whole molecule; when all bond polarizability tensors are represented by matrices in this coordinate system, the matrix representing in this system the total polarizability tensor is simply the sum of these matrices.

B. In-Plane van der Waals–London Interactions and the Configuration of Hydrogen-Bonded Base-Pairs

Besides its obvious significance for the elucidation of the factors responsible for the stability of the double helix of DNA, an extensive theoretical investigation of the interactions related to hydrogen bonding between the purine and pyrimidine bases was greatly stimulated by a series of experimental findings. In particular, the discovery by Hoogsteen (1959, 1963a,b) that methylated derivatives of adenine and thymine (both carrying the substituent at their glycosidic nitrogen) cocrystallize as a hydrogen-bonded complex whose configuration is, however, different from the Watson–Crick one, observed in the nucleic acids, stimulated a large number of investigations on the cocrystallization of purine and pyrimidine bases. Among the most outstanding results in this field are: (1) the observation that while the derivatives of adenine and thymine cocrystallize in at least two different complexes (Haschemeyer and Sobell, 1963, 1965; Mathews and Rich, 1964a,b; Katz *et al.*, 1965) both different from the Watson–Crick one, the derivatives of guanine and cytosine cocrystallize only following the Watson–Crick pairing scheme (Sobel *et al.*, 1963; Haschemeyer and Sobell, 1965); and (2) the observation that, as yet, cocrystallization of the nucleic acid bases could be obtained only with base pairs showing complementarity in the Watson–Crick sense, no cocrystallization occurring e.g., between guanine and thymine, adenine and cytosine, cytosine and thymine, or guanine and adenine (Haschemeyer and Sobell, 1965).

As a parallel development, the determination of the molecular and crystal structures of a number of biological purine and pyrimidine bases, and more recently (*vide infra*), the discovery that the bases are susceptible to forming hydrogen bonded pairs in nonaqueous solvents (e.g. chloroform dimethylsulfoxide or carbon tetrachloride), and to some extent also, the study of the properties of synthetic polynucleotides and of their interactions, have emphasized the importance of hydrogen bonding and its significance for the overall configuration.

The variety of results obtained in a number of cases raised, among others, the important problem of determining which of the hydrogen-bonded complexes correspond to intrinsic greater stability and which must, on the contrary, be attributed to the influence of environmental factors such as those present in crystals, in solvents, or in the helical structures of polynucleotides.

Because of the difficulty in answering this question experimentally, it seems particularly useful to contribute to its solution by evaluating theoretically the relative stabilities of a series of fundamental configurations of hydrogen-bonded purine and pyrimidine base pairs. As the calculations refer to isolated base-pairs they represent their intrinsic stabilities.

The essential results obtained so far (B. Pullman *et al.*, 1966, 1967b) are summed up in Table X. The main conclusions which may be drawn from their examination are the following:

TABLE X

IN-PLANE VAN DER WAALS–LONDON INTERACTION ENERGIES IN BASE-PAIRS (kcal/mole)

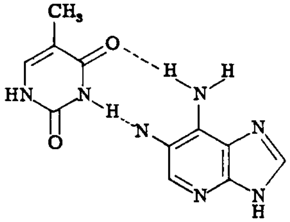
No.	Base-pair	E_{pp}	$E_{p\alpha}$	E_L	E_M
	Adenine-thymine				
I		−4.61	−0.27	−0.77	−5.65

TABLE X—contd.

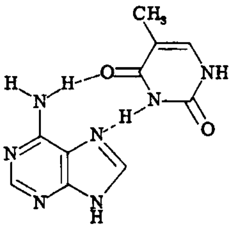
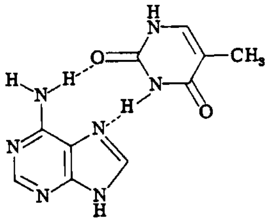
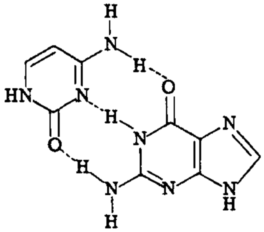
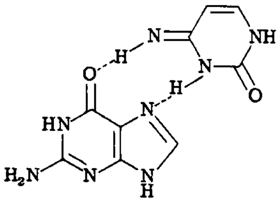
No.	Base-pair	$E_{\rho\rho}$	$E_{\rho\alpha}$	E_L	E_M
II	Adenine-thymine 	−5.85	−0.22	−0.98	−7.05
III	Adenine-thymine 	−5.64	−0.18	−1.03	−6.85
IV	Guanine-cytosine 	−15.91	−2.02	−1.25	−19.18
V	Guanine-cytosine 	−3.98	−1.33	−0.44	−5.75

TABLE X—contd.

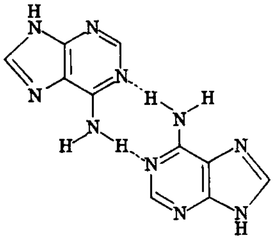
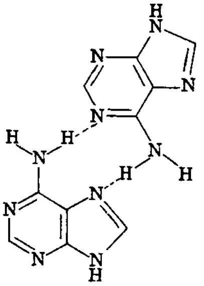
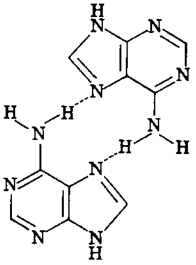
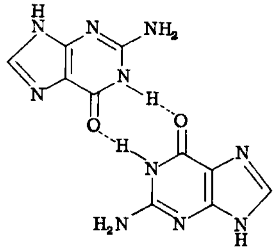
No.	Base-pair	E_{pp}	$E_{p\alpha}$	E_L	E_M
VI	Adenine-adenine 	−5.23	−0.11	−0.45	−5.79
VII	Adenine-adenine 	−4.69	−0.13	−0.54	−5.36
VIII	Adenine-adenine 	−1.20	−0.18	−0.82	−2.20
IX	Guanine-guanine 	−13.37	−0.62	−0.53	−14.52

TABLE X—contd.

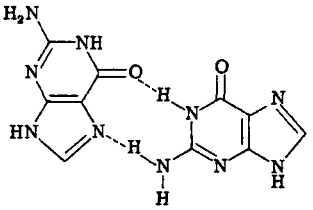
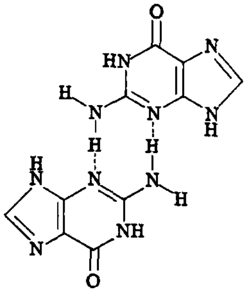
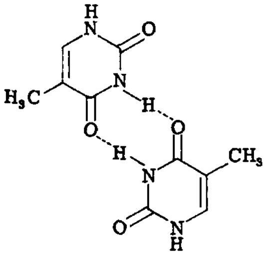
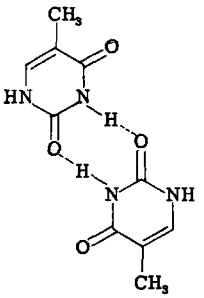
No.	Base-pair	$E_{\rho\rho}$	$E_{\rho\alpha}$	E_L	E_M
X	Guanine-guanine 	−5.50	−0.55	−0.17	−6.22
XI	Guanine-guanine 	−5.79	−0.73	−0.63	−7.15
XII	Thymine-thymine 	−2.80	−0.29	−0.81	−3.90
XIII	Thymine-thymine 	−2.18	−0.13	−1.03	−3.34

TABLE X—contd.

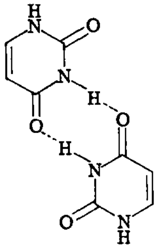
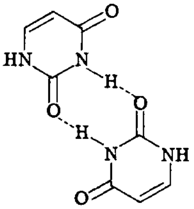
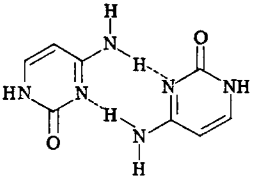
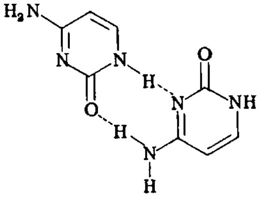
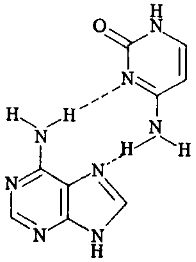
No.	Base-pair	E_{pp}	$E_{p\alpha}$	E_L	E_M
XIV	Uracil-uracil 	−2.86	−0.28	−0.62	−3.76
XV	Uracil-uracil 	−2.11	−0.12	−0.87	−3.10
XVI	Cytosine-cytosine 	−10.65	−1.09	−1.23	−12.97
XVII	Cytosine-cytosine 	−11.23	−1.04	−0.58	−12.85
XVIII	Adenine-cytosine 	−6.20	−0.59	−0.96	−7.75

TABLE X—contd.

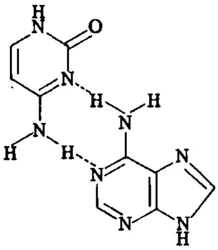
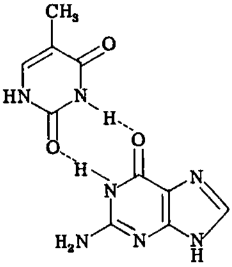
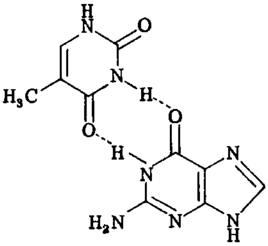
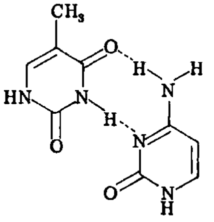
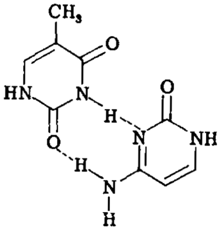
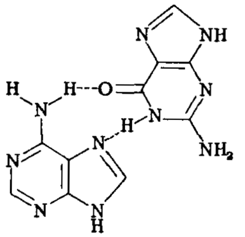
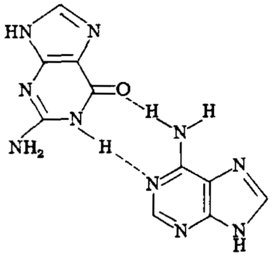
No.	Base-pair	$E_{\rho\rho}$	$E_{\rho\alpha}$	E_L	E_M
XIX	Adenine-cytosine 	−7.89	−0.60	−0.87	−9.36
XX	Guanine-thymine 	−4.41	−0.50	−0.58	−5.49
XXI	Guanine-thymine 	−6.24	−0.58	−0.58	−7.40
XXII	Cytosine-thymine 	−3.80	−1.15	−1.59	−6.54

TABLE X—contd.

No.	Base-pair	E_{pp}	$E_{p\pi}$	E_L	E_M
XXIII	Cytosine-thymine 	−2.85	−1.05	−1.63	−5.53
XXIV	Adenine-guanine 	−4.35	−0.56	−0.62	−5.53
XXV	Adenine-guanine 	−6.44	−0.50	−0.56	−7.50

(1) Among the three configurations considered for the adenine-thymine pairing, I, II, and III, the most stable one *per se* is configuration II corresponding to the structure of the cocrystallization product observed by Hoogsteen (1959, 1963a). It is followed in the order of decreasing stability by configuration III, in which thymine is still linked to N_7 of adenine but in which the hydrogen bonding with the amine group of adenine is through O_2 rather than O_4 of the pyrimidine. This configuration is present in complexes formed between adenine and 5-bromouracil derivatives (Haschemeyer and Sobell, 1963; Katz *et al.*, 1965) and seems also to be found in the structure of the three stranded helix poly(A + 2U) (Miles, 1964). The Watson-Crick arrangement of the bases corresponds to the smallest energy of interaction and is thus probably imposed in the nucleic acids by the

exigencies produced for a regular double-stranded helix with the guanine-cytosine pair.

(2) In the guanine-cytosine pairing, the Watson–Crick arrangement IV is much more stable than the hypothetical arrangement V, never observed yet, in which cytosine would be "on the other side" of guanine. It is also much more stable than any of the adenine-thymine arrangements.

(3) Among the three configurations, VI, VII, and VIII, considered for the autoassociation of adenine, VI and VII are of equal predicted stability. Configuration VII seems to be the one observed in the crystal structure of 9-methyladenine (Stewart and Jensen, 1964) although it was believed not long ago that this structure corresponded to model VI (Stewart and Davidson, 1963). The predominance of VII must be attributed to environmental factors such as the influence of the extended hydrogen bonded network or even, may be, to the role of the methyl group. Configuration VIII corresponds to relatively low stability. This mutual arrangement of adenines is nevertheless observed in the helical form of polyadenylic acid (Rich *et al.*, 1961). It must, however, be realized that the calculations refer to the association of two neutral adenine molecules while in poly A at low pH adenine is protonated at N_1 and, moreover, that the experimental results refer to a solution and to a polymer. It may nevertheless be reasonably concluded that this state of affairs confirms the view following which the stability of the double helix of polyadenylic acid at acid pH is due to a large extent to the electrostatic interactions between the extra positive charges on the bases and the negative charges of the phosphate groups.

(4) Three configurations have been considered for the guanine-guanine autoassociation: configuration IX suggested to occur in polyguanylic acid (Pochon and Michelson, 1965), configuration X suggested to be involved in gels of guanylic acid (Gellert *et al.*, 1962), and the curious configuration XI, observed in the crystal structure of guanine hydrochloride dihydrate (Iball and Wilson, 1963). Of these three structures IX is much more stable, in fact very stable on an absolute scale, a situation perhaps not without significance, in the limits of the obvious restrictions, for the relatively great stability of polyguanylic acid (Pochon and Michelson, 1965). The existence of structure XI in the crystal of guanine hydrochloride dihydrate must therefore be attributed to strong particular environmental effects.

(5) Two possible configurations, XII and XIII, have been considered in connection with the crystal structure of 1-methylthymine (Hoogsteen, 1963b). Of these two structures XII, which is actually observed, is, theoretically, the most stable one.

(6) Similarly of the two configurations XIV and XV considered for the hydrogen bonded dimers of uracil, it is the configuration XIV, the more

stable which is observed in the crystal structure of N_1-methyl-uracil (Green *et al.*, 1962).

(7) Two configurations have also been considered for the autoassociation of cytosine: configuration XVI observed in the crystal of N-methyl cytosine (Mathews and Rich, 1964a) (the structure being, however, somewhat unusual, the two bases not lying in the same plane), and configuration XVII observed in the crystal of cytosine (Barker and Marsh, 1964). The outstanding feature of these two configurations is the high value of the predicted stabilities.

(8) The next eight configurations studied, XVIII–XXV, correspond to hypothetical associations between bases noncomplemetary in the Watson–Crick sense. The first four of them, XVIII–XXI, concern a purine-pyrimidine interaction, the next four, XXII–XXV, pyrimidine or purine autoassociations. It is obvious that hydrogen bonds can, in principle, be established in all these configurations. The most plausible associations have been considered explicitly and it can be seen that they involve, in principle, considerable stabilization energies. As mentioned, however, already these associations have not as yet been observed and, in particular, could not be produced in cocrystallization reactions. Neither do they seem to be formed in solution. Explicit statement of this state of affairs has at least been made by Shoup *et al.* (1966) as regards the absence of interaction between G and T, C and T, and A and G in dimethyl-sulfoxide. As a possible explanation for this failure, we would like to suggest the difference which appears between the two classes of base pairs, the complementary and the noncomplementary ones, when the interaction energies of the cross-associations are compared with those of the auto-associations of the constituent bases. Thus, it may be observed (Table XI) that the stabilization of the adenine-thymine association, although relatively moderate is nevertheless greater than that of the adenine-adenine or thymine-thymine auto-associations. Similarly, although the stabilization of the guanine and cytosine auto-associations is relatively very strong, that of the guanine-cytosine association is still stronger. On the contrary, all the remaining cross-associations appear always weaker than the autoassociations of one of their constituent, which following the case, is guanine or cytosine. Table XII indicates that the same result prevails when the values of the cross-associations are compared with the mean values of the corresponding two auto-associations instead of being compared with the values of the one strongest autoassociation. This general situation points to the conclusion that it is the strength of the guanine-guanine and cytosine-cytosine auto-interactions which may possibly be responsible for preventing the associations of the noncomplementary bases.

TABLE XI

IN-PLANE INTERACTION ENERGIES FOR HYDROGEN-BONDED PAIRS (kcal/mole)

A—A	−5.8	A—T	−7.0
T—T	−5.2		
G—G	−14.5	G—C	−19.2
C—C	−13		
A—A	−5.8	A—C	−7.8
C—C	−13		
G—G	−14.5	G—T	−7.4
T—T	−5.2		
C—C	−13	C—T	−6.5
T—T	−5.2		
A—A	−5.8	A—G	−7.5
G—G	−14.5		

A—T	>	A—A T—T
G—C	>	G—G C—C
A—C	<	C—C
G—T	<	G—G
C—T	<	C—C
A—G	<	G—G

TABLE XII

INTERACTION ENERGIES IN HYDROGEN-BONDED PAIRS (kcal/mole)

	Mean value			
A—A T—T	−5.5	<	A—T	−7.0
G—G C—C	−13.8	<	G—C	−19.2
A—A C—C	−9.4	>	A—C	−7.8
G—G T—T	−9.9	>	G—T	−7.4
C—C T—T	−9.1	>	C—T	−6.5
A—A G—G	−10.2	>	A—G	−7.5

At this point it may be useful to indicate that very recent results from a number of laboratories on the interaction of free bases or of their nucleosides in nonaqueous solvents, in which hydrogen-bonded pairs are formed, confirm the essential theoretical predictions.

Thus Katz and Penman (1966), Shoup *et al.* (1966), and Pitha *et al.* (1966) all confirm that associations by hydrogen bonding between guanine and cytosine are stronger that those between adenine and thymine or adenine and uracil; Hamlin *et al.* (1965) and Küchler and Derkosch (1966) confirm that the H-bonding interactions between adenine and uracil are stronger than the self-associations of two adenines or two uracils, and Katz and Penman (1966) also confirm that the H-bonding interactions between guanine and cytosine are stronger than the self-associations of two guanines or two cytosines. It may also be interesting to add that the difference predicted by our calculations for the interaction energies between G—C and G—T is of the same order of magnitude, $\sim$14 kcal/mole, as that evaluated in a different way by Simon (1965).

All these experimental results seem thus to indicate that insofar as our present available knowledge goes, the calculations on the van der Waals–London interactions for the in-plane hydrogen bonded base-pairs, although carried out for interactions in vacuum, seem to be valid also, at least insofar as the relative strengths of the interactions in a given solvent are concerned, for base-pairs formed in solution. In no way does this mean that we consider the solvent effects to be negligible. As illustrated in particular in our work as the van der Waals–London interaction energies between free bases in solution (Claverie *et al.*, 1967), these last effects are very important. Neither do we wish to presume that such should always be the case. The conclusion just summarizes the present state of affairs.

This type of work has recently been extended, both experimentally and theoretically to the investigation of the H-bonding interactions between base analogs. Such an extension offers broad possibilities for the verification of the theory. Among the essential experimental results deduced from studies on free bases or nucleosides are the following ones (the signs $\lessgtr$ indicating the relative strength of the interactions):

Hypoxanthine-cytosine $<$ guanine-cytosine (Pitha *et al.*, 1966)

Guanine-6-azacytosine $<$ (slightly) guanine-cytosine (Pitha *et al.*, 1966).

Adenine-thymine $<$ 2, 6-diaminopurine-thymine $\ll$ guanine-cytosine (Shoup *et al.*, 1966).

As can be seen from Table XIII the results of the theoretical calculations are in complete agreement with these findings.

TABLE XIII

IN-PLANE INTERACTION ENERGIES (kcal/mole)

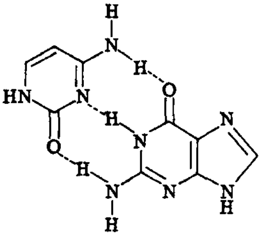
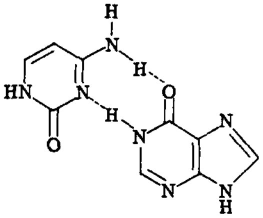
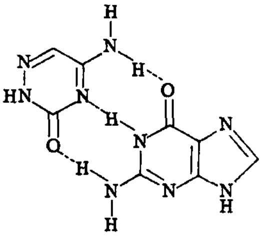
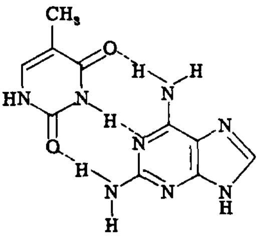
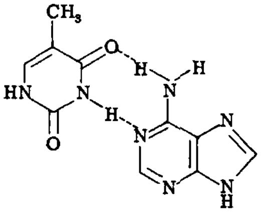
Base-pair	$E_{\rho\rho}$	$E_{\rho\alpha}$	E_L	E_M
Guanine-cytosine 	−15.91	−2.02	−1.25	−19.18
Hypoxanthine-cytosine 	−12.28	−1.24	−0.72	−14.24
Guanine-6-azacytosine 	−14.73	−1.88	−1.25	−17.86
2,6-diaminopurine-thymine 	−4.6	−0.2	−0.7	−5.5

TABLE XIII—cont.

Base-pair	E_{pp}	$E_{p\alpha}$	E_L	E_M
2,6-diaminopurine-thymine 	−6.51	−0.20	−1.18	−7.89

Sometimes conclusions are being tentatively drawn also about the probable strength of the in-plane interaction in H-bonded pairs from the study of the secondary structure of polyribonucleotides or from the study of the interactions between polyribonucleotides. In these cases the conclusions are, however, more subject to caution because of the role of the *vertical* interactions between the stacked bases. Before trying to evaluate the possible *respective role* of these two types of interactions, we have to consider in more detail the information and the calculations available for the vertical interactions.

C. Vertical Interactions between Stacked Bases

In view of the presently available evidence, these types of interactions are particularly interesting in connection with three problems: in the first place in connection, of course, with their fundamental importance for the understanding of the stability of the helical structure of DNA (De Voe and Tinoco, 1962), in the second place, with two more recent types of studies. One concerns the existence of oligo- and poly-nucleotides (e.g., poly A and poly C at neutral *pH*) and still more of *s*-RNA in single stranded helical forms which are believed to be stabilized to a large extent by base stacking (Warshaw and Tinoco, 1965; Cantor and Tinoco, 1965; Van Holde *et al.*, 1965; Brahms *et al.*, 1966; Michelson *et al.*, 1966; Poland *et al.*, 1966; Fasman *et al.*, 1965). The second concerns the establishment of stacking type interactions in *aqueous* solutions of free bases or their nucleosides (Ts'o *et al.*, 1962, 1963, 1964; Ts'o and Lu, 1964; Ts'o and Chan, 1964; Ts'o, 1964; Schweizer *et al.*, 1965; Jardetzky, 1964) or between purines and oligo- or polynucleosides (Chan *et al.*, 1966; Huang and Ts'o, 1966; Howard *et al.*, 1966).

As, in this review, we are essentially interested in the factors contributing to the stability of the structure of the nucleic acids, we shall not discuss here the results concerning the stacking of free bases in aqueous solution. The detailed discussion of this problem, including the role of the solvent, has been given by Claverie *et al.* (1967). We shall limit ourselves to the problem of the stacking of the bases in single stranded di- and polyribonucleotides. Finally, the next and last section will deal with the DNA double helix itself.

A partially helical single-stranded structure involving the stacking of the bases was proposed for poly C (Fasman *et al.*, 1964) and poly A (Witz and Luzzati, 1965; Michelson *et al.*, 1966) both in solution at neutral *pH* and for *s*-RNA itself (Fasman *et al.*, 1965). The structure of poly U seems to be more disputed: following Szer (1966) it exists as a random coil at room temperature but exhibits a certain degree of ordered state at 0°; following Witz and Luzzati (1965), its structure seems analogous to poly A although more flexible. Following a recent electro-optical study by Jakabhazy and Fleming (1966), the degree of order in the structure of poly U, even at low temperature and low *pH*, is at best an order of magnitude smaller than that of poly A under similar conditions. Poly G may possibly exist as a double stranded helix (Pochon and Michelson, 1965).

On the other hand, Warshaw and Tinoco (1965) studied the base stacking in homo- and hetero-dinucleoside phosphates containing A, G, C, and U) and found the interesting result that dinucleosides containing U exhibited no stacking, while all the others were stacked. Trinucleoside phosphates were also studied by Cantor and Tinoco (1965) with similar results.

More precise data about the energies involved in the stacking of the bases are available only for the interaction of adenine moieties. Thus a single stranded helical structure involving the stacking of the bases was also proposed by Van Holde *et al.* (1965) for poly N^6-hydroxyethyladenylic acid and diadenylic acid, which cannot form hydrogen bonds. The authors evaluated $\Delta H \simeq -8$ kcal/mole and $\Delta S \simeq -28$ e.u./mole for the transition A*p*A unstacked → A*p*A stacked. Further investigations concerning adenylic acid oligomers and poly A (Brahms *et al.*, 1966) lead to a model of a non-cooperative interaction between the bases, the thermodynamic characteristics being almost the same as for diadenylic acid; the corresponding ΔF is small (at most 1 kcal/mole between 0°C and 25°C). An analogous study of poly A by Leng and Felsenfeld (1966) leads to the same qualitative conclusions; the enthalpy change obtained by these authors from variation of hypochromism with temperature is higher (about -10 kcal/mole), but they also report the result of calorimetric measurements which gave a smaller value (about -6.8 kcal/mole). A study by Applequist and Damle

(1966) indicates the value -9.4 ± 2 kcal/mole. Poland *et al.* (1966) made a statistical analysis of the stacking process involving the possibility of cooperativity and fitting the parameters to the experimental data, found that the real process was almost completely noncooperative with $\Delta H = -6.5$ kcal/mole and $\Delta S = -21.4$ e.u./mole.

Theoretical calculations of the van der Waals–London interaction energies between stacked bases have been carried out by Claverie *et al.* (1967) and assumed to represent the corresponding ΔH in vacuum. The essential calculations refer to the four dinucleotides A*p*A, U*p*U, C*p*C, G*p*G, assuming: (1) the geometry of the DNA helix with an interplane distance of 3.4 Å, and (2) the same arrangement followed, however, in the case of C*p*C and U*p*U by a rotation of 180° around the glycosidic bond of the upper base (turning-over). Indeed, according to molecular models (Poland *et al.*, 1966) such rotations are quite possible in single strands, especially for pyrimidine bases, since the glycosidic bond coincides with a symmetry axis of the benzene ring, so that there is no particular steric hindrance involved. Such a rotation would be less easy for the purine bases included in a strand, the freedom for a rotation being naturally greater in a dinucleotide.

The results of the calculations are reported in Table XIV. It is apparent that agreement with the experimental distinction between A, G, and C which stack and U, which does not or stacks less, can only be obtained on the assumption that one of the cytosines is "turned over" around the glycosidic linkage. Without such a "turning over" the oligo- or polynucleotides of cytosine should not exhibit a tendency to stack. It may be observed that, in difference to cytosine, the "turning over" of an

TABLE XIV

INTERACTION ENERGIES IN SINGLE-STRANDED HOMODINUCLEOTIDES (kcal/mole)

Interacting bases		E_{pp}	$E_{p\alpha}$	E_L	E_M
A—A		+0.67	−0.44	−9.72	−9.49
G—G		+5.12	−1.35	−10.96	−7.19
C—C		+6.69	−1.78	−4.67	+0.24
U—U		+0.49	−0.42	−3.39	−3.32
T—T		+0.55	−0.48	−4.54	−4.51
C—C	after turning one base 180° around the glycosidic bond	−3.49	−0.91	−2.87	−7.27
U—U		+1.60	−0.57	−1.79	−0.76
T—T		+1.06	−0.52	−2.68	−2.14

uracil diminishes the tendency of stacking in the polymers of this base.

Changes in the relative disposition may also be considered for the purine bases. It is easily shown that they would not noticeably modify the interaction energy for a strand of adenines, owing to the smallness of E_{pp}; they could lead to a supplementary stabilization for guanine, but which would not be as large as if the two interacting guanines were free, because the presence of the phosphate chain does not allow them to orient their dipoles in an anti-parallel position at a sufficiently short distance.

It may also be observed that the stacking energy calculated for the interaction of two adenines is quite of the order of magnitude of the measured enthalpy.

It seems interesting to consider to what an extent residual interactions are being preserved in the random coils of the polyribonucleotides. The answer to this query is given in Table XV, in which the calculations refer to a "random dinucleotide," with an extended chain stretching the distance between the two bases to 7.3 Å; the results quoted represent the strongest interactions for such configurations which involve a rotation of the bases in their planes around the phosphate chains. The rotation angle is 180° for the dinucleotides of A, C, and U and 135° or 225° for the dinucleotide of G.

TABLE XV

INTERACTION ENERGIES IN "RANDOM COIL" DINUCLEOTIDES (kcal/mole)

Dinucleotide	E_{pp}	$E_{p\alpha}$	E_L	E_M
A—A	−0.23	−0.01	−0.07	−0.31
G—G	−0.46	−0.02	−0.05	−0.53
C—C	−1.30	−0.03	−0.05	−1.38
U—U	−0.20	−0.01	−0.05	−0.26

D. Interaction of the Base Pairs in the DNA Helix

Finally, we reproduce numerical results in Table XVI on the interactions between the nearest neighbour base pairs of the DNA helix, These have been studied originally by De Voe and Tinoco (1962) in the "dipole" approximation. They are revaluated here in the "monopole" approximation. The notations are those utilized by De Voe and Tinoco, the arrows which designate the direction of the chain pointing from the 3′ carbon on one sugar to the 5′ carbon on the adjacent sugar: e.g., $\overrightarrow{\mathrm{TA}}$ represents

T-sugar-3′-phosphate-5′-sugar-A. Table XVI needs some important precisions. It is the first four columns of numbers which relate the calculations concerned specifically with the stacking, vertical interactions. Column four indicates the values of the total stacking energy. Although this energy is particularly high for some couples of neighbor G—C pairs and particularly low for some couples of neighbour A—T pairs, it is nevertheless not possible to relate its value in a regular way to say the G—C content of the helix. It is, however, evident that the total interaction energy between near-neighbor base-pairs must involve also the in-plane horizontal interaction energies between the hydrogen bonded bases. When the average contribution of the in plane interactions (deduced from the values listed in Table X for the Watson–Crick pairing of guanine-cytosine (−19.2 kcal/mole) and

TABLE XVI

NEAREST-NEIGHBOUR BASE-PAIR INTERACTIONS IN THE DNA HELIX IN A VACUUM (kcal/2 MOLES OF BASE)

Adjacent base-pairs	Vertical interactions			Total stacking energy	Average contribution of the in-plane interactions	Total interaction energy
	E_{pp}	$E_{p\alpha}$	E_L			
↑ C—G G—C ↓	+0.9	−2.0	−10.2	−11.3	−19.2	−30.5
↑ G—C C—G ↓	−1.6	−2.5	−4.0	−8.5	−19.2	−27.7
↑ G—C G—C ↓	+2.6	−2.0	−8.3	−7.7	−19.2	−26.9
↑ A T G—C ↓	+1.2	−0.8	−10.3	−9.9	−12.2	−22.1
↑ A—T C—G ↓	−0.6	−1.7	−4.9	−7.2	−12.2	−19.4
↑ T—A C—G ↓	−0.1	−1.7	−5.2	−7.0	−12.2	−19.2
↑ T—A G—C ↓	+1.8	−1.0	−7.8	−7.0	−12.2	−19.2
↑ A—T A—T ↓	+0.5	−0.5	−7.4	−7.4	−5.5	−12.9
↑ A—T T—A ↓	+0.4	−0.3	−6.2	−6.1	−5.5	−11.6
↑ T—A A—T ↓	+1.5	−0.7	−5.8	−5.0	−5.5	−10.5

adenine-thymine (−5.5 kcal/mole)) are being added to the vertical interactions, one obtains the last column which indicates then the *total* interaction energy for each group of adjacent base pairs.

It is now evident from these last results that the different combinations of the base-pairs may be clearly divided into three groups. The most stable combinations are those formed of the G—C pairs only. Next in order of decreasing stabilities come the mixed combinations made out of an A—T and a G—C pair. Finally, the less stable combinations are those containing only A—T pairs.

It must be emphasized that this result, evidently consistent with the well-established greater thermal stability of nucleic acid rich in guanine-cytosine over those rich in adenine-thymine (Marmur and Doty, 1959), appears only upon *the summation of the stacking and the in-plane interaction energies* and is due to the fact that the electrostatic interactions *in* the G—C pair are much greater (by 13.9) kcal) than those *in* the A—T pair. It may be recalled that the "dipole" approximation (De Voe and Tinoco, 1962) does not lead to such a clearcut result and predicts, e.g., a relatively low total energy of interaction for the combination $\left|\uparrow\begin{matrix}\text{G—C}\\ \text{C—G}\end{matrix}\downarrow\right|$. This apparent "anomaly" is due to the fact that the difference in the values of the in-plane interactions in the G—C and the A—T pair is much smaller in the dipole approximation (=4.1 kcal/mole) than in the monopole approximation.

E. Horizontal versus Vertical Interaction Energies

The last results of the preceding section enable us to bring a tentative answer to the long debated question of whether it is the horizontal, in-plane interactions between the hydrogen bonded bases or the vertical interactions between the stacked bases which are responsible for the overall stability of the doubly-helical structure of DNA. The calculations indicate that the two types of interaction are apparently of a comparable order of magnitude and contribute therefore nearly equivalently to the overall stability. It may be observed that while the electrostatic $E_{\rho\rho}$ term makes the predominant contribution to the in-plane interactions it is the dispersion E_L term which contributes mostly to the stacking type interactions.

Although we did not discuss here in any detail the contribution of the solvent effect to this stability, and although information about this last effect seems much less quantitative than that concerning the van der Waals–London interactions, they nevertheless indicate (Kestner and Sinanoğlu, 1963; Sinanoğlu and Abdulnur, 1964, 1965; Claverie *et al.*, 1967) that the contribution of the solvation effects are certainly far from negligible and possibly of the same order of magnitude as those of the horizontal or vertical interactions. The overall stability may then be the resultant of three nearly equal contributions.

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REFERENCES

APPLEQUIST, J., and DAMLE, V. (1966). *J. Am. Chem. Soc.* **88**, 3895.

BARKER, D. L., and MARSH, R. E. (1964). *Acta Cryst.* **17**, 1497.

BAUDET, J., BERTHIER, G., and PULLMAN, B. (1962). *Compt. Rend.* **254**, 762.

BEAVEN, G. H., HOLIDAY, E. R., and JOHNSON, E. A. (1955). *In* "The Nucleic Acids" (E. Chargaff and J. N. Davidson, eds.), Vol. 1. p. 493. Academic Press, New York.

BERGMANN, F., and DIKSTEIN, S. (1955). *J. Am. Chem. Soc.* **77**, 691.

BERSOHN, R., and ISENBERG, I. (1964). *J. Chem. Phys.* **40**, 3175.

BERTHIER, G., MILLIÉ, P., and VEILLARD, A. (1965). *J. Chim. Phys.* **62**, 8.

BERTHOD, H., and PULLMAN, A. (1965). *J. Chim. Phys.* **62**, 942.

BERTHOD, H., and PULLMAN, A. (1966). *Compt. Rend.* **262**, 76.

BERTHOD, H., GIESSNER-PRETTRE, C., and PULLMAN, A. (1966a). *Theoret. Chim. Acta* **5**, 53.

BERTHOD, H., GEISSNER-PRETTRE, C., and PULLMAN, A. (1966b). *Compt. Rend.* **262**, 2657.

BERTHOD, H., GIESSNER-PRETTRE, C., and PULLMAN, A. (1967). *Intern. J. Quantum Chem.* **1**, 123.

BRADLEY, D. F., LIFSON, S., and HONIG, B. (1964). *Electron. Aspects Biochem., Proc. Intern. Symp. Ravello, Italy, 1963* p. 77. Academic Press, New York.

BRAHMS, J., MICHELSON, A. M., and VAN HOLDE, K. E. (1966). *J. Mol. Biol.* **15**, 467.

BRIEGLEB, G. (1964). *Angew. Chem. Intern. Ed. Engl.* **3**, 617.

CALLIS, P. R., ROSA, E. J., and SIMPSON, W. T. (1964). *J. Am. Chem. Soc.* **86**, 2292.

CANTOR, C. R., and TINOCO, I., JR. (1965). *J. Mol. Biol.* **13**, 65.

CAVALIERI, L. F., FOX, J. J., STONE, A., and CHANG, N. (1954). *J. Am. Chem. Soc.* **76**, 1119.

CHAN, S. I., SCHWEIZER, M. P., TS'O, P. O. P., and HELMKAMP, G. K. (1964). *J. Am. Chem. Soc.* **86**, 4182.

CHAN, S. I., BANGESTER, B. W., and PETER, H. H. (1966). *Proc. Natl. Acad. Sci. U.S.* **55**, 720.

CLARK, L. B., and TINOCO, I., JR. (1965). *J. Am. Chem. Soc.* **87**, 11.

CLARK, L. B., PESCHEL, G. G., and TINOCO, I., JR. (1965). *J. Phys. Chem.* **69**, 3615.

CLAVERIE, P., PULLMAN, B., and CAILLET, J. (1967). *J. Theoret. Biol.* **12**, 419.

COHEN, B. J., and GOODMAN, L (1965) *J. Am. Chem. Soc.* **87**, 5487.

DEL RE, G. (1958). *J. Chem. Soc.* p. 4031.

DEL RE, G., and PARR, R. G. (1963). *Phys. Rev.* **35**, 604.

De Voe, H., and Tinoco, I., Jr. (1962). *J. Mol. Biol.* **4**, 500.
Douzou, P., Francq, J., Hauss, M., and Ptak, M. (1961). *J. Chim. Phys.* **58**, 926.
Drobnik, J., and Augenstein, L. (1966a). *Photochem. Photobiol.* **5**, 13.
Drobnik, J., and Augenstein, L. (1966b). *Photochem. Photobiol.* **5**, 83.
Elving, P. J., Struck, W. A., and Smith, D. L. (1965). *Mises Point Chim. Anal. Org. Pharm. Bromatol.* **14**, 145.
Fernandez-Alonso, J. I. (1964). *In* "The Structure and Properties of Biomolecules and Biological Systems" (J. Duchesne, ed.), p. 3. Wiley (Interscience), New York.
Fasman, G. D., Lindblow, C., and Grossman, L. (1964). *Biochemistry* **3**, 1015.
Fasman, G. D., Lindblow, C., and Seaman, E. (1965) *J. Mol. Biol.* **12**, 630.
Gellert, M., Lipsett, M. N., and Davies, D. R. (1962). *Proc. Natl. Acad. Sci. U.S.* **48**, 2013.
Gersch, N. T., and Jordan, D. O. (1965). *J. Mol. Biol.* **13**, 138.
Giessner-Prettre, C., and Pullman, B. (1965). *Compt. Rend.* **261**, 2521.
Green, D. W., Mathews, F. S., and Rich, A. (1962). *J. Biol. Chem.* **237**, 3573.
Hamlin, R. M., Jr., Lord, R. C., and Rich, A. (1965). *Science* **148**, 1734.
Haschemeyer, A. E. V., and Sobell, H. M. (1963). *Proc. Natl. Acad. Sci. U.S.* **50**, 872.
Haschemeyer, A. E. V., and Sobell, H. M. (1964). *Nature* **202**, 969.
Haschemeyer, A. E. V., and Sobell, H. M. (1965). *Acta. Cryst.* **18**, 525.
Hélène, C. (1966). Thesis, Paris.
Hélène, C., Douzou, P., and Michelson, A. M. (1965). *Biochim. Biophys. Acta* **109**, 261.
Hélène, C., Douzou, P., and Michelson, A. M. (1966). *Proc. Natl. Acad. Sci. U.S.* **55**, 376.
Hinze, J., and Jaffé, H. H. (1962). *J. Am. Chem. Soc.* **84**, 540.
Hoogsteen, K. (1959). *Acta Cryst.* **12**, 822.
Hoogsteen, K. (1963a). *Acta Cryst.* **16**, 907.
Hoogsteen, K. (1963b). *Acta Cryst.* **16**, 28.
Howard, F. B., Frazier, J., Singer, M. F., and Miles, H. T. (1966). *J. Mol. Biol.* **15**, 415.
Huang, W. M., and Ts'o, P. O. P. (1966). *J. Mol. Biol.* **16**, 523.
Iball, J., and Wilson, H. R. (1963). *Nature* **198**, 1193.
Jakabhazy, S. Z., and Fleming, S. W. (1966). *Biopolymers* **4**, 793.
Jardetzky, O. (1964). *Biopolymers Symp.* **1**, 501.
Julg, A. (1958). *J. Chim. Phys.* **55**, 413.
Katz, Z., and Penman, S. (1966). *J. Mol. Biol.* **15**, 220.
Katz, L., Tomita, K., and Rich, A. (1965). *J. Mol. Biol.* **13**, 340.
Kestner, N. R., and Sinanoğlu, O. (1963). *J. Chem. Phys.* **38**, 1730.
Kon, H. (1955). *Bull. Chem. Soc. Japan* **28**, 275.
Kotelnikova, A. V., and Solomatina, V. V. (1966). *Biochemistry USSR* (*English Transl.*) **30**, 700; see *Biokhimiya* **30**, 816 (1900).
Küchler, E., and Derkosch, J. (1966). *Z. Naturforsch.* **21B**, 209.
Kwiatkowski, S. (1966). *Acta Phys. Polon.* **29**, 573.
Ladik, J. (1964). *Electron. Aspects Biochem. Proc. Intern. Symp. Ravello, Italy, 1963* p. 203. Academic Press, New York.
Ladik, J., and Appel, K. (1966). *Theoret. Chim. Acta* **4**, 132.
Lawley, P. D., and Brookes, P. (1963). *Biochem. J.* **89**, 127.
Le Fèvre, R. J. W. (1965). *Advan. Phys. Org. Chem.* **3**, 1.
Leng, M., and Felsenfeld, G. (1966). *J. Mol. Biol.* **15**, 455.
Longworth, J. W. (1962). *Biochem. J.* **84**, 104.

LONGWORTH, J. W., RAHN, R. O., and SHULMAN, R. G. (1966). *J. Chem. Phys.* **45**, 2930.

LÖWDIN, P.-O. (1950). *J. Chem. Phys.* **18**, 365.

LÖWDIN, P.-O. (1964). *Electron. Aspects Biochem., Proc. Intern. Symp. Ravello, Italy, 1963* p. 167. Academic Press, New York.

LÖWDIN, P.-O. (1965). *Advan. Quantum Chem.* **2**, 213.

LYKOS, P. G. (1961). *J. Chem. Phys.* **35**, 1249.

MCCLURE, D. (1949). *J. Chem. Phys.* **17**, 905.

MCWEENY, R. (1955). *Proc. Roy. Soc.* **A227**, 288.

MACHMER, P., and DUCHESNE, J. (1965). *Nature* **206**, 618.

MANTIONE, M. J., and PULLMAN, B. (1966a). *Biochim. Biophys. Acta* **91**, 387.

MANTIONE, M. J., and PULLMAN, B. (1966b). *Compt. Rend.* **262**, 1492.

MARMUR, J., and DOTY, P. (1959). *Nature* **183**, 1427.

MASON, S. F. (1954). *J. Chem. Soc.* p. 2071.

MATHEWS, F. S., and RICH, A. (1964a). *Nature* **201**, 179.

MATHEWS, F. S., and RICH, A. (1964b). *J. Mol. Biol.* **8**, 89.

MICHELSON, A. M., ULBRICHT, T. L. V., EMERSON, R. T., and SWAN, R. J. (1966). *Nature* **209**, 873.

MILES, H. T. (1964). *Proc. Natl. Acad. Sci. U.S.* **51**, 1104.

NAGATA, C., IMAMURA, A., TAGASHIRA, Y., and KODAMA, M. (1965). *Bull. Chem. Soc. Japan* **38**, 1638.

NAKAJIMA, T., and PULLMAN, A. (1958a). *J. Chim. Phys.* **55**, 793.

NAKAJIMA, T., and PULMAN, B. (1958b). *Bull. Soc. Chim. France* p. 1502.

NAKAJIMA, T., and PULLMAN, B. (1959). *Bull. Soc. Chim. France* p. 663.

NASH, H. A., and BRADLEY, D. F. (1965). *Biopolymers* **3**, 261.

NESBET, R. K. (1964). *Biopolymers Symp.* **1**, 129.

PARISER, R. (1953). *J. Chem. Phys.* **21**, 568.

PARISER, R. (1956). *J. Chem. Phys.* **24**, 250.

PARISER, R., and PARR, R. G. (1953). *J. Chem. Phys.* **21**, 767.

PARR, R. G. (1963). "Quantum Theory of Molecular Electronic Structure." Benjamin, New York.

PITHA, J., NORMAN JONES, R., and PITHOVA, P. (1966). *Can. J. Chem.* **44**, 1045.

POCHON, F., and MICHELSON, A. M. (1965). *Proc. Natl. Acad. Sci. U.S.* **53**, 1425.

POLAND, D. C., VOURNAKIS, J. N., and SCHERAGA, H. A. (1966). *Biopolymers* **4**, 223.

POPLE, J. A. (1953). *Trans. Faraday Soc.* **49**, 1375.

PULLMAN, A. (1963). *Compt. Rend.* **256**, 5435.

PULLMAN, A. (1964a). *Electron Aspects Biochem., Proc. Intern. Symp. Ravello, Italy, 1963* p. 135. Academic Press, New York.

PULLMAN, A. (1964b), *J. Chim. Phys.* **62**, 1666.

PULLMAN, A. (1964c). *Biochim. Biophys. Acta* **87**, 365.

PULLMAN, A. (1965a). *In* "Moden Quantum Chemistry" (O. Sinanoğlu, ed.), Vol. III, p. 283. Academic Press, New York.

PULLMAN, A. (1965b). *In* "Molecular Biophysics" (B. Pullman and M. Weissbluth, eds.), p. 81. Academic Press, New York.

PULLMAN, A., and PULLMAN, B. (1958a). *Bull. Soc. Chim. France* p. 766.

PULLMAN, A., and PULLMAN, B. (1958b). *Compt. Rend.* **246**, 611.

PULLMAN, A., and PULLMAN, B. (1959). *Bull. Soc. Chim. France* p. 594.

PULLMAN, A., and PULLMAN, B. (1967). *In* "Quantum Theory of Atoms, Molecules, and the Solid State" (P.-O. Löwdin, ed.). p. 345, Academic Press, New York.

PULLMAN, A., and ROSSI, M. (1964). *Biochim. Biophys. Acta* **88**, 211.

PULLMAN, A., PULLMAN, B., and BERTHIER, G. (1956). *Compt. Rend.* **243**, 380.
PULLMAN, B. (1964). *J. Cellular Comp. Physiol.* **64**, Suppl. 1, 91.
PULLMAN, B. (1965). *In* "Molecular Biophysics" (B. Pullman and M. Weissbluth, eds.), p. 117. Academic Press, New York.
PULLMAN, B., and DUPUY, N. (1966). *Compt. Rend.* **262**, 2773.
PULLMAN, B., and DUPUY, N. (1967). *Theoret. Chim. Acta* (in press).
PULLMAN, B., and MANTIONE, M. J. (1964). *Biochim. Biophys. Acta* **91**, 387.
PULLMAN, B., and MANTIONE, M. J. (1965a). *Biochim. Biophys. Acta* **95**, 668.
PULLMAN, B., and MANTIONE, M. J. (1965b). *Compt. Rend.* **260**, 5643; **261**, 5679.
PULLMAN, B., and PULLMAN, A. (1958a). *Proc. Natl. Acad. Sci. U.S.* **44**, 1197.
PULLMAN, B., and PULLMAN, A. (1958b). *Bull. Soc. Chim. France* p. 973.
PULLMAN, B., and PULLMAN, A. (1959). *Biochim. Biophys. Acta* **36**, 343.
PULLMAN, B., and PULLMAN, A. (1963). "Quantum Biochemistry." Wiley (Interscience), New York.
PULLMAN, B., CLAVERIE, P., and CAILLET, J. (1965). *Science* **147**, 1305.
PULLMAN, B., CLAVERIE, P., and CAILLET, J. (1966). *Proc. Natl. Acad. Sci. U.S.* **55**, 904.
PULLMAN, B., CLAVERIE, P., and CAILLET, J. (1967a). *Proc. Natl. Acad. Sci. U.S.* **57**, 1663.
PULLMAN, B., CLAVERIE, P., and CAILLET, J. (1967b). *J. Mol. Biol.* **22**, 373.
RAHN, R. O., LONGWORTH, J. W., EISINGER, J., and SHULMAN, R. G. (1964). *Proc. Natl. Acad. Sci. U.S.* **51**, 1299.
REIN, R., and HARRIS, F. E. (1964). *J. Chem. Phys.* **41**, 3393.
REIN, R., and HARRIS, F. E. (1965). *J. Chem. Phys.* **42**, 2177; **43**, 4415.
RICH, A., DAVIES, D. R., CRICK, F. H. C., and WATSON, D. (1961). *J. Mol. Biol.* **3**, 71.
ROOTHAAN, C. C. J. (1951). *Rev. Mod. Phys.* **23**, 69.
RUEDENBERG, K. (1961). *J. Chem. Phys.* **34**, 1861.
SCHWEIZER, M. P., CHAN, S. I., and TS'O, P. O. P. (1965). *J. Am. Chem. Soc.* **87**, 5241.
SHOUP, R. R., MILES, H. T., and BECKER, E. D. (1966). *Biochem. Biophys. Res. Commun.* **23**, 194.
SIMMONS, H. E. (1964). *J. Chem. Phys.* **40**, 3554.
SIMON, Z. (1965). *J. Theoret. Biol.* **9**, 414.
SINANOĞLU, O., and ABDULNIR, S. (1964). *Photochem. Photobiol.* **3**, 333.
SINANOĞLU, O., and ABDULNUR, S. (1965). *Federation Proc.* **24**, S12.
SOBELL, H. M., TOMITA, K., and RICH, A. (1963) *Proc. Natl. Acad. Sci. U.S.* **49**, 885.
STEWART, R. F., and DAVIDSON, N. (1963). *J. Chem. Phys.* **39**, 255.
STEWART, R. F., and DAVIDSON, N. (1964). *Biopolymers Symp.* **1**, 465.
STEWART, R. F., and JENSEN, L. H. (1964). *J. Chem. Phys.* **40**, 2071.
STRUCK, W. A., and ELVING, P. J. (1964). *J. Am. Chem. Soc.* **86**, 1229.
STRUCK, W. A., and ELVING, P. J. (1965). *Biochemistry* **4**, 1343.
SUKHORUKOV, B. I., and POLTEV, V. I. (1963) *Biophysics* (*USSR*) (*English Transl*) **9**, 154.
SZER, W. (1966). *J. Mol. Biol.* **16**, 585.
TS'O, P. O. P. (1964). *In* "The Nucleohistones" (J. Bonner and P. O. P. Ts'o, eds.), p. 149. Holden-Day, San Francisco, California.
TS'O, P. O. P., and CHAN, S. I. (1964). *J. Am. Chem. Soc.* **86**, 4176.
TS'O, P. O. P., and LU, P. (1964). *Proc. Natl. Acad. Sci. U.S.* **51**, 17.
TS'O, P. O. P., HELMKAMP, G. K., and SANDER, C. (1962). *Proc. Natl. Acad. Sci. U.S.* **48**, 686.
TS'O, P. O. P., MELVIN, I. S., and OLSON, A. C. (1963). *J. Am. Chem. Soc.* **85**, 1289.

Ts'o, P. O. P., Chan, S. I., Schweizer, M. P., and Helmkamp, G. K. (1964). *J. Am. Chem. Soc.* **86**, 4182.

Van Holde, K. E., Brahms, J., and Michelson, A. M. (1965). *J. Mol. Biol.* **12**, 726.

Veillard, A., and Pullman, B. (1963). *J. Theoret. Biol.* **4**, 37.

Voet, D., Gratzer, W. B., Cox, R. A., and Doty, P. (1963). *Biopolymers* **1**, 193.

Warshaw, M. M., and Tinoco, I., Jr. (1965). *J. Mol. Biol.* **13**, 54.

Witz, J., and Luzzati, V. (1965). *J. Mol. Biol.* **11**, 620.

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