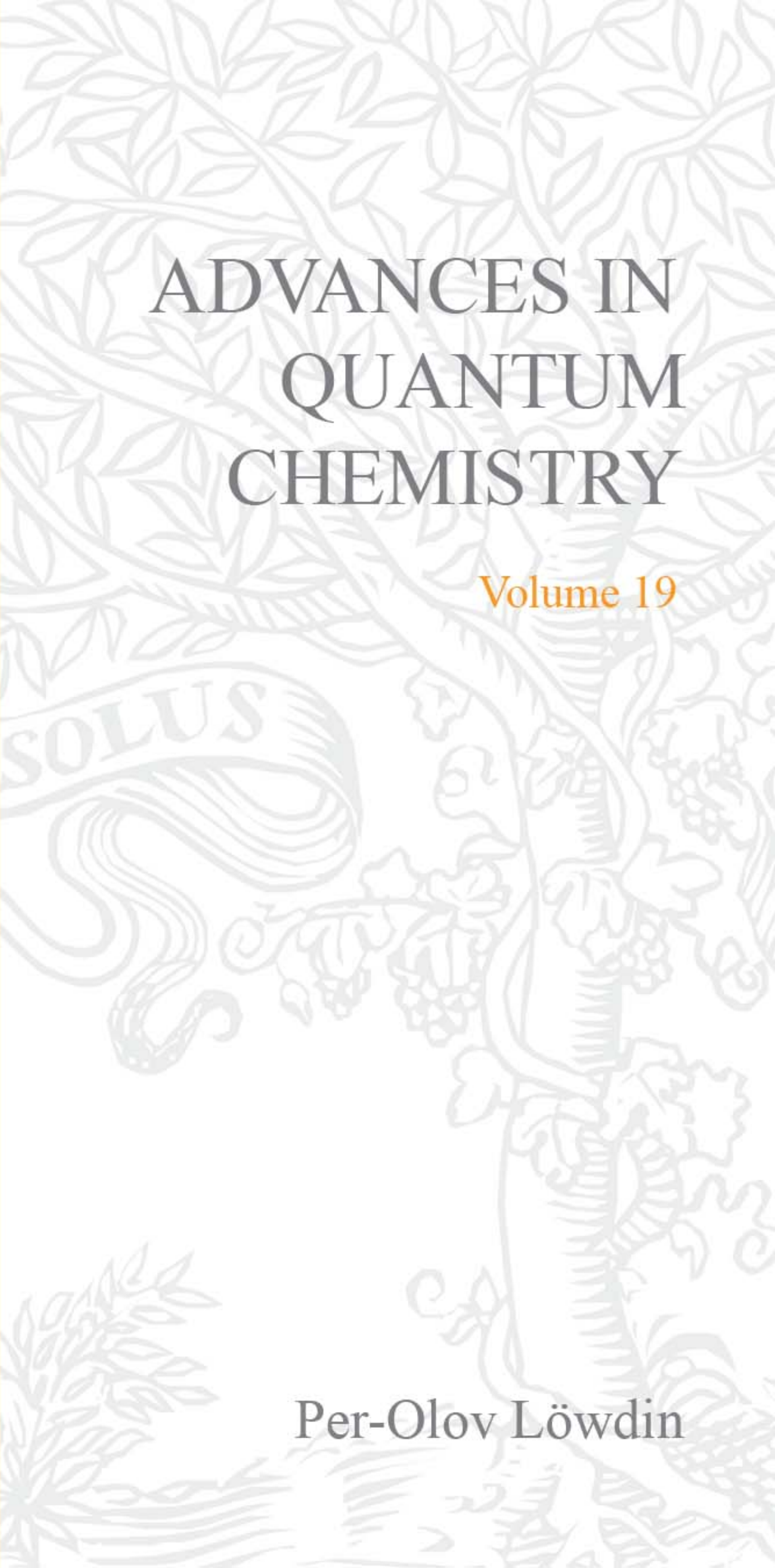

ADVANCES IN QUANTUM CHEMISTRY

Volume 19

Per-Olov Löwdin

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VOLUME 19

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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 of 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 of 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 for both 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 twentieth volume is now being prepared. However, in order to control production costs and speed publication time, a new format is being planned involving camera-ready manuscripts. A special announcement about the new format follows.

The Editor would like to thank the authors for their contributions, which give an interesting picture of the current range from studies of the use of the Lie algebra in quantum theory, overestimates of the neutrino mass, to relativistic effects in atoms and molecules and the calculation of lifetimes of metastable states by means of the method of complex scaling.

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.

PER-OLOV LÖWDIN

ANNOUNCEMENT OF NEW FORMAT

Starting with Volume 20, the *Advances in Quantum Chemistry* published by Academic Press, will assume a new format. As before, all contributions will be *by invitation only*, but—to control costs—all authors will be asked to submit their manuscripts in *photoready form* in a format specified by the publisher. This procecure will eliminate copyediting, typesetting, and proofreading, and, in this way, will hopefully reduce the publication time to 6–8 months.

We further plan to publish two volumes of the *Advances* per year: one *regular volume* in the same style as before, and one *thematic volume* concerned with one specific subject, for example, computational methods in quantum chemistry, theoretical organic chemistry, quantum pharmacology and drug design, density functional theory, and relativistic quantum chemistry.

I will remain Editor-in-Chief, but there will also be two Associate Editors: Professors John R. Sabin and Michael C. Zerner of the Florida Quantum Theory Project, where the main editorial office will be established with the address: 362 Williamson Hall, University of Florida, Gainesville, Florida 32611. Telephone: (904) 392-1597; Telex: 5106016813 QTP UF UD; Bitnet: OHRN at UFFSC.

There has further been established an *Editorial Board* and an *Advisory Editorial Board* (the latter on a rotating basis) of eminent specialists in the field to suggest authors to be invited to make contributions both to the regular and thematic volumes and to help with questions such as publication policies.

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Lie Algebraic Methods and Their Applications to Simple Quantum Systems

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I. Introduction

The algebraic methods were first introduced in the context of the new matrix mechanics around 1925. The importance of the concept of angular momentum in quantum mechanics, in contrast to classical mechanics (see, e.g., Wigner, 1964), was soon recognized and the necessary formalism was developed principally by Wigner, Weyl, and Racah. The algebraic treatment of the angular momentum can be found nowdays in almost every textbook on quantum mechanics, often in parallel with the differential equation approach. In contrast, this cannot be said about another basic quantum mechanical system, namely the hydrogen atom, which is almost universally treated by the latter approach only. Yet, both the algebraic approach to the hydrogen atom by Pauli (1926) and the differential equation approach due to Schrödinger (1926b) originated almost at the same time. Since this latter approach was more accessible to physicists, and the significance of the symmetry concepts in the microscopic world was not fully appreciated at the time, the algebraic approach for the determination of the hydrogen atom energy spectrum was largely forgotten and the algebraic techniques in general were in abeyance for three decades. The revival of these techniques came with the development of quantum mechanics of elementary particles, since for these systems the explicit form of the Hamiltonian is unknown and one can only make certain more or less plausible assumptions about its symmetry. In the midst of various

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* Killam Research Fellow 1987–8.

attempts to solve this difficult problem, the elementary particle physicists examined several noncompact Lie algebras in the mid-1950s, hoping that they would provide a clue to the classification of elementary particles. Although this hope did not materialize, and in fact these were Lie algebras of compact Lie groups which enabled such a classification (see, e.g., Gell-Mann and Ne'eman, 1964), the noncompact groups turned out to be relevant as the so-called dynamical groups for atomic physics. We note at this occasion that various compact groups—particularly their "prototype," the unitary group, or rather their Lie algebras—are also extensively used in both nuclear (Moshinsky, 1968) and atomic and molecular (see, e.g., Paldus, 1974, 1976, 1981, 1986; Paldus and Jeziorski, 1988) many-body problems. However, in this review we shall concentrate on the dynamical groups relevant to various one-body (or pseudo one-body) problems which are noncompact.

A close relationship of the angular momentum and the $so(3)$ algebra dates certainly to the prequantum mechanics era, while the realization that $SO(4)$ is the symmetry group of the Kepler problem was first demonstrated by Fock (1935). Soon afterward Bargmann (1936) showed that the generators of Fock's $SO(4)$ transformations were the angular momentum and Runge–Lenz vectors.[1] Following the developments in the late 1950s and early 1960s mentioned above, the original algebraic approach of Pauli (1926) was considerably simplified and systematized using the language and concepts of Lie algebras. A completely new aspect was the introduction of dynamical groups in field theory and particle physics (Barut and Bohm, 1965; Dothan *et al.*, 1965). In particular the noncompact groups $O(2, 1)$ *and* $O(4, 2)$ (Barut, 1971) enabled a simple and elegant treatment of the hydrogen atom and other simple quantum mechanical systems. The $so(4, 2)$ Lie algebra also enables an effective perturbation theory treatment of the hydrogen atom in external fields. Here the pioneering work of Bednár (1973) should be mentioned.

We wish to recall at this point that group theoretical methods, although greatly developed by pioneers of quantum mechanics (Wigner, 1931; Weyl, 1931), were subsequently in abeyance for a long time as mentioned earlier. In fact, a number of physicists expressed a certain proudness when claiming that they can "get along without it" (Condon and Shortley, 1935, pp. 10–11), and the approach was even referred to as a "group pest" by some. It is interesting to observe a rather dramatic change in this attitude during the last decade which is perhaps best documented by comparing the old and new editions of Condon and Shortley's atomic structure theory [Condon and Shortley, (1935) vs. Condon and Odabasi (1980)], the latter containing two extensive chapters on

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[1] In quantum mechanical context this invariant of the Kepler problem is often referred to as a Runge–Lenz–Pauli vector. In classical mechanics context it is also sometimes referred to as a Laplace–Runge–Lenz vector.

group theory. Nevertheless, the above-mentioned elegant and simple treatments of the hydrogen atom and similar problems have yet to make their way into more elementary texts on quantum mechanics. One of the reasons for the slow acceptance of these techniques, as well as for the original neglect of the group theoretical and algebraic methods, is undoubtedly related to their abstract character and inherent complexity. Indeed, a proper understanding of Lie group structure requires an intimate knowledge of not only the standard theory of finite groups, but also of topology and manifold theory. Nevertheless, the basic concepts are quite simple, particularly when presented in the context of physical applications, and at the much simpler Lie algebra level, since the group structure is unnecessary for many useful applications. This is precisely the standpoint taken in this review, in which we shall attempt to present a very simple and hopefully pedagogical as well as motivated approach to this topic. We also note that the importance of the commutator concept in axiomatic structure of quantum theory has been discussed by Löwdin (1982b, p. 294).

We shall introduce the $so(2, 1)$ algebra alongside the well-known $so(3)$ algebra of the angular momentum theory, assuming some familiarity of the reader with the latter. We shall then successively construct the higher algebras, namely $so(4)$, $so(4, 1)$, and $so(4, 2)$, by "merging" two or more smaller algebras already at hand. Let us outline this "merging" procedure in more detail (Cizek and Paldus, 1977; see also Section II). Starting with two smaller algebras A and B, the merging enables us to construct a larger algebra which contains both algebras A and B as its subalgebras (cf. Section II). Assuming that A and B are defined through the same realizations (cf. Section II). In terms of quantum mechanical operators of coordinate and momenta, as will be the case in our considerations, we consider the union of A and B, $A \cup B$, and form all the commutators of their elements $A_i \in A$, $B_j \in B$, namely $C_k^{(1)} = A_iB_j - B_jA_i \equiv [A_i, B_j]$. Some of the $C_k^{(1)}$ values will belong to either A or B, but some may be expected to belong neither to A nor to B. We thus extend $A \cup B$ by these elements, namely, we consider the set $A \cup B \cup C^{(1)}$, where $C^{(1)} = \{C_k^{(1)}\}$ is the set of all commutators of $A \cup B$. We now repeat this procedure considering the commutators $C_k^{(2)}$ of all elements of $A \cup B \cup C^{(1)}$, and form $A \cup B \cup C^{(1)} \cup C^{(2)}$. Continuing in this way, there are two possible outcomes: (1) after a finite number of steps, the set $A \cup B \cup C^{(1)} \cup \cdots \cup C^{(k)}$ will be closed with respect to the binary operation of forming the commutators, i.e., the commutators of all of its elements will again belong to the set, or (2) the procedure will not close after a finite number of steps. In the first case we shall have constructed a new finite dimensional Lie algebra, assuming that initial algebras A and B are of a finite dimension. Let us qualitatively illustrate the outcome of this procedure on an important example, which is treated in detail in subsequent sections. We have mentioned above that $SO(4)$ is a general symmetry group for the Kepler problem, and thus is relevant to the hydrogen atom problem. We shall see that the noncompact group $O(2, 1)$, the two-dimensional Lorenz group, or its unimodular subgroup $SO(2, 1)$, represents the spectrum-generating group for the hydrogen atom radial Schrödinger equation. The $so(4)$ Lie algebra has 6 generators [and can, in fact, be represented as a direct sum of two $so(3)$ algebras, each with 3 generators representing the components of the angular momentum], while the $so(2, 1)$ algebra has 3 generators. By merging $so(4)$ with $so(2, 1)$ we get the $so(4, 2)$ algebra with 15 generators, which is the Lie algebra of the full dynamical group of the hydrogen atom, also called the conformal group Lie algebra, treated in some detail in Section VIII.

Two sections of this review (Sections IX and X) are devoted to the exploitation of dynamical symmetries in perturbation studies[2] of various simple quantum mechanical systems, particularly of the hydrogen atom in electric or magnetic fields and of long-range forces in a one-electron diatomic molecule. In all these problems one starts with an unperturbed spherically symmetric Hamiltonian and applies perturbation theory for a strong, symmetry-breaking perturbation. Consequently, one is faced with two basic difficulties: (1) the existence of a continuum for hydrogen-like ions and (2) the divergence of the resulting perturbation series. The latter problem is largely extraneous to the dynamical group approach to which this review is devoted and thus will not be considered here. It suffices to say that nowdays there exist numerous techniques which enable one to extract useful information from divergent series, assuming that one can compute their terms to sufficiently high orders (Cizek and Vrscay, 1982; Vrscay, 1983; Cizek and Vrscay, 1984).

Finally, an Addendum (p. 70) has been added during the final processing of the manuscript and presents some most recent applications concerning charmonium and harmonium systems in the N-dimensional case. This section was written by F. Vinette.

We intend to publish in future volumes of the *Advances in Quantum Chemistry* two separate reviews on these problems, one on the large-order perturbation theory (LOPT) and one on continued fractions at large order (CFLO).

The first difficulty referred to above is the source of numerous technical problems in many perturbation theory applications. For the systems treated in this review, these difficulties can be avoided by exploiting the Dalgarno and Lewis (1955) procedure (see also Schiff, 1968, p. 263). However, it is a remarkable aspect of the Lie algebraic approach that the continuum problem can be simply avoided by introducing a nonunitary transformation, which can

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[2] For a comprehensive account and many remarkable developments of general perturbation theory, see Löwdin (1962, 1963, 1964, 1965, 1966, 1968, 1982a) and Löwdin and Goscinski (1971).

be essentially regarded as a coordinate scaling. Applying this transformation we obtain the unperturbed Hamiltonian, which has only a discrete spectrum, so that the subsequent perturbation theory calculations are straightforward.

II. General Discussion of Lie Algebras

Lie groups and their associated Lie algebras play a central role in quantum mechanics (Wybourne, 1974; Gilmore, 1974; Schiff, 1968; Barut, 1971; Hamermesh, 1962; Bohm, 1979). Their areas of application include fundamental quantum field theories, elementary particle symmetry and conservation laws, special function theory (Miller, 1968; Vilenkin, 1968), angular momentum theory (Biedenharn and Louck, 1981a,b), and, more recently, the practical development of the unitary group approach to configuration interaction (Paldus, 1974, 1976, 1981) and the systematic study of large-order perturbation theory via the Lie algebra $so(4, 2)$ (Cizek and Vrscay, 1982, and references therein). This latter application is the primary goal in this review.

Our main interest is in Lie algebras, rather than their corresponding Lie groups, as they arise more naturally as a practical tool for the systematic calculation of matrix elements of various quantum mechanical operators. In this section we shall introduce some definitions and terminology concerning Lie algebras and their representations and realizations. First we shall present the general definition of a Lie algebra and then specialize to the important case when the Lie algebra multiplication is given by the commutator of two operators or matrices. We shall discuss some basic identities involving commutators and present an extensive list of useful ones involving position and momentum operators (Appendix A) for our applications. Finally we shall introduce the important concepts of realizations and representations of a Lie algebra.

It should be emphasized that a detailed knowledge of Lie algebras is not essential to the understanding of the applications we shall consider, since all of our results will be presented in a simple pedagogical manner using only the familiar concepts of vector spaces, operators, matrices, and commutators (see, e.g., Hamermesh, 1962; Saletan and Cromer, 1971).

A. Definition of a Lie Algebra

A Lie algebra over a field F is a vector space V over F equipped with a law of composition (Lie multiplication) denoted by $[A, B]$ which has the following properties:

(1) $[A, B] \in V$
(2) $[A, B + C] = [A, B] + [A, C]$
(3) $\alpha[A, B] = [\alpha A, B] = [A, \alpha B]$

(4) $[A, A] = 0$
(5) $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

for all $\alpha \in F$ and $A, B, C \in V$.

The first property (1) guarantees the *closure* of the Lie algebra under the Lie multiplication. Properties (2) and (3) combine this multiplication with the multiplication by the scalars of the vector space V, and imply the usual bilinearity properties

$$\left[\sum_i \alpha_i A_i, \sum_j \beta_j B_j\right] = \sum_{i,j} \alpha_i \beta_j [A_i, B_j] \tag{1}$$

Properties (1)–(3) together define an algebra where the multiplication is usually denoted by AB rather than by $[A, B]$. Different kinds of algebras can be defined by imposing other properties in addition to (1)–(3). For example, a *commutative* algebra has the additional property that $AB = BA$ and an *associative* algebra has the associative property $A(BC) = (AB)C$. An algebra having both these additional properties would be called a commutative associative algebra. Thus, for a Lie algebra the additional properties are given by properties (4) and (5) and we see that a Lie algebra is neither commutative, since $[A + B, A + B] = 0$ implies the anticommutative property $[A, B] = -[B, A]$, nor associative. In fact, property (5) replaces the usual associative property and is called the Jacobi identity.

In quantum mechanics we often encounter associative algebras of operators and matrices which are noncommutative. For example, the set of all $n \times n$ matrices over the real or complex number fields is an n^2-dimensional vector space which is also an associative, noncommutative algebra whose multiplication is just the usual matrix multiplication. Also, the subset of all diagonal $n \times n$ matrices is a commutative algebra.

Lie algebras can often be constructed from associative algebras of operators or matrices. In fact, the Lie algebras we shall consider for physical applications can all be constructed in this manner. Thus, given an associative algebra with multiplication defined by AB we can define the Lie product by the commutator, or Lie bracket of A and B

$$[A, B] = AB - BA \tag{2}$$

It is now easily verified that the general properties (2)–(5) of a Lie algebra are formally satisfied by this commutator multiplication, so that only the closure property (1) needs to be verified in each particular case. It should also be noted that commutators arise naturally in quantum mechanics.

As a simple example of a Lie algebra consider the three-dimensional vector space with the unit basis vectors e_1, e_2, e_3, each pointing along one of the mutually perpendicular coordinate axes. Define $[e_i, e_j] = e_i \times e_j$, the usual vector cross-product, and a three-dimensional Lie algebra is obtained. Many other examples arise from matrix algebras. For example, the algebra of all $n \times n$ matrices mentioned above can be used to construct a Lie algebra simply by defining the commutator $[A, B] = AB - BA$ in terms of the ordinary matrix product AB, since the closure property (1) is obviously satisfied. This algebra is called a general linear algebra of order n and is designated as gl(n). It is interesting to note that the subset of all antisymmetric matrices is an $n(n-1)/2$-dimensional vector space but is not an algebra with respect to the usual matrix multiplication since the product of two antisymmetric matrices is not generally an antisymmetric matrix. Thus, the closure property (1) fails to hold. However, this subset is a Lie algebra with respect to the commutator multiplication, since

$$[A, B]^t = (AB - BA)^t = -(AB - BA) = -[A, B]$$

if A,.B are antisymmetric matrices, where t denotes the matrix transpose, and hence the closure property holds.

Since a Lie algebra has an underlying vector space structure we can choose a basis set $\{E_i : i = 1, \ldots, N\}$ for the Lie algebra. Furthermore, because of the bilinearity properties Eq. (1), the Lie algebra is completely defined by specifying the commutators of these basis elements:

$$[E_i, E_j] = \sum_k c_{ijk} E_k : i, j, k = 1, \ldots, N \tag{3}$$

These relations are called the *defining commutation relations* for the Lie algebra and the coefficients c_{ijk} are called the *structure constants.* A different choice of basis leads to a different but equivalent set of structure constants. We also say that the E_i are *generators* of the Lie algebra. The rather difficult problem of classifying different Lie algebras will not be considered here (see, e.g., Wybourne, 1974; Gilmore, 1974), since those we shall use arise quite naturally from physical considerations.

Finally, we would like to mention that the set of operators which commute with all elements of the Lie algebra is very useful in the study of Lie algebras (cf. Section III). In general these operators do not belong to the Lie algebra and are called *Casimir operators.*

B. Physical Realizations of a Lie Algebra

Once a Lie algebra has been defined in the abstract sense via the defining commutation relations Eq. (3), it is of practical interest to find physical realizations of the generators in terms of position and momentum operators, which also satisfy these defining commutation relations. We shall call such a set of concrete operators a *realization of the Lie algebra.* In practice, as we shall see, we often work backwards by starting with a set of concrete operators which do not close under commutation [i.e., property (1) is not satisfied] and adding to our set any new operators which are necessary to close out the commutation relations. In this manner we obtain a realization of some Lie algebra. This is also a standard procedure for combining or merging two realizations of two different Lie algebras into a realization of a bigger Lie algebra (cf. Section I).

As an example consider the important three-dimensional Lie algebra often denoted as $so(3)$ or $su(2)$, whose defining commutation relations can be cast in the form

$$[E_1, E_2] = iE_3 \qquad [E_2, E_3] = iE_1 \qquad [E_3, E_1] = iE_2 \tag{4}$$

Well-known realizations of the generators of this Lie algebra are given by the three components of the orbital angular momentum vector $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$, the three components of the spin $\boldsymbol{S} = \frac{1}{2}\boldsymbol{\sigma}$ realized in terms of the Pauli spin matrices (Schiff, 1968), or the total one-electron angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$. The components of each of these vector operators satisfy the defining commutation relations Eq. (4) if we use atomic units. We should also note that the vector cross-product example mentioned earlier also satisfies Eq. (4) if we define $E_j = ie_j$; $j = 1, 2, 3$.

Associated with each operator realization of a Lie algebra we generally have a vector space on which these operators act. For the realization given by $\boldsymbol{L}$ this might be either an abstract space of angular momentum states $|lm\rangle$, $l = 0, 1, \ldots$; $m = -l, -l+1, \ldots, l$ or a concrete realization of them as spherical harmonic functions $Y_{lm}(\theta, \phi)$. We can then consider the matrix elements of the operators with respect to this vector space of states and this leads to the important concept of a *matrix representation* of a Lie algebra.

C. Matrix Representation of a Lie Algebra

Given a Lie algebra with defining commutation relations Eq. (3), we can consider the generators E_i as operators acting on some n-dimensional vector space W. If $\{|i\rangle : i = 1, \ldots, n\}$ is a basis set for W then

$$E_k|j\rangle = \sum_i |i\rangle\langle i|E_k|j\rangle; \qquad i, j = 1, \ldots, n; \qquad k = 1, \ldots, N \tag{5}$$

where $\langle i|E_k|j\rangle$ is a matrix element of E_k. Denoting by $\boldsymbol{E}_k$ the matrix representing E_k it is easily shown that

$$[\boldsymbol{E}_i, \boldsymbol{E}_j] = \sum_k c_{ijk}\boldsymbol{E}_k \tag{6}$$

and we say that the matrices $\boldsymbol{E}_i$ generate a *matrix representation* of the Lie algebra since they have the same defining commutation relations.

When the representation space is not precisely specified, we often talk about a *realization* of a Lie algebra rather than the representation (cf. also

Section II,B). For example, the realization of Eq. (4) given by the spin $\boldsymbol{S}$ is a matrix realization since S can act in different spin spaces yielding representations of different dimension. A similar situation arises in group theory. For example, the three-dimensional rotation group has a familiar matrix realization in terms of Euler angles (Saletan and Cromer, 1971) which is also a matrix representation of the group, and again we can have matrix representations of any dimension. We should also mention here that each Lie algebra corresponds to one or more Lie groups although we shall not need this correspondence for our applications. In fact the realization of Eq. (4) in terms of $\boldsymbol{L}$ gives the Lie algebra of the three-dimensional rotation group.

The problem of classifying all matrix representations of a given Lie algebra is an important but difficult one. The first step is to classify all the *irreducible representations* (irreps). Then any matrix representation can be constructed using the irreps as building blocks. Thus, given any matrix representation of a Lie algebra we can always obtain an equivalent one by applying a similarity transformation to all the matrices representing the generators. If we can do this in such a way that all the matrices have an identical block diagonal structure then we say that the representation is *reducible* since the block matrices will form smaller dimensional matrix representations of the Lie algebra. For example, if each $\boldsymbol{E}_i$ has the form

$$\boldsymbol{E}_i = \begin{pmatrix} \boldsymbol{A}_i & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{B}_i \end{pmatrix}$$

where $\boldsymbol{A}_i$ and $\boldsymbol{B}_i$ are $l \times l$ and $m \times m$ matrices, respectively, then it is easily verified that the $\boldsymbol{A}_i$ form a matrix representation and so do the $\boldsymbol{B}_i$. If we cannot obtain such a reduction by any similarity transformation then we say that the representation is *irreducible*. Put another way, if the vector space W on which the operators E_i act has no nontrivial subspaces which are mapped into themselves by all the E_i (invariant subspaces), then the representation is irreducible. We shall use this definition in later sections to construct irreps of several physically important Lie algebras. A particularly important role will be played by unitary irreducible representations (cf. the finite group case) which we shall refer to for brevity as "unirreps."

III. Representation Theory of *so*(2, 1)

In this section we shall present a simple unified approach to the matrix representation theory of the *so*(2, 1) and *so*(3) Lie algebras (Barut and Fronsdal, 1965; Barut, 1971; Wybourne, 1974; Barut and Raczka, 1977). These Lie algebras have a similar structure and the general representation theory for both are closely related. However, when we specialize to the unitary representations by requiring that the generators be Hermitian, *so*(2, 1) and *so*(3) are quite different. In fact it is well known that all unitary irreducible representations (unirreps) of *so*(3) are finite dimensional (Biedenharn and Louck, 1981a). On the other hand we shall see that all nontrivial unirreps of *so*(2, 1) are infinite dimensional (Barut and Fronsdal, 1965). It is surprising that the unirreps of *so*(2, 1) are not as well known as those of *so*(3), since there is a large number of applications to simple quantum systems (Barut, 1971; Wybourne, 1974). Pedagogical approaches to the realization of the *so*(2, 1) generators in terms of coordinate and momentum operators have recently been given with a number of applications (Cizek and Paldus, 1977; Fernandez and Castro, 1984).

We shall present a simple account of the representation theory from a general point of view without using any particular realizations of the generators. The construction of realizations is deferred to Section V. First, the defining commutation relations are used to obtain the general representations of the generators on an abstract vector space of states. This purely algebraic approach is often used for *so*(3) in textbooks on quantum mechanics (see, e.g., Messiah, 1970, Vol. II) or angular momentum theory (Biedenharn and Louck, 1981a) and works just as easily for *so*(2, 1). We shall see in the general case that irreps of both *so*(2, 1) and *so*(3) fall into several classes: infinite dimensional ones which may be unbounded, bounded above, or bounded below, and finite dimensional ones. Next we shall introduce a scalar product and require that the Lie algebra generators be Hermitian with respect to it in order to obtain the unirreps. As mentioned above the unirreps of *so*(2, 1) will be different from those of *so*(3). Finally, we shall classify the unirreps, and give their explicit representations, and indicate which ones are most useful for applications to quantum mechanics.

A. General Representations

The defining commutation relations for the generators of *so*(2, 1) and *so*(3) are given by

$$[J_1, J_2] = i\gamma J_3 \tag{7a}$$

$$[J_2, J_3] = iJ_1 \tag{7b}$$

$$[J_3, J_1] = iJ_2 \tag{7c}$$

where $\gamma = 1$ refers to *so*(3) and $\gamma = -1$ refers to *so*(2, 1). The Casimir operator, which commutes with all generators, is given by

$$J^2 = \gamma(J_1^2 + J_2^2) + J_3^2 \tag{8}$$

For $\gamma = 1$ this is just the familar square of the angular momentum vector ($J^2 = \boldsymbol{J} \cdot \boldsymbol{J}$). For the study of spectral properties of these operators it is convenient to use the ladder operators $J_\pm = J_1 \pm iJ_2$. Then, the defining relations Eqs. (7a)–(7c) can be expressed in terms of $J_\pm$ and J_3:

$$[J_+, J_-] = 2\gamma J_3 \tag{9a}$$

$$[J_3, J_\pm] = \pm J_\pm \tag{9b}$$

and the Casimir operator can be written in the form

$$J^2 = \gamma J_+ J_- + J_3^2 - J_3 \tag{10}$$

It is well known (Messiah, 1970, Vol. I) that a set of mutually commuting operators can be simultaneously diagonalized. For $so(2, 1)$ and $so(3)$ the maximum number of such operators is two. For $so(3)$ ($\gamma = 1$) we could choose any of the pairs $\{J^2, J_i\}$, $i = 1, 2, 3$, and the representation theory would be the same in each case. However, for $so(2, 1)$ ($\gamma = -1$) each such choice of a pair of mutually commuting operators leads to a different set of inequivalent representations.

In our applications we are mainly interested in the *bound* states of simple quantum systems. The choice $\{J^2, J_3\}$ is necessary for a proper description of such states whereas the other choices would be more suitable for the description of the *continuum* states arising from scattering theory (Wybourne, 1974). Thus, we shall choose a representation space of states $|kq\rangle$ on which J^2 and J_3 are simultaneously diagonal:

$$J^2|kq\rangle = k(k + 1)|kq\rangle \tag{11}$$

$$J_3|kq\rangle = q|kq\rangle \tag{12}$$

Note the formal correspondence here with the familiar angular momentum theory where k and q are interpreted as the angular momentum and magnetic quantum numbers, respectively. It now follows from Eq. (9b) that J_+ (J_-) are raising (lowering) operators for q:

$$J_+|kq\rangle = A_{kq}|k, q + 1\rangle \tag{13}$$

$$J_-|kq\rangle = B_{kq}|k, q - 1\rangle \tag{14}$$

If we now let Eqs. (9a) and (10) act on $|kq\rangle$ and use Eqs. (11)–(14), then

$$A_{kq}B_{k,q+1} = \gamma(k - q)(k + q + 1) \tag{15a}$$

$$A_{k,q-1}B_{kq} = \gamma(k + q)(k - q + 1) \tag{15b}$$

and we choose the solution

$$A_{kq} = \gamma(k - q),\ B_{kq} = k + q \tag{16}$$

Other solutions are possible but they are all equivalent to this one. For example, we could choose $A_{kq} = -\gamma(k - q)$, $B_{kq} = -(k + q)$, or in any case we could associate the factor γ with B_{kq} rather than A_{kq}. However, all such choices are related to each other and to Eq. (16) by the phase change $(-1)^q$ of the basis vectors. We could choose $A_{kq} = \gamma(k + q + 1)$, $B_{kq} = k - q + 1$, but this choice is related to the previous ones by the change $k \to -k - 1$, which leaves the eigenvalue $Q = k(k + 1)$ of J^2 unchanged. Since Eqs. (11) and (12) will remain the same in any representation we need only consider Eqs. (13) and (14), which now become

$$J_+|kq\rangle = \gamma(k - q)|k, q + 1\rangle \tag{17a}$$

$$J_-|kq\rangle = (k + q)|k, q - 1\rangle \tag{17b}$$

B. Irreducible Representations: General Case

The subspaces $V(Q) = \{|kq\rangle : k(k + 1) = Q\}$ are invariant under the action of J_3, $J_\pm$ since none of these operators can change the values of k and thus Q. Furthermore, since $Q = k(k + 1)$ is invariant to the replacement $k \to -k - 1$, we obtain the further reduction $V(Q) = V_k \oplus V_{-k-1}$ into invariant subspaces $V_k = \{|kq\rangle : q \in C\}$, where C denotes the complex number field, unless $Q = -\frac{1}{4}$ (i.e., $k = -\frac{1}{2}$). Thus, for each k we can look at the possible eigenvalue spectra S_k of J_3 in order to further classify irreducible representations. Since J_+ and J_- raise and lower, respectively, the eigenvalue q in unit steps, these eigenvalue spectra have the general form $S(q_0) = \{q = q_0 + m, m = \text{integer}\}$ for some conveniently chosen reference value q_0. There are four cases to consider.

1. *Unbounded Spectrum*

If neither $k - q = 0$, nor $k + q = 0$ for any q, we obtain infinite dimensional irreps with unbounded J_3 eigenvalue spectra, since from Eq. (17) it follows that $J_\pm|kq\rangle \neq 0$. These conditions are equivalent to $k \pm q_0 \neq$ integer. The parameter q_0 is continuous and can be uniquely chosen so that its real part satisfies $-\frac{1}{2} \leq \mathrm{Re}(q_0) < \frac{1}{2}$. Each such q_0 gives a different J_3 eigenvalue spectrum. The other irrep series $-k - 1$ mentioned above gives the same J_3 eigenvalue spectra. Thus, the infinite dimensional irreps of this type are labelled by Q and q_0 and denoted by $D(Q, q_0)$.

2. *Spectrum Bounded Below*

If $J_-|kq\rangle = 0$ for some q but $J_+|kq\rangle \neq 0$ for any q then we obtain infinite dimensional irreps whose J_3 eigenvalue spectra are bounded from below. If we choose q_0 as the lowest eigenvalue, then the conditions are $k + q_0 = 0$, $k - q_0 - m \neq 0$ for $m = 0, 1, 2, \ldots$. Thus, the J_3 spectrum is $q = -k, -k + 1, -k + 2, \ldots$, where $2k \neq 0, 1, 2, \ldots$. Irreps of this type are denoted by $D^+(k)$.

3. *Spectrum Bounded Above*

This case is similar to the preceding case, except now the J_3 spectrum is bounded above. The conditions are

$$k - q_0 = 0, \qquad k + q_0 + m \neq 0, \qquad m = 0, -1, -2, \ldots$$

Thus, the J_3 spectrum is $q = k,\ k-1,\ k-2, \ldots,$ where again $2k \neq 0, 1, 2, \ldots$. Irreps of this type are denoted by $D^-(k)$.

4. *Bounded Spectrum*

Combining the second and third cases, we obtain finite dimensional irreps denoted by $D(k)$ with J_3 spectrum $q = -k, -k+1, \ldots, k$, where $2k = 0, 1, 2, \ldots$. These are the only finite dimensional irreps.

We should emphasize that the preceding classifications apply to both $so(2, 1)$ and $so(3)$. Also, some authors use $\psi = k + \frac{1}{2}$, rather than k, as a label, the advantage being that Q has the simpler form $Q = \psi^2 - \frac{1}{4}$ so that the two series associated with a given Q are negatives of each other, $k = \psi - \frac{1}{2}$ and $-k - 1 = -\psi - \frac{1}{2}$. Our choice has the advantage that it parallels more closely the familiar results of angular momentum theory. We also note that in the fourth case, for example, k can be an integer or a half-odd integer. In the latter case we are really dealing with the Lie algebras $su(1, 1)$ or $su(2)$ of the special unitary groups $SU(1, 1)$ and $SU(2)$, respectively, since for the three-dimensional rotation group $SO(3)$ we can only have the integral values of the angular momentum. However these Lie algebras are isomorphic to $so(2, 1)$ and $so(3)$, respectively, so we shall not normally distinguish them. To summarize, we have the following classification of the irreps of $so(1, 1)$ and $so(3)$:

$$D(Q, q_0)\begin{cases} q = q_0 \pm m, & m = 0, 1, 2, \ldots \\ -\frac{1}{2} \leq \mathrm{Re}(q_0) < \frac{1}{2} \\ k \pm q_0 \neq \text{integer} \end{cases} \tag{18a}$$

$$D^+(k)\begin{cases} q = -k + m, & m = 0, 1, 2, \ldots \\ 2k \neq 0, 1, 2, \ldots \end{cases} \tag{18b}$$

$$D^-(k)\begin{cases} q = k - m, & m = 0, 1, 2, \ldots \\ 2k \neq 0, 1, 2, \ldots \end{cases} \tag{18c}$$

$$D(k)\begin{cases} q = -k + m, & m = 0, 1, \ldots, 2k \\ 2k = 0, 1, 2, \ldots \end{cases} \tag{18d}$$

C. Unitary Irreducible Representations

In quantum mechanics our main interest is in the unirreps of Lie groups and these correspond to representations of the associated Lie algebras for which the generators are Hermitian operators. In our case the generators J_i and hence the Casimir operator J^2 must be Hermitian with respect to a suitable scalar product. Therefore we introduce a scalar product such that $J_i^\dagger = J_i$. Now, the raising and lowering operators $J_\pm$ are Hermitian conjugates

$$J_\pm^\dagger = J_\mp \tag{19}$$

with respect to this scalar product. This leads to several restrictions on the general irreps obtained above:

(1) Q, q must be real eigenvalues
(2) J_+J_- and J_-J_+ are positive definite Hermitian operators

$$\langle kq|J_+J_-|kq\rangle = \|J_-|kq\rangle\|^2 \geq 0 \tag{20a}$$

$$\langle kq|J_-J_+|kq\rangle = \|J_+|kq\rangle\|^2 \geq 0 \tag{20b}$$

Restriction (1) implies that q_0 is real and either k is real or $k = -\frac{1}{2} + i\beta, \beta \neq 0$. Substituting Eq. (17) into Eq. (20), restriction (2) gives the fundamental inequalities

$$\gamma(k \mp q)(k \pm q + 1) = \gamma[(k + \tfrac{1}{2})^2 - (q \pm \tfrac{1}{2})^2] \geq 0 \tag{21}$$

which must be satisfied by any unirrep. Note that the sign of these inequalities is different for $so(2, 1)(\gamma = -1)$ and $so(3)(\gamma = 1)$. Also, they are invariant under the substitution $k \to -k - 1$, which leaves Q unchanged.

The inequalities, Eq. (21), can be conveniently represented graphically as regions in the (k, q) plane bounded by the lines $k \mp q = 0$, $k \pm q + 1 = 0$, as shown in Fig. 1. In the vertically shaded regions the fundamental inequalities are satisfied for $so(2, 1)$ and in the horizontally shaded regions they are satisfied for $so(3)$. We shall consider $so(2, 1)$ and $so(3)$ separately.

For unirreps of $so(3)$ the case $k = -\frac{1}{2} + i\beta$, which is not represented in Fig. 1, is impossible since the fundamental inequalities cannot be satisfied for real q and β. Therefore k must be real and it follows that Eq. (21) can be satisfied only for a finite number of values of q. The J_3 eigenvalue spectra are thus given by Eq. (18d) with no further restrictions. These spectra lie on horizontal lines within the $so(3)$ regions of Fig. 1. In the region above the q axis they begin on the line $k + q = 0$ and on the line $k - q = 0$. From Fig. 1 it is clear that for each eigenvalue spectrum in the $so(3)$ region below the q axis there is an identical one in the upper $so(3)$ region. The corresponding unirreps $D(k)$ and $D(-k - 1)$ are equivalent since they have the same J_3 eigenvalue spectrum and thus a complete set of inequivalent unirreps is given, for example, by those corresponding to the upper $so(3)$ region only.

For unirreps of $so(2, 1)$ the situation is quite different. The fundamental inequalities cannot be satisfied if the J_3 eigenvalue spectrum is bounded unless $k = 0$, corresponding to the trivial one-dimensional unirrep. Thus, there are

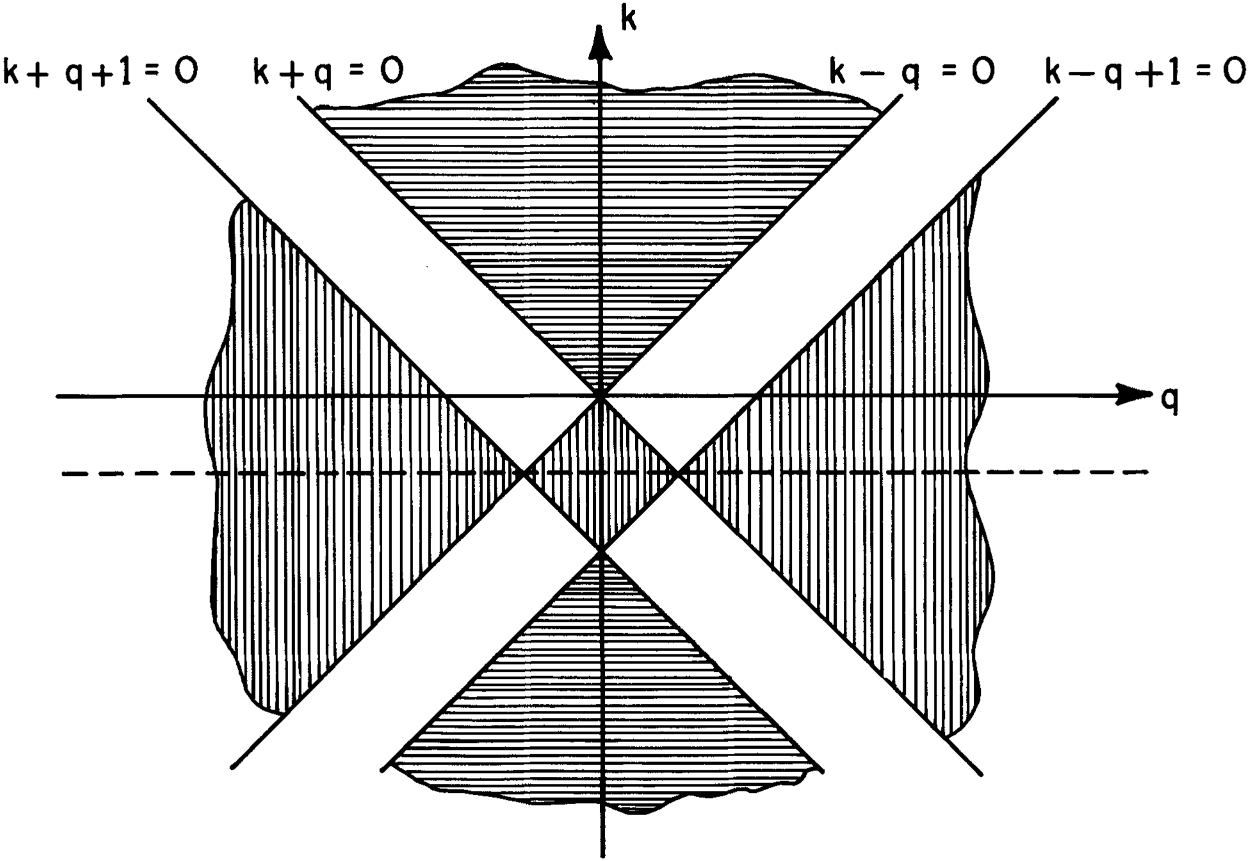

Fig. 1. Regions in the (k, q) plane where the J_3-eigenvalue spectrum corresponds to unitary irreducible representations of $so(3)$ (horizontal shading) and $so(2, 1)$ (vertical shading). See text for details.

no nontrivial finite-dimensional unirreps of $so(2, 1)$. For irreps of type $D^{\pm}(k)$ given in the general case by Eqs. (18b) and (18c) the fundamental inequalities can only be satisfied if $k < 0$ [$k > -1$ for the $D^{\pm}(-k-1)$]. For unirreps of type $D^{+}(k)$ the J_3 eigenvalue spectra begin on the line AB in Fig. 2 and extend in unit steps to the right into the allowable region BDF [for $D^{+}(-k-1)$ they begin on the line CD and extend to the right]. Similarly, for unirreps of type $D^{-}(k)$ the J_3 eigenvalue spectra begin on the line AG and extend to the left into the allowable region EGH [for $D^{-}(-k-1)$ they begin on CH and extend to the left]. Note that spectra which begin on any of the line segments AF, CF, CE, or AE immediately jump over the forbidden regions which are unshaded in Fig. 1.

Unirreps of $so(2, 1)$ having unbounded J_3 eigenvalue spectra arise from the general class $D(Q, q_0)$ given by Eq. (18a) and can be of two types. The so-called supplementary series of unirreps are denoted by $D_S(Q, q_0)$ and the principal series are denoted by $D_p(Q, q_0)$. The former arise when $-1 < k < 0$ and $-\frac{1}{2} \le q_0 \le \frac{1}{2}$. In this case k and q_0 lie within the diamond-shaped region AFCE of Fig. 2. The boundaries of this region are not included since $k + q_0 \neq$ integer. The interior of this region can be concisely described by either of the inequalities $|k + \frac{1}{2}| < \frac{1}{2} - |q_0|$ and $Q < |q_0|(|q_0| - 1)$, and it also follows that $-\frac{1}{4} < Q < 0$. Beginning at an arbitrary point in this region the J_3 eigenvalue spectrum extends in unit steps to the left and right into the

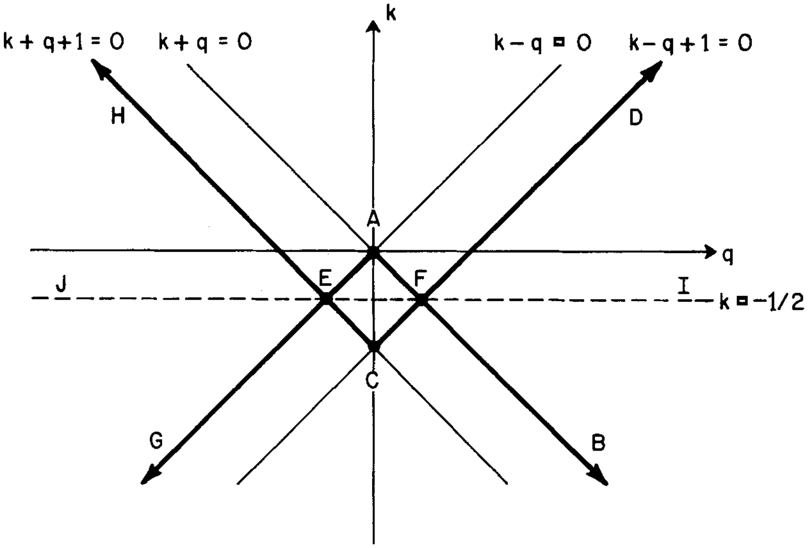

Fig. 2. Lines in the (k, q) plane on which the J_3-eigenvalue spectra begin for unitary irreducible representations of $so(2, 1)$. See text for details.

allowable regions EGH and BDF. Finally, the principal series arises when $k = -\frac{1}{2} + i\beta$ and $-\frac{1}{2} < q_0 < \frac{1}{2}$. In this case $Q = -\beta^2 - \frac{1}{4} < -\frac{1}{4}$. Thus, for any such q_0 on the line segment EF in Fig. 2 the J_3 eigenvalue spectrum extends to the left and right along the dashed line and each inequivalent unirrep of this type is characterized by β^2 and q_0.

For any unirreps of *so*(2, 1) of types $D^{\pm}$ or D_S, the dashed line $k = -\frac{1}{2}$ is a line of symmetry dividing the allowable regions in two. For any such unirrep there is an equivalent one on the opposite side of this line having the same J_3 eigenvalue spectrum. Thus, there are several ways to describe a complete set of inequivalent unirreps of each type. For example, for type D^+ we can choose (1) all $D^+(k)$ with spectra beginning on AB, (2) all $D^+(-k-1)$ with spectra beginning on CD, (3) all $D^+(-k-1)$ with spectra beginning on CF and all $D^+(k)$ beginning on FB, or (4) all $D^+(k)$ with spectra beginning on AF and all $D^+(-k-1)$ beginning on FD. Similar possibilities exist for type D^- using the lines AG, CH, CEG, or AEH. For type D_S we can choose either those arising from the triangle AEF or from the triangle FCE.

To summarize, the eigenvalue spectra and unirreps of *so*(2, 1) are classified as follows:

$$D^+(k)\begin{cases} q = -k + m, & m = 0, 1, 2, \ldots \\ k < 0 \end{cases} \tag{22a}$$

$$D^-(k)\begin{cases} q = k + m, & m = 0, -1, -2, \ldots \\ k < 0 \end{cases} \tag{22b}$$

$$D_S(Q, q_0)\begin{cases} q = q_0 + m, & m = 0, \pm 1, \pm 2, \ldots \\ Q < |q_0|(|q_0| - 1), & -\frac{1}{2} < q_0 < \frac{1}{2} \end{cases} \tag{22c}$$

$$D_p(Q, q_0)\begin{cases} q = q_0 + m, & m = 0, \pm 1, \pm 2, \ldots \\ Q = -\beta^2 - \frac{1}{4}, & -\frac{1}{2} < q_0 < \frac{1}{2} \end{cases} \tag{22d}$$

In Eqs. (22a) and (22b) we can also use the equivalent unirreps $D^{\pm}(-k-1)$ obtained by replacing k everywhere by $-k-1$.

To complete the unitary representation theory for *so*(2, 1) and *so*(3) it is only necessary to normalize the basis vectors $|kq\rangle$. Thus we define new basis vectors

$$|f^k_q\rangle = N_q|kq\rangle \tag{23}$$

such that

$$\langle f^{k'}_{q'}|f^k_q\rangle = \delta_{k'k}\delta_{q'q}$$

Introducing Eq. (23) into Eq. (17) we obtain

$$J_+|f^k_q\rangle = \gamma(k - q)(N_q/N_{q+1})|f^k_{q+1}\rangle \tag{24a}$$

$$J_-|f^k_q\rangle = (k + q)(N_q/N_{q-1})|f^k_{q-1}\rangle \tag{24b}$$

and the ratios of normalization factors can be obtained by substituting Eq. (23) into

$$\langle f^k_{q+1}|J_+|f^k_q\rangle = \langle f^k_q|J_-|f^k_{q+1}\rangle^* \tag{25}$$

to obtain

$$|N_q/N_{q+1}|^2 = \gamma(k+q+1)/(k^*-q) \tag{26}$$

Since q is always real we can multiply by $(k-q)(k^*-q)$ to obtain

$$|(k-q)N_q/N_{q+1}|^2 = \gamma(k-q)(k+q+1) \tag{27a}$$

Similarly

$$|(k+q)N_q/N_{q-1}|^2 = \gamma(k+q)(k-q+1) \tag{27b}$$

These results are consistent with the fundamental inequalities, Eq. (21). Choosing the positive square root in Eq. (27) we obtain the standard unirreps of $so(2, 1)$ and $so(3)$

$$J^2|kq\rangle = k(k+1)|kq\rangle \tag{28a}$$

$$J_3|kq\rangle = q|kq\rangle \tag{28b}$$

$$J_\pm|kq\rangle = [\gamma(k\mp q)(k\pm q+1)]^{1/2}|k, q\pm 1\rangle \tag{28c}$$

where we have returned to the original notation $|kq\rangle$ rather than $|f^k_q\rangle$, so that from now on all $|kq\rangle$ are orthonormal. We should note that in the case of the principal series, $D_p(Q, q_0)$ of unirreps of $so(2, 1)$, it is consistent to choose $N_q = 1$ for all q in Eq. (24), since the right-hand side of Eq. (26) becomes unity if we make the substitution $k = -\frac{1}{2} + i\beta$.

IV. Representation Theory of *so*(4)

The simplest approach to the matrix representation theory of $so(4)$, the Lie algebra of the rotation group in four dimensions, is to begin with the well-known subalgebra $so(3)$ generated by the three components of the angular momentum $\boldsymbol{J}$. Then we can use the familiar angular momentum basis $|\gamma jm\rangle$, where γ represents any additional quantum numbers necessary to specify the basis. For general representations there will be two such quantum numbers, but for the representations needed to describe hydrogenic states only one additional quantum number (the principle one, n) will be needed. We shall start with a brief summary of the $so(3)$ results and a brief review of the properties of scalar (S) and vector (V) operators with respect to $so(3)$ (Powell and Craseman, 1961; Slater, 1960, Appendix 31). Then we shall obtain the selection rules for their matrix elements and show that the matrix elements of a vector operator can be determined to within certain j-dependent factors by solving a simple pair of difference equations. Then the additional commutation relations needed to make **J**, **V** into a Lie algebra are presented and used to determine these j-dependent factors (Bohm, 1966, 1979; Naimark, 1964).

Thus, we shall obtain the general matrix representation theory of $so(4)$ and also $so(3, 1)$ in a straightforward manner. The requirement that the six generators of these Lie algebras be Hermitian imposes several restrictions on the general representations and will finally give a complete classification of the unirreps of $so(4)$ and $so(3, 1)$. Finally we shall mention two alternative approaches which are simpler but require more advanced aspects of angular momentum theory, since they involve the Wigner–Eckart theorem, Clebsch–Gordan coefficients, and 6-j symbols (Biedenharn and Louck, 1981a,b; Biedenharn, 1961; Wybourne, 1974; Adams *et al.*, 1982).

A. Brief Review of *so*(3)

The three components of the angular momentum $\boldsymbol{J}$ satisfy the commutation relations

$$[J_j, J_k] = i\epsilon_{jkl}J_l \tag{29}$$

where a summation over l is implied. The Levi–Civita symbol ϵ_{jkl} and its properties are defined in Appendix A. The J_i are the generators of the Lie algebra $so(3)$ of the three-dimensional rotation group [cf. Eq. (7) of Section III with $\gamma = 1$]. Introducing the raising and lowering operators $J_\pm = J_1 \pm iJ_2$, the commutation relations, Eq. (29), can be expressed as

$$[J_3, J_\pm] = \pm J_\pm \tag{30}$$

The Casimir operator for $so(3)$ commutes with all generators and is given by $J^2 = J_1^2 + J_2^2 + J_3^2$. The unitary irreducible representations are characterized by a single quantum number $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$, which also includes the spin representations of $su(2)$ corresponding to the special unitary group $SU(2)$ when $j = \frac{1}{2}, \frac{3}{2}, \ldots$, and are given by

$$J^2|jm\rangle = j(j+1)|jm\rangle \tag{31a}$$

$$J_3|jm\rangle = m|jm\rangle \tag{31b}$$

$$J_\pm|jm\rangle = \omega(j, \pm m)|j, m \pm 1\rangle \tag{31c}$$

where

$$\omega(j, m) = [(j+m+1)(j-m)]^{1/2} \tag{32}$$

These are the standard unirreps for which J^2 and J_3 are diagonal on each of the irreducible vector spaces

$$R^j = \{|jm\rangle : m = -j, \ldots, j\} \tag{33}$$

All of these results are well known and are derived in most textbooks on quantum mechanics (see, e.g., Messiah, 1970, Vol. II; Schiff, 1968). They also follow from the results of Section III, setting $k = j$ and $q = m$.

B. *so*(3) Scalar and Vector Operators

An operator S is an $so(3)$ scalar operator if

$$[S, J_i] = 0; \qquad i = 1, 2, 3 \tag{34}$$

This means that S is invariant under rotations. The matrix elements of S are easily obtained using Eq. (34). Thus

$$\langle j'm'|[S, J_3]|jm\rangle = (m - m')\langle j'm'|S|jm\rangle = 0$$

$$\langle j'm'|[S, J^2]|jm\rangle = [j(j+1) - j'(j'+1)]\langle j'm'|S|jm\rangle = 0$$

and therefore $m' = m$, $j' = j$. In fact the matrix elements of S are independent of m. This is easily shown using $[S, J_+] = 0$ and we obtain

$$\langle j'm'|S|jm\rangle = \delta_{j'j}\delta_{m'm}\langle j\|S\|j\rangle \tag{35}$$

where $\langle j\|S\|j\rangle$ is the reduced matrix element.

A vector operator $\boldsymbol{V}$ is called an $so(3)$ vector operator if its components satisfy the commutation relations

$$[J_j, V_k] = i\epsilon_{jkl}V_l; \qquad j, k, l = 1, 2, 3 \tag{36a}$$

which also implies that

$$\mathbf{J} \times \mathbf{V} + \mathbf{V} \times \mathbf{J} = 2i\mathbf{V} \tag{36b}$$

although the converse is not true (Biedenharn and Louck, 1981a; Landau and Lifshitz, 1977).

It is more convenient to work with the operators V_3, $V_\pm = V_1 \pm iV_2$ rather than V_1, V_2, V_3. Then the commutation relations, Eq. (36), can be expressed as

$$\begin{aligned} &[J_+, V_-] = 2V_3, \qquad [J_-, V_+] = -2V_3 \\ &[J_3, V_\pm] = \pm V_\pm, \qquad [J_\pm, V_3] = \mp V_\pm \\ &[J_+, V_+] = [J_-, V_-] = [J_3, V_3] = 0 \end{aligned} \tag{37}$$

We can now work out the following useful relationships involving $\boldsymbol{J}$ and $\boldsymbol{V}$:

$$(\boldsymbol{J} \cdot \boldsymbol{V}) = (\boldsymbol{V} \cdot \boldsymbol{J}) \tag{38a}$$

$$[(\boldsymbol{J} \cdot \boldsymbol{V}), J_i] = 0 \tag{38b}$$

$$[J^2, \boldsymbol{V}] = i(\boldsymbol{V} \times \boldsymbol{J} - \boldsymbol{J} \times \boldsymbol{V}) \tag{38c}$$

$$[J^2, \boldsymbol{J} \times \boldsymbol{V}] = 2i(J^2\boldsymbol{V} - (\boldsymbol{J} \cdot \boldsymbol{V})\boldsymbol{J}) \tag{38d}$$

$$[J^2, [J^2, \boldsymbol{V}]] = 2(J^2\boldsymbol{V} - 2(\boldsymbol{J} \cdot \boldsymbol{V})\boldsymbol{J} + \boldsymbol{V}J^2) \tag{38e}$$

The result, Eq. (38b), shows that $(\boldsymbol{J} \cdot \boldsymbol{V})$ is an $so(3)$ scalar operator so its matrix elements are obtained from Eq. (35). To obtain Eq. (38c) the general operator identity $[AB, C] = A[B, C] + [A, C]B$, the commutation relations, Eq. (36a), and the definition $(\boldsymbol{J} \times \boldsymbol{V})_i = \epsilon_{ijk} J_j V_k$ for the components of a vector product can be used. The result, Eq. (38d), is most easily obtained using the properties of ϵ_{ijk} given in Appendix A. Finally, Eq. (38e) is easily obtained from Eqs. (38c) and (38d). We shall use Eq. (38e) to obtain the j-selection rules for matrix elements of a vector operator.

C. Selection Rules for Vector Operators

Our goal is to calculate the matrix elements of V_3, $V_\pm$. First we determine the selection rules for an $so(3)$ vector operator. The selection rules for m are easily obtained. From $[J_3, V_\pm] = \pm V_\pm$ it follows that

$$(m' - m \mp 1)\langle j'm'|V_\pm|jm\rangle = 0$$

so matrix elements of $V_\pm$ vanish unless $m' = m \pm 1$. Similarly, $[J_3, V_3] = 0$ implies that matrix elements of V_3 vanish unless $m' = m$.

The j-selection rules are more difficult to obtain. The trick is to take matrix elements of the double commutator identity Eq. (38e). Apparently this trick is due to Dirac, Pauli, and Guttinger (see, e.g., Slater, 1960, Appendix 31). Using Eq. (31), the left side of Eq. (38e) can be expressed as

$$\begin{aligned}\langle j'm'|[J^2, [J^2, \boldsymbol{V}]]|jm\rangle &= [j'(j' + 1) - j(j + 1)]\langle j'm'|[J^2, \boldsymbol{V}]|jm\rangle \\ &= [j'(j' + 1) - j(j + 1)]^2\langle j'm'|\boldsymbol{V}|jm\rangle\end{aligned}$$

For the right side of Eq. (38e) we obtain

$$\begin{aligned}&2\langle j'm'|J^2\boldsymbol{V} - 2(\boldsymbol{J} \cdot \boldsymbol{V})\boldsymbol{J} + \boldsymbol{V}J^2|jm\rangle \\ &\quad = 2[j'(j' + 1) + j(j + 1)]\langle j'm'|\boldsymbol{V}|jm\rangle - 4\langle j'm'|(\boldsymbol{J} \cdot \boldsymbol{V})\boldsymbol{J}|jm\rangle\end{aligned}$$

Comparing these results and simplifying the factors involving j, j' we obtain

$$\begin{aligned}[(j'-j)^2-1][(j'+j+1)^2-1]\langle j'm'|\boldsymbol{V}|jm\rangle &= -4\langle j'm'|(\boldsymbol{J} \cdot \boldsymbol{V})\boldsymbol{J}|jm\rangle \\ &= -4\langle j||(\boldsymbol{J} \cdot \boldsymbol{V})||j\rangle\langle j'm'|\boldsymbol{J}|jm\rangle\end{aligned}$$

where the last equation results from the fact that $\boldsymbol{J} \cdot \boldsymbol{V}$ is an $so(3)$ scalar operator. There are two cases to consider:

1. If $j' \neq j$ then $\langle j'm'|\boldsymbol{J}|jm\rangle = 0$ since $\boldsymbol{J}$ cannot change the j quantum number. But $(j' + j + 1)^2 \neq 1$ so we must have $(j' - j)^2 - 1 = 0$, which implies $j' = j \pm 1$.
2. If $j' = j$ we obtain

$$\langle jm'|\boldsymbol{V}|jm\rangle = [j(j + 1)]^{-1}\langle j||\boldsymbol{J} \cdot \boldsymbol{V}||j\rangle\langle jm'|\boldsymbol{J}|jm\rangle$$

This is just the so called vector rule. In general $\langle jm'|V|jm\rangle$ is nonzero unless special properties of V give $\langle j||\boldsymbol{J}\cdot \boldsymbol{V}||j\rangle = 0$ (for example, in the hydrogenic realization considered in Section VII, $\boldsymbol{V}$ is the Runge–Lenz vector and $\boldsymbol{J}\cdot\boldsymbol{V} = 0$).

To summarize, the selection rules for *so*(3) vector operators are

$$\langle j'm'|V|jm\rangle = 0 \qquad \text{unless} \quad j' = j-1, j, j+1 \tag{39a}$$

$$\langle j'm'|V_\pm|jm\rangle = 0 \qquad \text{unless} \quad m' = m \pm 1 \tag{39b}$$

$$\langle j'm'|V_3|jm\rangle = 0 \qquad \text{unless} \quad m' = m \tag{39c}$$

In general, Eq. (39a) holds for any component of V so it also holds for $V_\pm$. Thus, the matrix representation of a component of an *so*(3) vector operator has a particularly simple form.

D. Matrix Representation of *so*(3) Vector Operators

We shall now determine the matrix elements of V_+. Then, using the commutation relations, Eq. (37), we can easily obtain matrix elements of V_3 and V_-. Taking matrix elements of $[J_+, V_+] = 0$ and using $J_+|jm\rangle = \omega(j, m)|j, m+1\rangle$ and its Hermitian conjugate we obtain

$$\omega(j', m')\langle j', m'-1|V_+|jm\rangle = \omega(j, m)\langle j'm'|V_+|j, m+1\rangle$$

From the m-selection rules these V_+ matrix elements vanish unless $m' = m+2$. There are three cases to consider ($j' = j+1, j, j-1$). In case $j' = j+1$ we obtain

$$\frac{\langle j+1, m+1|V_+|jm\rangle}{[(j+m+1)]^{1/2}} = \frac{\langle j+1, m+2|V_+|j, m+1\rangle}{[(j+m+3)]^{1/2}}$$

Dividing both sides by $[j+m+2]^{1/2}$ we conclude that these ratios are independent of m so

$$\langle j+1, m+1|V_+|jm\rangle = -d_j[(j+m+1)(j+m+2)]^{1/2}$$

for some j-dependent factor d_j. Similarly, for $j' = j$ and $j' = j-1$ we obtain

$$\langle j, m+1|V_+|jm\rangle = -a_j[(j-m)(j+m+1)]^{1/2}$$

$$\langle j-1, m+1|V_+|jm\rangle = c_j[(j-m-1)(j-m)]^{1/2}$$

for some j-dependent factors a_j, c_j. Actually only two of the three sets of coefficients a_j, c_j, d_j are needed (Bohm, 1979; Naimark, 1964) since a j-dependent phase change of the basis vectors shows that we can choose

$$d_j = c_{j+1}$$

Thus, for example, we can choose to use a_j, c_j and we shall assume from now on that such a choice of phase has been made. It is now easy to obtain matrix elements of V_3 using $V_3 = -\frac{1}{2}[J_-, V_+]$. Then matrix elements of V_- are obtained using $V_- = [J_-, V_3]$. The results are most conveniently expressed in terms of the action of V_3, $V_\pm$ on the basis vectors

$$V_3|jm\rangle = \alpha(j, m)c_j|j-1, m\rangle - ma_j|jm\rangle + \alpha(j+1, m)c_{j+1}|j+1, m\rangle \tag{40a}$$

$$\begin{aligned} V_+|jm\rangle = {} & \beta(j-1, m)c_j|j-1, m+1\rangle - \omega(j, m)a_j|j, m+1\rangle \\ & - \gamma(j+1, m)c_{j+1}|j+1, m+1\rangle \end{aligned} \tag{40b}$$

$$\begin{aligned} V_-|jm\rangle = {} & -\beta(j-1, -m)c_j|j-1, m-1\rangle - \omega(j, -m)a_j|j, m-1\rangle \\ & + \gamma(j+1, -m)c_{j+1}|j+1, m-1\rangle \end{aligned} \tag{40c}$$

where

$$\alpha(j, m) = [(j-m)(j+m)]^{1/2} \tag{41a}$$

$$\beta(j, m) = [(j-m+1)(j-m)]^{1/2} \tag{41b}$$

$$\gamma(j, m) = [(j+m+1)(j+m)]^{1/2} \tag{41c}$$

$$\omega(j, m) = [(j+m+1)(j-m)]^{1/2} \tag{41d}$$

This is as far as we can go with the representation of vector operators without requiring further properties of $\boldsymbol{V}$ in order to obtain the explicit form of the coefficients a_j and c_j. The additional properties we shall use are the commutation relations needed to make the six components of $\boldsymbol{J}$ and $\boldsymbol{V}$ into the Lie algebra $so(4)$.

E. Matrix Representation Theory of *so*(4) and *so*(3, 1)

To make $\boldsymbol{J}$, $\boldsymbol{V}$ into generators of a Lie algebra we require that the commutators $[V_i, V_j]$ be expressible in terms of J_i and V_i. The possibilities we shall consider are given by

$$[J_j, J_k] = i\epsilon_{jkl}J_l \tag{42a}$$

$$[J_j, V_k] = i\epsilon_{jkl}V_l \tag{42b}$$

$$[V_j, V_k] = i\sigma\epsilon_{jkl}J_l \tag{42c}$$

These are the defining commutation relations for three Lie algebras (depending on the value of σ) since they are closed under commutation. For $\sigma = 1$ we obtain $so(4)$, the Lie algebra of the four-dimensional rotation group. For $\sigma = -1$ the Lie algebra of the homogeneous Lorentz group is obtained (Naimark, 1964) and for $\sigma = 0$ the Lie algebra of the three-dimensional Euclidean group is obtained (Bohm, 1966). In the latter case $\boldsymbol{V}$ can be interpreted as linear momentum. Our primary interest is in $so(4)$ although the representation theory of all three Lie algebras can be obtained in a uniform manner due to the similarity of the commutation relations, Eqs. (42a) and (42b), in all three cases.

The additional commutation relations, Eq. (42c), can be used to determine the coefficients a_j and c_j, Eq. (40). Rewriting them in terms of $V_\pm$ gives

$$[V_3, V_\pm] = \pm\sigma J_\pm \tag{43a}$$

$$[V_+, V_-] = 2\sigma J_3 \tag{43b}$$

In fact we need only consider one of these three commutation relations since using the Jacobi identity (cf. Section II) it can be shown that

$$[V_3, V_-] = \tfrac{1}{2}[[[V_3, V_+], J_-], J_-]$$

$$[V_+, V_-] = [[V_3, V_+], J_-]$$

Thus we consider only the commutation relation $[V_3, V_+] = \sigma J_+$ and apply it to the basis vectors $|jm\rangle$. After some algebra involving the substitution of Eqs. (40a), (40b), and (31), we obtain a linear relationship among several of the $|jm\rangle$. Since these basis vectors are linearly independent we set their coefficients equal to zero and the result is a pair of difference equations which must be satisfied by the coefficients a_j and c_j:

$$[ja_j - (j+2)a_{j+1}]c_{j+1} = 0 \tag{44}$$

$$a_j^2 - (2j+3)c_{j+1}^2 + (2j-1)c_j^2 = \sigma \tag{45}$$

To solve these equations we note that there is a smallest j in the representation space since $j \geq 0$. Therefore

$$j = j_0, j_0 + 1, \ldots \qquad (2j_0 = \text{integer}) \tag{46}$$

From Eq. (40c) we can also assume that

$$c_{j_0} = 0 \tag{47}$$

otherwise $|j_0 - 1, m - 1\rangle$ is in the representation space, a contradiction. In Eq. (44) we now have two possibilities

(a) $c_{j_0} = 0, c_{j_0+1} \neq 0, \ldots, c_{j_0+k} \neq 0, c_{j_0+k+1} = 0$
(b) $c_{j_0} = 0, c_j \neq 0 \qquad$ for all $\quad j > j_0$

It is clear that in case (a) the representations are finite dimensional and in (b) they are infinite dimensional. In either case Eq. (44) is equivalent to

$$ja_j - (j+2)a_{j+1} = 0$$

Multiply by $j+1$ and define $\alpha_j = j(j+1)a_j$ to obtain a simple difference equation $\alpha_j - \alpha_{j+1} = 0$ whose solution is $\alpha_j = \alpha_{j_0} = j_0(j_0+1)a_{j_0}$. Therefore

$$a_j = j_0(j_0+1)a_{j_0}[j(j+1)]^{-1}$$

which can be more conveniently expressed as

$$a_j = j_0\eta[j(j+1)]^{-1}; \qquad j \geq j_0 \tag{48}$$

for some constants j_0 and η. The second difference equation is now easily solved. Multiply it by $2j+1$, define $\tau_j = (2j-1)(2j+1)c_j^2$, and substitute Eq. (48) to obtain

$$\tau_{j+1} - \tau_j = -\sigma[(j+1)^2 - j^2] - j_0^2\eta^2[(j+1)^{-2} - j^{-2}]$$

Now sum from j_0 to $j-1$ to obtain

$$\tau_j - \tau_{j_0} = \sigma[j_0^2 - j^2] + j_0^2\eta^2[j_0^{-2} - j^{-2}]$$

Since $c_{j_0} = 0$ then $\tau_{j_0} = 0$ and we obtain the solution

$$c_j^2 = (j_0^2 - j^2)(\sigma j^2 - \eta^2)[j^2(4j^2-1)]^{-1}; \qquad j \geq j_0 \tag{49}$$

Thus, Eqs. (48) and (49) determine the coefficients a_j and c_j in Eq. (40) and the two parameters j_0, η classify the irreducible representations. They will be finite dimensional only if $\sigma j^2 - \eta^2 = 0$ for some j. For $so(4)$ we have finite dimensional representations if $\eta = \pm(j_0 + k)$, $k = 1, 2, 3, \ldots$ and infinite dimensional ones otherwise. Similarly for $so(3, 1)$ we have finite dimensional irreps only if $\eta = \pm i(j_0 + k)$. If we denote the irreps by $R(j_0, \eta)$ and the basis vectors by $|(j_0\eta)jm\rangle$, then in either case the reduction under the action of the $so(3)$ generators is

$$R(j_0, \eta) \xrightarrow[so(3)]{} R^{j_0} \oplus R^{j_0+1} \oplus \cdots$$

with a finite or infinite direct sum as the case may be. In terms of matrices this means that each $so(3)$ generator has a block diagonal matrix structure and each block is one of the $so(3)$ representation matrices.

F. Unitary Representations of *so*(4) and *so*(3, 1)

We are primarily interested in the unitary irreducible representations (cf. Section III). In this case the generators J_i and V_i must be Hermitian ($J_i^\dagger = J_i$, $V_i^\dagger = V_i$). As in the $so(2, 1)$ case this imposes restrictions on the types of irreps we have obtained in the general case. Since V_3 is Hermitian then

$$\langle jm|V_3|jm\rangle = \langle jm|V_3^\dagger|jm\rangle$$

so from Eq. (40a), a_j must be real. Similarly

$$\langle j-1, m|V_3|jm\rangle = \langle j-1, m|V_3^\dagger|jm\rangle$$

so c_j must be real ($c_j^* = c_j$). Therefore in Eqs. (48) and (49), η must be real (unless $j_0 = 0$) and $c_j^2 > 0$.

For $so(4)$ this means that $j^2 - \eta^2 < 0$ so the j values are bounded above and only finite-dimensional unirreps are possible. We can let

$$\eta = |j_0| + k; \qquad k = 1, 2, 3, \ldots \tag{50}$$

and assume that j_0 can have either sign. Then the permissible values of j are

$$j = |j_0|, |j_0| + 1, \ldots, \eta - 1 \tag{51}$$

Substituting into Eq. (40) we finally obtain the standard form for unirreps of $so(4)$:

$$V_3|\gamma jm\rangle = \alpha(j, m)c_j^\gamma|\gamma, j-1, m\rangle - ma_j^\gamma|\gamma\, jm\rangle + \alpha(j+1, m)c_{j+1}^\gamma|\gamma, j+1, m\rangle \tag{52a}$$

$$V_+|\gamma jm\rangle = \beta(j-1, m)c_j^\gamma|\gamma, j-1, m+1\rangle - \omega(j, m)a_j^\gamma|\gamma, j, m+1\rangle - \gamma(j+1, m)c_{j+1}^\gamma|\gamma, j+1, m+1\rangle \tag{52b}$$

$$V_-|\gamma jm\rangle = -\beta(j-1, -m)c_j^\gamma|\gamma, j-1, m-1\rangle - \omega(j, -m)a_j^\gamma|\gamma, j, m-1\rangle + \gamma(j+1, -m)c_{j+1}^\gamma|\gamma, j+1, m-1\rangle \tag{52c}$$

where

$$a_j^\gamma = a_j^{(j_0\eta)} = j_0\eta[j(j+1)]^{-1} \tag{53a}$$

$$c_j^\gamma = c_j^{(j_0\eta)} = [(j^2 - j_0^2)(\eta^2 - j^2)]^{1/2}[j^2(4j^2-1)]^{-1/2} \tag{53b}$$

We should also note that the two values $\pm j_0$ give the same j spectrum, Eq. (51), but correspond to inequivalent unirreps since the coefficients a_j^γ will have opposite signs.

For $so(3, 1)$ we can proceed in a similar manner (Naimark, 1964) using $\eta^2 + j^2 > 0$ and η real if $j_0 \neq 0$. There are two cases: (a) if $j_0 \neq 0$ then η is an arbitrary real number and the c_j are all nonzero for $j > j_0$. This gives a class of infinite dimensional unirreps ($j_0 = 0$, η real can also be included here); (b) if $j_0 = 0$ then $\eta = i\beta$, where $-1 < \beta < 1$. Negative values of β give unirreps equivalent to the ones with positive values of β so only the nonnegative values need be considered. Also, j can have only integral values and only infinite dimensional unirreps are obtained.

Thus, we obtain only finite dimensional unirreps for $so(4)$ and only infinite dimensional ones for $so(3, 1)$. For our applications to perturbation theory we shall only need the so called hydrogenic case (cf. Section VII) where V is the Laplace–Runge–Lenz vector. For the realization of the generators in this manner we shall show that $j_0 = 0$ and η is the principal quantum number. The unirreps of $so(3, 1)$ may be of interest in scattering problems which deal with the continuum states of the hydrogen atom.

G. Casimir Operators for *so*(4) and *so*(3, 1)

The Casimir operators of a Lie algebra are important since they commute with all generators and can therefore be simultaneously diagonalized. The Casimir operators for $so(4)$ or $so(3, 1)$ are given by

$$C_1 = \sigma J^2 + V^2 \tag{54}$$

$$C_2 = (V \cdot J) = (J \cdot V) \tag{55}$$

It is easily shown that $[C_i, J_j] = [C_i, V_j] = 0$. They can be expressed in terms of $J_\pm$, $V_\pm$:

$$C_1 = \sigma J_+ J_- + V_+ V_- + V_3^2 + \sigma J_3(J_3 - 2)$$

$$C_2 = \tfrac{1}{2}(V_+ J_- + V_- J_+) + V_3 J_3$$

Then, using Eqs. (40) and (31a)

$$C_1 |jm\rangle = [(j+1)^2 a_j^2 + (4j^2 - 1)c_j^2 + \sigma(j^2 - 1)] |jm\rangle$$

$$C_2 |jm\rangle = -j(j+1)a_j |jm\rangle$$

Substituting the explicit results, Eqs. (48) and (49), we obtain

$$C_1 |\gamma jm\rangle = (\sigma j_0^2 + \eta^2 - \sigma) |\gamma jm\rangle \tag{56}$$

$$C_2 |\gamma jm\rangle = -j_0 \eta |\gamma jm\rangle \tag{57}$$

We shall use these results in Section VII to obtain the Bohr formula for the energy levels of the hydrogen atom.

H. Wigner–Eckart Theorem

The Wigner–Eckart theorem (Biedenharn and Louck, 1981a, p. 96) can be used to obtain Eq. (40) directly. According to this theorem the matrix elements in an angular momentum basis of a spherical tensor operator $V_q^{(k)}$ ($q = -k, -k+1, \ldots, k$) have a particularly simple structure given by[3]

$$\langle j'm' | V_q^{(k)} | jm \rangle = \langle jmkq | j'm' \rangle \langle j' \| V^{(k)} \| j \rangle \tag{58}$$

in terms of Clebsch–Gordan (CG) coefficients and reduced matrix elements. The so called geometrical part of the matrix element, depending on m', q, m, is given entirely by the CG coefficient. Thus properties of CG coefficients immediately give the selection rules $j' = |j - k|, \ldots, j + k$ and $m' = m + q$ for nonvanishing matrix elements. For a vector operator $k = 1$ and

$$\langle j'm' | V_q^{(1)} | jm \rangle = \langle jm1q | j'm' \rangle \langle j' \| V \| j \rangle, \tag{59}$$

where the spherical components of V are

$$V_{\pm 1}^{(1)} = \mp (2)^{-1/2} V_\pm, \qquad V_0^{(1)} = V_3 \tag{60}$$

Thus they are simply related to the components V_3, $V_\pm$ we have used previously. The CG coefficients in Eq. (59) are easily evaluated and essentially give the factors defined in Eq. (41), and the coefficients a_j, c_j, d_j introduced

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[3] Note that in atomic physics one often employs a different phase and normalization convention in defining the reduced matrix elements (see, e.g., Schiff, 1968, p. 223; Lindgren and Morrison, 1982, p. 41; Messiah, 1970, Vol. II, p. 1076 and others).

earlier are now given in terms of reduced matrix elements by

$$c_j = -\langle j-1\|V\|j\rangle[j(2j+1)]^{-1/2}$$
$$a_j = -\langle j\|V\|j\rangle[j(j+1)]^{-1/2}$$
$$d_j = -\langle j+1\|V\|j\rangle[(j+1)(2j+1)]^{-1/2}$$

As before we can show that $d_j = c_{j+1}$ can be assumed and we can solve the difference equations (44) and (45). Thus, the advantage in using the Wigner–Eckart theorem is the simple derivation of selection rules and the representation of a vector operator by Eq. (52).

I. Coupling Problem for *so*(4)

An even simpler approach is possible for *so*(4) that avoids the solution of difference equations and gives the matrix representation, Eqs. (52) and (53), directly in terms of 6-j symbols, which can be easily evaluated (Biedenharn and Louck, 1981b). If we define

$$\boldsymbol{M} = \tfrac{1}{2}(\boldsymbol{J} + \boldsymbol{V}) \tag{61a}$$

$$\boldsymbol{N} = \tfrac{1}{2}(\boldsymbol{J} - \boldsymbol{V}) \tag{61b}$$

then the defining commutation relations, Eq. (42), in the *so*(4) case can be expressed as

$$[M_j, M_k] = i\epsilon_{jkl}M_l \tag{62a}$$

$$[N_j, N_k] = i\epsilon_{jkl}N_l \tag{62b}$$

$$[M_j, N_k] = 0 \tag{62c}$$

Thus, $\boldsymbol{M}$ and $\boldsymbol{N}$ are two commuting angular momenta and $so(4) = so(3) \oplus so(3)$. Also, from Eq. (61)

$$\boldsymbol{J} = \boldsymbol{M} \oplus \boldsymbol{N} \tag{63}$$

and we can obtain the representation of *so*(4) by coupling the two angular momenta and finding the matrix elements of $J_\pm$, J_3, $V_\pm$, V_3 in the coupled basis using CG coefficients to relate the coupled basis to the uncoupled one.

The uncoupled basis is given by

$$|j_1m_1j_2m_2\rangle = |j_1m_1\rangle \otimes |j_2m_2\rangle$$

where

$$M^2|j_1m_1j_2m_2\rangle = j_1(j_1+1)|j_1m_1j_2m_2\rangle$$
$$M_3|j_1m_1j_2m_2\rangle = m_1|j_1m_1j_2m_2\rangle$$
$$N^2|j_1m_1j_2m_2\rangle = j_2(j_2+1)|j_1m_1j_2m_2\rangle$$
$$N_3|j_1m_1j_2m_2\rangle = m_2|j_1m_1j_2m_2\rangle$$

The coupled basis is defined in terms of CG coefficients by

$$|[j_1 j_2]jm\rangle = \sum_{\substack{m_1, m_2 \\ m_1 + m_2 = m}} \langle j_1 m_1 j_2 m_2 | jm \rangle | j_1 m_1 j_2 m_2 \rangle \tag{64}$$

where

$$j = |j_1 - j_2|, \ldots, j_1 + j_2; \qquad m = -j, \ldots, j$$

With respect to this basis $\boldsymbol{M}$ and $\boldsymbol{N}$ are vector operators so from the Wigner–Eckart theorem

$$\langle \gamma' j' m' | M_q^{(1)} | \gamma j m \rangle = \langle j m 1 q | j' m' \rangle \langle \gamma' j' \| \boldsymbol{M} \| \gamma j \rangle$$

Because of Eq. (63) we can evaluate the reduced matrix elements explicitly in terms of 6-j symbols (see, e.g., Biedenharn and Louck, 1981a, p. 103):

$$\begin{aligned} \langle \gamma' j' \| \boldsymbol{M} \| \gamma j \rangle &= \delta_{j_1' j_1} \delta_{j_2' j_2} (-1)^{j_1 + j_2 + j + 1} \\ &\quad \times [(2j+1)(2j'+1) j_1 (j_1+1)(2j_1+1)]^{1/2} \begin{Bmatrix} j' & j & 1 \\ j_1 & j_1 & j \end{Bmatrix} \end{aligned} \tag{65}$$

The matrix elements of $V_\pm$, V_3 can now be calculated using Eq. (60) and $\boldsymbol{V} = 2\boldsymbol{M} - \boldsymbol{J}$. Thus, we can directly derive Eqs. (52) and (53) if we make the connection

$$j_0 = j_1 - j_2 \tag{66a}$$

$$\eta = j_1 + j_2 + 1 \tag{66b}$$

between the parameter sets (j_0, η) and (j_1, j_2) used in the two approaches [Biedenharn (1961) uses $p = j_1 + j_2$ and $q = j_1 - j_2$ to describe unirreps of $so(4)$].

V. Realizations of *so*(2, 1)

In order to apply the representation theory of $so(2, 1)$ to physical problems we need to obtain realizations of the $so(2, 1)$ generators in either coordinate or momentum space. For our purposes the realizations in three-dimensional coordinate space are more suitable so we shall only consider them (for N-dimensional realizations, see Cizek and Paldus, 1977, and references therein). First we shall show how to build realizations in terms of the radial distance and momentum operators, r, p_r. These realizations are sufficiently general to express the radial parts of the Hamiltonians we shall consider linearly in the $so(2, 1)$ generators. Then we shall obtain the corresponding realizations of the $so(2, 1)$ unirreps which are bounded from below. The basis functions of the representation space are simply related to associated Laguerre polynomials. For finding the eigenvalue spectra it is not essential to obtain these explicit realizations of the basis functions, since all matrix elements can be calculated in a purely algebraic manner. In order that the $so(2, 1)$ generators be Hermitian it is necessary to introduce the so called "$1/r$ scalar product" rather than the usual one. Next we shall consider noncanonical scaling transformations (Zaitsev, 1969) in coordinate space and show how they can be obtained via the $so(2, 1)$ generators. Finally we shall use these transformations to show that $so(2, 1)$ is a spectrum-generating algebra for a class of second-order differential equations. In the next section we shall show that several important Hamiltonian eigenvalue problems belong to this class.

A. Realizations in Coordinate Space

The radial distance and momentum operators satisfy the simple commutation relation[4]

$$[r, p_r] = i \tag{67}$$

where

$$r = [x^2 + y^2 + z^2]^{1/2} \tag{68a}$$

$$p_r = -i\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) = -ir^{-1}\frac{\partial}{\partial r}r = r^{-1}[(\boldsymbol{r}\cdot\boldsymbol{p}) - i] \tag{68b}$$

We need to construct three operators in terms of r and p_r which satisfy $so(2, 1)$-defining commutation relations [cf. Eq. (7) for $\gamma = -1$]

$$[T_1, T_2] = -iT_3 \tag{69a}$$

$$[T_2, T_3] = iT_1 \tag{69b}$$

$$[T_3, T_1] = iT_2 \tag{69c}$$

A pedagogical approach in N-dimensional coordinate space has been given earlier (Cizek and Paldus, 1977), so we shall simply sketch the details in case $N = 3$.

The three operators r, rp_r, rp_r^2 satisfy the commutation relations (cf. Section Addendum, C)

$$[r, rp_r] = ir \tag{70a}$$

$$[rp_r, rp_r^2] = irp_r^2 \tag{70b}$$

$$[rp_r^2, r] = -2irp_r \tag{70c}$$

Thus, they are closed under commutation and form a three-dimensional Lie algebra. By taking the appropriate linear combinations of these operators we can obtain operators satisfying the $so(2, 1)$ defining commutation relations,

---

[4] $h/2\pi = 1$.

Eq. (69). The linear combinations

$$T_1 = \tfrac{1}{2}(rp_r^2 - r) \tag{71a}$$

$$T_2 = rp_r \tag{71b}$$

$$T_3 = \tfrac{1}{2}(rp_r^2 + r) \tag{71c}$$

give a realization of the $so(2, 1)$ generators. For our purposes this realization is not general enough. Recalling that

$$p^2 = p_r^2 + L^2 r^{-2} \tag{72}$$

where L^2 is the square of the orbital angular momentum, Eq. (71) can be expressed in the form

$$T_1 = \tfrac{1}{2}(rp^2 - L^2 r^{-1} - r) \tag{73a}$$

$$T_2 = rp_r \tag{73b}$$

$$T_3 = \tfrac{1}{2}(rp^2 - L^2 r^{-1} + r) \tag{73c}$$

However L^2, which is r independent, commutes with p^2, p_r^2, and functions of r. It could thus be replaced by a constant and we will still have a realization of $so(2, 1)$. For convenience we replace L^2 by $L^2 - \xi$ to obtain

$$T_1 = \tfrac{1}{2}(rp_r^2 + \xi r^{-1} - r) \tag{74a}$$

$$T_2 = rp_r \tag{74b}$$

$$T_3 = \tfrac{1}{2}(rp_r^2 + \xi r^{-1} + r) \tag{74c}$$

This realization is general enough for our purposes. Further generalizations are possible (cf. Cizek and Paldus, 1977; Barut and Bornzin, 1971), namely

$$T_1 = \tfrac{1}{2}[w^{-2} r^{2-w} p_r^2 + \xi r^{-w} - r^w] \tag{75a}$$

$$T_2 = w^{-1}[rp_r - i(w - 1)/2] \tag{75b}$$

$$T_3 = \tfrac{1}{2}[w^{-2} r^{2-w} p_r^2 + \xi r^{-w} + r^w] \tag{75c}$$

where $w = 1, 2, 3, \ldots$ and Eq. (74) is just a special case when $w = 1$. The realization for $w = 2$ is useful for the treatment of the isotropic harmonic oscillator-type Hamiltonians which we shall briefly consider in the next section (Wybourne, 1974; Cizek and Paldus, 1977; Fernandez and Castro, 1984).

B. Unirreps in Coordinate Space

For our applications we need the unirreps of $so(2, 1)$ from Section III which have the T_3 eigenvalue spectrum bounded from below. Thus we shall consider unirreps of type $D^+(-k - 1)$ defined by [cf. Eq. (28), $\gamma = -1$ and make the replacement $J \to T$]

$$T^2|kq\rangle = k(k+1)|kq\rangle \tag{76a}$$

$$T_3|kq\rangle = q|kq\rangle \tag{76b}$$

$$T_\pm|kq\rangle = [-(k \mp q)(k \pm q + 1)]^{1/2}|k, q \pm 1\rangle \tag{76c}$$

$$q = k + 1 + \mu; \qquad \mu = 0, 1, 2, \ldots; \qquad k > -1 \tag{76d}$$

where the basis vectors $|kq\rangle$ form an orthonormal set with respect to a suitably chosen scalar product. We also require that the $so(2, 1)$ generators T_i be Hermitian with respect to this scalar product.

In order to show that an operator X is Hermitian it is sufficient that it has real expectation values:

$$\langle f|X|f\rangle - \langle f|X|f\rangle^* = 0 \tag{77}$$

for the chosen scalar product, where the asterisk denotes complex conjugation. It can be shown (Messiah, 1970, Vol. I, p. 346) that the radial momentum operator p_r is Hermitian with respect to the usual scalar product

$$\langle f, g\rangle = \int_0^\infty f^*(r)g(r)r^2\,dr \tag{78}$$

arising from the radial part of a wave function in the three-dimensional spherical coordinate system we are using, if the class of functions $f(r)$ in Eqs. (77) and (78) satisfy

$$\lim_{r\to 0} rf(r) = \lim_{r\to\infty} rf(r) = 0$$

since

$$\langle f, p_r f\rangle - \langle f, p_r f\rangle^* = -i\int_0^\infty \frac{d}{dr}|rf(r)|^2\,dr$$

It is interesting to note that even though p_r is Hermitian it has no square integrable eigenfunctions.

If we apply the same analysis to the $so(2, 1)$ generator T_2, Eq. (75b), we find that it is not Hermitian with respect to the usual scalar product unless $w = 2$. However, if we define a new scalar product by

$$\langle f|g\rangle = \int_0^\infty f^*(r)g(r)r^w\,dr \tag{79}$$

then T_2 is Hermitian with respect to it since

$$\langle f|T_2|f\rangle - \langle f|T_2|f\rangle^* = -\frac{i}{w}\int_0^\infty \frac{d}{dr}|r^{(w+1)/2}f(r)|^2\,dr$$

which is zero for suitable boundary conditions on the function $f(r)$. In the important case $w = 1$ this is often called the "$1/r$ scalar product" since the integrand of the usual scalar product is multiplied by $1/r$ to obtain it.

In a similar manner we can show that the generators T_1 and T_3 are Hermitian with respect to the same scalar product, Eq. (79). Only the generator T_3 has square integrable eigenfunctions and this is the reason why we chose to diagonalize T^2 and T_3 in our study of the representation theory of $so(2, 1)$ (the notation J^2, J_3 was used in Section III).

If X is any $so(2, 1)$ generator we can define its matrix elements by

$$\langle f|X|g\rangle = \int_0^\infty f^*(r)Xg(r)r^w\,dr \tag{80}$$

The Casimir operator T^2 and the raising and lowering operators $T_\pm$ can be expressed explicitly as [cf. Eq. (8)]

$$\begin{aligned} T^2 &= T_3^2 - T_1^2 - T_2^2 \\ &= (T_3 - T_1)(T_3 + T_1) - [T_3, T_1] - T_2^2 \\ &= \xi + \frac{1 - w^2}{4w^2} = \xi + W(W - 1), \end{aligned} \tag{81}$$

$$T_\pm = T_3 \pm W - r^w \pm w^{-1} r \frac{\partial}{\partial r} \tag{82a}$$

where

$$W = (w + 1)/2w \tag{82b}$$

As expected, the Casimir operator reduces to a constant (operator).

The eigenvalues q in Eq. (76b) are related to the parameters ξ and w by

$$k(k + 1) = \xi + W(W - 1); \qquad k > -1 \tag{83a}$$

$$q = k + 1 + \mu; \qquad \mu = 0, 1, 2, \ldots \tag{83b}$$

so the lowest eigenvalue of T_3 is

$$q_0 = k + 1 = \tfrac{1}{2}\{1 \pm [4\xi + (2W - 1)^2]^{1/2}\} \tag{83c}$$

The generator T_3 can be expressed as the second-order differential operator

$$T_3 = -\frac{1}{2w^2} r^{2-w}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\xi}{2r^w} + \frac{r^w}{2} \tag{84}$$

and the eigenvalue problem, Eq. (76b), could be solved by the standard textbook methods using series solutions to obtain explicit forms for the basis functions $|kq\rangle$ of the $so(2, 1)$ representation. In the algebraic appraoch it is not necessary to obtain any of these explicit solutions in order to calculate matrix elements, since by expressing the operators whose matrix elements are desired in terms of $so(2, 1)$ generators, we can use Eq. (76) to calculate the matrix elements. If explicit solutions to Eq. (76b) are desired they are most easily obtained using the raising and lowering operators $T_\pm$ in the following manner.

Since $|k, k+1\rangle$ is the eigenfunction of T_3 having the lowest eigenvalue it follows that

$$T_-|k, k+1\rangle = 0 \tag{85}$$

Substituting Eq. (82) and replacing T_3 by its eigenvalue $k+1$ we obtain a separable first-order differential equation which is easily solved to give

$$f_{k,k+1}(r) \equiv |k, k+1\rangle = c_w r^{w(k+1-W)} e^{-r^w} \tag{86}$$

The normalization constant c_w is obtained by using Eq. (79) ($\langle f|f\rangle = 1$):

$$c_w = w^{1/2}2^{k+1}[(2k+1)!]^{-1/2} \tag{87}$$

Now we can apply the raising operator T_+ successively to this solution to obtain the explicit form of any T_3 eigenfunction. From Eq. (76) it follows that

$$\begin{gathered}|kq\rangle = c_{kq}(T_+)^{q-k-1}|k, k+1\rangle \\ c_{kq} = [(q-1-k)!(q+k)!/(2k+1)!]^{-1/2} \\ |kq\rangle = c_{kq}\left[\prod_{j=1}^{q-k-1}\left(q - j + W - r^w + \frac{r}{w}\frac{d}{dr}\right)\right] f_{k,k+1}(r)\end{gathered} \tag{88}$$

where the factors are written in the order for which j increases from left to right. These factors can be simplified with the operator identity

$$e^{-r^w}\left(\frac{r}{w}\cdot\frac{d}{dr}\right) = \left[\frac{r}{w}\cdot\frac{d}{dr} + r^w\right]e^{-r^w}$$

to push the exponential factors through each factor from left to right:

$$|kq\rangle = c_{kq}e^{r^w}\left[\prod_{j=1}^{q-k-1}\left(q - j + W + \frac{r}{w}\frac{d}{dr}\right)\right]e^{-r^w}f_{k,k+1}(r)$$

Substituting $\rho = r^w$, reversing the order of the factors since they now commute, and using the operator identity

$$\rho^\alpha\left(\alpha + 1 + \rho\frac{d}{d\rho}\right) = \frac{d}{d\rho}\rho^{\alpha+1}$$

we obtain

$$|kq\rangle = c_w c_{kq} e^\rho \rho^{-k-W}\left(\frac{d}{d\rho}\right)^{q-k-1}\rho^{q+k}e^{-2\rho}$$

Finally, using the Rodrigues formula for associated Laguerre polynomials (cf. Abramowitz and Stegun, 1965; Powell and Craseman, 1961)

$$L_{q-k-1}^{(2k+1)}(\rho) = [(q-k-1)!]^{-1} e^{\rho} \rho^{-2k-1} \left(\frac{d}{d\rho}\right)^{q-k-1} \rho^{q+k} e^{-\rho}$$

we obtain

$$|kq\rangle = N_{kq} e^{-r^w} (2r^w)^{k-W+1} L_{q-k-1}^{(2k+1)}(2r^w) \tag{89a}$$

$$N_{kq} = w^{1/2} 2^W [(q-k-1)!/(q+k)!]^{1/2} \tag{89b}$$

C. Transformation of Operators and Functions

In order to apply the *so*(2, 1) unirreps to physical problems we need to use scaling transformations. An operator T_S effects a scaling transformation on a function $f(r)$ if

$$\tilde{f}(r) = T_S f(r) = f(\lambda r); \qquad \lambda > 0 \tag{90}$$

It is convenient to let

$$\lambda = e^{\alpha} \tag{91}$$

so that α can be any real number. Corresponding to these transformations we have scaling transformations of operators X defined by

$$\tilde{X} = T_S X T_S^{-1} \tag{92}$$

These scaling transformations can be defined in terms of the *so*(2, 1) generator T_2. In fact, expanding $f(e^{\alpha} r)$ in a Taylor series in α about $\alpha = 0$ and using $d/d\alpha = r\, d/dr$ it can be shown that (Schiff, 1968)

$$e^{\alpha r\, d/dr} f(r) = f(e^{\alpha} r)$$

Using the explicit realization, Eqs. (68b) and (75b), it follows that

$$e^{i\alpha T_2} f(r) = e^{\alpha W} f(e^{\alpha/w} r) \tag{93}$$

so scaling transformations are essentially generated by $e^{i\alpha T_2}$.

From Eq. (92) we obtain the operator transformations

$$\tilde{X} = e^{i\alpha T_2} X e^{-i\alpha T_2}. \tag{94}$$

Using the operator identity Eq. (A.16), a number of useful scaling transformations can be derived:

$$\tilde{r} = e^{\alpha/w} r \tag{95}$$

$$\tilde{p}_r = e^{-\alpha/w} p_r, \qquad \tilde{\mathbf{p}} = e^{-\alpha/w} \mathbf{p} \tag{96}$$

$$\tilde{T}_3 = T_3 \cosh \alpha - T_1 \sinh \alpha \tag{97}$$

Note that Eqs. (95) and (96) are realization dependent since they depend on w, whereas Eq. (97) is a general result depending only on the $so(2, 1)$ commutation relations.

D. *so*(2, 1) as a Spectrum-Generating Algebra

Let us consider the class of second-order differential equations

$$[\tfrac{1}{2}w^{-2}p_r^2 + \tfrac{1}{2}\xi r^{-2} - \eta r^{w-2} - \tau r^{2w-2}]R(r) = 0 \tag{98}$$

For $w = 1$ or 2 they have the general form of a radial eigenvalue problem arising from some Hamiltonian. In fact, the radial parts of the nonrelativistic hydrogenic Hamiltonian, Klein–Gordon, and second-order iterated Dirac Hamiltonians with $1/r$ potential can all be expressed in this form for $w = 1$ and suitable choices of the parameters ξ, η, τ. Similarly, the three-dimensional isotropic harmonic oscillator radial equation has this form for $w = 2$.

If we multiply Eq. (98) on the left by $2r^{2-w}$ and use Eq. (75) we obtain an equation which is linear in T_1 and T_3:

$$[(1 + 2\tau)T_1 + (1 - 2\tau)T_3 - 2\eta]R(r) = 0 \tag{99}$$

Since we can solve the T_3 eigenvalue problem we can solve Eq. (99) if T_1 can be eliminated. We can write Eq. (99) in the form

$$[T_1 \sinh\alpha + T_3 \cosh\alpha - 2\eta(-8\tau)^{-1/2}]R(r) = 0$$

where

$$\sinh\alpha = (1 + 2\tau)(-8\tau)^{-1/2} \tag{100a}$$

$$\cosh\alpha = (1 - 2\tau)(-8\tau)^{-1/2} \tag{100b}$$

Then using Eq. (97)

$$[e^{-i\alpha T_2}T_3 e^{i\alpha T_2} - 2\eta(-8\tau)^{-1/2}]R(r) = 0$$

or

$$e^{-i\alpha T_2}[T_3 - 2\eta(-8\tau)^{-1/2}]e^{i\alpha T_2}R(r) = 0$$

and we obtain the T_3 eigenvalue problem

$$[T_3 - \eta(-2\tau)^{-1/2}]\tilde{R}(r) = 0 \tag{101}$$

where

$$\tilde{R}(r) = R(e^{\alpha/w}r) = e^{-\alpha W}e^{i\alpha T_2}R(r) \tag{102}$$

and the scaling parameter is given from Eq. (100) by

$$\lambda = e^{\alpha} = (-2\tau)^{-1/2} \tag{103}$$

The T_3 eigenvalues are given by Eq. (83) with

$$q = \eta\lambda \tag{104}$$

and the eigenvalues of the original differential equation (98) are given by

$$\tau = -\tfrac{1}{2}\eta^2 q^{-2}; \qquad w = 1 \tag{105}$$

$$\eta = q\lambda^{-1}; \qquad w = 2 \tag{106}$$

Finally, the T_3 eigenfunctions are given by Eq. (89) with

$$\tilde{R}_{kq}(r) = N_{kq} e^{-r^w}(2r^w)^{k-W+1} L_{q-k-1}^{(2k+1)}(2r^w) \tag{107}$$

and the eigenfunctions of Eq. (98) are

$$R_{kq}(r) = ce^{-i\alpha T_2}\tilde{R}_{kq}(r) \tag{108}$$

where the constant c is included since the exponential transformation is nonunitary for $w \neq 2$. It is determined by normalizing Eq. (108) with respect to the usual scalar product, Eq. (78). In case $w = 1$ we obtain

$$\begin{aligned} 1 = \langle R_{kq}, R_{kq}\rangle &= c^2 e^{\alpha}\langle \tilde{R}_{kq}|r|\tilde{R}_{kq}\rangle \\ &= c^2 e^{\alpha}\langle \tilde{R}_{kq}|T_3 - T_1|\tilde{R}_{kq}\rangle \\ &= c^2 e^{\alpha} < \tilde{R}_{kq}|T_3|\tilde{R}_{kq}\rangle = c^2\lambda q \end{aligned}$$

Thus

$$c = (\lambda q)^{-1/2}; \quad w = 1 \tag{109a}$$

$$c = 1; \qquad w = 2 \tag{109b}$$

and the eigenfunctions of Eq. (98) are

$$R_{kq}(r) = c\lambda^{-W}\tilde{R}_{kq}(r\lambda^{-1/w}) \tag{110}$$

$$= c\lambda^{-W} N_{kq} e^{-r^w\lambda^{-1}}(2r^w\lambda^{-1})^{k-W+1} L_{q-k-1}^{(2k+1)}(2r^w\lambda^{-1}) \tag{111}$$

The scaling transformation which converts Eq. (98) to Eq. (101) can be introduced in a simpler manner from the passive viewpoint by using two coordinate systems: the physical coordinate system, defined by r, p_r, and a scaled coordinate system (Cizek and Paldus, 1977). The details are given in Appendix B, Section XIII.

VI. Application of *so*(2, 1) to Physical Systems

In this section we shall apply the realizations of *so*(2, 1) to physical systems, such as the nonrelativistic Coulomb problem, the three-dimensional isotropic harmonic oscillator, Schrödinger's relativistic equation (Klein–Gordon equation), and several forms of the Dirac equation with Coulomb potential (Barut, 1971; Barut and Bornzin, 1971; Bacry and Richard, 1967; Cizek and Paldus, 1977; Lánik, 1969). The s-states for the three-dimensional Morse potential can also be treated using $so(2, 1)$ (Wybourne, 1974), although we shall not consider this problem here.

In the preceding section we found the eigenvalues and eigenfunctions of a class of second-order differential equations by algebraic methods. Since the radial parts of the above-mentioned physical systems belong to this class we simply need to identify the parameters ξ, η, τ in each case and we have solved all these problems in a uniform manner. This illustrates the power of algebraic methods and the use of $so(2, 1)$ as a spectrum-generating algebra. In fact, for our applications to perturbation theory, we do not need to know the explicit forms of the eigenfunctions since the representation of $so(2, 1)$ allows us to calculate any desired matrix elements.

A. Nonrelativistic Hydrogenic Hamiltonian

In atomic units the Hamiltonian for the nonrelativistic Coulomb problem with nuclear charge Z is given by

$$\begin{aligned} H &= \tfrac{1}{2}p^2 - Zr^{-1} \\ &= \tfrac{1}{2}p_r^2 + \tfrac{1}{2}L^2r^{-2} - Zr^{-1} \end{aligned} \tag{112}$$

where L is the orbital angular momentum and r, p_r are defined in Eq. (68). Separating variables and replacing L^2 by its eigenvalue $l(l + 1)$, we obtain the radial eigenvalue equation

$$[\tfrac{1}{2}p_r^2 + \tfrac{1}{2}l(l + 1)r^{-2} - Zr^{-1} - E]R(r) = 0 \tag{113}$$

where the complete wave functions are given in terms of normalized spherical harmonics by

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi) \tag{114}$$

Equation (113) has the form of Eq. (98) if we put

$$w = 1, \qquad \xi = l(l + 1), \qquad \eta = Z, \qquad \tau = E \tag{115}$$

From Eq. (105) the energy eigenvalues are given by

$$E_q = -\tfrac{1}{2}Z^2q^{-2} \tag{116}$$

where $q = q_0 + \mu$; $\mu = 0, 1, 2, \ldots$ [cf. Eq. (76d)], and the lowest value of q is given by Eq. (83c) using the upper sign:

$$q_0 = k + 1 = l + 1 \tag{117}$$

Thus, we can identify q with the principal quantum number n to obtain the usual Bohr formula

$$E_n = -\tfrac{1}{2}Z^2 n^{-2}; \qquad n = 1, 2, 3, \ldots \tag{118}$$

Using l, n instead of k, q, the normalized T_3 eigenfunctions are given by Eqs. (89b) and (107):

$$\tilde{R}_{ln}(r) = N_{ln} e^{-r}(2r)^l L_{n-l-1}^{(2l+1)}(2r) \tag{119}$$

and from Eqs. (108) and (109a) the usual radial eigenfunctions are ($\lambda = nZ^{-1}, \quad w = 1, \quad W = 1$)

$$\begin{aligned} R_{ln}(r) &= Z^{3/2} n^{-2} \tilde{R}_{ln}(Zrn^{-1}) \\ &= Z^{3/2} n^{-2} N_{nl} e^{-Zrn^{-1}} (2Zrn^{-1})^l L_{n-l-1}^{(2l+1)}(2Zrn^{-1}) \end{aligned} \tag{120}$$

The same result follows directly from Eq. (111) since $\lambda = n/Z$.

There is a significant difference between these usual eigenfunctions and the T_3 eigenfunctions when we consider perturbation theory problems for bound states. Normally we would use the eigenfunctions of Eq. (120) as a basis in which to expand perturbed eigenfunctions. However the set, Eq. (120), is not complete. It is well known that the continuum eigenfunctions of Eq. (112) are needed to ensure completeness, even for the expansion of bound states. On the other hand it can be shown that the T_3 eigenfunctions, Eq. (119), do form a complete set for the expansion of bound states (Klahn and Bingel, 1977; Clay, 1979). They are also related to Sturmians (Löwdin and Shull, 1956; Shull and Löwdin, 1959; Rotenberg, 1970). Thus, the use of T_3 eigenfunctions in perturbation theory nicely avoids the "problem of the continuum" inherent in the conventional approach. The presence of r/n in Eq. (120) is largely responsible for the incompleteness of the usual radial functions, whereas the T_3 eigenfunctions of Eq. (119) depend on r rather than r/n.

B. Isotropic Harmonic Oscillator

The Hamiltonian for the three-dimensional harmonic oscillator can be written in the form

$$H = \tfrac{1}{2}p^2 + \tfrac{1}{2}\omega^2 r^2 \tag{121}$$

and the radial equation is

$$[\tfrac{1}{2}p_r^2 + \tfrac{1}{2}l(l+1)r^{-2} + \tfrac{1}{2}\omega^2 r^2 - E]R(r) = 0 \tag{122}$$

Dividing by 4 and comparing with Eq. (98) we obtain

$$\begin{aligned} &w = 2, \qquad \xi = \tfrac{1}{4}l(l+1), \qquad \eta = \tfrac{1}{4}E \\ &\tau = -\tfrac{1}{8}\omega^2, \qquad \lambda = 2/\omega \end{aligned} \tag{123}$$

and the T_3 eigenvalue spectrum is given by Eq. (83), so that

$$q_0 = k + 1 = \tfrac{1}{2}(l + \tfrac{3}{2}) \tag{124}$$

$$q = \tfrac{1}{2}(n + \tfrac{3}{2}) \tag{125}$$

where

$$n = l + 2\mu; \qquad \mu = 0, 1, 2, \ldots \tag{126}$$

can be identified with the principal quantum number. From Eq. (106) the energy levels are

$$E_n = 4\eta = 4q\lambda^{-1} = 2q\omega = \omega(n + \tfrac{3}{2}) \tag{127}$$

Finally, the T_3 eigenfunctions are given by Eq. (107) with $w = 2$, $W = 3/4$;

$$\tilde{R}_{kq}(r) = N_{kq}e^{-r^2}(2r^2)^{k+1/4}L_{q-k-1}^{(2k+1)}(2r^2) \tag{128}$$

and the eigenfunctions of the original radial equation are

$$R_{kq}(r) = (2/\omega)^{-3/4}\tilde{R}_{kq}((2/\omega)^{-1/2}r), \tag{129}$$

where

$$k = \tfrac{1}{2}l - \tfrac{1}{4}, \qquad q = \tfrac{1}{2}(n + \tfrac{3}{2}) \tag{130}$$

This is the usual textbook form (see, e.g., Powell and Craseman, 1961). The only difference between Eqs. (128) and (129) is a change in units, since in case $w = 2$ the *so*(2, 1) generators are Hermitian with respect to the usual scalar product [cf. Eq. (79)]. On the other hand, for the hydrogen atom the scaling parameter (i.e., $\lambda = n/Z$) depends on the principal quantum number.

It is interesting to note that there is a close connection between the radial equations of the hydrogen atom and the harmonic oscillator. In fact they can be transformed into each other by a change of independent (r) and dependent (R) variables. This transformation in the N-dimensional case has been given explicitly by Cizek and Paldus (1977, Appendix I). In the three-dimensional case, if we substitute

$$r = 2(\rho/E)^{1/2}, \qquad R(r) = \rho^{1/4}P(\rho) \tag{131}$$

into the harmonic oscillator radial equation (122) we obtain

$$[\tfrac{1}{2}p_\rho^2 + \tfrac{1}{32}[4l(l + 1) - 3]\rho^{-2} - \rho^{-1} + 2\omega^2E^{-2}]P(\rho) = 0 \tag{132}$$

which has the same form as the hydrogen atom radial equation (113) [p_ρ is given by Eq. (68b) with r replaced by ρ]. Other relationships between the hydrogen atom, the four-dimensional harmonic oscillator, and a pair of two-dimensional coupled harmonic oscillators have been explored (Kibler and Negadi, 1983, 1984b).

C. Klein–Gordon Equation

The Klein–Gordon equation (Schrödinger's relativistic equation) has been used in the description of a relativistic particle with spin zero (see, e.g., Schiff, 1968) and can be treated using the *so*(2, 1) algebraic methods (Barut, 1971; Cizek and Paldus, 1977, and references therein). It is obtained from the energy–momentum relationship

$$(E - e\phi)^2 = p^2c^2 + m^2c^4 \tag{133}$$

For the Coulomb potential $\phi = -Zr^{-1}$ using atomic units and the fine structure constant $\alpha = 1/c$ we obtain

$$\left[\frac{1}{2}p_r^2 + \frac{1}{2}(L^2 - \alpha^2Z^2)r^{-2} - \alpha^2ZEr^{-1} + \frac{1}{2c^2}(c^4 - E^2)\right]R(r) = 0 \tag{134}$$

This has the form of Eq. (98) with

$$\begin{aligned} w &= 1, \qquad \xi = l(l+1) - \alpha^2Z^2 \\ \eta &= \alpha^2ZE, \qquad \tau = \frac{1}{2c^2}(E^2 - c^4) \end{aligned} \tag{135}$$

so the energy eigenvalues are given by Eq. (105):

$$E = c^2[1 + \alpha^2Z^2q^{-2}]^{-1/2} \tag{136}$$

Using Eq. (83) the T_3 eigenvalues can be expressed as

$$q = n + g_l; \qquad n = l+1, l+2, \ldots \tag{137}$$

where n is the principal quantum number and the correction to the nonrelativistic result $q = n$ is

$$g_l = \frac{2l+1}{2}\left\{\left[1 - \left(\frac{2\alpha Z}{2l+1}\right)^2\right]^{1/2} - 1\right\} \tag{138}$$

Thus the energy levels can be expressed as

$$\begin{aligned} E_{nl} &= c^2\left[1 + \frac{\alpha^2Z^2}{n^2}\left(1 + \frac{g_l}{n}\right)^{-2}\right]^{-1/2} \\ &= c^2 - \frac{Z^2}{2n^2} + \cdots \end{aligned} \tag{139}$$

If desired, the explicit form of the scaled wave functions (eigenfunctions of T_3) and the usual ones can be obtained from Eqs. (107) and (111) by substituting $w = W = 1$, and using n, l as labels rather than q, k, noting that

$$\begin{aligned} q &= n + g_l, \qquad k = l + g_l \\ \alpha\lambda &= \{1 + (n/\alpha Z)^2[1 + g_l/n]^2\}^{1/2} \end{aligned} \tag{140}$$

D. Dirac–Coulomb Equation

The Dirac–Coulomb equation for a central potential has the form

$$H = c\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta c^2 + V(r) \tag{141}$$

where α_1, α_2, α_3, and β are 4×4 anticommuting Dirac matrices (see, e.g., Schiff, 1968). The $so(2, 1)$ algebraic method can be applied directly to Eq. (141) in two-component form (see, e.g., Cizek and Paldus, 1977). An alternate approach which we shall outline (Biedenharn, 1962) involves converting Eq. (141) to a second-order differential equation for the radial functions.

The eigenvalue problem is most conveniently expressed in the form

$$O_+\Psi \equiv \beta(H - E)\Psi = 0 \tag{142}$$

where Ψ is a four-component spinor wave function. Using the radial momentum p_r and the radial $\boldsymbol{\alpha}$ matrix

$$\alpha_r = r^{-1}(\boldsymbol{\alpha} \cdot \boldsymbol{r}) \tag{143}$$

which is independent of r, the Dirac Hamiltonian can be expressed as

$$H = c\alpha_r p_r + icr^{-1}\alpha_r \beta K + \beta c^2 + V(r) \tag{144}$$

where

$$K = \beta(\boldsymbol{\Sigma} \cdot \boldsymbol{L} + 1) \tag{145}$$

and

$$\boldsymbol{S} = \tfrac{1}{2}\boldsymbol{\Sigma} \tag{146}$$

is the spin. The operator K commutes with the Hamiltonian so it is a constant of motion. It can be shown that

$$K^2 = L^2 + \beta K = J^2 + \tfrac{1}{4} \tag{147}$$

where

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S} \tag{148}$$

is the total angular momentum. Thus K^2 has eigenvalues $(j + \frac{1}{2})^2$ for $j = 1/2$, $3/2, \ldots$, so K has eigenvalues $\pm 1, \pm 2, \ldots$. In fact the sign of K is related to the relativistic parity of the wave functions. Our main interest is in obtaining the energy levels in a Coulomb field algebraically so we shall not consider the explicit form of the wave functions.

For a Coulomb potential we have

$$V = -Zr^{-1}$$

$$O_- = c\beta\boldsymbol{\alpha} \cdot \boldsymbol{p} - c^2 + \beta(V - E) \tag{149}$$

Then the equation

$$O_- O_+ \Phi = 0 \tag{150}$$

can be expressed in the form

$$[\tfrac{1}{2}p_r^2 + \tfrac{1}{2}\Gamma(\Gamma - 1)r^{-2} - \alpha^2 ZEr^{-1} - (1/2c^2)(E^2 - c^4)]\Phi = 0 \tag{151}$$

where α is the fine structure constant. The operator Γ commutes with K and is defined by

$$\Gamma = \beta K + i\alpha Z\alpha_r \tag{152}$$

$$\Gamma^2 = K^2 - \alpha^2 Z^2 \tag{153}$$

The second-order equation (150) is equivalent to the original Dirac equation in the sense that if Φ is any solution of Eq. (151) then $O_-\Phi$ is a solution of the Dirac Eq. (142), since O_- and O_+ commute. Conversely, any solution of Eq. (142) is a solution of Eq. (150). If we choose a basis such that Γ and K are diagonalized then

$$\Gamma^2 = \gamma^2, \qquad \Gamma = -\omega\gamma \tag{154}$$

where

$$\gamma = [(j + \tfrac{1}{2})^2 - \alpha^2 Z^2]^{1/2}, \qquad \omega = \pm 1 \tag{155}$$

Comparing Eqs. (151) and (98) we obtain

$$\begin{aligned} w &= 1, \qquad \xi = \Gamma(\Gamma - 1) = \gamma(\gamma + \omega) \\ \eta &= \alpha^2 ZE, \qquad \tau = (1/2c^2)(E^2 - c^4) \end{aligned} \tag{156}$$

Thus the T_3 eigenvalues can be expressed as

$$q = n + g_j; \qquad n = l + 1, l + 2, \ldots \tag{157}$$

where g_j is the same function, Eq. (138), that we obtained in the Klein–Gordon case but with l replaced by j, and the orbital angular momentum is given by

$$l = j + \tfrac{1}{2}\omega \tag{158}$$

Finally, the energy levels are

$$E_{nj} = c^2[1 + (\alpha^2 Z^2/n^2)(1 + g_j/n)^{-2}]^{-1/2}$$

VII. Realizations of *so*(4)

In this section we shall first introduce the Laplace–Runge–Lenz vector X and show that it provides, in addition to the *so*(3) orbital angular momentum generators L_i, three constants of motion for the hydrogenic Hamiltonian H. Thus, the six operators X_i, L_i commute with H. They do not close under commutation to form a Lie algebra since H appears explicitly in the commutation relations. However, if H is replaced by one of its bound-state energy eigenvalues E_n, a realization of *so*(4) is obtained. This energy-dependent realization was first considered by Pauli (see, e.g., Van der

Waerden, 1968) and can be used to rederive the Bohr formula for the energy levels. Corresponding to each energy level a unirrep of *so*(4) is obtained. The basis functions for each such unirrep are just the hydrogenic wave functions belonging to the energy level.

This realization is not suitable for perturbation problems with unperturbed Hamiltonian H since it cannot be easily merged with the *so*(2, 1) realization in order to calculate matrix elements between states belonging to different energy levels. We shall show how to convert it via a scaling transformation into an energy independent realization that can be merged with *so*(2, 1). Finally, we shall obtain the matrix elements of the *so*(4) generators for this scaled realization using the results of Section IV, since they are needed for perturbation applications.

A. Laplace–Runge–Lenz Vector

The classical Laplace–Runge–Lenz vector is

$$\boldsymbol{X} = \boldsymbol{p} \times \boldsymbol{L} - Zr^{-1}\boldsymbol{r} \tag{159}$$

It is a constant of the motion for the classical Kepler problem (Saletan and Cromer, 1971). The magnitude of $\boldsymbol{X}$ is proportional to the eccentricity of the orbit and $\boldsymbol{X}$ points in the direction of the major axis. Using the correspondence principle Pauli first showed that its quantum mechanical analog,

$$\begin{aligned} \boldsymbol{X} &= \tfrac{1}{2}(\boldsymbol{p} \times \boldsymbol{L} - \boldsymbol{L} \times \boldsymbol{p}) - Zr^{-1}\boldsymbol{r} \\ &= \tfrac{1}{2}\boldsymbol{r}p^2 - \boldsymbol{p}(\boldsymbol{r} \cdot \boldsymbol{p}) + \boldsymbol{r}H \end{aligned} \tag{160}$$

commutes with the hydrogenic Hamiltonian

$$H = \tfrac{1}{2}p^2 - Zr^{-1} \tag{161}$$

Thus, the components of $\boldsymbol{X}$ and $\boldsymbol{L}$ commute with H and satisfy the following commutation relations

$$[L_j, L_k] = i\epsilon_{jkl}L_l \tag{162a}$$

$$[L_j, X_k] = i\epsilon_{jkl}X_l \tag{162b}$$

$$[X_j, X_k] = (-2H)i\epsilon_{jkl}L_l \tag{162c}$$

and the identities

$$X^2 = 2H(L^2 + 1) + Z^2 \tag{163a}$$

$$(\boldsymbol{X} \cdot \boldsymbol{L}) = (\boldsymbol{L} \cdot \boldsymbol{X}) = 0 \tag{163b}$$

Except for the factor $-2H$, Eqs. (162a)–(162c) are the defining commutation relations for the Lie algebra *so*(4) given in Section IV.

B. Realizations of *so*(4) in Coordinate Space

In order to obtain a realization of $so(4)$, the factor $-2H$ must be removed from Eq. (162c). There are two possibilities: H can be replaced by one of its continuum or bound-state energy eigenvalues. The former choice leads to a realization of $so(3, 1)$ and the latter to a realization of $so(4)$. Thus, if we replace H by the bound-state energy E_n, and define the modified Laplace–Runge–Lenz vector

$$V = (-2E_n)^{-1/2}\mathbf{X} \tag{164}$$

then the components of $\boldsymbol{L}$ and $\boldsymbol{V}$ satisfy the commutation relations of $so(4)$ [cf. Eq. (42) with $\boldsymbol{J}$ replaced by $\boldsymbol{L}$ and $\sigma = 1$]. Corresponding to Eq. (163) we get

$$V^2 = -(L^2 + 1) - Z^2(2E_n)^{-1} \tag{165a}$$

$$(\boldsymbol{L} \cdot \boldsymbol{V}) = (\boldsymbol{V} \cdot \boldsymbol{L}) = 0 \tag{165b}$$

The two $so(4)$ Casimir operators [Eqs. (54) and (55)] are

$$C_1 = L^2 + V^2 = -1 - Z^2(2E_n)^{-1} \tag{166a}$$

$$C_2 = (\boldsymbol{L} \cdot \boldsymbol{V}) = 0 \tag{166b}$$

The general unirreps of $so(4)$ obtained in Section IV can be labeled either by the pair j_0, η such that $l = |j_0|, |j_0| + 1, \ldots, \eta - 1$, or by the pair j_1, j_2 such that $l = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2$. The relationship between the two sets of labels is $j_0 = j_1 - j_2, \eta = j_1 + j_2 + 1$. Then the eigenvalues of the Casimir operators are from Eqs. (166), (56), and (57)

$$j_0^2 + \eta^2 - 1 = -1 - Z^2(2E_n)^{-1} \tag{167a}$$

$$j_0\eta = 0 \tag{167b}$$

It follows that $j_0 = 0$ and $\eta = n$ is the principal quantum number. In fact, Eq. (167a) directly gives the Bohr formula for the energy levels.

Thus, we obtain a special class of so-called diagonal representations of $so(4)$ characterized by $j_0 = 0$ (or $j_1 = j_2$). This is analogous to the situation in angular momentum theory where only integral values of orbital angular momentum are possible. The half-odd-integral values are ruled out because of the particular realization of $\boldsymbol{L}$ in terms of coordinates and momenta.

Thus, our hydrogenic representations are completely characterized by the principal quantum number $n = 2j_1 + 1$. The basis functions for each representation can be denoted by

$$|nlm\rangle = |(0, n)lm\rangle; \qquad l = 0, 1, \ldots, n - 1 \tag{168a}$$

or by

$$|nlm\rangle = |[j_1, j_1]lm\rangle; \qquad l = 0, 1, \ldots, 2j_1 \tag{168b}$$

where $m = -l, -l+1, \ldots, l$. The former notation emphasizes the principal quantum number and is more appropriate, whereas the latter emphasizes that $so(4)$ representations can be constructed from the coupling of two angular momenta.

It follows that $so(4)$, like $so(2, 1)$, is also a spectrum-generating algebra for the hydrogenic atom. Moreover, the so-called accidental degeneracy of the energy levels is easily explained using $so(4)$. From angular momentum theory the predicted degeneracy of E_n is just $2l + 1$. But from Eq. (168b) the degeneracy is $(2j_1 + 1)^2 = n^2$, the correct value. This extra degeneracy is a simple consequence of the three additional constants of motion provided by the components of the Laplace–Runge–Lenz vector. A similar situation exists for the three-dimensional isotropic harmonic oscillator (Schiff, 1968) where the orbital angular momentum degeneracy does not account for the full degeneracy of the energy levels.

For each value of the principal quantum number n we obtain an $n^2 \times n^2$ dimensional matrix unirrep of $so(4)$ with basis functions given by Eq. (168). If desired they can be expressed explicitly in terms of spherical harmonics. The matrix elements of the $so(4)$ generators can easily be obtained from the general results, Eqs. (52) and (53) of Section IV. Raising and lowering operators can also be defined in terms of $\boldsymbol{L}$ and $\boldsymbol{V}$ for the quantum numbers l and m, but $so(4)$ cannot provide raising and lowering operators for n, so we cannot calculate algebraically the matrix elements of operators between states belonging to different energy levels. We have already seen that the $so(2, 1)$ operators $T_\pm$ are raising and lowering operators for n and this suggests that we merge our $so(2, 1)$ and $so(4)$ realizations into a realization of a bigger Lie algebra, which contains raising and lowering operators for all three quantum numbers. This would mean that all bound states of the hydrogenic atom are contained in a single unirrep of some bigger Lie algebra.

The $so(4)$ realization which we have just constructed is not suitable for merging with $so(2, 1)$. The primary difficulty is the energy dependence of the realization of $\boldsymbol{V}$ given by Eq. (164). In Section V we have shown that the $so(2, 1)$ generator T_3 is related to the hydrogenic Hamiltonian via a scaling transformation of the form given in Eq. (94), and this suggests that we apply the same scaling transformation to the $so(4)$ generators $\boldsymbol{L}$ and $\boldsymbol{V}$ to obtain a scaled realization of $so(4)$.

We can express $\boldsymbol{V}$ in the form

$$\boldsymbol{V} = (-2E_n)^{-1/2}[\tfrac{1}{2}\boldsymbol{r}p^2 - \boldsymbol{p}(\boldsymbol{r}\cdot\boldsymbol{p}) + \boldsymbol{r}E_n] \tag{169}$$

If we apply the scaling transformation, Eq. (94), with $w = 1$ and

$$e^\alpha = (-2E_n)^{-1/2} = nZ^{-1} \tag{170}$$

then using $\tilde{\boldsymbol{r}} = e^\alpha \boldsymbol{r}$ and $\tilde{\boldsymbol{p}} = e^{-\alpha}\boldsymbol{p}$ we obtain

$$\boldsymbol{A} \equiv \tilde{\boldsymbol{V}} = \tfrac{1}{2}\boldsymbol{r}p^2 - \boldsymbol{p}(\boldsymbol{r}\cdot\boldsymbol{p}) - \tfrac{1}{2}\boldsymbol{r} \tag{171}$$

which is the scaled Laplace–Runge–Lenz vector. Since $\boldsymbol{r}$ and $\boldsymbol{p}$ transform inversely, the angular momentum vector $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is invariant to scaling. Thus, we obtain an energy-independent realization of the *so*(4) Lie algebra with defining commutation relations

$$[L_j, L_k] = i\epsilon_{jkl}L_l \tag{172a}$$

$$[L_j, A_k] = i\epsilon_{jkl}A_l \tag{172b}$$

$$[A_j, A_k] = i\epsilon_{jkl}L_l \tag{172c}$$

There is a close connection between the set $\{H, \boldsymbol{L}, \boldsymbol{V}\}$ and the set $\{T_3, \boldsymbol{L}, \boldsymbol{A}\}$ obtained from it via the scaling transformation. The *so*(4) Lie algebra generated by $\{\boldsymbol{L}, \boldsymbol{V}\}$ is the dynamical invariance (symmetry) algebra for the hydrogenic Hamiltonian, whereas $\{\boldsymbol{L}, \boldsymbol{A}\}$ plays the same role for the T_3 operator. In fact

$$[L_i, T_3] = [A_i, T_3] = 0; \qquad i = 1, 2, 3 \tag{173}$$

Corresponding to Eqs. (165) and (166) the scaled *so*(4) realization has the special properties

$$A^2 + L^2 + 1 = T_3^2 \tag{174a}$$

$$C_1 = L^2 + A^2 = -1 + T_3^2 \tag{174b}$$

$$C_2 = (\boldsymbol{L} \cdot \boldsymbol{A}) = (\boldsymbol{A} \cdot \boldsymbol{L}) = 0 \tag{174c}$$

It follows that for each energy level E_n we can replace T_3 by its eigenvalue n to obtain $C_1 = -1 + n^2$ and this shows that the unirreps of *so*(4) corresponding to the scaled realization can be labeled by n.

C. Matrix Elements for Scaled Hydrogenic Realization

The matrix elements of the *so*(4) generators A_3, $A_\pm$ for the scaled hydrogenic realization are easily obtained from the general results [Section IV, Eqs. (52) and (53)] by substituting $j = l$, $j_0 = 0$, $\eta = n$. Thus,

$$a_l^n = 0 \tag{175}$$

which is a consequence of the special property $(\boldsymbol{L} \cdot \boldsymbol{A}) = 0$ of the realization, and

$$c_l^n = [(n^2 - l^2)/(4l^2 - 1)]^{1/2} \tag{176}$$

Therefore

$$\begin{aligned} A_3|nlm\rangle &= [(l-m)(l+m)]^{1/2}c_l^n|n, l-1, m\rangle \\ &\quad + [(l-m+1)(l+m+1)]^{1/2}c_{l+1}^n|n, l+1, m\rangle \end{aligned} \tag{177a}$$

$$\begin{aligned} A_+|nlm\rangle &= [(l-m)(l-m-1)]^{1/2}c_l^n|n, l-1, m+1\rangle \\ &\quad - [(l+m+1)(l+m+2)]^{1/2}c_{l+1}^n|n, l+1, m+1\rangle \end{aligned} \tag{177b}$$

$$A_-|nlm\rangle = -[(l+m)(l+m-1)]^{1/2}c_l^n|n, l-1, m-1\rangle + [(l-m+1)(l-m+2)]^{1/2}c_{l+1}^n|n, l+1, m-1\rangle \quad (177c)$$

and for L_3, $L_\pm$,

$$L_3|nlm\rangle = m|nlm\rangle \quad (178a)$$

$$L_+|nlm\rangle = [(l-m)(l+m+1)]^{1/2}|n, l, m+1\rangle \quad (178b)$$

$$L_-|nlm\rangle = [(l+m)(l-m+1)]^{1/2}|n, l, m-1\rangle \quad (178c)$$

$$L^2|nlm\rangle = l(l+1)|nlm\rangle \quad (178d)$$

$$(L^2 + A^2 + 1)|nlm\rangle = n^2|nlm\rangle \quad (178e)$$

D. Hydrogenic Tower of States

It follows from Eq. (177b) that

$$A_+|n, l-1, l-1\rangle = k_{nl}|nll\rangle \quad (179a)$$

$$k_{nl} = -[2l(n^2 - l^2)/(2l+1)]^{1/2} \quad (179b)$$

This shows that A_+ is a raising operator connecting states with $m = l$. In fact, all such states can be generated from $|n00\rangle$ with the formula

$$|nll\rangle = K_{nl}(A_+)^l|n00\rangle, \quad (180a)$$

$$K_{nl} = (k_{n1}k_{n2}\cdots k_{nl})^{-1} \quad (180b)$$

This is indicated in Fig. 3, where the n^2 states are shown for $n = 3$ in a triangular $so(4)$ subtower corresponding to one of the $so(4)$ unirreps.

All states on the right edge of the triangle are generated from the top one by successive application of A_+. The horizontal lines of the triangle each

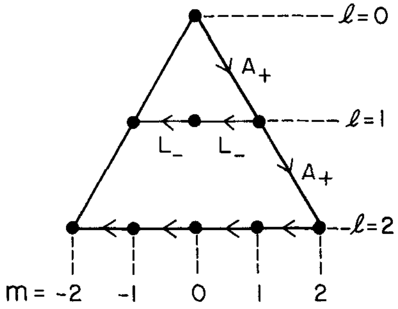

Fig. 3. An $so(4)$ subtower representing the n^2 scaled hydrogenic eigenfunctions which form a basis for a unitary irreducible representation of $so(4)$. All states can be obtained from the top one by the appropriate application of the A_+ and L_- operators. See text for details.

correspond to a unirrep of *so*(3) and the states in each line are generated from the rightmost one by successive application of L_-. This follows from Eq. (178c):

$$L_-|n, l, m + 1\rangle = b_{lm}|nlm\rangle \tag{181a}$$

$$b_{lm} = [(l + m + 1)(l - m)]^{1/2} \tag{181b}$$

Thus,

$$|nlm\rangle = B_{lm}(L_-)^{l-m}|nll\rangle \tag{182a}$$

$$B_{lm} = (b_{lm}b_{l,m+1}\cdots b_{l,l-1})^{-1} \tag{182b}$$

Combining these results we see that any state in a subtower can be obtained from the top one using

$$|nlm\rangle = K_{nl}B_{lm}(L_-)^{l-m}(A_+)^l|n00\rangle \tag{183}$$

This result could be used to obtain explicit forms algebraically for all bound-state hydrogenic eigenfunctions.

We can combine the results with Eq. (76c) (with $k = l, q = n$), which implies that

$$|nlm\rangle = C_{ln}(T_+)^{n-l-1}|l + 1, lm\rangle \tag{184a}$$

$$C_{ln} = [(n - l - 1)!(n + l)!/(2l + 1)!]^{-1/2} \tag{184b}$$

for hydrogenic states. Thus,

$$|n00\rangle = C_{0n}(T_+)^{n-1}|100\rangle \tag{185}$$

where

$$C_{0n} = [(n - 1)!n!]^{-1/2}$$

and all bound states can be expressed in terms of the ground state:

$$|nlm\rangle = N_{nlm}(L_-)^{l-m}(A_+)^l(T_+)^{n-1}|100\rangle \tag{186a}$$

$$\begin{aligned} N_{nlm} &= K_{nl}B_{lm}C_{0l} \\ &= (-1)^l[2^l l!(n - 1)!]^{-1}[2l + 1]^{1/2}[(n - l - 1)!(l + m)!]^{1/2} \\ &\quad \times [(n + l)!(l - m)!]^{-1/2} \end{aligned} \tag{186b}$$

This leads to the pictorial representation of all bound hydrogenic states given in Fig. 4.

The *so*(4) subtowers are all linked together at the top through the action of T_+ so that successive application of T_+ to the top state of a subtower produces the top state of the next subtower. Thus, by merging *so*(4) and *so*(2, 1) we should be able to find a larger Lie algebra for which all hydrogenic bound states are contained in a single unirrep.

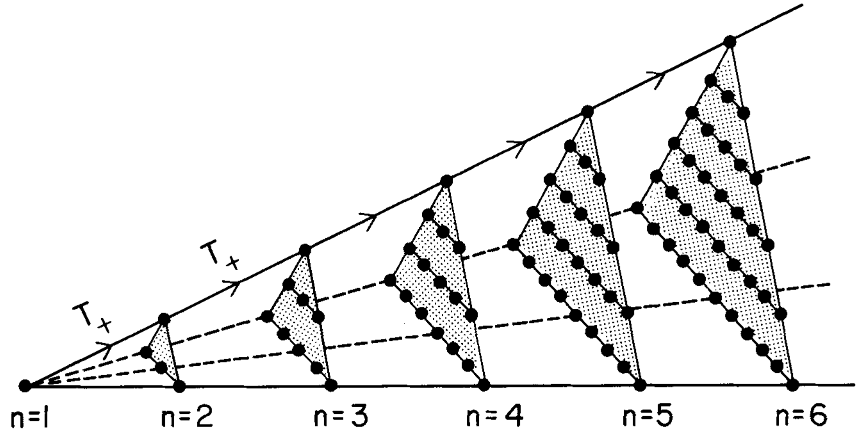

Fig. 4. The collection of $so(4)$ subtowers for $n = 1, 2, 3, \ldots$ forms an $so(4, 2)$ tower of scaled hydrogenic eigenfunctions such that all eigenfunctions belong to a single unitary irreducible representation of $so(4, 2)$. The top state in any $so(4)$ subtower can be reached by successive application of the $so(2, 1)$ operator T_+ to the ground state. See text for details.

VIII. Realizations of $so(4, 2)$

In this section we shall complete our goal of providing a complete algebraic framework for perturbation problems based on the unperturbed hydrogenic Hamiltonian. The most general type of perturbation is a function of the coordinates and momenta so it is desirable to obtain simple expressions for them in terms of generators of some Lie algebra. We have seen that $so(2, 1)$ provides the simple expression $r = T_3 - T_1$ for the radial distance and that $so(2, 1)$ and $so(4)$ provide raising and lowering operators for the three quantum numbers n, l, and m. In order to obtain simple expressions for the coordinates we need to merge $so(2, 1)$ and $so(4)$ together into a bigger Lie algebra.

First we shall combine $so(4)$ and the $so(2, 1)$ generator T_2. To close out all commutation relations among the operators $\boldsymbol{L}$, $\boldsymbol{A}$, T_2 it is necessary to introduce an additional $so(3)$ vector operator $\boldsymbol{B}$. The result is the Lie algebra $so(4, 1)$ having the ten generators $\boldsymbol{L}$, $\boldsymbol{A}$, $\boldsymbol{B}$, T_2. We also obtain the simple expression $\boldsymbol{r} = \boldsymbol{B} - \boldsymbol{A}$. Next we combine T_1 and T_3 with the $so(4, 1)$ generators. Again another $so(3)$ vector operator $\boldsymbol{\Gamma}$ is needed to close out the commutation relations. Thus, we finally obtain the Lie algebra $so(4, 2)$ and a realization of it defined by the 15 generators $\boldsymbol{L}$, $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{\Gamma}$, T_1, T_2, and T_3.

Using either $so(4, 1)$ or $so(4, 2)$ we can find infinite dimensional unirreps for which all bound-state scaled hydrogenic wave functions form a basis. The Lie algebra $so(4, 2)$ is more suitable for our purposes since we have the simple expressions $r = T_3 - T_1$, $\boldsymbol{r} = \boldsymbol{B} - \boldsymbol{A}$. We can then calculate matrix elements of all 15 generators, and hence of any perturbation expressible in terms of the coordinates, by simple matrix multiplication (see, e.g., Bednár, 1973; Adams *et al.*, 1982).

A. Hydrogenic Realization of *so*(4, 1)

To merge *so*(4) and T_2 we must evaluate the commutators of T_2 with $\boldsymbol{L}$ and A. Since $T_2 = rp_r$ [cf. Eq. (73)] acts only on the radial part of a wave function and L acts only on the angular part, it follows that

$$[T_2, L_j] = 0; \qquad j = 1, 2, 3 \tag{187a}$$

This can also be shown by direct calculation of the commutators using the rules outlines in Appendix A. However, for the components of A we obtain

$$[T_2, A_j] = iB_j \tag{187b}$$

where

$$\boldsymbol{B} = \boldsymbol{A} + \boldsymbol{r} = \tfrac{1}{2}\boldsymbol{r}p^2 - \boldsymbol{p}(\boldsymbol{r} \cdot \boldsymbol{p}) + \tfrac{1}{2}\boldsymbol{r} \tag{187c}$$

is a new vector operator. Thus, we must include $\boldsymbol{B}$ to close out the commutation relations. To check for closure we must now evaluate the commutators of $\boldsymbol{B}$ with the remaining operators $\boldsymbol{L}$, $\boldsymbol{A}$, T_2. The results are

$$[L_j, L_k] = i\epsilon_{jkl}L_l \tag{188a}$$

$$[L_j, A_k] = i\epsilon_{jkl}A_l \tag{188b}$$

$$[A_j, A_k] = i\epsilon_{jkl}L_l \tag{188c}$$

which are just the commutation relations for the *so*(4) subalgebra, and

$$[L_j, B_k] = i\epsilon_{jkl}B_l \tag{188d}$$

$$[B_j, B_k] = -i\epsilon_{jkl}L_l \tag{188e}$$

$$[A_j, B_k] = i\delta_{jk}T_2 \tag{188f}$$

$$[T_2, L_j] = 0 \tag{188g}$$

$$[T_2, A_j] = iB_j \tag{188h}$$

$$[T_2, B_j] = iA_j \tag{188i}$$

These are the defining commutation relations for the Lie algebra *so*(4, 1) in terms of the 10 generators $\boldsymbol{L}$, $\boldsymbol{A}$, $\boldsymbol{B}$, and T_2. We also note that Eqs. (188a), (188d), and (188e) are the defining commutation relations for an *so*(3, 1) Lie algebra (subalgebra) generated by $\boldsymbol{L}$ and $\boldsymbol{B}$. The importance of this realization of *so*(4, 1) is that we now have the simple expressions

$$x_i = B_i - A_i; \qquad i = 1, 2, 3 \tag{189}$$

for the coordinates in terms of generators of *so*(4, 1).

The representation theory of $so(4, 1)$ is considerably more involved than for $so(4)$, so we shall not present the details here (see, e.g., Strom, 1965; Kihlberg and Strom, 1965; Bohm, 1966; Vitale, 1968). We need only the following results.

(1) The two independent Casimir operators for $so(4, 1)$ are given by

$$Q = T_2^2 + B^2 - A^2 - L^2 \tag{190}$$

$$W = X^2 - Y^2 \tag{191}$$

where[5]

$$\mathbf{X} = T_2\mathbf{L} - \mathbf{A} \times \mathbf{B} \tag{192}$$

$$Y = \tfrac{1}{2}[\mathbf{L}\cdot(\mathbf{A} + \mathbf{B}) + (\mathbf{A} + \mathbf{B})\cdot\mathbf{L}] \tag{193}$$

(2) There are two classes of infinite dimensional unirreps of $so(4, 1)$ adapted to the subalgebra decomposition $so(4, 1) \supset so(4) \supset so(3)$:

$$D^{\mathrm{I}}; \qquad Q \geq 0; \qquad W = 0, \tag{194}$$

$$D^{\mathrm{I}} \xrightarrow[so(4)]{} R[0, 0] \oplus R[\tfrac{1}{2}, \tfrac{1}{2}] \oplus R[1, 1] \oplus \cdots$$

and

$$D^{\mathrm{II}}(s); \qquad Q = -(s-1)(s+2); \qquad s = 1, 2, 3, \ldots; \qquad W = 0 \tag{195}$$

$$D^{\mathrm{II}}(s) \xrightarrow[so(4)]{} R\left[\frac{s}{2}, \frac{s}{2}\right] \oplus R\left[\frac{s+1}{2}, \frac{s+1}{2}\right] \oplus \cdots$$

where $R[j_1, j_2]$ is a general unirrep of $so(4)$ defined in Section IV in terms of the two angular momentum quantum numbers j_1 and j_2.

To determine which class of unirreps we are dealing with, we must evaluate the Casimir operators Q and W for our hydrogenic realization of $so(4, 1)$. It can be shown by direct calculation using Eqs. (73), (171), and (189) that

$$L^2 = T_3^2 - T_2^2 - T_1^2 \tag{196}$$

$$A^2 = T_1^2 + T_2^2 - 1 \tag{197}$$

$$B^2 = T_3^2 - T_2^2 + 1 \tag{198}$$

for the hydrogenic realization. Substitution into Eq. (190) gives $Q = 2$, so we will have a type I unirrep if $W = 0$. It can be shown using the $so(4, 1)$ commutation relations that

$$\mathbf{B}(\mathbf{L}\cdot\mathbf{A}) - (\mathbf{L}\cdot\mathbf{A})\mathbf{B} = -i\mathbf{X} \tag{199}$$

$$\mathbf{A}(\mathbf{L}\cdot\mathbf{B}) - (\mathbf{L}\cdot\mathbf{B})\mathbf{A} = i\mathbf{X} \tag{200}$$

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[5] Note that here X defines a different quantity than the Runge–Lenz vector, Eq. (159).

$$(\boldsymbol{A} \cdot \boldsymbol{X}) - (\boldsymbol{X} \cdot \boldsymbol{A}) = -3i(\boldsymbol{L} \cdot \boldsymbol{B}) \tag{201}$$

$$(\boldsymbol{B} \cdot \boldsymbol{X}) - (\boldsymbol{X} \cdot \boldsymbol{B}) = -3i(\boldsymbol{L} \cdot \boldsymbol{A}) \tag{202}$$

These results are independent of the particular realization and show that if any one of $(\boldsymbol{L} \cdot \boldsymbol{A})$, $(\boldsymbol{L} \cdot \boldsymbol{B})$, or X is zero, then the other two are also zero. For our realization we know that $(\boldsymbol{L} \cdot \boldsymbol{A}) = 0$. Since we always have $(\boldsymbol{L} \cdot \boldsymbol{A}) = (\boldsymbol{A} \cdot \boldsymbol{L})$ and $(\boldsymbol{L} \cdot \boldsymbol{B}) = (\boldsymbol{B} \cdot \boldsymbol{L})$ then it follows from Eq. (191) that $W = 0$. Thus we are dealing with a type I unirrep defined by $Q = 2$ and $W = 0$. The reduction of this unirrep with respect to $so(4)$, given by Eq. (194), shows that all the $so(4)$ subtowers shown in Fig. 4 are contained in a single unirrep of $so(4, 1)$ [$j_1 = j_2$, $n = 2j_1 + 1$; cf. Eq. (66)]. The basis for $R[0, 0]$ is the ground state, the basis for $R[\frac{1}{2}, \frac{1}{2}] = R(0, 2)$ is the set of states having energy E_1, and so on. In general each $so(4)$ unirrep $R[k/2, k/2] = R(0, k + 1)$ corresponds to the $so(4)$ subtower having energy E_n with $n = k + 1$.

B. Hydrogenic Realization of *so*(4, 2)

To merge T_1 and T_3 with the $so(4, 1)$ generators we need to evaluate their commutators with these generators. Since the $so(2, 1)$ generators commute with the angular momentum components L_i we first consider commutators with $\boldsymbol{A}$ and $\boldsymbol{B}$ in order to check for closure of all commutation relations. By direct calculation

$$[T_1, A_j] = i\Gamma_j \tag{203}$$

$$[T_1, B_j] = 0 \tag{204}$$

$$[T_3, A_j] = 0 \tag{205}$$

$$[T_3, B_j] = -i\Gamma_j \tag{206}$$

where

$$\boldsymbol{\Gamma} = r\boldsymbol{p} \tag{207}$$

is a new vector operator needed to close out the commutation relations. Finally we must evaluate the commutators of $\boldsymbol{\Gamma}$ with T_1, T_2, T_3, $\boldsymbol{L}$, $\boldsymbol{A}$, and $\boldsymbol{B}$ to ensure closure. Thus

$$[\Gamma_j, L_k] = i\epsilon_{jkl}\Gamma_l \tag{208}$$

which shows that $\boldsymbol{\Gamma}$ is another $so(3)$ vector operator, and

$$[\Gamma_j, A_k] = -i\delta_{jk}T_1 \tag{209}$$

$$[\Gamma_j, B_k] = -i\delta_{jk}T_3 \tag{210}$$

$$[\Gamma_j, T_1] = -iA_j \tag{211}$$

$$[\Gamma_j, T_2] = 0 \tag{212}$$

$$[\Gamma_j, T_3] = -iB_j \tag{213}$$

and

$$[\Gamma_j, \Gamma_k] = -i\epsilon_{jkl}L_l \tag{214}$$

which shows, along with Eq. (208), that $\boldsymbol{L}$, $\boldsymbol{\Gamma}$ generate an *so*(3, 1) Lie algebra.

Thus, we obtain a realization of the Lie algebra *so*(4, 2) having the 15 generators $\boldsymbol{L}$, $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{\Gamma}$, T_1, T_2, and T_3. The realization is given by

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \tag{215a}$$

$$\boldsymbol{A} = \tfrac{1}{2}\boldsymbol{r}p^2 - \boldsymbol{p}(\boldsymbol{r} \cdot \boldsymbol{p}) - \tfrac{1}{2}\boldsymbol{r} \tag{215b}$$

$$\boldsymbol{B} = \tfrac{1}{2}\boldsymbol{r}p^2 - \boldsymbol{p}(\boldsymbol{r} \cdot \boldsymbol{p}) + \tfrac{1}{2}\boldsymbol{r} \tag{215c}$$

$$\boldsymbol{\Gamma} = r\boldsymbol{p} \tag{215d}$$

$$T_1 = \tfrac{1}{2}(rp^2 - r) = \tfrac{1}{2}(rp_r^2 + L^2r^{-1} - r) \tag{215e}$$

$$T_2 = \boldsymbol{r} \cdot \boldsymbol{p} - i = rp_r \tag{215f}$$

$$T_3 = \tfrac{1}{2}(rp^2 + r) = \tfrac{1}{2}(rp_r^2 + L^2r^{-1} + r) \tag{215g}$$

Since there is a large number of defining commutation relations for *so*(4, 2) it is desirable to have a compact notation for them. The commutation relations can be expressed in a convenient form if we define an antisymmetric set of operators

$$L_{ab} = -L_{ba}; \qquad a, b = 1, 2, \ldots, 6 \tag{216}$$

using the matrix correspondence

$$L_{ab} \leftrightarrow \begin{bmatrix} 0 & L_3 & -L_2 & A_1 & B_1 & \Gamma_1 \\ & 0 & L_1 & A_2 & B_2 & \Gamma_2 \\ & & 0 & A_3 & B_3 & \Gamma_3 \\ & & & 0 & T_2 & T_1 \\ & & & & 0 & T_3 \\ & & & & & 0 \end{bmatrix} \tag{217}$$

If we introduce the diagonal metric matrix

$$g_{ab} = \begin{cases} 0; & a \neq b \\ 1; & a = b = 1, 2, 3, 4 \\ -1; & a = b = 5, 6 \end{cases} \tag{218}$$

then the complete set of *so*(4, 2) commutation relations can be expressed as

$$[L_{ab}, L_{cd}] = i(g_{ac}L_{bd} + g_{bd}L_{ac} - g_{bc}L_{ad} - g_{ad}L_{bc}) \tag{219}$$

The set of all nonzero commutators can be more simply expressed as

$$[L_{ab}, L_{ad}] = ig_{aa}L_{bd}; \qquad a \neq b \neq d \tag{220}$$

where no summation over index "a" is implied.

The form of the matrix, Eq. (217), is arranged so that the most important subalgebras are apparent: if $a, b = 1, 2, 3$ we obtain $so(3)$; if $a, b = 1, 2, 3, 4$ we obtain $so(4)$; and if $a, b = 1, 2, \ldots, 5$ we obtain $so(4, 1)$. Other subalgebras, which may be important for applications to continuum states, can be found. We have already seen that $\boldsymbol{L}$, $\boldsymbol{B}$ generate an $so(3, 1)$ subalgebra. Physically, $\boldsymbol{B}$ is obtained by scaling the Laplace–Runge–Lenz vector $V = (2H)^{-1/2}\boldsymbol{X}$, Eq. (160) [cf. Eq. (164)] for positive energy eigenvalues of H rather than the negative energy ones. Realizations of $so(4, 2)$ obtained in this way may be of interest in algebraic studies of scattering theory.

We shall not consider the general representation theory of $so(4, 2)$ (Barut and Bohm, 1970). It is clear from our construction of the hydrogenic realization that we have all bound-state hydrogenic eigenfunctions within a single unirrep of $so(4, 2)$, since this is true for the subalgebra $so(4, 1)$. We only note that there are three independent Casimir operators for $so(4, 2)$ given by the rather complicated expressions (see, e.g., Barut, 1971, p. 45)

$$Q_2 = \tfrac{1}{2}L_{ab}L^{ab} \tag{221}$$

$$Q_3 = \tfrac{1}{48}\epsilon_{abcdef}L^{ab}L^{cd}L^{ef} \tag{222}$$

$$Q_4 = L_{ab}L^{bc}L_{cd}L^{da} \tag{223}$$

where summation over all indices is implied, ε_{abcdef} is completely antisymmetric in all indices such that $\varepsilon_{123456} = 1$, $\epsilon_{213456} = -1$, and superscript indices are obtained from subscripted ones by raising the indices with the metric tensor g^{ab}, i.e.,

$$L^{ab} = g^{ac}g^{bd}L_{cd} \tag{224}$$

$$g^{ab} = g_{ab} \tag{225}$$

The first two Casimir operators can easily be expressed in conventional form

$$Q_2 = L^2 + A^2 - B^2 - \Gamma^2 + T_3^2 - T_1^2 - T_2^2, \tag{226}$$

$$Q_3 = -T_1(\boldsymbol{B}\cdot\boldsymbol{L}) + T_2(\boldsymbol{\Gamma}\cdot\boldsymbol{L}) + T_3(\boldsymbol{A}\cdot\boldsymbol{L}) + \boldsymbol{A}\cdot(\boldsymbol{B}\times\boldsymbol{\Gamma}) \tag{227}$$

Using Eqs. (196), (197), and (198) and a similar result

$$\Gamma^2 = T_3^2 - T_1^2 + 1 \tag{228}$$

valid for the hydrogenic realization, it follows that

$$Q_2 = -3 \tag{229}$$

The Casimir operator Q_3 is also easily evaluated. Since $(\boldsymbol{A} \cdot \boldsymbol{L}) = (\boldsymbol{B} \cdot \boldsymbol{L}) = 0$ for our realization, and $(\boldsymbol{\Gamma} \cdot \boldsymbol{L}) = 0$ follows from $(\boldsymbol{p} \cdot \boldsymbol{L}) = 0$, we obtain $Q_3 = -\boldsymbol{A} \cdot (\boldsymbol{B} \times \boldsymbol{\Gamma})$. Direct calculation shows that $\boldsymbol{B} \times \boldsymbol{\Gamma}$ has $\boldsymbol{L}$ as a left-hand factor so

$$Q_3 = 0 \tag{230}$$

Finally, a somewhat lengthy calculation shows that

$$Q_4 = 0 \tag{231}$$

Thus for our hydrogenic realization all Casimir operators have constant values so we are dealing with a single unirrep of $so(4, 2)$ symmetry adapted according to the subalgebra chain

$$so(4, 2) \supset so(4, 1) \supset so(4) \supset so(3)$$

C. Representation of *so*(4, 2): Hydrogenic Case

In order to obtain the $so(4, 2)$ representation corresponding to the hydrogenic case we must specify the action of the 15 generators on the scaled bound-state hydrogenic wave functions $|nlm\rangle$. We have already done this for the generators $\boldsymbol{L}$, $\boldsymbol{A}$ of $so(4)$ [cf. Eqs. (177) and (178)]. For T_1, T_2, T_3 it follows from Eq. (76) with $k = l$, $q = n$ that

$$T^2|nlm\rangle = l(l + 1)|nlm\rangle \tag{232a}$$

$$T_3|nlm\rangle = n|nlm\rangle \tag{232b}$$

$$T_{\pm}|nlm\rangle = [-(l \mp n)(l \pm n + 1)]^{1/2}|n \pm 1, lm\rangle \tag{232c}$$

To evaluate the action of the remaining generators $\boldsymbol{B}$, $\boldsymbol{\Gamma}$ on the basis functions it is convenient to use B_3, $B_{\pm} = B_1 \pm iB_2$, Γ_3, $\Gamma_{\pm} = \Gamma_1 \pm i\Gamma_2$. Then using Eqs. (188h) and (206)

$$B_3 = -\tfrac{1}{2}[T_+ - T_-, A_3] \tag{233}$$

$$B_{\pm} = -\tfrac{1}{2}[T_+ - T_-, A_{\pm}], \tag{234}$$

$$\Gamma_3 = i[T_3, B_3] \tag{235}$$

$$\Gamma_{\pm} = i[T_3, B_{\pm}] \tag{236}$$

Thus, the matrix elements of B_3, $B_{\pm}$ can be calculated from Eqs. (233) and (234), and the known results for A_3, $A_{\pm}$, Eqs. (176) and (177), using simple matrix multiplication. Then the matrix elements of Γ_3, $\Gamma_{\pm}$ can be evaluated in a similar manner using Eqs. (235) and (236). The results are given by

$$\begin{aligned} U_3|nlm\rangle = {} & f\alpha(l, m)a(n, l)|n - 1, l - 1, m\rangle \\ & + g\alpha(l, m)b(n, l)|n + 1, l - 1, m\rangle \\ & + f\alpha(l + 1, m)b(n - 1, l + 1)|n - 1, l + 1, m\rangle \\ & + g\alpha(l + 1, m)a(n + 1, l + 1)|n + 1, l + 1, m\rangle \end{aligned} \tag{237}$$

$$\begin{aligned} U_{\pm}|nlm\rangle = &\pm f\beta(l-1, \pm m)a(n, l)|n-1, l-1, m \pm 1\rangle \\ &\pm g\beta(l-1, \pm m)b(n, l)|n+1, l-1, m \pm 1\rangle \\ &\mp f\beta(l+1, \mp m)b(n-1, l+1)|n-1, l+1, m \pm 1\rangle \\ &\mp g\beta(l+1, \mp m)a(n+1, l+1)|n+1, l+1, m \pm 1\rangle \end{aligned} \tag{238}$$

where

$$f = g = 1 \qquad \text{for} \qquad U = B \tag{239}$$

$$f = -i, \qquad g = i \qquad \text{for} \quad U = \Gamma \tag{240}$$

and

$$\alpha(l, m) = [(l-m)(l+m)]^{1/2} \tag{241}$$

$$\beta(l, m) = [(l-m+1)(l-m)]^{1/2} \tag{242}$$

$$a(n, l) = \tfrac{1}{2}[(n+l)(n+l-1)/(4l^2-1)]^{1/2} \tag{243}$$

$$b(n, l) = \tfrac{1}{2}[(n-l+1)(n-l)/(4l^2-1)]^{1/2} \tag{244}$$

We can now calculate matrix elements of any operator which is expressible in terms of the 15 generators of $so(4, 2)$.

IX. Algebraic Perturbation Formalism for Hydrogenic Systems

In this section we shall discuss in some detail the formalism needed to apply the $so(4, 2)$ algebraic methods to problems whose unperturbed Hamiltonian is hydrogenic. First a scaling transformation is applied to obtain a new Hamiltonian whose unperturbed part is just the $so(2, 1)$ generator T_3, which has a purely discrete spectrum. Next we use the scaled hydrogenic eigenfunctions of T_3 as a basis for the expansion of the exact wave function. This discrete basis is complete with respect to the expansion of bound-state wave functions whereas the usual bound-state eigenfunctions do not form a complete set: continuum functions must also be included to ensure completeness (cf. Section VI,A).

Thus, perturbation theory based on the scaled hydrogenic basis can provide better accuracy and, when combined with the convenient calculation of matrix elements using $so(4, 2)$ algebraic methods, results in an effective technique for large-order perturbation theory (Cizek and Vrscay, 1982; Clay, 1979; Vrscay, 1977; Bednár, 1973; Adams *et al.*, 1980; Cizek *et al.*, 1980a,b; Silverstone *et al.*, 1979).

A. Scaling the Hamiltonian

We consider Hamiltonians of the form

$$H = H_0 + \lambda V \tag{245}$$

where λ is the perturbation parameter, V is the perturbation, and H_0 is the hydrogenic Hamiltonian

$$H_0 = \tfrac{1}{2}p^2 - Zr^{-1} \tag{246}$$

The unperturbed eigenvalue problem can be expressed as

$$H_0 \phi_{nlm} = E_n \phi_{nlm} \tag{247}$$

$$E_n = -\tfrac{1}{2}Z^2 n^{-2} \tag{248}$$

with the usual hydrogenic eigenfunctions as the unperturbed basis. Generally, continuum states must also be included since they can have a significant effect on the results. The eigenvalue problem for H is

$$[H_0 - E_n + \lambda V - \Delta E_n]\Psi = 0 \tag{249}$$

where

$$E = E_n + \Delta E_n \tag{250}$$

is the unknown energy.

In order to apply the algebraic methods based on $so(4, 2)$ it is necessary to carry out a noncanonical and nonunitary transformation of Eq. (249). Thus, multiplying on the left by r and applying the scaling transformation (cf. Section V and Appendix B) to operators and functions

$$\tilde{\mathbf{r}} = e^{\alpha_n}\mathbf{r} \tag{251}$$

$$\tilde{\mathbf{p}} = e^{-\alpha_n}\mathbf{p} \tag{252}$$

$$e^{i\alpha T_2}\Psi(\mathbf{r}) = e^{\alpha_n}\Psi(e^{\alpha_n}\mathbf{r}) = e^{\alpha_n}\tilde{\Psi}(\mathbf{r}) \tag{253}$$

using the convention of Eq. (90), where

$$e^{\alpha_n} = nZ^{-1} \tag{254}$$

$$E_n = -\tfrac{1}{2}e^{-2\alpha_n} \tag{255}$$

we obtain the eigenvalue problem (see Appendix B for alternative derivation)

$$[K + \lambda W - \Delta E_n S]\tilde{\Psi} = 0 \tag{256}$$

where

$$K = T_3 - n \tag{257}$$

$$W = e^{2\alpha_n} r \tilde{V}(r) \tag{258}$$

$$S = e^{2\alpha_n} r \tag{259}$$

Except for the operator S, Eq. (256) is a secular equation in standard form with unperturbed part K and perturbation W. Because of S, however, Eq. (256) looks like a generalized secular equation typical of perturbation theory using a nonorthogonal basis, where S would be interpreted as the overlap matrix between the basis functions. This is not the case, since our basis functions are eigenfunctions of T_3 and are orthonormal with respect to the "$1/r$ scalar product" we are using. Thus, we can use the formalism of perturbation theory with a nonorthogonal basis but without the added complexity involved in using such a basis. In fact the matrix elements of S are easily calculated.

B. Nondegenerate Perturbation Formalism

We shall restrict the discussion here to nondegenerate perturbation theory for the ground-state case. However, there is no formal difficulty extending the method to degenerate cases if we wish to treat excited states (Cizek and Vrscay, 1982; Adams *et al.*, 1980).

Putting $n = 1$ in Eqs. (256)–(259) and using Eq. (254) we obtain

$$K = T_3 - 1 \tag{260}$$

$$W = Z^{-2} r \tilde{V}(r) \tag{261}$$

$$S = Z^{-2} r \tag{262}$$

The exact wave function can be expanded as

$$\tilde{\Psi} = \sum_{i=0}^{\infty} \lambda^i \tilde{\Psi}^{(i)} \tag{263}$$

in terms of the ith-order corrections to the wave functions and

$$\tilde{\Psi}^{(0)} = C_0 |100\rangle \tag{264}$$

The constant C_0 is usually chosen to be unity. Similarly, the perturbation correction to the energy can be expanded as

$$\Delta E = \sum_{i=1}^{\infty} \lambda^i E^{(i)} \tag{265}$$

in terms of the ith-order corrections $E^{(i)}$ to the ground-state energy $E^{(0)} = -\frac{1}{2}$.

We can also demand that the ith-order corrections to the wave function be $1/r$ orthogonal to the unperturbed ground state:

$$\langle \tilde{\Psi}^{(0)} | \tilde{\Psi}^{(i)} \rangle = 0; \qquad i \geq 1 \tag{266}$$

Substituting these results into Eq. (256) and collecting terms belonging to the same power of λ, we obtain

$$K\tilde{\Psi}^{(k)} = -W\tilde{\Psi}^{(k-1)} + \sum_{i=1}^{k} E^{(i)} S \tilde{\Psi}^{(k-i)} \tag{267}$$

or

$$E^{(k)} S \tilde{\Psi}^{(0)} = K\tilde{\Psi}^{(k)} + W\tilde{\Psi}^{(k-1)} - \sum_{i=1}^{k-1} E^{(i)} S \tilde{\Psi}^{(k-i)} \tag{268}$$

Projecting the last result onto the unperturbed ground state gives

$$E^{(k)}\langle\tilde{\Psi}^{(0)}|S|\tilde{\Psi}^{(0)}\rangle = \langle\tilde{\Psi}^{(0)}|K|\tilde{\Psi}^{(k)}\rangle + \langle\tilde{\Psi}^{(0)}|W|\tilde{\Psi}^{(k-1)}\rangle - \sum_{i=1}^{k-1} E^{(i)}\langle\tilde{\Psi}^{(0)}|S|\tilde{\Psi}^{(k-i)}\rangle \tag{269}$$

which simplifies, since

$$\langle\tilde{\Psi}^{(0)}|K|\tilde{\Psi}^{(k)}\rangle = \langle\tilde{\Psi}^{(0)}|T_3 - 1|\tilde{\Psi}^{(k)}\rangle = 0$$

$$\langle\tilde{\Psi}^{(0)}|S|\tilde{\Psi}^{(0)}\rangle = Z^{-2}\langle 100|T_3 - T_1|100\rangle = Z^{-2}$$

Thus, we obtain a recursive formula for the energy corrections

$$E^{(k)} = Z^2\langle\tilde{\Psi}^{(0)}|W|\tilde{\Psi}^{(k-1)}\rangle - Z^2\sum_{i=1}^{k-1}\langle\tilde{\Psi}^{(0)}|S|\tilde{\Psi}^{(k-i)}\rangle E^{(i)} \tag{270}$$

To obtain a similar formula from Eq. (267) for the wave function corrections it is convenient to introduce the Green function for the operator K defined by

$$G = \sum_{\substack{nlm \\ n\neq 1}} \frac{|nlm\rangle\langle nlm|}{n-1} \tag{271}$$

It is a pseudo-inverse for K since

$$KG|\tilde{\Psi}\rangle = GK|\tilde{\Psi}\rangle = |\tilde{\Psi}\rangle - C_{100}|100\rangle \tag{272}$$

for any $\tilde{\Psi}$ of the form

$$|\tilde{\Psi}\rangle = \sum_{nlm} C_{nlm}|nlm\rangle \tag{273}$$

Thus G is an inverse of K for all such functions which have no component along the unperturbed ground state. From Eq. (266) the wave function corrections are of this type so we can apply G to Eq. (267) to obtain the recursive formula

$$\tilde{\Psi}^{(k)} = \sum_{i=1}^{k} GS\tilde{\Psi}^{(k-i)}E^{(i)} - GW\tilde{\Psi}^{(k-1)} \tag{274}$$

Equations (270) and (274) provide a practical scheme for the systematic calculation of the energy and wave function corrections to large order. It should be noted that in order to obtain the kth-order correction to the energy it is necessary to calculate the first $k - 1$ corrections to the wave function.

On the other hand it is known from variational methods (Hirschfelder *et al.*, 1964; Dupont-Bourdelet *et al.*, 1960), treating λ as a variational parameter, that if the wave function is known to order k then the energy can be found to order $2k + 1$. In our case it is possible to calculate the first $2k + 1$ corrections to the energy using the symmetric perturbation formula (Vrscay, 1977)

$$\begin{aligned} Z^{-2}E^{(m+n+1)} = {} & \langle \tilde{\Psi}^{(m)} | W | \tilde{\Psi}^{(n)} \rangle \\ & - \sum_{a=1}^{m} \sum_{b=1}^{n} \langle \tilde{\Psi}^{(a)} | S | \tilde{\Psi}^{(b)} \rangle E^{(m+n+1-a-b)} \\ & - \sum_{a=1}^{m} \langle \tilde{\Psi}^{(0)} | S | \tilde{\Psi}^{(a)} \rangle E^{(m+n+1-a)} \\ & - \sum_{b=1}^{n} \langle \tilde{\Psi}^{(0)} | S | \tilde{\Psi}^{(b)} \rangle E^{(m+n+1-b)} \end{aligned} \tag{275}$$

Setting $m = n$ gives the odd-order corrections while $m = n - 1$ gives the even-order ones. Even though the matrix elements in Eq. (275) are more complicated than those in Eq. (270), which always involve the unperturbed ground state on the left, Eq. (275) is superior for applications where large-order energy corrections are required, since as the order increases the difficulty in calculating and storing the wave function corrections is much greater than is the evaluation of matrix elements in Eq. (275) for lower orders.

C. Evaluation of Matrix Elements

In a particular application of the $so(4, 2)$ perturbation formalism the type of matrix elements required is determined by the form of the scaled perturbation W, Eq. (261). In any case, matrix elements of r are needed for the matrix elements of S [cf. Eq. (262)]. They can be obtained using

$$r = T_3 - T_1 = T_3 - \tfrac{1}{2}(T_+ + T_-) \tag{276}$$

and Eq. (232):

$$\begin{aligned} r|nlm\rangle = {} & -\tfrac{1}{2}[(n + l)(n - l - 1)]^{1/2}|n - 1, lm\rangle \\ & + n|nlm\rangle - \tfrac{1}{2}[(n - l)(n + l + 1)]^{1/2}|n + 1, lm\rangle \end{aligned} \tag{277}$$

so that r has a simple tridiagonal matrix structure on each subspace with l and m fixed.

Matrix elements of higher powers of r are often needed and can be obtained by matrix multiplication. Using the notation

$$(r^k)^{\mu 00}_{nlm} = \langle n + \mu, lm | r^k | nlm \rangle \tag{278}$$

then

$$(r^k)|nlm\rangle = \sum_{\substack{\mu = l+1-n \\ |\mu| \le k}}^{n} (r^k)^{\mu 00}_{nlm} |n + \mu, lm\rangle \tag{279}$$

where

$$(r^k)_{nlm}^{\mu 00} = \sum_{\substack{\mu' \\ |\mu-\mu'|\le 1}} (r^{k-1})_{nlm}^{\mu' 00} (r)_{n+\mu', lm}^{\mu-\mu', 00} \tag{280}$$

The Hermitian property

$$(r^k)_{nlm}^{-\mu, 00} = (r^k)_{n-\mu, lm}^{\mu 00} \tag{281}$$

reduces the number of matrix elements which need be considered. The results for $k = 1, 2, 3$ are given in Table I, Appendix C.

Matrix elements of powers of the coordinates can be obtained in a similar manner using $x_i = B_i - A_i$, Eq. (189), expressed in the form

$$x = x_1 = (1/2)(B_+ + B_- - A_+ - A_-) \tag{282}$$

$$y = x_2 = -(i/2)(B_+ - B_- - A_+ + A_-) \tag{283}$$

$$z = x_3 = B_3 - A_3 \tag{284}$$

The first two powers of z are needed for the LoSurdo–Stark and Zeeman Hamiltonians (Section X), for example. The results are

$$z|nlm\rangle = \sum_{\mu=-1}^{1} \sum_{\nu=\pm 1} (z)_{nlm}^{\mu\nu 0} |n+\mu, l+\nu, m\rangle \tag{285}$$

$$z^2|nlm\rangle = \sum_{\mu=-2}^{2} \sum_{\nu=0,\pm 2} (z^2)_{nlm}^{\mu\nu 0} |n+\mu, l+\nu, m\rangle \tag{286}$$

The matrix elements are given in Table II, Appendix C. For z there are three distinct matrix elements whereas the z^2 there are eight, taking into account the Hermiticity property

$$(z^k)_{nlm}^{-\mu, -\nu, 0} = (z^k)_{n-\mu, l-\nu, m}^{\mu\nu 0} \tag{287}$$

With respect to the orthonormal basis $|nlm\rangle$, matrix elements of polynomials in x, y, z usually contain square roots of rational numbers as factors. For large-order calculations using rational arithmetic it may be an advantage to introduce an artificial normalization to make all such matrix elements rational numbers. This can always be achieved. For example, the unnormalized basis

$$N_{nlm}|nlm\rangle \tag{288}$$

where

$$N_{nlm}^2 = \frac{(n+l)!(l-m)!}{(n-l-1)!(l+m)!} \cdot \frac{1}{2l+1} \tag{289}$$

can be used. The choice is not unique, however, and other possibilities may be more convenient in a particular application (see, e.g., Clay, 1979).

X. Application of Perturbation Theory to Hydrogenic Systems

A. LoSurdo–Stark Effect

Historically, the LoSurdo–Stark effect in hydrogen was the first problem to which Rayleigh–Schrödinger perturbation theory was applied in quantum mechanics (Schrödinger, 1926b). The difficulty in applying this conventional formalism is evident since it was not until 1973 that the correct value of $E^{(4)}$ was obtained (Alliluev and Malkin, 1974). Since then $E^{(n)}$ has been calculated in floating point form to $n = 150$ using a method based on the separability of the LoSurdo–Stark Hamiltonian in parabolic coordinates (Silverstone, 1978), to $n = 82$ in floating point form using the $so(4, 2)$ algebraic methods (Silverstone *et al.*, 1979), and to $n = 60$ in rational form (Privman, 1980), using the logarithmic derivative formulation (Aharonov and Au, 1979; Privman, 1981b).

In the $so(4, 2)$ algebraic approach we use Eqs. (256)–(259) for the ground state in the form

$$[K + (\lambda Z^{-3})rz - Z^{-2}\Delta E r]\tilde{\Psi} = 0 \tag{290}$$

We can set the charge $Z = 1$ since it can easily be put back into the final result if desired. Thus,

$$K = T_3 - 1 \tag{291}$$

$$W = rz \tag{292}$$

$$S = r \tag{293}$$

The matrix elements of W can be obtained from those of r and z given in Tables I and II (Appendix C) by simple matrix multiplication. They are defined by

$$rz|nlm\rangle = \sum_{\mu=-2}^{2} \sum_{\nu=\pm 1} (rz)_{nlm}^{\mu\nu 0}|n + \mu, l + \nu, m\rangle \tag{294}$$

and the five distinct matrix elements are given in Table III, Appendix C. Other matrix elements are obtained using the Hermititan property

$$(rz)_{nlm}^{-\mu,-\nu,0} = (rz)_{n-\mu,l-\nu,m}^{\mu\nu 0} \tag{295}$$

A special property of the perturbation series for the energy is that all odd-order corrections are zero. Thus, using Eq. (274) and the symmetric perturbation formula Eq. (275), the first few orders are

$$|\tilde{\Psi}^{(1)}\rangle = -2^{1/2}[|210\rangle - (1/4)|310\rangle] \tag{296}$$

$$\begin{aligned}|\tilde{\Psi}^{(2)}\rangle = {} & -(23/8)2^{1/2}|210\rangle + (7/4)3^{1/2}|300\rangle + (11/8)6^{1/2}|320\rangle \\ & - |400\rangle - (3/2)|420\rangle + (1/16)5^{1/2}|500\rangle \\ & + (1/16)14^{1/2}|520\rangle\end{aligned} \tag{297}$$

$$
\begin{aligned}
|\tilde{\Psi}^{(3)}\rangle = {} & -(305/16)2^{1/2}|210\rangle + (1529/64)2^{1/2}|310\rangle \\
& - (175/16)5^{1/2}|410\rangle - (21/4)5^{1/2}|430\rangle \\
& + (13/4)10^{1/2}|510\rangle + (9/4)10^{1/2}|530\rangle \\
& - (23/80)70^{1/2}|610\rangle - (9/10)5^{1/2}|630\rangle \\
& + (3/32)7^{1/2}|710\rangle + (3/32)6^{1/2}|730\rangle
\end{aligned}
\tag{298}
$$

and the asymptotic (divergent) series for the energy is

$$
\begin{aligned}
E &= -\frac{1}{2} - \frac{9}{4}\lambda^2 - \frac{3555}{64}\lambda^4 - \frac{2512779}{512}\lambda^6 - \cdots \\
&= -\frac{1}{2}\left[1 + 72\left(\frac{\lambda}{4}\right)^2 + 28440\left(\frac{\lambda}{4}\right)^4 + 40204464\left(\frac{\lambda}{4}\right)^6 + \cdots\right]
\end{aligned}
\tag{299}
$$

For the first form of the energy expansion the coefficients up to 20th order are given in Table V, Appendix C, and the coefficients using the second form of the expansion have been given to order 60 by Privman (1980).

B. Zeeman Effect

The study of the hydrogen atom in a uniform magnetic field (HAMF) is considerably more complex than the LoSurdo–Stark effect (see Cizek and Vrscay, 1982, and references therein). The Hamiltonian is not separable and reducible to a one-dimensional problem. For a field along the z axis the problem is inherently two-dimensional. Thus, the methods mentioned above which rely on the one-dimensional aspect of the LoSurdo–Stark effect and its separability in parabolic coordinates are special and not directly extendable to the Zeeman effect.

On the other hand the $so(4, 2)$ algebraic formalism can be directly applied. The Hamiltonian is given by

$$
H = \tfrac{1}{2}p^2 - Zr^{-1} + \tfrac{1}{2}\gamma L_3 + \tfrac{1}{8}\gamma^2(r^2 - z^2) \tag{300}
$$

where γ is the magnetic field strength for a uniform field in the z direction. The linear term vanishes for the ground state and only the quadratic term remains. Defining the perturbation parameter

$$
\lambda = \tfrac{1}{8}\gamma^2 \tag{301}
$$

Eqs. (256)–(259) become

$$
[K + (\lambda Z^{-4})W - Z^{-2}\Delta Er]\tilde{\Psi} = 0 \tag{302}
$$

$$
K = T_3 - 1 \tag{303}
$$

$$
W = r(r^2 - z^2) \tag{304}
$$

Again we can choose $Z = 1$ without loss of generality. The matrix elements of W are easily calculated from those of r, r^2, z^2 given in Tables I and II by matrix multiplication. The 11 distinct matrix elements are given in Table IV and the remaining ones can be obtained from the usual Hermitian conditions, which are given in Eq. (295).

The symmetric perturbation equations [Eq. (275)] give the following energy expansion:

$$\begin{aligned} E &= -\frac{1}{2} + \sum_{k=1}^{\infty} E^{(k)}\lambda^k \\ &= -\frac{1}{2} + 2\lambda - \frac{53}{3}\lambda^2 + \frac{5581}{9}\lambda^3 - \frac{21577397}{540}\lambda^4 + \cdots \end{aligned} \tag{305}$$

The coefficients $E^{(k)}$ were first calculated by Vrscay (1977) to order 40 in floating point form and later to order 100 (Avron *et al.*, 1979). The rational form to order 10 has been given by Clay (1979) and Avron *et al.* (1979) and is reproduced in Table VI, Appendix C.

We should mention that the combined LoSurdo–Stark–Zeeman effect using the Hamiltonian

$$H = \tfrac{1}{2}p^2 - Zr^{-1} + \tfrac{1}{2}\gamma L_3 + \tfrac{1}{8}\gamma^2(r^2 - z^2) + Fz \tag{306}$$

has recently been considered (Johnson *et al.*, 1983). These authors transform the inhomogeneous equations for double perturbation theory into difference equations to obtain a ground-state energy expansion of the form

$$E = \sum_{m,n=0}^{\infty} E^{(m,n)}F^{2m}(\gamma^2/8)^n \tag{307}$$

and results in floating point form are reported to order 5 in both m and n. The $so(4, 2)$ algebraic approach can also be applied to this problem by generalizing the nondegenerate perturbation formalism of Section IX to the double perturbation case (see, e.g., Hirschfelder *et al.*, 1964). Finally we note that the connection between the HAMF problem and the four-dimensional anharmonic oscillator has recently been considered (Kibler and Negadi, 1984a).

C. One-Electron Diatomic Ions

The study of one-electron diatomic ions is the simplest model for long-range intermolecular forces. The simplest cases, H_2^+ and HeH^{2+}, have been studied extensively using perturbation theory by Dalgarno and Lewis (1955) and Dalgarno and Stewart (1956a,b). Their now famous method (Hirschfelder *et al.*, 1964; Schiff, 1968; Schwartz, 1959) was to solve the inhomogeneous differential equations characterizing perturbation theory rather than deal directly with the formal perturbation series, thus avoiding problems of

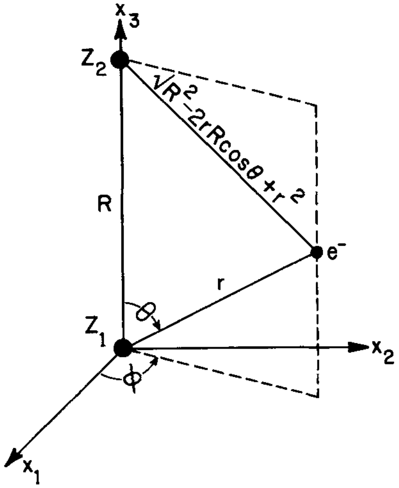

Fig. 5. Coordinate system used for one-electron diatomic atoms. The two nuclei are on the z axis with charges Z_1 and Z_2, separated by a distance R, and the electron (e^-) is a distance r from the origin. See text for details.

continuum states. However this method is not easily extendable to higher orders. On the other hand, the *so*(4, 2) algebraic method can be applied in large-order calculations more easily and systematically.

The general problem is to consider two nuclei having charges Z_1 and Z_2 separated by a distance R along the z-axis as shown in Fig. 5.

The unperturbed Hamiltonian is

$$H_0 = \tfrac{1}{2}p^2 - Z_1 r^{-1} \tag{308}$$

and the perturbation is

$$V = Z_1 Z_2 R^{-1} - Z_2 |\mathbf{R} - \mathbf{r}|^{-1} \tag{309}$$

For long-range interactions we are interested in the asymptotic expansion ($R \gg r$) in powers of R^{-1}:

$$V = Z_2(Z_1 - 1)R^{-1} - Z_2 \sum_{j=1}^{\infty} r^j R^{-j-1} P_j(\cos\theta) \tag{310}$$

where P_j is a Legendre polynomial. The conventional eigenvalue problem is given by

$$[H_0 - E_n + V - \Delta E_n]\Psi = 0 \tag{311}$$

using R^{-1} as a perturbation parameter. Multiplying by r and applying the scaling transformation (Section IX) we obtain for the ground state ($n = 1$)

$$[T_3 - 1 + W - Z_1^{-1}\Delta E Q_0]\tilde{\Psi} = 0 \tag{312}$$

where

$$W = Z_1^{-1}\{Z_2(Z_1 - 1)R^{-1}Q_0 - Z_2 \sum_{j=1}^{\infty} R^{-j-1}Q_j\} \tag{313}$$

$$Q_j = r^{j+1}Z_1^{-j-1}P_j(\cos\theta) \tag{314}$$

$$Q_0 = rZ_1^{-1} \tag{315}$$

There are two choices for the perturbation expansion of the energy

$$\Delta E = \sum_{k=1}^{\infty} E^{(k)}(Z_1, R^{-1})Z_2^k, \tag{316}$$

$$= \sum_{k=1}^{\infty} E^{(k)}(Z_1, Z_2)R^{-k} \tag{317}$$

using either Z_2 or R^{-1} as perturbation parameter. Formally, the first choice is simplest since the perturbation is linear in Z_2 and the energy coefficients are infinite series in R^{-1}. Dalgarno and Stewart (1956b) have expressed their results in this form for $k = 1$ to 5 accurate to $O(R^{-12})$.

For the systematic approach based on $so(4, 2)$ it is more convenient to use the second choice and calculate $E^{(k)}$. Thus, using the wave function expansion

$$\tilde{\Psi} = \sum_{k=0}^{\infty} R^{-k}\tilde{\Psi}^{(k)} \tag{318}$$

and Eq. (317), we obtain

$$(T_3 - 1)\tilde{\Psi}^{(0)} = 0 \tag{319}$$

$$Z_1(T_3 - 1)\tilde{\Psi}^{(1)} = [E^{(1)} - Z_2(Z_1 - 1)]Q_0\tilde{\Psi}^{(0)} \tag{320}$$

which implies that

$$|\tilde{\Psi}^{(0)}\rangle = |100\rangle \tag{321}$$

$$|\tilde{\Psi}^{(1)}\rangle = 0 \tag{322}$$

$$E^{(1)} = Z_2(Z_1 - 1) \tag{323}$$

using the orthogonality conditions [Eq. (266)]. For $k \geq 2$

$$Z_1(T_3 - 1)\tilde{\Psi}^{(k)} = Z_2 \sum_{j=1}^{k-1} Q_j\tilde{\Psi}^{(k-j-1)} + Q_0 \sum_{j=2}^{k} E^{(j)}\tilde{\Psi}^{(k-j)} \tag{324}$$

Projecting onto $|100\rangle$ gives the recurrence relation for the energy corrections

$$\begin{aligned} E^{(k)} = {} & -Z_1Z_2 \sum_{j=1}^{k-1} \langle 100|Q_j|\tilde{\Psi}^{(k-j-1)}\rangle \\ & - \sum_{j=2}^{k-1} \langle 100|r|\tilde{\Psi}^{(k-j)}\rangle E^{(j)} \end{aligned} \tag{325}$$

and the Green function [Eq. (271)] gives the wave function corrections

$$\tilde{\Psi}^{(k)} = Z_1^{-1} Z_2 \sum_{j=1}^{k-1} G Q_j \tilde{\Psi}^{(k-j-1)} + Z_1^{-2} \sum_{j=2}^{k} E^{(j)} G r \tilde{\Psi}^{(k-j)} \tag{326}$$

Calculations based on these formulas have been carried out to order $k = 12$ using rational arithmetic, to order $k = 20$ in floating point form (Clay, 1979), and to order $k = 45$ (Cizek *et al.*, 1980b). The results can be expressed in the form

$$\tilde{\Psi}^{(k)} = \sum_{nj} \sum_{pq} S_{nj}^{1/2} A_{nj}^{k} Z_2^{q} Z_1^{-p} |nj0\rangle \tag{327}$$

$$E^{(k)} = \sum_{pq} E_{pq}^{(k)} Z_2^{q} Z_1^{-p} \tag{328}$$

The perturbation corrections to the wave function for $Z_1 = Z_2$ are given in Table VII, Appendix C, up to fifth order and the corrections to the energy are given in rational form to fifth order in Table VIII, Appendix C. More extensive tabulations in floating point form have been given by Clay (1979).

D. Screened Coulomb Potentials

The general class of potentials of the form

$$U(r) = -Zr^{-1} \sum_{j=0}^{\infty} V_j r^j \lambda^j; \qquad V_0 = 1 \tag{329}$$

are referred to as screened Coulomb potentials (McEnnan *et al.*, 1976) and the Hamiltonian can be expressed in the form

$$H = \tfrac{1}{2}p^2 - Zr^{-1} + V(r) \tag{330}$$

where

$$V(r) = -Zr^{-1} \sum_{j=1}^{\infty} V_j r^j \lambda^j \tag{331}$$

and λ is the perturbation parameter. These problems can all be treated using the *so*(4, 2) algebraic approach (Bechler, 1977). We shall consider the case

$$U(r) = -r^{-1} e^{\lambda r} \tag{332}$$

Application of the scaling transformation of Section IX to the ground state gives

$$[K + W - \Delta E S]\tilde{\Psi} = 0 \tag{333}$$

where K and S are given by Eqs. (260) and (262) with $Z = 1$, and

$$W = 1 - e^{-\lambda r} = \sum_{j=1}^{\infty} W_j \lambda^j \tag{334}$$

$$W_j = (-1)^{j+1} r^j / j! \tag{335}$$

The perturbation equations for the wave functions and energy corrections can be developed as in the preceding subsection and the results are

$$|\tilde{\Psi}^{(0)}\rangle = |100\rangle \tag{336}$$

$$|\tilde{\Psi}^{(1)}\rangle = 0 \tag{337}$$

$$E^{(1)} = \langle 100|W_1|100\rangle = 1 \tag{338}$$

$$E^{(2)} = \langle 100|W_2|100\rangle = -3/4 \tag{339}$$

and

$$\tilde{\Psi}^{(k)} = \sum_{j=2}^{k} G(E^{(j)}r - W_j)\tilde{\Psi}^{(k-j)}; \qquad k \geq 2 \tag{340}$$

$$\begin{aligned} E^{(k)} &= \langle 100|W_k|100\rangle + \sum_{j=1}^{k-2} \langle 100|W_j|\tilde{\Psi}^{(k-j)}\rangle \\ &\quad - \sum_{j=1}^{k-2} E^{(j)}\langle 100|r|\tilde{\Psi}^{(k-j)}\rangle; \qquad k \geq 3 \end{aligned} \tag{341}$$

The series for the energy has the form

$$E = -\frac{1}{2} + \sum_{k=1}^{\infty} E^{(k)}\lambda^k \tag{342}$$

and the energy coefficients are given in Table IX, Appendix C, in rational form to order $k = 16$. Privman (1981a) has calculated the coefficients to order 40 in rational form using the one-dimensional logarithmic derivative approach. His results are reported in Rydberg atomic units rather than the Hartree atomic units we have been using, so his energy coefficients E_k are related to the ones in Table IX by

$$E_k = 2^{k-1}E^{(k)} \tag{343}$$

Recently this problem was also studied by Vrscay (1983).

E. Charmonium Potentials

It is believed that the main feature of the interaction between charmed quarks and antiquarks is given by a nonrelativistic confining potential of the form (Eichten *et al.*, 1978)

$$U(r) = -Zr^{-1} + \lambda r^q \tag{344}$$

so the *so*(4, 2) algebraic method of Section IX can again be applied with $Z = 1$ and

$$W = r^{q+1} \tag{345}$$

using Eqs. (274) and (275) for the wave function and energy corrections in the form

$$E = -\frac{1}{2} + \sum_{k=1}^{\infty} E^{(k)}\lambda^k$$
$$= -\frac{1}{2} + \sum_{k=1}^{\infty} E_k 2^{1-k}\lambda^k \qquad (346)$$

The coefficients E_k in the two cases $q = 1$ and $q = 2$ are integers and are given in Table X, Appendix C, to order $k = 10$. Results to order $k = 20$ for these two cases have also been reported by Privman (1981a). Very recently, perturbation theory to high order for generalized charmonium potential was carried out by Vrscay (1984, 1985).

Addendum. The Application of *so*(2, 1) to the Study of Charmonium and Harmonium in *N*-Dimension with the Use of Symbolic Computation[6]

Section X of the present review article is devoted to the application of perturbation theory to hydrogenic systems with different external potentials such as screened Coulomb potential and charmonium potential. The Lie algebraic approach is shown to be very useful in such cases, since it avoids the difficulties due to the presence of a discrete spectrum and of a continuum: the divergence of the perturbation series can then be efficiently treated. Since the preceding sections of the present review article were written, we have been investigating other applications of Lie algebraic methods to hydrogenic systems where the advantages of that approach would be clearly notable. Motivated by the comprehensive paper of MacDonald and Ritchie (1986), we pursued the study of the two-dimensional hydrogen atom in an external magnetic field. This problem is of interest not only in quantum chemistry but also in solid-state physics, as it represents a model for the treatment of shallow donor levels for semiconductor impurities near the center of a potential well. MacDonald and Ritchie obtained perturbation series expansions for the cases of weak and strong magnetic field: up to the fourth order for the high-field limit but, surprisingly, only the first-order low-field correction. In addition, they employed two-point Padé approximants to interpolate between these two limiting cases.

The hydrogen atom in a linear external field (charmonium) and in a quadratic external field (harmonium) has already been studied by Vrscay (1983, 1984, 1985). In both cases, Lie algebraic methods provided a considerable number of coefficients in the perturbation series expansion for small values of the coupling constant. However, these results were obtained for a

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[6] This section was written by F. Vinette.

three-dimensional case only. Cizek and Vinette (1987) thus considered the N-dimensional hydrogen atom in external fields of the type λr and λr^2 and obtained expressions, with the help of symbolic computation, for the perturbation energy up to the fourth order for an arbitrary-state atom. The physically relevant case of the two-dimensional hydrogen atom in a magnetic field is then easily obtained by substituting $N = 2$. These results are summarized below.

Consider the Schrödinger equation for the N-dimensional hydrogen atom in a radial external field λr^a, where $a = 1$ corresponds to charmonium and $a = 2$ corresponds to harmonium,

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r} + \lambda r^a\right]\Psi = E\Psi \tag{347}$$

After a scaling transformation $\hat{R} = r/n$, the hydrogenic radial eigenvalue problem, given by Eq. (256), becomes

$$[K + \lambda W - \Delta ES]\Psi = 0 \tag{348}$$

where K and R are given in terms of $so(2, 1)$ generators T_i as in Eqs. (257) and (276), and

$$\begin{aligned}
W &= n^{a+2}R^{a+1} \\
S &= n^2 R \\
\xi &= k(k+1) = (N-1)(N-3)/4 + l(l+N-2) \\
k &= l + N/2 - 3/2 \\
n &= k + 1 + n_r = l + N/2 - 1/2 + n_r
\end{aligned}$$

In these equations, n is a principal quantum number labeling the state considered, l is an angular momentum quantum number, and n_r is a radial quantum number.

Applying a modified Rayleigh–Schrödinger perturbation theory, one obtains the following expressions for the first four coefficients in the expansion of the perturbation energy. For charmonium, this gives (Cizek and Vinette, 1987)

$$\begin{aligned}
\Delta E_1 &= (3/2)n^2 - (1/2)\xi \\
\Delta E_2 &= -(1/8)n^2(7n^4 + 5n^2 - 3\xi^2) \\
\Delta E_3 &= (1/16)n^4(33n^6 + 75n^4 - 7n^2\xi^2 - 10\xi^3) \\
\Delta E_4 &= -(1/64)n^6(465n^8 + 2275n^6 + 440n^4 - 99n^4\xi^2 \\
&\quad - 90n^2\xi^3 - 180n^2\xi^2 - 84\xi^4)
\end{aligned} \tag{349}$$

Similarly, for harmonium, (Cizek and Vinette, 1987)

$$
\begin{aligned}
\Delta E_1 &= (1/2)n^2(5n^2 + 1 - 3\xi) \\
\Delta E_2 &= -(1/16)n^6(143n^4 + 345n^2 + 28 - 90n^2\xi - 21\xi^2 - 126\xi) \\
\Delta E_3 &= (1/16)n^{10}(1530n^6 + 11145n^4 + 8645n^2 + 484 - 1305n^4\xi \\
&\quad - 6825n^2\xi - 33\xi^3 + 33\xi^2 - 2706\xi) \\
\Delta E_4 &= -(1/1024)n^{14}(1502291n^8 + 22937530n^6 + 54811295n^4 \\
&\quad + 25371140n^2 + 1137344 - 1640100n^6\xi + 251370n^4\xi^2 \\
&\quad - 19742520n^4\xi - 3060n^2\xi^3 + 2184330n^2\xi^2 - 31859700n^2\xi \\
&\quad - 4005\xi^4 - 7260\xi^3 + 1425540\xi^2 - 7286640\xi) \qquad (350)
\end{aligned}
$$

These results were then numerically checked with those of Vrscay (1983, 1985) by suitably replacing the values for k and n. Finally, the substitution of $N = 2$, $n = 0$, and $\xi = 0$ provided the additional information for the construction of two-point Padé approximants. The results were compared with the numerical solution of the radial Schrödinger equation for the ground state, obtaining excellent agreement (Adams, 1987).

Although all necessary calculations could have been performed by hand, they were greatly facilitated by the use of the symbolic computation language MAPLE (Char *et al.*, 1986), which yielded the above simple expressions in terms of all parameters. With such an assistance we were able to obtain similar general expressions for the nth-order perturbation energy correction as well as to calculate additional mean values of observables other than the energy (Vinette and Cizek, 1987).

Appendix A. Operator and Commutator Identities

A. Levi–Civita Symbol

The Levi–Civita symbol is denoted by ϵ_{ijk} and is antisymmetric in all three indices. It is defined by

$$
\epsilon_{ijk} = \begin{cases} 1 & \text{if } ijk \text{ is an even permutation of } 123 \\ -1 & \text{if } ijk \text{ is an odd permutation of } 123 \\ 0 & \text{if two or more of } i, j, k, \text{ are equal} \end{cases} \qquad (A.1)
$$

Its primary use in our applications is for expressing various commutation relations in compact form and performing calculations involving them. The Levi–Civita symbol also arises naturally in vector analysis. Thus, if e_i, $i = 1$, 2, 3, are three mutually perpendicular unit vectors defining a right-handed coordinate system, then

$$
e_i \times e_j = \epsilon_{ijk} e_k \qquad (A.2)
$$

where a summation is implied over k. Because of the defining properties, Eq. (A.1), this sum contains only one term. It follows that the Levi–Civita symbol can be defined by

$$(e_i \times e_j) \cdot e_k = \epsilon_{ijk} \tag{A.3a}$$

which is just the signed volume of the unit cube.

As mentioned in Section II, these unit vectors generate a Lie algebra if we define

$$[e_i, e_j] = \epsilon_{ijk} e_k \tag{A.3b}$$

The Levi–Civita symbol has the following useful properties:

$$\epsilon_{ijm}\epsilon_{klm} + \epsilon_{jkm}\epsilon_{ilm} + \epsilon_{kim}\epsilon_{jlm} = 0 \tag{A.4}$$

$$\epsilon_{ijm}\epsilon_{klm} = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \tag{A.5}$$

$$\epsilon_{ilm}\epsilon_{klm} = 2\delta_{ik} \tag{A.6}$$

$$\epsilon_{ilm}\epsilon_{ilm} = 6 \tag{A.7}$$

where δ_{ij} is the usual Kronecker delta symbol. In these formulas and elsewhere we shall always assume summation over repeated indices. Equation (A.4) is a simple consequence of the Jacobi identity [property (5) in Section II,A], applied to the generators e_i of the Lie algebra [Eq. (A.3b)], and also follows from the well known vector identity

$$(\boldsymbol{a} \times \boldsymbol{b}) \times \boldsymbol{c} = (\boldsymbol{a} \cdot \boldsymbol{c})\boldsymbol{b} - (\boldsymbol{b} \cdot \boldsymbol{c})\boldsymbol{a} \tag{A.8}$$

which implies that

$$(\boldsymbol{a} \times \boldsymbol{b}) \times \boldsymbol{c} + (\boldsymbol{b} \times \boldsymbol{c}) \times \boldsymbol{a} + (\boldsymbol{c} \times \boldsymbol{a}) \times \boldsymbol{b} = 0 \tag{A.9}$$

Equation (A.5) follows by applying

$$(\boldsymbol{a} \times \boldsymbol{b}) \cdot (\boldsymbol{c} \times \boldsymbol{d}) = (\boldsymbol{a} \cdot \boldsymbol{c})(\boldsymbol{b} \cdot \boldsymbol{d}) - (\boldsymbol{a} \cdot \boldsymbol{d})(\boldsymbol{b} \cdot \boldsymbol{c}) \tag{A.10}$$

to the basis vectors e_i. Finally, Eq. (A.6) is obtained by setting $j = l$ in Eq. (A.5) and summing over l, and Eq. (A.7) follows from Eq. (A.6) by setting $k = i$ and summing over i, noting that $\delta_{jj} = 3$.

B. Useful Commutator Identities

The following general commutator identities are quite useful for simplifying the commutation relations, which occur in the determination of realizations of a Lie algebra. The well-known relations

$$[AB, C] = A[B, C] + [A, C]B \tag{A.11}$$

$$[A, BC] = B[A, C] + [A, B]C \tag{A.12}$$

can be used to simplify commutators involving products of operators. More generally we can show that for arbitrary polynomial functions f, g of the indicated operators

$$f(A)[g(A), B] = [g(A), f(A)B] \tag{A.13}$$

$$[A, g(B)]f(B) = [Af(B), g(B)] \tag{A.14}$$

which can be effectively used to move operators in and out of commutators. A useful special case involves a power of an operator

$$[A, B^n] = \sum_{k=0}^{n-1} B^k[A, B]B^{n-k-1} \tag{A.15}$$

which can be proved by induction on n.

In our discussion of scaling transformations in Section V we have to evaluate operator transformations of the form $e^{-B}Ae^{B}$ [cf. Eq. (94)]. To evaluate such expressions define

$$f(\lambda) = e^{-\lambda B}Ae^{\lambda B}$$

Differentiating we obtain

$$f'(\lambda) = e^{-\lambda B}[A, B]e^{\lambda B}$$

$$f''(\lambda) = e^{-\lambda B}[[A, B], B]e^{\lambda B}$$

and in general

$$f^{(n)}(\lambda) = e^{-\lambda B}[\cdots[[A, B], B], \ldots, B]e^{\lambda B}$$

where the multiple commutator contains B exactly n times. We can now expand $f(\lambda)$ in a Taylor series:

$$f(\lambda) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0)\lambda^n$$

Setting $\lambda = 1$ gives the useful operator identity

$$e^{-B}Ae^{B} = A + [A, B] + \frac{1}{2!}[[A, B], B] + \frac{1}{3!}[[[A, B], B], B] + \cdots \tag{A.16}$$

which can be used to obtain the scaling transformations given in Eqs. (95)–(97).

C. Commutators Involving Position and Momentum

In Sections V–VII we considered the construction of realizations of $so(2, 1)$, $so(4)$, and $so(4, 2)$, respectively. In order to evaluate the commutators among the generators of these Lie algebras to verify that we did indeed obtain a realization, it is necessary to evaluate some rather complex commutators involving position and momentum coordinates. Thus, we shall collect here a number of useful commutators to facilitate this task.

The basic commutation relations involving the position (x_i), momentum (p_i), and angular momentum (L_i) components are

$$[x_j, x_k] = [p_j, p_k] = 0 \tag{A.17}$$

$$[x_j, p_k] = i\delta_{jk} \tag{A.18}$$

$$[L_j, L_k] = i\epsilon_{jkl}L_l \tag{A.19}$$

All commutators can be obtained using these results. In particular, the following commutators involving p_i are useful:

$$[p_j, L_k] = i\epsilon_{jkl}p_l, \; [x_j, L_k] = i\epsilon_{jkl}x_l \tag{A.20}$$

$$[p, f(r)] = -irr^{-1}f'(r) = -i\nabla f \tag{A.21}$$

$$[p, r^{-n}] = inrr^{-n-2} \tag{A.22}$$

$$[p_j, x_k r^{-n}] = ir^{-n}[nx_j x_k r^{-2} - \delta_{jk}] \tag{A.23}$$

$$[p_j, x_j r^{-n}] = i(n-3)r^{-n} \tag{A.24}$$

where f is a function of the radial distance, r, and the last result implies summation over j. Commutators involving p^2, $\boldsymbol{r} \cdot \boldsymbol{p}$ are also useful:

$$[\boldsymbol{r}, p^2] = 2i\boldsymbol{p} \tag{A.25}$$

$$[f(r), p^2] = 2ir^{-1}f'(r)(\boldsymbol{r} \cdot \boldsymbol{p} - i) + f''(r) \tag{A.26}$$

$$[\boldsymbol{r}, \boldsymbol{r} \cdot \boldsymbol{p}] = i\boldsymbol{r} \tag{A.27}$$

$$[\boldsymbol{p}, \boldsymbol{r} \cdot \boldsymbol{p}] = -i\boldsymbol{p} \tag{A.28}$$

$$[f(r), \boldsymbol{r} \cdot \boldsymbol{p}] = irf'(r) \tag{A.29}$$

$$[\boldsymbol{r} \cdot \boldsymbol{p}, p^2] = 2ip^2 \tag{A.30}$$

Finally, some important commutators involving the angular momentum are

$$[L_j, f(r)] = 0, \qquad [L, r^2] = [L, p^2] = 0 \tag{A.31}$$

$$[L^2, x_j] = 2i(\boldsymbol{r} \times \boldsymbol{L})_j + 2x_j \tag{A.32}$$

$$[L^2, p_j] = 2i(\boldsymbol{p} \times \boldsymbol{L})_j + 2p_j \tag{A.33}$$

Some additional identities are (in vector notation)

$$\boldsymbol{p} \cdot \boldsymbol{r} = \boldsymbol{r} \cdot \boldsymbol{p} - 3i \tag{A.34}$$

$$\boldsymbol{r} \cdot \boldsymbol{L} = \boldsymbol{L} \cdot \boldsymbol{r} = \boldsymbol{p} \cdot \boldsymbol{L} = \boldsymbol{L} \cdot \boldsymbol{p} = 0 \tag{A.35}$$

$$\boldsymbol{L} \times \boldsymbol{L} = i\boldsymbol{L} \tag{A.36}$$

$$\boldsymbol{p} \times \boldsymbol{L} = \boldsymbol{r}p^2 - \boldsymbol{p}[(\boldsymbol{r} \cdot \boldsymbol{p}) - i] \tag{A.37}$$

$$\boldsymbol{r} \times \boldsymbol{L} = -\boldsymbol{p}r^2 + [(\boldsymbol{r} \cdot \boldsymbol{p}) - i]\boldsymbol{r} = \boldsymbol{r}(\boldsymbol{r} \cdot \boldsymbol{p}) - r^2\boldsymbol{p} \tag{A.38}$$

$$\boldsymbol{r} \times \boldsymbol{L} + \boldsymbol{L} \times \boldsymbol{r} = 2i\boldsymbol{r} \tag{A.39}$$

$$\boldsymbol{p} \times \boldsymbol{L} + \boldsymbol{L} \times \boldsymbol{p} = 2i\boldsymbol{p} \tag{A.40}$$

Appendix B. Scaling Transformations

In Section V we introduced scaling transformations from the active group theoretic viewpoint using the operator transformation, Eq. (94). Such transformations can be more directly achieved by introducing the following scaling transformation (Cizek and Paldus, 1977)

$$r = \lambda R; \qquad p_r = \lambda^{-1} P_R \tag{B.1}$$

Let us consider a perturbed hydrogenic radial equation [cf. Eqs. (249) and (98) with $w = 1$] in physical space:

$$(\tfrac{1}{2}p_r^2 + \tfrac{1}{2}\xi r^{-2} - Zr^{-1} + \zeta V(r) - E - \Delta E)\psi(r) = 0 \tag{B.2}$$

where the perturbation parameter is now designated by ζ. Multiplying by r on the left and introducing the scaling transformation, Eq. (B.1), we obtain

$$\lambda^{-1}[\tfrac{1}{2}RP_R^2 + \tfrac{1}{2}\xi R^{-1} - \lambda Z + \zeta\lambda^2 RV(\lambda R) - \lambda^2 R(E + \Delta E)]\psi(\lambda R) = 0 \tag{B.3}$$

Thus multiplying by λ and requiring that

$$2\lambda^2 E = -1 \tag{B.4}$$

we can rewrite Eq. (B.3) as follows

$$[T_3 - \lambda Z + \zeta W - \Delta E S]\psi(\lambda R) = 0 \tag{B.5}$$

where we now used T_3 of the $so(2, 1)$ realization defined in the scaled coordinate system,

$$\begin{aligned} T_1 &= \tfrac{1}{2}(RP_R^2 + \xi R^{-1} - R) \\ T_2 &= RP_R \\ T_3 &= \tfrac{1}{2}(RP_R^2 + \xi R^{-1} + R) \end{aligned} \tag{B.6}$$

and where we defined

$$\begin{aligned} W &= \lambda^2 RV(\lambda R) \\ S &= \lambda^2 R \end{aligned} \tag{B.7}$$

If we now consider the unperturbed problem, $\zeta = 0$, so that $\Delta E = 0$, we see immediately from Eq. (B.5) that λZ must be an integer. Thus, setting $n = \lambda Z$ so that

$$\lambda \equiv \lambda_n = n/Z \tag{B.8}$$

we find Bohr's formula for the unperturbed energy, Eq. (4),

$$E_n = -\tfrac{1}{2}\lambda_n^{-2} = -Z^2/2n^2$$

and we can write the perturbed problem, Eq. (B.5), as follows

$$[T_3 - n + \zeta W - \Delta E_n S]\psi(\lambda_n R) = 0$$

with

$$W = n^2 Z^{-2} R V(nZ^{-1}R)$$

$$S = n^2 Z^{-2} R$$

which should be compared with Eqs. (256)–(259). This derivation is much simpler than the usual approach to which we adhered to in the main text.

Appendix C. Matrix Elements and Perturbation Coefficients

In this appendix we collect together tables of matrix elements of r, r^2, r^3, z, z^2, rz, and $r(r^2 - z^2)$ in the scaled hydrogenic basis and perturbation corrections to the ground-state energy for the LoSurdo–Stark, Zeeman, screened Coulomb, and charmonium Hamiltonians and the one-electron diatomic ion.

TABLE I

MATRIX ELEMENTS OF POWERS OF r IN THE SCALED HYDROGENIC BASIS[a]

$$(r)_{nlm}^{100} = -(1/2)[(n-l)(n+l+1)]^{1/2}$$

$$(r)_{nlm}^{000} = n$$

$$(r^2)_{nlm}^{200} = (1/4)[(n-l)(n-l+1)(n+l+1)(n+l+2)]^{1/2}$$

$$(r^2)_{nlm}^{100} = -[(2n+1)/2][(n-l)(n+l+1)]^{1/2}$$

$$(r^2)_{nlm}^{000} = (3n^2 - X)/2$$

$$(r^3)_{nlm}^{300} = -(1/8)[(n-l)(n-l+1)(n-l+2)]^{1/2} \times [(n+l+1)(n+l+2)(n+l+3)]^{1/2}$$

$$(r^3)_{nlm}^{200} = [(3n+3)/4][(n-l)(n-l+1)]^{1/2} \times [(n+l+1)(n+l+2)]^{1/2}$$

$$(r^3)_{nlm}^{100} = -(3/8)(5n^2 + 5n + 2 - X)[(n-l)(n+l+1)]^{1/2}$$

$$(r^3)_{nlm}^{000} = n(5n^2 + 1 - 3X)/2$$

[a] See text for details $[X = l(l+1)]$.

TABLE II

MATRIX ELEMENTS OF z AND z^2 IN THE SCALED HYDROGENIC BASIS[a]

$$\begin{aligned}(z)^{010}_{nlm} &= -[(2l+1)(2l+3)]^{-1/2}\\ &\quad \times [(l-m+1)(l+m+1)(n-l-1)(n+l+1)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z)^{1-10}_{nlm} &= (1/2)[(2l-1)(2l+1)]^{-1/2}\\ &\quad \times [(l-m)(l+m)(n-l+1)(n-l)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z)^{110}_{nlm} &= (1/2)[(2l+1)(2l+3)]^{-1/2}\\ &\quad \times [(l-m+1)(l+m+1)(n+l+1)(n+l+2)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z^2)^{220}_{nlm} &= [4(2l+3)]^{-1}[(2l+1)(2l+5)]^{-1/2}\\ &\quad \times [(l-m+1)(l-m+2)(l+m+1)(l+m+2)]^{1/2}\\ &\quad \times [(n+l+1)(n+l+2)(n+l+3)(n+l+4)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z^2)^{200}_{nlm} &= (1/4)[(2X-2m^2-1)/(4X-3)]\\ &\quad \times [(n-l+1)(n-l)(n+l+1)(n+l+2)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z^2)^{2-20}_{nlm} &= [4(2l-1)]^{-1}[(2l-3)(2l+1)]^{-1/2}\\ &\quad \times [(l-m-1)(l-m)(l+m-1)(l+m)]^{1/2}\\ &\quad \times [(n-l)(n-l+1)(n-l+2)(n-l+3)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z^2)^{120}_{nlm} &= -(2l+3)^{-1}[(2l+1)(2l+5)]^{-1/2}\\ &\quad \times [(l-m+1)(l-m+2)(l+m+1)(l+m+2)]^{1/2}\\ &\quad \times [(n-l-1)(n+l+1)(n+l+2)(n+l+3)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z^2)^{100}_{nlm} &= -[(2n+1)/2][(2X-2m^2-1)/(4X-3)]\\ &\quad \times [(n-l)(n+l+1)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z^2)^{1-20}_{nlm} &= -(2l-1)^{-1}[(2l-3)(2l+1)]^{-1/2}\\ &\quad \times [(l-m-1)(l-m)(l+m-1)(l+m)]^{1/2}\\ &\quad \times [(n-l)(n-l+1)(n-l+2)(n+l)]^{1/2}\end{aligned}$$

$$\begin{aligned}(z^2)^{020}_{nlm} &= (3/2)(2l+3)^{-1}[(2l+1)(2l+5)]^{-1/2}\\ &\quad \times [(l-m+1)(l-m+2)(l+m+1)(l+m+2)]^{1/2}\\ &\quad \times [(n-l-2)(n-l-1)(n+l+1)(n+l+2)]^{1/2}\end{aligned}$$

$$(z^2)^{000}_{nlm} = [(3n^2-X)/2](2X-2m^2-1)/(4X-3)$$

---

[a] See text for details $[X = l(l+1)]$.

TABLE III

MATRIX ELEMENTS OF THE LOSURDO–STARK PERTURBATION rz IN THE SCALED HYDROGENIC BASIS[a]

$$\begin{aligned}(rz)^{2-10}_{nlm} &= -(1/4)[(2l-1)(2l+1)]^{-1/2}\\ &\quad \times [(l-m)(l+m)]^{1/2}\\ &\quad \times [(n+l+1)(n-l)(n-l+1)(n-l+2)]^{1/2}\end{aligned}$$

$$\begin{aligned}(rz)^{210}_{nlm} &= -(1/4)[(2l+1)(2l+3)]^{-1/2}\\ &\quad \times [(l-m+1)(l+m+1)]^{1/2}\\ &\quad \times [(n-l)(n+l+1)(n+l+2)(n+l+3)]^{1/2}\end{aligned}$$

$$\begin{aligned}(rz)^{1-10}_{nlm} &= [(2n+l+1)/2][(2l-1)(2l+1)]^{-1/2}\\ &\quad \times [(l-m)(l+m)(n-l+1)(n-l)]^{1/2}\end{aligned}$$

$$\begin{aligned}(rz)^{110}_{nlm} &= [(2n-l)/2][(2l+1)(2l+3)]^{-1/2}\\ &\quad \times [(l-m+1)(l+m+1)(n+l+1)(n+l+2)]^{1/2}\end{aligned}$$

$$\begin{aligned}(rz)^{010}_{nlm} &= -(3n/2)[(2l+1)(2l+3)]^{-1/2}\\ &\quad \times [(l-m+1)(l+m+1)(n-l-1)(n+l+1)]^{1/2}\end{aligned}$$

---

[a] See text for details.

TABLE IV

MATRIX ELEMENTS OF THE ZEEMAN PERTURBATION $W = r(r^2 - z^2)$ IN THE SCALED HYDROGENIC BASIS[a]

$$
\begin{aligned}
(W)^{320}_{nlm} = {} & (1/8)(2l+3)^{-1}[(2l+1)(2l+5)]^{-1/2} \\
& \times [(l-m+1)(l-m+2)(l+m+1)(l+m+2)]^{1/2} \\
& \times [(n-l)(n+l+1)(n+l+2)(n+l+3)]^{1/2} \\
& \times [(n+l+4)(n+l+5)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{300}_{nlm} = {} & -(1/4)[(X+m^2-1)/(4X-3)] \\
& \times [(n-l)(n-l+1)(n-l+2)]^{1/2} \\
& \times [(n+l+1)(n+l+2)(n+l+3)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{3-20}_{nlm} = {} & (1/8)(2l-1)^{-1}[(2l-3)(2l+1)]^{-1/2} \\
& \times [(l-m-1)(l-m)(l+m-1)(l+m)]^{1/2} \\
& \times [(n-l)(n-l+1)(n-l+2)(n-l+3)]^{1/2} \\
& \times [(n-l+4)(n+l+1)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{220}_{nlm} = {} & -[(3n-2l)/4](2l+3)^{-1}[(2l+1)(2l+5)]^{-1/2} \\
& \times [(l-m+1)(l-m+2)(l+m+1)(l+m+2)]^{1/2} \\
& \times [(n+l+1)(n+l+2)(n+l+3)(n+l+4)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{200}_{nlm} = {} & [(3n+3)/2)][(X+m^2-1)/(4X-3)] \\
& \times [(n-l)(n-l+1)(n+l+1)(n+l+2)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{2-20}_{nlm} = {} & -[(3n+2l+2)/4](2l-1)^{-1}[(2l-3)(2l+1)]^{-1/2} \\
& \times [(l-m-1)(l-m)(l+m-1)(l+m)]^{1/2} \\
& \times [(n-l)(n-l+1)(n-l+2)(n-l+3)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{120}_{nlm} = {} & [5(3n-l)/8](2l+3)^{-1}[(2l+1)(2l+5)]^{-1/2} \\
& \times [(l-m+1)(l-m+2)(l+m+1)(l+m+2)]^{1/2} \\
& \times [(n-l-1)(n+l+1)(n+l+2)(n+l+3)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{100}_{nlm} = {} & -(3/4)(5n^2+5n+2-X)[(X+m^2-1)/(4X-3)] \\
& \times [(n-l)(n+l+1)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{1-20}_{nlm} = {} & (5/8)(3n+l+1)(2l-1)^{-1}[(2l-3)(2l+1)]^{-1/2} \\
& \times [(l-m-1)(l-m)(l+m-1)(l+m)]^{1/2} \\
& \times [(n-l)(n-l+1)(n-l+2)(n+l)]^{1/2}
\end{aligned}
$$

$$
\begin{aligned}
(W)^{020}_{nlm} = {} & -(5n/2)(2l+3)^{-1}[(2l+1)(2l+5)]^{-1/2} \\
& \times [(l-m+1)(l-m+2)(l+m+1)(l+m+2)]^{1/2} \\
& \times [(n-l-2)(n-l-1)(n+l+1)(n+l+2)]^{1/2}
\end{aligned}
$$

$$
(W)^{000}_{nlm} = n(5n^2+1-3X)(X+m^2-1)/(4X-3)
$$

[a] See text for details [$X = l(l+1)$].

TABLE V

PERTURBATION CORRECTIONS TO THE GROUND-STATE ENERGY UP TO 20TH ORDER FOR THE LOSURDO–STARK PERTURBATION[a]

k	$E^{(k)}$
2	−9/4
4	−3555/64
6	−2512779/512
8	−13012777803/16384
10	−25497693122265/131072
12	−138963659571727791/2097152
14	−50205724908148860576 3/16777216
16	−186261677408532267929 12715/1073741824
18	−108153747299254161399143616141/4294967296
20	−1540770888228329784458463316315781/137438953472

[a] See text for details.

TABLE VI

PERTURBATION CORRECTIONS TO THE GROUND-STATE ENERGY UP TO 10TH ORDER FOR THE ZEEMAN PERTURBATION[a]

k	$E^{(k)}$
1	2
2	−53/3
3	5581/9
4	−21577397/540
5	31283298283/8100
6	−13867513160861/27000
7	5337333446078164463/59535000
8	−9958606672915942111123017/50009400000
9	866294634238659755927420474 23/15752961000000
10	−6127873544613551793091647103033033/3308121810000000

[a] See text for details.

TABLE VII

PERTURBATION CORRECTIONS TO THE WAVE FUNCTION UP TO FIFTH ORDER FOR ONE-ELECTRON DIATOMIC MOLECULAR IONS AT LARGE SEPARATION[a]

k	n	j	p	q	S_{nj}	A^k_{nj}
2	2	1	3	1	2	1
	3	1	3	1	2	−1/4
3	3	2	4	1	6	3/4
	4	2	4	1	1	−1/2
4	2	0	6	2	2	−23/8
	3	0	6	2	3	7/4
	3	2	6	2	6	11/8
	4	0	6	2	1	−1
	4	2	6	2	1	−3/2
	4	3	5	1	5	2
	5	0	6	2	5	1/16
	5	2	6	2	14	1/16
	5	3	5	1	10	−3/8
5	2	1	7	2	2	53/4
	3	1	7	2	2	−97/8
	4	1	7	2	25	22/5
	4	3	7	2	5	63/10
	5	1	7	2	10	−79/80
	5	3	7	2	10	−81/40
	5	4	6	1	70	15/8
	6	1	7	2	70	1/20
	6	3	7	2	5	9/20
	6	4	6	1	7	−3/2

[a] See text for details.

TABLE VIII

PERTURBATION CORRECTIONS TO THE GROUND-STATE ENERGY UP TO 15TH ORDER FOR ONE-ELECTRON DIATOMIC MOLECULAR IONS AT LARGE SEPARATIONS[a]

k	p	q	$E_{pq}^{(k)}$
4	4	2	9/4
5	4	1	0
6	6	2	15/2
7	8	3	213/4
8	8	2	525/8
	10	4	3555/64
9	10	3	1773/2
10	10	2	8505/8
	12	4	67749/16
11	12	3	42435/2
	14	5	501579/64
12	12	2	218295/8
	14	4	11036490/64
	16	6	2512779/512
13	14	3	23204655/32
	16	5	718680/1
14	14	2	2027025/2
	16	4	529880103/64
	18	6	408802203/256
15	16	3	1082786355/32
	18	5	3375376965/64
	20	7	916443651/512

[a] See text for details.

TABLE IX

PERTURBATION CORRECTIONS TO THE GROUND-STATE ENERGY UP TO 16TH ORDER FOR THE SCREENED COULOMB POTENTIAL[a]

k	$E^{(k)}$
1	1
2	−3/4
3	1/2
4	−11/16
5	21/16
6	−290/96
7	1514/192
8	−69433/3072
9	321449/4608
10	−2343967/10240
11	24316577/30720
12	−2536041607/884736
13	47860811537/4423680
14	−145923785051/3440640
15	159957248809633/928972800
16	−42949294634584421/59454259200

[a] See text for details.

TABLE X

PERTURBATION CORRECTIONS TO THE GROUND-STATE ENERGY UP TO 10TH ORDER FOR THE CHARMONIUM POTENTIALS r and r^2[a]

k	$E_k(W = r^2)$	$E_k(W = r^3)$
1	3	12
2	−12	−1032
3	216	348864
4	−6360	−211519200
5	245952	188054861568
6	−11433984	−225337358179584
7	610773696	348078597814278144
8	−36514015968	−674026573693938697728
9	2402441159040	1603169878479744477327360
10	−171993510639744	−4606772576062370817254928384

[a] See text for details.

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On the Change of Spectra Associated with Unbounded Similarity Transformations of a Many-Particle Hamiltonian and the Occurrence of Resonance States in the Method of Complex Scaling. Part I. General Theory

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If a self-adjoint operator, like the many-particle Hamiltonian H, undergoes an unbounded similarity transformation $\bar{H} = UHU^{-1}$, it loses its self-adjoint character, and its spectrum is subject to change: some eigenvalues are persistent, others may be lost, and new eigenvalues may occur also in the complex plane. It is shown how these spectral changes are related to the fact that the original eigenfunctions are transformed not only within the ordinary L^2 Hilbert space but also out of and into this space. Under certain conditions, the complex eigenvalues correspond to physical resonance states with a finite lifetime. If, further, the transformation U satisfies the special condition $(U^\dagger)^{-1} = U^*$, the transformed Hamiltonian has the important symmetry property $\bar{H}^\dagger = \bar{H}^*$, which greatly simplifies the theory. It is shown that the method of complex scaling provides an example of such a special transformation. Some applications will be given in a second paper.

I. Introduction

When one solves the Schrödinger equation $H\Psi = E\Psi$ for a self-adjoint Hamiltonian H subject to the standard boundary conditions, one obtains a spectrum $\{E\}$ of real eigenvalues E which are either discrete (corresponding to closed states) or continuous (corresponding to scattering states). However, if one changes the boundary conditions to include incoming waves, which by way of a "scatterer" are turned into outgoing waves, the Hamiltonian H is no longer self-adjoint and may have *complex eigenvalues* E corresponding to resonance states with a finite lifetime (*1*).

The theory of the resonance states was greatly simplified when it was discovered (*2*) that they could be described by quadratically integrable eigenfunctions associated with complex eigenvalues of a transformed Hamiltonian $\bar{H} = UHU^{-1}$, obtained from the original Hamiltonian H by an unbounded similarity transformation U. During the last 15 years, there has been a tremendous development in the theory of such dilated Hamiltonians obtained by "complex scaling," which was reviewed at the 1978 Sanibel workshop (*3*). Since then a great deal of work has been carried out, including practical applications (*4*).

The transformed Hamiltonian $\bar{H} = UHU^{-1}$ is no longer self-adjoint and the original spectrum $\{E\}$ has been changed: some energy eigenvalues are persistent, others may be lost, and new eigenvalues may occur also in the complex plane. Under certain conditions, this approach may provide a shortcut to find physical resonance states associated with the original Hamiltonian and special boundary condition. In this first paper, we will try to get a general understanding of the reasons for these spectral changes both in the exact theory and in the approximate treatment of eigenvalues and eigenfunctions. We will here try to take full advantage of the fact that, under certain conditions, the transformed Hamiltonian has the important symmetry property $\bar{H}^\dagger = \bar{H}^*$, which greatly simplifies the theory.

In Part II, we will consider the same problems on the Hartree–Fock level, and some numerical illustrations will be given.

II. Bounded Similarity Transformations

A. General Aspects

Let us start with some purely formal considerations. Let us consider a linear space $A = \{F\}$ and an operator U defined on this space, which maps it onto itself in a one-to-one way, so that

$$UF = G, \qquad F = U^{-1}G \tag{1.1}$$

Let us further consider a linear operator T defined on $A = \{F\}$ which maps this space on itself. In such a case, one may define an associated operator $\bar{T}$ defined on $A = \{F\}$ through the relation

$$\bar{T} = UTU^{-1} \tag{1.2}$$

which is referred to as a *similarity transformation.* If C is an eigenelement to T associated with the eigenvalue λ, so that

$$TC = \lambda C \tag{1.3}$$

then the transformed element

$$\bar{C} = UC \tag{1.4}$$

is an eigenelement to the operator $\bar{T}$, since one has

$$\bar{T}\bar{C} = \lambda\bar{C} \tag{1.5}$$

Since the reverse is also true, the operators T and $\bar{T}$ have evidently the same eigenvalues. In the treatment of the general stability problem (*5*), one observes that, if the projector O reduces T, so that

$$OT = TO \tag{1.6}$$

then the transformed projector $\bar{O} = UOU^{-1}$ reduces $\bar{T}$, since

$$\begin{aligned}\bar{O}\bar{T} &= UOU^{-1} \cdot UTU^{-1} \\ &= UOTU^{-1} = UTOU^{-1} \\ &= UTU^{-1} \cdot UOU^{-1} = \bar{T}\bar{O}\end{aligned} \tag{1.7}$$

In many connections, it is convenient to introduce an abstract *binary product* $\langle F_1 | F_2 \rangle$ associated with ordered pairs of elements of the linear space $A = \{F\}$, which is defined as linear in the second position, Hermitian symmetric, and positive definite:

$$\langle F | F_1\alpha_1 + F_2\alpha_2 \rangle = \langle F | F_1 \rangle \alpha_1 + \langle F | F_2 \rangle \alpha_2 \tag{1.8}$$

$$\langle F_2 | F_1 \rangle = \langle F_1 | F_2 \rangle^* \tag{1.9}$$

$$\langle F | F \rangle \geq 0, \qquad \text{and} \quad = 0, \qquad \text{iff} \quad F = \bar{0} \tag{1.10}$$

Using this concept, one may now introduce the *adjoint operator* $T^\dagger$ to the operator T through the relation

$$\langle F_1 | TF_2 \rangle = \langle T^\dagger F_1 | F_2 \rangle \tag{1.11}$$

If the adjoint operator $T^\dagger$ has the eigenelement D associated with the eigenvalue μ, so that

$$T^\dagger D = \mu D \tag{1.12}$$

one gets immediately (*5*)

$$\lambda\langle D|C\rangle = \langle D|TC\rangle = \langle T^\dagger|DC\rangle = \mu^*\langle D|C\rangle \tag{1.13}$$

i.e.,

$$(\lambda - \mu^*)\langle D|C\rangle = 0 \tag{1.14}$$

This means that, if $\mu \neq \lambda^*$, one has the orthogonality relation $\langle D|C\rangle = 0$, whereas, if $\langle D|C\rangle \neq 0$, one has $\mu = \lambda^*$. The operators T and $\bar{T}$ have hence complex conjugate eigenvalues and, after proper normalization, the sets $\mathbf{C} = \{C\}$ and $\mathbf{D} = \{D\}$ become *biorthonormal:*

$$\langle \mathbf{D}|\mathbf{C}\rangle = \mathbf{1} \tag{1.15}$$

From Eq. (1.6) it follows further that, if the projector O reduced T, then the adjoint projector $O^\dagger$ reduces $T^\dagger$.

For the adjoint of the transformed operator $\bar{T}$ defined by Eq. (1.2), one gets immediately

$$\bar{T}^\dagger = (U^{-1})^\dagger T^\dagger U^\dagger \tag{1.16}$$

It follows directly that the transformed element

$$\bar{D} = (U^\dagger)^{-1}D \tag{1.17}$$

is an eigenelement to $\bar{T}^\dagger$ associated with the eigenvalue $\mu = \lambda^*$:

$$\bar{T}^\dagger\bar{D} = \mu\bar{D} \tag{1.18}$$

For the transformed sets $\bar{\mathbf{C}} = U\mathbf{C}$ and $\bar{\mathbf{D}} = (U^\dagger)^{-1}\mathbf{D}$, one gets the biorthonormality relation

$$\langle \bar{\mathbf{D}}|\bar{\mathbf{C}}\rangle = \langle (U^\dagger)^{-1}\mathbf{D}|U\mathbf{C}\rangle = \langle \mathbf{D}|\mathbf{C}\rangle = \mathbf{1} \tag{1.19}$$

which shows an important invariance property of the transformed eigenelements.

If one introduces the norm $\|F\| = \langle F|F\rangle^{1/2}$ of an element F of the linear space $A = \{F\}$, one obtains the relation

$$\|UF\| = \langle F|U^\dagger U|F\rangle^{1/2} \tag{1.20}$$

where the operator $U^\dagger U = V$ may be described as a "metric operator." Using the method of polar decomposition (*6*), one may write the operator U in the form

$$U = W(U^\dagger U)^{1/2} = WV^{1/2} \tag{1.21}$$

where $W = U(U^\dagger U)^{-1/2}$ is a unitary operator satisfying the relation $W^\dagger W = WW^\dagger = 1$.

The operator U is said to be *bounded* with respect to the norm $\|F\|$, if there exists a finite number $K(U)$ with the property

$$||UF|| \leq K(U) \cdot ||F|| \tag{1.22}$$

For such a bounded operator, the spectral and general stability properties of the linear operator T stay essentially invariant under the transformation Eq. (1.2), and, for self-adjoint and normal operators, one has a series of well-known theorems. Before proceeding to the unbounded transformations, we will briefly review some additional properties of the bounded similarity transformations.

B. The Bivariational Principle

In the same way that a self-adjoint operator satisfies a variational principle, a pair of adjoint operators T and $T^\dagger$ satisfy a bivariational principle (*5*), which may also be applied to the transformed operators $\bar{T}$ and $\bar{T}^\dagger$. Let us start by considering the variational expressions

$$I = \frac{\langle D_a | T | C_a \rangle}{\langle D_a | C_a \rangle}; \qquad I^* = \frac{\langle C_a | T^\dagger | D_a \rangle}{\langle C_a | D_a \rangle} \tag{1.23}$$

which are complex conjugate quantities, hence it is sufficient to consider one of them. Here the functions C_a and D_a are approximate eigenfunctions to the operators T and $T^\dagger$, respectively, and the index "a" indicates their approximate nature. We will assume that they are first-order variations around the exact solutions, so that

$$C_a = C + \delta C, \qquad D_a = D + \delta D \tag{1.24}$$

where

$$(T - \lambda \cdot 1)C = 0, \qquad (T - \lambda \cdot 1)^\dagger D = 0 \tag{1.25}$$

in accordance with Eqs. (1.5) and (1.18). Using these eigenvalue relations, one obtains directly

$$\begin{aligned} I &= \lambda + \frac{\langle D_a | T - \lambda \cdot 1 | C_a \rangle}{\langle D_a | C_a \rangle} \\ &= \lambda + \frac{\langle \delta D | T - \lambda \cdot 1 | \delta C \rangle}{\langle D_a | C_a \rangle} \end{aligned} \tag{1.26}$$

Since there is obviously no first-order variation in the last member, one gets

$$\delta I = 0 \tag{1.27}$$

which is the bivariational principle. It is easily shown (*5*) that, if this principle is fulfilled for all variations δC and δD, then Eq. (1.27) is equivalent with the eigenvalue relations in Eq. (1.25).

C. Dual Choice of Bases; The Secular Equations

One may use the bivariational principle to calculate approximate eigenfunctions and eigenvalues to the operators $\bar{T}$ and $\bar{T}^\dagger$. For this purpose, we will introduce two linearly independent sets of order m

$$\boldsymbol{\Psi} = \{\Psi_1, \Psi_2, \ldots, \Psi_m\}, \qquad \boldsymbol{\Phi} = \{\Phi_1, \Phi_2, \ldots, \Phi_m\} \tag{1.28}$$

which have the additional property that their "overlap matrix" $\boldsymbol{\Delta} = \langle \boldsymbol{\Phi} \,|\, \boldsymbol{\Psi} \rangle$ is *nonsingular* and has an inverse. Using these bases, one may now try to expand the approximate eigenfunctions in the form

$$C_{\mathrm{a}} = \boldsymbol{\Psi}\mathbf{c}, \qquad D_{\mathrm{a}} = \boldsymbol{\Phi}\mathbf{d} \tag{1.29}$$

Substituting these expansions into the bivariational expression, Eq. (1.23), one obtains

$$\begin{aligned} I &= \frac{\langle C_{\mathrm{a}} | T | D_{\mathrm{a}} \rangle}{\langle C_{\mathrm{a}} | D_{\mathrm{a}} \rangle} \\ &= \frac{\mathbf{d}^\dagger \langle \boldsymbol{\Phi} | T | \boldsymbol{\Psi} \rangle \mathbf{c}}{\mathbf{d}^\dagger \langle \boldsymbol{\Phi} \,|\, \boldsymbol{\Psi} \rangle \mathbf{c}} = \frac{\mathbf{d}^\dagger \mathbf{T} \mathbf{c}}{\mathbf{d}^\dagger \boldsymbol{\Delta} \mathbf{c}} \end{aligned} \tag{1.30}$$

where

$$\mathbf{T} = \langle \boldsymbol{\Phi} | T | \boldsymbol{\Psi} \rangle, \qquad \boldsymbol{\Delta} = \langle \boldsymbol{\Phi} \,|\, \boldsymbol{\Psi} \rangle \tag{1.31}$$

Using the bivariational principle to determine the column vectors **c** and **d**, one gets immediately the linear relations

$$\mathbf{T}\mathbf{c} = I\, \boldsymbol{\Delta}\mathbf{c}, \qquad \mathbf{T}^\dagger \mathbf{d} = I^*\, \boldsymbol{\Delta}^* \mathbf{d} \tag{1.32}$$

where the possible I values are given by the m roots to the secular equation:

$$P(Z) \equiv |\mathbf{T} - Z \cdot \boldsymbol{\Delta}| = 0 \tag{1.33}$$

By solving the homogeneous relations, Eq. (1.32), for the column vectors **c** and **d**, one obtains the approximate solutions, Eq. (1.29), associated with the bivariational principle.

It is evident that the same approach may be used to find also the approximate eigenvalues $\bar{I}$ and $\bar{I}^*$ and eigenfunctions $\bar{C}_{\mathrm{a}}$ and $\bar{D}_{\mathrm{a}}$ to the transformed operators $\bar{T}$ and $\bar{T}^\dagger$, in which case one would introduce two linearly independent sets $\bar{\boldsymbol{\Psi}}$ and $\bar{\boldsymbol{\Phi}}$ of order m and express the approximate eigenfunctions in the form

$$\bar{C}_{\mathrm{a}} = \bar{\boldsymbol{\Psi}}\bar{\mathbf{c}}, \qquad \bar{D}_{\mathrm{a}} = \bar{\boldsymbol{\Phi}}\mathbf{d} \tag{1.34}$$

In many cases, it seems natural to introduce the dual bases $\bar{\boldsymbol{\Psi}}$ and $\bar{\boldsymbol{\Phi}}$ through the relations

$$\bar{\boldsymbol{\Psi}} = U\boldsymbol{\Psi}, \qquad \bar{\boldsymbol{\Phi}} = (U^\dagger)^{-1}\boldsymbol{\Phi} \tag{1.35}$$

For the associate matrices $\bar{\mathbf{T}}$ and $\bar{\boldsymbol{\Delta}}$, one obtains in such a case

$$\begin{aligned}\bar{\mathbf{T}} &= \langle\bar{\boldsymbol{\Phi}}|\bar{T}|\bar{\boldsymbol{\Psi}}\rangle = \langle(U^{\dagger})^{-1}\boldsymbol{\Phi}|UTU^{-1}|U\boldsymbol{\Psi}\rangle \\ &= \langle\boldsymbol{\Phi}|T|\boldsymbol{\Psi}\rangle = \mathbf{T} \qquad (1.36)\\ \bar{\boldsymbol{\Delta}} &= \langle\bar{\boldsymbol{\Phi}}|\bar{\boldsymbol{\Psi}}\rangle = \langle(U^{\dagger})^{-1}\boldsymbol{\Phi}|U\boldsymbol{\Psi}\rangle \\ &= \langle\boldsymbol{\Phi}|\boldsymbol{\Psi}\rangle = \boldsymbol{\Delta} \qquad (1.37)\end{aligned}$$

i.e., the matrices $\mathbf{T}$ and $\boldsymbol{\Delta}$ in the Eq. (1.32) stay unchanged. Hence one has $\bar{I} = I$ and

$$\bar{\mathbf{c}} = \mathbf{c}, \qquad \bar{\mathbf{d}} = \mathbf{d} \qquad (1.38)$$

which implies that also the approximate eigenfunctions undergo the transformations

$$\bar{C}_{\mathrm{a}} = UC_{\mathrm{a}}, \qquad \bar{D}_{\mathrm{a}} = (U^{\dagger})^{-1}D_{\mathrm{a}} \qquad (1.39)$$

which are characteristic for the exact solutions according to Eqs. (1.4) and (1.17), respectively.

D. Outer Projections

It should be observed that one can conveniently describe the calculation of approximate eigenfunctions in terms of truncated basis sets by using the concept of "outer projections" (7) of the operators involved. If $\boldsymbol{\Psi} = \{\Psi_k\}$ and $\boldsymbol{\Phi} = \{\Phi_k\}$ for $k = 1, 2, \ldots, m$ are the dual bases chosen, the operator

$$\begin{aligned}Q &= |\boldsymbol{\Psi}\rangle\langle\boldsymbol{\Phi}|\boldsymbol{\Psi}\rangle^{-1}\langle\boldsymbol{\Phi}| \\ &= \sum_{k,l=1}^{m} |\Psi_k\rangle\, d_{kl}\langle\Phi_l| \qquad (1.40)\end{aligned}$$

where $\mathbf{d} = \boldsymbol{\Delta}^{-1} = \langle\boldsymbol{\Phi}|\boldsymbol{\Psi}\rangle^{-1}$ has the properties

$$Q^2 = Q, \qquad \mathrm{Tr}\, Q = m, \qquad Q^{\dagger} \neq Q \qquad (1.41)$$

Unless the sets $\boldsymbol{\Psi}$ and $\boldsymbol{\Phi}$ span the same space, the operator Q is usually not self-adjoint and it may hence be described as a *skew projector* associated with an oblique projection of nonorthogonal character. It is immediately seen that it has the particular properties

$$Q\boldsymbol{\Psi} = \boldsymbol{\Psi}, \qquad Q^{\dagger}\boldsymbol{\Phi} = \boldsymbol{\Phi} \qquad (1.42)$$

Introducing the "outer projection" T' of the operator T with respect to the projector Q through the relation

$$T' = QTQ \qquad (1.43)$$

and, using Eq. (1.42), one finds directly

$$\begin{aligned}\mathbf{T}' &= \langle \mathbf{\Phi} | T' | \mathbf{\Psi} \rangle = \langle \mathbf{\Phi} | QTQ | \mathbf{\Psi} \rangle \\ &= \langle Q^\dagger \mathbf{\Phi} | T | Q\mathbf{\Psi} \rangle = \langle \mathbf{\Phi} | T | \mathbf{\Psi} \rangle = \mathbf{T}\end{aligned} \tag{1.44}$$

i.e., the operators T and T' have the same matrix representation with respect to the dual bases $\mathbf{\Psi}$ and $\mathbf{\Phi}$. Using the relations [Eq. (1.32)] one finds further that the approximate solutions C_a and D_a are now the *exact* eigenfunctions to the operators T' and $(T')^\dagger$:

$$T'C_a = IC_a, \qquad (T')^\dagger D_a = I^* D_a \tag{1.45}$$

It is interesting to observe that the outer projection $\bar{T}' = OTO$ of the transformed operator $\bar{T} = UTU^{-1}$ may always be written as a similarity transformation with respect to the operator U of an outer projection $T' = QTQ$ of the original operator T, so that

$$\bar{T}' = UT'U^{-1} \tag{1.46}$$

This follows from the fact that

$$\begin{aligned}T' &= U^{-1}\bar{T}'U = U^{-1}O\bar{T}OU \\ &= U^{-1}OUTU^{-1}OU = QTQ\end{aligned} \tag{1.47}$$

where

$$Q = U^{-1}OU, \qquad O = UQU^{-1} \tag{1.48}$$

The projectors Q and O are hence connected by the same similarity transformation. In the treatment of the transformed operator $\bar{T}$, this corresponds to the special choice [Eq. (1.35)] of the dual bases. One gets directly

$$\begin{aligned}\bar{Q} &= |\bar{\mathbf{\Psi}}\rangle\langle\bar{\mathbf{\Phi}}|\bar{\mathbf{\Psi}}\rangle^{-1}\langle\bar{\mathbf{\Phi}}| \\ &= U|\mathbf{\Psi}\rangle\langle\mathbf{\Phi}|\mathbf{\Psi}\rangle\langle\mathbf{\Phi}|U^{-1} = UQU^{-1} = O\end{aligned} \tag{149}$$

It is clear that the concept of "outer projections" permits us to formulate the approximate treatment of the eigenfunctions and eigenvalues based on the bivariational principle in an exact manner.

E. Complex Symmetric Operators

In the treatment of a pair of adjoint operators T and $T^\dagger$ there are sometimes certain connections which greatly simplify the treatment of the eigenvalue problem, as, for example, the relation $T^\dagger = T^*$. In order to define this relation and particularly the operator T^* properly, we will start this section by assuming that the linear operator T is defined on a linear space $A = \{F\}$, the elements of which are complex functions of certain variables.

Let us further assume that this space is stable under *complex conjugation* $*$, so that, if the function F belongs to the space, also the complex conjugated function F^* belongs to the space. In such a case, one can define the *complex conjugate* T^* of the operator T through the relation

$$T^*F = (TF^*)^* \tag{1.50}$$

In the particular case when $T = T^*$, one says that the operator T is *real*. On the other hand, if the operator T satisfies the relation

$$T^\dagger = T^* \tag{1.51}$$

the operator T is said to be *complex symmetric*. Taking the complex conjugate of the eigenvalue relation $TC = \lambda C$, one obtains $T^*C^* = \lambda^* C^*$ and

$$T^\dagger C^* = \lambda^* C^* \tag{1.52}$$

and this implies that

$$D = C^* \tag{1.53}$$

i.e., the eigenfunctions to T and $T^\dagger$ are complex conjugate. It is evident that such a property will greatly simplify the treatment of the eigenvalue problem.

The simplest example of a complex symmetric operator is the nonrelativistic many-particle Hamiltonian H for an atomic, molecular, or solid-state system, which consists essentially of the kinetic energy of the particles and their mutual Coulomb interaction. Since such a Hamiltonian is both self-adjoint and real, one obtains

$$H = H^\dagger, \qquad H = H^* \tag{1.54}$$

and

$$H^\dagger = H^* \tag{1.55}$$

i.e., such a Hamiltonian is also complex symmetric. It should be observed, however, that if the system contains electromagnetic fields, this property is lost, and one has to use the more general theory.

Let us now also consider the transformed operator $\bar{T} = UTU^{-1}$ as well as the associated operators:

$$\bar{T}^\dagger = (U^\dagger)^{-1} T^\dagger U^\dagger, \qquad \bar{T}^* = U^* T^* (U^*)^{-1} \tag{1.56}$$

It is evident that if the operator U satisfies the specific relation

$$(U^\dagger)^{-1} = U^* \tag{1.57}$$

then the relation

$$\bar{T}^\dagger = \bar{T}^* \tag{1.58}$$

is true also for the transformed operator $\bar{T}$. In such a case, one has also

$$\bar{D} = \bar{C}^* \tag{1.59}$$

It is clear that, in studying the eigenfunctions C and D to the operators T and $T^\dagger$, which satisfy the relation Eq. (1.51), it may be convenient to choose the two basic sets $\boldsymbol{\Phi}$ and $\boldsymbol{\Psi}$ as complex conjugate:

$$\boldsymbol{\Phi} = \boldsymbol{\Psi}^* \tag{1.60}$$

For the associated matrix, $\mathbf{T} = \langle \boldsymbol{\Phi} | T | \boldsymbol{\Psi} \rangle$, one finds directly

$$\begin{aligned} \mathbf{T}^\dagger &= \langle \boldsymbol{\Phi} \,|\, T\boldsymbol{\Psi} \rangle^\dagger = \langle T\boldsymbol{\Psi} \,|\, \boldsymbol{\Phi} \rangle = \langle \boldsymbol{\Psi} \,|\, T^\dagger \boldsymbol{\Phi} \rangle \\ &= \langle \boldsymbol{\Psi} \,|\, T^* \boldsymbol{\Psi}^* \rangle = \langle \boldsymbol{\Psi}^* \,|\, T\boldsymbol{\Psi} \rangle^* = \mathbf{T}^* \end{aligned} \tag{1.61}$$

or

$$\tilde{\mathbf{T}} = \mathbf{T}, \qquad T_{kl} = T_{lk} \tag{1.62}$$

i.e., $\mathbf{T}$ is *symmetric matrix*, having complex elements. For the overlap matrix $\boldsymbol{\Delta} = \langle \boldsymbol{\Phi} \,|\, \boldsymbol{\Psi} \rangle$, one obtains in the same way $\boldsymbol{\Delta}^\dagger = \langle \boldsymbol{\Psi} \,|\, \boldsymbol{\Phi} \rangle = \langle \boldsymbol{\Phi} \,|\, \boldsymbol{\Psi} \rangle^* = \boldsymbol{\Delta}^*$, i.e.,

$$\tilde{\boldsymbol{\Delta}} = \boldsymbol{\Delta} \qquad \text{or} \qquad \Delta_{kl} = \Delta_{lk} \tag{1.63}$$

Comparing the two relations given in Eq. (1.32) and using Eqs. (1.62) and (1.63), one obtains directly

$$\mathbf{d} = \mathbf{c}^* \tag{1.64}$$

and this means that even the approximate solutions C_a and D_a are complex conjugate.

In treating the transformed operators $\bar{T} = UTU^{-1}$ and $\bar{T}^\dagger = \bar{T}^*$, it may further seem natural to introduce the dual bases:

$$\bar{\boldsymbol{\Psi}} = U\boldsymbol{\Psi}, \qquad \bar{\boldsymbol{\Phi}} = (U^\dagger)^{-1}\boldsymbol{\Phi} = U^*\boldsymbol{\Psi}^* = \bar{\boldsymbol{\Psi}}^* \tag{1.65}$$

For the associate matrices $\bar{\mathbf{T}}$ and $\bar{\boldsymbol{\Delta}}$, one obtains

$$\begin{aligned} \bar{\mathbf{T}} &= \langle \bar{\boldsymbol{\Phi}} | \bar{T} | \bar{\boldsymbol{\Psi}} \rangle = \langle (U^\dagger)^{-1}\boldsymbol{\Phi} | UTU^{-1} | U\boldsymbol{\Psi} \rangle \\ &= \langle \boldsymbol{\Phi} | T | \boldsymbol{\Psi} \rangle = \mathbf{T} \end{aligned} \tag{1.66}$$

$$\begin{aligned} \bar{\boldsymbol{\Delta}} &= \langle \bar{\boldsymbol{\Phi}} \,|\, \bar{\boldsymbol{\Psi}} \rangle = \langle (U^\dagger)^{-1}\boldsymbol{\Phi} \,|\, U\boldsymbol{\Psi} \rangle \\ &= \langle \boldsymbol{\Phi} \,|\, \boldsymbol{\Psi} \rangle = \boldsymbol{\Delta} \end{aligned} \tag{1.67}$$

i.e., the matrices $\mathbf{T}$ and $\boldsymbol{\Delta}$ stay unchanged. The same applies to the column vectors $\mathbf{c}$ and $\mathbf{d}$

$$\bar{\mathbf{c}} = \mathbf{c}, \qquad \bar{\mathbf{d}} = \mathbf{d} \tag{1.68}$$

and this means that also the approximate solutions satisfy the relations

$$\bar{C}_a = UC_a, \qquad \bar{D}_a = (U^\dagger)^{-1}D_a = U^*C_a^* = \bar{C}^* \tag{1.69}$$

By using the bivariational principle and proper choice of bases, it is hence possible to transfer some of the characteristic properties of the exact eigenfunctions to the approximate ones.

It is evident that the symmetry property $\bar{T}^\dagger = \bar{T}^*$ greatly simplifies the theory, and in the next section we will study it from a slightly different and perhaps deeper point of view. A similarity transformation, where the operator U satisfies the relation, Eq. (1.57), will be referred to as a *restricted similarity transformation.* In order to show that such transformations exist, it is sufficient to write U in the exponential form

$$U = e^{\Omega} \tag{1.70}$$

Since $(U^\dagger)^{-1} = e^{-\Omega^\dagger}$ and $U^* = e^{\Omega^*}$, it is clear that the relation, Eq. (1.57), is fulfilled, if the operator Ω satisfies the condition

$$\Omega^\dagger = -\Omega^* \tag{1.71}$$

i.e., the operator Ω is *complex antisymmetric.* The momentum operator $p = i\hbar\,\partial/\partial x$ is self-adjoint $p^\dagger = p$, but it has also the property $p^* = -p$ which gives $p^\dagger = -p^*$. Any self-adjoint operator $\Omega = \Omega(x, p)$, which is a function of the operators x and p and which is *odd* in the powers of p, is hence going to satisfy the condition, Eq. (1.57).

F. Complex Conjugate Biorthonormal Sets

The eigenfunctions $\mathbf{C} = \{C_k\}$ and $\mathbf{D} = \{D_k\}$ to the operators T and $T^\dagger$ have, according to Eq. (1.15), the special property of being biorthonormal, i.e., $\langle \mathbf{D} | \mathbf{C} \rangle = \mathbf{1}$. If $T^\dagger = T^*$, one has at the same time $\mathbf{D} = \mathbf{C}^*$, and this gives the relation

$$\langle \mathbf{C}^* | \mathbf{C} \rangle = \mathbf{1} \tag{1.72}$$

A set $\mathbf{C}$ having this property is said to be complex conjugate biorthonormal.

It is further evident that it would greatly simplify the overlap problem if one could introduce dual bases $\boldsymbol{\varphi}$ and $\boldsymbol{\varphi}^*$ which would be biorthonormal. For this purpose, we will start out from a linearly independent set $\boldsymbol{\phi} = \{\phi_1, \phi_2, \ldots, \phi_m\}$ of order m and put

$$\boldsymbol{\varphi} = \boldsymbol{\phi}\mathbf{A} \tag{1.73}$$

where $\mathbf{A} = \{A_{kl}\}$ is a quadratic matrix to be determined. We will further assume that the overlap matrix

$$\boldsymbol{\Delta} = \langle \boldsymbol{\phi}^* | \boldsymbol{\phi} \rangle \tag{1.74}$$

is *nonsingular.* It should be observed that, even if the matrix $\langle\phi|\phi\rangle$ is nonsingular due to the fact that the set ϕ is linearly independent, one still has to check that the matrix $\mathbf{\Delta}$ is nonsingular. One gets immediately the relation

$$\begin{aligned}\langle\varphi^*|\varphi\rangle &= \langle\phi^*\mathbf{A}^*|\phi\mathbf{A}\rangle = (\mathbf{A}^*)^\dagger\langle\phi^*|\phi\rangle\,\mathbf{A}\\ &= \tilde{\mathbf{A}}\,\mathbf{\Delta}\mathbf{A} = \mathbf{1}\end{aligned} \tag{1.75}$$

where $\tilde{\mathbf{\Delta}} = \mathbf{\Delta}$. *This means that, if one can construct a square root*

$$\mathbf{A} = \mathbf{\Delta}^{-1/2} = \langle\phi^*|\phi\rangle^{-1/2} \tag{1.76}$$

which is symmetric, then the set

$$\varphi = \phi\langle\phi^*|\phi\rangle^{-1/2} \tag{1.77}$$

is going to be complex conjugate biorthonormal. The details of constructing the square root are treated in Appendix A.

With this choice of basis, the first relation [Eq. (1.32)] simplifies to the form

$$\mathbf{Tc} = l\mathbf{c} \tag{1.78}$$

where

$$\mathbf{T} = \langle\varphi^*|T|\varphi\rangle \tag{1.79}$$

is a symmetric matrix with complex elements.

It is evident that the solution $\mathbf{A} = \mathbf{\Delta}^{-1/2}$ given by Eq. (1.76) is a special solution to Eq. (1.75). Putting $\mathbf{A}' = \mathbf{AB}$, one finds that $\mathbf{A}'$ represents the general solution, provided that the matrix $\mathbf{B}$ satisfies the relation $\tilde{\mathbf{B}}\mathbf{B} = \mathbf{1}$, or

$$(\mathbf{B}^\dagger)^{-1} = \mathbf{B}^* \tag{1.80}$$

which is obviously the matrix analog of the condition Eq. (1.57).

If, finally, the set $\phi = \{\phi_k\}$ is chosen *real,* then the matrix $\mathbf{\Delta} = \langle\phi^*|\phi\rangle = \langle\phi|\phi\rangle$ becomes automatically nonsingular, and the relation Eq. (1.77) defines a real orthonormal set φ, which is obtained from ϕ by means of the method of "symmetric orthonormalization" (8).

III. Unbounded Similarity Transformations and the Associated Change of Boundary Conditions

A. Some General Aspects on the Boundary Conditions Associated with the Eigenvalue Problem

In physics, it is customary to formulate the eigenvalue problem of a self-adjoint many-particle Hamiltonian H and the associated boundary conditions which define its spectrum $\{E\}$, in terms of the mathematical framework based on the theory of the *Hilbert space.* Before proceeding, it may hence be worthwhile to briefly review some of the fundamental concepts in this connection.

According to von Neumann (*9*), an abstract *Hilbert space* $\mathscr{H}$ is a linear space $A = \{x\}$ having a binary product $\langle x_1 | x_2 \rangle$, which satisfies the conditions, Eqs. (1.8)–(1.10), and which further contains all its limit points in the norm $\|x\| = \langle x | x \rangle^{1/2}$ and is separable. The last assumption means that there exists an enumerable set $\mathscr{H}' = \{x_k\}$ which is everywhere dense in $\mathscr{H}$ and which ensures the existence of at least one complete orthonormal set $\boldsymbol{\varphi} = \{\varphi_k\}$ spanning the space.

There are two realizations of the abstract Hilbert space which are frequently used in physics: the sequential Hilbert space $\mathscr{H}_0$, and the L^2 Hilbert space. The *sequential Hilbert space* $\mathscr{H}_0$ consists of all infinite column vectors $\mathbf{c} = \{c_k\}$ with complex elements having a finite norm $\|\mathbf{c}\|$, so that

$$\|\mathbf{c}\|^2 = \mathbf{c}^\dagger \mathbf{c} = \sum_{k=1}^{\infty} |c_k|^2 < \infty \tag{2.1}$$

and the binary product

$$\langle \mathbf{d} | \mathbf{c} \rangle = \mathbf{d}^\dagger \mathbf{c} = \sum_{k=1}^{\infty} d_k^* c_k \tag{2.2}$$

The elements of the L^2 *Hilbert space* are the complex functions $\Psi = \Psi(X)$ of a composite real variable $X = \{x_1, x_2, \ldots, x_N\}$ having a finite norm $\|\Psi\|$, so that

$$\|\Psi\| = \int |\Psi(X)|^2 \, dX < \infty \tag{2.3}$$

where the integral has to be carried out in the sense of Lebesgue—hence the symbol L. This Hilbert space hence consists of all complex functions Ψ which are absolutely quadratically integrable—hence the symbol L^2. It has a binary product defined through the relation

$$\langle \Psi_1 | \Psi_2 \rangle = \int \Psi_1^*(X) \Psi_2(X) \, dX \tag{2.4}$$

It should be observed that, in physics, the elements x_k of the composite real variable $X = \{x_1, x_2, \ldots, x_N\}$ often themselves contain several variables. For instance, in the so-called coordinate picture, each element x_k has the form $x_k = (\mathbf{r}_k, \zeta_k)$, where $\mathbf{r}_k$ is the three-dimensional coordinate for particle k and ζ_k is the coordinate for its spin, isotopic spin, etc., taking only discrete values. It should be observed that, in the relations given by Eqs. (2.3) and (2.4), the integration symbol $\int dX$ indicates Lebesgue integration over all space coordinates involved between $-\infty$ and $+\infty$ and summation over all the discrete variables.

The connection between the two Hilbert spaces $\mathscr{H}_0$ and L^2 used in physics is established by using the existence of at least one orthonormal basis $\varphi = \{\varphi_k(X)\}$ in L^2, which leads to the expansion theorem

$$\Psi(X) = \sum_{k=1}^{\infty} \psi_k(X) c_k = \varphi \mathbf{c} \tag{2.5}$$

with $c_k = \langle \varphi_k | X \rangle$, where the infinite series is convergent in the norm, so that

$$\lim_{n \to \infty} \left\| \Psi - \sum_{k=1}^{n} \varphi_k c_k \right\| = 0 \tag{2.6}$$

For further details as to the isomorphism between the three Hilbert spaces $\mathscr{H}$, $\mathscr{H}_0$, and L^2, the reader is referred to von Neumann's book (*9*).

If, further, T is a linear operator defined on the L^2 space $\{\Psi\}$, one says that an element $\Psi = \Psi(X)$ belongs to the *domain* $D(T)$ of the operator T, if both T and its image $T\Psi$ belong to L^2; the set $\{T\Psi\}$ is then referred to as the *range* of the operator T. It should be observed that a bounded operator T as a rule has the entire Hilbert space as its domain—or may be extended to achieve this property—whereas an unbounded operator T has a more restricted domain. In the latter case, we will let the symbol $C(T)$ denote the *complement* to the domain $D(T)$ with respect to the Hilbert space. A function $\Psi = \Psi(X)$ is hence an element of $C(T)$, if it belongs to L^2, whereas this is not true for its image $T\Psi$.

According to Eq. (1.11), the adjoint operator $T^\dagger$ with respect to the binary product Eq. (2.4) is now defined through the relation

$$\langle \Psi_1 | T\Psi_2 \rangle = \langle T^\dagger \Psi_1 | \Psi_2 \rangle \tag{2.7}$$

which is meaningful provided that Ψ_2 and Ψ_1 belong to the domains of the operators T and $T^\dagger$, respectively. In the following discussion, we will always assume that these domains, $D(T)$ and$D(T^\dagger)$, have been extended as far as is ever possible within the L^2 Hilbert space.

The problem treated in this paper is complicated by the fact that the linear operator T is supposed to be linearly defined on a linear space $A = \{F\}$ of all complex functions $F = F(X)$ of a real composite variable $X = \{x_1, x_2, \ldots, x_N\}$, of which the L^2 Hilbert space is only a small subspace. We will refer to this space $A = \{F\}$ as the *definition space* of the operator T. Since it contains all complex functions, it is stable under complex conjugation $*$, and, according to Eq. (1.50) one has $T^*F = (TF^*)^*$, which means that also the complex conjugate operator T^* is defined on this space.

The adjoint operator $T^\dagger$ is defined only on the domain $D(T^\dagger)$ inside the L^2 Hilbert space. In the important case, when the operator T is complex symmetric within the domain $D(T^\dagger)$, so that $T^\dagger = T^*$, one has first of all

$D(T^\dagger) = D(T^*) = D(T)$. Second, one may try to extend the definition of $T^\dagger$, first to the entire Hilbert space, and second to the entire definition space $A = \{F\}$, by using the relation

$$T^\dagger = T^* \tag{2.8}$$

everywhere. In such a case, it should be observed, however, that the relation Eq. (2.7), or

$$\begin{aligned}\langle \Psi_1 \,|\, T\Psi_2 \rangle &= \langle T^\dagger \Psi_1 \,|\, \Psi_2 \rangle = \langle T^* \Psi_1 \,|\, \Psi_2 \rangle \\ &= \langle T\Psi_1^* \,|\, \Psi_2^* \rangle^* \end{aligned}\tag{2.9}$$

looses its meaning as soon as the two functions Ψ_1 and Ψ_2 are no longer elements of $D(T)$. Hence a great deal of caution is necessary in treating the adjoint operator $T^\dagger$ outside its original domain.

Let us now review the eigenvalue problem for the adjoint pair of operators T and $T^\dagger$

$$TC = \lambda C, \qquad T^\dagger D = \mu D \tag{2.10}$$

and let us discuss the boundary conditions for the eigenelements C and D in somewhat greater detail. In the case when the operator T is complex symmetric, so that $T^\dagger = T^*$, one has immediately $D = C^*$ and $\mu = \lambda^*$, and it is sufficient to discuss only the first relation, Eq. (2.10).

A real or complex eigenvalue λ is said to be discrete if the corresponding eigenfunction $C = C(X)$ belongs to the L^2 Hilbert space. In the conventional scattering theory, one would say that a real or complex eigenvalue λ belongs to the continuum if the corresponding solution $C(\lambda; X)$ does not belong to L^2 but $|C(\lambda; x)|$ stays finite also at infinity, i.e., at a very large distance from the scatterer. Here we will use an alternative formulation, in which $C(\lambda; X)$ does not belong to L^2 but is a derivative with respect to λ of a *primitive function* $\Xi(\lambda; X)$ which itself belongs to L^2:

$$C(\lambda; X) = \frac{d\Xi(\lambda; X)}{d\lambda} \tag{2.11}$$

Hence

$$\Xi(\lambda; X) = \int_{\lambda_0}^{\lambda} C(\lambda; X)\, d\lambda \tag{2.12}$$

where the integral may be a contour integral over the continuous eigenvalues and is an element in L^2; we note that this is essentially a generalization of the idea of the "wave packet" in the continuum in quantum mechanics.

It is evident that, since $C = C(\lambda; X)$ is not an element of L^2, it may not be expanded in the basis φ according to Eq. (2.6). However, it may be shown (*10*) that, if one introduces the coefficients c_k through the formula

$$c_k(\lambda) = d/d\lambda \langle \varphi_k | \Xi(\lambda) \rangle \tag{2.13}$$

one has—point for point in the variable X—the relation

$$C(\lambda; X) = \sum_{k=1}^{\infty} \varphi_k(X) c_k \tag{2.14}$$

where the series in the right-hand member is convergent in the ordinary sense and not in the norm. To be more precise, however small the positive member ϵ is chosen to be, one has

$$\left| C(\lambda; X) - \sum_{k=1}^{m} \varphi_k(X) c_k(\lambda) \right| < \epsilon \tag{2.15}$$

whenever $n > N(\epsilon; X)$; we note further that the function $N(\epsilon; X)$ always depends on X and that the convergence can never be uniform. The wave functions $C = C(\lambda; X)$ are hence not ordinary limit points of the L^2 Hilbert space but limit points in terms of the absolute value. We note that even if the series Eq. (2.14) is convergent for every value of the composite variable X, the series

$$\sum_{k=1}^{\infty} |c_k(\lambda)|^2 \tag{2.16}$$

is always divergent.

It should be observed that, in the approximate treatment of the eigenvalue problem based on the bivariational principle and the use of a truncated basis $\varphi = \{\varphi_1, \varphi_2, \ldots, \varphi_m\}$ in L^2, so that

$$C_a(X) = \sum_{k=1}^{m} \varphi_k(X) c_k \tag{2.17}$$

the approximations C_a to both the discrete and the continuous eigenfunctions are situated in L^2. From the practical point of view, they differ in one aspect, however: when the number m indicating the order of the truncated basis becomes larger and larger, the series

$$\sum_{k=1}^{m} |c_k|^2 \tag{2.18}$$

tends to a specific value for the approximations to a discrete eigenfunction, whereas it becomes larger and larger for the approximations to an eigenfunction associated with the continuum. The approximate eigenvalues l associated with the latter functions also have a tendency to cluster in a line or contour to form the first approximation of the continuous part of the spectrum. Even if one has no idea of the rigorous properties of the spectrum $\{\lambda\}$ of a specific operator T, the bivariational approximation for higher and higher m values may at least give a first hint as to the true form of the exact spectrum.

It should finally be observed that, for instance, in atomic and molecular physics we are accustomed to treating the ground state and the low-lying excited states of the systems as completely separated from the continuum. This depends on the fact that, in studying these systems, one is usually successful in separating the motion of the center of the mass of the system from the "internal" motions of the particles involved. In reality, one has to include also the translational motion of the system, which has a continuous energy spectrum ranging from 0 to $+\infty$, in the total energies, and this implies that all the discrete energies in reality are imbedded in a continuum.

So far, we have included in the definition space $A = \{F\}$ only complex functions $F = F(X)$ of the real compositive variable $X = \{x_1, x_2, \ldots, x_N\}$. We will now extend this space by also including complex functions $F = F(Z)$ of a composite complex variable $Z = \{z_1, z_2, \ldots, z_N\}$, and we will introduce such functions essentially through complex similarity transformations.

B. Complex Transformations

Let us now consider the linear space $A' = \{F\}$ which consists of all complex functions $F = F(Z)$ of a complex composite variable $Z = \{z_1, z_2, \ldots, z_N\}$. Let us then define the N-particle operator U, which maps these functions on other functions $G = G(Z)$ in a one-to-one way, so that

$$UF(Z) = G(Z), \qquad F(Z) = U^{-1}G(Z) \tag{2.19}$$

A typical example is the "complex scaling" defined through the relation

$$UF(Z) = \eta^{3N/2}F(\eta Z) = \eta^{3N/2}F(\eta z_1, \eta z_2, \ldots, \eta z_N) \tag{2.20}$$

where η is a fixed complex parameter; this transformation will be treated in greater detail in Section III.

It should be observed that since the operators T to be discussed include differential operators, it may be practical from the very beginning to assume that the functions $F(Z)$ and $G(Z)$ are *analytic functions* of all the complex variables involved.

The L^2 Hilbert space $\{\Psi\}$ is a subspace of the linear space A', and we note that the operator U transforms the elements $\Psi(X)$ into complex functions of the composite complex variable Z, so that

$$\bar{\Psi} = U\Psi(X) = \bar{\Psi}(Z) \tag{2.21}$$

In studying the matrix elements of the operator U defined through the relation

$$\begin{aligned}\langle\Psi_1 \mid U\Psi_2\rangle &= \int \Psi_1^*(X)U\Psi_2(X)\,dX \\ &= \int \Psi_1^*(X)\bar{\Psi}_2(Z)\,dX \qquad (2.22)\end{aligned}$$

each individual coordinate of the real composite variable $X = \{x_1, x_2, \ldots, x_N\}$ is integrated over the entire real axis from $-\infty$ to $+\infty$ in the sense of Lebesgue. In going over to integrands which are partly functions of complex variables, it is sometimes tempting to go over to contour integrals in the complex plane, and, in such a case, it is of course necessary to use the appropriate generalization of the concept of Lebesgue integration. We will further discuss this problem in Section III.

In conclusion, it should be observed that in many applications it is possible to express the N-particle transformation U in terms of one-particle transformations u, e.g., in the product form

$$U = u(1)u(2)\cdots u(N) \qquad (2.23)$$

which is particularly important, since it preserves in a simple way the symmetry of the wave functions $\Psi = \Psi(X)$. In such a case, the operator u maps complex functions $f(z)$ of the complex variable z on other functions $g(z)$ in a *one-to-one* way:

$$uf(z) = g(z), \qquad f(z) = u^{-1}g(z) \qquad (2.24)$$

We note that z is here a complex composite variable corresponding to the real composite variable $x = (\mathbf{r}, \zeta)$. It is evident that the complex scaling operator U defined by Eq. (2.20) is of the product form Eq. (2.23), provided that the one-particle operator u is defined through the relation

$$uf(z) = \eta^{3/2}f(\eta z) \qquad (2.25)$$

Here the operator u may be further resolved into the product of three complex scaling operators v, each one working on its own coordinate ξ, so that

$$vf(\xi) = \eta^{1/2}f(\eta\xi) \qquad (2.26)$$

At this point it should be observed that even if it is natural to assume that all the functions $F = F(Z)$ in the definition space $A' = \{F\}$ are analytic functions of the composite complex variable $Z = \{z_1, z_2, \ldots, z_N\}$, one has still to be very careful in the definition of the complex transformation U. Some of the complications which may occur are well illustrated by the simple example of complex scaling as defined in Eq. (2.26).

For the sake of simplicity, we will consider an analytic function $f = f(z)$ of a single complex variable z. It is well known that except for the integer functions and the meromorphic functions defined in the entire complex plane, such an analytic function usually has a natural domain restricted by a boundary of singularities, over which it cannot be analytically continued. This means that even in the case of complex scaling $v = v(\eta)$—for certain values of η—the transformation may take the variable ηz outside the domain of analyticity, and the operation is then meaningless. As an example, we may consider the analytic functions $f = f(z)$ which are defined only within the unit circle $|z| \leq 1$, with this circle as natural boundary, and it is then evident that the complex scaling is meaningful only for $|\eta| \leq 1$.

In the physical applications, one is starting from wave functions $\psi = \psi(x)$ which are originally defined only on the real axis, i.e., for $-\infty < x < +\infty$, and, in order to use the method of complex scaling, it is then necessary to continue these functions analytically from the real axis out in the complex plane. Some of these problems have been studied in greater detail by mathematicians (*2*), but they are also of essential interest to theoretical physicists.

One should also be aware of the fact that for the general complex transformation U, there may exist wave functions $\Psi = \Psi(X)$ defined on the real axis which are quadratically integrable, but which cannot be analytically continued in such a way that the symbol $U\Psi$ becomes meaningful. In discussing an unbounded operator U and its domain $D(U)$, it may then be practical to introduce the complement $C(U)$ only with respect to the part of the L^2 Hilbert space, for which the operator U may be properly defined. A more detailed discussion of these problems is outside the scope of this review. In the following discussion, we will not further specify the form of the transformation U.

C. Transformations Out of and Into the L^2 Hilbert Space

Let us consider the linear operator T which is formally defined on the linear space $A' = \{F\}$ consisting of all complex functions $F = F(Z)$ of the composite complex variable $Z = \{z_1, z_2, \ldots, z_N\}$, and let U be a nonsingular linear transformation working on this space. Let us now investigate the properties of the transformed operator

$$\bar{T} = UTU^{-1} \tag{2.27}$$

particularly when U is an *unbounded* operator. It is evident that $\bar{T}$ is also defined on the linear space $A' = \{F\}$. However, in connection with the study of the eigenvalue problem for the operator $\bar{T}$, it is important to investigate how it works on the L^2 Hilbert space $\{\Psi\}$.

If U is an unbounded operator, it has a specific domain $D(U)$ in the L^2 Hilbert space. We note further that the range $R(U)$ of the operator U is the same as the domain of the inverse operator U^{-1}, and vice versa. Hence, one has in a condensed form the relations

$$R(U) = UD(U) = D(U^{-1}) \tag{2.28}$$

$$R(U^{-1}) = U^{-1}D(U^{-1}) = D(U) \tag{2.29}$$

We previously introduced the symbol $C(U)$ for the complement of the domain $D(U)$ with respect to the L^2 Hilbert space, and it is thus evident that the elements in the image set $A(U) = UC(U)$ must be situated outside the L^2 Hilbert space and that one has the reciprocity relations

$$A(U) = UC(U), \qquad C(U) = U^{-1}A(U) \tag{2.30}$$

implying that if the operator U transforms an element out of the L^2 Hilbert space, then the operator U^{-1} will transform the image back into the Hilbert space.

If F is an arbitrary element in the linear space $A' = \{F\}$, the following four possibilities may occur:

$$\begin{array}{lll} F \in L^2, & UF \in L^2, & F \in D(U) \\ F \in L^2, & UF \notin L^2, & F \in C(U) \\ F \notin L^2, & UF \in L^2, & F \in A(U^{-1}) \\ F \notin L^2, & UF \notin L^2, & F \in B(U) \end{array} \tag{2.31}$$

In the treatment of the eigenvalue problem for the transformed operator, the set $B(U)$ will be of little interest to us, whereas the set $A(U^{-1})$ is going to be of essential importance.

Our discussion is complicated by the fact that, in the definition Eq. (2.27) of the transformed operator $\bar{T}$, the operator T occurs in the middle. If Ψ is an element of the L^2 Hilbert space, then the result $\Psi''' = \bar{T}\Psi$ is obtained by three successive mappings,

$$\Psi' = U^{-1}\Psi; \qquad \Psi'' = T\Psi'; \qquad \Psi''' = U\Psi'' \tag{2.32}$$

where we will now require that the result Ψ''' is also an element of L^2.

Let us first consider the case when the intermediate elements Ψ' and Ψ'' are situated in L^2. In such a case, the element Ψ must be situated in $D(U^{-1})$. If the operator T is a bounded operator, so that $\|T\Psi'\| \leq K(T) \cdot \|\Psi'\|$, one also gets

$$\|TU^{-1}\Psi\| \leq K(T) \cdot \|U^{-1}\Psi\| \tag{2.33}$$

implying that the domain $D(TU^{-1})$ of the operator TU^{-1} is the same as the domain $D(U^{-1})$ of the operator U^{-1}. The image $\Psi'' = TU^{-1}\Psi$ is in the range $R(U^{-1}) = D(U)$, which implies that the final result $\Psi''' = U\Psi''$ is in L^2.

If the operator T is unbounded, the situation becomes more complicated, since one must now require that Ψ must be in the domain of U^{-1} as well as in the domain of TU^{-1}. We will let the symbol $D(T; U^{-1})$ mean a subset of $D(TU^{-1})$, which is such that if Ψ is within $D(T; U^{-1})$, then the image $\Psi'' = TU^{-1}\Psi$ is still within $R(U^{-1}) = D(U)$ and $\Psi''' = U\Psi''$ is in L^2. One has the inequality

$$D(U^{-1}) \supset D(TU^{-1}) \supset D(T; U^{-1}) \tag{2.34}$$

and it is evident that $D(T; U^{-1})$ must be part of the domain of the operator $\bar{T}$.

Let us next consider the case when the intermediate elements Ψ' and Ψ'' are situated *outside* L^2. In such a case, the element Ψ is situated in the complement $C(U^{-1})$, whereas the image $\Psi' = U^{-1}\Psi$ is situated in the set $A(U)$. We will further let $C(T; U^{-1})$ denote a subset of $C(U^{-1})$ having the property that, if Ψ is an element of $C(T; U^{-1})$, then not only the image $\Psi' = U^{-1}\Psi$ but also the next image $\Psi'' = T\Psi'$ belong to the set $A(U)$. This implies that the final result $\Psi''' = U\Psi''$ is in L^2.

This discussion shows that the two subsets $D(T; U^{-1})$ and $C(T; U^{-1})$ together form the domain of the transformed operator $T = UTU^{-1}$. The two alternative pathways of the mappings involved are schematically illustrated in Fig. 1. It is clear that if the element Ψ is in $D(T; U^{-1})$, then the result $\Psi''' = \bar{T}\Psi$ is in $D(U^{-1})$, whereas if the element Ψ *is in* $C(T; U^{-1})$, then the result $\Psi''' = \bar{T}\Psi$ is in $C(U^{-1})$.

D. Eigenvalue Problem of the Transformed Hamiltonian and the Parent Relations

In the case when the original Hamiltonian H is self-adjoint, $H^\dagger = H$, and the transformed Hamiltonian $\bar{H}$ has the form

$$\bar{H} = UHU^{-1} \tag{2.35}$$

we will consider the eigenvalue problems

$$H\Psi = E\Psi; \qquad \bar{H}\bar{\Psi} = \bar{E}\bar{\Psi} \tag{2.36}$$

For the discrete eigenvalues E, it is assumed that the eigenfunctions Ψ and $\bar{\Psi}$ belong to L^2, whereas, for the continuum, one will use the condition Eq. (2.11). If one introduces the formal transformation $\bar{\Psi} = U\Psi$, it is evident that the second relation, Eq. (2.36), follows from the first with $\bar{E} = E$, and any change in the spectra must hence be related to changes in the boundary conditions.

It is clear that if Ψ belongs to the domain $D(U)$, then the function $\bar{\Psi} = U\Psi$ also belongs to L^2 and $\bar{E} = E$ is a *persistent discrete eigenvalue.* On the other hand, if Ψ belongs to the complement $C(U)$, the function $\bar{\Psi} = U\Psi$ is outside L^2 and it cannot be an eigenfunction to $\bar{H}$; hence E becomes a *lost eigenvalue,* one that does not necessarily belong to the spectrum of $\bar{H}$.

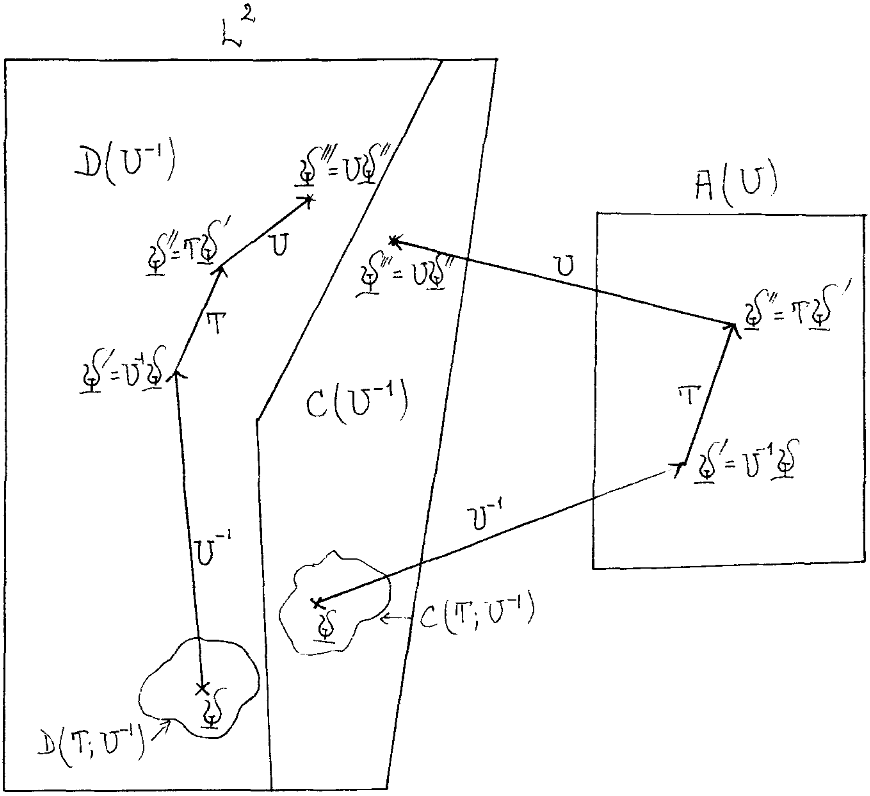

Fig. 1. Schematic illustration of the alternative pathways for the mapping $\bar{T} = UTU^{-1}$ within the L^2 space, and out of L^2, and then back again via the set $A(U) = U^{-1}C(U^{-1})$; they are referred to as the "inside" and "outside" paths. The reader may find it interesting to study whether there are other possibilities.

Since the transformed operator H is no longer self-adjoint, one may expect that it may have also *complex eigenvalues* $\bar{E}$ which lack counterparts in the spectrum $\{E\}$ of the original Hamiltonian and which may hence be described as *new eigenvalues*. In such a case, we will consider the transformation

$$F = U^{-1}\Psi \tag{2.37}$$

where F will be called the *parent function* of the eigenfunction Ψ, which is either in L^2 or fulfills the condition Eq. (2.11) for the continuum. It is clear that the function Ψ cannot belong to the domain $D(U^{-1})$ of the operator U^{-1}, since the function F would then be identical with the eigenfunction Ψ in L^2 and one would have $\bar{E} = E =$ real value, which is a contradiction if $\bar{E}$ is assumed to be complex.

In this case the eigenfunction $\bar{\Psi}$ must hence belong to the complement $C(U^{-1})$ and the parent function F must then be situated in the set $A(U^{-1})$ *outside* the L^2 Hilbert space. Substituting the relation $\bar{\Psi} = UF$ into the second relation of Eq. (2.36) and multiplying the left by U^{-1}, one obtains

$$HF = \bar{E}F \tag{2.38}$$

where $\bar{E}$ is a complex number. The relation given by Eq. (2.38) is a differential equation for the original Hamiltonian and looks like an eigenvalue relation, with the essential difference that the function F should now be an element of the set $A(U^{-1})$ outside the L^2, which implies that F is subject to the condition that UF should belong to L^2. In the following discussion, we will refer to Eq. (2.38) as a *parent relation* to the eigenvalue problem $\bar{H}\bar{\Psi} = \bar{E}\bar{\Psi}$.

We will next consider the adjoint operator $\bar{H}^{\dagger}$ to the transformed Hamiltonian $\bar{H}$ defined through the relation

$$(\bar{H})^{\dagger} = (U^{\dagger})^{-1}HU^{\dagger} \tag{2.39}$$

which is essentially defined only within the proper domains of the L^2 Hilbert space and hence *not* on the original space A'. The associated eigenvalue problem has the form

$$\bar{H}^{\dagger}\bar{\Phi} = \mu\bar{\Phi} \tag{2.40}$$

where $\bar{\Phi}$ should belong to L^2 or—in the case of the continuum—satisfy the condition Eq. (2.11). If one introduces the formal transformation

$$\bar{\Phi} = (U^{\dagger})^{-1}\Psi \tag{2.41}$$

it is clear that the relation given by Eq. (2.40) follows directly from the first relation given by Eq. (2.36) with $\mu = E$, and any changes in the spectra must hence be associated with changes in the boundary conditions.

It is evident that if the function Ψ belongs to the domain $D[(U^{\dagger})^{-1}]$ of the operator $(\mathrm{U}^{\dagger})^{-1}$, then the image $\bar{\Phi} = (U^{\dagger})^{-1}\Psi$ belongs to L^2, and $\mu = E$ is a *persistent discrete eigenvalue.* Similarly, if Ψ belongs to the complement $C[(U^{\dagger})^{-}]$ of the operator $(U^{\dagger})^{-1}$, the image $\bar{\Phi} = (U^{\dagger})^{-1}\Psi$ is outside L^2 and cannot be an eigenfunction to $\bar{H}^{\dagger}$; hence E becomes a *lost eigenvalue*, one that does not necessarily belong to the spectrum of $\bar{H}^{\dagger}$.

In the case when Eq. (2.40) has a *complex eigenvalue* μ for $\bar{\Phi}$ in L^2—or satisfying the condition Eq. (2.11) for continuous eigenvalues—instead of Eq. (2.41) we will introduce the transformation

$$G = U^{\dagger}\bar{\Phi} \tag{2.42}$$

where G will be referred to as the *parent function* to the eigenfunction $\bar{\Phi}$. It is evident that $\bar{\Phi}$ cannot be situated in the domain $D(U^{\dagger})$ to the operator $U^{\dagger}$, since the image G would then be identical to the eigenfunction Ψ in L^2, which would lead to the contradictory conclusion $\mu = E =$ real value.

In the case when the eigenvalue μ is complex, the eigenfunction $\bar{\Phi}$ must be situated in the complement $C(U^\dagger)$ associated with the operator $U^\dagger$, and the image Eq. (2.42) will then be situated in the set $A[(U^\dagger)^{-1}]$ *outside* L^2. Substituting the relation $\bar{\Phi} = (U^\dagger)^{-1}G$ into Eq. (2.40) and multiplying on the left by $U^\dagger$, one obtains

$$HG = \mu G \tag{2.43}$$

which is analogous to Eq. (2.39) with the boundary condition that the parent function G should now belong to the set $A[(U^\dagger)^{-1}]$, i.e., $U^\dagger G$ should belong to L^2. Equation (2.43) will be referred to as the *second parent relation.*

Since both $\bar{\Psi}$ and $\bar{\Phi}$ belong to L^2, the binary product $\langle\bar{\Phi}|\bar{\Psi}\rangle$ will always exist according to Schwarz's inequality. In the following discussion, we will always assume that not all the binary products $\langle\bar{\Phi}|\bar{\Psi}\rangle$ are vanishing. For a specific pair, $\bar{\Phi}$ and $\bar{\Psi}$, having $\langle\bar{\Phi}|\bar{\Psi}\rangle \neq 0$, it is convenient to introduce the new function $\bar{\Phi}' = \bar{\Phi}\langle\bar{\Phi}|\bar{\Psi}\rangle^{-1}$, which gives the so-called binormalization

$$\langle\bar{\Phi}'|\bar{\Psi}\rangle = 1 \tag{2.44}$$

In the following discussion, we will assume that the eigenfunctions $\{\bar{\Phi}\}$ and $\{\bar{\Psi}\}$ have been essentially ordered in binormalized pairs (*5*). In analogy with Eq. (1.14), one gets

$$\begin{aligned}\bar{E}\langle\bar{\Phi}|\bar{\Psi}\rangle &= \langle\bar{\Phi}|\bar{H}\bar{\Psi}\rangle = \langle\bar{H}^\dagger\bar{\Phi}|\bar{\Psi}\rangle\\ &= \langle\mu\bar{\Phi}|\bar{\Psi}\rangle = \mu^*\langle\bar{\Phi}|\bar{\Psi}\rangle\end{aligned} \tag{2.45}$$

or

$$(\bar{E} - \mu^*)\langle\bar{\Phi}|\bar{\Psi}\rangle = 0 \tag{2.46}$$

Hence one has $\mu = E^*$ if $\langle\bar{\Phi}|\bar{\Psi}\rangle \neq 0$, whereas if $\mu \neq E^*$ one has $\langle\bar{\Phi}|\bar{\Psi}\rangle = 0$. One has then also the general biorthonormality property expressed by the relation Eq. (1.19).

It is evident that the spectra of $\bar{H}$ and $\bar{H}^\dagger$ are essentially complex conjugate. For a persistent real eigenvalue $\bar{E} = E$, one has

$$\langle\bar{\Phi}|\bar{\Psi}\rangle = \langle(U^\dagger)^{-1}\Psi|U\Psi\rangle = \langle\Psi|\Psi\rangle = 1 \tag{2.47}$$

whereas, for a complex eigenvalue $\bar{E}$, one *cannot* use the transformation

$$\langle\bar{\Phi}|\bar{\Psi}\rangle = \langle(U^\dagger)^{-1}G|UF\rangle = \langle G|F\rangle \tag{2.48}$$

since the binary product $\langle G|F\rangle$ simply does not exist.

In conclusion, we note that the two parent relations, Eqs. (2.38) and (2.43), may now summarized in the two equations:

$$HF = \bar{E}F, \qquad HG = \bar{E}^*G \tag{2.49}$$

with the boundary conditions that F and G should belong to the sets $A(U^{-1})$ and $A[(U^{\dagger})^{-1}]$, which means that UF and $U^{\dagger}G$ should belong to L^2.

E. The Symmetry Property $\bar{H}^{\dagger} = \bar{H}^*$

Let us now consider the special case when the original Hamiltonian H is not only self-adjoint, $H^{\dagger} = H$, but also real, $H = H^*$, so that

$$H^{\dagger} = H = H^* \tag{2.50}$$

Taking the complex conjugate of the eigenvalue relation $H\Psi = E\Psi$, one obtains $H\Psi^* = E\Psi^*$, which means that, without loss of generality, the eigenfunctions Ψ may be assumed to be real. If one further assumes that the operator U is *restricted* to fulfill the condition Eq. (1.57) or

$$U^{\dagger} = (U^*)^{-1} \tag{2.51}$$

then the transformed operator $\bar{H} = UHU^{-1}$ is complex symmetric, so that

$$\bar{H}^{\dagger} = \bar{H} \tag{2.52}$$

Instead of the relation given by Eq. (2.39), one may now define the adjoint operator $\bar{H}^{\dagger}$ through the relation $\bar{H}^{\dagger} = \bar{H}^* = U^*H(U^*)^{-1}$, which may be extended to the entire original space A'.

It is interesting to observe that the set $A[(U^{\dagger})^{-1}] = A(U^*)$ is the complex conjugate of the set $A(U)$. This means that if one takes the complex conjugate of the first relation, Eq. (2.49), one obtains $HF^* = \bar{E}^*F^*$, where F^* is situated in the set $A(U^*)$. Considering the boundary conditions for the two relations given in Eq. (2.49), one obtains

$$G = F^* \tag{2.53}$$

This implies an essential simplification of the entire eigenvalue problem, since it will now be sufficient to consider only one of the two parent relations in Eq. (2.49), for instance

$$HF = \bar{E}F, \qquad F \in A(U^{-1}) \tag{2.54}$$

In the case of the real persistent eigenvalues, one has

$$\bar{\Psi} = U\Psi, \qquad \bar{\Phi} = (U^{\dagger})^{-1}\Psi = U^*\Psi = \bar{\Psi}^* \tag{2.55}$$

and in the case of complex eigenvalues one obtains

$$\bar{\Psi} = UF, \qquad \bar{\Phi} = (U^{\dagger})^{-1}G = U^*F^* = \bar{\Psi}^* \tag{2.56}$$

For the eigenfunctions to $\bar{H}$ and $\bar{H}^{\dagger} = \bar{H}^*$, one gets

$$\bar{\Phi} = \bar{\Psi}^* \tag{2.57}$$

in accordance with the general theory developed in a previous section.

The transformed operator $\bar{H}$ may also have complex eigenvalues $\bar{E}$ which form a continuum, in which case the eigenfunctions $\bar{\Psi}$ do not belong to L^2 but are derivatives with respect to $\bar{E}$ of a primitive function $\bar{\Xi}$ in L^2 according to Eq. (2.11). (For some examples of continuous spectra, see Appendix B.)

It should finally be observed that an *unbounded* transformation U which is restricted to satisfy the relations given by Eq. (1.57) or (2.51) must necessarily be *complex*. In the case of a real transformation, i.e., $U^* = U$, one has

$$U^\dagger = U^{-1} \tag{2.58}$$

i.e., the transformation U becomes unitary and hence automatically bounded, i.e., $\|U\Psi\| = \|\Psi\|$, and, since such a transformation leaves the spectrum unchanged, it is of less interest in studying the resonances associated with complex eigenvalues.

F. Calculation of Approximate Eigenvalues and Eigenfunctions to the Transformed Hamiltonian $\bar{H}$

In order to calculate the approximate solutions to the eigenvalue problem

$$\bar{H}\bar{\Psi} = \bar{E}\bar{\Psi} \tag{2.59}$$

for the transformed Hamiltonian $\bar{H} = UHU^{-1}$, we will now use the general methods developed in Section I, leading to homogeneous equations of the type Eq. (1.32) or

$$(\bar{\mathbf{H}} - \bar{\mathbf{\Delta}} \cdot I)\mathbf{c} = \mathbf{0} \tag{2.60}$$

where

$$\bar{\mathbf{H}} = \langle \mathbf{\Phi} | \bar{H} | \mathbf{\Psi} \rangle, \qquad \mathbf{\Delta} = \langle \mathbf{\Phi} | \mathbf{\Psi} \rangle \tag{2.61}$$

One of the main problems here is the proper choice of the dual bases $\mathbf{\Psi} = \{\psi_1, \psi_2, \ldots, \psi_m\}$ and $\mathbf{\Phi} = \{\phi_1, \phi_2, \ldots, \phi_m\}$, and—in the particular case when $\bar{H}^\dagger = \bar{H}^*$—it is natural to choose $\mathbf{\Phi} = \mathbf{\Psi}^*$. In such a case, the fundamental matrices $\bar{\mathbf{H}}$ and $\bar{\mathbf{\Delta}}$ both become complex symmetric

$$\tilde{\bar{\mathbf{H}}} = \bar{\mathbf{H}}, \qquad \tilde{\bar{\mathbf{\Delta}}} = \bar{\mathbf{\Delta}} \tag{2.62}$$

which is convenient also from the computational point of view. We will now discuss various types of choices of the dual bases ψ and ψ^* and their consequences.

1. *The Trivial Choice of Bases*

In a study of the original Hamiltonian H, it may be natural to start from a linearly independent set $\boldsymbol{\theta} = \{\Theta_1, \Theta_2, \ldots, \Theta_m\}$ consisting of m real functions $\Theta_k = \Theta_k(X)$ as a truncated basis in the L^2 space, and to use the standard procedures. In studying the transformed Hamiltonian $\bar{H} = UHU^{-1}$, the results obtained in Section I and particularly the relations given in Eq. (1.65) suggest that one may try to introduce the dual bases:

$$\boldsymbol{\psi} = U\boldsymbol{\theta}, \qquad \boldsymbol{\phi} = (U^{\dagger})^{-1}\boldsymbol{\theta} = U^{*}\boldsymbol{\theta} = \boldsymbol{\psi}^{*} \tag{2.63}$$

For the associated matrices of Eq. (2.61), one obtains according to Eqs. (1.66) and (1.67)

$$\bar{\mathbf{H}} = \langle\boldsymbol{\phi}|\bar{H}|\boldsymbol{\psi}\rangle = \langle\boldsymbol{\theta}|H|\boldsymbol{\theta}\rangle = \mathbf{H} \tag{2.64}$$

$$\bar{\boldsymbol{\Delta}} = \langle\boldsymbol{\phi}\,|\,\boldsymbol{\psi}\rangle = \langle\boldsymbol{\theta}\,|\,\boldsymbol{\theta}\rangle = \boldsymbol{\Delta} \tag{2.65}$$

i.e., the matrices $\bar{\mathbf{H}}$ and $\bar{\boldsymbol{\Delta}}$ associated with the transformed Hamiltonian are identical with the original matrices $\mathbf{H}$ and $\boldsymbol{\Delta}$, and all the approximate eigenvalues l are persistent and real. Since the special choice Eq. (2.63) does not give any new information about the properties of the transformed Hamiltonian H, we will call it the *real trivial choice.*

One could hope to do somewhat better by introducing a truncated basis $\boldsymbol{\theta}$ which consists of *m complex functions.* Since we are interested in utilizing the property $H^{\dagger} = H = H^{*}$, we will further assume that the set $\boldsymbol{\theta}$ is *stable under complex conjugation* $*$, which means that the individual functions in the set $\boldsymbol{\theta}^{*}$ are situated in the space spanned by the set $\boldsymbol{\theta}$, so that

$$\boldsymbol{\theta}^{*} = \boldsymbol{\theta}\boldsymbol{\alpha}, \qquad \boldsymbol{\theta} = \boldsymbol{\theta}^{*}\boldsymbol{\alpha}^{*} \tag{2.66}$$

where the second relation is the complex conjugate of the first; this implies that $\boldsymbol{\alpha}^{*} = \boldsymbol{\alpha}^{-1}$. Since the set $\boldsymbol{\theta}$ is linearly independent, the matrix $\langle\boldsymbol{\theta}\,|\,\boldsymbol{\theta}\rangle$ is nonsingular, and it follows then directly that also the overlap matrix $\boldsymbol{\Delta} = \langle\boldsymbol{\theta}^{*}\,|\,\boldsymbol{\theta}\rangle = \boldsymbol{\alpha}^{\dagger}\langle\boldsymbol{\theta}\,|\,\boldsymbol{\theta}\rangle$ is nonsingular. In such a case, one has also the relations

$$\boldsymbol{\alpha} = \langle\boldsymbol{\theta}\,|\,\boldsymbol{\theta}\rangle^{-1}\langle\boldsymbol{\theta}\,|\,\boldsymbol{\theta}^{*}\rangle, \qquad \boldsymbol{\alpha}^{-1} = \langle\boldsymbol{\theta}\,|\,\boldsymbol{\theta}^{*}\rangle^{-1}\langle\boldsymbol{\theta}\,|\,\boldsymbol{\theta}\rangle \tag{2.67}$$

Starting from the complex sets $\boldsymbol{\theta}$ and $\boldsymbol{\theta}^{*}$ and using Eq. (1.65), we will now try to introduce the dual bases:

$$\boldsymbol{\psi} = U\boldsymbol{\theta}, \qquad \boldsymbol{\phi} = (U^{\dagger})^{-1}\boldsymbol{\theta}^{*} = U^{*}\boldsymbol{\theta}^{*} = \boldsymbol{\psi}^{*} \tag{2.68}$$

For the associated matrices of Eq. (2.61), one obtains according to Eqs. (1.66) and (1.67)

$$\bar{\mathbf{H}} = \langle\boldsymbol{\phi}|\bar{H}|\boldsymbol{\psi}\rangle = \langle\boldsymbol{\theta}^{*}|H|\boldsymbol{\theta}\rangle = \mathbf{H} \tag{2.69}$$

$$\bar{\boldsymbol{\Delta}} = \langle\boldsymbol{\phi}\,|\,\boldsymbol{\psi}\rangle = \langle\boldsymbol{\theta}^{*}\,|\,\boldsymbol{\theta}\rangle = \boldsymbol{\Delta} \tag{2.70}$$

where $\mathbf{H}$ and $\boldsymbol{\Delta}$ are the matrices associated with the original Hamiltonian H occurring in a bivariational treatment of this operator using the complex sets $\boldsymbol{\theta}$ and $\boldsymbol{\theta}^{*}$. The matrices $\mathbf{H}$ and $\boldsymbol{\Delta}$ are complex symmetric, but, since they are not self-adjoint, they may certainly have complex eigenvalues. We note, however, that the homogeneous equations system, Eq. (2.60), may now be written in the form

$$\begin{aligned}(\bar{\mathbf{H}} - I\bar{\mathbf{\Delta}})\mathbf{c} &= \langle \boldsymbol{\theta}^* | H - I \cdot 1 | \boldsymbol{\theta} \rangle \mathbf{c} \\ &= \boldsymbol{\alpha}^\dagger \langle \boldsymbol{\theta} | H - I \cdot 1 | \boldsymbol{\theta} \rangle \mathbf{c} \qquad (2.71) \\ &= \boldsymbol{\alpha}^\dagger \{ \langle \boldsymbol{\theta} | H | \boldsymbol{\theta} \rangle - I \langle \boldsymbol{\theta} | \boldsymbol{\theta} \rangle \} \mathbf{c} = \mathbf{0}\end{aligned}$$

Since $\boldsymbol{\alpha}^\dagger$ has an inverse matrix, it is first of all clear that the bivariational treatment of the original Hamiltonian based on the two complex sets $\boldsymbol{\theta}$ and $\boldsymbol{\theta}^*$ gives the same eigenvalues I and eigenvectors $\mathbf{c}$ as the variational treatment based on a single complex set $\boldsymbol{\theta}$. However, since the matrices $\langle \boldsymbol{\theta} | H | \boldsymbol{\theta} \rangle$ and $\langle \boldsymbol{\theta} | \boldsymbol{\theta} \rangle$ are both Hermitian symmetric, the eigenvalues I determined by Eq. (2.71) are all going to be real. In this case, the approximate eigenvalues I of the transformed Hamiltonian $\bar{H}$ determined by Eq. (2.60) are all going to be persistent and real. Since the special choice, Eq. (2.68), is not going to provide any new information about the transformed Hamiltonian $\bar{H}$, we will call it the *complex trivial choice.*

In the formulation of the approximate theory based on outer projections of the type given by Eq. (1.43), it is interesting to observe that the fundamental projector Q defined by Eq. (1.40) in the bivariational treatment of the original Hamiltonian takes the special form

$$\begin{aligned}Q &= |\boldsymbol{\theta}\rangle \langle \boldsymbol{\theta}^* | \boldsymbol{\theta} \rangle^{-1} \langle \boldsymbol{\theta}^* | \\ &= |\boldsymbol{\theta}\rangle [\boldsymbol{\alpha}^\dagger \langle \boldsymbol{\theta} | \boldsymbol{\theta} \rangle]^{-1} \boldsymbol{\alpha}^\dagger \langle \boldsymbol{\theta} | \\ &= |\boldsymbol{\theta}\rangle \langle \boldsymbol{\theta} | \boldsymbol{\theta} \rangle^{-1} (\boldsymbol{\alpha}^\dagger)^{-1} \boldsymbol{\alpha}^\dagger \langle \boldsymbol{\theta} | \\ &= |\boldsymbol{\theta}\rangle \langle \boldsymbol{\theta} | \boldsymbol{\theta} \rangle^{-1} \langle \boldsymbol{\theta} | \qquad (2.72)\end{aligned}$$

i.e., Q is identical with the self-adjoint projector associated with the ordinary variational treatment. It should perhaps be mentioned that if the space spanned by the complex set $\boldsymbol{\theta}$ is *not stable* under complex conjugation $*$, the bivariational treatment of the original Hamiltonian H may lead to complex approximate eigenvalues I, for which the imaginary parts will gradually disappear, as the set $\boldsymbol{\theta}$ tends to become complete and hence also stable under complex conjugation. These complex eigenvalues, which depend only on the character of the approximation, thus have no importance in the study of the transformed operator H (see also Appendix C).

2. *The Dual Choice of Bases for $\bar{H}$*

It is evident that if we are interested in physical resonances associated with complex eigenvalues of the transformed Hamiltonian $\bar{H} = UHU^{-1}$, we have to avoid the trivial choices of bases. It follows directly from the so-called parent relations, Eq. (2.49), that if we like to relate the eigenvalue problem of the transformed operator $\bar{H}$ to similar relations for the original Hamiltonian H, the boundary conditions have to be drastically changed—particularly in the case of complex eigenvalues. However, since the eigenvalue problem for the operator $\bar{H}$ is here expressed with boundary conditions related to the L^2 Hilbert space, it should be possible to treat this problem using the general methods developed in Section I, without any reference to the original Hamiltonian H.

Since one has the general property $\bar{H}^\dagger = \bar{H}^*$, it is convenient to introduce a dual basis $\boldsymbol{\psi}$ and $\boldsymbol{\phi}$ having the property $\boldsymbol{\phi} = \boldsymbol{\psi}^*$. For this purpose, we will now introduce a linearly independent set $\boldsymbol{\theta} = \{\Theta_1, \Theta_2, \ldots, \Theta_m\}$ consisting of m complex functions, which have the additional property that the overlap matrix $\bar{\boldsymbol{\Delta}} = \langle \boldsymbol{\theta}^* \,|\, \boldsymbol{\theta} \rangle$ is nonsingular, and make the dual choice of bases:

$$\boldsymbol{\psi} = \boldsymbol{\theta}, \qquad \boldsymbol{\phi} = \boldsymbol{\theta}^* \tag{2.73}$$

For the fundamental matrices given by Eq. (2.61), one obtains

$$\bar{\mathbf{H}} = \langle \boldsymbol{\theta}^* | \bar{H} | \boldsymbol{\theta} \rangle, \qquad \boldsymbol{\Delta} = \langle \boldsymbol{\theta}^* \,|\, \boldsymbol{\theta} \rangle \tag{2.74}$$

The truncated basis $\boldsymbol{\theta}$ is said to be trivial if all the functions Θ_k are situated in the domain $D(U^{-1})$ of the unbounded operator U^{-1}, and, in this case, one can carry out the transformations

$$\bar{\mathbf{H}} = \langle (U^{-1}\boldsymbol{\theta})^* | H | (U^{-1}\boldsymbol{\theta}) \rangle, \qquad \bar{\boldsymbol{\Delta}} = \langle (U^{-1}\boldsymbol{\theta})^* | (U^{-1}\boldsymbol{\theta}) \rangle \tag{2.75}$$

which are analogous to Eqs. (2.64) and (2.65). On the other hand, the truncated basis $\boldsymbol{\theta}$ is said to be *nontrivial* if part of the functions in the set are situated in the complement $C(U^{-1})$ to the domain $D(U^{-1})$ with respect to the L^2 Hilbert space. Since this implies that part of the functions $U^{-1}\boldsymbol{\theta}$ are situated in the set $A(U)$ outside the L^2 space, the formulas given by Eq. (2.75) are no longer valid. This means also that the approximate solution

$$\bar{\Psi}_{\mathrm{a}} = \boldsymbol{\theta}\mathbf{c} \tag{2.76}$$

gets a chance to fulfill the same boundary conditions as the exact eigenfunction $\bar{\Psi}$ in the case of a complex eigenvalue $\bar{E}$, since the approximate parent function $\bar{F}_{\mathrm{a}} = U^{-1}\bar{\Psi}_{\mathrm{a}} = (U^{-1}\boldsymbol{\theta})\mathbf{c}$—defined in analogy to Eq. (2.37)—is now going to be situated in class $A(U)$.

If the set $\boldsymbol{\theta}$ does not originally span a space which is stable under complex conjugation $*$, it is easy to extend the set to achieve this property: one simply considers the functions in the combined set $\{\boldsymbol{\theta}; \boldsymbol{\theta}^*\}$ in order, from the first one, eliminating all functions which are linear combinations of the previous ones. This gives a new set $\boldsymbol{\theta}'$ consisting of linearly independent functions having the desired stability property.

Without loss of generality, one can thus always construct a truncated basis $\boldsymbol{\theta}$ which spans a space stable under complex conjugation $*$. In such a case, Eqs. (2.66), (2.71), and (2.72) are valid, and this means that the eigenvalue problem may be solved by studying the homogeneous equations

$$\langle\boldsymbol{\theta}|\bar{H} - I \cdot 1|\boldsymbol{\theta}\rangle\mathbf{c} = \mathbf{0} \tag{2.77}$$

involving matrix elements with respect to a single complex basis $\boldsymbol{\theta}$ only. In such a case, the simple symmetry properties given by Eq. (2.62) may be lost, but, as we will see, there is still one more possibility left.

3. *The Simple Choice of Basis for $\bar{H}$*

The above discussion indicates that in the bivariational study of the transformed operator $\bar{H} = UHU^{-1}$ having the property $\bar{H}^\dagger = \bar{H}^*$, it is natural to introduce dual bases $\boldsymbol{\theta}$ and $\boldsymbol{\theta}^*$, which span not only part of the domain $D(U^{-1})$ but also part of the complement $C(U^{-1})$ of the operator U^{-1}. It was also shown that if $\boldsymbol{\theta}$ spans a space which is stable under complex conjugation $*$, one would get the same results by using the basis $\boldsymbol{\theta}$ alone.

In this situation, one can achieve a further simplification by observing that it is not necessary to choose the linearly independent set $\boldsymbol{\theta}$ complex; instead one can start from a real set $\boldsymbol{\varphi} = \{\varphi_1, \varphi_2, \ldots, \varphi_m\}$, which is chosen as a truncated part of a *real complete orthonormal basis* for the L^2 Hilbert space. The existence of such bases is well known. This means that in the approximate treatment of the eigenvalue problem for $\bar{H}$, the relation, Eq. (2.73), is now replaced by the simpler relation

$$\boldsymbol{\psi} = \boldsymbol{\phi} = \boldsymbol{\varphi} \tag{2.78}$$

which will be referred to as the *simple choice of basis*. Since $\boldsymbol{\varphi} = \boldsymbol{\varphi}^*$, it is evident that the space spanned by the set $\boldsymbol{\varphi}$ is stable under complex conjugation, and it is further clear that the overlap matrix $\boldsymbol{\Delta} = \langle\boldsymbol{\varphi}^*|\boldsymbol{\varphi}\rangle = \langle\boldsymbol{\varphi}|\boldsymbol{\varphi}\rangle = \mathbf{1}$ is automatically nonsingular. The approximate eigenfunction may now be expressed in the form

$$\bar{\Psi}_{\mathrm{a}} = \boldsymbol{\varphi}\mathbf{c} \tag{2.79}$$

where the column vector $\mathbf{c}$ is determined by the homogeneous equation system given by Eq. (2.60), or

$$(\bar{\mathbf{H}} - I \cdot \mathbf{1})\mathbf{c} = \mathbf{0} \tag{2.80}$$

with

$$\bar{\mathbf{H}} = \langle\boldsymbol{\varphi}|\bar{H}|\boldsymbol{\varphi}\rangle \tag{2.81}$$

We note that the matrix $\bar{\mathbf{H}}$ is still complex symmetric, so that $\bar{H}_{kl} = \bar{H}_{lk}$, but also that it is usually not Hermitian, which means that it can very well have complex eigenvalues.

It should further be observed that the set $\{\varphi\mathbf{a}\}$ for all values of m and rational values of the complex elements in the column vectors $\mathbf{a}$ form an enumerable set $\mathscr{H}'$, which is *everywhere dense* in the entire Hilbert space, including the domain $D(U^{-1})$ and its complement $C(U^{-1})$. We note that all numerical applications are, in fact, based on this theorem.

In conclusion, it should be observed that the secular equation

$$\bar{P}(Z) \equiv |\bar{\mathbf{H}} - Z \cdot \mathbf{1}| = 0 \tag{2.82}$$

associated with the homogeneous system, Eq. (2.80), has only discrete eigenvalues $Z = I_1, I_2, \ldots, I_m$ associated with eigenfunctions $\bar{\Psi}_a = \varphi\mathbf{c}$, which are all absolutely quadratically integrable, so that

$$\langle\bar{\Psi}_a|\bar{\Psi}_a\rangle = \mathbf{c}^\dagger\mathbf{c} = \sum_{k=1}^{m} |c_k|^2 \tag{2.83}$$

When the number m increases, and the set φ tends to become complete, the approximations will become better and better, and one can then expect that the complex eigenvalues I_k are approximations both to the continuous eigenvalues $\bar{E}$ of $\bar{H}$ in the complex plane as well as to the true resonances. The criterion for the distinction between these two types has been discussed in connection with Eq. (2.18).

Even if computer applications verify the convergence of the approximations as the number m increases and the set φ tends to become complete, it would be highly valuable to have some strict mathematical criteria for the accuracy of the various stages of the approximations. Some research along these lines is presently in progress (*11*), but much more is needed to obtain simple and satisfactory results.

If the unbounded operator $U = U(\alpha)$ is a function of one or more parameters $\alpha = \{\alpha_1, \alpha_2, \ldots\}$, the same is true for the transformed Hamiltonian $\bar{H} = UHU^{-1} = \bar{H}(\alpha)$ and the associated matrix Eq. (2.81), and—keeping the truncated basis φ fixed—one can then plot the eigenvalues $I = I(\alpha)$ of the matrix $\bar{\mathbf{H}} = \bar{\mathbf{H}}(\alpha)$ as functions of the parameters $\alpha = \{\alpha_1, \alpha_2, \ldots\}$ and observe the appearance of new eigenvalues and disappearance of old ones as discontinuous phenomena.

G. Resolvent Method

Since, in physics, the Hamiltonian H is usually not bounded from above, it is in principle an *unbounded operator* with a specific domain $D(H)$, and it is thus in certain ways more complicated to handle than a bounded operator. Instead of the Hamiltonian, one often considers its resolvent

$$R(Z) = (Z \cdot 1 - H)^{-1} \tag{2.84}$$

where z is a complex variable. Outside the circles $|z - E| \geq \rho$, with radius ρ around the eigenvalues E in the complex plane, the resolvent $R(z)$ is bounded, and one has particularly $||R\Psi|| \leq (1/\rho)||\Psi||$. Since

$$\{R(z)\}^{\dagger} = R(z^*) = \{R(z)\}^* \tag{2.85}$$

the resolvent is also complex symmetric. It should be observed that the resolvent $R(z)$ has the same eigenfunctions Ψ as the Hamiltonian but that the associated eigenvalues are $(z - E)^{-1}$ with the multiplicity unchanged. Instead of the eigenvalue problem, one often studies the so-called Weinstein function

$$W(z) = \langle\varphi|R(z)|\varphi\rangle = \langle\varphi|(z - H)^{-1}|\varphi\rangle \tag{2.86}$$

for an arbitrary normalized reference function φ, which has simple poles for $z = E$, i.e., for the eigenvalues.

Let us also consider the resolvent $\bar{R}(z)$ for the transformed Hamiltonian $\bar{H} = UHU^{-1}$. It follows directly from the definition that

$$\begin{aligned}\bar{R}(z) &= (z \cdot 1 - \bar{H})^{-1} = \{U(z \cdot 1 - H)U^{-1}\}^{-1} \\ &= U(z \cdot 1 - H)^{-1}U^{-1} = UR(z)U^{-1}\end{aligned} \tag{2.87}$$

and this implies that if U is a restricted unbounded transformation satisfying the condition given by Eq. (1.57), one has the general property

$$\{\bar{R}(z)\}^{\dagger} = \{\bar{R}(z)\}^* \tag{2.88}$$

Even the resolvent $\bar{R}(z)$ for the transformed Hamiltonian $\bar{H}$ is hence complex symmetric, and this feature simplifies also this type of approach.

IV. Method of Complex Scaling

A. Complex Scaling as an Example of a Restricted Unbounded Transformation

In this section we will consider the method of complex scaling (*2*) as a typical example of an unbounded similarity transformation of the restricted type. It is here sufficient to consider a single one-dimensional particle with the real coordinate $x(-\infty < x < +\infty)$, since the N-particle operator U in a $3N$-dimensional system may then be built up by using the product constructions given by Eqs. (2.23) and (2.25).

If $f = f(z)$ is a function of the variable z, the operator $u = u(\eta)$ is defined through the relation

$$u(\eta)f(z) = \eta^{1/2}f(\eta z) \tag{3.1}$$

where the parameter η serves as a complex "scale factor." In order to show that this transformation is *unbounded*, it is sufficient to show that there exists at least one function $\psi = \psi(x)$ in L^2, for which the image $u\psi$ does not belong to L^2. For this purpose, we will consider the function

$$\psi(x) = \frac{1}{\sqrt{2\pi k}} \frac{e^{ikx} - 1}{x}, \qquad k > 0 \tag{3.2}$$

which is an element of L^2 normalized so that $\|\psi\| = 1$. Putting $\eta = a + ib$, one obtains immediately for the transformed function

$$\begin{aligned} \bar{\psi} = u(\eta)\psi(x) &= \frac{1}{\sqrt{2\pi\eta k}} \frac{e^{ik\eta x} - 1}{x} \\ &= \frac{1}{\sqrt{2\pi\eta k}} \frac{e^{ikax - kbx} - 1}{x} \end{aligned} \tag{3.3}$$

which blows up exponentially for either $x = +\infty$ or $x = -\infty$ if $b < 0$ or $b > 0$, respectively. For $b \neq 0$, the function $\bar{\psi}$ is not an element of L^2, hence the transformation $u = u(\eta)$ is *unbounded* whenever the scale factor η is complex. In the special case, where η is real, the transformation $u = u(\eta)$ becomes bounded and unitary, but this case is of less interest in this discussion.

From the definition Eq. (3.1) it follows immediately that the operator has the following special properties

$$\begin{aligned} &u(1) = 1, \qquad [u(\eta)]^{-1} = u(\eta^{-1}) \\ &u(\eta_1)u(\eta_2) = u(\eta_2)u(\eta_1) = u(\eta_1\eta_2) \end{aligned} \tag{3.4}$$

and it is then evident that the operators $u(\eta)$ form a one-parameter Abelian group.

In order to derive the adjoint operator $u^\dagger$, we will now study the expression $\langle uf \,|\, g\rangle$ for a function $f(x)$ in the domain $D(u)$ and another function $g(x)$ in L^2. Putting $z = \eta^* x$ and using Cauchy's theorem about contour integrals, one obtains—provided that the integrand becomes sufficiently small on the outside arcs—that

$$\begin{aligned} \langle uf \,|\, g\rangle &= \int_{-\infty}^{+\infty} [\eta^{1/2} f(\eta x)]^* g(x)\, dx \\ &= \int_{-\infty}^{+\infty} (\eta^*)^{1/2} f^*(\eta^* x) g(x)\, dx = \int_{-\infty}^{+\infty} (\eta^*)^{1/2} f^*(z) g[(\eta^*)^{-1} z]\, dx \\ &= \int_{L(\eta^*)} f^*(z)(\eta^*)^{-1/2} g[(\eta^*)^{-1} z)\, dz \\ &= \int_{-\infty}^{+\infty} f^*(x) u[(\eta^*)^{-1}] g(x)\, dx = \langle f \,|\, u^\dagger g\rangle \end{aligned} \tag{3.5}$$

Here $L(\eta^*)$ is the contour the complex variable $z = \eta^* x$ goes through when the real variable x goes from $-\infty$ to $+\infty$. This transformation is valid only if the function $g(x)$ belongs to the domain of the operator $u[(\eta^*)^{-1}]$, and it is then easily shown that one may change the integration path from the line $L(\eta^*)$ back to the real axis. Hence one has the relation

$$[u(\eta)]^\dagger = u[(\eta^*)^{-1}] = [u^{-1}(\eta)]^* \tag{3.6}$$

which shows that the complex scaling is a restricted transformation which satisfies the condition, Eq. (1.57).

Since Eq. (3.6) is a very important property, we will also give an alternative proof. For this purpose, we will use the notation

$$\eta = e^\theta, \qquad v(\theta) = u(\eta) = u(e^\theta) \tag{3.7}$$

The relations given by Eq. (3.4) are now replaced by the relations

$$\begin{aligned} v(\theta) = 1; \qquad [v(\theta)]^{-1} = v(-\theta); \\ v(\theta_1)v(\theta_2) = v(\theta_2)v(\theta_1) = v(\theta_1 + \theta_2) \end{aligned} \tag{3.8}$$

The operators $v(\theta)$ form again a one-parameter Abelian group, which seems to have simple exponential properties. In analogy with Eq. (1.70), we may now write $v(\theta)$ in the form

$$v(\theta) = e^{h(\theta)} \tag{3.9}$$

where the exponent $h(\theta)$ has the property $h(\theta_1 + \theta_2) = h(\theta_1) + h(\theta_2)$. Taking the derivative of this relation with respect to θ_2, one obtains $h'(\theta_1 + \theta_2) = h'(\theta_1)$, i.e., the derivative $h'(\theta) = \omega$ is independent of θ. Hence one has $h(\theta) = \theta\omega$, and the operator $v(\theta)$ takes the form

$$v(\theta) = e^{\theta\omega} \tag{3.10}$$

In order to calculate the explicit form of the operator ω, we consider the relation

$$v(\theta)f(x) = e^{\theta\omega}f(x) = e^{\theta/2}f(e^\theta x) \tag{3.11}$$

Taking the derivative with respect to the parameter θ, one obtains

$$\omega e^{\theta\omega}f(x) = \tfrac{1}{2}e^{\theta/2}f(e^\theta x) + e^{\theta/2}f'(e^\theta x)e^\theta x \tag{3.12}$$

Putting $\theta = 0$, one gets

$$\omega f(x) = \tfrac{1}{2}f(x) + xf'(x) \tag{3.13}$$

and ω must hence necessarily have the form

$$\omega = \frac{1}{2} + x\frac{d}{dx} = \frac{1}{2}\left(\frac{d}{dx}x + x\frac{d}{dx}\right) \tag{3.14}$$

$$= \frac{2\pi i}{h}\frac{1}{2}(px + xp) = iA \tag{3.15}$$

where

$$A = \frac{\pi}{h}(px + xp) \tag{3.16}$$

is a well-known self-adjoint operator in quantum theory; in fact, it is the operator that is associated with the proof of the virial theorem, which may also be proved by real scaling. Hence one has the formula

$$v(\theta) = e^{\theta\omega} = e^{i\theta A} \tag{3.17}$$

where $A^\dagger = A$, $A^* = -A$, and $A^\dagger = -A^*$. Taking the adjoint of this relation one obtains

$$[v(\theta)]^\dagger = e^{-i\theta^* A^\dagger} = e^{i\theta^* A^*} = [v^{-1}(\theta)]^* \tag{3.18}$$

which gives another proof for the fundamental relation, Eq. (3.6); one can also write

$$[v(\theta)]^\dagger = e^{-i\theta^* A} = v(-\theta^*) \tag{3.19}$$

Using Eq. (1.70), one finds further that $\Omega = i\theta A$, and it is evident that the condition Eq. (1.71) is automatically fulfilled.

B. Change of the Spectrum under Complex Rotation

For the strict underlying theory of the change of the spectrum of the Hamiltonian $H = T + V$, where $T = p^2/2m$ is the kinetic energy operator and $V = V(x)$ is the potential, the reader is referred to the original mathematical papers (*2*); here we will make only a few elementary remarks. We will assume that the original Hamiltonian is self-adjoint and real, and that the ground state and low-lying excited states form a *discrete part* of the spectrum followed by a *continuum* on the real axis from 0 to $+\infty$. The transformed Hamiltonian $\bar{H}$ is now defined through the relation

$$\bar{H} = u(\eta)Hu^{-1}(\eta) = H(\eta) \tag{3.20}$$

and may be considered as a function of the complex scaling parameter $\eta = a + ib = \rho e^{i\alpha}$. Since the condition, Eq. (3.6), is satisfied, the transformed

Hamiltonian has the property $\bar{H}^{\dagger} = \bar{H}^{*}$, which gives

$$[H(\eta)]^{\dagger} = H(\eta^{*}) \tag{3.21}$$

If the potential $V = V(x)$ vanishes sufficiently rapidly at $x = \pm\infty$, and is otherwise well behaved (*2*), it is evident that the kinetic energy term $T(\eta) = \eta^{-2}T$ is going to dominate the behavior of the continuous spectrum, which will be moved out an angle (-2α) in the complex plane. If, further, the continuum on the real axis is degenerate, and consists of several "branches," each branch will be rotated an angle (-2α) around its real starting point. According to the general theory (*2*), the discrete energy eigenvalues for the ground state and the low-lying excited states will be *persistent* eigenvalues, whereas *new eigenvalues* associated with physical resonances may be revealed in the complex plane as the angle α increases and the "continuum ray" passes them (see Fig. 2).

Even in the approximate treatment using the bivariational principle and a truncated finite basis, it is usually easily checked that the eigenfunctions Ψ_a corresponding to the *persistent* eigenvalues belong to the domain $D(u^{-1})$ of

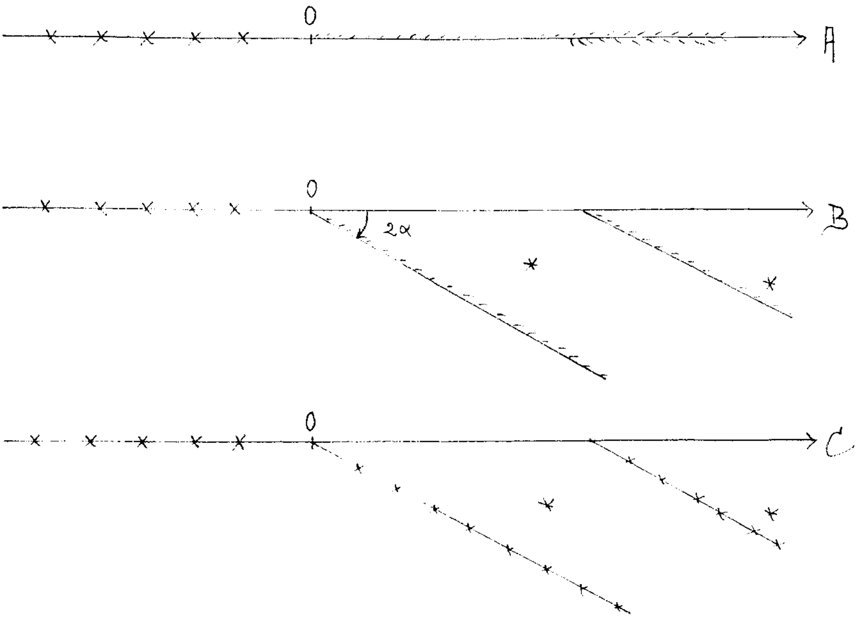

Fig. 2. The change of the energy spectrum under complex scaling. (*A*) The spectrum of the original Hamiltonian; (B) the exact spectrum of the dilated Hamiltonian; (C) the approximate spectrum with all the eigenvalues discrete as obtained by the bivariational principle and a truncated finite basis.

the operator $u^{-1} = u(\eta^{-1})$, whereas the eigenfunctions $\bar{\Psi}_a$ corresponding to the *new* eigenvalues in the complex plane—the approximations to the resonances as well as to the complex continua—are situated in the complement $C(u^{-1})$. Finally, the *lost* eigenvalues are represented by the real continua, which have completely disappeared.

C. Complex Scaling in Polar Coordinates

A single particle in three dimensions may be described in terms of cartesian coordinates (x, y, z) or polar coordinates (r, θ, φ) with the connection formulas

$$x = r \sin \theta \cos \varphi, \qquad y = r \sin \theta \sin \varphi, \qquad z = r \cos \theta \tag{3.22}$$

where $0 \leq r < +\infty$, $0 \leq \theta \leq \pi$, $0 \leq \varphi < 2\pi$. In this case, one may define the complex scaling $u_3(\eta)$ as a product [Eq. (2.25)] of three elementary scalings of the cartesian coordinates involved, so that

$$u_3(\eta) f(x, y, z) = \eta^{3/2} f(\eta x, \eta y, \eta z) \tag{3.23}$$

Multiplying the three relations given by Eq. (3.22) by η, it seems natural to assume that the complex scaling in polar coordinates corresponds to the transformation

$$r' = \eta r, \qquad \theta' = \theta, \qquad \varphi' = \varphi \tag{3.24}$$

where r' is now a complex coordinate which—for the sake of uniqueness—we will limit to the upper half-plane, so that $\mathrm{Re}(r') \geq 0$. This means that, for $\mathrm{Re}(\eta) > 0$, we will have the definition

$$u_3(\eta) g(r, \theta, \varphi) = \eta^{3/2} g(\eta r, \theta, \varphi) \tag{3.25}$$

We note that even the scale factor $\eta = -1$ should be permitted, and, in the real case, it corresponds to the transformation $r' = r$, $\theta' = \pi - \theta$, $\varphi' = \varphi \pm \pi$. This means that, for $\mathrm{Re}(\eta) < 0$, it may be convenient to use the definition

$$r' = -\eta r, \qquad \theta' = \pi - \theta, \qquad \varphi' = \varphi \pm \pi \tag{3.26}$$

It should finally be observed that, in cartesian and polar coordinates, one has $dv = dx\, dy\, dz = r^2 \sin \theta\, dr\, d\theta\, d\varphi$. If there is no risk for misunderstanding, we will in the following discussion omit the index 3 in the operator $u_3(\eta)$.

D. Scaling of an Atomic or Molecular Hamiltonian

Let us now consider a system, which consists of N electrons having the mass m, and P atomic nuclei having the mass m_g and the atomic number Z_g, i.e., a total of $(N + P)$ particles. Denoting the particles by the indices k and l, the nonrelativistic Hamiltonian for such a system has the form

$$H = \sum_k \frac{\mathbf{p}_k^2}{2m_k} + \sum_{k<l} \frac{e_k e_l}{r_{kl}} = T + V \tag{3.27}$$

where the summations over k and l go from 1 to $(N + P)$. Here T represents the kinetic energy of the system and V its Coulomb energy. The total operator U is then built up from $3(N + P)$ elementary scalings, and, for the transformation of a wave function $\Psi = \Psi(x_1, x_2, \ldots, x_{N+P})$, one obtains

$$U\Psi(x_1, x_2, \ldots, x_{N+P}) = \eta^{3(N+P)/2}\Psi(\eta x_1, \eta x_2, \ldots, \eta x_{N+P}) \tag{3.28}$$

as well as

$$\begin{aligned} \bar{H} &= U(\eta)HU^{-1}(\eta) = \eta^{-2}\sum_k \frac{\mathbf{p}_k^2}{2m_k} + \eta^{-1}\sum_{k<l}\frac{e_k e_l}{r_{kl}} \\ &= \eta^{-2}T + \eta^{-1}V \end{aligned} \tag{3.29}$$

In the approximate treatment based on the bivariational principle and the use of a finite truncated (real or complex) orthonormal basis φ, one obtains for the corresponding matrices

$$\bar{\mathbf{H}} = \eta^{-2}\mathbf{T} + \eta^{-1}\mathbf{V} \tag{3.30}$$

It is thus easy, at least in principle, to relate the properties of the matrix of the transformed Hamiltonian to the properties of the matrices $\mathbf{T}$ and $\mathbf{V}$ of the original Hamiltonian. Keeping the basis φ fixed, one can then plot the approximate eigenvalues I as functions of the scale factor $\eta = \rho e^{i\alpha}$ and observe the appearance and disappearance of eigenvalues as the "rotation angle" α increases.

In most applications, it is convenient to separate the indices of the electrons from the indices of the atomic nuclei, which are here considered as point charges. In the following discussion, we will let the electrons be denoted by the indices i and j, which run from 1 to N, and the nuclei by the indices g and h, which run from 1 to P. The nonrelativistic Hamiltonian, Eq. (3.27), now takes the form

$$\begin{aligned} H = {} & \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_g \frac{\mathbf{p}_g^2}{2m_g} + \sum_{i<j}\frac{e^2}{r_{ij}} \\ & - e^2\sum_i\sum_g \frac{Z_g}{r_{ig}} + e^2\sum_{g<h}\frac{Z_g Z_h}{r_{gh}} \end{aligned} \tag{3.31}$$

In the so-called Born–Oppenheimer approximation, the nuclei are supposed to have so large masses m_g that their kinetic energy may be neglected and their positions $(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_p)$ may be considered as fixed. In such a case, the original Hamiltonian simplifies to the form

$$\begin{aligned} H &= e^2 \sum_{g<h} \frac{Z_g Z_h}{R_{gh}} + \sum_i \frac{\mathbf{p}_i^2}{2m} - e^2 \sum_i \sum_g \frac{Z_g}{r_{ig}} + \sum_{i<j} \frac{e^2}{r_{ij}} \\ &= H_{(0)} + \sum_i H_i + \sum_{i<j} H_{ij} \end{aligned} \tag{3.32}$$

where

$$H_i = \frac{\mathbf{p}_i^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{ig}}, \qquad H_{ij} = \frac{e^2}{r_{ij}} \tag{3.33}$$

are the one- and two-electron operators involved. For the scaling of the wave function $\Psi = \Psi(x_1, x_2, \ldots, \mathbf{R})$, one now obtains

$$U\Psi(x_1, x_2, \ldots, x_N; \mathbf{R}) = \eta^{3N/2}\Psi(\eta x_1, \eta x_2, \ldots, \eta x_N; \eta\mathbf{R}) \tag{3.34}$$

where $\mathbf{R}$ stands for the composite $(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_p)$. For the transformed Hamiltonian $\bar{H}$, one has

$$\begin{aligned} &\bar{H}_{(0)} = \eta^{-1} H_{(0)}; \qquad \bar{H}_{ij} = \eta^{-1} H_{ij} \\ &\bar{H}_i = \eta^{-2} \frac{\mathbf{p}_i^2}{2m} - \eta^{-1} e^2 \sum_g \frac{Z_g}{r_{ig}} \end{aligned} \tag{3.35}$$

For applications to atomic systems, this approach is apparently working very well, whereas the applications to molecular systems still have a long way to go, depending on the fact that we are not yet familiar with the handling of the complex scaling of internuclear coordinates.

E. Various Types of Basis Sets

In treating an N-electron system, it may be convenient to introduce a truncated one-electron basis $\varphi = \{\varphi_k\}$ of order M and to build an N-electron basis consisting of the $\binom{M}{N}$ Slater determinants $\mathbf{D} = \{D_K\}$ formed by a selection $K = \{k_1, k_2, \ldots, k_N\}$ of N different one-electron functions out of the basis $\varphi = \{\varphi_k\}$. In such a case, it is sufficient to study the properties of the one-electron set φ with respect to the operator $u = u_3(\eta)$.

From our previous discussion, it follows that it is essential that this truncated basis φ spans not only the domain $D(u^{-1})$ of the operator $u^{-1} = u(\eta^{-1})$ but also its complement $C(u^{-1})$, which is defined through the feature that the image $u^{-1}C(u^{-1})$ is situated *outside* L^2 in the set $A(u) = u^{-1}C(u^{-1})$ (see Fig. 1).

In a treatment using polar coordinates, it may be convenient to introduce a basis of the form

$$\varphi_{nlm}(r, \theta, \varphi) = \frac{f_{nl}(r)}{r} Y_{lm}(\theta, \varphi) = \chi_{nl}(r) Y_{lm}(\theta, \varphi) \tag{3.36}$$

where Y_{lm} are the standard spherical harmonics, and $\chi_{nl}(r) = f_{nl}(r)/r$ is the radial part with the normalization

$$\int_0^\infty |\chi_{nl}(r)|^2 r^2 \, dr = \int_0^\infty |f_{nl}(r)|^2 \, dr = 1 \tag{3.37}$$

Let us now study various types of radial functions $\chi(r)$, where, for the sake of simplicity, we will omit the indices. For Slater-type orbitals (STOs), one has

$$\chi(r) = Ar^p e^{-qr} \tag{3.38}$$

where p and q are positive numbers (but not necessarily integers). One gets directly, for $\eta = \rho e^{i\alpha}$,

$$\begin{aligned} F &= u^{-1}(\eta)\chi(r) = \eta^{-3/2}\chi(\eta^{-1}r) \\ &= \eta^{-3/2}A(\eta^{-1}r)^p e^{-q\rho^{-1}e^{-i\alpha}r} \\ &= \eta^{-(p+3/2)}Ar^p e^{-q\rho^{-1}r\cos\alpha + iq\rho^{-1}r\sin\alpha} \end{aligned} \tag{3.39}$$

and it is evident that F belongs to L^2, and $\chi(r)$ to $D(u^{-1})$, as long as $\cos\alpha > 0$, i.e., whenever $-\pi/2 < \alpha < +\pi/2$. When this condition is fulfilled, a finite set of STOs will hence only approximate functions in the domain $D(u^{-1})$ of the operator $u^{-1} = u(\eta^{-1})$.

Let us next consider a set of Gaussian orbitals of the type

$$\chi(r) = Ar^p e^{-qr^2} \tag{3.40}$$

where the parameters p and q are positive. One gets directly

$$\begin{aligned} F &= u^{-1}(\eta)\chi(r) = \eta^{-3/2}\chi(\eta^{-1}r) \\ &= \eta^{-(p+3/2)}Ar^p e^{-q\rho^{-2}r^2\cos 2\alpha + iq\rho^{-2}r^2\sin 2\alpha}, \end{aligned} \tag{3.41}$$

and it is evident that F belongs to L^2, if $\cos 2\alpha > 0$, i.e., when $-\pi/4 < \alpha < +\pi/4$. If this condition is fulfilled, a finite set of Gaussians will hence only approximate functions in the domain $D(u^{-1})$.

If one tries to introduce higher exponentials of the type

$$\chi(r) = Ar^p e^{-qr^s} \tag{3.42}$$

where s is a positive integer, one finds similarly that $F = u^{-1}\chi(r)$ is in L^2, whenever $\cos s\alpha > 0$, i.e., when $-\pi/2s < \alpha < +\pi/2s$. For sufficiently small values of α, even the higher exponentials are going to approximate functions in $D(u^{-1})$.

On the other hand, if we consider the so-called Fourier–Plancherel functions in one dimension defined by Eq. (3.2), all of them are situated in the complement $C(u^{-1})$ as soon as the rotation angle is different from zero ($\alpha \neq 0$). It is evident that, in polar coordinates, the exponential factor $\exp(ikr)$ is going to have similar properties, since one has

$$\begin{aligned} u^{-1}e^{ikr} &= \eta^{-3/2}e^{ik\eta^{-1}r} \\ &= \eta^{-3/2}e^{ik\rho^{-1}r\cos\alpha + k\rho^{-1}r\sin\alpha} \end{aligned} \tag{3.43}$$

where the second term in the exponent will lead to an exponential blow up for $r = +\infty$, whenever $\sin\alpha > 0$, i.e., when $0 < \alpha < \pi$.

If $\chi = \chi(r)$ is an arbitrary basis function in L^2, which is normalized to unity according to Eq. (3.37), then the function

$$\chi'(r) = e^{ikr}\chi(r) \tag{3.44}$$

is also normalized to unity and belongs to L^2. However, even if $\chi(r)$ belongs to $D(u^{-1})$, it may very well happen that the image $F' = u^{-1}\chi'(r)$ is situated outside L^2, and that $\chi'(r)$ is hence situated in $C(u^{-1})$. Functions of the type Eq. (3.34) are known in the literature as Siegert functions.

As an example, we will consider the combination of the exponential factor and a Slater-type orbital defined by Eq. (3.28)

$$\chi'(r) = Ar^pe^{(ik-q)r} \tag{3.45}$$

where k, p, and q are positive parameters. For the image $F = u^{-1}\chi'(r)$, one obtains directly

$$\begin{aligned} F &= \eta^{-(p+3/2)}Ar^pe^{(ik-q)\rho^{-1}r(\cos\alpha - i\sin\alpha)} \\ &= \eta^{-(p+3/2)}Ar^pe^{\rho^{-1}r(-q\cos\alpha + k\sin\alpha + ik\cos\alpha + iq\sin\alpha)} \end{aligned} \tag{3.46}$$

It is then evident that the image F will be situated in L^2, if $-q\cos\alpha + k\sin\alpha < 0$, whereas it will be situated outside L^2, if $-q\cos\alpha + k\sin\alpha > 0$. Let us assume that the angle α has been fixed in the interval $-\pi/2 < \alpha < +\pi/2$, which means $\cos\alpha > 0$. It follows immediately that the Siegert function, Eq. (3.35), is situated in the complement $C(u^{-1})$ whenever

$$q/k < tg\alpha$$

If one tries the same procedure with Gaussian orbitals, it will not work, since the qr^2 term will be dominating for large values of r. However, if one choses a complex value of q, so that $q = q_1 + iq_2$ with $q_1 > 0$, the function given by Eq. (3.40) is still in L^2. For the image $F = u^{-1}\chi(r)$, one then obtains

$$\begin{aligned} F &= \eta^{-(p+3/2)}Ar^pe^{-\rho^{-2}r^2(q_1+iq_2)(\cos 2\alpha - i\sin 2\alpha)} \\ &= \eta^{-(p+3/2)}Ar^pe^{-\rho^{-2}r^2(q_1\cos 2\alpha + q_2\sin 2\alpha - iq\sin 2\alpha + iq_2\cos 2\alpha} \end{aligned} \tag{3.47}$$

which indicates that F is in L^2, if $q_1 \cos 2\alpha + q_2 \sin 2\alpha > 0$, and outside L^2, if $q_1 \cos 2\alpha + q_2 \sin 2\alpha < 0$. Provided that α is fixed in the interval $-\pi/4 < \alpha < +\pi/4$, one finds that the Gaussian Eq. (3.30) with $q = q_1 + iq_2$ is situated in the complement $C(u^{-1})$ whenever

$$q_1 + q_2 tg2\alpha < 0 \tag{3.48}$$

The discussion shows that if one wants to span both the domain $D(u^{-1})$ and the complement $C(u^{-1})$ approximately fairly well without introducing very large basis sets, it may be worthwhile to introduce different types of complex components both in the Slater-type orbitals and in the Gaussians.

F. Stabilization Graphs

The general theory (2) tells us that the new complex eigenvalues $\bar{E}$ corresponding to resonances may appear whenever the rotation angle α becomes sufficiently large, so that the point $\bar{E}$ is situated in the area of angle (-2α) which has been passed by the "continuum ray." In the limiting case of an infinite complete basis, the eigenvalue becomes independent of $\bar{E}$, and one has directly

$$\frac{\partial \bar{E}}{\partial \eta} = \frac{\partial^2 \bar{E}}{\partial \eta^2} = \frac{\partial^3 \bar{E}}{\partial \eta^3} = \cdots = 0 \tag{3.49}$$

for all derivatives with respect to η. Even if the basis is truncated and finite, one can expect that the approximate eigenvalue should show some tendency of convergence, and the relations given by Eq. (3.39) form the background for the use of *stabilization graphs.*

We note that, first of all, the first derivative of $\bar{E}$ has to be vanishing and that the relation

$$\partial \bar{E}/\partial \eta = 0 \tag{3.50}$$

resembles the bivariational principle in which one varies the complex scaling parameter η. In the case of a real scale parameter ($\eta = \rho$), Hylleraas (*12*) used relations of the type given by Eq. (3.29) to improve his variational wave functions, and Fock (*13*) used the same approach to prove the validity of the virial theorem. Later these considerations were generalized, also to the method of complex scaling, by Brändas *et al.* (*14*).

The use of the stabilization graphs represents one of the most popular methods for dealing with the method of complex scaling in the current literature, particularly since these graphs indicate the occurrence of complex eigenvalues corresponding to resonances, even when α is not large enough to reveal their existence. It has been pointed out by Simons (*15*) that one may even be able to calculate the complex resonances from the quantities of the *real stabilization graphs* $\bar{E} = \bar{E}(\rho)$ for which $\alpha = 0$. The reason for this is not yet fully known, but it may be related to the fact that the occurrence of a complex eigenvalue in some way is a description of the existence of certain *spectral concentrations* on the real axis of the original Hamiltonian, which should show up also in other connections.

G. Concluding Remarks

It is hardly necessary to emphasize that the present review is a fairly simple exercise in linear algebra and is intended to familiarized theoretical physicists and chemists working on the quantum theory of matter with the fundamental properties of the unbounded similarity transformations as applied to N-electron systems. Special attention has been given to the change of the spectra and how it is related to the domain of the transformation applied and to the fact that the eigenfunctions may be transformed not only within the L^2 Hilbert space, but also out of and into this space (see Fig. 1).

The mathematicians have concentrated their interest on the transformed Hamiltonian for a single particle in one dimension, and they have solved the problem of the domain changes by the introduction of the Nelson class (*16*), which contains all functions on which the operator $v(\theta) = e^{i\theta A}$, given by Eq. (3.17), is analytically defined for all complex θ. Even if a great deal of strict mathematical work is now devoted to the problem of a single particle in three dimensions, it will probably take a fair amount of time until all the fundamental theorems have been strictly proved for N-electron systems.

A great deal of work has also been devoted to the study of the resolvent $R(z) = (z \cdot 1 - H)^{-1}$ and of the analytic properties of the Weinstein function $W(z) = \langle\varphi|R(z)|\varphi\rangle$ defined by Eq. (2.86), where φ is a normalized reference function. The resolvent was originally introduced in connection with the solution of the inhomogeneous equation

$$(H - z \cdot 1)\Psi_Z = a\varphi \tag{3.51}$$

subject to the boundary condition

$$\langle\varphi\,|\,\Psi_Z\rangle = 1 \tag{3.52}$$

Hence one has $\Psi_Z = -aR(z)\varphi$, where $a = -\langle\varphi|R(z)|\varphi\rangle^{-1}$. Since $a = 0$ corresponds to the homogeneous Schrödinger equation for $z = E$, it is clear that the eigenvalues $z = E$ correspond to the poles of the Weinstein function. One gets directly

$$\Psi_Z = \frac{R(z)\varphi}{\langle\varphi|R(z)|\varphi\rangle} \tag{3.53}$$

which takes the form ∞/∞ when z approaches an eigenvalue E. One may calculate the limiting value by means of the so-called *partitioning* technique (*17*). Introducing the projector $O = |\varphi\rangle\langle\varphi|$ and the projector $P = 1 - O$ for its orthogonal complement, one obtains

$$O\varphi = \varphi; \qquad O\Psi_Z = \varphi; \qquad P\varphi = 0; \qquad P\Psi_Z = \Psi_Z - \varphi \tag{3.54}$$

Letting the operator P work on the inhomogeneous Eq. (3.51), one obtains the relation $P(H - z \cdot 1)\Psi_Z = PH\Psi_Z - z(\Psi_Z - \varphi) = 0$, which has the formal explicit solution

$$\Psi_Z = (1 - PH/z)^{-1}\varphi \tag{3.55}$$

which is another form of the quotient, Eq. (3.53). Multiplying the inhomogeneous Eq. (3.53) on the left by $\langle\varphi|$, one obtains

$$a = \langle\varphi|H|\Psi_Z\rangle - z = \langle\varphi|H(1 - PH/z)^{-1}|\varphi\rangle - z \tag{3.56}$$

The zero points of this function correspond to the poles of the Weinstein function and give the eigenvalues $z = E$.

Let us, for a moment, consider a single particle in one dimension with a Hamiltonian of the type $H = p^2/2m + V(x)$. This is a second-order differential operator, and this means that the general solution to the inhomogeneous Eq. (3.51)—considered as a second-order differential equation—will consist of a linear superposition of two special solutions, where the coefficients will depend on the boundary conditions introduced. As a specific example, one could think of the two solutions to the JWKB problem, their connection formulas, and the Stoke's phenomenon for the coefficients.

It is obvious that if one is interested in the analytic properties of the solutions given by Eq. (3.53) or (3.55) and their dependence on the complex variable Z, it may be convenient to introduce a *twofold Riemann surface* and to discuss the possible analytic continuation as well as the poles of the resolvent—or the corresponding Weinstein function—on this surface. It takes a great deal of mathematical skill and carefulness to discuss these problems for a single particle in one dimension, and it is considerably more difficult to study them for a single particle in three dimensions—not to mention the proper handling of an N-electron system.

This means that, for a long time, the theoretical physicists or chemists interested in evaluating the properties of, e.g., new materials by means of many-particle quantum theory may have to rely on formal methods which are fairly strict from the point of view of theoretical physics, but which lack the proofs for the existence theorems characteristic for rigorous mathematics. Hence a great deal of effort will go into the calculation of quantities which are not known really to exist from the mathematical point of view, but which exist at least practically from a computational point of view.

Appendix A. Construction of Dual Complex Conjugate Biorthonormal Sets

Let us start from a linearly independent set $\mathbf{\Phi} = \{\Phi_1, \Phi_2, \ldots, \Phi_m\}$ consisting of complex functions; the set has the additional property that the overlap matrix $\mathbf{\Delta} = \langle \mathbf{\Phi}^* | \mathbf{\Phi} \rangle$ is nonsingular, i.e., that $|\mathbf{\Delta}| \neq 0$. Let γ be the similarity transformation, which brings $\mathbf{\Delta}$ to classical canonical form $\boldsymbol{\lambda}$ with the eigenvalues on the diagonal and 0s and 1s on the line above the diagonal:

$$\gamma^{-1}\mathbf{\Delta}\gamma = \boldsymbol{\lambda} \tag{A.1}$$

where the matrix $\boldsymbol{\lambda}$ consists of Jordan blocks, the sizes of which are described by the so-called Ségré characteristics. The matrix $\mathbf{\Delta}^{-1/2}$ is then defined by the relation

$$\mathbf{t} = \mathbf{\Delta}^{-1/2} = \gamma\boldsymbol{\lambda}^{-1/2}\gamma^{-1} \tag{A.2}$$

where we will now define the square root $\boldsymbol{\lambda}^{-1/2}$ in somewhat greater detail. For this purpose, we will consider a specific Jordan block

$$\boldsymbol{\lambda}_k = \begin{bmatrix} \lambda_k & 1 & 0 & \cdot & \cdot & \cdot & \cdot \\ 0 & \lambda_k & 1 & 0 & \cdot & \cdot & \cdot \\ 0 & 0 & \lambda_k & 1 & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \lambda_k \end{bmatrix} = \lambda_k \cdot \mathbf{1} + \mathbf{J}_1 \tag{A.3}$$

of order p_k, where λ_k is the eigenvalue and $\mathbf{J}_1$ is a matrix with the element 0 everywhere except for a series of 1s on the line above the diagonal. It is easily checked that the matrix $\mathbf{J}_2 = \mathbf{J}_1^2$ consists of a series of 1s two steps above the diagonal, and similarly that $\mathbf{J}_l = \mathbf{J}_1^l$ consists of a series of 1s which are l steps above the diagonal. For $l = p_k$, the matrix $\mathbf{J}_l$ has only vanishing elements, and the matrix $\mathbf{J}_1$ is hence *nilpotent* of order p_k:

$$\mathbf{J}_1^{p_k} = \mathbf{0} \tag{A.4}$$

The eigenvalue λ_k is nonvanishing, since the matrix $\mathbf{\Delta}$ was assumed to be nonsingular. We will further let the symbol $\lambda_k^{+1/2}$ denote a specific square root, which is positive if the number λ_k is real and positive, and which is situated in the upper half of the complex plane if λ_k is complex, so that $I\{\lambda_k^{1/2}\} \geq 0$. Even other conventions are, of course, possible. Writing Eq. (A.3) in the form

$$\boldsymbol{\lambda}_k = \lambda_k\{\mathbf{1} + \lambda_k^{-1}\mathbf{J}_1\} \tag{A.5}$$

one may then construct a specific square root $\boldsymbol{\lambda}_k^{-1/2}$ by means of the binomial theorem, which leads to a finite expansion consisting of p_k terms:

$$\begin{aligned}\boldsymbol{\lambda}_k^{-1/2} &= \lambda_k^{-1/2}\{\mathbf{1} + \lambda_k^{-1}\mathbf{J}_1\}^{-1/2} \\ &= \lambda_k^{-1/2}\{\mathbf{1} - \tfrac{1}{2}\lambda_k^{-1}\mathbf{J}_1 + \tfrac{3}{8}\lambda_k^{-2}\mathbf{J}_2 - \tfrac{5}{16}\lambda_k^{-3}\mathbf{J}_3 \pm \cdots\}\end{aligned} \tag{A.6}$$

Making this construction for all the Jordan blocks occurring in the matrix $\boldsymbol{\lambda}$, one obtains a specific square root $\boldsymbol{\lambda}^{-1/2}$, which, substituted in the relation given by Eq. (A.2), leads to the matrix $\mathbf{t} = \boldsymbol{\Delta}^{-1/2}$. We will now show that if the overlap matrix $\boldsymbol{\Delta}$ is symmetric, so that $\tilde{\boldsymbol{\Delta}} = \boldsymbol{\Delta}$, then the matrix $\mathbf{t} = \boldsymbol{\Delta}^{-1/2}$ has the same property:

$$\tilde{\mathbf{t}} = \mathbf{t} \tag{A.7}$$

It should be observed that the classical canonical form $\boldsymbol{\lambda}$ is by no means symmetric, except in the special case when it happens to be diagonal. The transposed matrix $\tilde{\boldsymbol{\lambda}}$ has the same elements as $\boldsymbol{\lambda}$ on the diagonal, but the 0s and 1s are now on the line one step below the diagonal. For a specific Jordan block of order p, one obtains from Eq. (A.3)

$$\tilde{\boldsymbol{\lambda}}_k = \lambda_k \cdot \mathbf{1} + \tilde{\mathbf{J}}_1 \tag{A.8}$$

It is now easily checked that, if $\mathbf{P}_k$ is a permutation matrix which reverses the order of the basic element associated with this specific Jordan block, so that

$$\mathbf{P}_k = \begin{pmatrix} & & & & & & 1 \\ & & & & & 1 & \\ & & & & 1 & & \\ & & & 1 & & & \\ & & 1 & & & & \\ & 1 & & & & & \\ 1 & & & & & & \end{pmatrix} \tag{A.9}$$

then one has the connection

$$\mathbf{P}_k^{-1}\tilde{\mathbf{J}}_1\mathbf{P}_k = \mathbf{J}_1 \tag{A.10}$$

where $\tilde{\mathbf{P}}_k = \mathbf{P}_k^{-1} = \mathbf{P}_k$. The same similarity transformation holds also for the powers $\tilde{\mathbf{J}}_2, \tilde{\mathbf{J}}_3, \ldots$, etc., and, for the square root, Eq. (A.6), this gives

$$\begin{aligned}\widetilde{(\boldsymbol{\lambda}_k^{-1/2})} &= \lambda_k^{-1/2}\{\mathbf{1} - \tfrac{1}{2}\lambda_k^{-1}\tilde{\mathbf{J}}_1 + \tfrac{3}{8}\lambda_k^{-2}\tilde{\mathbf{J}}_2 \mp \cdots\} \\ &= \mathbf{P}_k\lambda_k^{-1/2}\{\mathbf{1} - \tfrac{1}{2}\lambda_k^{-1}\mathbf{J}_1 + \tfrac{3}{8}\lambda_k^{-2}\mathbf{J}_2 + \cdots\}\mathbf{P}_k^{-1} \\ &= \mathbf{P}_k\boldsymbol{\lambda}_k^{-1/2}\mathbf{P}_k^{-1}\end{aligned} \tag{A.11}$$

If, finally, $\mathbf{P}$ is the permutation matrix built up in block-diagonal form from all the submatrices $\mathbf{P}_k$ associated with the various Jordan blocks, one obtains

$$\mathbf{P}^{-1}\tilde{\lambda}\mathbf{P} = \lambda, \qquad \tilde{\lambda} = \mathbf{P}\lambda\mathbf{P}^{-1} \tag{A.12}$$

i.e., the permutation matrix **P** characterizes the similarity transformation, which brings the transposed matrix $\tilde{\lambda}$ to canonical form.

We will now use the fact that the original overlap matrix $\boldsymbol{\Delta}$ is symmetric, so that $\tilde{\boldsymbol{\Delta}} = \boldsymbol{\Delta}$. Taking the transpose of Eq. (A.1), one obtains

$$\tilde{\gamma}\,\tilde{\boldsymbol{\Delta}}(\tilde{\gamma})^{-1} = \tilde{\lambda} = \mathbf{P}\lambda\mathbf{P}^{-1} \tag{A.13}$$

i.e.,

$$\mathbf{P}^{-1}\tilde{\gamma}\,\boldsymbol{\Delta}(\tilde{\gamma})^{-1}\mathbf{P} = \lambda \tag{A.14}$$

Hence it is always possible to find a matrix γ which has the special property $\gamma = (\tilde{\gamma})^{-1}\mathbf{P}$ or

$$(\tilde{\gamma})^{-1}\mathbf{P} = \gamma, \qquad \mathbf{P}^{-1}\tilde{\gamma} = \widetilde{\gamma^{-1}} \tag{A.15}$$

Taking the transpose of the matrix **t** defined by Eq. (A.2) and using Eqs. (A.11) and (A.15), we obtain

$$\begin{aligned}\tilde{\mathbf{t}} &= (\tilde{\gamma})^{-1}(\lambda^{-1/2})\tilde{\gamma} = (\tilde{\gamma})^{-1}\mathbf{P}\lambda^{-1/2}\mathbf{P}^{-1}\tilde{\gamma}\\ &= \gamma\lambda^{-1/2}\gamma^{-1} = \mathbf{t}\end{aligned} \tag{A.16}$$

Hence even the matrix **t** is a symmetric matrix with complex elements.

We note finally that, if the basic set $\boldsymbol{\Phi}$ is chosen to consist of *real* functions, the overlap matrix $\boldsymbol{\Delta} = \langle \boldsymbol{\Phi}^* | \boldsymbol{\Phi} \rangle$ is real and symmetric, i.e., one has also $\boldsymbol{\Delta}^\dagger = \boldsymbol{\Delta}$. In such a case, the classical canonical form is diagonal, and all the Jordan blocks are of order $p = 1$, which greatly simplifies the treatment.

Appendix B. Examples of Tranformed Operators Having a Continuous Spectrum: The Momentum *p* and the Kinetic Energy $T = p^2/2m$

In the eigenvalue relation $TC = \lambda C$, where $T^\dagger = T$, the eigenfunction C is said to belong to the continuum if C does not belong to L^2 but $|C|$ is still finite at infinity. An alternative formulation is that C is a derivative of a function $\Xi(\lambda)$, which itself belongs to L^2:

$$C = d\Xi(\lambda)/d\lambda \tag{B.1}$$

Hence

$$\Xi(\lambda) = \int_{\lambda_0}^{\lambda} C(\lambda)\, d\lambda \tag{B.2}$$

is an element in L^2, and we note that this is essentially the idea of the "wave packet" in the continuum in quantum mechanics.

Let us now consider the transformed operator $\bar{T} = UTU^{-1}$. Since the transformation $\bar{C} = UC$ corresponds to the transformation $\bar{\Xi} = U\Xi$, one can conclude that $\bar{\lambda} = \lambda$ is a persistent eigenvalue provided that $\bar{C}$ does not belong to L^2, whereas the function $\bar{\Xi}$ does. At the same time, one sees that, in order to obtain a complex eigenvalue $\bar{\lambda}$ belonging to the continuum, the image $U^{-1}\bar{\Xi}$ cannot belong to L^2—instead it should belong to the class $A(U)$.

As examples, we will consider the momentum operator p and the kinetic energy operator $T = p^2/2m$ for a single particle in one dimension. Introducing atomic units with $\hbar = h/2\pi = 1$ and $m = 1$, one obtains $p = -i\,\partial/\partial x$. The operator p is self-adjoint with respect to the L^2 binary product, since one has

$$\begin{aligned}\langle p\psi_1 | \psi_2\rangle &= \int_{-\infty}^{+\infty} (p\psi_1)^* \psi_2\, dx = \int_{-\infty}^{+\infty} i\frac{\partial \psi_1^*}{\partial x}\psi_2\, dx \\ &= i[\psi_1^*\psi_2]_{-\infty}^{+\infty} - i\int_{-\infty}^{+\infty} \psi_1^* \frac{\partial \psi_2}{\partial x}\, dx = \int_{-\infty}^{+\infty} \psi_1^*(p\psi_2)\, dx \\ &= \langle \psi_1 | p\psi_2\rangle \end{aligned} \tag{B.3}$$

where we have used the fact that the L^2 elements ψ_1 and ψ_2 vanish at infinity. The eigenvalue relation

$$p\psi = \lambda\psi \tag{B.4}$$

considered as a differential equation has solutions ψ for all values of λ, real or complex:

$$\psi = Ae^{i\lambda x} \tag{B.5}$$

Putting $\lambda = a + ib$ and observing that x is real, $-\infty < x < +\infty$, one obtains

$$|\psi| = |A|e^{-bx} \tag{B.6}$$

which blows up for either $x = +\infty$ or $x = -\infty$ unless $b = 0$. Hence the eigenvalues $\lambda = a$ are situated on the real axis, and one has a continuous spectrum in λ on the real axis reaching from $-\infty$ to $+\infty$. At the same time, one obtains for the integrated wave packet

$$\Xi(\lambda) = A\frac{e^{i\lambda x} - 1}{i\lambda} \tag{B.7}$$

which gives

$$|\Xi(\lambda)|^2 = |A|^2\frac{(e^{-bx} - \cos ax)^2 + \sin^2 ax}{x^2} \tag{B.8}$$

This means that Ξ does not belong to L^2 unless $b = 0$. For $b = 0$, one obtains particularly

$$|\Xi(\lambda)|^2 = |A|^2 2 \frac{1 - \cos ax}{x^2} \tag{B.9}$$

which means that Ξ belongs to L^2.

As an example, we will consider the complex scaling defined by Eqs. (1.35) and (3.1). One gets directly

$$\bar{\Xi} = u\Xi = \eta^{1/2}\Xi(\eta x) = \eta^{1/2} A \frac{e^{i(\eta\lambda)x}}{i\eta x} \tag{B.10}$$

where η is a complex parameter: $\eta = \rho e^{i\alpha}$. Our previous variable λ is now replaced by the variable $\lambda' = \eta\lambda$, and it is then evident that $\bar{\Xi}$ can belong to L^2, if and only if $\lambda' = \eta\lambda$ is real, which gives

$$\bar{\lambda} = a\rho^{-1}e^{-i\alpha} \tag{B.11}$$

Hence the continuum has been rotated an angle $(-\alpha)$ in the complex plane. In this particular case, one has

$$\bar{\Xi} = \eta^{-1/2} A \frac{e^{iax} - 1}{ix} \tag{B.12}$$

which is an element of L^2. However, if we are interested in finding out where this function comes from, we must consider the reverse transformation

$$\begin{aligned} F = u^{-1}\bar{\Xi} = \eta^{-1/2}\bar{\Xi}(\eta^{-1}x) &= \eta^{-1} A \frac{e^{i(\eta^{-1}a)x} - 1}{i\eta^{-1}x} \\ &= A \frac{e^{i\rho^{-1}ax\cos\alpha + \rho^{-1}ax\sin\alpha} - 1}{ix} \end{aligned} \tag{B.13}$$

and, for $\alpha \neq 0$, this function does not belong to L^2; in fact, it belongs to class $A(U)$. One can get another aspect on this problem by considering the operator $\bar{p} = UpU^{-1}$. Since one has

$$\bar{p} = \eta^{-1}p \tag{B.14}$$

it is evident that $\bar{p}$ and p must have the same eigenfunctions, whereas the eigenvalues are subject to the transformation

$$\bar{\lambda} = \eta^{-1}\lambda = (\rho^{-1}\lambda)e^{-i\alpha} \tag{B.15}$$

Let us now also consider the example of the kinetic energy operator $T = p^{2/2} = -\frac{1}{2}\partial^2/\partial x^2$ under complex scaling. The differential equation

$$T\Psi = E\Psi \tag{B.16}$$

has the general solution

$$\Psi = A_1 e^{ix\sqrt{2E}} + A_2 e^{-ix\sqrt{2E}} \tag{B.17}$$

for all values of E, complex or real. It is immediately clear that unless the parameter E is real and positive ($E \geq 0$), the absolute value of Ψ is going to blow up for either $x = +\infty$ or $x = -\infty$. Hence T has a continuous spectrum situated on the positive real axis. For the scaled operator $\bar{T} = UTU^{-1}$ one gets directly

$$\bar{T} = \eta^{-2} T \tag{B.18}$$

which means that $\bar{T}$ has the same eigenfunctions as T with the eigenvalues transformed according to the formula

$$\bar{E} = \eta^{-2} E = (E/\rho^2) e^{-2i\alpha} \tag{B.19}$$

In this case, the continuum is rotated an angle (-2α) with respect to the positive real axis. A study of the associated functions Ξ and $\bar{\Xi}$ gives a good illustration of the theory.

For the sake of simplicity, we will put $E = \omega^2/2$ or $\omega = \sqrt{2E}$, where we will choose ω positive for positive E and otherwise use the same square root convention as in Appendix A. For the primitive function associated with the first term in Eq. (B.17), one obtains

$$\Xi = \int_0^E e^{ix\sqrt{2E}}\, dE = \int_0^\omega e^{ix\omega}\omega\, d\omega$$
$$= \frac{e^{ix\omega}(1 - i\omega x) - 1}{x^2} \tag{B.20}$$

which belongs to L^2. It is also easily shown that this function belongs to the complement $C(u^{-1})$ unless $\alpha = 0$. Similar results hold for the second term in Eq. (B.17).

Appendix C: Example of Complex Eigenvalues Occurring as a Result of the Approximations Introduced

In Section II, we warned about the fact that complex eigenvalues to the transformed operator $\bar{H} = UHU^{-1}$ may occur essentially as a result of the approximations introduced, and that the imaginary parts may converge to zero as the number of basis functions increases and the basis becomes complete. In this appendix, we will study a simple example of this phenomenon, where we have made a simple choice of basis for $\bar{H}$ but limited ourselves to a single basis function $\Theta_1 = \Psi$, where Ψ is an exact normalized eigenfunction to the original Hamiltonian $H = T + V$, where T is the kinetic energy operator and V the Coulomb energy, associated with the eigenvalue E, so that $H\Psi = E\Psi$. According to the virial theorem, one obtains for the corresponding expectation values

$$\langle T \rangle = -E, \qquad \langle V \rangle = +2E \tag{C.1}$$

The transformed Hamiltonian $\bar{H} = UHU^{-1}$ is then given by Eq. (3.29), and for its expectation value $\langle \bar{H} \rangle = \langle \Psi | \bar{H} | \Psi \rangle$ one obtains

$$\begin{aligned} \langle \bar{H} \rangle &= -E\eta^{-2} + 2E\eta^{-1} \\ &= E - E(\eta^{-1} - 1)^2 \end{aligned} \tag{C.2}$$

It is hence evident that this expectation value is going to be complex, even if E is a persistent real eigenvalue. Let us now plot the function

$$f = \langle \bar{H} \rangle / E - 1 = -(\eta^{-1} - 1)^2 \tag{C.3}$$

as a function of the angle α in the parameter $\eta = e^{i\alpha}$. For the real and imaginary parts of $f = x + iy$, one gets directly

$$\begin{aligned} x &= 2\cos\alpha - 2\cos^2\alpha = 2\cos\alpha(1 - \cos\alpha) \\ y &= \sin 2\alpha - 2\sin\alpha = -2\sin\alpha(1 - \cos\alpha) \end{aligned} \tag{C.4}$$

which gives $y/x = -tg\alpha$. In planar polar coordinates $x = r\cos\varphi$, $y = r\sin\varphi$, one obtains

$$r = \sqrt{x^2 + y^2} = 2(1 - \cos\alpha), \qquad \varphi = -\alpha \tag{C.5}$$

and it is then easy to plot $f = x + iy$ as a function of α (see Fig. 3).

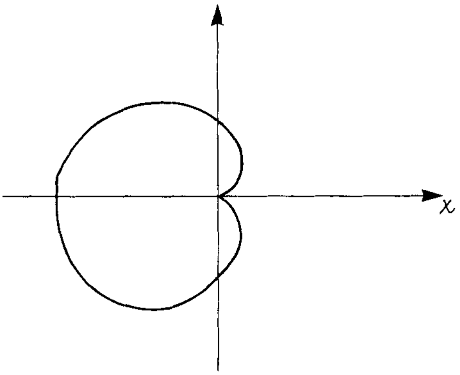

Fig. 3. The function $f = -(\eta^{-1} - 1)^2$ for $\eta = e^{i\alpha}$ as a function of α.

In a similar way, one can plot the eigenvalues of the matrix $\bar{\mathbf{H}} = \eta^{-2}\mathbf{T} + \eta^{-1}\mathbf{V}$ for any choice of basis $\boldsymbol{\theta}$ as functions of the parameter $\eta = \rho e^{i\alpha}$. Since the eigenvalues I are in general going to be complex, it is evidently necessary to carefully distinguish between the approximations to real persistent eigenvalues, to continuous eigenvalues in the complex plane, and to true physical resonances.

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Spin-Orbit Coupling and Other Relativistic Effects in Atoms and Molecules

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I. Introduction

The calculation of accurate wave functions for systems containing heavy elements requires addressing the difficulties of the treatment of large numbers of electrons and the subtleties of electron correlation. In addition, because of the large magnitudes of spin-orbit coupling and other relativistic effects in heavy atoms, some form of the Dirac formalism must be incorporated. One approach by which difficulties can be reduced to manageable ends is detailed in this article. This is not intended as a general review of relativity in chemistry or quantum mechanics, nor even of effective potential procedures, but is rather a critical discussion, including a limited number of applications, of the background, approximations, and implications of techniques developed by the present authors and collaborators and colleagues. The particular approach given here is by no means the only avenue to the *ab inito* studv of heavy-element systems, but it is one of the most extensively tested and, perhaps, the one by which the most sophisticated heavy-element molecular calculations to date have been carried out.

In light-atom systems, a high level of accuracy is realized if potential energy curves are calculated in the $\Lambda-S$ coupling scheme in which spin-orbit coupling effects are neglected. In heavy-atom systems, however, the pertubation of $\Lambda-S$ potential energy curves by spin-orbit coupling is significant. This is illustrated in Fig. 1, where the 0_g^+, 0_u^-, and 1_u states of Tl_2 are shown along

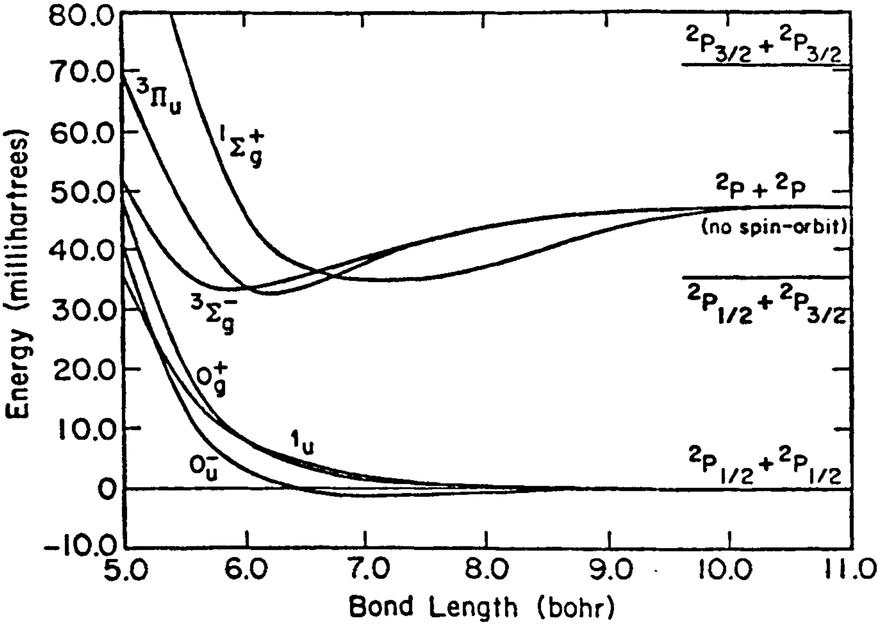

Fig. 1. *Ab initio* potential energy curves for 0_g^+, 0_u^-, and 1_u states of Tl_2, with $^3\Sigma_g^-$, $3\Pi_u$, and $^1\Sigma_g^+$ curves (computed without spin-orbit coupling) for comparison.

with the $^3\Sigma_g^+$, $^3\Pi_u$, and $^1\Sigma_g^+$ states from which they originate. As can be seen in the figure, bond strengths, bond lengths, and potential energy curve shapes are dramatically different when spin-orbit coupling and other relativistic effects are considered. Pitzer (*1,2*) has discussed these effects in detail and Pyykkö and Desclaux (*3*) have shown that they are also important in understanding ionization potentials, electron affinities, and valency changes.

Spin-orbit effects on ionization potentials, as discussed by Pyykkö and Desclaux (*3*), are seen when the successive first ionization potentials of Pb ($6s^2 6p^2$) and Bi ($6s^2 6p^3$) are compared to their lighter congeners. As observed by Frick *et al.* (*4*) the first ionization potentials increase in the sequence np^2 to np^3 for all of the lighter atoms ($n \leq 5$). They did not observe this increase, however, in the Pb to Bi sequence. This is understood if spin-orbit coupling effects are taken into account. After spin-orbit splitting is accounted for, the electron occupations are Pb ($6s^2 6p_{1/2}^2$) and Bi ($6s^2 6p_{1/2}^2 6p_{3/2}$) (*1*). The $p_{3/2}$ orbital is higher in energy than the $p_{1/2}$ orbital, so the ionization potential does not increase when the third p electron is added. The electron occupation in Bi also illustrates a valency change effect, since there is one electron outside of a closed $p_{1/2}$ shell. In the case of electron affinities, Pyykkö and Desclaux point out that the anomolously large value for Tl can be attributed to the stability of the closed $6p_{1/2}$ shell in the presence of one open-shell $6p_{3/2}$ electron (*3*). Most of the molecular calculations that have included spin-orbit effects prior to the last 5 years have involved light atoms. In such systems, relativistic effects, including spin-orbit splitting, are small and have been treated by perturbation theory.

The formalism for treating light atom systems begins with the Breit equation. The atomic spin-orbit Hamiltonian is given by (*5*)

$$H^{\mathrm{SO}} = (\alpha^2/2)\left[\sum_i (Z/r_i^3)(\mathbf{l}_i \cdot \mathbf{s}_i) - \sum_{i \neq j} (1/r_{ij}^3)(\mathbf{r}_{ij} \times \mathbf{p}_i) \cdot (\mathbf{s}_i + 2\mathbf{s}_j)\right] \qquad (1)$$

where α is the fine structure constant and the second term is identified with the so-called spin-other-orbit interaction. Blume and Watson, employing the above Hamiltonian and nonrelativistic Hartree–Fock wave functions, have calculated spin-orbit coupling constants for many of the first- and second-row Group A elements and first-row transition elements (*6,7*). The spin-orbit coupling constants A are given by

$$E_J - E_{J-1} = AJ \qquad (2)$$

where J is the total angular momentum quantum number. Fraga and coworkers, employing the same procedure, have calculated coupling constants for atoms from B through the third transition row (*8*). The agreement with experiment is reasonably good until elements containing $4s$ and $4p$ electrons are studied. Results of Blume and Watson, shown in Table I, indicate that spin-orbit coupling effects become particularly large at this point, and that treating them as perturbations is not as good an approximation as it is for the lighter elements. Part of the deviation in agreement with experiment can also be attributed to the lack of terms that account for spin–spin splitting effects (*5–7*), which also increase with atomic number. Many other calculations, employing perturbation methods similar to that described above, have been performed yielding good agreement with experiment for light atoms (*9,10*).

Calculations of spin-orbit coupling constants of diatomic molecules based on nonrelativistic wave functions have been performed by Walker and Richards (*11,12*) by extending the techniques of Blume and Watson. A review of this formalism, including diatomic calculations through 1979, is given in the monograph by Richards *et al.* (*13*). Calculated spin-orbit coupling constants for diatomic molecules comprised of elements of the first and second rows agree favorably with experiment (*13*). Calculations on molecules containing heavy elements, however, are not reported. In such cases, one expects the $\Lambda - S$ coupling scheme to be less appropriate, and the use of perturbation theory less accurate. Although *ab initio* all-electron calculations have been carried out

TABLE I

Spin-Orbit Coupling Constants *A* of Selected Elements[a]

Element	Configuration	Observed (cm^{-1})	Calculated (cm^{-1})
B	$2p^1$	10.7	9.7
C	$2p^2$	15 ± 2	13.4
N^+	$2p^2$	45 ± 4	41.8
O^{2+}	$2p^2$	105 ± 8	99.2
F^{3+}	$2p^2$	210 ± 16	200
O	$2p^4$	−74 ± 6	−80
F^+	$2p^4$	−160 ± 10	−168
F	$2p^5$	−269	−265
Sc^{2+}	$3d^1$	79	86
Ti^{2+}	$3d^2$	60 ± 1	61
V^{2+}	$3d^3$	56	57
Cr^{2+}	$3d^4$	58 ± 4	59
Fe^{2+}	$3d^6$	−102 ± 8	−114
Co^{2+}	$3d^7$	−176 ± 10	−189
Ni^{2+}	$3d^8$	−322 ± 19	−343
Cu^{2+}	$3d^9$	−829	−830
Al	$3p^1$	75	61
Si	$3p^2$	75 ± 2	64
S	$3p^4$	−187 ± 11	−184
Cl	$3p^5$	−587	−545
Ga	$4p^1$	551	460
Ge	$4p^2$	440	399
Se	$4p^4$	−934	−825
Br	$4p^5$	−2456	−2194

[a] From Ref. 7.

using the Dirac–Fock (DF) formalism for the heavy elements (*14*), to date only one study has been published in which it has been applied in *ab initio* all-electron calculations using a multicenter basis set to a molecule containing at least one heavy element (*15*). The difficulty of carrying out even the self-consistent field (SCF) step demonstrates that such calculations will be impractical for some time to come. It is also true that electron correlation generally cannot be neglected.

The computational complexity for all-electron molecular DF calculations is extremely high for several reasons. These include the large number of electrons, additional integrals due to each molecular spinor having both a large and small component, the large number of configurations necessary at the configuration interaction (CI) level due to the increased number of valence electrons from shells with different angular momenta, and the additional configuration mixing due to relativistic interactions. If the basis sets are not large enough, the calculated results can be misleading and inaccurate.

Another difficulty with all-electron relativistic calculations lies in the nature of the one-electron four-component spinors. They are complex in general and exhibit behavior near the nucleus which is difficult to describe with conventional basis functions. For example, the large component of a molecular spinor having s or $p_{1/2}$ population behaves like $1/r^{\gamma}$ near a point nucleus while the small component behaves like $Z/r^{1+\gamma}$ where $\gamma = Z^2\alpha^2/2$ (*16*). Still another difficulty with all-electron relativistic calculations is that the energy expectation values no longer have the property of being upper bounds to the total energy. This can result in variational collapse in attempting to use variational methods.

Furthermore, in contrast to the case of molecules made up solely of light atoms, heavy-element systems require the inclusion of extensive configuration mixing for reasons other than those usually attributed solely to electron correlation. In molecules containing heavy elements, the angular momentum coupling is rarely approximated accurately as pure j–j or pure L–S, but rather is intermediate between these limiting cases. Thus, configurations may be required just for the purpose of ensuring convergence to a desired electronic state. For strictly pragmatic reasons, it is often the case that considerable approximations must be made to render heavy-element molecular calculations tractable. Considering the margin for error in even the highest quality light-element work, such approximations must be chosen with care to avoid a critical loss of accuracy.

Several reviews have been written dealing with *ab initio* and semiempirical quantum chemical calculations including relativistic effects (*1–3,17–20*).

II. Reliable Effective Core Potentials

The underlying assumption behind all methods for defining effective core potentials (EP) is the frozen core approximation. That is, the intrinsic reliability of core–valence separability. However, substantial savings are not realized by this approximation alone because of the radical oscillations of the valence orbitals in the region near the nuclei. Although the number of electrons to be treated explicitly is reduced, the number of required basis functions [in the linear combination of atomic orbitals (LCAO) sense] is essentially unchanged. Most EP procedures avoid this pitfall by replacing the valence orbitals with pseudoorbitals, which are smooth and nodeless in the core region, but approximately resemble the true valence orbitals at larger radii (*20–23*). Thus one freezes not only the core orbitals but also that fraction of the valence electron density responsible for the inner oscillatory behavior.

Once a nodeless orbital has been generated the one-electron atomic Fock equation is easily "inverted" to produce a (radially) local operator, the EP, which represents the core–valence interactions (*22,23*).

In this area, a great deal of pioneering work was done by Goddard and co-workers (*22*), who, in turn, based their approach on that of Phillips and Kleinman (*21*). Detailed comparisons of nonrelativistic EP calculations with those from all-electron work has, however, demonstrated that the Phillips–Kleinman approach is inadequate for computing many molecular properties, including dissociation energies and bond lengths (*23,24*). Christiansen *et al.* have clearly shown that the difficulties arise as a result of the unreasonable partitioning of the core and valence electron space in the definition of the pseudoorbitals (*25*).

The precise form of the pseudoorbitals is essentially arbitrary, except for the constraint that nodes be eliminated. Pragmatic and reliability requirements, however, place certain conditions on the definition. In terms of the effect on molecular energies, and therefore spectroscopic properties, the accuracy of the EP approximation depends critically on the shape of the pseudoorbitals in the valence region. One problem with the Phillips–Kleinman approach is that the pseudoorbitals so generated consistently underestimate the atomic electron density in the valence region. Since the difference between the pseudoorbital and the original atomic orbital represents electron density which will be frozen in subsequent calculations, valence as well as core electron density is effectively frozen. It is critically important that the pseudoorbital precisely match the true orbital amplitude in the valence region. Although bumps in the core region of the pseudoorbital have little effect on the reliability of the EP, it should be remembered that one of the purposes for employing a pseudoorbital is to reduce the size of the subsequent molecular basis set to be used in calculations on molecules. Irregularities in the core region diminish this objective. Thus the pseudoorbital should be chosen to be as smooth as possible over its entire range.

To define the EPs, the pseudoorbitals are derived from numerical Hartree–Fock (*26*) and Dirac–Fock (*27*) wave functions. In the valence region the pseudoorbitals match precisely the atomic orbitals or spinors. Restricting the present discussion to the nonrelativistic case, a pseudoorbital is represented in the core region by a power series (usually five to seven terms) in r with a leading power of approximately $l + 2$ (considerable flexibility is possible), where l is the usual orbital angular momentum quantum number. The power series is chosen to match the amplitude and the first three or more derivatives of the atomic orbital at an intermediate matching radius. The remaining flexibility is used to normalize the pseudoorbital. The matching radius is chosen to be as close to the nucleus as possible while maintaining a smooth and nodeless inner function. Smoothness is enforced by allowing at most two inflections in the pseudoorbital over its entire range, and at most three inflections in the derivative. Pseudoorbitals defined in this manner are termed "shape consistent" (*25*) or "norm conserving" (*28*) and are given by

$$\chi_v(r) = f_v(r) + \phi_v(r) \tag{3}$$

where f_v is zero outside the core region with χ_v transforming smoothly into the exact valence orbital ϕ_v at some $r = r_m$.

A separate EP must be generated for each l value. When generalized to take into account the various orbital symmetries the total (nonrelativistic) EP has the form

$$U^{\mathrm{EP}} = \sum_{l=0}^{\infty} \sum_{m=-1}^{l} U_l(r)|lm\rangle\langle lm| \tag{4}$$

where the projection operators $|lm\rangle\langle lm|$ ensure that the individual terms operate on molecular basis functions of the proper angular symmetry. This general form was given by Goddard and co-workers for use with Phillips–Kleinman pseudopotentials (*22*). It has been found that, in practice, the infinite sum can be truncated at an l value which is one greater than that represented by the core with no appreciable loss in accuracy. The truncated potential can be written

$$U^{\mathrm{EP}} = U_L^{\mathrm{EP}} + \sum_{l=0}^{L} \sum_{m=-l}^{l} [U_l^{\mathrm{EP}}(r) - U_L^{\mathrm{EP}}(r)]|lm\rangle\langle lm| \tag{5}$$

where L is the maximum l value and $U_L(r)$ is the so-called "residual" EP.

Although the goal here is the extension of molecular electronic structure techniques into the realm of heavy elements, it is important that as much as possible of the reliability of light-element work be retained. The accuracy of the effective potential approximation can most readily be determined by careful comparisons of molecular EP results with those obtained from all-electron calculations. At the present time this can be done easily only for the nonrelativistic case. Although comparisons can be made with experimentally determined properties, it should be kept in mind that in general highly accurate valence wave functions are required.

As demonstrated by Kahn and co-workers, Phillips–Kleinman types of EPs often yield poor results when computing molecular properties (*23*). This was found to be particularly true for the halide dimers. Figures 2 and 3 show dissociation curves for F_2 and Cl_2 computed using all-electron and EP two-configuration wave functions. The shape-consistent and all-electron results are in excellent agreement, whereas the curves obtained using Phillips–Kleinman (PK) types of EPs (*23*) ("Kahn E.P."), and even those based on a "corrected" PK EP (*24*) ("Hay E.P."), show dramatic deviations, particularly at short bond lengths. It should be noted that the discrepancies between the

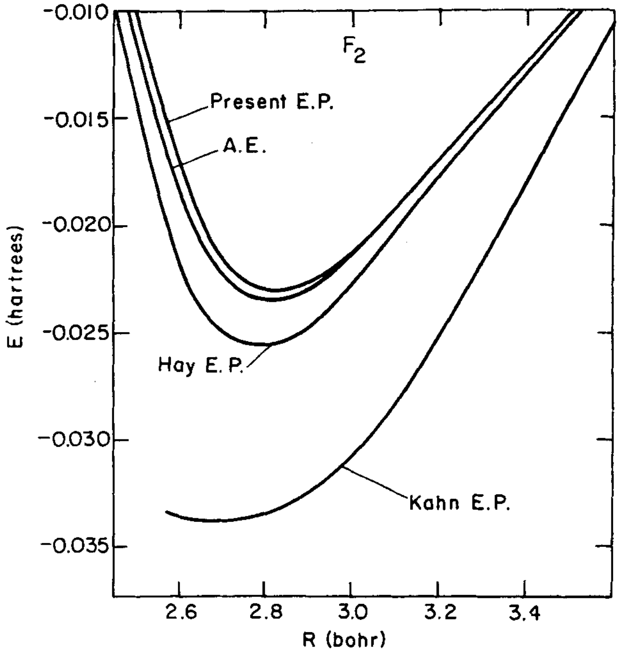

Fig. 2. Potential energy curves of F_2 from all-electron (A.E.) and effective potential (E.P.) calculations using two-configuration MCSCF wave functions.

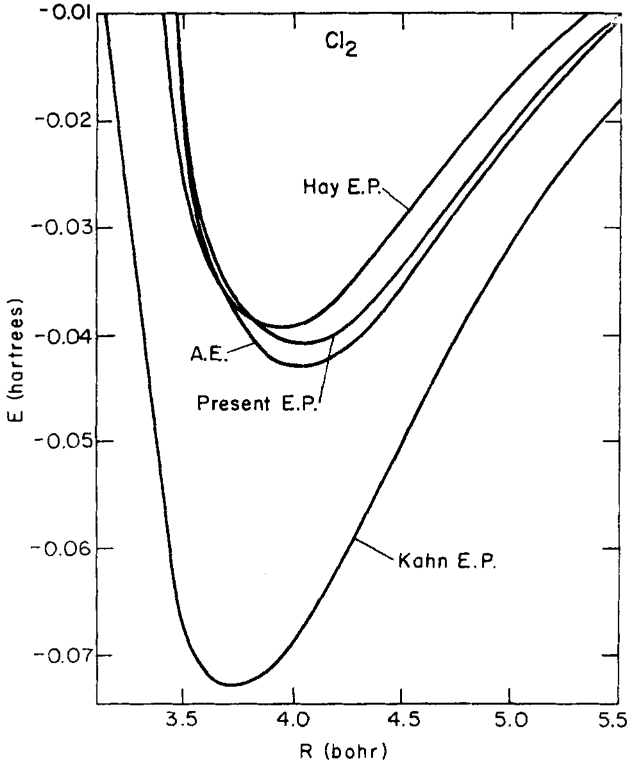

Fig. 3. Potential energy curves of Cl_2 from all-electron (A.E.) and effective potential (E.P.) calculations using two-configuration MCSCF wave functions.

TABLE II

BOND LENGTHS (a.u.) AND DISSOCIATION ENERGIES (kcal/mol) OF F_2 AND Cl_2 FROM TWO-CONFIGURATION MCSCF WAVE FUNCTIONS[a]

	F_2		Cl_2	
Wave function	R_e	D_e	R_e	D_e
All electron	2.84	14.8	4.04	27.0
Shape-consistent EP	2.86	14.6	4.04	25.7
Phillips–Kleinman EP	2.70	21.2	3.70	45.7

[a] From Ref. 25.

shape-consistent and all-electron results are no longer than might be expected from minor variations in basis sets. Spectroscopic properties of F_2 and Cl_2 are listed in Table II.

III. Relativistic Effective Core Potentials—Formal Aspects

The method discussed here for the inclusion of relativistic effects in molecular electronic structure calculations is grounded in the Dirac–Fock approximation for atomic wave functions (*29*). The premise is that the major relativistic effects of the Dirac Hamiltonian are manifested in the core region, involving the core electrons, and that these effects propagate to the valence electrons. In addition, there are direct relativistic effects on valence electrons penetrating into the core region. Insofar as this is true, the valence electrons can be treated using a nonrelativistic Hamiltonian to which is added an operator, the relativistic effective core potential (REP). The REP formally, incorporates relativistic effects due to core electrons and to interactions of valence electrons with core electrons in an internally consistent way.

The formalism parallels to some extent the nonrelativistic arguments of Kahn *et al.* (*23*). We begin with the relativistic Hamiltonian

$$H^{\text{rel}} = \sum_i h_{\text{D}}(i) + \sum_{i>j} r_{ij}^{-1} \tag{6}$$

where i and j index electrons. Many-electron relativistic effects, which may be approximated by including the Breit interaction terms (*29*), are omitted. (In all methods developed to date, such effects are included in the form of a first-order energy correction computed using a zeroth-order wave function resulting from H^{rel} as defined above.) The precise form of the Dirac one-electron Hamiltonian is

$$h_{\text{D}} = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 - Z/r \tag{7}$$

where, in atomic units, $c = 1/\alpha$, with α being the hyperfine structure constant, $\mathbf{p}$ the momentum operator $i\nabla$, Z the atomic number, and r the electron–nucleus interparticle distance. The two matrix operators are defined by

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma}^P \\ \boldsymbol{\sigma}^P & 0 \end{bmatrix} \quad \text{and} \quad \boldsymbol{\beta} = \begin{bmatrix} \mathbf{I} & 0 \\ 0 & -\mathbf{I} \end{bmatrix} \tag{8}$$

where $\boldsymbol{\sigma}^P$ is the Pauli spin matrix and $\mathbf{I}$ is a unit matrix of rank two. The zero of energy for Eq. (7) is that of the free electron.

The eigenfunctions of h_D are four-component Dirac spinors

$$\psi_{nkm}(r, \theta, \phi) = r^{-1}\begin{bmatrix} P_{nk}(r)\chi_{km}(\theta, \phi) \\ iQ_{nk}(r)\chi_{-km}(\theta, \phi) \end{bmatrix} \tag{9}$$

where the angular factors are defined by

$$\chi_{km}(\theta, \phi) = \sum_{\sigma = \pm 1/2} C(\lambda \tfrac{1}{2} j;\, m - \sigma, \sigma) Y_{\lambda}^{m-\sigma}(\theta, \phi)\varphi_{1/2}^{\sigma} \tag{10}$$

In Eq. (10) $Y_{\lambda}^{m-\sigma}$ are spherical harmonics, $\varphi_{1/2}^{\sigma}$ are Pauli spinors, and $C(\lambda\frac{1}{2}j;\, m - \sigma, \sigma)$ are Clebsch–Gordan coefficients. The index λ is defined as $\lambda = |\gamma + \frac{1}{2}| - \frac{1}{2}$, where γ is either $+k$ or $-k$. Here k is the relativistic quantum number, equal to $\pm(j + \frac{1}{2})$ as $j = l \mp \frac{1}{2}$, j is the total angular momentum quantum number, and l is the orbital angular momentum quantum number.

In an analogous fashion to the atomic Hartree–Fock equations, the angular variables can be separated and integrated out using the Wigner–Eckart theorem in the Dirac equation to yield a set of coupled differential equations depending on r (*29*).

$$(dP_{nk}/dr) + kP_{nk}/r - 2/\alpha + \alpha[V(r) - \varepsilon_{nk}]Q_{nk} = 0 \tag{11}$$

$$(dQ_{nk}/dr) - kQ_{nk}/r + \alpha[V(r) - \varepsilon_{nk}]P_{nk} = 0 \tag{12}$$

To construct the Dirac–Fock equations, it is assumed that the wave function for an atom having N electrons may be expressed as an antisymmetrized product of four-component Dirac spinors of the form shown in Eq. (9). For cases where a single antisymmetrized product is an eigenfunction of the total angular momentum operator J^2, the N-electron atomic wave function may be written

$$\Psi^{\mathrm{R}} = \hat{A}[(\psi_1^{\mathrm{c}}\psi_2^{\mathrm{c}} \cdots \psi_m^{\mathrm{c}})(\psi_1^{\mathrm{v}}\psi_2^{\mathrm{v}} \cdots \psi_n^{\mathrm{v}})] \tag{13}$$

The first product in brackets refers to m core electrons and the second to n valence electrons. $\hat{A}$ is the antisymmetrization and normalization operator. The total energy is then given by

$$E_{\mathrm{T}}^{\mathrm{R}} = \langle \psi^{\mathrm{R}} | H^{\mathrm{rel}} | \psi^{\mathrm{R}} \rangle = E_{\mathrm{c}}^{\mathrm{R}} + E_{\mathrm{v}}^{\mathrm{R}} + E_{\mathrm{cv}}^{\mathrm{R}} \tag{14}$$

which is separable into contributions due to core, valence, and core–valence interaction energies. As in the nonrelativistic case (*23,25*), the last two terms may be combined using a modified Hamiltonian and a wave function representing the valence electrons

$$E_v + E_{cv} = \langle \psi_v^R | H_v^{rel} | \psi_v^R \rangle \tag{15}$$

where

$$H_v^{rel} = \sum_v \left\{ h_D(v) + \sum_c [J_c(v) - K_c(v)] \right\} + \sum_{v>v'} r_{vv'}^{-1} \tag{16}$$

in which $J_c(v)$ and $K_c(v)$ are Coulomb and exchange operators. Here H_v^{rel} includes the original Dirac one-electron Hamiltonian for the valence electrons plus additional terms that represent the effect of the core on the valence orbitals.

If it is assumed that the orbitals representing the core and valence electrons comprise an orthonormal set, the Dirac–Fock equation for a single valence electron is

$$\sum_c \varepsilon_{cv} \psi_c + \left[h_D + \sum_c (J_c - K_c) \right] \psi_v = \varepsilon_v \psi_v \tag{17}$$

where ε_v is the valence orbital energy and ε_{cv} is an off-diagonal Lagrange multiplier. The atomic orbitals ψ_c and ψ_v are four-component Dirac spinors as defined in Eq. (9).

If we then partition the valence spinor in a manner analogous to Eq. (3) (*25*),

$$\psi_v = \chi_v^R - f_v \tag{18}$$

the valence electron wave equation can be written as

$$\sum_c \varepsilon_{cv} \psi_c + \varepsilon_v f_v - \left[h_D + \sum_c (J_c - K_c) \right] f_v + \left[h_D + \sum_c (J_c - K_c) \right] \chi_v^R = \varepsilon_v \chi_v^R \tag{19}$$

or

$$(h_D + U^{core}) \chi_v^R = \varepsilon_v \chi_v^R \tag{20}$$

where U^{core} is the REP in the form of a 4×4 matrix that operates on the nodeless four-component spinors χ_v^R. That is, U^{core} represents a combination of the core–valence interaction along with core–valence orthogonality operator, in addition to corrections for the valence spinor partitioning of Eq. (18).

The REP U^{core} may be expanded in the angular factors of Eq. (9) and used to construct the analogs of Eqs. (11) and (12) in terms of the radial pseudo wave function (*30*)

$$d/dr\begin{bmatrix} P_{\text{v}}^{\text{ps}}(r) \\ Q_{\text{v}}^{\text{ps}}(r) \end{bmatrix} = \begin{bmatrix} -k_{\text{v}}/r & 2/\alpha + \alpha[\varepsilon_{\text{v}} - U_{\text{v}}^{Q}(r)] \\ -\alpha[\varepsilon_{\text{v}} - U_{\text{v}}^{P}(r)] & k_{\text{v}}/r \end{bmatrix}\begin{bmatrix} P_{\text{v}}^{\text{ps}}(r) \\ Q_{\text{v}}^{\text{ps}}(r) \end{bmatrix} \tag{21}$$

The REPs $U_{\text{v}}^{P}(r)$ and $U_{\text{v}}^{Q}(r)$ may, in principle, be extracted using any pseudo wave function having components P_{v}^{ps} and Q_{v}^{ps}. However, the resulting REPs would exhibit discontinuities at points corresponding to nodes in P_{v}^{ps}. Thus nodeless pseudospinors are necessary. In Eq. (18), f_{v} is chosen as in Eq. (3) so as to cancel the corelike oscillation in P_{v}^{ps}, the large component of $\chi_{\text{v}}^{\text{R}}$. In the relativistic case, however, f_{v} can also be used to cancel Q_{v}^{ps} completely. The justification is that Q_{v}^{ps} has a small amplitude in the valence region, and experience indicates that the resulting errors are negligible (*30*). The one-electron radial equation then becomes

$$[h_{\text{v}}(r) + U_{\text{v}}^{\text{REP}}(r)]P_{\text{v}}^{\text{ps}} = \varepsilon_{\text{v}}P_{\text{v}}^{\text{ps}}(r) \tag{22}$$

where h_{v} is the nonrelativistic Schrödinger Hamiltonian for the valence electron; (a procedure for retaining the small component in the REP has been proposed (*31*).]

Atoms having more than one valence electron are treated in a parallel fashion using two-component pseudospinors [Eq. (18)] and the many-electron analog of Eqs. (20)–(22) to yield

$$U_{lj}^{\text{REP}} = \tfrac{1}{2}\nabla^2 + Z/r - W_{lj} + \varepsilon_{lj})\chi_{lj}/\chi_{lj} \tag{23}$$

In Eq. (23), W_{lj} represents coulomb and exchange potential, involving pseudospinor χ_{lj} and all remaining pseudospinors.

It is clear from Eq. (22) that a different REP arises for each pseudospinor. The complete REP is conveniently expressed in terms of products of radial functions and angular momentum projection operators, as has been done for the nonrelativistic Hartree–Fock case (*23*). Atomic orbitals having different total angular momentum j but the same orbital angular momentum l are not degenerate in j–j coupling. Therefore the REP is expressed as

$$U^{\text{REP}} = \sum_{l=0}^{\infty}\ \sum_{j=|l-1/2|}^{|l+1/2|}\ \sum_{m=-j}^{j} U_{lj}^{\text{REP}}(r)|ljm\rangle\langle ljm| \tag{24}$$

The projection operator $|ljm\rangle\langle ljm|$ is comprised of the two-component angular functions of Eq. (10).

The radially dependent REPs of Eq. (23) are obtained from the following equation, which is an analog of one that arises in the Dirac–Fock formalism (29),

$$
\begin{aligned}
&[-\tfrac{1}{2}(d^2/dr^2) + l_{\mathrm{A}}(l_{\mathrm{A}}+1)/2r_1^2 + U_{l_{\mathrm{A}}j_{\mathrm{A}}}(r_1) - Z/r_1]P_{\mathrm{A}}(r_1) \\
&\quad + \Bigg[(N_{\mathrm{A}}-1)\int |P_{\mathrm{A}}(r_2)|^2(r_>^{-1})dr_2 - \tfrac{1}{2}\{(N_{\mathrm{A}}-1)/2j_{\mathrm{A}}\} \\
&\quad \times \sum_{\nu>0}(2j_{\mathrm{A}}+1)\Gamma_{j_{\mathrm{A}}\nu j_{\mathrm{A}}}\int |P_{\mathrm{A}}(r_2)|^2(r_<^{\nu}/r_>^{\nu+1})dr_2 \\
&\quad + \sum_{\mathrm{A}'\neq\mathrm{A}} N_{\mathrm{A}'}\int |P_{\mathrm{A}'}(r_2)|^2(r_>^{-1})dr_2\Bigg]P_{\mathrm{A}}(r_1) \\
&\quad - \left[\frac{1}{2}\sum_{\mathrm{A}'\neq\mathrm{A}} N_{\mathrm{A}'}\sum_{\nu}\Gamma_{j_{\mathrm{A}}\nu j_{\mathrm{A}'}}\int P_{\mathrm{A}}(r_2)^*P_{\mathrm{A}'}(r_2)(r_<^{\nu}/r_>^{\nu+1})dr_2\right]P_{\mathrm{A}'}(r_1) \\
&= \varepsilon_{\mathrm{A}}P_{\mathrm{A}}(r_1) + \sum_{\mathrm{A}'\neq\mathrm{A}} N_{\mathrm{A}'}\,\delta(k_{\mathrm{A}'}k_{\mathrm{A}'})P_{\mathrm{A}'}(r_1)\varepsilon_{\mathrm{AA}'}
\end{aligned}
\tag{25}
$$

where l_{A}, j_{A}, k_{A}, and N_{A} denote the orbital angular momentum quantum number, the total angular momentum quantum number, the relativistic quantum number, and the number of electrons, respectively, of the shells A and A′. $P_{\mathrm{A}}(r)$ and $P_{\mathrm{A}'}(r)$ refer to pseudospinors, and ε_{A} and $\varepsilon_{\mathrm{AA}'}$ are diagonal and off-diagonal Lagrange multipliers. The independent variables $r_<$ and $r_>$ are the smaller and the larger of r_1 and r_2, respectively, and ν satisfies the triangular condition

$$|j_{\mathrm{A}} - j_{\mathrm{A}'}| \leq \nu \leq |j_{\mathrm{A}} + j_{\mathrm{A}'}| \tag{26}$$

with the additional requirement

$$
\begin{aligned}
j_{\mathrm{A}} + j_{\mathrm{A}'} + \nu &= \text{even} \qquad \text{if} \quad \mathrm{A} \neq \mathrm{A}' \\
&= \text{odd} \qquad \text{if} \quad \mathrm{A} = \mathrm{A}'
\end{aligned}
\tag{27}
$$

where A and A′ are signs of relativistic quantum numbers k_{A} and $k_{\mathrm{A}'}$, respectively. $\Gamma_{j_{\mathrm{A}}\nu j_{\mathrm{A}'}}$ is defined in terms of $3j$ symbols by

$$\Gamma_{j_{\mathrm{A}}\nu j_{\mathrm{A}'}} = 2\begin{bmatrix} j_A & \nu & j_{A'} \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{bmatrix} \tag{28}$$

In theory, an infinite number of calculations for highly excited states is required to complete the expansion of the EP given by Eq. (24), since there are only a few occupied valence orbitals in neutral atoms. This difficulty also exists in the nonrelativistic case and is resolved by using the closure property of the projection operator with the assumption that radial parts of EPs are the same for all orbitals having higher angular momentum quantum numbers than are present in the core. The same approximation is applicable in the present approach if relativistic effects are not too different for electrons in the highly excited orbitals. We expect that this is the case since those electrons spend less time near the nucleus. If this assumption is valid, the REP may be given by

$$U^{\mathrm{REP}} = U^{\mathrm{REP}}_{LJ}(r) + \sum_{l=0}^{L-1} \sum_{|l-1/2|}^{l+1/2} \sum_{m=-j}^{j} [U^{\mathrm{REP}}_{lj}(r) - U^{\mathrm{REP}}_{LJ}(r)]|ljm\rangle\langle ljm| \qquad (29)$$

Equation (29) is an analog of Eq. (5) for the case of atomic basis functions represented as two-component spinors.

A weighted average REP (AREP) that is precisely of the form of Eq. (5) is (*32*)

$$U^{\mathrm{AREP}} = U^{\mathrm{AREP}}_{L} + \sum_{l=0}^{L-1} \sum_{m=-l}^{l} [U^{\mathrm{AREP}}_{l}(r) - U^{\mathrm{AREP}}_{L}(r)]|lm\rangle\langle lm| \qquad (30)$$

where

$$U^{\mathrm{AREP}}_{l} = (2l+1)^{-1}[lU^{\mathrm{REP}}_{l,l-1/2} + (l+1)U^{\mathrm{REP}}_{l,l+1/2}(r)] \qquad (31)$$

The AREP has the advantage that it may be used in standard molecular calculations that are based on Λ–S coupling. The AREP may be interpreted as containing the relativistic effects included in the Dirac Hamiltonian, with the exception of spin-orbit coupling. This form is the same as that presented by Kahn *et al.* (*33*) which is based on the relativistic treatment of Cowan and Griffin (*34*). The Hamiltonian employed by Cowan and Griffin is based on the Pauli approximation to the Dirac Hamiltonian with the omission of the spin-orbit term.

Definitions of the REP and AREP, Eqs. (29) and (30), can be combined to reveal a useful form for the spin-orbit operator (*35*),

$$H^{\mathrm{SO}} = \sum_{l}\sum_{m}\sum_{j}[U^{\mathrm{REP}}_{lj}(r) - U^{\mathrm{AREP}}_{l}(r) - U^{\mathrm{REP}}_{LJ}(r) + U^{\mathrm{AREP}}_{L}(r)]|lmj\rangle\langle lmj| \qquad (32)$$

or

$$\begin{aligned} H^{\mathrm{SO}} = \sum_{l=1}^{L} \Delta U^{\mathrm{REP}}_{l}(r) \Bigg[&\{l/(2l+1)\} \sum_{m=-l-1/2}^{l+1/2} |l, l+\tfrac{1}{2}, m\rangle\langle l, l+\tfrac{1}{2}, m| \\ &-\{(l+1)/(2l+1)\} \sum_{m=-l+1/2}^{l-1/2} |l, l-\tfrac{1}{2}, m\rangle\langle l, l-\tfrac{1}{2}, m| \Bigg] \qquad (33) \end{aligned}$$

where

$$\Delta U^{\mathrm{REP}}_{l}(r) = U^{\mathrm{REP}}_{l,l+1/2}(r) - U^{\mathrm{REP}}_{l,l-1/2}(r) \qquad (34)$$

This form of H^{SO} has been applied with considerable success to atoms (*36,37*), to molecules containing only light elements (*38*), and to heavy-atom molecules (*39*).

An alternative equivalent form of H^{SO} has been proposed *(40)* that is more appropriate for use with a standard polyatomic integrals program that computes angular and radial integrals *(41)*. It is derived by transforming the projection operators $|ljm\rangle\langle ljm|$ to a form involving only projection operators $|lm\rangle\langle lm|$ and the spin operator **s**. The spin-orbit operator then becomes *(40)*

$$H^{SO} = \mathbf{s} \cdot \sum_{l=1}^{L} \{2/(2l+1)\} \Delta U_l^{REP}(r) \sum_{m=-l}^{l} |lm\rangle\langle lm|\mathbf{l}|lm\rangle\langle lm| \tag{35}$$

which can be expressed as

$$H^{SO} = \sum_{l} \varepsilon_l(r) \mathbf{l} \cdot \mathbf{s} \sum_{m} |lm\rangle\langle lm| \tag{36}$$

The $U_{lj}^{REP}(r)$, $U_l^{AREP}(r)$, and terms $\Delta U_l^{REP}(r)$ in H^{SO} of Eqs. (23), (31), and (34) or Eq. (6), respectively, are derived in the form of numerical functions consistent with the large components of Dirac spinors as calculated using the Dirac–Fock program of Desclaux *(27)*. These operators have been used in their numerical form in applications to diatomic systems where basis sets of Slater-type functions are employed *(39,42,43)*. It is often more convenient to represent the operators as expansions in exponential or Gaussian functions *(32)*. The general form of an expansion involving M terms is

$$U_l^{AREP}(r) = r^{-2} \sum_{i=1}^{M} C_{li} r^{n_{li}} \exp(-\alpha_{li} r^x) \tag{37}$$

where $x = 1$ for exponential and $x = 2$ for Gaussian functions and the n_{li} are integers. The numerical forms of these operators are fitted using a nonlinear least-squares technique, thereby yielding optimum values of the C_{li} and α_{li}. The residual potential U_L^{AREP} is fitted directly. The $U_l^{AREP}(l < L)$ are first modified, by subtracting off the residual potential and then fitted. The spin-orbit operators of Eq. (33) are represented as fits of the difference potentials U_l^{SO}, which are defined by $(2l+1)^{-1}\Delta U_l^{REP}$. Similar expansions may be used to represent U_{lj}^{REP} and ΔU_l^{REP}. Examples of a REP, the corresponding REP-based spin-orbit operator, and a valence basis set of Gaussian-type orbitals are provided in Tables III and IV. The expansions and basis set all refer to the lead atom, which is represented as having 68 core electrons, $[\mathrm{Xe}]4f^{14}$, and 14 valence electrons, $5d^{10}6s^2 6p^2$.

In applications to atoms and molecules the REPs in the form of Eq. (29) or the AREPs in the form of Eq. (4) are used in the valence Hamiltonian

$$H = \sum_{\mu=1}^{n} \left[-\frac{1}{2}\nabla_\mu^2 + \sum_i (-Z_i/r_{i\mu} + U_i^{EP}) \right] + \sum_{\mu>\nu}^{n_v} r_{\mu\nu}^{-1} \tag{38}$$

where n_v is the number of valence electrons, and U_i^{EP} refers to a relativistic, an averaged relativistic, or a nonrelativistic effective potential that represents the

TABLE III

GAUSSIAN EXPANSIONS, AREP, AND SPIN-ORBIT OPERATORS FOR Pb[a]

$L-l$	n	α	U^{AREP}	U^{SO}
$s-g$	2	1.0513	45.001518	
	2	1.2136	−142.817217	
	2	1.5929	280.339943	
	2	2.2755	−305.931084	
	2	3.4159	275.888336	
	2	5.0455	−126.195870	
	1	8.1018	58.640396	
	0	29.9294	6.276546	
$p-g$	2	0.3446	0.195629	−0.026525
	2	1.0122	−60.526899	1.671710
	2	1.2147	201.290903	11.379299
	2	1.6575	−254.737303	−39.841366
	2	2.4011	231.821089	50.649842
	2	3.4683	−120.335833	−29.381577
	1	4.7190	43.356446	2.256756
	0	14.2448	5.935587	−0.209541
$d-g$	2	0.8860	−1.356637	−0.137145
	2	2.4297	49.747395	0.712443
	2	3.0903	−160.286327	2.834768
	2	4.4506	325.697735	−8.105807
	2	6.8596	−339.073044	6.600976
	2	10.5118	199.774546	8.512031
	1	8.9278	40.334296	−1.172489
	0	30.4126	7.639982	0.114494
$f-g$	2	0.7430	37.605412	−33.879691
	2	0.9349	−24.430166	7725.742188
	2	0.9371	−38.516580	−7731.144775
	2	1.3505	60.979285	49.801095
	2	2.4532	−10.033807	−18.201314
	2	3.9905	52.056166	9.141817
	1	8.4453	39.917824	−1.293316
	0	19.7761	5.474869	0.138303
g	2	1.3001	−1.414344	−0.087112
	2	3.1872	−13.280216	0.146252
	2	9.5488	−54.137527	−0.104059
	2	23.6841	−138.126621	0.789745
	2	81.0422	−376.411697	1.201032
	1	260.1822	−54.858120	3.521041

[a] See Eq. (37).

TABLE IV
TRIPLE-ZETA BASIS SET OF GAUSSIAN-TYPE ORBITALS FOR Pb

l	ζ	Coefficient
s	0.6041	−0.707754
	0.2863	0.980269
	0.0880	0.586696
p	0.7575	−0.091765
	0.1843	0.578739
	0.0616	0.544185
d	1.5860	0.575724
	0.6013	0.457275
	0.2195	0.108943

core electrons of atom i. If the U_i^{EP} are nonrelativistic or averaged relativistic EPs, the wave function for the n_v-electron system may be represented in terms of spin orbitals and standard electronic codes may be employed for their calculation. The only alteration in the procedure for using such codes is the necessity to incorporate an additional set of one-electron integrals involving the basis functions and the EP (*23,30*). This is most straightforwardly accomplished by the addition of these integrals to previously computed nuclear attraction integrals.

If the REPs of Eq. (29) are used, the presence of the projection operators $|ljm\rangle\langle ljm|$ dictates that the valence wave functions must be comprised or expressable in terms of two-component atomic spinors (TCASs) (*43*). Whereas the incorporation of a nonrelativistic EP or an AREP requires only the computation of a new set of one-electron integrals over atomic orbitals, the use of U^{REP} and TCAS requires the computation of all one- and two-electron integrals over two-component atomic orbitals. Malli and Oreg have derived the relationship between diatomic molecular integrals in a basis set of four-component Dirac spinors [Eq. (9)] and spin orbitals that are products of complex Slater-type functions (STFs) and α and β spin functions (*44*). These relationships involve integrals with respect to the STFs and factors that include the proper Clebsch–Gordan coefficients that render the resulting wave function an eigenfunction of the total angular momentum operator. This ω–ω coupling procedure has been specialized to the case of basis sets of TCAS for closed- and open-shell SCF (*43*) and multiconfiguration SCF (MCSCF) (*45*) calculations on linear molecules.

The symmetry properties of diatomic molecules in the double group representation may be found in the work by Malli and Oreg (*44*). However, the molecular spinors which are eigenfunctions of the REP of Eq. (29) have only two components while the Dirac spinors have four components. In linear molecules, the angular symmetry of a state of a molecule is defined by the total electronic angular momentum Ω, as in Hund's case c, and that of ith molecular orbitals by $m_i = \pm\omega_i$ (*46*). The two spinors with $m_j = +\omega_i$ and $m_i = -\omega_i$ are degenerate and constitute a shell. Because spin is incorporated, each molecular spinor can accommodate only one electron. With these characteristics, one can derive the SCF theory for the two-component molecular spinors (TCMSs) for diatomic molecules by following the procedures that have been formulated for conventional nonrelativistic molecular calculations (*43*).

For a molecular state that may be represented by a single Slater determinant, the total wave function of the system is approximated by

$$\Phi = \hat{A}[\phi^1\phi^2\cdots\phi^n] \tag{39}$$

where $\hat{A}$ is the antisymmetrization and normalization operator and the ϕ are one-electron molecular spinors. The total energy of the molecular state is

$$E = \langle\Phi|H|\Phi\rangle \tag{40}$$

provided Φ is normalized. As in the nonrelativistic case, each one-electron molecular spinor, $\phi_{i\lambda'}$ is expanded in a basis set of two-component atomic spinors, $\chi_{\lambda p'}$ (TCAS)

$$\varphi^{\pm}_{i\lambda} = \sum c^{\pm}_{i\lambda,p}\chi_{\lambda p} \tag{41}$$

where λ is the symmetry index ω, i is the index for orbitals of the same symmetry, and + and − refer to the sign of m. The TCASs are defined by

$$\chi^{\pm}_{\lambda p} = \chi_{\lambda p}(n_p, l_p, j_p, \pm\lambda) = R_{\lambda p}(r) \sum_{\sigma=\pm 1/2} C(l\tfrac{1}{2}j; \pm\lambda-\sigma, \sigma)Y^{\pm\lambda-\sigma}_{lp}\varphi^{\sigma}_{1/2} \tag{42}$$

where $R_{\lambda_p}(r)$ is a radial function. When Slater-type functions are used for the basis, $\chi_{\lambda p}$ becomes

$$\chi_{\lambda p}(n_p, l_p, j_p, \pm\lambda) = N_p r^{n_p-1}e^{-\zeta_p r}\begin{bmatrix} C(l_p\tfrac{1}{2}j_p; \pm\lambda-\tfrac{1}{2}, \tfrac{1}{2}) & Y^{\pm\lambda-1/2}_{lp} \\ C(l_p\tfrac{1}{2}j_p; \pm\lambda+\tfrac{1}{2}, -\tfrac{1}{2}) & Y^{\pm\lambda+1/2}_{lp} \end{bmatrix} \tag{43}$$

where N_p is the normalization factor and the angular parts are rewritten to demonstrate the two-component properties of the basis spinors.

Following the nonrelativistic theory for open shells (*47*), we express the total energy as

$$E = D^{\dagger}_{\mathrm{T}}HD_{\mathrm{T}} + \tfrac{1}{2}D^{\dagger}_{\mathrm{T}}PD_{\mathrm{T}} - \tfrac{1}{2}D^{\dagger}_{\mathrm{O}}QD_{\mathrm{O}} \tag{44}$$

where H is composed of matrix elements of the valence Hamiltonian, including the REPs with respect to TCASs, D_{T} and D_{O} are the total and the open-shell density matrices, respectively, and P and Q are the closed- and the open-shell supermatrices. The summations implied in Eq. (44) and the definition of density matrices are given by Roothaan and Bagus (*47*). The computational methods for the one-electron matrix elements are described in Ref. 30.

Matrix elements of the supermatrices P and Q are defined by

$$P_{\lambda pq,\mu rs} = J_{\lambda pq,\mu rs} - \tfrac{1}{2}[K^{+}_{\lambda pq,\mu rs} + K^{-}_{\lambda pq,\mu rs}] \tag{45}$$

and

$$Q_{\lambda pq,\mu rs} = A_{\lambda\mu}J_{\lambda pq,\mu rs} + B_{\lambda\mu}K^{+}_{\lambda pq,\mu rs} + C_{\lambda\mu}K^{-}_{\lambda pq,\mu rs} \tag{46}$$

where $A_{\lambda\mu}$, $B_{\lambda\mu}$ and $C_{\lambda\mu}$ are open-shell vector coupling coefficients and $J_{\lambda pq,\mu rs}$ and $K_{\lambda pq,\mu rs}$ are coulomb and exchange integrals. In Eqs. (45) and (46)

$$J_{\lambda pq,\mu rs} = \int \chi^{+}_{\lambda p}(1)^{*}\chi^{+}_{\mu r}(2)^{*}r^{-1}_{12}\chi^{+}_{\lambda q}(1)\chi^{+}_{\mu s}(2)\,d\tau \tag{47}$$

and

$$K^{\pm}_{\lambda pq,\mu rs} = \int \chi^{+}_{\lambda p}(1)^{*}\chi^{\pm}_{\mu r}(2)^{*}r^{-1}_{12}\chi^{\pm}_{\mu s}(1)\chi^{+}_{\lambda p}(2)\,d\tau \tag{48}$$

where the order of signs is preserved. $J_{\lambda pq,\mu rs}$ and $K_{\lambda pq,\mu rs}$ can be calculated from the two-electron integrals over STFs by taking proper linear combinations (*30,47*).

Energy expressions given by Eqs. (44)–(48) are possible because of the assumed shell structure. This equivalence constraint may be expressed as

$$c^{+}_{i\lambda p} = c^{-}_{i\lambda p} \qquad \text{for} \quad \text{all } p \tag{49}$$

If the shell structure is not conserved, the number of matrix elements to be included in the energy expression will be increased considerably and yield nonequivalent + and − orbitals for open-shell configurations. When the variational procedure is applied to the energy, one obtains equations that are essentially the same as the nonrelativistic equations [Eqs. (13)–(16) of Ref. 47]. Since all the deviations from the conventional SCF equations are included in Eqs. (44)–(49), the SCF equations for the TCMSs are omitted.

The open-shell configurations which can be treated with the present formalism are limited to the cases where Q defined by Eq. (47) is adequate for the energy expression; specifically, each open shell must belong to a different symmetry. Since the only type of relativistic open-shell is one with a single electron, vector coupling coefficients may be obtained for any open-shell case as long as each open shell belongs to a different symmetry. Coefficients appropriate for ω–ω coupling calculations are listed in Table V (*43*). Once the

TABLE V

OPEN-SHELL VECTOR COUPLING COEFFICIENTS FOR THE ω–ω STATES REPRESENTED BY A SLATER DETERMINANT OF TWO-COMPONENT SPINORS

	$A_{\lambda\mu}$	$B_{\lambda\mu}$	$C_{\lambda\mu}$
$\lambda = \mu$	1	$-1/2$	$-1/2$
$\lambda \neq \mu$	—	—	—
$\Omega_i = \lambda + \mu$[a]	0	$1/2$	$-1/2$
$\Omega_i = \lvert\lambda - \mu\rvert$[a]	0	$-1/2$	$1/2$

[a] If $\Omega_i = \lambda + \mu$ for the interaction of two open shells, the signs of the m values are the same for both orbitals. If $\Omega_i = |\lambda - \mu|$, the signs of the m values are opposite.

proper transformation is carried out for one- and two-electron matrix elements, an existing SCF program can be modified for use with TCMSs.

This formalism may be extended to simple multiconfiguration SCF calculations using standard nonrelativistic computer codes (*48*). For instance, in the simplest case involving the two-electron promotion from one closed shell to another, the coupling is of the form

$$H_{ij} = K^{+}_{\lambda ii,\mu jj} + K^{-}_{\lambda ii,\mu jj}, \tag{50}$$

where i and j are the indices of the two shells by which the configurations differ. Using the transformed integral set described above, only minor modifications in the nonrelativistic MCSCF procedure are required (*45*).

Unfortunately, due to the fact that the angular momentum coupling is just as unlikely to be pure j–j as pure L–S, single-configuration SCF or even small MCSCF calculations are not appropriate in many cases for molecules containing atoms from the lower portion of the periodic table. For the heavier elements, the coupling is more often intermediate between the two extremes. To deal effectively with these intermediate coupling cases at the MCSCF level requires calculations including large numbers of configurations. To date such calculations have not been published.

Although the intermediate coupling problem has not received much attention at the SCF level, several methods have been developed in which the spin-orbit coupling is introduced into a normal Λ–S coupling calculation in a final configuration interaction step. In these procedures normal Λ–S coupling and SCF and CI calculations employing the AREP of Eqs. (30) and (31) (or their equivalent) are carried out for all of the Λ–S states thought to be important. A CI matrix is then formed using the Λ–S wave functions as the basis. The spin-orbit matrix elements are added in and the matrix diagonalized (*49*). To date the spin-orbit matrix elements in such calculations have been determined semiempirically. However, Eq. (33) or (35) could be used to determine the matrix elements rigorously.

Procedures of this type are probably adequate for molecules containing atoms no heavier than the second transition row, for which the spin-orbit effects are usually only a small correction (i.e., the coupling is very nearly Hund's case a). However, for many of the heavier elements, the spin-orbit corrections are large enough that it may be quite difficult to determine the important $\Lambda-S$ states without extensive trial calculations. In addition, the number of $\Lambda-S$ states required for a reasonably accurate description of the coupling may be excessive, making the above procedure impractical. Finally, for the heaviest elements the spin-orbit coupling effects are of the same magnitude as the electron correlation corrections and it may be mathematically inappropriate to treat spin-orbit coupling as a final perturbation. That is, for the heaviest elements, spin-orbit terms should probably be present in the initial CI step of the calculation.

The procedure employed currently in molecular calculations is to carry out normal $\Lambda-S$ coupling SCF calculations using the AREPs of Eqs. (30) and (31), to derive the molecular orbital basis set as a starting point for CI calculations. The usual atomic orbital (AO) to molecular orbital (MO) integral transformation is carried out and the CI matrix formed. However, instead of the relatively simple $\Lambda-S$ coupling configuration list, the configuration expansion is augmented to cover the entire intermediate coupling range. In the simplest cases, this is achieved by selecting a set of reference configurations which spans the coupling range for the outermost valence electrons (typically 10 to 20 terms have been used) (*39*). Additional configurations are generated by promoting electrons from the reference configurations using the $\Lambda-S$ coupling electron correlation conventions. In more complicated cases, it may be necessary to carry out numerous trial calculations or, preferably, some sort of limited full-valence CI calculation in the intermediate coupling regime, to determine the important reference configurations (*50*).

Since the final configuration lists may be an order of magnitude or more longer than those required for equivalent light-element work, configuration selection techniques have been extensively employed (*50*). The CI matrix is generated in the usual manner except that now the full REP (AREP plus spin-orbit operator) is included in the molecular Hamiltonian. A complication of this approach is that some matrix elements that arise due to the spin-orbit operator are complex when computed in terms of the basis sets of atomic spin-orbitals generally employed in $\Lambda-S$ coupling calculations. That is, the CI matrix is Hermitian, but complex, and standard diagonalization programs cannot be used. However, in the REP formalism, there are few imaginary or complex elements to deal with. Furthermore, iterative diagonalization procedures, such as that developed by Davidson (*51*), are easily modified to take such problems into account with relatively little loss in speed. Although this procedure is somewhat crude when compared to CI procedures used in light-element calculations, it is the only approach for dealing extensively with intermediate coupling which has as yet been implemented.

One not so obvious problem with the shape-consistent REP formalism (or any nodeless pseudoorbital approach) is that some molecular properties are determined primarily by the electron density in the core region (some molecular moments, Breit corrections, etc.) and cannot be computed directly from the valence-only wave function. For Phillips–Kleinman (*21*) types of wave functions, Daasch *et al.* (*52*) have shown that the core electron density can be approximated quite accurately by adding in the atomic core orbitals and then Schmidt orthogonalizing the valence orbitals to the core. This new set of orbitals (core plus orthogonalized valence) is a reasonable approximation to the all-electron set and can be used to compute the desired properties. This will not work for the shape-consistent case because f_v from Eq. (18) cannot be accurately described in terms of the core orbitals alone. On the other hand, it is clear from that equation that the corelike portion of the valence orbitals could be reintroduced by adding in f_v (*53*),

$$\psi_v^{R'} = \chi_v^R - \sum \frac{\langle \chi_v^R | \psi_{c_i} \rangle}{\langle f_{v_i} | \psi_{c_i} \rangle} f_{v_i} \tag{51}$$

where the sum is over all angular symmetry types in the core. ψ_{c_i} is the outermost core spinor of i symmetry. In the strictest sense, the ψ_{c_i} and f_{v_i} are four-component spinors. The modified valence orbitals (or spinors) could then be Schmidt orthogonalized to the core functions (as in Daasch *et al.*) and the combined set used to compute molecular properties. Although this approach has as yet not been implemented, the excellent results (*52*) obtained for the Phillips–Kleinman case is a cause for optimism.

Other complications are associated with the partitioning of the core and valence space, which is a fundamental assumption of effective potential approximations. For instance, for the transition elements, in addition to the outermost *s* and *d* subshells, the next inner *s* and *p* subshells must also be included in the valence space in order to accurately compute certain properties (*54*). A related problem occurs in the alkali and alkaline earth elements, involving the outer *s* and next inner *s* and *p* subshells. In this case, however, the difficulties are related to core–valence correlation. Muller *et al.* (*55*) have developed semiempirical core polarization treatments for dealing with intershell correlation. Similar techniques have been used in pseudopotential calculations (*56*). These approaches assume that intershell correlation can be represented by a simple polarization of one shell (core) relative to the electrons in another (valence) and, therefore, the correlation energy adjustment will be given by a simple polarizability expression,

$$V_{\mathrm{cpp}} = -\tfrac{1}{2}\alpha_c \mathbf{f}_c \cdot \mathbf{f}_c \tag{52}$$

where α_c is the polarizability of the core, c, and $\mathbf{f}_c$ is the empirically adjusted field at the core due to external electrons (or additional nuclei) at $\mathbf{r}_c$. Preliminary work has shown that this basic approach can be implemented in a nonempirical fashion using REPs (*57*). The polarization potential, $V_{\mathrm{cpp}}(r_c)$, is first computed as the energy shift of the core due to the presence of a negative charge (the valence electron) at various radial positions. An approximate adiabatic correction is then applied. This potential can then be used with the above expression and core polarizability to define the effective field due to an external point charge. As apposed to the all-electron work by Muller *et al.*, the REP approach allows the alkali elements to be treated as one-electron atoms. This would make molecular calculations (Rb_2, Cs_2, etc.), or even cluster calculations, particularly simple. Core polarization potentials might also prove appropriate for treating core–valence correlation (primarily between the outer *s* and *p* and the next inner *d* subshells) for main-group elements to the right of transition rows. The work of Stoll *et al.*, though semiempirical, appears to support this conclusion (*56*). If this turns out to be the case, then, with the exception of intermediate coupling difficulties, calculations involving heavy main-group elements should be no more difficult than those for the first row.

IV. Spin-Orbit Coupling and Relativistic Effective Potentials—Applications

Figure 4 shows dissociation curves for the Xe dimer and dimer ion obtained from all-valence electron calculations using shape-consistent EPs and AREPs (*58*). The corresponding nonrelativistic all-electron calculations of Wadt are included for comparison (*59*). The agreement between the EP and all-electron results is exceptionally good. This is true even for the ionic state, which differs significantly from the atomic states from which the EPs were generated. This demonstrates the transferability of the shape-consistent EPs relative to variations in electronic configurations. Except for the absence of the spin-orbit contributions, the AREP calculations are fully relativistic within the Dirac formalism. Thus the small shift of the AREP curves toward shorter internuclear distances is a result of relativistic effects. If sufficiently small, the spin-orbit splitting (estimated by either semiempirical or *ab initio* means) can be reintroduced into the AREP molecular calculations using perturbation procedures, as discussed above.

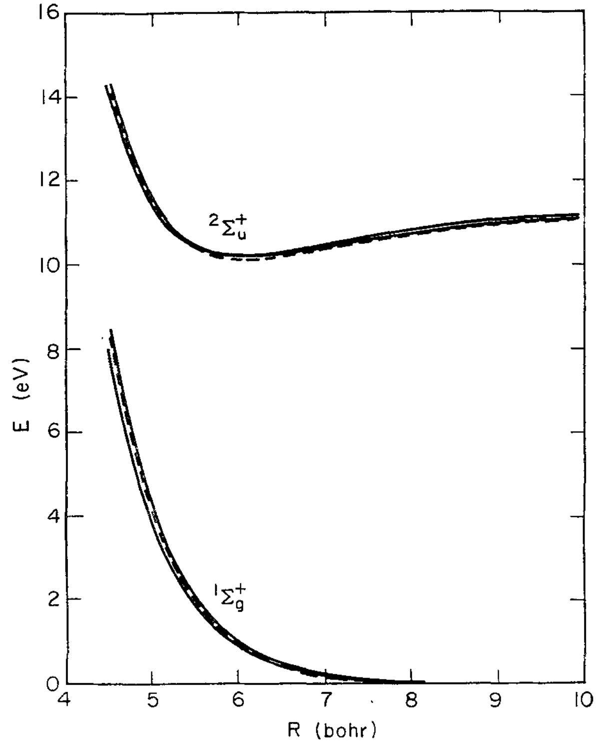

Fig. 4. All-electron, effective potential, and average relativistic effective core potential configuration-interaction potential-energy curves of Xe_2 and Xe_2^+. Dashed curves are from all-electron calculations and AREP curves are less repulsive than EP.

Some of the earliest all-electron molecular calculations that included a rigorous treatment of relativistic effects were done by Desclaux and Pyykkö using the one-center numerical Dirac–Fock approach (*60–62*). They computed both relativistic and nonrelativistic (by adjusting the speed of light) molecular properties. The differences are useful indicators of the magnitudes of the relativistic effects. For Group 13, they computed hydride bond-length contractions of approximately 0.002, 0.02, 0.07, and 0.2 a.u. for Al, Ga, In, and Tl, respectively. These values correspond rather closely to the relativistic valence orbital contractions published by Desclaux (*14*) and suggest that orbital contractions and bond lengths are intimately related.

More recently Ziegler, Snijders, and co-workers have suggest that the bond-length contraction is independent of the orbital contraction but rather it is a “direct” result of the Dirac Hamiltonian (*63,64*). They observed that the contraction could be computed from the nonrelativistic molecular wave function by replacing the Schrödinger Hamiltonian with a relativistic one. The energy then is the "first-order" relativistic energy. Comparisons were made using both the one-center approach of Desclaux and Pyykkö and using the Hartree–Fock–Slater (HFS) method. These results were verified using the molecular generalization of the Cowan–Griffin atomic procedure (*65*). In detailed calculations, Ziegler *et al.* indicated that the contraction occurred as a result of the relativistic stabilization of the electron density build up near the nuclei, which in turn resulted from the overlap of the valence orbitals on one center with the core on another (*63*). Katriel *et al.* have shown in all-electron calculations on Li_2 and Na_2 and their cations, that the requirement that the valence orbitals be orthogonal to the core orbitals is responsible for the increase in the valence-other core overlap as the internuclear distance decreases (*66*). This provides a confirmation of the findings of Ziegler *et al.* (*63,64*) and Martin (*65*). The interpretation of these studies has not been universally accepted. First, most comparisons were done using the rather approximate HFS procedure. But, more importantly, it is not clear that the molecular buildup of electron density near the nuclei differs altogether from the relativistic AO contraction. Schwarz and co-workers have argued that the bond-length contraction can be obtained in either of two equivalent ways: by the first-order energy method employed by Zeigler *et al.* (nonrelativistic wave function and relativistic Hamiltonian), or by replacing the nonrelativistic wave function with its relativistic counterpart which includes the orbital contraction (relativistic wave function and nonrelativistic Hamiltonian) (*67*).

This analysis has been tested for Xe_2^+ and Au_2 within the effective core potential approximation (*68*). Four sets of calculations have been carried out: nonrelativistic, first-order relativistic, fully relativistic, and first-order nonrelativistic (relativistic wave function with nonrelativistic Hamiltonian). The computed R_e values were 3.01, 2.67, 2.58, and 3.14 Å, respectively, for Au_2 and 3.24, 3.18, 3.19, and 3.24 Å for Xe_2^+. For these cases then, the analysis of Schwarz *et al.* is clearly inappropriate. It may be the case that the nonrelativistic electronic "contraction" stabilized in first-order calculations is independent of the usual relativistic AO contraction. However since the "contraction" is only stable in the presence of the relativistic Hamiltonian, it is still a relativistic orbital contraction, but now at a molecular level.

The origin of relativistic bond-length contraction is still somewhat of an open question. First, the precise mechanism by which it occurs has not been determined unequivocally. In addition, the computed magnitudes often vary by as much a factor of two or more from calculation to calculation.

To date, the best *ab initio* all-electron molecular calculations involving "heavy" elements are those of Lee and McLean, who published LCAO–MO SCF relativistic calculations on AgH and AuH (*15*). They reported relativistic bond-length contractions of 0.08 and 0.25 Å, respectively, and increases in dissociation energies of 0.08 and 0.25 eV. For comparison, Ross and Ermler carried out shape-consistent REP calculations on AgH and AuH (*69*). They obtained bond-length contractions of 0.06 and 0.23 Å, respectively.

Some of the earliest relativistic molecular calculations involving more than one heavy element were done by Lee *et al.* on the ground state of Au_2 using Phillips- and Kleinmann-based AREPs (*70*). The Au_2 bond is anomalously strong when compared to that of Cu_2 and Ag_2. The relativistic correction to the bond strength was computed at the SCF level by Lee *et al.* to be approximately 1 eV. This corresponds to a "nonrelativistic" bond strength of about 1.3 eV for Au_2 (the experimental D_e is 2.3 eV). The bond strengths of Cu_2 and Ag_2 are 2.1 and 1.5 eV, respectively. The anomaly is due almost entirely to relativity.

Ross and Ermler completed ground-state calculations on Au_2 using the more reliable shape-consistent potentials discussed above (*69*). Employing configuration interaction expansions equivalent to those of Lee *et al.* (*70*), they obtained a bond length 0.14 Å longer. When compared to nonrelativistic all-electron calculations (*70*), these bond-length contractions are twice as large and in good agreement for the respective hydrides. Similar calculations were performed on Ag_2, yielding a 0.5 Å bond-length contraction.

The importance of spin-orbit coupling on the formation of chemical bonds and its incorporation in *ab initio* procedures was brought up by Pitzer in 1979 (*2*). However, it is a much more difficult problem to deal with computationally (as compared to the bond contraction) and only recently have accurate calculations for heavy-element systems appeared in the literature.

For molecules involving only the lighter elements, or even heavier elements, provided bonding is dominated by s character, spin-orbit effects can be added as a final correction to standard Hund's case a coupling calculations. The principal difficulty of this approach is in determining the spin-orbit matrix elements. In all-electron procedures, they can be calculated using the usual Breit–Pauli operator. [See Langhoff and Kern for a review of such procedures (*71*).] But for effective potential calculations the all-electron operator is no longer appropriate and various semiempirical and effective operator schemes have been devised.

The spin-orbit operator in the Breit–Pauli approximation is given by (*49,71*)

$$H^{\mathrm{SO}} = (\alpha^2/2)\left[\sum_{i,K}(Z_K/r_{K_i}^3)(\mathbf{r}_{K_i}\times\mathbf{p}_i)\cdot\mathbf{s}_i + \sum_{i,j\neq i}(1/r_{ij}^3)(\mathbf{r}_{ij}\times\mathbf{p}_i)\cdot(\mathbf{s}_i+2\mathbf{s}_j)\right] \qquad (53)$$

where α is the fine structure constant, i and j index the electrons, and K indexes the nuclei, $\mathbf{r}_{K_i} = |\mathbf{r}_i - \mathbf{r}_K|$ and $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. If the two-electron spin-orbit interaction is neglected, the spin-orbit Hamiltonian becomes

$$H'^{\mathrm{SO}} = (\alpha^2/2)\sum_{i,K}(Z_K/r_{K_i}^3)\mathbf{l}_{K_i}\cdot\mathbf{s}_i = \sum_{i,K}\xi_K(r_{K_i})(\mathbf{l}_{K_i}\cdot\mathbf{s}_i) \qquad (54)$$

Equation (54) is the basis for the semiempirical methods to be discussed below. Several approximations have been used for $\xi_K(r_{K_i})$. In all of the methods, the matrix elements of H^{SO} are evaluated with respect to a wave function variationally optimized in $\Lambda - S$ coupling. The spin-orbit matrix is then diagonalized for the various values of the total angular momentum of the system.

One of the most commonly employed procedures has been to simply extrapolate the molecular coupling from the available atomic parameters using the so-called atoms-in-molecules approach (*72*). Here $\xi(r_i)$ is assumed to be constant for electrons with the same n and l quantum numbers. The values of ξ are then assumed to be equal to the spin-orbit coupling constants ζ_{nl}, which are derived from atomic spectral data. This approach has been employed by Wadt (*73*) in all-electron studies, and by other groups (*32,74*) in effective potential calculations involving the rare-gas dimers and dimer ions. Ermler and co-workers used this approach coupled with AREP calculations to determine spectroscopic properties for various states of Au_2 (*42*), Hg_2, and HgTl (*75*).

Another method, devised by Cohen *et al.* to determine oxygen-rate gas collision parameters is to define an effective spin-orbit operator that includes r dependence, Z_{eff}/r^3, where the value of Z_{eff} is adjusted to match experimental data (*76*). Langhoff has compared this technique with all-electron calculations using the full microscopic spin-orbit Hamiltonian for the rare-gas–oxide potential curves and found very good agreement (*77*). This operator has also been employed in REP calculations on Si (*73*), UF_6 (*78*), UO_2^+ and ThO_2 (*79*), and UF_5 (*80*). The REPs employed in these calculations are based on Cowen–Griffin atomic orbitals, which include the relativistic mass–velocity and Darwin effects but do not include spin-orbit effects. Wadt (*73*), has made comparisons with calculations on Si by Stevens and Krauss (*81*), who employed the *ab initio* REP-based spin-orbit operator of Ermler *et al.* (*35*).

The calculations on UF_6 show good agreement with experiment for properties such as the relative energies of the states of UF_6^- (to within 0.1 to 0.2 eV), but disagree with experiment considerably for quantities such as the electron affinity of UF_6, where the calculated values differ by more than 2 eV (*78*). In the calculations on the isoelectronic species UO_2^+ and ThO_2, the calculated geometries (linear and bent, respectively) agree with experiment (*79*). Finally, in the calculations on UF_5, the effects of spin-orbit coupling are illustrated in that the calculated ground-state geometry is changed from square pyramidal to trigonal bipyramidal when spin-orbit coupling is included (*80*).

This method yields good qualitative and, in some cases, quantitative results. It is especially useful in cases in which Cowan–Griffin orbital-based REPs, such as in this case, are employed because *ab initio* spin-orbit operators are not appropriate, since spin-orbit terms are not considered in the derivation of the REPs. However, this approach has been criticized in that the rigorous REP-based spin-orbit operator [Eq. (35)] does not as a rule exhibit r^{-3} behavior, as assumed for the Z_{eff} approach. For this reason, the above approach (*73,76*) may not be internally consistent. Furthermore, now that general polyatomic Gaussian integral codes are available (*40*), the REP-based spin-orbit operator can be applied as easily as the Z_{eff} form.

Basch *et al.* employ a "phenomonological" spin-orbit operator of the same form as Eq. (54), in which it is assumed that ξ is constant and that only valence electron interactions are important in determining spin-orbit splitting energies (*82*). The value of ξ is found through a variational procedure employing experimental term energy levels. This spin-orbit operator has been used to transform $\Lambda-S$ potential energy curves into Ω representations in REP calculations on PbHe and PbXe. It was found that the bonding was generally weakened by transforming to Ω representations.

In another approach, Shim and Gingerich, in all-electron calculations on Pd_2, assume that the radial integrals $\xi(r_i)$ are constant and equal (*83*). A value of 1412 cm^{-1} was obtained from the work of Laporte and Inglis, who applied the Landé interval rule to experimental spectra (*84*). They found that the energy range of the low-lying states of Pd_2 is increased over threefold. They show how this affects the value of the dissociation energy, as determined by employing mass spectrometric data. Values of 83 and 99 kcal/mol are calculated, omitting and including spin-orbit coupling, respectively. Additional calculations on a variety of molecules are needed to more firmly establish the expected accuracy when this operator is employed.

The *ab initio* REP-based spin-orbit operator derived from the Dirac–Fock equations has been employed in several calculations. Stevens and Krauss (*81*) provided careful comparisons with all-electron work for atomic carbon and silicon. As shown in Table VI, Ross *et al.* have calculated the spin-orbit splittings of doubled states for the elements in Groups 13 and 17 in REP SCF calculations (*36*). Table VII shows that the calculated spin-orbit splittings agree well with experiment and with comparable all-electron Dirac–Fock calculations. The comparisons in Table VII also reveal that the relativistic mass–velocity and Darwin terms are important in calculating spin-orbit splittings in heavy elements. This can be seen by comparing Hartree–Fock spin-orbit splittings with those due to the REP-based spin-orbit operator. The latter include mass–velocity and Darwin effects, whereas the former do not. The disagreement between experiment and Hartree–Fock spin-orbit splittings becomes extremely large in the case of heavy elements. Calculated spin-orbit splittings for Li through Ar have been reported by Pacios and Christiansen (*53*). Spin-orbit splittings for the first, second, and third transition rows are shown in Tables VIII, IX, and X, respectively (*85*). As can be seen in the tables, the calculated results agree well with experiment and with

TABLE VI

Spin-Orbit Splitting for Doublet States (cm^{-1})

			Dirac–Fock				
Element	H^{SO}[a]	REP[b]	I[c]	II[d]	III[e]	IV[f]	Expt.[g]
B	19	19	20	15	20	15	16
Al	125	125	126	120	120	112	112
Ga	842	803	803	788	801	784	826
In	2146	2052	2147	2121	2142	2113	2213
Tl	7324	7545	7693	7684	7509	7597	7792
F	434	401	411	364	411	364	404
Cl	970	941	922	918	877	872	881
Br	3924	3794	3762	3692	3738	3668	3684
I	7891	7723	7705	7666	7737	7640	7603
At	22225	22697	23990	23741	23952	23712	—

[a] First-order spin-orbit splitting due to H^{SO}.

[b] Energy difference between $J = 1/2$ and $J = 3/2$ states using numerical REPs and basis sets of two-component spinors.

[c] Valence shell orbitals optimized, excluding Breit corrections.

[d] Valence shell orbitals optimized, including Breit corrections.

[e] All orbitals optimized, excluding Breit corrections.

[f] All orbitals optimized, including Breit corrections.

[g] From C. E. Moore, *Natl. Bur. Stand. Circ.* No. 467, Vol. I (1949); Vol. II (1952); Vol. III (1958).

TABLE VII

Comparison of Computed Spin-Orbit Splittings for Columns 13 and 17[a]

	REP–DF(I)		HF–expt.	
Element	Difference	Percentage	Difference	Percentage
Ga	0	0.0	−130	−15.7
In	−95	−4.4	−439	−19.8
Tl	−148	−1.9	−2677	−34.4
Br	32	0.8	−360	−9.8
I	18	0.2	−1147	−15.1
At	−1293	−5.4	—	—

	H^{SO}–expt.		REP–expt.	
Element	Difference	Percentage	Difference	Percentage
Ga	16	1.9	−23	−2.8
In	−67	−3.0	−161	−7.3
Tl	−468	−6.0	−247	−3.2
Br	240	6.5	110	3.0
I	288	3.8	120	1.6
At	—	—	—	—

[a] Column headings as defined in Table VI; difference units in cm^{-1}.

TABLE VIII

First Transition-Row Spin-Orbit Splittings[a]

Element	Configuration	H^{SO}	REP	DF	Expt.[b]
K	p_1	38	47	48	58
Ca^+	p^1	172	198	203	223
Sc	d^1	146	143	174	168
Ti^+	d^1	350	389	400	232
Ti^{3+}	d^1	374	421	434	384
Cu	d^9	1875	1878	2140	2043
Zn^+	d^9	2477	2513	2833	2719
Ge^+	p^1	1806	1756	1779	1767
Kr^+	p^5	5691	5543	5470	5371

[a] Column headings as defined in Table VI; units in cm^{-1}.

[b] From C. E. Moore, *Natl. Bur. Stand. Circ.* No. 467, Vol. I (1949); Vol. II (1952); Vol. III (1958).

TABLE IX

Second Transition-Row Spin-Orbit Splittings[a]

Element	Configuration	H^{SO}	REP	DF	Expt.[b]
Rb	p^5	7460	7419	7390	6820
Sr^+	p^1	594	674	689	801
Y	d^1	658	456	473	530
Zr^+	d^1	—	—	1200	1250
Ag	d^9	4289	4349	4503	4471
Cd^+	d^9	5644	5579	5708	5635
Sn^+	p^1	4375	4211	4228	4251
Xe^+	p^5	11,100	10,792	10,755	10,537

[a] Column headings as defined in Table VI; units in cm^{-1}.

[b] From C. E. Moore, *Natl. Bur. Stand. Circ.* No. 467, Vol. I (1949); Vol. II (1952); Vol. III (1958).

TABLE X

Third Transition-Row Spin-Orbit Splittings[a]

Element	Configuration	H^{SO}	REP	DF	Expt.[b]
Cs	p^5	13,729	13,798	13,892	9810
Ba^+	p^1	1220	1375	1401	1691
La	d^1	1430	965	1047	1053
Au	d^9	12,228	12,536	11,938	12,274
Hg^+	d^9	13,660	13,931	14,727	15,038
Pb^+	p^1	13,920	13,887	14,234	14,081
Rn^+	p^5	26,780	26,963	32,005	30,895

[a] Column headings as defined in Table VI; units in cm^{-1}.

[b] From C. E. Moore, *Natl. Bur. Stand. Circ.* No. 467, Vol. I (1949); Vol. II (1952); Vol. III (1958).

comparable all-electron Dirac–Fock calculations, showing the accuracy of the REP-based spin-orbit operator, as well as the reliability of the REPs employed.

A complication concerning the use of the REP-based spin-orbit operator has to do with computing Breit corrections. As can be seen from Tables VI and VII, this can be quite important for the lightest elements. However, because the all-electron Breit operator (*29*) weights the core region heavily, such corrections cannot be computed from valence wave functions using such an operator. One method of computing the Breit correction would be to reintroduce the core portion of the wave function, as suggested by Pacios *et al.* (*53*) using Eq. (51). A simpler approach, however, has been employed by Stevens and Krauss (*38,81*). They proposed an effective Breit operator obtained by scaling the REP-based spin-orbit operator so as to reproduce the atomic Dirac–Fock plus Breit splittings. This approach has been used with considerable success in light-element work and is also probably appropriate for heavier elements.

The REP-based spin-orbit operator has been used implicitly in a number of ω–ω coupling molecular SCF calculations. Lee *et al.* were the first to use this approach in calculations on atomic Xe and Au (*30*) and in molecular calculations on Au_2^+, TlH, PbSe, and PbS (*43*). Schwarz and co-workers have developed a similar molecular ω–ω coupling technique employing more approximate effective potential operators (*16,86*). Christiansen and Pitzer extended the technique to do small ω–ω coupling MCSCF calculations on TlH (*43,87*), Tl_2 (*88*), and Pb_2 (*89*). Spin-orbit effects on bonding are particularly important for molecules containing thallium. Ross and Ermler have reported ω–ω SCF calculations on Ag_2 and Au_2 employing REPs (*69*). Calculations were also performed in the Λ–S coupling scheme. No difference was observed in the calculated spectroscopic constants, indicating that the bonding in both molecules primarily involves the valence *s* electrons.

The mechanism by which spin-orbit coupling can impact molecular bonding becomes more obvious if the wave function is reformulated in terms of molecular spinors (Hund's case c coupling). One should keep in mind, however, that even for the heaviest elements the angular momentum coupling is generally intermediate between case a and case c, and the following picture is therefore an oversimplification.

The $p_{1/2}$ spinors are combinations of σ-type and π-type spin orbitals (ignoring the small components) with coefficients of $(1/3)^{1/2}$ and $(2/3)^{1/2}$, respectively. Therefore, a molecular spinor formed as a sum or difference of atomic $p_{1/2}$ spinors on two centers will be one-third σ bonding and two-thirds π antibonding, or just the reverse. In either case, one would expect only a weak bond to form. On the other hand, the $p_{3/2}$ atomic spinors are $(2/3)\sigma$ and $(1/3)\pi$. Because of the difference in the signs of the components, combinations of $p_{1/2}$

and $p_{3/2}$ spinors can be made to obtain pure σ or pure π spin orbitals, and this, of course, occurs for the lighter elements. However, for the heavier elements, such as Tl, Pb, and Bi, the energy gap between the 1/2 and 3/2 spinors is approximately 1 eV and the appropriate mixing is not nearly as readily achieved. For this reason, one would expect only very weak bonds to form between two Tl atoms or between Pb atoms, which in their ground atomic states have only $p_{1/2}$ electrons. For Pb the problem is somewhat more complicated in that the two $p_{1/2}$ electrons form a closed subshell. From this point of view, Pb is somewhat comparable to Be. Bismuth, on the other hand, in addition to the closed $p_{1/2}$ subshell, has a single $p_{3/2}$ electron and therefore a single π bond can be readily formed between two Bi atoms. This is in contrast to the one σ and two π bonds of N_2. Similar combinations can, of course, be made for heteronuclear molecules. For instance, TlBi would be expected to form a single stable bond that is roughly one-half σ and one-half π. Furthermore one would expect to see some effect, though probably not as dramatic, in bonds between a heavier element and a lighter one, such as in TlH.

The above discussion presumes that $p_{1/2}$-to-$p_{3/2}$ promotion is unlikely due to the large energy separation and for this reason L–S coupling is no longer completely appropriate. Unfortunately, in most cases purely j–j coupling is also inappropriate. Perhaps the best example of this is Pb_2, for which ω–ω coupling SCF or even MCSCF calculations suggest little or no bonding (*89*), whereas intermediate coupling CI calculations by Balasubramanian and Pitzer (*90*) yield a bond energy of Pb_2 to be 0.88 eV. The Pb_2 bond energy is known with some degree of certainty to be about 0.9 eV (*91*). For the heavier elements the coupling is typically intermediate between the two extremes and, in practice, the formulation of the wave function must be sufficiently flexible to cover the full L–S to j–j range for the various electronic states. If the wave function is written as a linear expansion (as in configuration interaction calculations), the expansion terms must be chosen such that both electron correlation and intermediate angular momentum coupling are incorporated.

TlH is one of the simplest molecules for which one would expect to observe substantial intermediate angular momentum coupling effects. Dissociation curves for six low-lying states of TlH were determined by Christiansen *et al.* (*39*) using Λ–S coupling SCF calculations followed by spin-orbit CI (as discussed in an earlier section). The results of these calculations along with the experimental results of Ginter and Battino (*92*) are given in Table XI. The lowest two 0_g^+ curves are compared with the experimentally determined curves in Fig. 5. The excellent agreement indicates the reliability of this particular computational technique. The inner walls of the computed curves are somewhat too repulsive, due at least in part to the neglect of d-shell promotions in the spin-orbit CI calculation.

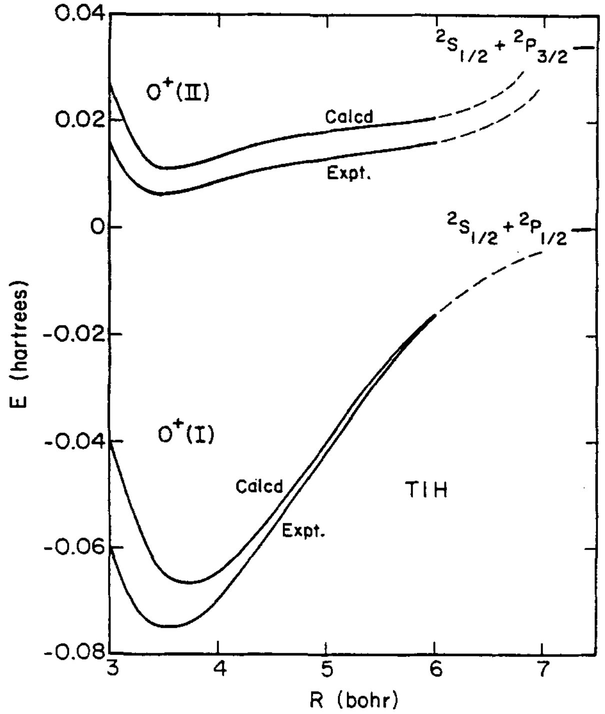

Fig. 5. Experimental and calculated configuration-interaction potential-energy curves for the two lowest 0^+ states of TlH.

TABLE XI

SPECTROSCOPIC CONSTANTS FOR LOW-LYING BOUND STATES OF TlH[a]

State	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	T_e (cm^{-1})
0^+(I) calc.	1.99	1.81	1300	0
0^+(I) expt.	1.87	1.97	1391	0
0^- calc.	1.95	0.24	795	16600
0^+(II) calc.	1.91	0.61	−1000	17100
0^+(II) expt.	1.91	0.74	−760	17723
2 calc.	1.90	0.035	740	21800
1(II) calc.	3.1	—	−200	23400
1(II) expt.	2.9	—	−140	24180

[a] From Ref. 88.

As one might expect, the lowest 0^+ state is dominated by $^1\Sigma^+$ character near the equilibrium geometry, whereas the excited 0^+ state is primarily $^3\Pi$ (presumably the "orthogonal triplet", earlier conjectured to be in part, responsible for the strong ground-state bond (*93*)). However, at large internuclear distances, the reverse is true. This is, as one would expect, based on the large component coefficients for the $p_{1/2}$ spinor. The peculiar shape of the excited 0^+ curve is due then to avoided crossing of $^3\Pi - {^1\Sigma^+}$.

From the discussion of atomic spinors, one would expect the ground-state bond to be considerably weaker than it would have been had the effects of spin-orbit coupling not been taken into account. Indeed, Pitzer and Christiansen have shown in MCSCF calculations that the spin-orbit coupling reduces the bond strength by about 25% (*87*). Due to the relativistic stabilization of the 6*s* atomic spinor, a sizable energy gap exists between the 6*s* and 6*p* electrons in Tl. This so-called "inert pair" effect for the 6*s* electrons delegates most of the bonding interaction to the 6*p* electrons. When spin-orbit coupling is included, the $6p_{1/2}$ (one-third σ character and two-thirds π character) is the lowest energy atomic orbital available for bonding. Since the bonding with H can only be σ, a bond solely with a $p_{1/2}$ spinor would yield one-third of a "normal" σ bond.

Pyper has pointed out that the π component of the $p_{1/2}$ spinor will interact with the H through an "orthogonal triplet" bond (*93*). He estimates the strength of this bond to be about one-half the strength of a normal σ bond. Hence, using his estimate, a bond solely with the $p_{1/2}$ atomic spinor will have about two-thirds the strength of a normal σ bond. Christiansen and Pitzer tested this hypothesis by performing AREP MCSCF ($\Lambda-S$) and two sets of REP MCSCF ($\omega-\omega$) calculations (*88*). One set of REP MCSCF calculations included $p_{3/2}$ functions, while the other did not. The REP MCSCF calculation without the $p_{3/2}$ functions only accounted for 36% of the bond energy of a normal σ bond at 5 bohr. Thus the "orthogonal triplet" bond is only 3% of a normal σ bond, and not 50%. Allowing for participation by the $p_{3/2}$ spinors yields 62% of a full σ bond, indicating there is some promotion to the $p_{3/2}$ orbital. Also, in the calculation including $p_{3/2}$ spinors, 85% of the experimental dissociation energy was obtained in the calculation and R_e was calculated to within 0.1 Å of experiment (*45*).

Calculations on Tl_2 also illustrate the dramatic effects of spin-orbit coupling on bonding (*88*). Both $\Lambda-S$ and $\omega-\omega$ calculations were performed. The $\Lambda-S$ calculations showed appreciable bonding while the $\omega-\omega$ calculations predicted very weak bonding. This is portrayed in Fig. 1. The spin-orbit coupling lowers the atomic asymptote well below the $\Lambda-S$ coupling bond. The $^3\Pi_u$ state gives rise to the 0_u^- and 1_u states, whereas the 0_g^+ comes from $^3\Sigma_g^-$ and $^1\Sigma_g^+$. These calculations also indicate that, although the neutral molecule is only weakly bonded, the $(1/2)_g$ state of the molecular ion has a bond strength of about 0.5 eV, which is consistent with mass spectral data.

Very weak bonding is observed in the neutral dimer. The studies on Tl_2 and TlH, show the capability of this REP-based approach to yield information that would be unattainable without the inclusion of relativistic effects.

A difficulty in invoking the ω–ω coupling scheme in relativistic calculations is that CI computational codes that are based on configurations that are eigenfunctions of Ω have yet to be developed. Esser has published a CI procedure but, to date, it has not been extensively applied in molecular calculations (*94*). It has been used in atomic calculations, yielding some interesting results. Esser, in the context of the model potential approach of Hafner and Schwartz, performed both L–S and j–j atomic CI calculations on the ground and various excited states of Hg and Pb (*94*). The results of the calculations, through analyses of the weights of certain configurations, showed that Hg is more accurately represented in L–S coupling and Pb is more accurately represented in the j–j scheme. In the case of molecules, it will be true in certain cases that the intermediate coupling states are more concisely represented in ω–ω coupling versus Λ–S coupling. In such instances, it would be computationally advantageous to perform the CI calculations based on ω–ω coupling. A major advantage of this approach is that spin-orbit coupling is dealt with directly, and bonding effects, such as those discussed in the TlH calculations, can be readily studied.

Intermediate coupling calculations have been used to compute spectroscopic constants for a number of diatomic molecules, including TlH (*39*), Pb_2 (*90*), Sn_2 (*91*), SnO (*95*), PbO (*96*), PbH (*97*), SnH (*98*), Bi_2 (*50*), PtH (*99*), UH (*100*), PbF (*101*), and Tl_2 (*102*). These applications indicate that this procedure is successful in calculating spectroscopic constants in good agreement with experiment, in assigning ground states, in characterizing transitions observed in experimental spectra, and in predicting electronic states. It has also been employed to study comparative magnitudes of relativistic effects, including spin-orbit effects, to illustrate the role of spin-orbit coupling in bonding in heavy-atom systems, and to calculate more accurate bond energies in conjunction with mass-spectral data. In addition, through examining the magnitude of CI coefficients this method has been used to reveal the amount of mixing of Λ–S states necessary to describe a particular intermediate angular momentum coupling state, as well as which molecules can be adequately described by Λ–S coupling and which cannot. Various CI coefficents also show the change in character of the CI wave function with bond length (spin-orbit effects generally increasing while molecular extra-correlation effects decrease with increasing bond length). Finally, this method has been used to show the effects of spin-orbit coupling on bond order, R_e, and ω_e.

Intermediate coupling calculations have been used to determine the spectroscopic properties and dissociation curves for several low-lying states of Tl_2 (*102*). All three lowest energy states are bound, but only weakly. In contrast to TlH, the angular momentum coupling for the lowest energy states of Tl_2 is dominated by ω–ω coupling. The weak bond in the 0_u^- ground state is in direct conflict with the value by Balducci and Piacente (0.6 ± 0.15 eV) (*103*) based on mass-spectral data. However, a reinterpretation of the mass-spectral data using the molecular parameters from the four lowest energy states gives a bond of about 0.37 eV (±0.15), which is in marginal agreement with the computed values, assuming similar error limits.

Balasubramanian and Pitzer have carried out calculations for several states of Sn_2 and Pb_2 using the same intermediate coupling procedure as discussed above (*90*). These calculations provide an interesting comparison, with the spin-orbit splitting increasing (going from Sn to Pb) by about a factor of four. For Sn_2 the splitting is much smaller than the bond energy. Sn_2 is reasonably well represented in Λ–S coupling, with the spin-orbit effects being a mild perturbation, whereas for Pb_2, spin-orbit coupling reduces the ground-state bond strength by a factor of two. However, as stated earlier, simple ω–ω coupling alone is also inadequate. For the low-energy states, the coupling in Pb_2 is quite intermediate.

As stated above, information can be obtained concerning the intermediate nature of the angular momentum coupling from the relative values of CI coefficients for the various reference configurations employed. Balasubramanian and Pitzer, in calculations on Sn_2 and Pb_2, presented an example of how examining the coefficients can illustrate the magnitude of relativistic effects and can be used to estimate whether or not a molecule can be described adequately by pure Λ–S or ω–ω coupling (*90*). The mixing of Λ–S states is much greater in Pb_2 than in Sn_2, indicating that Sn_2 is better represented than Pb_2 in pure Λ–S coupling, and that relativistic effects are much greater in Pb_2 than in Sn_2. They also examined the difference in magnitudes of spin-orbit coupling between SnO (*95*) and PbO (*96*) and between PbH (*97*) and SnH (*98*).

Another application of intermediate coupling calculations has been to use the calculated results to reevaluate dissociation energies derived using the third-law method and mass- spectral data. Balasubramanian and Pitzer have shown how this can be accomplished in their calculations on Sn_2 and Pb_2 (*90*). This method requires the molecular partition function, which can be written

$$q = q_{tr}(T, P) \sum_i q_{rot}(T, R_{e,i}) q_{vib}(T, \omega_{e,i}) g_i e^{-\Delta\varepsilon_i/kT} \tag{55}$$

where the sum is over all electronic states that make significant contributions, $\Delta\varepsilon_i$ is the electronic excitation energy relative to the ground state, g_i is the electronic state degeneracy, and q_{rot} and q_{vib} are the rotational and vibrational partition functions for the *i*th electronic state (*90*). An improved value of the partition function for Sn_2 and Pb_2 can be calculated by including in the summation the 1_g, 2_u, and 1_u electronic states, which are all at low enough energy to contribute to the partition function at the temperature of the mass-spectral measurements (*104*). The correction term to D_0, the dissociation energy relative to the ground vibrational level, appropriate to this situation, is given by (*105*)

$$\delta D_0 = RT \ln(q'/q'') \tag{56}$$

where q'' includes the 1_g, 2_u, and 1_u electronic states and q' does not. This equation was originally derived by Gurvich and Korobov and applied to O_2 (*105*). Balasubramanian and Pitzer recalculated the partition function for Sn_2 using experimental values for spectroscopic constants when available and calculated spectroscopic constants for the remainder. Adding the correction term to the experimental D_0 obtained from mass-spectral data (*104*), they obtained 1.93 eV, which agrees well with the calculated value of 1.86 eV. Christiansen, in calculations on Tl_2, employing a similar treatment, re-evaluated mass-spectral data and found that the experimental dissociation energy was lowered from the original value by 0.37 eV (*102*).

Christiansen has completed spin-orbit CI calculations for the ground state of Bi_2 (*50*). In comparison to Tl and Pb, in $j-j$ coupling Bi has a single $p_{3/2}$ electron, and one would expect to see somewhat reduced effects due to spin-orbit coupling. In fact, the ground state is dominated by the ${}^1\Sigma_g^+$ triple-bonding configuration (as in N_2); however, the spin-orbit coupling mixes in considerable ${}^3\Pi$ character (about 25%). The ${}^3\Pi_g$ and ${}^1\Sigma_g^+$ curves (see Fig. 6) are very nearly parallel to the 0_g^+ curve. The ground-state coupling, though still intermediate, is dominated by $\Lambda-S$.

For the Tl, Pb, and Bi series of homonuclear diatomics, the impact of spin-orbit coupling decreases as electrons are added to the $6p$ shell. This is as one would expect in terms of the additional electrostatic interactions.

Another trend that has been observed in intermediate coupling calculations is that, for a given molecular state, $\Lambda-S$ coupling is generally more important for the equilibrium atomic separation and becomes less important as the interatomic distance is increased. That is, bonding tends to favor $\Lambda-S$ coupling (or vice versa). This is particularly apparent for the TlH and Bi_2 ground states.

In several of the calculations cited earlier, calculated spectral transitions have been compared to experimental spectra to aid in assigning transitions. In the calculations on SnO, Balasubramanian and Pitzer (*96*), on the basis of calculated T_e values, agree with the conclusion of Deutsch and Barrow (*106*) in assigning experimentally observed emission bands to the transitions from the ${}^3\Pi(0^+)$ and ${}^3\Pi(1)$ states to the ground state. Balasubramanian and Pitzer disagree, however, with the assignments of Capelle and Linton (*107*), who assign observed emission bands around 2000 cm^{-1} to the ${}^3\Sigma^+(1) \rightarrow {}^1\Sigma^+(0^+)$ transition. An example of this method, acting as a check on experimentally

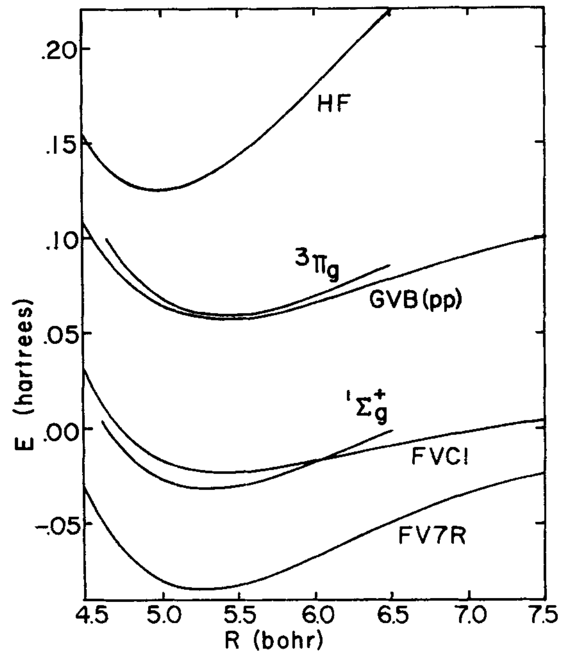

Fig. 6. Average relativistic effective core potential and relativistic effective core potential energy curves for two states of Bi_2. HF, Hartree–Fock; GVB(pp), eight-configuration perfect-pairing generalized valence bond; FVCI, full-valence CI based on the GVB(pp) wave functions; FV7R, full-valence CI plus single and double promotions to virtual MOs relative to seven-dominant configurations. (The FVCI and FV7R calculations include the REP-based spin-orbit operator.)

assigned spectral transitions, is provided by Christiansen in calculations on the nine low-lying states of Tl_2 (*102*). A transition observed in the thermal emission spectrum (*108*) at 136 cm^{-1} is too high to correspond to any of the states Christiansen investigated. This implies that the transition may actually not be due to Tl_2. Krauss and Stevens have predicted the existence of unobserved states for parts of the infrared and visible electronic spectra of UO^+ using REP-based calculations (*109*).

There are some limitations to employing the intermediate coupling spin-orbit CI procedure that should be noted. The first is that the effects of spin-orbit coupling on the nature of the molecular orbitals cannot be directly included, in contrast to the ω–ω coupling scheme, which does include such effects. Second, in order to represent intermediate coupling states, a rather large number of reference configurations must be employed. This, in turn, limits the size of the valence space and the extent of the CI procedure due to computational restraints. This is a somewhat serious limitation because a larger valence space and/or more extended CI calculations are required to calculate accurate spectroscopic constants in some cases. Finally, the general limitations associated with the use of effective core potentials, such as the frozen-core approximation and the difficulty of incorporating core–valence correlation and polarization effects, must be considered.

Most of the present discussion has been concerned with applications of REPs within the framework of otherwise essentially orbital-based calculations. On the other hand, a recent application (*110*) involved a quantum Monte Carlo (QMC) procedure. [A useful overview of Monte Carlo electronic structure work has been given by Ceperly and Alder (*111*).] Currently, QMC offers little, if any, competition for conventional calculations in that the computer time required to reduce statistical errors to acceptable limits increases rapidly as a function of atomic number and is excessive for all but the smallest systems. Recent fluorine calculations required nearly 100 hours of supercomputer time (*112*). Although, on the surface, it would appear totally impractical, the appeal of this approach in the context of heavy-element work is its avoidance of extensive basis sets and enormous configuration expansions that plague present studies.

Most QMC work to date is based on the important sampling modification of the Schrödinger equation (*113*) in imaginary time, t,

$$\partial f/\partial t = \tfrac{1}{2}\nabla^2 f - \nabla \cdot (f \nabla \ln \psi_\mathrm{T}) - [H\psi_\mathrm{T}/\psi_\mathrm{T} - E_\mathrm{T}]f \qquad (57)$$

where H is the usual Hamiltonian, ψ_T is a trial wave function and $f = \psi\psi_\mathrm{T}$, a product of ψ_T with the actual solution, ψ, of the Schrödinger equation. The equation is simulated by a combination of random-particle movement, birth, and death, as well as drift, with the reference energy, E_T, adjusted to maintain stability. Electronic energies are ultimately obtained as an average of the local energies, $H\psi_\mathrm{T}/\psi_\mathrm{T}$.

The sources of difficulty are obvious. For all but the lightest elements, the atomic Hamiltonian may contain a large number of singularities due to electrostatic interactions between electrons and between electrons and nuclei. Additional singularities in the drift and local energies can occur at nodes in the wave function. Unless ψ_T is a reasonably good approximation to ψ, the singularities will become overwhelmingly apparent in the local energies, leading to large statistical errors in the average. The more densely packed the electrons become (and this will be most serious in the core region), the more acute the difficulties become.

Clearly, much of the trouble could be eliminated by replacing the nucleus and core electrons by an REP. This may be conveniently done by defining a local potential (the REPs are nonlocal in that they contain angular momentum projection operators) in terms of the trial wave function.

$$V = U^{\mathrm{REP}}\psi_\mathrm{SD}/\psi_\mathrm{SD} \qquad (58)$$

where ψ_SD is the Slater determinant from ψ_T. The above approximation has recently been used to compute the electron affinity for potassium (*110*), and the total error—due to the use of AREPs, core polarization potentials, and Eq. (58)—was only 0.02 eV (0.48 as opposed to 0.50 eV experimental). The entire calculation required about 10 hours of MicroVAX computer time and gave a statistical error of 0.01 eV, as opposed to the approximately 100 supercomputer hours and order of magnitude larger error seen in the recent fluorine electron affinity study. By comparison, the all-electron QMC equivalent, the K calculation, might require a "Cray decade" or more. Interestingly, although the difficulty of REP QMC will increase as one moves across a given row of the periodic table, it will decrease as one moves down a column, since the number of valence electrons remains unchanged whereas the valence wave function becomes more diffuse.

V. Conclusions

An accurate procedure for performing calculations that incorporate spin-orbit and other relativistic effects, and that represents intermediate coupling states for molecules containing heavy atoms, is based on $\Lambda-S$ coupling in conjunction with the use of the *ab initio* REP-based spin-orbit operator and extended configuration interaction. The coupling scheme is more familiar than $\omega-\omega$ coupling to chemists and physicists. In addition, the complexity of calculations necessary to achieve reliable results is computationally tractable.

An *ab initio* alternative to performing such $\Lambda-S$ REP CI calculations is to perform $\omega-\omega$ REP CI calculations. The MCSCF and CI codes are currently under development. When they become available, this method will provide a viable and, in many cases, preferable alternative to the spin-orbit CI procedure based on $\Lambda-S$ coupling. In particular, when molecules containing heavy and super-heavy elements are studied, it is reasonable to expect the number of reference configurations needed to describe the intermediate coupling state to be less in the $\omega-\omega$ framework than in the $\Lambda-S$ framework, since as the atomic number increases the coupling tends more toward the $\omega-\omega$ limit. Correlated calculations in $\omega-\omega$ coupling would also be useful in verifying the results of $\Lambda-S$ calculations since both should give an accurate description of the molecule, as long as the necessary reference configurations are present and the extend of the CI is adequate.

Computer codes have been developed for use in the $\omega-\omega$ framework for SCF (*43*) and MCSCF (*45*) calculations. Calculations employing these codes can be of great utility because, although they cannot be expected to produce results as accurate as large-scale spin-orbit CI calculations, they can yield a great deal of information about the nature of the bonding and molecular orbitals in chemical systems. This is illustrated by the calculations on TlH discussed above (*45*).

All-electron Dirac–Fock procedures are also capable of producing accurate molecular wave functions (*16*). However, it is not feasible at present to use this method as a standard tool for heavy-element systems because of the computational constraints. This approach can result in calculations of questionable value due to the use of inadequate basis sets and modest levels of CI. Such calculations may not only be inaccurate, but, can be misleading if used for comparisons with REP calculations. Carefully selected "benchmark" calculations would be extremely useful for checking results of REP-based studies.

Semiempirical spin-orbit operators play an important role in all-electron and in REP calculations based on Cowen–Griffin pseudoorbitals. These operators are based on rather severe approximations, but have been shown to give good results in many cases. An alternative is to employ the complete microscopic Breit–Pauli spin-orbit operator, which adds considerably to the complexity of the problem because of the necessity to include two-electron terms. However, it is also inappropriate in heavy-element molecules unless used in the presence of mass–velocity and Darwin terms.

In summary, the recommended method for the inclusion of spin-orbit coupling and other relativistic effects for molecules containing heavy elements, considering computational complexity and accuracy factors, is one based on *ab initio* REPs. Future developments should include more extensive spin-orbit and CI procedures in the Λ–S framework, the development and implementation of CI computational codes in ω–ω coupling, the incorporation of reliable methods for the treatment of core–valence polarization and correlation effects, and selected "benchmark" all-electron calculations.

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Analytical Calculation of Geometrical Derivatives in Molecular Electronic Structure Theory

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I. Introduction

A. Perspective

The development of and computational implementation of analytical expressions for the derivatives of *ab initio* electronic energy surfaces and molecular properties have undergone rapid growth in recent years. This growth reflects the central role these derivatives play in understanding chemical reactions and in interpreting many spectroscopic experiments. Low-order derivatives are now calculated analytically in a routine fashion for a variety of wave functions, greatly increasing the amount of information that can be conveniently extracted from approximate electronic wave functions. The purpose of this article is to review the techniques currently available for the analytical calculation of molecular energy and property derivatives.

The analytical calculation of energy derivatives has recently been reviewed by Pulay (1987) and Gaw and Handy (1984), and the analytical calculation of property derivatives by Amos (1987). The calculation of derivatives has traditionally been expressed in a generalized Fock-operator formalism, and this approach is also taken by the above authors. This makes it easier to look at developments in a historical perspective. However, the Fock-operator technique suffers from some disadvantages. One problem is the use of redundant variational parameters, requiring a complicated handling of Lagrange multipliers. Another disadvantage is the lack of separation between the effects of geometry-dependent basis sets (variable metrics) and the physical relaxation of the wave function in the presence of a geometrical perturbation. Because of this the underlying simplicity of the derivative expressions become obscured, and generalizations to time-dependent geometrical derivatives (e.g., geometrical derivatives of frequency-dependent polarizabilities) become difficult if not impossible.

The response function approach (Jørgensen and Simons, 1981) to the calculation of geometrical derivatives does not suffer from these disadvantages. In this formalism, wave functions are parametrized by exponential transformations of a reference state. This ensures that only independent variations are considered, eliminating the need for Lagrange multipliers. Furthermore, by expressing the Hamiltonian in the language of second quantization, the geometry dependence of the basis set can be isolated in the Hamiltonian and incorporated in the perturbation operator describing the nuclear distortion. In this way the geometry dependence of the basis set is treated in the same way for all wave functions and can be considered before the choice of wave function is made. Also, since the geometry dependence is incorporated in the Hamiltonian, a geometrical distortion may be treated as an ordinary external perturbation in the same way as, for example, electric field perturbations. The extension of the analytical calculation of geometrical derivatives to time-dependent molecular properties therefore becomes straightforward. However, this topic is outside the scope of the present review. [For details about time-dependent properties, see Olsen and Jørgensen (1985).] The use of independent variables and the isolation of the geometry dependence of the basis set in the Hamiltonian also make it easy to see structural similarities and differences between various wave functions, and hence to recognize their advantages and disadvantages. Also, the similarities between wave function optimizations and derivative calculations become apparent when the response function approach is used.

The response function approach has been used for many years to describe molecular properties where the perturbations leave the metric unchanged (the basis set remains fixed in space). The use of response functions to calculate geometrical derivatives was initiated by Jørgensen and Simons (1983) and independently described by Helgaker and Almlöf (1984). Since then many developments have been made using this approach. However, this progress has received little attention in the recent reviews by Gaw and Handy (1984), Pulay (1987), and Amos (1987). Since the response function approach offers a very direct insight into the calculation of geometrical derivatives, we feel that a review which focuses on this approach is appropriate and may help to clarify some of the confusion in this field, and may also provide the unfamiliar reader with a simple introduction to the calculation of geometrical derivatives in quantum chemistry.

The emphasis in this review is on theoretical and technical aspects. We set up a mathematical framework within which the expressions for the various derivatives can be conveniently derived, and discuss efficient computer implementations of these expressions. There is no discussion of the relationship between the calculated numbers and observed quantities, or of the accuracy of the various wave function approximations. For this we refer to the reviews by Fogarasi and Pulay (1984), Hess *et al.* (1986), Amos (1987), and Schlegel (1987). Also, little attention is given to the important field of integral evaluation, which is well covered by Saunders (1983) and Gaw and Handy (1984).

B. Outline

We consider a molecular system at a reference geometry X_0 in state $|X_0\rangle$ with total energy

$$W(X_0) = \langle X_0|H(X_0)|X_0\rangle \tag{1}$$

where $H(X_0)$ is the Hamiltonian. The total energy at a displaced geometry $X = X_0 + \mu$ may be expanded around X_0 (see Appendix A for notation)

$$\begin{aligned} W(X_0 + \mu) &= \langle X_0 + \mu|H(X_0 + \mu)|X_0 + \mu\rangle \\ &= W^{(0)} + \mu W^{(1)} + \tfrac{1}{2}\mu\mu W^{(2)} + \tfrac{1}{6}\mu\mu\mu W^{(3)} + \cdots \end{aligned} \tag{2}$$

where $W^{(0)}$ is the total energy at X_0, $W^{(1)}$ is the molecular gradient, $W^{(2)}$ is the molecular Hessian, and $W^{(3)}$ is the first molecular anharmonicity. In this review we discuss the analytical evaluation of these derivatives when $|X_0\rangle$ is approximated by multiconfiguration self-consistent field (MCSCF), configuration interaction (CI), coupled-cluster (CC), and Møller–Plesset perturbation theory (MPPT) wave functions. Most attention is given to the lower derivatives, as efficient computer implementations exist only in those cases.

The total energy has an explicit geometry dependence in the nuclear–electron and nuclear–nuclear interaction terms, and an implicit geometry dependence in the wave function. In approximate calculations where finite nuclear-fixed basis sets are used, the total energy has an explicit dependence also in the basis set. Using the technique of second quantization, the geometry dependence of the basis set may be transferred to the Hamiltonian. In Section II we describe how the Hamiltonian at $X_0 + \mu$ may be expanded around X_0

$$H(X_0 + \mu) = H^{(0)} + \mu H^{(1)} + \tfrac{1}{2}\mu\mu H^{(2)} + \tfrac{1}{6}\mu\mu\mu H^{(3)} + \cdots \tag{3}$$

where the coefficients $H^{(n)}$ contain all the geometry dependence originating from the use of the finite basis set. In some approaches (e.g., limited CI and CC) the molecular orbitals are determined in HF or MCSCF calculations prior to the calculation of the wave function. This orbital preoptimization creates an additional geometry dependence in the basis set, which is also transferred to the Hamiltonian.

In Sections III–VI the nuclear displacement operators $H^{(n)}$ are treated as perturbation operators and response function theory is used to determine the implicit geometry dependence of the wave function to each order in the nuclear displacement:

$$|X_0 + \mu\rangle = |X_0\rangle^{(0)} + \mu|X_0\rangle^{(1)} + \tfrac{1}{2}\mu\mu|X_0\rangle^{(2)} + \tfrac{1}{6}\mu\mu\mu|X_0\rangle^{(3)} + \cdots \tag{4}$$

By combining the order-by-order expansions of the Hamiltonian and the wave function we identify the geometrical derivatives $W^{(n)}$ and discuss computer implementations of these expressions.

In Section VII we describe how expressions for geometrical derivatives of molecular properties may be derived using the formalism developed for energy derivatives. We also discuss alternative definitions that may be used to determine geometrical derivatives of molecular properties for wave functions which do not satisfy the Hellmann–Feynman relationship for the property in question. Finally, in Section VIII we describe how translational and rotational symmetries may be used to reduce the cost of derivative calculations.

II. Hamiltonian Expansion

A. Hamiltonian at the Reference Geometry

The basic elements of the second-quantization formalism are the annihilation and creation operators (Linderberg and Öhrn, 1973). The annihilation operator a_p annihilates an electron in orbital ϕ_p (which we assume real), while the creation operator a_p^+ (the conjugate of a_p) creates an electron in orbital ϕ_p. These operators satisfy the anticommutation relations

$$[a_p, a_q]_+ = 0 \tag{5}$$

$$[a_p^+, a_q^+]_+ = 0 \tag{6}$$

$$[a_p^+, a_q]_+ = \delta_{pq} \tag{7}$$

if the orbitals ϕ_p are orthonormal. Omitting the nuclear–nuclear repulsion part the Hamiltonian is

$$H = \sum_{pq} h_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} e_{pqrs} \tag{8}$$

where

$$E_{pq} = \sum_{\sigma} a_{p\sigma}^+ a_{q\sigma} \tag{9}$$

are generators of the unitary group and

$$e_{pqrs} = E_{pq} E_{rs} - \delta_{rq} E_{ps} \tag{10}$$

In Eq. (9) the summation is over spin. In atomic units the one- and two-electron Hamiltonian integrals are obtained by integration over electronic coordinates according to

$$h_{pq} = \langle \phi_p(\xi_1) | h(\xi_1) | \phi_q(\xi_1) \rangle \tag{11}$$

$$g_{pqrs} = \langle \phi_p(\xi_1)\phi_q(\xi_1) | \xi_{12}^{-1} | \phi_r(\xi_2)\phi_s(\xi_2) \rangle \tag{12}$$

where ξ_1 denotes the coordinates of electron 1 and $\xi_{12} = |\xi_1 - \xi_2|$. The one-electron operator $h(\xi)$ is given by

$$h(\xi) = -\frac{1}{2}\nabla_\xi^2 - \sum_{\mathrm{A}} \frac{Z_{\mathrm{A}}}{|\xi - X_{\mathrm{A}}|} \tag{13}$$

where Z_{A} denotes the charge and X_{A} the position of nucleus A. In the linear combination of atomic orbitals (LCAO) approach the orbitals ϕ_p are expanded in a set of nonorthogonal atomic orbitals χ_μ fixed on the atomic nuclei:

$$\phi_p = \sum_{\mu} C_{p\mu}\chi_\mu \tag{14}$$

The integrals are calculated in terms of the atomic orbitals (AOs) and are subsequently transformed to the orthonormal basis. In some cases it may be more efficient to evaluate the expressions in the nonorthogonal AO basis. We return to this problem when we consider the calculation of the individual geometry derivatives. For the time being we assume that the Hamiltonian is expressed in the orthonormal molecular orbital (MO) basis. The second-quantized Hamiltonian [Eq. (8)] is a projection of the full Hamiltonian onto the space spanned by the molecular orbitals ϕ_p, i.e., the space in which calculations are carried out.

B. Orbital Connections

So far we have considered the Hamiltonian at one geometry, as appropriate for single-point calculations. However, if we wish to calculate the derivatives of the energy with respect to variations in the geometry, we must also consider the geometry dependence of the Hamiltonian. This introduces certain complications, which are treated in the remainder of this section.

The Hamiltonian integrals depend on the molecular geometry in two ways. The first is trivial and arises because the Coulomb interactions between the electrons and the nuclei depend on the geometry. The second is more complicated and arises because the orbitals are themselves functions of the geometry. The reason for this is that the MOs are expanded in a finite set of AOs fixed on the nuclear centers. A consequence of using a finite set of AOs is that we are presented with a different basis set at each geometry.

To study the geometry dependence of the Hamiltonian in any detail, we must first find a way to relate or "connect" orbitals at neighboring geometries X. In other words we must establish a one-to-one correspondence between orbitals at neighboring points. Rules that accomplish this are called orbital connections (Helgaker, 1986). In the LCAO approach the situation may be pictured as follows. At each geometry we have a set of AOs from which an infinite set of orthogonally equivalent orbital bases can be constructed. As the geometry changes we must pick out exactly one of these orbital bases at each geometry X. In this way an orthogonal orbital connection is established. (A connection is called orthogonal if it preserves orthonormality between the orbitals.) We further require that the connection is continuous and differentiable.

One may also wish to impose an additional requirement on the connection, namely that it is translationally and rotationally invariant. This may seem to be a trivial requirement. However, a connection is conveniently defined in terms of atomic Cartesian displacements rather than in terms of a set of nonredundant internal coordinates. This implies that each molecular geometry may be described in an infinite number of translationally and rotationally equivalent ways. The corresponding connections may be different and therefore not translationally and rotationally invariant. In other words, the orbital basis is not necessarily uniquely determined by the internal coordinates when the connections are defined in terms of Cartesian coordinates. Conversely, a rotationally invariant connection picks up the same basis set regardless of how the rotation is carried out and so the basis is uniquely defined by the internal coordinates. [For a discussion of translationally and rotationally invariant connections, see Carlacci and McIver (1986).]

In cases where fully orbital-optimized wave functions are used [e.g., MCSCF or AGP (antisymmetrized geminal power)] it does not matter what particular orbital basis is chosen at a given geometry as long as the connection is orthogonal. For example, at any geometry an MCSCF wave function can be constructed from an arbitrary orthonormal basis by parametrizing the MCSCF state in terms of exponential orthogonal configuration and orbital transformations of a nonoptimized reference state [see Eq. (49)]. The parameters of the orthogonal transformations are determined from the variational principle. Usually we change the orbital basis in each iteration of MCSCF wave function optimizations, and the final MCSCF state is expressed in a basis for which the exponential orthogonal transformation corresponds to the identity transformation. In principle, however, we can carry out an MCSCF calculation at any geometry using an arbitrary set of orthonormal orbitals (Olsen *et al.*, 1983). From this it follows that we are free to choose whatever orthogonal connection we find most convenient.

In certain cases (e.g., limited CI and CC) the wave function at each geometry is expressed in terms of orbitals that are defined by some procedure independent of the actual wave function. This puts an extra constraint on our connection, namely that in addition to being orthonormal it must also connect these predefined orbitals.

C. Geometry Dependence of the Hamiltonian

First $X = X_0$ is chosen as the reference geometry and a set of orthonormal MOs are determined as linear combinations of AOs:

$$\phi_p(X_0) = \sum_{\mu} C^{(0)}_{p\mu}\chi_\mu(X_0) \tag{15}$$

The orthonormality of the MOs implies

$$S_{pq}(X_0) = \langle \phi_p(\xi; X_0) \,|\, \phi_q(\xi; X_0)\rangle = \sum_{\mu\nu} C^{(0)}_{p\mu}C^{(0)}_{q\nu}S^{\mathrm{AO}}_{\mu\nu}(X_0) = \delta_{pq} \tag{16}$$

where integration is over the electronic coordinates ξ. When the geometry changes the unmodified molecular orbitals $\phi_p(X)$ (UMOs) are no longer orthonormal:

$$S_{pq}(X) = \sum_{\mu\nu} C^{(0)}_{p\mu}C^{(0)}_{q\nu}S^{\mathrm{AO}}_{\mu\nu}(X) \neq \delta_{pq} \tag{17}$$

Provided the overlap matrix $S(X)$ is nonsingular we can define a set of orthonormal molecular orbitals (OMOs)

$$\psi(X) = U(X)S^{-1/2}(X)\phi(X) \tag{18}$$

where $S^{-1/2}(X)$ ensures that the connection is orthogonal (Helgaker and Almlöf, 1984) and the orthogonal matrix $U(X)$ makes the connection general (Helgaker, 1986) so that we can pick up any set of orthonormal orbitals, for example, a set of orbitals determined in an optimization prior to the wave function calculation. In the MCSCF case we may set $U(X)$ equal to the identity matrix, as any orthogonal connection can be used, and the OMOs $\psi(X)$ are then defined completely in terms of the unmodified molecular orbitals through the $S^{-1/2}$ matrix. A parametrization equivalent to Eq. (18) to be used in a Fock-operator formalism has been given by King *et al.* (1984).

Using the OMOs we may construct a Hamiltonian which is defined at all geometries (Jørgensen and Simons, 1983; Helgaker and Almlöf, 1984; Simons *et al.*, 1984)

$$H(X) = \sum_{pq} \tilde{h}_{pq}(X)E_{pq}(X) + \frac{1}{2}\sum_{pqrs} \tilde{g}_{pqrs}(X)e_{pqrs}(X) \tag{19}$$

where the geometry dependence of $E_{pq}(X)$ and $e_{pqrs}(X)$ will be discussed later.

The integrals which appear in this expression are given in terms of the UMOs as

$$\tilde{h}(X)_{pq} = \sum_{\alpha\beta} h_{\alpha\beta}(X) Y_{p\alpha}(X) Y_{q\beta}(X) \tag{20}$$

$$\tilde{g}(X)_{pqrs} = \sum_{\alpha\beta\gamma\delta} g_{\alpha\beta\gamma\delta}(X) Y_{p\alpha}(X) Y_{q\beta}(X) Y_{r\gamma}(X) Y_{s\delta}(X) \tag{21}$$

where we have introduced the connection matrix $Y(X)$

$$Y(X) = U(X) S^{-1/2}(X) \tag{22}$$

(We use indices $pqrs$ and $\alpha\beta\gamma\delta$ for general molecular orbitals and $\mu\nu\lambda\sigma$ for atomic orbitals.) The UMO integrals in Eqs. (20) and (21) are given as [compare the expression for the overlap matrix, Eq. (17)]

$$h_{pq}(X) = \sum_{\mu\nu} C^{(0)}_{p\mu} C^{(0)}_{q\nu} h^{\mathrm{AO}}_{\mu\nu}(X) \tag{23}$$

$$g_{pqrs}(X) = \sum_{\mu\nu\lambda\sigma} C^{(0)}_{p\mu} C^{(0)}_{q\nu} C^{(0)}_{r\lambda} C^{(0)}_{s\sigma} g^{\mathrm{AO}}_{\mu\nu\lambda\sigma}(X) \tag{24}$$

Note that in these integrals the geometry dependence is isolated in the atomic integrals.

We are now ready to discuss the geometry expansion of the Hamiltonian, Eq. (19). Both the integrals and the operators in this Hamiltonian are geometry dependent. In particular the geometry dependence of the operators $E_{pq}(X)$ and $e_{pqrs}(X)$ arises due to the geometry dependence of the orbitals. However, for our purposes we may treat these operators as geometry *independent* (Jørgensen and Simons, 1983; Helgaker and Almlöf, 1984). This can be seen in the following way.

The creation and annihilation operators always appear in expectation and transition densities such as $\langle\mu|a_p^+ a_q^+ a_s a_r|\nu\rangle$ where $|\mu\rangle$ and $|\nu\rangle$ are electronic configurations, i.e., space- and/or spin-symmetrized ordered products of creation operators working on the vacuum state. In the simplest case we have

$$|\mu\rangle = \prod_{p\in\mu} a_p^+|\mathrm{vac}\rangle \tag{25}$$

where the vacuum state is characterized by

$$a_p|\mathrm{vac}\rangle = 0 \tag{26}$$

The element $\langle\mu|a_p^+ a_q^+ a_s a_r|\nu\rangle$ may be written as a vacuum expectation value of a string of creation and annihilation operators such as $\langle\mathrm{vac}|a_{\mu_1} a_{\mu_2} \cdots a_{\mu_N} a_p^+ a_q^+ a_s a_r a_{\nu_N}^+ \cdots a_{\nu_2}^+ a_{\nu_1}^+|\mathrm{vac}\rangle$. According to Wick's theorem such vacuum expectation values can be expressed as a sum over all totally contracted terms, each of which depends only on the overlap between the orbitals. Since these are δ_{pq} for orthonormal orbitals, we see that the vacuum expectation values are geometry independent, provided the orbitals are orthonormal at all geometries. Since we use orthogonal connections this condition is fulfilled, and we may neglect the geometry dependence of the creation and annihilation operators in our derivations.

We may now expand the Hamiltonian in geometrical distortions about the reference geometry

$$H(X_0 + \mu) = H^{(0)} + \mu H^{(1)} + \tfrac{1}{2}\mu\mu H^{(2)} + \tfrac{1}{6}\mu\mu\mu H^{(3)} + \cdots \tag{27}$$

where, following the discussion above, each term has the form

$$H^{(n)} = \sum_{pq} \tilde{h}_{pq}^{(n)} E_{pq} + \frac{1}{2} \sum_{pqrs} \tilde{g}_{pqrs}^{(n)} e_{pqrs} \tag{28}$$

The geometry dependence of the Hamiltonian is isolated in the integrals. It only remains to determine the explicit form of $\tilde{h}_{pq}^{(n)}$ and $\tilde{g}_{pqrs}^{(n)}$.

If in Eq. (22) we introduce the matrices

$$Q = \ln U \tag{29}$$

$$R = \ln S^{-1/2} \tag{30}$$

where Q is antisymmetric and R symmetric, the Hamiltonian integrals can be written in an expansion in Q and R reminiscent of the Baker–Campbell–Hausdorff (BCH) commutator expansion for operators (Simons *et al.*, 1984). If we let I denote either the one- or the two-electron integrals, the OMO integrals may be written as

$$\begin{aligned}\tilde{I} = I &+ \{Q + R, I\} + \tfrac{1}{2}\{Q, Q, I\} + \{Q, \{R, I\}\} + \tfrac{1}{2}\{R, R, I\} \\ &+ \tfrac{1}{6}\{Q, Q, Q, I\} + \tfrac{1}{2}\{Q, Q, \{R, I\}\} + \tfrac{1}{2}\{Q, \{R, R, I\}\} \\ &+ \tfrac{1}{6}\{R, R, R, I\} + \cdots\end{aligned} \tag{31}$$

where we have used the notation for one-index transformations given in Appendix B, for example

$$\{A, h\}_{pq} = \sum_{\alpha}(A_{p\alpha}h_{\alpha q} + A_{q\alpha}h_{p\alpha}) \tag{32}$$

From the BCH expansion one may arrive at the expressions for the derivatives of the integrals $\tilde{I}$

$$\tilde{I} = \tilde{I}^{(0)} + \mu\tilde{I}^{(1)} + \tfrac{1}{2}\mu\mu\tilde{I}^{(2)} + \tfrac{1}{6}\mu\mu\mu\tilde{I}^{(3)} + \cdots \tag{33}$$

by expanding

$$I = I^{(0)} + \mu I^{(1)} + \tfrac{1}{2}\mu\mu I^{(2)} + \tfrac{1}{6}\mu\mu\mu I^{(3)} + \cdots \tag{34}$$

$$Q = \mu Q^{(1)} + \tfrac{1}{2}\mu\mu Q^{(2)} + \tfrac{1}{6}\mu\mu\mu Q^{(3)} + \cdots \tag{35}$$

$$R = \mu R^{(1)} + \tfrac{1}{2}\mu\mu R^{(2)} + \tfrac{1}{6}\mu\mu\mu R^{(3)} + \cdots \tag{36}$$

where $Q^{(0)}$ and $R^{(0)}$ are zero, as the OMO integrals are identical to the UMO integrals at the reference geometry. Identifying terms to same order we obtain

$$\tilde{I}^{(0)} = I^{(0)} \tag{37}$$

$$\tilde{I}^{(1)} = I^{(1)} + \{Q^{(1)} + R^{(1)}, I^{(0)}\} \tag{38}$$

$$\begin{aligned}\tilde{I}^{(2)} = I^{(2)} &+ 2\{Q^{(1)} + R^{(1)}, I^{(1)}\} + \{Q^{(2)} + R^{(2)}, I^{(0)}\} \\ &+ \{Q^{(1)}, Q^{(1)}, I^{(0)}\} + \{R^{(1)}, R^{(1)}, I^{(0)}\} + 2\{Q^{(1)}, \{R^{(1)}, I^{(0)}\}\}\end{aligned} \tag{39}$$

$$\begin{aligned}\tilde{I}^{(3)} = I^{(3)} &+ 3\{Q^{(1)} + R^{(1)}, I^{(2)}\} + 3\{Q^{(2)} + R^{(2)}, I^{(1)}\} \\ &+ \{Q^{(3)} + R^{(3)}, I^{(0)}\} + 3\{Q^{(1)}, Q^{(1)}, I^{(1)}\} + 6\{Q^{(1)}, \{R^{(1)}, I^{(1)}\}\} \\ &+ 3\{R^{(1)}, R^{(1)}, I^{(1)}\} + 3\{Q^{(1)}, Q^{(2)}, I^{(0)}\} + 3\{Q^{(1)}, \{R^{(2)}, I^{(0)}\}\} \\ &+ 3\{Q^{(2)}, \{R^{(1)}, I^{(0)}\}\} + 3\{R^{(1)}, R^{(2)}, I^{(0)}\} \\ &+ \{Q^{(1)}, Q^{(1)}, Q^{(1)}, I^{(0)}\} + \{R^{(1)}, R^{(1)}, R^{(1)}, I^{(0)}\} \\ &+ 3\{Q^{(1)}, Q^{(1)}, \{R^{(1)}, I^{(0)}\}\} + 3\{Q^{(1)}, \{R^{(1)}, R^{(1)}, I^{(0)}\}\}\end{aligned} \tag{40}$$

For (MC) SCF wave functions it is not necessary to include Q in the above expressions. The correct expressions are then obtained simply by omitting all terms containing derivatives of Q.

To calculate the above integrals one must know $Q^{(n)}$ and $R^{(n)}$. The derivatives of the rotation matrix Q are obtained by solving the appropriate response equations, as discussed in later sections. In some cases the explicit evaluation of $Q^{(n)}$ can be avoided by using the technique of Handy and Schaefer (1984). The expressions for $R^{(n)}$ in terms of the derivatives of the overlap matrix may be obtained by expanding R as

$$R = -\tfrac{1}{2}\Delta + \tfrac{1}{4}\Delta^2 - \tfrac{1}{6}\Delta^3 + \cdots \tag{41}$$

where Δ is defined as

$$S = 1 + \Delta \tag{42}$$

By expanding Δ in powers of μ and identifying terms to same order, we obtain (Helgaker and Almlöf, 1984)

$$R^{(1)} = -\tfrac{1}{2}S^{(1)} \tag{43}$$

$$R^{(2)} = -\tfrac{1}{2}S^{(2)} + \tfrac{1}{2}S^{(1)}S^{(1)} \tag{44}$$

$$R^{(3)} = -\tfrac{1}{2}S^{(3)} + \tfrac{3}{4}S^{(1)}S^{(2)} + \tfrac{3}{4}S^{(2)}S^{(1)} - S^{(1)}S^{(1)}S^{(1)} \tag{45}$$

where $S^{(n)}$ can be calculated using standard techniques for calculation of atomic orbital integrals.

D. Calculation of Atomic Orbital Integrals

It is not our purpose to discuss in detail methods for evaluation of molecular integrals. At present two techniques are in general use—the Rys quadrature method introduced by Dupuis *et al.* (1976), and the incomplete gamma function method as formulated by McMurchie and Davidson (1978). Efficient computer codes for calculating derivative integrals exist using both techniques. For example, the GAUSSIAN 86 (Frisch *et al.*, 1984), HONDO (Dupuis *et al.*, 1976), GRADSCF (Komornicki, 1980), and CADPAC (Amos, 1984a) programs all use the Rys quadrature method, while ABACUS (Helgaker *et al.*, 1986a) uses the McMurchie–Davidson scheme. Neither method appears to be superior. [For reviews and comparisons of the two approaches, see Saunders (1983) and Hegarty and van der Velde (1983).] A good discussion of integral evaluation with emphasis on derivatives has been given by Gaw and Handy (1984). Recently, an interesting new recursive scheme for calculation of integrals has been presented by Obara and Saika (1986). However, too little experience is available to judge the merits of the Obara–Saika scheme.

III. Derivatives from Multiconfiguration Self-Consistent-Field Wave Functions

A. MCSCF Electronic Energy

We assume that an MCSCF calculation has been carried out at the reference geometry X_0 and denote the MCSCF state at this geometry by $|\mathrm{MC}\rangle$. The MCSCF state may be expressed as

$$|\mathrm{MC}\rangle = \sum_{\nu} C_{\nu}^{\mathrm{MC}} |\nu\rangle \tag{46}$$

where C^{MC} are the expansion coefficients of the determinants

$$|\nu\rangle = \prod_{r \in \nu} a_r^{+} |\mathrm{vac}\rangle \tag{47}$$

where $\{a_r^{+}\}$ refer to the orthonormal set of MCSCF orbitals $\{\psi_r\}$. The orthogonal complement set of states $\{|k\rangle\}$ to $|\mathrm{MC}\rangle$ may be written as

$$|k\rangle = \sum_{\nu} C_{\nu}^{k} |\nu\rangle \tag{48}$$

where the coefficients $C = \{C^{\mathrm{MC}}, C^{k}\}$ form an orthogonal matrix. The MCSCF state $|\mathrm{MC}(\mu)\rangle$ at a displaced geometry $X_0 + \mu$ may be obtained by an orthogonal transformation of the state $|\mathrm{MC}\rangle$ at the reference geometry

$$|\mathrm{MC}(\mu)\rangle = \exp(-\kappa)\exp(-P)|\mathrm{MC}\rangle \tag{49}$$

where (Dalgaard, 1979)

$$\exp(-P) = \exp\left[-\sum_{k\neq \mathrm{MC}} P_k(|k\rangle\langle \mathrm{MC}| - |\mathrm{MC}\rangle\langle k|)\right]$$

$$= \exp\left[-\sum_{k\neq \mathrm{MC}} P_k(R_k^+ - R_k)\right] \tag{50}$$

describes the orthogonal transformation in the configuration space and (Jørgensen and Linderberg, 1970; Levy, 1970)

$$\exp(-\kappa) = \exp\left[-\sum_{r>s} \kappa_{rs}(E_{rs} - E_{sr})\right] \tag{51}$$

describes the orthogonal transformation in the orbital space. Only nonredundant orbital rotations (Dalgaard and Jørgensen, 1978; Hoffmann *et al.*, 1984) are included in κ. With the ansatz of Eq. (49) we may express an arbitrary state spanned by the orbital and configuration space in terms of a particular set of nonredundant orbital $\{\kappa_{rs}\}$ and state $\{P_k\}$ parameters. One of these sets represents the optimized state at the displaced geometry (Jørgensen and Simons, 1983; Helgaker and Almlöf, 1984).

The total energy of the MCSCF state at the displaced geometry is

$$W(X_0 + \mu, \kappa, P) = \langle \mathrm{MC}(\mu)|H(X_0 + \mu)|\mathrm{MC}(\mu)\rangle$$

$$= \langle \mathrm{MC}| \exp(P)\exp(\kappa)H(X_0 + \mu)\exp(-\kappa)\exp(-P)|\mathrm{MC}\rangle \tag{52}$$

where the orbital connection of the Hamiltonian contains only finite basis reorthonormalization contributions. The variational parameters $\{\kappa_{rs}; r > s\}$ and $\{P_k; k \neq \mathrm{MC}\}$, and the operators $E^+ = \{E_{rs}; r > s\}$ and $R^+ = \{R_k^+; k \neq \mathrm{MC}\}$ may be arranged as column vectors

$$\lambda = \begin{pmatrix} \kappa \\ P \end{pmatrix} \tag{53}$$

$$\Lambda = \begin{pmatrix} E^+ - E \\ R^+ - R \end{pmatrix} \tag{54}$$

Inserting the Hamiltonian expansion [Eq. (27)] in Eq. (52) and using the BCH expansion, we obtain

$$\begin{aligned} W(X_0 + \mu, \lambda) = {} & E^{(0)} + \mu E^{(1)} + \tfrac{1}{2}\mu\mu E^{(2)} + \tfrac{1}{6}\mu\mu\mu E^{(3)} \\ & + \mu f^{(1)}\lambda + \tfrac{1}{2}\mu\mu f^{(2)}\lambda + \tfrac{1}{6}\mu\mu\mu f^{(3)}\lambda \\ & + \tfrac{1}{2}G^{(0)}\lambda\lambda + \tfrac{1}{2}\mu G^{(1)}\lambda\lambda + \tfrac{1}{4}\mu\mu G^{(2)}\lambda\lambda \\ & + \tfrac{1}{6}K^{(0)}\lambda\lambda\lambda + \tfrac{1}{6}\mu K^{(1)}\lambda\lambda\lambda \\ & + \tfrac{1}{24}L^{(0)}\lambda\lambda\lambda\lambda + \cdots \end{aligned} \tag{55}$$

where

$$E^{(i)} = \langle \mathrm{MC}|H^{(i)}|\mathrm{MC}\rangle \tag{56}$$

$$f^{(i)} = \langle \mathrm{MC}|[\Lambda, H^{(i)}]|\mathrm{MC}\rangle \tag{57}$$

$$G^{(i)} = \langle \mathrm{MC}|[\Lambda, \Lambda, H^{(i)}]|\mathrm{MC}\rangle \tag{58}$$

are the electronic energy, gradient, and Hessian, and where

$$K^{(i)} = \langle \mathrm{MC}|[\Lambda, \Lambda, \Lambda, H^{(i)}]|\mathrm{MC}\rangle \tag{59}$$

$$L^{(i)} = \langle \mathrm{MC}|[\Lambda, \Lambda, \Lambda, \Lambda, H^{(i)}]|\mathrm{MC}\rangle \tag{60}$$

are the third and fourth electronic derivatives. In Eqs. (58)–(60) we have used the symmetric commutators (Olsen *et al.*, 1983). The gradient $f^{(0)}$ is zero since the MCSCF energy is stationary at X_0.

B. MCSCF Response Equations

The geometry dependence of the variational parameters λ is determined from the requirement that the total energy in Eq. (55) must be stationary in the perturbed field:

$$dW(X_0 + \mu, \lambda)/d\lambda = 0 \tag{61}$$

We obtain

$$\begin{aligned} -G^{(0)}\lambda = {} & \mu f^{(1)} + \tfrac{1}{2}\mu\mu f^{(2)} + \tfrac{1}{6}\mu\mu\mu f^{(3)} + \mu G^{(1)}\lambda + \tfrac{1}{2}\mu\mu G^{(2)}\lambda \\ & + \tfrac{1}{2}K^{(0)}\lambda\lambda + \tfrac{1}{2}\mu K^{(1)}\lambda\lambda + \tfrac{1}{6}L^{(0)}\lambda\lambda\lambda + \cdots \end{aligned} \tag{62}$$

The variational parameters may be expanded in a power series in the nuclear displacement

$$\lambda = \mu\lambda^{(1)} + \tfrac{1}{2}\mu\mu\lambda^{(2)} + \tfrac{1}{6}\mu\mu\mu\lambda^{(3)} + \cdots \tag{63}$$

where the zeroth-order term vanishes as the MCSCF state $|\mathrm{MC}\rangle$ is optimized at X_0. Solving Eq. (62) to each order in μ gives

$$-G^{(0)}\lambda^{(1)} = f^{(1)} \tag{64}$$

$$-G^{(0)}\lambda^{(2)} = f^{(2)} + 2G^{(1)}\lambda^{(1)} + K^{(0)}\lambda^{(1)}\lambda^{(1)} \tag{65}$$

$$\begin{aligned} -G^{(0)}\lambda^{(3)} = {} & f^{(3)} + 3G^{(1)}\lambda^{(2)} + 3G^{(2)}\lambda^{(1)} \\ & + 3K^{(0)}\lambda^{(2)}\lambda^{(1)} + 3K^{(1)}\lambda^{(1)}\lambda^{(1)} \\ & + L^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} \end{aligned} \tag{66}$$

These equations describe how the MCSCF state responds through first, second, and third orders to a nuclear displacement.

The first-order MCSCF response equations were first derived by Dalgaard and Jørgensen (1978). For geometrical perturbations these equations were derived by Osamura *et al.* (1982a) using a Fock-operator approach.

C. MCSCF Energy Derivatives

Inserting the power-series expansion of λ [Eq. (63)] in the total energy expression in Eq. (55) allows us to identify the geometrical derivatives for the MCSCF wave function as

$$W^{(1)} = E^{(1)} \tag{67}$$

$$\begin{aligned} W^{(2)} &= E^{(2)} + 2f^{(1)}\lambda^{(1)} + G^{(0)}\lambda^{(1)}\lambda^{(1)} \\ &= E^{(2)} + f^{(1)}\lambda^{(1)} \end{aligned} \tag{68}$$

$$\begin{aligned} W^{(3)} &= E^{(3)} + 3f^{(1)}\lambda^{(2)} + 3f^{(2)}\lambda^{(1)} \\ &\quad + 3G^{(0)}\lambda^{(2)}\lambda^{(1)} + 3G^{(1)}\lambda^{(1)}\lambda^{(1)} + K^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} \\ &= E^{(3)} + 3f^{(2)}\lambda^{(1)} + 3G^{(1)}\lambda^{(1)}\lambda^{(1)} \\ &\quad + K^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} \end{aligned} \tag{69}$$

In the identification of $W^{(3)}$ we have used the first-order response equations [Eq. (64)] to eliminate $\lambda^{(2)}$. From Eqs. (68) and (69) we see that the first-order correction to the wave function determines the energy through third order. In general the nth-order response of the wave function determines the energy through order $2n + 1$.

The MCSCF gradient expression was first given by Pulay (1977). The MCSCF Hessian and first anharmonicity expressions were derived by Pulay (1983) using a Fock-operator approach, and by Jørgensen and Simons (1983) and Simons and Jørgensen (1983) using a response function approach.

D. Implementation of MCSCF Derivative Expressions

1. *MCSCF Gradients*

From Eq. (67) we see that the expression for the molecular gradient is

$$W^{(1)} = \langle \mathrm{MC}|H^{(1)}|\mathrm{MC}\rangle \tag{70}$$

where $H^{(1)}$ contains the first derivatives of the OMO integrals $\tilde{I}^{(1)}$. An explicit expression for these derivatives is obtained by combining Eqs. (38) and (43) of Section II. This gives us

$$\tilde{I}^{(1)} = I^{(1)} - \tfrac{1}{2}\{S^{(1)}, I^{(0)}\} \tag{71}$$

since the rotational part of the connection may be omitted for MCSCF wave functions. The Hamiltonian may therefore be written

$$H^{(1)} = H^{[1]} - \tfrac{1}{2}(S^{(1)}, H^{[0]}) \tag{72}$$

where we have used the square bracket superscript notation as explained in Appendix A, and the notation for operators containing one-index transformed integrals as introduced in Appendix B. Inserting this expression in Eq. (70), we obtain

$$W^{(1)} = \mathrm{Tr}\, Dh^{(1)} + \tfrac{1}{2}\mathrm{Tr}\, dg^{(1)} - \mathrm{Tr}\, S^{(1)}F^{[0]} \tag{73}$$

where we have used Eq. (D.4) and the notation for trace operations and density elements as given in Appendix D. Also we have used the identity [Eq. (F.1)]

$$\langle \mathrm{MC}|(S^{(1)}, H^{[0]})|\mathrm{MC}\rangle = 2\mathrm{Tr}\, S^{(1)}F^{[0]} \tag{74}$$

Here $F^{[n]}$ is the Fock matrix, which is discussed in detail in Appendix E.

The gradient expression given above is not particularly useful since it appears in the MO basis. Following the discussion in Appendix C about covariant and contravariant representations, we may rewrite the gradient as

$$W^{(1)} = \mathrm{Tr}\, D_{\mathrm{ao}}h^{(1)}_{\mathrm{AO}} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}}g^{(1)}_{\mathrm{AO}} - \mathrm{Tr}\, S^{(1)}_{\mathrm{AO}}F^{[0]}_{\mathrm{ao}} \tag{75}$$

where ao denotes contravariant and AO covariant components. Since all derivative integrals now appear in the covariant AO representation in which they are calculated, no integral transformation is required. The MCSCF gradient was first implemented by Goddard *et al.* (1979) and Kato and Morokuma (1979).

2. *MCSCF Hessians*

The MCSCF Hessian as given by Eq. (68) contains two terms. The first contribution

$$E^{(2)} = \langle \mathrm{MC}|H^{(2)}|\mathrm{MC}\rangle \tag{76}$$

may be treated in the same way as the molecular gradient $\langle \mathrm{MC}|H^{(1)}|\mathrm{MC}\rangle$. The integrals

$$\tilde{I}^{(2)} = I^{(2)} - \{S^{(1)}, I^{(1)}\} - \tfrac{1}{2}\{S^{(2)} - S^{(1)}S^{(1)}, I^{(0)}\} + \tfrac{1}{4}\{S^{(1)}, \{S^{(1)}, I^{(0)}\}\} \tag{77}$$

give rise to the operator

$$H^{(2)} = H^{[2]} - (S^{(1)}, H^{[1]}) - \tfrac{1}{2}(S^{(2)} - S^{(1)}S^{(1)}, H^{[0]}) + \tfrac{1}{4}(S^{(1)}, (S^{(1)}, H^{[0]})) \tag{78}$$

Taking the expectation value of this operator we obtain

$$\begin{aligned} E^{(2)} = {} & \mathrm{Tr}\, Dh^{(2)} + \tfrac{1}{2}\mathrm{Tr}\, dg^{(2)} - 2\mathrm{Tr}\, S^{(1)}F^{[1]} \\ & - \mathrm{Tr}[(S^{(2)} - S^{(1)}S^{(1)})F^{[0]}] + \tfrac{1}{2}\mathrm{Tr}[S^{(1)}(S^{(1)}, F^{[0]})] \end{aligned} \tag{79}$$

where $(S^{(1)}, F^{[0]})$ is the Fock matrix constructed from one-index transformed integrals (see Appendix E). As for the molecular gradient some of the terms are best calculated in the AO basis. A convenient working expression is

$$\begin{aligned} E^{(2)} = {} & \mathrm{Tr}\, D_{\mathrm{ao}}h^{(2)}_{\mathrm{AO}} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}}g^{(2)}_{\mathrm{AO}} - \mathrm{Tr}\, S^{(2)}_{\mathrm{AO}}F^{[0]}_{\mathrm{ao}} \\ & - 2\mathrm{Tr}\, S^{(1)}F^{[1]} + \mathrm{Tr}(S^{(1)}S^{(1)}F^{[0]}) + \tfrac{1}{2}\mathrm{Tr}[S^{(1)}(S^{(1)}, F^{[0]})] \end{aligned} \tag{80}$$

in which all second-derivative integrals appear in the covariant AO representation.

The evaluation of the second contribution to the MCSCF Hessian requires the construction of $f^{(1)}$ and the solution of the linear set of equations [Eq. (64)]:

$$G^{(0)}\lambda^{(1)} + f^{(1)} = 0 \tag{81}$$

Before discussing the solution of these equations, we consider the evaluation of $f^{(1)}$.

The orbital components of $f^{(1)}$ may be written as [see Eq. (E.2)]

$$f^{(1)}_{pq} = 2(F^{(1)}_{pq} - F^{(1)}_{qp}) \tag{82}$$

where $F^{(1)}$ is the Fock matrix calculated from the Hamiltonian $H^{(1)}$ of Eq. (72) [see Eq. (E.1)]. Then $F^{(1)}$ may be decomposed as

$$F^{(1)} = F^{[1]} - \tfrac{1}{2}(S^{(1)}, F^{[0]}) \tag{83}$$

where $F^{[1]}$ and $(S^{(1)}, F^{[0]})$ are the Fock matrices constructed from the UMO integrals $I^{(1)}$ and the one-index transformed integrals $\{S^{(1)}, I^{(0)}\}$, respectively. The calculation of these matrices is described in Appendix E.

The configuration part of $f^{(1)}$

$$f^{(1)}_k = \langle \mathrm{MC}|[R^+_k - R_k, H^{(1)}]|\mathrm{MC}\rangle = -2\langle \mathrm{MC}|H^{(1)}|k\rangle \tag{84}$$

refers to the orthogonal complement set of states $\{|k\rangle\}$ and may, for small configuration expansions, be calculated straightforwardly using, for example, the states obtained by diagonalizing the Hamiltonian matrix. For larger configuration spaces it is convenient to calculate $f^{(1)}_k$ from the configuration space equivalent of Eq. (84) [$\langle \mathrm{MC}|H^{(1)}|\nu\rangle$] (Lengsfield and Liu, 1981; Lengsfield, 1982). This requires no further consideration if all vectors multiplied on $f^{(1)}$ are orthogonal to $|\mathrm{MC}\rangle$. If this is not the case the $|\mathrm{MC}\rangle$ component of Eq. (84) must be projected out

$$f^{(1)}_\nu = -2\langle \nu|H^{(1)}|\mathrm{MC}\rangle + 2C^{\mathrm{MC}}_\nu\langle \mathrm{MC}|H^{(1)}|\mathrm{MC}\rangle \tag{85}$$

Note that $\langle \mathrm{MC}|H^{(1)}|\mathrm{MC}\rangle$ is the molecular gradient. The configuration part of $f^{(1)}$ may thus be evaluated in the configuration basis requiring $I^{(1)}$ and $\{S^{(1)}, I^{(0)}\}$ in the MO basis with all four indices active.

For small configuration expansions the linear equations [Eq. (81)] can be solved by constructing the MCSCF electronic Hessian $G^{(0)}$ in an explicit representation of the orthogonal complement. For larger expansions $G^{(0)}$ cannot be constructed explicitly. The solution must then be determined by an iterative method. In the algorithm described below new trial vectors are obtained using a modification of the conjugate-gradient algorithm (Hestenes, 1980).

In an iterative scheme linear transformations are carried out on trial vectors using $G^{(0)}$ as transformation matrix:

$$\sigma_i = G^{(0)} b_i \tag{86}$$

Assume that in the nth iteration we have generated n orthonormal trial vectors orthogonal to $|\mathrm{MC}\rangle$

$$\{b_1, b_2, \ldots, b_n\} \tag{87}$$

and calculated the transformed vectors

$$\{\sigma_1, \sigma_2, \ldots, \sigma_n\} \tag{88}$$

The reduced linear equations

$$G^{\mathrm{R}} \lambda^{\mathrm{R}} + f^{\mathrm{R}} = 0 \tag{89}$$

where

$$G^{\mathrm{R}}_{ij} = \tilde{b}_i G^{(0)} b_j = \tilde{b}_i \sigma_j \tag{90}$$

$$f^{\mathrm{R}}_i = \tilde{b}_i f^{(1)} \tag{91}$$

determine the best solution λ^{R} in the basis of the trial vectors. To obtain a new trial vector we divide the residual

$$\delta^{(1)} = G^{(0)}\left(\sum_i b_i \lambda^{\mathrm{R}}_i\right) + f^{(1)} = \sum_i \sigma_i \lambda^{\mathrm{R}}_i + f^{(1)} \tag{92}$$

by the diagonal Hessian elements, orthonormalize the resulting vector against $|\mathrm{MC}\rangle$ and the previous trial vectors, and add it to the basis of trial vectors. The iterative procedure is continued until the residual is smaller than a preset threshold.

For large configuration expansions the linear transformation Eq. (86) is the time-consuming step in the iterative scheme. For convenience we write the linear transformation as

$$\begin{pmatrix} {}^{\mathrm{c}}\sigma \\ {}^{\mathrm{o}}\sigma \end{pmatrix} = \begin{pmatrix} {}^{\mathrm{cc}}G^{(0)} & {}^{\mathrm{co}}G^{(0)} \\ {}^{\mathrm{oc}}G^{(0)} & {}^{\mathrm{oo}}G^{(0)} \end{pmatrix} \begin{pmatrix} {}^{\mathrm{c}}b \\ {}^{\mathrm{o}}b \end{pmatrix} \tag{93}$$

where superscripts c and o denote the configuration and orbital blocks, respectively. After some simple algebra the working equations are seen to be (Olsen *et al.*, 1983)

$$\sum_\nu G^{(0)}_{\mu,\nu} b_\nu = 2(\langle \mu | H^{(0)} | B \rangle - b_\mu E^{(0)}) \tag{94}$$

$$\sum_\nu G^{(0)}_{pq,\nu} b_\nu = -2(\langle \mathrm{MC} | [E_{pq}, H^{(0)}] | B \rangle + \langle B | [E_{pq}, H^{(0)}] | \mathrm{MC} \rangle) \tag{95}$$

$$\sum_{r>s} G^{(0)}_{\mu,rs} b_{rs} = -2\langle \mu | K | \mathrm{MC} \rangle \tag{96}$$

$$\sum_{r>s} G^{(0)}_{pq,rs} b_{rs} = 2\langle \mathrm{MC} | [E_{pq}, K] | \mathrm{MC} \rangle \tag{97}$$

where

$$|B\rangle = \sum_{\mu} b_{\mu} |\mu\rangle \tag{98}$$

$$K = ({}^{o}b, H^{(0)}) \tag{99}$$

A linear transformation of a configuration vector ${}^{c}b$ thus requires the construction of a configuration gradient with $|B\rangle$ as the reference state [Eq. (94)], and the construction of an orbital gradient with a symmetric transition density matrix [Eq. (95)]. A linear transformation on an orbital vector ${}^{o}b$ requires the construction of a configuration gradient [Eq. (96)] and an orbital gradient [Eq. (97)] from the one-index transformed Hamiltonian K.

A straightforward implementation of the above algorithm converges slowly mainly because of large off-diagonal elements in the orbital–orbital block ${}^{oo}G^{(0)}$ of the Hessian. The following three techniques can be used to speed up convergence (Helgaker *et al.*, 1986a).

1. Solve for several or all Cartesian displacements simultaneously. Sharing trial vectors reduces the number of vectors that must be generated.
2. Split the trial vectors into two sets, one which spans the orbital part of the solution only and one which spans the configuration part only. Usually a large number of orbital trial vectors is needed while the configuration vectors converge much faster.
3. For the current approximate configuration part of the solution vector, find the exact solution of the orbital part. This reduces the number of configuration gradients $\langle \mu | K | \mathrm{MC} \rangle$ [Eq. (96)] that must be calculated.

The relaxation contribution to the MCSCF molecular Hessian

$$-f^{(1)}(G^{(0)})^{-1}f^{(1)} = f^{(1)}\lambda^{(1)} \tag{100}$$

may be evaluated straightforwardly as written if the exact solution of the response equation is known. If the solution vectors are determined iteratively to a preset residual norm then errors in Eq. (100) will be linear in the residual error. However, Eq. (100) may be written in a different form, which (at essentially no extra cost) gives errors quadratic in the residual error (Sellers, 1986). We refer to Appendix G for a detailed discussion of linear and quadratic errors.

The first implementations of general MCSCF Hessians were reported by Hoffmann *et al.* (1984) and shortly after by Page *et al.* (1984a). A program capable of handling large configuration spaces using the techniques described in this section has been presented by Helgaker *et al.* (1986a).

3. *MCSCF First Anharmonicities*

The first anharmonicity [Eq. (69)] contains four terms. Using Eq. (40) the first term may be written as

$$\begin{aligned} E^{(3)} = \langle \mathrm{MC} | & H^{[3]} + 3(R^{(1)}, H^{[2]}) + 3(R^{(2)}, H^{[1]}) \\ & + 3(R^{(1)}, R^{(1)}, H^{[1]}) + (R^{(3)}, H^{[0]}) \\ & + 3(R^{(1)}, R^{(2)}, H^{[0]}) + (R^{(1)}, R^{(1)}, R^{(1)}, H^{[0]}) | \mathrm{MC} \rangle \qquad (101) \end{aligned}$$

where $R^{(1)}$, $R^{(2)}$, and $R^{(3)}$ [see Eqs. (43)–(45)] are easily calculated. Using the same techniques as for the gradient and the Hessian we obtain

$$\begin{aligned} E^{(3)} = {} & \mathrm{Tr}\, D_{\mathrm{ao}} h^{(3)}_{\mathrm{AO}} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}} g^{(3)}_{\mathrm{AO}} + 6\mathrm{Tr}\, R^{(1)}_{\mathrm{ao}} F^{[2]}_{\mathrm{AO}} \\ & + 6\mathrm{Tr}\, R^{(2)} F^{[1]} + 6\mathrm{Tr}[R^{(1)}(R^{(1)}, F^{[1]})] + 2\mathrm{Tr}\, R^{(3)} F^{[0]} \\ & + 3\mathrm{Tr}[R^{(1)}(R^{(2)}, F^{[0]})] + 3\mathrm{Tr}[R^{(2)}(R^{(1)}, F^{[0]})] \\ & + 2\mathrm{Tr}[R^{(1)}(R^{(1)}, (R^{(1)}, F^{[0]}))] \qquad (102) \end{aligned}$$

The terms containing second and third derivative integrals may be evaluated in the AO basis, while those containing first derivative integrals require two general and two active indices in the MO basis.

The second term in Eq. (69) is $f^{(2)}\lambda^{(1)}$, where the electronic gradient $f^{(2)}$ is constructed from the Hamiltonian

$$\begin{aligned} H^{(2)} = {} & H^{[2]} - (S^{(1)}, H^{[1]}) - \tfrac{1}{2}(S^{(2)}, H^{[0]}) \\ & + \tfrac{1}{4}(S^{(1)}, (S^{(1)}, H^{[0]})) + \tfrac{1}{2}(S^{(1)}S^{(1)}, H^{[0]}) \qquad (103) \end{aligned}$$

The contributions to $f^{(2)}$ from $H^{[1]}$ and $H^{[0]}$ may be easily evaluated if $I^{(1)}$ are available in the MO basis with two general and two active indices, and $I^{(0)}$ with three general and one active indices. The contribution from $H^{[2]}$ may be calculated in the AO basis, as will now be discussed. Using Eqs. (D.7) and (F.5), we obtain

$$\begin{aligned} f^{[2]}\lambda^{(1)} & = {}^{\mathrm{c}}f^{[2]\mathrm{c}}\lambda^{(1)} + {}^{\mathrm{o}}f^{[2]\mathrm{o}}\lambda^{(1)} \\ & = -2\mathrm{Tr}\, D^{\mathrm{P}}_{\mathrm{ao}} h^{(2)}_{\mathrm{AO}} - \mathrm{Tr}\, d^{\mathrm{P}}_{\mathrm{ao}} g^{(2)}_{\mathrm{AO}} + 2\mathrm{Tr}\, \kappa^{(1)}_{\mathrm{ao}} F^{[2]}_{\mathrm{AO}} \qquad (104) \end{aligned}$$

where

$$|P\rangle = \sum_k |k\rangle P^{(1)}_k \qquad (105)$$

The evaluation of $f^{(2)}\lambda^{(1)}$ thus requires the same differentiated integrals in the MO basis as does the evaluation of $E^{(3)}$.

The third term in Eq. (69) should be calculated carrying out the linear transformation $G^{(1)}\lambda^{(1)}$. [The reason this and similar terms discussed later should be calculated using linear transformations is that we only need to know the projection of $G^{(1)}$ onto the solution vectors $\lambda^{(1)}$, and not $G^{(1)}$ itself. Constructing $G^{(1)}$ explicitly constitutes a much heavier task than carrying out linear transformations in a direct fashion.] The transformation $G^{(1)}\lambda^{(1)}$ is identical to $G^{(0)}b$ described in Eqs. (94)–(97), except that the $I^{(0)}$ integrals are replaced by $\tilde{I}^{(1)}$. The linear transformation requires $I^{(1)}$ and $\{S^{(1)}, I^{(0)}\}$ with two general and two active indices. The requirements on the integrals are therefore the same as in the calculation of $E^{(3)}$.

The evaluation of the last term in Eq. (69) requires linear transformations $K^{(0)}\lambda^{(1)}\lambda^{(1)}$ to be carried out. Such transformations were described by Olsen *et al.* (1982) for small configuration spaces with an explicit representation of the orthogonal complement space in connection with cubically convergent MCSCF optimization techniques. For larger configuration spaces it is better to work in the configuration-based representation given by Olsen and Jørgensen (1985).

To summarize, the first anharmonicity may be evaluated for an MCSCF wave function with second and third derivative integrals in the AO basis, first derivative integrals in the MO basis with two general and two active indices, and undifferentiated integrals with three general and one active indices.

E. Hartree–Fock Derivatives

Some simplifications occur in the MCSCF derivative expressions for single-configuration self-consistent field wave functions. The most important is that the calculations can be carried out in the AO basis as discussed below.

After omitting all contributions to the MCSCF derivatives which arise from variations in the configuration space, the remaining terms either already appear in the AO basis (e.g., all terms $\langle \mathrm{MC}|H^{[n]}|\mathrm{MC}\rangle$), or they are expressed in terms of Fock matrices. In the MCSCF case these matrices are partly calculated in the MO basis. In contrast, SCF Fock matrices (which may be calculated from the inactive Fock matrices) are straightforwardly calculated in the AO basis, as described in Appendix E. (This is also true for SCF Fock matrices constructed from multiply one-index transformed integrals.) This implies that SCF derivatives can be calculated completely in the AO basis. We give some examples to make this point clear.

Consider first the SCF response equations [Eq. (64)]. The construction of $f^{(1)}$ [see Eqs. (82) and (83)] requires the calculation of ${}^{i}F^{[1]}$ and $(S^{(1)}, {}^{i}F^{[0]})$, i.e., the calculation of inactive Fock matrices from differentiated integrals and from one-index transformed integrals. Both matrices may be calculated in the AO basis (see Appendix E). Furthermore, the solution of the response equations requires linear transformations of orbital trial vectors. Equation

(97) shows how the transformed vectors may be obtained from one-index transformed Fock matrices. We conclude that the SCF response equations may be solved with no reference to MO integrals (Bacskay, 1981).

The evaluation of $E^{(n)}$ requires the construction of Fock matrices from multiply one-index transformed integrals. For example, $E^{(3)}$ contains the term

$$\langle \mathrm{HF}|(R^{(1)}, R^{(1)}, R^{(1)}, H^{[0]})|\mathrm{HF}\rangle = 2\mathrm{Tr}[R^{(1)}(R^{(1)}, (R^{(1)}, {}^{\mathrm{i}}F^{[0]}))] \tag{106}$$

which requires the calculation of inactive Fock matrices from integrals which have been one-index transformed twice. These matrices may be calculated in the AO basis as described in Eq. (E.17).

All contributions to the molecular derivatives involving the higher electronic derivatives [Eqs. (59) and (60)] may be treated as direct linear transformations and calculated in terms of inactive Fock matrices containing multiply one-index transformed integrals. For example, the first anharmonicity contains the term

$$\begin{aligned} K^{(0)}\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} &= \langle \mathrm{HF}|[\Lambda, \Lambda, \Lambda, H^{(0)}]|\mathrm{HF}\rangle\lambda^{(1)}\lambda^{(1)}\lambda^{(1)} \\ &= \langle \mathrm{HF}|[\kappa^{(1)}, \kappa^{(1)}, \kappa^{(1)}, H^{(0)}]|\mathrm{HF}\rangle \\ &= \langle \mathrm{HF}|(\kappa^{(1)}, \kappa^{(1)}, \kappa^{(1)}, H^{(0)})|\mathrm{HF}\rangle \\ &= 2\mathrm{Tr}[\kappa^{(1)}(\kappa^{(1)}, (\kappa^{(1)}, {}^{\mathrm{i}}F^{[0]}))] \end{aligned} \tag{107}$$

which is calculated in the same way as Eq. (106), i.e., from inactive Fock matrices containing integrals which have been one-index transformed twice.

The expression for HF gradients was first derived by Bratož (1958), and the first practical implementation was reported by Pulay (1969, 1970). HF Hessians were first implemented by Thomsen and Swanstrøm (1973), based on the work by Bratož (1958) and Gerratt and Mills (1968). The first practical implementation was reported by Pople *et al.* (1979). Third derivative expressions were derived by Moccia (1970). Further developments and the first implementation of third derivatives were reported by Gaw *et al.* (1984). Very recently analytical fourth derivatives have been programmed by Gaw and Handy (1987).

IV. Derivatives from Multireference Configuration Interaction Wave Functions

A. MRCI Electronic Energy

We consider a multireference CI (MRCI) wave function calculated from a set of MCSCF orbitals. The CI reference state is denoted by $|\mathrm{CI}\rangle$ at X_0 and by $|\mathrm{CI}(\mu)\rangle$ at the displaced geometry $X_0 + \mu$. In addition to the reorthonormalization part, the MRCI orbital connection contains the MCSCF orbital rotation parameters κ. The MCSCF responses $\kappa^{(n)}$ through third order are given as the orbital components of the solution vectors $\lambda^{(n)}$ in Eqs. (64)–(66). The CI state at the displaced geometry may be expressed in terms of the CI state at the undisplaced geometry

$$|\mathrm{CI}(\mu)\rangle = \exp(-P)|\mathrm{CI}\rangle \tag{108}$$

where

$$P = \sum_{k \neq \mathrm{CI}} P_k(|k\rangle\langle \mathrm{CI}| - |\mathrm{CI}\rangle\langle k|) = \sum_{k \neq \mathrm{CI}} P_k \Lambda_k \tag{109}$$

The set of states $\{|k\rangle\}$ constitutes an orthonormal basis for the orthogonal complement to $|\mathrm{CI}\rangle$.

The total energy of the CI state at the displaced geometry is

$$\begin{aligned} W(X_0 + \mu, P) &= \langle \mathrm{CI}(\mu)|H(X_0 + \mu)|\mathrm{CI}(\mu)\rangle \\ &= \langle \mathrm{CI}| \exp(P) H(X_0 + \mu) \exp(-P)|\mathrm{CI}\rangle \end{aligned} \tag{110}$$

Inserting the Hamiltonian expansion [Eq. (27)] and using the BCH expansion, we obtain

$$\begin{aligned} W(X_0 + \mu, P) = {} & E^{(0)} + \mu E^{(1)} + \tfrac{1}{2}\mu\mu E^{(2)} + \tfrac{1}{6}\mu\mu\mu E^{(3)} \\ & + \mu f^{(1)} P + \tfrac{1}{2}\mu\mu f^{(2)} P + \tfrac{1}{2} G^{(0)} PP + \tfrac{1}{2}\mu G^{(1)} PP + \cdots \end{aligned} \tag{111}$$

The matrices $f^{(i)}$ and $G^{(i)}$ are defined as in Eqs. (57) and (58) but with average values taken with respect to $|\mathrm{CI}\rangle$ and with no orbital excitation operators in Λ [Eq. (109)]. Note that both $f^{(0)}$ and $K^{(0)}$ are zero as $|\mathrm{CI}\rangle$ is optimized at X_0, i.e., $\langle \mathrm{CI}|H(X_0)|k\rangle = 0$.

B. MRCI Response Equations

The geometry dependence of the P parameters is obtained from the requirement that the total energy in Eq. (111) must be stationary in the perturbed field

$$dW(X_0 + \mu, P)/dP = \mu f^{(1)} + \tfrac{1}{2}\mu\mu f^{(2)} + G^{(0)} P + \mu G^{(1)} P + \cdots = 0 \tag{112}$$

The parameters P may be expanded in a power series in the nuclear displacement

$$P = \mu P^{(1)} + \tfrac{1}{2}\mu\mu P^{(2)} + \cdots \tag{113}$$

where the zeroth-order term vanishes as the CI state is optimized at X_0. Solving Eq. (112) to first and second orders we obtain

$$-G^{(0)} P^{(1)} = f^{(1)} \tag{114}$$

$$-G^{(0)} P^{(2)} = f^{(2)} + 2G^{(1)} P^{(1)} \tag{115}$$

These equations describe how the CI state responds through first and second orders to a nuclear displacement.

The first-order CI response equations were derived by Jørgensen and Simons (1983) using a response function approach and reformulated by Fox *et al.* (1983) using a Fock-operator approach.

C. MRCI Energy Derivatives

The geometrical derivatives may be identified by inserting the power series expansion of P [Eq. (113)] into the CI energy expression [Eq. (111)]. We obtain

$$W^{(1)} = E^{(1)} \tag{116}$$

$$W^{(2)} = E^{(2)} + f^{(1)}P^{(1)} \tag{117}$$

$$W^{(3)} = E^{(3)} + 3f^{(2)}P^{(1)} + 3G^{(1)}P^{(1)}P^{(1)} \tag{118}$$

The energy through third order is thus determined by the first-order correction to the wave function. In general the nth-order correction to the wave function determines the energy through order $(2n + 1)$. Comparing these equations with their MCSCF counterparts [Eqs. (67)–(69)], we note their structural similarity. However, the elements entering the CI and MCSCF derivative expressions are defined differently. The orbital connections (and therefore $H^{(n)}$) in both cases contain reorthonormalization contributions, but in the CI case $H^{(n)}$ also contains the MCSCF orbital responses. Differences also occur in the definitions of $E^{(i)}$, $f^{(i)}$, $G^{(i)}$, and $K^{(i)}$, reflecting the different variational parameters of the two wave functions. We finally note that the $K^{(0)}$ contribution vanishes in the CI third derivative expression, as opposed to the MCSCF case where the many-body orbital operators make this term nonvanishing.

The CI gradient expression was derived and implemented by Krishnan *et al.* (1980) and Brooks *et al.* (1980). The generalization to MRCI is due to Osamura *et al.* (1981, 1982a,b). The Hessian expression was derived by Jørgensen and Simons (1983) and implemented by Fox *et al.* (1983). Recently, a more efficient implementation has been reported by Lee *et al.* (1986). MRCI derivative expressions up to fourth order have been derived by Simons *et al.* (1984). The introduction of the Handy–Schaefer technique (Handy and Schaefer, 1984) greatly improved the efficiency of CI derivative calculations. The calculation of CI derivatives within the Fock-operator formalism has recently been reviewed by Osamura *et al.* (1987).

D. Implementation of MRCI Derivative Expressions

1. *MRCI Gradients*

Using Eq. (38), the CI gradient [Eq. (116)] may be written as

$$W^{(1)} = \langle \mathrm{CI}|H^{[1]} - \tfrac{1}{2}(S^{(1)}, H^{(0)}) + (\kappa^{(1)}, H^{(0)})|\mathrm{CI}\rangle \tag{119}$$

where $\kappa^{(1)}$ is the first-order MCSCF orbital response [the orbital part of Eq. (64)]. The first two terms may be calculated as in the MCSCF case, i.e.,

$$\langle \mathrm{CI}|H^{[1]} - \tfrac{1}{2}(S^{(1)}, H^{(0)})|\mathrm{CI}\rangle = \mathrm{Tr}\, D_{\mathrm{ao}} h_{\mathrm{AO}}^{(1)} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}} g_{\mathrm{AO}}^{(1)} - \mathrm{Tr}\, S_{\mathrm{AO}}^{(1)} F_{\mathrm{ao}}^{[0]} \tag{120}$$

The evaluation of the third term may be simplified as described by Handy and Schaefer (1984):

$$\begin{aligned} \langle \mathrm{CI}|(\kappa^{(1)}, H^{(0)})|\mathrm{CI}\rangle &= 2\mathrm{Tr}\, \kappa^{(1)} F^{(0)} \\ &= \kappa^{(1)\mathrm{o}} f_{\mathrm{CI}}^{(0)} = \zeta^{(0)} f_{\mathrm{MC}}^{(1)} \end{aligned} \tag{121}$$

where ${}^{\mathrm{o}}f_{\mathrm{CI}}^{(0)}$ is the CI orbital gradient calculated from $I^{(0)}$, and $f_{\mathrm{MC}}^{(1)}$ is the full MCSCF electronic gradient calculated from $\tilde{I}^{(1)}$. Here $\zeta^{(0)}$ is the solution of the MCSCF response equations associated with the CI orbital gradient ${}^{\mathrm{o}}f_{\mathrm{CI}}^{(0)}$:

$$\begin{bmatrix} {}^{\mathrm{cc}}G_{\mathrm{MC}}^{(0)} & {}^{\mathrm{co}}G_{\mathrm{MC}}^{(0)} \\ {}^{\mathrm{oc}}G_{\mathrm{MC}}^{(0)} & {}^{\mathrm{oo}}G_{\mathrm{MC}}^{(0)} \end{bmatrix} \begin{bmatrix} {}^{\mathrm{c}}\zeta^{(0)} \\ {}^{\mathrm{o}}\zeta^{(0)} \end{bmatrix} = -\begin{bmatrix} 0 \\ {}^{\mathrm{o}}f_{\mathrm{CI}}^{(0)} \end{bmatrix} \tag{122}$$

The orbital part of $\zeta^{(0)} f_{\mathrm{MC}}^{(1)}$ may be rewritten as [see Eqs. (F.3) and (F.1)] (Rice and Amos, 1985)

$$\begin{aligned} {}^{\mathrm{o}}\zeta^{(0)\mathrm{o}} f_{\mathrm{MC}}^{(1)} &= \langle \mathrm{MC}|({}^{\mathrm{o}}\zeta^{(0)}, H^{(1)})|\mathrm{MC}\rangle \\ &= -\mathrm{Tr}\{{}^{\mathrm{o}}\zeta^{(0)}, D^{\mathrm{MC}}\} h^{(1)} - \tfrac{1}{2}\mathrm{Tr}\{{}^{\mathrm{o}}\zeta^{(0)}, d^{\mathrm{MC}}\} g^{(1)} \end{aligned} \tag{123}$$

where D^{MC} and d^{MC} are the MCSCF density elements. The configuration part of $\zeta^{(0)} f_{\mathrm{MC}}^{(1)}$ becomes [see Eq. (D.7)] (Shepard, 1987)

$$\begin{aligned} {}^{\mathrm{c}}\zeta^{(0)\mathrm{c}} f_{\mathrm{MC}}^{(1)} &= -2\langle \mathrm{MC}|H^{(1)}|\zeta^{(0)}\rangle \\ &= -2\mathrm{Tr}\, D^{\mathrm{MC}\zeta} \tilde{h}^{(1)} - \mathrm{Tr}\, d^{\mathrm{MC}\zeta} \tilde{g}^{(1)} \end{aligned} \tag{124}$$

where

$$|\zeta^{(0)}\rangle = \sum_k {}^{\mathrm{c}}\zeta_k^{(0)} |k\rangle \tag{125}$$

and $D^{\mathrm{MC}\zeta}$ and $d^{\mathrm{MC}\zeta}$ are the appropriately defined transition density matrices. Combining Eqs. (120), (123), and (124) we find

$$W^{(1)} = \mathrm{Tr}\, D_{\mathrm{ao}}^{\mathrm{eff}} h_{\mathrm{AO}}^{(1)} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}}^{\mathrm{eff}} g_{\mathrm{AO}}^{(1)} - \mathrm{Tr}\, S_{\mathrm{AO}}^{(1)} F_{\mathrm{ao}}^{\mathrm{eff}} \tag{126}$$

where we have introduced the effective density elements

$$D^{\mathrm{eff}} = D - 2D^{\mathrm{MC}\zeta} - \{{}^{\mathrm{o}}\zeta^{(0)}, D^{\mathrm{MC}}\} \tag{127}$$

and similarly for the two-electron densities. The Fock matrix in Eq. (126) is constructed from the effective densities. Hence the CI gradient can be calculated very efficiently, requiring no transformation of derivative integrals and the solution of only a single set of MCSCF response equations.

2. *MRCI Hessians*

The MRCI Hessian [Eq. (117)] contains two terms. Using Eq. (39) we obtain for the first term

$$\begin{aligned} E^{(2)} = \langle \mathrm{CI} | H^{[2]} &+ (2\kappa^{(1)} - S^{(1)}, H^{[1]}) \\ &+ (\kappa^{(2)}, H^{(0)}) + (-\tfrac{1}{2}S^{(2)} + \tfrac{1}{2}S^{(1)}S^{(1)}, H^{(0)}) \\ &+ (\kappa^{(1)}, \kappa^{(1)}, H^{(0)}) + \tfrac{1}{4}(S^{(1)}, (S^{(1)}, H^{(0)})) - (\kappa^{(1)}, (S^{(1)}, H^{(0)})) | \mathrm{CI} \rangle \qquad (128) \end{aligned}$$

Using a similar technique as for the MCSCF Hessian we write this equation as

$$\begin{aligned} E^{(2)} = \mathrm{Tr}\, D_{\mathrm{ao}} h_{\mathrm{AO}}^{(2)} &+ \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}} g_{\mathrm{AO}}^{(2)} + \mathrm{Tr}[(4\kappa^{(1)} - 2S^{(1)})F^{[1]}] \\ &+ 2\mathrm{Tr}\, \kappa^{(2)} F^{[0]} - \mathrm{Tr}\, S_{\mathrm{AO}}^{(2)} F_{\mathrm{ao}}^{[0]} + \mathrm{Tr}(S^{(1)} S^{(1)} F^{[0]}) \\ &+ 2\mathrm{Tr}[\kappa^{(1)}(\kappa^{(1)}, F^{[0]})] - \mathrm{Tr}[(2\kappa^{(1)} - \tfrac{1}{2}S^{(1)})(S^{(1)}, F^{[0]})] \qquad (129) \end{aligned}$$

Except for the term containing $\kappa^{(2)}$ all terms in this expression may be evaluated as in the MCSCF case with little extra cost. The evaluation of the $\kappa^{(2)}$ term may be simplified as described by Handy and Schaefer (1984). We obtain (Lee *et al.*, 1986)

$$2\mathrm{Tr}\, \kappa^{(2)} F^{[0]} = \zeta^{(0)}(f_{\mathrm{MC}}^{(2)} + 2G_{\mathrm{MC}}^{(1)} \lambda_{\mathrm{MC}}^{(1)} + K_{\mathrm{MC}}^{(0)} \lambda_{\mathrm{MC}}^{(1)} \lambda_{\mathrm{MC}}^{(1)}) \qquad (130)$$

where $\zeta^{(0)}$ is identical to the Handy–Schaefer vector which appears in the CI gradient calculation. The $\zeta^{(0)} f_{\mathrm{MC}}^{(2)}$ term in Eq. (130) is treated in the same way as $\zeta^{(0)} f_{\mathrm{MC}}^{(1)}$ for gradients, resulting in the expression

$$\mathrm{Tr}\, D_{\mathrm{ao}}^{\mathrm{eff}} h_{\mathrm{AO}}^{(2)} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}}^{\mathrm{eff}} g_{\mathrm{AO}}^{(2)} - \mathrm{Tr}\, S_{\mathrm{AO}}^{(2)} F_{\mathrm{ao}}^{\mathrm{eff}} \qquad (131)$$

which takes care of all contributions from second derivative integrals. Hence no transformation of second derivative integrals is required. The remaining two terms in Eq. (130) are best calculated by computing $G_{\mathrm{MC}}^{(1)} \zeta^{(0)}$ and $K_{\mathrm{MC}}^{(0)} \zeta^{(0)}$ first.

The evaluation of the second term $f^{(1)} P^{(1)}$, of the MRCI Hessian [Eq. (117)] requires the construction of $f^{(1)}$ and the solution of the linear equations

$$G^{(0)} P^{(1)} + f^{(1)} = 0 \qquad (132)$$

The electronic gradient $f^{(1)}$ (which has no orbital part) has the same structure as the configuration part of the MCSCF electronic gradient [Eq. (84)] and may be constructed in the configuration basis, requiring $I^{(1)}$, $\{S^{(1)}, I^{(0)}\}$, and $\{\kappa^{(1)}, I^{(0)}\}$ in the MO basis. (The $\{\kappa^{(1)}, I^{(0)}\}$ integrals are needed since the orbital connection includes the MCSCF orbital reoptimization effects.)

The linear equations may be solved using the same iterative technique as in the MCSCF case. The direct transformations are simplified since only the configuration block ${}^{cc}G$ is present. The relaxation contribution to the Hessian

$$-f^{(1)}(G^{(0)})^{-1}f^{(1)} = f^{(1)}P^{(1)} \tag{133}$$

may be calculated as $f^{(1)}P^{(1)}$ when the exact solution vectors $P^{(1)}$ are known. When only approximate solutions are available, it is better to use a modified expression which gives errors quadratic in the errors of the solution vectors (see Appendix G).

3. *MRCI First Anharmonicities*

The CI first anharmonicity contains three terms [Eq. (118)], the first of which

$$E^{(3)} = \langle \mathrm{CI}|H^{(3)}|\mathrm{CI}\rangle \tag{134}$$

may be further decomposed into three parts

$$T_1 = \langle \mathrm{CI}|H^{[3]} + 3(\kappa^{(1)} + R^{(1)}, H^{[2]})|\mathrm{CI}\rangle \tag{135}$$

$$T_2 = \langle \mathrm{CI}|(\kappa^{(3)}, H^{[0]}) + (\kappa^{(2)}, A^{(1)}) + \tfrac{3}{2}(\kappa^{(1)}, (\kappa^{(2)}, H^{[0]}))|\mathrm{CI}\rangle \tag{136}$$

$$T_3 = \langle \mathrm{CI}|(R^{(3)}, H^{[0]}) + (R^{(2)}, B^{(1)}) + (R^{(1)}, C^{(2)}) + (\kappa^{(1)}, D^{(2)})|\mathrm{CI}\rangle \tag{137}$$

We have here introduced the effective Hamiltonians

$$A^{(1)} = 3H^{[1]} + 3(R^{(1)}, H^{[0]}) + \tfrac{3}{2}(\kappa^{(1)}, H^{[0]}) \tag{138}$$

$$B^{(1)} = 3H^{[1]} + \tfrac{3}{2}(R^{(1)}, H^{[0]}) \tag{139}$$

$$C^{(2)} = (R^{(1)}, 3H^{[1]} + (R^{(1)}, H^{[0]})) + \tfrac{3}{2}(R^{(2)}, H^{[0]}) \tag{140}$$

$$\begin{aligned} D^{(2)} = {} & (\kappa^{(1)}, 3H^{[1]} + 3(R^{(1)}, H^{[0]}) + (\kappa^{(1)}, H^{[0]})) \\ & + 3(R^{(1)}, 2H^{[1]} + (R^{(1)}, H^{[0]})) + 3(R^{(2)}, H^{[0]}) \end{aligned} \tag{141}$$

which are straightforwardly calculated from $g^{(0)}$ and $g^{(1)}$ in the MO basis and from $\kappa^{(1)}$. Let us consider each of the three terms T_1, T_2, and T_3 in turn.

The first contribution is

$$T_1 = \mathrm{Tr}\, D_{\mathrm{ao}} h_{\mathrm{AO}}^{(3)} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}} g_{\mathrm{AO}}^{(3)} + \mathrm{Tr}\, D_{\mathrm{ao}}^{(1)} h_{\mathrm{AO}}^{(2)} + \tfrac{1}{2}\mathrm{Tr}\, d_{\mathrm{ao}}^{(1)} g_{\mathrm{AO}}^{(2)} \tag{142}$$

where we have introduced the effective density matrices

$$D^{(1)} = 3\{-\kappa^{(1)} + R^{(1)}, D\} \tag{143}$$

and similarly for two-electron densities. No integral transformation is needed, but $3N - 6$ effective densities must be constructed and transformed to the contravariant AO representation. Later more terms will be added to the densities [Eq. (143)] to eliminate all transformations of second and third derivative two-electron integrals.

The second term T_2 contains all contributions to $E^{(3)}$ arising from $\kappa^{(2)}$ and

$\kappa^{(3)}$. The calculation of $\kappa^{(2)}$ and $\kappa^{(3)}$ may be avoided by using the Handy–Schaefer technique. We first write

$$\begin{aligned} T_2 &= 2\mathrm{Tr}\,\kappa^{(3)}F^{[0]} + 2\mathrm{Tr}[\kappa^{(2)}(F^A + F^\kappa)] \\ &= \kappa^{(3)}\,{}^{0}f^{[0]} + \kappa^{(2)}\,{}^{0}f^{A\kappa} \end{aligned} \tag{144}$$

where $F^{[0]}$ is the usual CI Fock matrix, F^A are the $3N-6$ Fock matrices constructed from the effective Hamiltonians $A^{(1)}$, and F^κ are the $3N-6$ Fock matrices constructed from the one-index transformed density elements $\{-\frac{3}{2}\kappa^{(1)}, D\}$ and $\{-\frac{3}{2}\kappa^{(1)}, d\}$. The vector ${}^{0}f^{[0]}$ and the $3N-6$ vectors ${}^{0}f^{A\kappa}$ are the orbital gradients calculated from $F^{[0]}$ and $F^A + F^\kappa$. Using the Handy–Schaefer technique and carrying out some rearrangements we obtain

$$T_2 = \zeta^{(0)}\rho^{(3)} + \zeta^{(1)}\rho^{(2)} \tag{145}$$

where $\zeta^{(0)}$ is the Handy–Schaefer vector which appears in CI gradients and Hessians, and the $\zeta^{(1)}$ are the solutions of the $3N-6$ MCSCF response equations

$$-G^{(0)}_{\mathrm{MC}}\zeta^{(1)} = 3G^{(1)}_{\mathrm{MC}}\zeta^{(0)} + 3K^{(0)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}}\zeta^{(0)} + \begin{bmatrix} 0 \\ {}^{0}f^{A\kappa} \end{bmatrix} \tag{146}$$

We have further used the notation

$$\rho^{(2)} = f^{(2)}_{\mathrm{MC}} + 2G^{(1)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}} + K^{(0)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}} \tag{147}$$

$$\rho^{(3)} = f^{(3)}_{\mathrm{MC}} + 3G^{(2)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}} + 3K^{(1)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}} + L^{(0)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}}\lambda^{(1)}_{\mathrm{MC}} \tag{148}$$

where $\rho^{(2)}$ is simply the right-hand side of the second-order MCSCF response equations [Eq. (65)], and $\rho^{(3)}$ is the right-hand side of the third-order response equations [Eq. (66)], with both terms containing $\lambda^{(2)}_{\mathrm{MC}}$ omitted. Hence we may calculate T_2 according to Eq. (145) by solving $3N-6$ response equations in addition to those needed for the CI Hessian.

The explicit calculation of $\rho^{(2)}$ and $\rho^{(3)}$ is a formidable task, but the calculation of their contributions to $E^{(3)}$ can be simplified considerably. Most importantly, $\zeta^{(0)}f^{(3)}_{\mathrm{MC}}$ may be handled in the same way as $\zeta^{(0)}f^{(1)}_{\mathrm{MC}}$ for gradients and $\zeta^{(0)}f^{(2)}_{\mathrm{MC}}$ for Hessians, i.e., by modifying the densities multiplying $\tilde{I}^{(3)}_{\mathrm{AO}}$ from Eq. (134). (In fact, the same densities can be used.) In a similar fashion we may account for $\zeta^{(1)}f^{(2)}_{\mathrm{MC}}$ by modifying the densities $D^{(1)}_{\mathrm{ao}}$ and $d^{(1)}_{\mathrm{ao}}$ multiplying $\tilde{I}^{(2)}_{\mathrm{AO}}$ from Eq. (134). Finally, by using a similar technique one may avoid calculating $3G^{(2)}_{\mathrm{MC}}\zeta^{(0)}\lambda^{(1)}_{\mathrm{MC}}$ by adding additional corrections to $D^{(1)}_{\mathrm{ao}}$ and $d^{(1)}_{\mathrm{ao}}$.

The third term T_3 is straightforwardly calculated according to

$$T_3 = 2\mathrm{Tr}\,R^{(3)}F^{[0]} + 2\mathrm{Tr}\,R^{(2)}F^B + 2\mathrm{Tr}\,R^{(1)}F^C + 2\mathrm{Tr}\,\kappa^{(1)}F^D \tag{149}$$

where F^B, F^C, and F^D are the Fock matrices constructed from the effective Hamiltonians $B^{(1)}$, $C^{(2)}$, and $D^{(2)}$. This completes the discussion of $E^{(3)}$.

The remaining two contributions to $W^{(3)}$ depend on $P^{(1)}$ which is available from the Hessian calculation. The first of the two contributions is

$$3f^{(2)}P^{(1)} = -6\langle CI|H^{(2)}|P^{(1)}\rangle \tag{150}$$

where

$$|P^{(1)}\rangle = 3\sum_k |k\rangle P_k^{(1)}. \tag{151}$$

This term may be calculated in the same way as the $E^{(2)}$ contribution to the MRCI Hessian discussed above [Eq. (129)]. The only difference is that we must construct one set of transition densities between $|\text{CI}\rangle$ and $|P^{(1)}\rangle$ for each independent perturbation $P^{(1)}$, and the Fock matrices in Eq. (129) must be calculated from these densities. Furthermore, the term containing $\kappa^{(2)}$ [see Eq. (129)] may be treated by the Handy–Schaefer technique in the same way as the $\kappa^{(2)}$ contribution to $E^{(3)}$ discussed above. This is easily achieved by adding $-6F^P$ to $F^A + F^\kappa$ in Eq. (144), where F^P are the $3N-6$ Fock matrices calculated from the densities between $|\text{CI}\rangle$ and $|P^{(1)}\rangle$.

The last contribution to $W^{(3)}$, $3G^{(1)}P^{(1)}P^{(1)}$, is best calculated by first carrying out the linear transformations $G^{(1)}P^{(1)}$ in a direct fashion, requiring first derivative integrals in the MO basis.

Let us summarize. The calculation of CI first anharmonicities requires no storage or transformation of second and third derivative two-electron integrals, but the full set of first derivative MO integrals is needed. One must construct and transform one set of effective density elements for third derivative integrals and $3N-6$ sets of effective densities for second derivative integrals. In addition to the $3N-6$ MCSCF orbital responses $\kappa^{(1)}$ and the Handy–Schaefer vector $\zeta^{(0)}$ needed for the Hessian, the first anharmonicity requires the solution of $3N-6$ response equations to obtain $\zeta^{(1)}$.

V. Derivatives from Coupled-Cluster Wave Functions

A. CC Electronic Energy

We assume that we have carried out a Hartree–Fock calculation at the reference geometry X_0 and used the orbitals to determine a coupled-cluster wave function

$$|\text{CC}\rangle = \exp(T)|\text{HF}\rangle \tag{152}$$

The cluster operator of an N-electron system is

$$T = T_1 + T_2 + \cdots + T_N \tag{153}$$

where, for example,

$$T_1 = \sum_{ai} t_i^a a_a^+ a_i \tag{154}$$

$$T_2 = \frac{1}{4} \sum_{abij} t_{ij}^{ab} a_a^+ a_b^+ a_j a_i \tag{155}$$

are the one- and two-electron cluster operators. The indices *ij* and *ab* refer to occupied and unoccupied orbitals in the HF reference function $|\mathrm{HF}\rangle$. In practice, the cluster operator is truncated at some low excitation level, usually after T_2. We will in the following use the general cluster operator, which we write as

$$T = t\tau \tag{156}$$

where t contains the cluster amplitudes and τ the operators.

The CC total energy is determined by projecting the CC Schrödinger equation

$$\exp(-T)H(X_0)\exp(T)|\mathrm{HF}\rangle = W(X_0)|\mathrm{HF}\rangle \tag{157}$$

from the left against $\langle\mathrm{HF}|$

$$\begin{aligned} W(X_0) &= \langle\mathrm{HF}|\exp(-T)H(X_0)\exp(T)|\mathrm{HF}\rangle \\ &= \langle\mathrm{HF}|H(X_0)|\mathrm{CC}\rangle \end{aligned} \tag{158}$$

where we have used the fact that

$$\langle\mathrm{HF}|\exp(-T) = \langle\mathrm{HF}| \tag{159}$$

Similarly the CC amplitudes are determined by projecting the Schrödinger equation from the left against all excitations included in the cluster operator, for example, all single and double excitations from the HF reference function. If we denote this set of excited states by $|*\rangle$, the cluster amplitude equations have the form

$$\langle *|\exp(-T)H(X_0)\exp(T)|\mathrm{HF}\rangle = 0 \tag{160}$$

where we have used the fact that

$$\langle *|\mathrm{HF}\rangle = 0 \tag{161}$$

At a displaced geometry $X_0 + \mu$ the coupled-cluster state may be expressed as

$$|\mathrm{CC}(\mu)\rangle = \exp[T(\mu)]|\mathrm{HF}\rangle \tag{162}$$

where the cluster amplitudes are geometry dependent

$$T(\mu) = t(\mu)\tau \tag{163}$$

Since HF orbitals are used, the orbital connection and thus $H^{(n)}$ contain reorthonormalization as well as reoptimization contributions. The HF orbital response parameters are obtained by solving Eqs. (64)–(66).

B. CC Response Equations

The geometry dependence of the cluster amplitudes is determined by considering the geometry dependence of the cluster amplitude equations

$$\langle * |\, \exp[-T(\mu)] H(X_0 + \mu) \exp[T(\mu)] | \mathrm{HF} \rangle = 0 \tag{164}$$

We expand $T(\mu)$ around X_0

$$T(\mu) = T^{(0)} + \mu T^{(1)} + \tfrac{1}{2}\mu\mu T^{(2)} + \cdots \tag{165}$$

where

$$T^{(n)} = t^{(n)}\tau \tag{166}$$

Inserting this expansion and the Hamiltonian expansion [Eq. (27)] in the amplitude equations, we obtain to first and second orders

$$\langle * |\, \exp(-T^{(0)})(H^{(1)} - [T^{(1)}, H^{(0)}]) \exp(T^{(0)}) | \mathrm{HF} \rangle = 0 \tag{167}$$

$$\begin{aligned} \langle * |\, \exp(-T^{(0)})(H^{(2)} - 2[T^{(1)}, H^{(1)}] - [T^{(2)}, H^{(0)}] \\ + [T^{(1)}, T^{(1)}, H^{(0)}]) \exp(T^{(0)}) | \mathrm{HF} \rangle = 0 \end{aligned} \tag{168}$$

If we introduce the notation

$$\langle \hat{*} | = \langle * |\, \exp(-T^{(0)}) \tag{169}$$

and the effective Hamiltonian

$$H^{(2)}_{\mathrm{eff}} = H^{(2)} - 2[T^{(1)}, H^{(1)}] + [T^{(1)}, T^{(1)}, H^{(0)}] \tag{170}$$

we may write the above amplitude response equations as (Jørgensen and Simons, 1983)

$$\langle \hat{*} | H^{(1)} | \mathrm{CC} \rangle = \langle \hat{*} | [\tau, H^{(0)}] | \mathrm{CC} \rangle t^{(1)} \tag{171}$$

$$\langle \hat{*} | H^{(2)}_{\mathrm{eff}} | \mathrm{CC} \rangle = \langle \hat{*} | [\tau, H^{(0)}] | \mathrm{CC} \rangle t^{(2)} \tag{172}$$

The first set of equations determines the first-order response of the cluster amplitudes. Once this has been determined we may construct the effective operator $H^{(2)}_{\mathrm{eff}}$ and determine the second-order amplitude response using the same set of equations (with $H^{(1)}$ replaced by $H^{(2)}_{\mathrm{eff}}$). These equations may be solved using an iterative technique. The key steps would be the calculation of transformed trial vectors,

$$\sigma^{(i)} = \langle \hat{*} | [\tau, H^{(0)}] | \mathrm{CC} \rangle b^{(i)} \tag{173}$$

the calculation of an optimal solution vector for the linear equations in a reduced space, and the determination of a new trial vector using, for example, the conjugate gradient algorithm.

C. CC Energy Derivatives

The total CC energy at a displaced geometry is

$$W(X_0 + \mu) = \langle \mathrm{HF} | \exp[-T(\mu)] H(X_0 + \mu) \exp[T(\mu)] | \mathrm{HF} \rangle \tag{174}$$

However, since Eq. (164) is fulfilled at all geometries, we may calculate the energy from the alternative expression

$$W(X_0 + \mu) = \langle \Lambda | \exp[-T(\mu)] H(X_0 + \mu) \exp[T(\mu)] | \mathrm{HF} \rangle \tag{175}$$

where

$$\langle \Lambda | = \langle \mathrm{HF} | + \lambda \langle * | \tag{176}$$

and λ is arbitrary. To simplify the calculation of energy derivatives, we choose λ so that

$$\langle \hat{\Lambda} | [\tau, H^{(0)}] | \mathrm{CC} \rangle = 0 \tag{177}$$

where we have used the short-hand notation

$$\langle \hat{\Lambda} | = \langle \Lambda | \exp(-T^{(0)}) \tag{178}$$

The left-hand side of Eq. (177) has a structure similar to the electronic gradient vector in variational wave function calculations. Unlike variational calculations, Eq. (177) cannot be used to determine the response parameters $t^{(n)}$ in a CC calculation. However, for the calculation of the nth geometrical derivative $W^{(n)}$, Eq. (177) eliminates $t^{(n)}$, which would otherwise appear in the calculation. In fact, we show below that the calculation of $(3N\text{-}6)^n$ response amplitudes $t^{(n)}$ is replaced by the solution of one set of linear equations of similar but simpler structure. By inserting Eq. (176) in Eq. (177) and rearranging terms, we see that λ fulfills the equations

$$\lambda \langle \hat{*} | [\tau, H^{(0)}] | \mathrm{CC} \rangle = -\langle \mathrm{HF} | [\tau, H^{(0)}] | \mathrm{CC} \rangle \tag{179}$$

which may be solved using standard iterative techniques. The linear transformations of trial vectors $b^{(i)}$ are accomplished by constructing the intermediate states

$$\langle \hat{b}^{(i)} | = b^{(i)} \langle \hat{*} | \tag{180}$$

in the iterative procedure.

The energy derivatives are now obtained by inserting the expansions for $T(\mu)$ and $H(X_0 + \mu)$ in Eq. (175) and identifying terms to same order. To first and second orders we obtain

$$W^{(1)} = \langle \hat{\Lambda} | H^{(1)} | \mathrm{CC} \rangle \tag{181}$$

$$W^{(2)} = \langle \hat{\Lambda} | H^{(2)}_{\mathrm{eff}} | \mathrm{CC} \rangle \tag{182}$$

where we have used Eq. (177) to simplify the expressions and $H^{(2)}_{\mathrm{eff}}$ is the effective Hamiltonian [Eq. (170)]. Here $H^{(1)}$ is independent of the cluster amplitudes, and $H^{(2)}_{\mathrm{eff}}$ depends on $t^{(1)}$ only. In general $W^{(n)}$ may be calculated from $t^{(i)}$, where $i \leq n - 1$. Note that the solution of one (the same) single set of equations simplifies the calculation of derivatives to any order.

The gradient $W^{(1)}$ may be calculated using a procedure similar to that for MCSCF and MRCI wave functions, since $H^{(1)}$ is an operator of rank 2. The molecular gradient becomes

$$\begin{aligned} W^{(1)} &= \langle \hat{\Lambda} | H^{[1]} + (\kappa^{(1)} - \tfrac{1}{2} S^{(1)}, H^{(0)}) | \mathrm{CC} \rangle \\ &= \mathrm{Tr}\, D^{\mathrm{eff}}_{\mathrm{ao}} h^{(1)}_{\mathrm{AO}} + \tfrac{1}{2} \mathrm{Tr}\, d^{\mathrm{eff}}_{\mathrm{ao}} g^{(1)}_{\mathrm{AO}} - \mathrm{Tr}\, S^{(1)}_{\mathrm{AO}} F^{\mathrm{eff}}_{\mathrm{ao}} \\ &\quad + 2\mathrm{Tr}\, \kappa^{(1)} F^{\mathrm{eff}} \end{aligned} \tag{183}$$

where the effective density elements are (Fitzgerald *et al.*, 1986)

$$D^{\mathrm{eff}}_{pq} = \langle \hat{\Lambda} | E_{pq} | \mathrm{CC} \rangle \tag{184}$$

$$d^{\mathrm{eff}}_{pqrs} = \langle \hat{\Lambda} | e_{pqrs} | \mathrm{CC} \rangle \tag{185}$$

and the effective Fock matrix F^{eff} is constructed from these densities. The orbital relaxation term may be rewritten as

$$2\mathrm{Tr}\, \kappa^{(1)} F^{\mathrm{eff}} = \sum_{p>q} \kappa^{(1)}_{pq} f^{\mathrm{eff}}_{pq} \tag{186}$$

where f^{eff} is an effective orbital gradient

$$f^{\mathrm{eff}}_{pq} = 2(F^{\mathrm{eff}}_{pq} - F^{\mathrm{eff}}_{qp}) \tag{187}$$

Finally, this term may be simplified using the Handy–Schaefer technique. We obtain

$$\kappa^{(1)} f^{\mathrm{eff}} = \zeta^{(0)} f^{(1)}_{\mathrm{HF}} \tag{188}$$

where $\zeta^{(0)}$ is the Handy–Schaefer vector

$$G^{(0)}_{\mathrm{HF}} \zeta^{(0)} = -f^{\mathrm{eff}} \tag{189}$$

The explicit calculation of $\zeta^{(0)} f^{(1)}_{\mathrm{HF}}$ is avoided by modifying the densities D^{eff} and d^{eff} by one-index transformed HF densities $-\{\zeta^{(0)}, D^{\mathrm{HF}}\}$ and $-\{\zeta^{(0)}, d^{\mathrm{HF}}\}$, as was done for CI gradients. We conclude that the CC molecular gradient may be determined in the same way as CI gradients if the solution vector to Eq. (179) is used to construct the effective one- and two-electron density matrices [Eqs. (184) and (185)]. Note that differentiated integrals are needed in the AO basis only.

The molecular Hessian has the form

$$W^{(2)} = \langle \hat{\Lambda} | H^{(2)} - 2[T^{(1)}, H^{(1)}] + [T^{(1)}, T^{(1)}, H^{(0)}] | \mathrm{CC} \rangle \tag{190}$$

Since $H^{(2)}$ is a rank 2 operator the first term in this expression may be calculated using the technique described for the evaluation of the molecular gradient, using the same effective density matrices. The second and third terms require the solution vectors $t^{(1)}$ of Eq. (171). As the commutators $[\tau, H^{(0)}]$ in Eq. (171) and $[T^{(1)}, H^{(1)}]$ and $[T^{(1)}, T^{(1)}, H^{(0)}]$ in Eq. (190) contain operators of third and higher ranks, it does not appear practical to calculate these terms using a density matrix formulation. Since the implementation of CC molecular Hessians has not yet started, we do not discuss the evaluation of CC molecular Hessians in more detail.

The CC molecular gradient and Hessian expressions were derived by Jørgensen and Simons (1983). Using the Handy–Schaefer technique, Adamowicz *et al.* (1984) and Bartlett (1986) simplified the expressions for the gradient. The only implementations are the CC molecular gradients reported by Fitzgerald *et al.* (1985) and by Lee *et al.* (1987).

VI. Derivatives from Møller–Plesset Perturbation Theory

A. MPPT Electronic Energy

Møller–Plesset perturbation theory (MPPT) uses the orbitals and orbital energies obtained from a closed-shell Hartree–Fock–Roothaan (HFR) calculation. The HFR (or canonical) orbitals correspond to the eigenvectors of the inactive Fock matrix

$$\sum_{\sigma} \langle \mathrm{HF} | [a^{+}_{p\sigma}, [a_{q\sigma}, H]]_{+} | \mathrm{HF} \rangle = 2\varepsilon_p \delta_{pq} \tag{191}$$

and the eigenvalues ε_p are the orbital energies

$$\varepsilon_p = h_{pp} + 2\sum_{i} \mathscr{P}_{ppii} \tag{192}$$

where $\mathscr{P}_{pqrs}$ are the Roothaan–Bagus (1963) supermatrix integrals

$$\mathscr{P}_{pqrs} = g_{pqrs} - \tfrac{1}{4} g_{prqs} - \tfrac{1}{4} g_{psrq} \tag{193}$$

In this section we use indices *pqrs* to denote arbitrary (occupied or unoccupied) orbitals, *ijkl* to denote occupied orbitals, and *abcd* to denote unoccupied orbitals.

The diagonal form of the Fock matrix implies

$$\sum_{\sigma}\langle \mathrm{HF}|[a_{i\sigma}^{+}, [a_{a\sigma}, H]]_{+}|\mathrm{HF}\rangle = \sum_{\sigma}\langle \mathrm{HF}|a_{i\sigma}^{+}a_{a\sigma}H|HF\rangle$$
$$= \sum_{\sigma}\langle \mathrm{HF}|[a_{i\sigma}^{+}a_{a\sigma}, H]|\mathrm{HF}\rangle = \frac{1}{2}f_{ia} = 0 \tag{194}$$

and the total energy is therefore stationary. The diagonal form of the occupied–occupied and unoccupied–unoccupied blocks of the Fock matrix is an additional requirement on the orbitals in an HFR calculation. This requirement does not affect the total energy, but is necessary to define the orbital energies for the subsequent MPPT treatment. This has an important consequence for the MPPT orbital connection: the orbitals must satisfy the HFR equations at all geometries and not simply the SCF response equations in Section III,B.

In MPPT we construct the Hamiltonian from canonical HF orbitals and decompose it into two pieces

$$H = F + V \tag{195}$$

where the Fock operator

$$F = \sum_{p} \varepsilon_p E_{pp} \tag{196}$$

is the zeroth-order Hamiltonian and

$$V = \frac{1}{2}\sum_{pqrs} g_{pqrs} e_{pqrs} - 2\sum_{pqi} \mathcal{P}_{pqii} E_{pq} \tag{197}$$

the fluctuation potential. The reference state $|\mathrm{HF}\rangle$ together with all single, double, and possibly higher excitations from $|\mathrm{HF}\rangle$ constitute the set of zeroth-order states.

MPPT total energies are expressed in terms of integrals in the canonical basis and orbital energies. To second order (MP2) we obtain

$$\Delta W = W - \langle \mathrm{HF}|H|\mathrm{HF}\rangle = \sum_{r} \frac{\langle \mathrm{HF}|V|r\rangle\langle r|V|\mathrm{HF}\rangle}{\Delta\varepsilon_r} \tag{198}$$

where $|r\rangle$ is the set of all doubly excited states, such as $a_{a\alpha}^{+}a_{b\alpha}^{+}a_{j\alpha}a_{i\alpha}|\mathrm{HF}\rangle$ and

$$\Delta\varepsilon_r = \Delta\varepsilon_{iajb} = \varepsilon_i - \varepsilon_a + \varepsilon_j - \varepsilon_b \tag{199}$$

In the following section we discuss the analytical calculation of gradients and Hessians of MP2 energies.

B. Coupled Perturbed Hartree–Fock Equations

The predefined orbitals of an MP2 calculation are determined by requiring Eq. (191) to be fulfilled at all geometries. At a displaced geometry $X_0 + \mu$ we have

$$\sum_{\sigma}\langle \mathrm{HF}(\mu)|[a^{+}_{p\sigma}(\mu), [a_{q\sigma}(\mu), H(X_0 + \mu)]]_{+}|\mathrm{HF}(\mu)\rangle = 2\varepsilon_p(\mu)\delta_{pq} \tag{200}$$

where $\{a^{+}_{p\sigma}(\mu)\}$ are the canonical Hartree–Fock creation operators and $|\mathrm{HF}(\mu)\rangle$ the Hartree–Fock state at the displaced geometry. These are related to the operators and the state at the reference geometry as

$$a^{+}_{p\sigma}(\mu) = \exp(-\kappa)a^{+}_{p\sigma}\exp(\kappa) \tag{201}$$

$$|\mathrm{HF}(\mu)\rangle = \exp(-\kappa)|\mathrm{HF}\rangle \tag{202}$$

where

$$\kappa = \sum_{p>q}\kappa_{pq}(E_{pq} - E_{qp}) \tag{203}$$

is the orbital rotation operator. To ensure a complete diagonalization of the inactive Fock matrix, the operator κ contains all possible rotations, also those that are redundant in an energy optimization. Inserting Eqs. (201) and (202) in Eq. (200) we obtain

$$\sum_{\sigma}\langle \mathrm{HF}|[a^{+}_{p\sigma}, [a_{q\sigma}, \exp(\kappa)H(X_0 + \mu)\exp(-\kappa)]]_{+}|\mathrm{HF}\rangle = 2\varepsilon_p(\mu)\delta_{pq} \tag{204}$$

We now expand the orbital energies, the rotational parameters, and the Hamiltonian in Cartesian displacements, insert these expansions in the equation above, and identify terms to same order. The expansions of ε and κ are

$$\varepsilon(\mu) = \varepsilon^{(0)} + \mu\varepsilon^{(1)} + \tfrac{1}{2}\mu\mu\varepsilon^{(2)} + \cdots \tag{205}$$

$$\kappa = \mu\kappa^{(1)} + \tfrac{1}{2}\mu\mu\kappa^{(2)} + \cdots \tag{206}$$

where $\kappa^{(0)}$ vanishes since an HFR calculation has been carried out at the reference geometry. The expansion of the Hamiltonian is that given in Section II with the rotational part of the connection omitted. Inserting these expansions in Eq. (204) and collecting terms to same order, we obtain the first-order coupled perturbed (CP) SCF equations

$$\sum_{\sigma}\langle \mathrm{HF}|[a^{+}_{p\sigma}, [a_{q\sigma}, [\kappa^{(1)}, H^{(0)}]]]_{+}|\mathrm{HF}\rangle + \sum_{\sigma}\langle \mathrm{HF}|[a^{+}_{p\sigma}, [a_{q\sigma}, H^{(1)}]]_{+}|\mathrm{HF}\rangle = 2\varepsilon^{(1)}_p\delta_{pq} \tag{207}$$

and the second-order CPSCF equations

$$
\begin{aligned}
&\sum_{\sigma}\langle \mathrm{HF}|[a^{+}_{p\sigma}, [a_{q\sigma}, [\kappa^{(2)}, H^{(0)}]]]_{+}|\mathrm{HF}\rangle \\
&\quad + \sum_{\sigma}\langle \mathrm{HF}|[a^{+}_{p\sigma}, [a_{q\sigma}, H^{(2)}]]_{+}|\mathrm{HF}\rangle \\
&\quad + 2\sum_{\sigma}\langle \mathrm{HF}|[a^{+}_{p\sigma}, [a_{q\sigma}, [\kappa^{(1)}, H^{(1)}]]]_{+}|\mathrm{HF}\rangle \\
&\quad + \sum_{\sigma}\langle \mathrm{HF}|[a^{+}_{p\sigma}, [a_{q\sigma}, [\kappa^{(1)}, [\kappa^{(1)}, H^{(0)}]]]]_{+}|\mathrm{HF}\rangle \\
&= 2\varepsilon^{(2)}_{p}\delta_{pq}
\end{aligned}
\tag{208}
$$

We first consider the first-order CPSCF equations in more detail. In our usual notation, we obtain for the first term on the left-hand side of Eq. (207) using Eq. (E.15),

$$
\begin{aligned}
2(\kappa^{(1)}, {}^{i}F^{(0)})_{pq} &= 2\{\kappa^{(1)}, {}^{i}F^{(0)}\}_{pq} + 8\sum_{ir}\mathscr{P}^{(0)}_{pqir}\kappa^{(1)}_{ir} \\
&= 2(\varepsilon^{(0)}_{q} - \varepsilon^{(0)}_{p})\kappa^{(1)}_{pq} + 8\sum_{ia}\mathscr{P}^{(0)}_{pqia}\kappa^{(1)}_{ia}
\end{aligned}
\tag{209}
$$

since ${}^{i}F^{(0)}$ is diagonal and $\kappa^{(1)}$ antisymmetric. The second term on the left-hand side is simply $2\,{}^{i}F^{(1)}_{pq}$, and the CPSCF equations therefore become

$$
2(\varepsilon^{(0)}_{p} - \varepsilon^{(0)}_{q})\kappa^{(1)}_{pq} + 2\varepsilon^{(1)}_{p}\delta_{pq} + 8\sum_{ai}\mathscr{P}^{(0)}_{pqai}\kappa^{(1)}_{ai} = 2\,{}^{i}F^{(1)}_{pq}
\tag{210}
$$

Equation (210) may be viewed as a set of linear equations of the structure in Fig. 1. The only nonvanishing elements are the diagonal elements and the elements of the column vectors corresponding to the unoccupied–occupied indices. The diagonal elements of the pp block are equal to two, and the diagonal elements of the $a > b$ and $i > j$ blocks are $2(\varepsilon^{(0)}_{a} - \varepsilon^{(0)}_{b})$ and $2(\varepsilon^{(0)}_{i} - \varepsilon^{(0)}_{j})$. To solve the CPSCF equations we first determine $\kappa^{(1)}_{ai}$ from the occupied–unoccupied block of Eq. (210)

$$
\sum_{bj} G^{(0)}_{aibj}\kappa^{(1)}_{bj} = -f^{(1)}_{ai}
\tag{211}
$$

where

$$
G^{(0)}_{aibj} = 4\delta_{ab}\delta_{ij}(\varepsilon^{(0)}_{a} - \varepsilon^{(0)}_{i}) + 16\mathscr{P}^{(0)}_{aibj}
\tag{212}
$$

$$
f^{(1)}_{ai} = -4\,{}^{i}F^{(1)}_{ai}
\tag{213}
$$

These equations are identical to the first-order SCF response equations [Eq. (64)] in the canonical orbital basis. Once the unoccupied–occupied orbital rotations $\kappa^{(1)}_{ai}$ have been determined, we can use Eq. (210) to obtain explicit expressions for the occupied–occupied $\kappa^{(1)}_{ij}$ and unoccupied–

unoccupied $\kappa_{ab}^{(1)}$ components of $\kappa^{(1)}$, as well as for the orbital energies $\varepsilon_p^{(1)}$:

$$\kappa_{ij}^{(1)} = \left({}^{i}F_{ij}^{(1)} - 4\sum_{ck} \mathscr{P}_{ijck}^{(0)} \kappa_{ck}^{(1)} \right) \Big/ (\varepsilon_i^{(0)} - \varepsilon_j^{(0)}) \tag{214}$$

$$\kappa_{ab}^{(1)} = \left({}^{i}F_{ab}^{(1)} - 4\sum_{ck} \mathscr{P}_{abck}^{(0)} \kappa_{ck}^{(1)} \right) \Big/ (\varepsilon_a^{(0)} - \varepsilon_b^{(0)}) \tag{215}$$

$$\varepsilon_p^{(1)} = {}^{i}F_{pp}^{(1)} - 4\sum_{ck} \mathscr{P}_{ppck}^{(0)} \kappa_{ck}^{(1)} \tag{216}$$

Note the similar structure of the equations for $\kappa_{ij}^{(1)}$ and $\kappa_{ab}^{(1)}$. This completes the solution of the first-order CPSCF equations.

Higher order CPSCF equations may be treated in a similar fashion. The second-order equations [Eq. (208)] become

$$2(\varepsilon_p^{(0)} - \varepsilon_q^{(0)})\kappa_{pq}^{(2)} + 2\varepsilon_p^{(2)}\delta_{pq} + 8\sum_{ai} \mathscr{P}_{pqai}^{(0)} \kappa_{ai}^{(2)} = 2u_{pq}^{(2)} \tag{217}$$

where

$$u_{pq}^{(2)} = {}^{i}F_{pq}^{(2)} + 2(\kappa^{(1)}, {}^{i}F^{(1)})_{pq} + (\kappa^{(1)}, (\kappa^{(1)}, {}^{i}F^{(0)}))_{pq} \tag{218}$$

can be calculated from $\kappa^{(1)}$. For the occupied–unoccupied components of $\kappa^{(2)}$ these equations reduce to the second-order SCF response equations in the canonical basis

$$\sum_{bj} G_{aibj}^{(0)} \kappa_{bj}^{(2)} = 4u_{ai}^{(2)} \tag{219}$$

Once these equations have been solved, we may determine the remaining components of $\kappa^{(2)}$ and $\varepsilon^{(2)}$ from the equations

$$\kappa_{ij}^{(2)} = \left(u_{ij}^{(2)} - 4\sum_{ck} \mathscr{P}_{ijck}^{(0)} \kappa_{ck}^{(2)} \right) \Big/ (\varepsilon_i^{(0)} - \varepsilon_j^{(0)}) \tag{220}$$

$$\kappa_{ab}^{(2)} = \left(u_{ab}^{(2)} - 4\sum_{ck} \mathscr{P}_{abck}^{(0)} \kappa_{ck}^{(2)} \right) \Big/ (\varepsilon_a^{(0)} - \varepsilon_b^{(0)}) \tag{221}$$

$$\varepsilon_p^{(2)} = u_{pp}^{(2)} - 4\sum_{ck} \mathscr{P}_{ppck}^{(0)} \kappa_{ck}^{(2)} \tag{222}$$

Using the Fock operator formalism, the first-order CPSCF equations were derived by Bratož (1958) and Gerratt and Mills (1968). Pople *et al.* (1979) implemented these equations using an iterative method.

C. MP2 Energy Derivatives

The MP2 energy at a displaced geometry is

$$W(X_0+\mu) = \langle \mathrm{HF}|H(X_0+\mu)|\mathrm{HF}\rangle + \sum_r \frac{\langle \mathrm{HF}|V(X_0+\mu)|r\rangle\langle r|V(X_0+\mu)|\mathrm{HF}\rangle}{\Delta\varepsilon_r(\mu)} \tag{223}$$

where the orbital connection, in addition to the reorthonormalization part, contains canonical orbital rotation parameters (from the CPSCF equations). The fluctuation potential and the denominators satisfy the geometry expansions

$$V(X_0 + \mu) = V^{(0)} + \mu V^{(1)} + \tfrac{1}{2}\mu\mu V^{(2)} + \cdots \tag{224}$$

$$\frac{1}{\Delta\varepsilon_r(\mu)} = \frac{1}{\Delta\varepsilon_r^{(0)}} - \mu\frac{\Delta\varepsilon_r^{(1)}}{(\Delta\varepsilon_r^{(0)})^2} - \frac{1}{2}\mu\mu\left[\frac{\Delta\varepsilon_r^{(2)}}{(\Delta\varepsilon_r^{(0)})^2} - 2\frac{(\Delta\varepsilon_r^{(1)})^2}{(\Delta\varepsilon_r^{(0)})^3}\right] + \cdots \tag{225}$$

Inserting the expansions for $H(X_0 + \mu)$, $V(X_0 + \mu)$, and $(\Delta\varepsilon_r(\mu))^{-1}$ in the MP2 expression and collecting terms to same order, we obtain

$$\begin{aligned} W^{(1)} = {} & \langle \mathrm{HF}|H^{(1)}|\mathrm{HF}\rangle + 2\sum_r \frac{\langle \mathrm{HF}|V^{(1)}|r\rangle\langle r|V^{(0)}|\mathrm{HF}\rangle}{\Delta\varepsilon_r^{(0)}} \\ & - \sum_r \frac{\langle \mathrm{HF}|V^{(0)}|r\rangle\langle r|V^{(0)}|\mathrm{HF}\rangle\Delta\varepsilon_r^{(1)}}{(\Delta\varepsilon_r^{(0)})^2} \end{aligned} \tag{226}$$

for the molecular gradient and

$$\begin{aligned} W^{(2)} = {} & \langle \mathrm{HF}|H^{(2)}|\mathrm{HF}\rangle + 2\sum_r \frac{\langle \mathrm{HF}|V^{(2)}|r\rangle\langle r|V^{(0)}|\mathrm{HF}\rangle}{\Delta\varepsilon_r^{(0)}} \\ & - \sum_r \frac{\langle \mathrm{HF}|V^{(0)}|r\rangle\langle r|V^{(0)}|\mathrm{HF}\rangle\Delta\varepsilon_r^{(2)}}{(\Delta\varepsilon_r^{(0)})^2} + 2\sum_r \frac{\langle \mathrm{HF}|V^{(1)}|r\rangle\langle r|V^{(1)}|\mathrm{HF}\rangle}{\Delta\varepsilon_r^{(0)}} \\ & - 4\sum_r \frac{\langle \mathrm{HF}|V^{(1)}|r\rangle\langle r|V^{(0)}|\mathrm{HF}\rangle\Delta\varepsilon_r^{(1)}}{(\Delta\varepsilon_r^{(0)})^2} \\ & + 2\sum_r \frac{\langle \mathrm{HF}|V^{(0)}|r\rangle\langle r|V^{(0)}|\mathrm{HF}\rangle(\Delta\varepsilon_r^{(1)})^2}{(\Delta\varepsilon_r^{(0)})^3} \end{aligned} \tag{227}$$

for the molecular Hessian. We emphasize that in the above expressions the connection contains orbital reoptimization as well as reorthonormalization contributions. The SCF molecular Hessian $\langle \mathrm{HF}|H^{(2)}|\mathrm{HF}\rangle$ in the above expression is therefore identical to the expression [Eq. (68)] given in Section III, since in Section III the connection contains only reorthonormalization contributions.

The MP2 gradient expression was derived and implemented by Pople *et al.* (1979). Second derivative expressions were given by Jørgensen and Simons (1983). Handy *et al.* (1985, 1986) and Harrison *et al.* (1986) simplified the gradient and Hessian expressions using the Handy–Schaefer technique and reported implementations of these expressions.

D. Implementation of MP2 Derivative Expressions

Before considering the molecular gradient and Hessian in detail, we note that the MP2 energy at the displaced geometry $X_0 + \mu$ may be written

$$\Delta W = \sum_{iajb} \frac{\tilde{g}_{iajb}(\mu)\tilde{k}_{iajb}(\mu)}{\Delta\varepsilon_{iajb}(\mu)} = \sum_{iajb} \tilde{t}_{iajb}(\mu)\tilde{g}_{iajb}(\mu) \tag{228}$$

where

$$\tilde{k}_{iajb}(\mu) = 2\tilde{g}_{iajb}(\mu) - \tilde{g}_{ibja}(\mu) \tag{229}$$

$$\tilde{t}_{iajb}(\mu) = \tilde{k}_{iajb}(\mu)/\Delta\varepsilon_{iajb}(\mu) \tag{230}$$

We also note that

$$\sum_{iajb} \frac{\tilde{g}^{(m)}_{iajb}\tilde{k}^{(n)}_{iajb}}{f_{iajb}} = \sum_{iajb} \frac{\tilde{g}^{(n)}_{iajb}\tilde{k}^{(m)}_{iajb}}{f_{iajb}} \tag{231}$$

whenever the function f_{iajb} is symmetric in a and b.

1. *MP2 Gradients*

Using the notation introduced above, the MP2 gradient [Eq. (226)] may be written

$$\Delta W^{(1)} = 2\sum_{iajb} t^{(0)}_{iajb}\tilde{g}^{(1)}_{iajb} - \sum_{iajb} t^{(0)}_{iajb} g^{(0)}_{iajb} \frac{\Delta\varepsilon^{(1)}_{iajb}}{\Delta\varepsilon^{(0)}_{iajb}} \tag{232}$$

where the derivatives of the OMO integrals are

$$\tilde{g}^{(1)}_{iajb} = g^{(1)}_{iajb} + \{\kappa^{(1)} - \tfrac{1}{2}S^{(1)}, g^{(0)}\}_{iajb} \tag{233}$$

Inserting Eq. (233) in Eq. (232) and rearranging terms, we obtain

$$\Delta W^{(1)} = 2\sum_{iajb} t^{(0)}_{iajb} g^{(1)}_{iajb} + 2\mathrm{Tr}\ \kappa^{(1)}\Phi^{(0)} - \mathrm{Tr}\ S^{(1)}\Phi^{(0)} + Z^{(0)}\varepsilon^{(1)} \tag{234}$$

where we have introduced the notation

$$\Phi_{ip} = 2\sum_{ajb} \tilde{t}_{iajb}\tilde{g}_{pajb} \tag{235}$$

$$\Phi_{ap} = 2\sum_{ijb} \tilde{t}_{iajb}\tilde{g}_{ipjb} \tag{236}$$

and

$$Z_i = -2\sum_{ajb} \tilde{t}_{iajb}\tilde{g}_{iajb}/\Delta\varepsilon_{iajb} \tag{237}$$

$$Z_a = 2\sum_{ijb} \tilde{t}_{iajb}\tilde{g}_{iajb}/\Delta\varepsilon_{iajb} \tag{238}$$

to simplify the expression. Note that Φ_{pq} has the same structure as the total Fock matrix [Eq. (E.1)] if we interpret $\tilde{t}_{iajb}$ as density elements, and also that $\operatorname{Tr}\Phi = 4\,\Delta W$.

We now collect together the contributions from $\kappa^{(1)}$ and $\varepsilon^{(1)}$ by introducing the vectors

$$\xi^{(1)} = \begin{cases} \varepsilon_p^{(1)} & (p = q) \\ \kappa_{pq}^{(1)} & (p > q) \end{cases} \tag{239}$$

and

$$\gamma^{(0)} = \begin{cases} Z_p^{(0)} & (p = q) \\ 2(\Phi_{pq}^{(0)} - \Phi_{qp}^{(0)}) & (p > q) \end{cases} \tag{240}$$

In the context of the previous sections, $\gamma_{pq}^{(0)}$ $(p > q)$ can be interpreted as the MP2 orbital gradient [compare Eq. (E.2)]. The molecular gradient now becomes

$$\Delta W^{(1)} = 2 \sum_{iajb} t_{iajb}^{(0)} g_{iajb}^{(1)} - \operatorname{Tr} S^{(1)}\Phi^{(0)} + \xi^{(1)}\gamma^{(0)} \tag{241}$$

Since $\xi^{(1)}$ is the solution of the CPSCF equations [Eq. (210)] (see Fig. 1)

$$A\xi^{(1)} = 2{}^{i}F^{(1)} \tag{242}$$

we may rewrite the last term in Eq. (241) as

$$\xi^{(1)}\gamma^{(0)} = 2{}^{i}F^{(1)}\zeta^{(0)} \tag{243}$$

where $\zeta^{(0)}$ is the Handy–Schaefer vector $\gamma^{(0)}A^{-1}$. (Note that A is not sym-

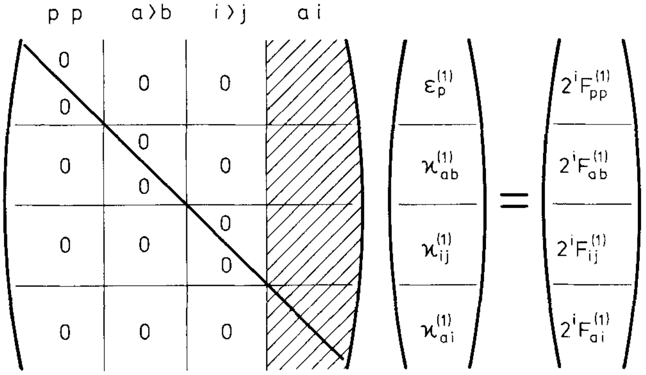

Fig. 1. The structure of the CPSCF linear equations. The only nonvanishing matrix elements are the diagonal elements and the elements of the column vectors for the unoccupied–occupied (*ai*) indices.

metric.) The final expression for the MP2 gradient is then

$$\Delta W^{(1)} = 2\sum_{iajb} t^{(0)}_{iajb} g^{(1)}_{iajb} + 2\,{}^{i}F^{(1)}\zeta^{(0)} - \operatorname{Tr} S^{(1)}\Phi^{(0)} \tag{244}$$

The first term is calculated in the AO basis, requiring the transformation of $t^{(0)}_{iajb}$ to the contravariant representation. The second term contains the contribution

$$2\,{}^{i}F^{[1]}\zeta^{(0)} = 2\sum_{p\geq q} \zeta^{(0)}_{pq}{}^{i}F^{(1)}_{pq} = \sum_{pq} Y^{(0)}_{pq} h^{(1)}_{pq} + 2\sum_{pqi} Y^{(0)}_{pq} \mathscr{P}^{(1)}_{pqii} \tag{245}$$

where

$$Y^{(0)} = \begin{cases} \zeta^{(0)}_{pq} & (p > q) \\ 2\zeta^{(0)}_{pp} & (p = q) \\ \zeta^{(0)}_{qp} & (p < q) \end{cases} \tag{246}$$

The two-electron contribution to Eq. (245) may be combined with the first term in Eq. (244) before transforming the effective densities to the contravariant AO representation. In this way transformations of differentiated AO integrals are completely avoided (Rice and Amos, 1985). In addition, the second term in Eq. (244) contains contributions from differentiated overlap matrices $-(S^{(1)}, {}^{i}F^{(0)})\zeta^{(0)}$, which are easily calculated in the AO basis using the techniques described in Appendix E. The last contribution to Eq. (244) is easily calculated having transformed the Fock matrix $\Phi^{(0)}$ to the contravariant AO representation.

2. *MP2 Hessians*

The expression for the MP2 Hessian is

$$\begin{aligned} \Delta W^{(2)} = {} & 2\sum_{iajb} t^{(0)}_{iajb}\tilde{g}^{(2)}_{iajb} - \sum_{iajb} t^{(0)}_{iajb} g^{(0)}_{iajb}\left(\frac{\Delta\varepsilon^{(2)}_{iajb}}{\Delta\varepsilon^{(0)}_{iajb}}\right) \\ & + 2\sum_{iajb} \frac{\tilde{g}^{(1)}_{iajb}\tilde{k}^{(1)}_{iajb}}{\Delta\varepsilon^{(0)}_{iajb}} - 4\sum_{iajb} t^{(0)}_{iajb}\tilde{g}^{(1)}_{iajb}\left(\frac{\Delta\varepsilon^{(1)}_{iajb}}{\Delta\varepsilon^{(0)}_{iajb}}\right) \\ & + 2\sum_{iajb} t^{(0)}_{iajb} g^{(0)}_{iajb}\left(\frac{\Delta\varepsilon^{(1)}_{iajb}}{\Delta\varepsilon^{(0)}_{iajb}}\right)^{2} \end{aligned} \tag{247}$$

Assuming that the $\varepsilon^{(1)}$ and $\kappa^{(1)}$ are available from the CPSCF equations and the $\tilde{g}^{(1)}$ are available in the MO basis, the last three contributions to the Hessian [Eq. (247)] can be calculated in a straightforward manner.

The second derivative integrals have the structure

$$\tilde{g}^{(2)} = g^{(2)} + \{\kappa^{(2)} + R^{(2)}, g^{(0)}\} + g^{(2)}_{rest} \tag{248}$$

where

$$g^{(2)}_{\text{rest}} = 2\{\kappa^{(1)} + R^{(1)}, g^{(1)}\} + \{\kappa^{(1)}, \{\kappa^{(1)}, g^{(0)}\}\} + \{R^{(1)}, \{R^{(1)}, g^{(0)}\}\} \\ + 2\{\kappa^{(1)}, \{R^{(1)}, g^{(0)}\}\} \tag{249}$$

and the first two contributions to the Hessian [Eq. (247)] may therefore be written as

$$T_{12} = T_1 + T_2 \tag{250}$$

where

$$T_1 = 2\sum_{iajb} t^{(0)}_{iajb} g^{(2)}_{iajb} + 2\text{Tr}\, R^{(2)}\Phi^{(0)} + 2\text{Tr}\, \kappa^{(2)}\Phi^{(0)} + Z^{(0)}\varepsilon^{(2)} \tag{251}$$

$$T_2 = 2\sum_{iajb} t^{(0)}_{iajb} [g^{(2)}_{\text{rest}}]_{iajb} \tag{252}$$

We now consider the calculation of these terms.

The term T_1 has the same structure as the MP2 gradient and may be treated in the same manner. If we introduce the vector

$$\xi^{(2)} = \begin{cases} \varepsilon^{(2)}_p & (p = q) \\ \kappa^{(2)}_{pq} & (p > q) \end{cases} \tag{253}$$

we may write

$$2\text{Tr}\, \kappa^{(2)}\Phi^{(0)} + Z^{(0)}\varepsilon^{(2)} = \xi^{(2)}\gamma^{(0)} \tag{254}$$

where $\gamma^{(0)}$ is defined as in the MP2 gradient calculation. This term contains all contributions from $\kappa^{(2)}$ and $\varepsilon^{(2)}$. Since $\xi^{(2)}$ is the solution of the second-order CPSCF equations [Eq. (217)]

$$A\xi^{(2)} = 2u^{(2)} \tag{255}$$

we obtain

$$\xi^{(2)}\gamma^{(0)} = 2u^{(2)}\zeta^{(0)} \tag{256}$$

where $\zeta^{(0)}$ is the Handy–Schaefer vector available from the gradient calculation. T_1 may therefore be written as

$$T_1 = 2\sum_{iajb} t^{(0)}_{iajb} g^{(2)}_{iajb} + 2\text{Tr}\, R^{(2)}\Phi^{(0)} + 2u^{(2)}\zeta^{(0)} \tag{257}$$

and calculated in the same manner as the MP2 gradient. In particular we may combine the second derivative integrals in $u^{(2)}$ with those in the first term in Eq. (257), and calculate the combined contribution in the AO basis using the same effective contravariant densities as in the gradient calculation. Hence no transformation of second derivative two-electron integrals is needed (Handy *et al.*, 1986).

The term T_2 [Eq. (252)] may be calculated in a variety of ways, noting that all contributions to $g^{(2)}_{\text{rest}}$ are already available in the MO basis. One may either carry out the one-index transformations according to Eq. (249) and then combine $g^{(2)}_{\text{rest}}$ with the densities $t^{(0)}_{iajb}$. Alternatively, one may construct intermediate MP2 Fock matrices from differentiated and one-index transformed integrals and calculate T_2 according to

$$\begin{aligned} T_2 = {} & 8\text{Tr}\,\kappa^{(1)}\Phi^{[1]} - 4\text{Tr}\,S^{(1)}\Phi^{[1]} \\ & + 4\text{Tr}[\kappa^{(1)}(\kappa^{(1)}, \Phi^{(0)})] + \text{Tr}[S^{(1)}(S^{(1)}, \Phi^{(0)})] \\ & - 4\text{Tr}[\kappa^{(1)}(S^{(1)}, \Phi^{(0)})] \end{aligned} \tag{258}$$

In these expressions differentiation and one-index transformations refer to the g integrals only of the Fock matrix [Eqs. (235) and (236)], treating the t elements as densities. The Fock matrix $\Phi^{[1]}$ may be constructed in the AO basis, transforming the density elements in $\Phi^{[1]}_{ip}$ and $\Phi^{[1]}_{ap}$ to the contravariant representation. If $\Phi^{[1]}$ is constructed in the AO basis the requirement on first derivative integrals in the MO basis is reduced to two occupied and two unoccupied indices (Handy *et al.*, 1986). Note that $T_1 + T_2$ [Eqs. (257) and (258)] has the same structure as the $E^{(2)}$ part of the MRCI Hessian (129).

VII. Derivatives of Molecular Properties

In this section we discuss the analytical calculation of geometrical derivatives of molecular properties. The emphasis is on properties related to variations in the electric field.

The techniques for calculating property derivatives are very similar to those for energy derivatives and we therefore refer to the literature given in previous sections. However, it is appropriate here to list the first implementations of analytical property derivative expressions which have been reported: SCF dipole gradients (Amos, 1984b), SCF polarizability gradients (Frisch *et al.*, 1986), MCSCF dipole gradients (Helgaker *et al.*, 1986b), and MP2 dipole gradients (Simandiras *et al.*, 1987; Harrison *et al.*, 1986). In addition, the technique of Komornicki and McIver (1979) should be mentioned. In their approach, dipole gradients are obtained by finite field calculations on analytically calculated gradients.

A. Alternative Descriptions of Dipole Moments and Frequency-Independent Polarizabilities

We consider a molecule at geometry X_0 in eigenstate $|X_0\rangle$ of the Hamiltonian $H(X_0)$ given in Eq. (8). When a homogeneous time-independent electric field is applied, the Hamiltonian becomes

$$\mathscr{H}(X_0) = H(X_0) - \varepsilon M(X_0) \tag{259}$$

where ε is the electric field strength and

$$M(X_0) = \sum_{pq} m_{pq}(X_0) E_{pq} \tag{260}$$

is the electric dipole operator (omitting the nuclear contribution). The dipole integrals are calculated as

$$m_{pq}(X) = \langle \psi_p(\xi; X) | \xi | \psi_q(\xi; X) \rangle \tag{261}$$

where the integration is over electronic coordinates ξ. The total energy of the system is

$$W(X_0, \varepsilon) = \langle X_0, \varepsilon | H(X_0) - \varepsilon M(X_0) | X_0, \varepsilon \rangle \tag{262}$$

where $|X_0, \varepsilon\rangle$ is the wave function of the system in the presence of the field. Expanding the energy in orders of the field strength we obtain

$$W(X_0, \varepsilon) = W^{(0)} - \varepsilon d(X_0) - \tfrac{1}{2}\varepsilon\varepsilon\alpha(X_0) + \cdots \tag{263}$$

where $d(X_0)$ is the dipole moment and $\alpha(X_0)$ the frequency-independent polarizability at the reference geometry. This expansion may be regarded as the definition of dipole moments and static polarizabilities.

The exact state satisfies the Hellmann–Feynman relationship

$$\frac{dW(X_0, \varepsilon)}{d\varepsilon} = -\langle X_0, \varepsilon | M(X_0) | X_0, \varepsilon \rangle \tag{264}$$

The electric properties may therefore also be defined by the expansion

$$\langle X_0, \varepsilon | M(X_0) | X_0, \varepsilon \rangle = d(X_0) + \varepsilon\alpha(X_0) + \cdots \tag{265}$$

Frequency-dependent properties are in fact usually defined by a time-dependent generalization of this equation. For example, when a periodic homogeneous electric field is applied, then the time development of $\langle X_0, \varepsilon | M(X_0) | X_0, \varepsilon \rangle$ defines the frequency-dependent properties. In the limit of a time-independent field the same equation then serves as a definition of frequency-independent properties.

The above definitions are equivalent only for wave functions which satisfy the Hellmann–Feynman relationship for electric field variations, for example, MCSCF wave functions. Limited CI and CC wave functions do not satisfy the conditions of the Hellmann–Feynman theorem, and properties calculated using the above two definitions are therefore different for these wave functions. There is, however, no *a priori* reason to prefer one definition over the other (Amos, 1987).

To illustrate the differences between these definitions we compare CI dipole moments calculated using the two approaches. The energy and dipole moment may be expanded in the field strength ε

$$W(\varepsilon) = \langle \mathrm{CI}(\varepsilon)|\mathscr{H}(\varepsilon)|\mathrm{CI}(\varepsilon)\rangle = W^{(0)} + \varepsilon W^{(1)} + \cdots \tag{266}$$

$$d(\varepsilon) = \langle \mathrm{CI}(\varepsilon)|M(\varepsilon)|\mathrm{CI}(\varepsilon)\rangle = d^{(0)} + \varepsilon d^{(1)} + \cdots \tag{267}$$

where $|\mathrm{CI}(\varepsilon)\rangle$ is the optimized wave function at ε and

$$\mathscr{H}(\varepsilon) = H(\varepsilon) - \varepsilon M(\varepsilon) \tag{268}$$

is the Hamiltonian operator. Since the MCSCF orbitals used in CI calculations depend on the electric field, the orbital connection and hence the operators $H(\varepsilon)$ and $M(\varepsilon)$ are field dependent. Expanding $H(\varepsilon)$, $M(\varepsilon)$, and $|\mathrm{CI}(\varepsilon)\rangle$ in ε and collecting terms to same order, we obtain the two alternative expressions for the dipole moment

$$-W^{(1)} = -\langle \mathrm{CI}|\mathscr{H}^{(1)}|\mathrm{CI}\rangle \tag{269}$$

$$d^{(0)} = \langle \mathrm{CI}|M^{(0)}|\mathrm{CI}\rangle \tag{270}$$

where $|\mathrm{CI}\rangle$ is the wave function at zero electric field. Differentiating $\mathscr{H}(\varepsilon)$ at $\varepsilon = 0$, we find

$$\mathscr{H}^{(1)} = H^{(1)} - M^{(0)} = -M^{(0)} + (\kappa^{(1)}, H^{(0)}) \tag{271}$$

since $H^{[1]}$ vanishes. Here $\kappa^{(1)}$ represents the first-order response of the orbitals to the electric field and may be determined from Eq. (64) if the operator $H^{(1)}$ in $f^{(1)}$ is replaced by $-M^{(0)}$. Inserting Eq. (271) in Eq. (269), we obtain

$$-W^{(1)} = \langle \mathrm{CI}|M^{(0)}|\mathrm{CI}\rangle - 2\mathrm{Tr}\,\kappa^{(1)}F^{(0)} \tag{272}$$

where $F^{(0)}$ is the CI Fock matrix. Comparing $-W^{(1)}$ and $d^{(0)}$, we see that

$$-W^{(1)} - d^{(0)} = -2\mathrm{Tr}\,\kappa^{(1)}F^{(0)} = -\sum_{p>q} \kappa^{(1)}_{pq} f^{(0)}_{pq} \tag{273}$$

where $f^{(0)}_{pq}$ is the CI orbital gradient. As this does not vanish, small differences occur between $-W^{(1)}$ and $d^{(0)}$ (Diercksen *et al.*, 1981). Using the Handy–Schaefer technique, the calculation of $\kappa^{(1)}$ for all three components of the field can be avoided. We finally note that for MCSCF wave functions, $-W^{(1)}$ and $d^{(0)}$ are identical, since $f^{(0)}_{pq}$ is zero for an MCSCF wave function.

B. Property Derivatives from Expansion of the Energy

We have previously considered the Hamiltonian as a function of the molecular geometry and described the expansion of the Hamiltonian in geometrical displacements μ. We now consider the Hamiltonian as a function of the electric field strength ε as well as geometrical displacements μ. Combining ε and μ into a single perturbational parameter

$$\eta = \begin{pmatrix} \mu \\ \varepsilon \end{pmatrix} \tag{274}$$

we may expand the Hamiltonian as

$$\begin{aligned} \mathscr{H}(X_0 + \mu, \varepsilon) &= H(X_0 + \mu, \varepsilon) - \varepsilon M(X_0 + \mu, \varepsilon) \\ &= \mathscr{H}^{(0)} + \eta \mathscr{H}^{(1)} + \tfrac{1}{2}\eta\eta\mathscr{H}^{(2)} + \cdots \end{aligned} \tag{275}$$

The components of $\mathscr{H}^{(n)}$ which refer to geometrical displacements only correspond to the $H^{(n)}$ that were discussed in Section II. The components of $\mathscr{H}^{(n)}$ which couple geometrical distortions and field variations correspond to derivatives of the one-electron operator $-\varepsilon M(X_0 + \mu)$ and are easily calculated.

The analytical expressions for the property derivatives may be obtained by substituting $\mathscr{H}^{(n)}$ for $H^{(n)}$ in the appropriate expressions given in Sections III–VI, since these expressions were derived with no assumptions about the internal structure of the Hamiltonian. For example, second-order MCSCF properties are given by [Eq. (68)]

$$W^{(2)} = E^{(2)} + f^{(1)}\lambda^{(1)} \tag{276}$$

where $\lambda^{(1)}$ is obtained by solving the response equations [Eq. (64)]

$$G^{(0)}\lambda^{(1)} = -f^{(1)} \tag{277}$$

We now interpret these equations as

$$\begin{bmatrix} W^{(20)} & W^{(11)} \\ W^{(11)} & W^{(02)} \end{bmatrix} = \begin{bmatrix} E^{(20)} & E^{(11)} \\ E^{(11)} & E^{(02)} \end{bmatrix} + \begin{bmatrix} f^{(10)} \\ f^{(01)} \end{bmatrix} [\lambda^{(10)}\lambda^{(01)}] \tag{278}$$

and

$$G^{(00)}[\lambda^{(10)}\lambda^{(01)}] = -[f^{(10)}f^{(01)}] \tag{279}$$

where double superscripts (mn) indicate m times differentiation with respect to μ and n times with respect to ε. From Eq. (278) we see that the dipole gradient may be calculated in two equivalent ways

$$\begin{aligned} W^{(11)} &= E^{(11)} + f^{(10)}\lambda^{(01)} \\ &= E^{(11)} + f^{(01)}\lambda^{(10)} \end{aligned} \tag{280}$$

where

$$E^{(11)} = \langle \mathrm{MC}|\mathscr{H}^{(11)}|\mathrm{MC}\rangle \tag{281}$$

In the MCSCF case the connection is independent of the field, and the

Hamiltonian therefore has field-independent integrals:

$$\mathscr{H}(X_0 + \mu, \varepsilon) = H(X_0 + \mu) - \varepsilon M(X_0 + \mu) \tag{282}$$

From this we see that

$$\mathscr{H}^{(11)} = -M^{(10)} = -M^{[10]} + \tfrac{1}{2}(S^{(10)}, M^{(00)}) \tag{283}$$

so that

$$E^{(11)} = -\mathrm{Tr}\; Dm^{(10)} + \mathrm{Tr}\; S^{(10)}F^{M} \tag{284}$$

where F^M is the Fock matrix constructed from the dipole operator $-M$ rather than the Hamiltonian H. The $E^{(11)}$ are easily calculated in the AO basis

$$E^{(11)} = -\mathrm{Tr}\; D_{\mathrm{ao}} m^{(10)}_{\mathrm{AO}} + \mathrm{Tr}\; S^{(10)}_{\mathrm{AO}} F^{M}_{\mathrm{ao}} \tag{285}$$

using covariant integrals. The electronic gradient is simply

$$f^{(01)} = -\langle \mathrm{MC} | [\Lambda, M^{(00)}] | \mathrm{MC} \rangle \tag{286}$$

which is easily constructed since only one-electron integrals are involved.

C. Property Derivatives from Expansion of the Dipole Moment

Calculations of property derivatives based on the expansion of the dipole moment follow an outline similar to the one used for the calculations based on the energy expansion. As an illustration we consider the MCSCF dipole gradient.

Ignoring the field dependence of the dipole operator (MCSCF orbital connections are field independent) we write

$$d(X_0 + \mu) = d^{(0)} + \mu d^{(1)} + \cdots \tag{287}$$

The dipole moment expectation value may be BCH expanded in the same way as the Hamiltonian expectation value:

$$d(X_0 + \mu) = \langle \mathrm{MC} | M(X_0 + \mu) | \mathrm{MC} \rangle + \lambda \langle \mathrm{MC} | [\Lambda, M(X_0 + \mu)] | \mathrm{MC} \rangle + \cdots \tag{288}$$

where we have used the notation of Section III. Expanding $M(X_0 + \mu)$ and λ in Cartesian displacements, we obtain

$$M(X_0 + \mu) = M^{(0)} + \mu M^{(1)} + \cdots \tag{289}$$

$$\lambda = \mu \lambda^{(1)} + \cdots \tag{290}$$

where $\lambda^{(0)}$ vanishes since $|\mathrm{MC}\rangle$ is optimized at X_0, and $\lambda^{(1)}$ is determined from the MCSCF response equations. Inserting the expansions for $d(X_0 + \mu)$, $M(X_0 + \mu)$, and λ in Eq. (288) and collecting terms to first order, we obtain

$$d^{(1)} = \langle \mathrm{MC} | M^{(1)} | \mathrm{MC} \rangle + \lambda^{(1)} \langle \mathrm{MC} | [\Lambda, M^{(0)}] | \mathrm{MC} \rangle \tag{291}$$

Since there is no orbital rotation connection, the first derivatives of the dipole operator become

$$M^{(1)} = M^{[1]} - \tfrac{1}{2}(S^{(1)}, M^{(0)}) \tag{292}$$

This gives

$$\langle \mathrm{MC}|M^{(1)}|\mathrm{MC}\rangle = \mathrm{Tr}\, Dm^{(1)} - \mathrm{Tr}\, S^{(1)}F^{M} \tag{293}$$

which is identical to $-E^{(11)}$ derived from the energy expansion [Eq. (284)]. Also $\langle \mathrm{MC}|[\Lambda, M^{(0)}]|\mathrm{MC}\rangle$ is identical to $-f^{(01)}$ derived from the energy expansion [Eq. (286)]. Hence we see that the expressions for MCSCF dipole gradients derived using the two approaches are identical, as they should be when the wave function satisfies the conditions of the Hellmann–Feynman theorem.

VIII. Translational and Rotational Symmetries

Derivatives of the energy and molecular properties are most conveniently calculated in Cartesian coordinates. Due to translational and rotational symmetries these Cartesian derivatives are not independent. For example, for forces only $3N - m$ ($m = 5, 6$) Cartesian components are independent. The remaining five or six components can be calculated by taking into consideration the translational and rotational symmetries of the energy. This has two useful applications. First, the number of derivatives that must be calculated *ab initio* may be reduced. This saving is especially important for small molecules. Alternatively, one may calculate all derivatives *ab initio* and simply use translational and rotational symmetries as a simple check on the calculation.

Over the years many discussions of translational and rotational symmetries have appeared in connection with calculation of energy and property derivatives (Page *et al.*, 1984b; Helgaker *et al.*, 1986b; Lee *et al.*, 1986). However, all of these have been restricted to special cases. We present here a method which is both simple and general.

Let $F^{(n)}$ denote the $(3N)^n$ nth-order geometrical partial derivatives of a function F of a molecular system. Let us assume that we know $(3N - m)^{n+1}$ appropriately chosen components of $F^{(n+1)}$ and all the components of $F^{(n)}$. We will now show that the $(3N)^{n+1} - (3N - m)^{n+1}$ unknown components of $F^{(n+1)}$ may be calculated in a simple fashion from the rotational and translational symmetries of $F^{(n)}$.

Let us denote the translational and rotational coordinates by $\{T_x, T_y, T_z, R_x, R_y, R_z\}$ or collectively by $\{r_i\}$. The $3N$ Cartesian coordinates are denoted by $\{x_i, y_i, z_i \,|\, i = 1, N\}$ or $\{\xi_i \,|\, i = 1, 3N\}$. Using the chain rule for differentiation we obtain

$$(\partial F^{(n)}_{i_1 i_2 \cdots i_n}/\partial r_j) = \sum_{k=1}^{3N} (\partial F^{(n)}_{i_1 i_2 \cdots i_n}/\partial \xi_k)(\partial \xi_k/\partial r_j) \tag{294}$$

We may write Eq. (294) in matrix form

$$T[m \times (3N)]A[3N] = B[m] \tag{295}$$

where

$$T_{ij} = \partial \xi_j/\partial r_i \tag{296}$$

$$A_i = \partial F^{(n)}_{j_1 j_2 \cdots j_n}/\partial \xi_i = F^{(n+1)}_{j_1 j_2 \cdots j_n i} \tag{297}$$

$$B_i = \partial F^{(n)}_{j_1 j_2 \cdots j_n}/\partial r_i \tag{298}$$

T can be calculated from the molecular geometry and B from the derivatives $F^{(n)}$, as discussed below. Assuming that we have picked out m independent Cartesian coordinates, we may reorder the columns of T so that the first m columns are linearly independent. In partitioned form we may write T as

$$T[m \times (3N)] = [T_{\mathrm{D}}(m \times m)T_{\mathrm{I}}(m \times (3N - m)] \tag{299}$$

where T_{D} is nonsingular. Reordering A in the same way

$$A[3N] = \begin{pmatrix} A_{\mathrm{D}}[m] \\ A_{\mathrm{I}}[3N - m] \end{pmatrix} \tag{300}$$

we find that Eq. (295) may be written as

$$T_{\mathrm{D}}A_{\mathrm{D}} + T_{\mathrm{I}}A_{\mathrm{I}} = B \tag{301}$$

or equivalently

$$A_{\mathrm{D}} = T_{\mathrm{D}}^{-1}(B - T_{\mathrm{I}}A_{\mathrm{I}}) \tag{302}$$

In order to use Eq. (302) to calculate m components of A_{D} it remains to describe the calculation of T and B.

The T matrix is easily constructed from the molecular geometry, using (the summations are over all atoms)

$$(\partial/\partial T_x) = \sum_k (\partial/\partial x_k) \tag{303}$$

$$(\partial/\partial T_y) = \sum_k (\partial/\partial y_k) \tag{304}$$

$$(\partial/\partial T_z) = \sum_k (\partial/\partial z_k) \tag{305}$$

$$(\partial/\partial R_x) = \sum_k [y_k(\partial/\partial z_k) - z_k(\partial/\partial y_k)] \tag{306}$$

$$(\partial/\partial R_y) = \sum_k [z_k(\partial/\partial x_k) - x_k(\partial/\partial z_k)] \tag{307}$$

$$(\partial/\partial R_z) = \sum_k [x_k(\partial/\partial y_k) - y_k(\partial/\partial x_k)] \tag{308}$$

which give explicitly the transformation coefficients $(\partial\xi_i/\partial r_j)$. To obtain expressions for B we need to consider the commutators between the partial derivatives of r_i and ξ_j. The only nonzero commutators are

$$[(\partial/\partial R_x), (\partial/\partial y_i)] = -(\partial/\partial z_i) \tag{309}$$

$$[(\partial/\partial R_x), (\partial/\partial z_i)] = (\partial/\partial y_i) \tag{310}$$

$$[(\partial/\partial R_y), (\partial/\partial x_i)] = (\partial/\partial z_i) \tag{311}$$

$$[(\partial/\partial R_y), (\partial/\partial z_i)] = -(\partial/\partial x_i) \tag{312}$$

$$[(\partial/\partial R_z), (\partial/\partial x_i)] = -(\partial/\partial y_i) \tag{313}$$

$$[(\partial/\partial R_z), (\partial/\partial y_i)] = (\partial/\partial x_i) \tag{314}$$

We use the notation

$$[(\partial/\partial r_i), (\partial/\partial \xi_j)] = a_{ij}(\partial/\partial \xi_{[i,j]}) \tag{315}$$

for a general commutator, where a_{ij} is 0, -1, or 1. Repeated use of Eq. (315) then gives

$$(\partial F^{(n)}_{j_1 j_2 \cdots j_n}/\partial r_i) = \sum_{k=1}^{n} a_{ij_k} F^{(n)}_{j_1 j_2 \cdots j_{k-1}[i,j_k]j_{k+1}\cdots j_n} + (\partial F/\partial r_i)^{(n)}_{j_1 j_2 \cdots j_n} \tag{316}$$

where we have used an obvious shorthand notation. Hence we see that the rotational derivatives of the elements of $F^{(n)}$ in general consist of $n + 1$ contributions. The first n contributions are obtained from $F^{(n)}$ simply by rotating one index at a time according to the commutator relationships between the rotational and Cartesian coordinates. The last contribution arises from the rotational properties of F. For the energy this term is zero. For other properties such as the dipole moment this contribution is nonzero and must be calculated from the translational and rotational properties of the considered molecular property.

To illustrate the technique we consider the derivatives of E_{xyz} with respect to rotation about the z axis (assuming that all coordinates belong to the same atom):

$$(\partial E_{xyz}/\partial R_z) = E_{[z,x]yz} + E_{x[z,y]z} + E_{xy[z,z]} = -E_{yyz} + E_{xxz} \tag{317}$$

where the last contribution in Eq. (316) vanishes.

The above method can be applied straightforwardly to calculate m dependent Cartesian forces (gradient elements) from $3N - m$ independent forces. The calculation of Hessian elements is somewhat more complicated. First we apply the method successively to each of the $(3N - m)$ rows, generating each time m-dependent Hessian elements belonging to the same row. The method can now be applied to the remaining m rows since the symmetry of the Hessian ensures that only m elements are unknown in each row. The above procedure may be carried out by solving two consecutive sets of linear equations.

IX. Concluding Remarks

Over the past decade the analytical calculation of geometrical derivatives has emerged as an indispensable tool in the study of molecular structure and dynamics. At the same time the emphasis in the field has changed. A few years ago the derivation of gradient expressions for correlated wave functions presented a significant challenge. Today such expressions have been successfully programmed and put to use in many laboratories. The emphasis is now on higher derivatives, as well as on simplifications and efficient reformulations of established techniques.

In this review we have presented derivative expressions for the most commonly used methods in molecular electronic structure theory, and we have discussed their computational implementations. It is seldom possible to give expressions which are optimal under all conditions, regardless of the number of electrons, basis functions, and configurations. We have focused on techniques which are simple and general, in particular those which can handle large basis sets and configuration expansions. Under certain conditions these may not be the most efficient. We believe, however, that the approach taken in this review constitutes a good basis for developing efficient procedures for calculation of geometrical derivatives under any particular set of circumstances.

Appendix A. Notation for Derivatives

We use $A^{(n)}$ to denote derivatives. The expansion of A in μ is written

$$A = A^{(0)} + \mu A^{(1)} + \tfrac{1}{2}\mu\mu A^{(2)} + \cdots \tag{A.1}$$

where we have used a shorthand tensor notation, for example,

$$\mu\mu A^{(2)} = \sum_{ij} \mu_i \mu_j A_{ij}^{(2)} \tag{A.2}$$

Square brackets in $A^{[n]}$ are used to indicate that in the expression for A we replace the undifferentiated integrals by the derivatives of the UMO integrals $h_{pq}^{(n)}$ and $g_{pqrs}^{(n)}$ (i.e., by the derivatives of the integrals with no connection matrix attached). For example, the derivatives of the Hamiltonian

$$H = \sum_{pq} \tilde{h}_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} \tilde{g}_{pqrs} e_{pqrs} \tag{A.3}$$

are given as

$$H^{(n)} = \sum_{pq} \tilde{h}^{(n)}_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} \tilde{g}^{(n)}_{pqrs} e_{pqrs} \tag{A.4}$$

since the geometry dependence of the operators E_{pq} and e_{pqrs} may be neglected (see Section II). In contrast, $H^{[n]}$ is given as

$$H^{[n]} = \sum_{pq} h^{(n)}_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} g^{(n)}_{pqrs} e_{pqrs} \tag{A.5}$$

which differs from $H^{(n)}$ since, for example,

$$\tilde{h}^{(1)}_{pq} = h^{(1)}_{pq} + \{Q^{(1)} + R^{(1)}, h^{(0)}\}_{pq} \tag{A.6}$$

Appendix B. Notation for One-Index Transformations

One-index transformations with A as the transformation matrix are defined as

$$\{A, B\}_{pq} = \sum_{\alpha} (A_{p\alpha} B_{\alpha q} + A_{q\alpha} B_{p\alpha}) \tag{B.1}$$

$$\{A, B\}_{pqrs} = \sum_{\alpha} (A_{p\alpha} B_{\alpha qrs} + A_{q\alpha} B_{p\alpha rs} + A_{r\alpha} B_{pq\alpha s} + A_{s\alpha} B_{pqr\alpha}) \tag{B.2}$$

in the one- and two-electron cases, respectively. Symmetrized one-index transformations are defined as

$$\{A_1, A_2, \ldots, A_n, B\} = \frac{1}{n!} P(1, 2, \ldots, n) \{A_1, \{A_2, \ldots, \{A_n, B\} \ldots,\}\} \tag{B.3}$$

where $P(1, 2, \ldots, n)$ is the permutation operator. We further use the notation (A, B) to indicate that in the expression for B the Hamiltonian integrals are replaced by the one-index transformed integrals. For example

$$(A, H^{[n]}) = \sum_{pq} \{A, h^{(n)}\}_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} \{A, g^{(n)}\}_{pqrs} e_{pqrs} \tag{B.4}$$

Appendix C. Covariant and Contravariant Representations

Using the Einstein summation convention the molecular electronic energy is

$$E = D_{pq}h_{pq} + \tfrac{1}{2}d_{pqrs}g_{pqrs} \tag{C.1}$$

in the MO basis. The energy can also be calculated in the AO basis (denoted by Greek letters $\mu\nu\lambda\sigma$) as

$$E = D^{\mu\nu}h_{\mu\nu} + \tfrac{1}{2}d^{\mu\nu\lambda\sigma}g_{\mu\nu\lambda\sigma} \tag{C.2}$$

where

$$D^{\mu\nu} = \sum_{pq} C_{p\mu}C_{q\nu}D_{pq} \tag{C.3}$$

$$h_{pq} = \sum_{\mu\nu} C_{p\mu}C_{q\nu}h_{\mu\nu} \tag{C.4}$$

and similarly in the two-electron case. Note that the AO density matrix and AO one-electron integral matrix are related to the MO basis in different ways. The AO density matrix is obtained from the MO basis by transforming with the orbital coefficients, and the MO integral matrix is obtained from the AO matrix using the same transformation. In the language of tensor theory the $D^{\mu\nu}$ are said to be the *contravariant* components of the density tensor in the AO basis, and the $h_{\mu\nu}$ are said to be the *covariant* components of the one-electron Hamiltonian in the AO basis. Upper and lower indices are used to distinguish between the contravariant and covariant tensor components.

The energy can also be calculated in the AO basis as

$$E = D_{\mu\nu}h^{\mu\nu} + \tfrac{1}{2}d_{\mu\nu\lambda\sigma}g^{\mu\nu\lambda\sigma} \tag{C.5}$$

where the covariant density matrix and the contravariant integrals are related to the MO basis as

$$D_{pq} = \sum_{\mu\nu} C_{p\mu}C_{q\nu}D_{\mu\nu} \tag{C.6}$$

$$h^{\mu\nu} = \sum_{pq} C_{p\mu}C_{q\nu}h_{pq} \tag{C.7}$$

and similarly in the two-electron case. Any other combination of covariant and contravariant components can also be used, for example,

$$E = D^{\mu}_{\cdot\nu}h_{\mu}^{\cdot\nu} + \tfrac{1}{2}d^{\mu\nu}_{\cdot\cdot\lambda\sigma}g_{\mu\nu}^{\cdot\cdot\lambda\sigma} \tag{C.8}$$

except that in the summations one contravariant index of one tensor should always be equated to one covariant index of the other. The expression Eq. (C.2) is the most useful since the Hamiltonian integrals are always calculated in the covariant AO basis.

The relationship between the contravariant and the covariant components is simple, for example,

$$h_{\mu\nu} = S_{\mu\lambda}S_{\nu\sigma}h^{\lambda\sigma} \tag{C.9}$$

$$h^{\mu\nu} = S^{\mu\lambda}S^{\nu\sigma}h_{\lambda\sigma} \tag{C.10}$$

where the $S_{\mu\nu}$ are the covariant components of the metric tensor (which corresponds to the usual AO overlap matrix) and $S^{\mu\nu}$ is the contravariant metric tensor (which corresponds to the inverse of the overlap matrix). There is no difference between contravariant and covariant components in the MO basis, as in this case the metric tensor corresponds to the unit tensor (the overlap matrix is the unit matrix).

Even though we do not invoke the full machinery of tensor analysis (Butkov, 1968), it is useful to keep the distinction between contravariant and covariant components clear. To avoid conflicting notation we do not use upper and lower indices to denote contravariant and covariant indices. Instead, we will use the suffix ao (lower case letters) on tensors whose indices are all contravariant, and AO (capital letters) on tensors whose indices are all covariant. No special suffix is used in the MO basis. For example, using the two- and four-index trace operators the energy is

$$E = \mathrm{Tr}\ Dh + \tfrac{1}{2}\mathrm{Tr}\ dg \tag{C.11}$$

in the MO basis, and

$$E = \mathrm{Tr}\ D_{\mathrm{ao}}h_{\mathrm{AO}} + \tfrac{1}{2}\mathrm{Tr}\ d_{\mathrm{ao}}g_{\mathrm{AO}} \tag{C.12}$$

in the AO basis using covariant integrals and contravariant density matrices.

Appendix D. Hamiltonian (Transition) Expectation Values

The average value of the Hamiltonian $H^{[n]}$ with respect to an MCSCF or MRCI wave function may be written as

$$\langle H^{[n]}\rangle = \sum_{pq} D_{pq}h_{pq}^{(n)} + \frac{1}{2}\sum_{pqrs} d_{pqrs}g_{pqrs}^{(n)} \tag{D.1}$$

where we have introduced the symmetrized one- and two-electron density matrices

$$D_{pq} = \tfrac{1}{2}\langle E_{pq} + E_{qp}\rangle \tag{D.2}$$

$$d_{pqrs} = \tfrac{1}{4}\langle e_{pqrs} + e_{pqsr} + e_{qprs} + e_{qpsr}\rangle \tag{D.3}$$

In terms of two- and four-index trace operations the expectation value may be written more compactly as

$$\langle H^{[n]}\rangle = \mathrm{Tr}\ Dh^{(n)} + \tfrac{1}{2}\mathrm{Tr}\ dg^{(n)} \tag{D.4}$$

The above expressions are also valid for expectation values of $H^{(n)}$ if we replace the integrals $I^{(n)}$ by the OMO integrals $\tilde{I}^{(n)}$. In many cases it is more useful to express Eq. (D.4) in the AO basis

$$\langle H^{[n]}\rangle = \mathrm{Tr}\ D_{\mathrm{ao}} h_{\mathrm{AO}}^{(n)} + \tfrac{1}{2}\mathrm{Tr}\ d_{\mathrm{ao}} g_{\mathrm{AO}}^{(n)} \tag{D.5}$$

with contravariant density matrices and covariant integrals. This expression is convenient since it does not require transformation of the AO (derivative) integrals to the MO basis. Also, in many cases integral storage is avoided since the integrals may be combined directly with the appropriate density elements and their contribution added to $\langle H^{[n]}\rangle$.

The configuration part of the electronic gradient is for both MCSCF and MRCI wave functions

$${}^{c}f_k^{(n)} = -2\langle 0|H^{(n)}|k\rangle \tag{D.6}$$

where $|0\rangle$ is the reference state and $\{|k\rangle\}$ the orthogonal complement set of states. Several alternative expressions may be given (Shepard, 1987) for the evaluation of

$$\begin{aligned}\sum_k {}^{c}f_k^{(n)} y_k &= -2\langle 0|H^{(n)}|y\rangle \\ &= -2\mathrm{Tr}\ D^y \tilde{h}^{(n)} - \mathrm{Tr}\ d^y \tilde{g}^{(n)} \\ &= -2\mathrm{Tr}\ D_{\mathrm{ao}}^y \tilde{h}_{\mathrm{AO}}^{(n)} - \mathrm{Tr}\ d_{\mathrm{ao}}^y \tilde{g}_{\mathrm{AO}}^{(n)}\end{aligned} \tag{D.7}$$

where

$$|y\rangle = \sum_k |k\rangle y_k \tag{D.8}$$

and

$$D_{pq}^y = \tfrac{1}{2}\langle 0|E_{pq} + E_{qp}|y\rangle \tag{D.9}$$

$$d_{pqrs}^y = \tfrac{1}{4}\langle 0|e_{pqrs} + e_{pqsr} + e_{qprs} + e_{qpsr}|y\rangle \tag{D.10}$$

are the symmetrized transition density matrices.

Appendix E. The Fock Matrix

The Fock matrix $F^{(n)}$ is defined as (Siegbahn *et al.*, 1981; Jensen and Ågren, 1986)

$$\begin{aligned}F_{pq}^{(n)} &= \sum_\sigma \langle a_{p\sigma}^{+}[a_{q\sigma}, H^{(n)}]\rangle \\ &= \sum_\beta D_{p\beta}\tilde{h}_{q\beta}^{(n)} + \sum_{\beta\gamma\delta} d_{p\beta\gamma\delta}\tilde{g}_{q\beta\gamma\delta}^{(n)}\end{aligned} \tag{E.1}$$

where the second expression is obtained by inserting the Hamiltonian and using the anticommutation relationships of the creation and annihilation operators. The Fock matrix $F^{[n]}$ is defined in the same way as $F^{(n)}$ except that $H^{[n]}$ is used instead of $H^{(n)}$. Hence all relationships derived for $F^{(n)}$ also hold for $F^{[n]}$ if we replace $\tilde{I}^{(n)}$ by $I^{(n)}$ in the expressions.

The Fock matrix appears naturally in the calculation of the orbital part of the electronic gradient:

$$\begin{aligned} f_{pq}^{(n)} &= \langle [E_{pq} - E_{qp}, H^{(n)}] \rangle = 2\langle [E_{pq}, H^{(n)}] \rangle \\ &= 2\sum_{\sigma} (\langle a_{p\sigma}^{+} [a_{q\sigma}, H^{(n)}] \rangle + \langle [a_{p\sigma}^{+}, H^{(n)}] a_{q\sigma} \rangle) \\ &= 2\sum_{\sigma} (\langle a_{p\sigma}^{+} [a_{q\sigma}, H^{(n)}] \rangle - \langle a_{q\sigma}^{+} [a_{p\sigma}, H^{(n)}] \rangle) \\ &= 2(F_{pq}^{(n)} - F_{qp}^{(n)}) \end{aligned} \tag{E.2}$$

In the MCSCF case the undifferentiated Fock matrix is symmetric since the orbital optimization ensures that $f_{pq}^{(0)} = 2(F_{pq}^{(0)} - F_{qp}^{(0)}) = 0$. The Fock matrix also appears in the calculation of expectation values of one-index transformed Hamiltonians (see Appendix F).

The construction of the Fock matrix may be simplified in the MCSCF case when the orbital space is partitioned in an inactive, an active, and a secondary space. Siegbahn *et al.* (1981) have shown that the Fock matrix elements then become

$$F_{iq}^{(n)} = 2({}^{i}F_{iq}^{(n)} + {}^{a}F_{iq}^{(n)}) \tag{E.3}$$

$$F_{tq}^{(n)} = \sum_{u} D_{tu}\, {}^{i}F_{qu}^{(n)} + Q_{tq}^{(n)} \tag{E.4}$$

$$F_{aq}^{(n)} = 0 \tag{E.5}$$

where we have introduced the inactive Fock matrix

$${}^{i}F_{pq}^{(n)} = \tilde{h}_{pq}^{(n)} + 2\sum_{i} \tilde{\mathscr{P}}_{pqii}^{(n)} \tag{E.6}$$

the active Fock matrix

$${}^{a}F_{pq}^{(n)} = \sum_{tu} D_{tu} \tilde{\mathscr{P}}_{pqtu}^{(n)} \tag{E.7}$$

and the auxiliary matrix

$$Q_{tq}^{(n)} = 2\sum_{uvx} d_{tuvx} \tilde{g}_{quvx}^{(n)} \tag{E.8}$$

In these expressions we have used the Roothaan–Bagus integrals (Roothaan and Bagus, 1963)

$$\tilde{\mathscr{P}}_{pqrs} = \tilde{g}_{pqrs} - \tfrac{1}{4}\tilde{g}_{prqs} - \tfrac{1}{4}\tilde{g}_{psrq} \tag{E.9}$$

We use the indices *ijkl* for inactive orbitals, *tuvx* for active orbitals, *abcd* for secondary orbitals, and *pqrs* for general (arbitrary) orbitals. Equations (E.3)–(E.5) are obtained recognizing that density matrix elements containing secondary indices vanish, and that elements containing inactive orbitals simplify as

$$D_{ip} = 2\delta_{ip} \tag{E.10}$$

$$d_{ijpq} = \delta_{ij} D_{pq} - \delta_{iq}\delta_{jp} \tag{E.11}$$

$$d_{pijq} = 2\delta_{ip}\delta_{jq} - \tfrac{1}{2}\delta_{ij} D_{pq} \tag{E.12}$$

The matrices ${}^{i}F^{(n)}$ and ${}^{a}F^{(n)}$ are easily calculated in the AO basis from the Roothaan–Bagus integrals. Conversely, the construction of $Q^{(n)}$ (and thus the total Fock matrix) requires MO integrals with one general and three active indices. The $Q^{(n)}$ matrix can be calculated as a matrix product if all density and integral elements for a given distribution *vx* are held in core at the same time.

The sum of the inactive and the active Fock matrices may be written as (Linderberg and Öhrn, 1973)

$$2({}^{i}F^{(n)}_{pq} + {}^{a}F^{(n)}_{pq}) = \sum_{\sigma} \langle [a^{+}_{p\sigma}, [a_{q\sigma}, H^{(n)}]]_{+} \rangle \tag{E.13}$$

which differs from the expression for the total Fock matrix (E.1) by the presence of the anticommutator.

The Fock matrix from one-index transformed integrals is

$$(A, F^{[n]})_{pq} = \sum_{\beta} D_{p\beta} \{A, h^{(n)}\}_{q\beta} + \sum_{\beta\gamma\delta} d_{p\beta\gamma\delta} \{A, g^{(n)}\}_{q\beta\gamma\delta} \tag{E.14}$$

In the MCSCF case this matrix may be calculated according to Eqs. (E.3)–(E.5), but using matrices ${}^{i}F^{[n]}$, ${}^{a}F^{[n]}$, and $Q^{[n]}$ containing one-index transformed integrals. For example, for the inactive Fock matrix we obtain

$$\begin{aligned}(A, {}^{i}F^{[n]})_{pq} &= \{A, {}^{i}F^{[n]}\}_{pq} + 4\sum_{ir} \mathscr{P}^{(n)}_{pqir} A_{ir} \\ &= \{A, {}^{i}F^{[n]}\}_{pq} + 4P(A)^{[n]}_{pq}\end{aligned} \tag{E.15}$$

where

$$P(A)^{[n]}_{pq} = \sum_{ir} \mathscr{P}^{(n)}_{pqir} A_{ir} \tag{E.16}$$

and similarly for the active Fock matrix. The first term is simply the one-index transformed inactive Fock matrix. The second term may be constructed in the AO basis with A in the contravariant representation. The construction of $(A, Q^{[n]})$ requires MO integrals with two general and two active indices.

The Fock matrix with doubly one-index transformed integrals may be calculated in the same way. In particular, the inactive and active Fock matrices may be calculated in the AO basis. For example, for the inactive Fock matrix we obtain

$$\begin{aligned}(B,(A,{}^{i}F^{[n]}))_{pq} &= \{B,(A,{}^{i}F^{[n]})\}_{pq} + 4\{A, P(B)^{[n]}\}_{pq}\\ &\quad + 4P(AB)^{[n]}_{pq} + 4\sum_{rs}\mathscr{P}^{(n)}_{pqrs}\left(\sum_{i} B_{ir}A_{is}\right)\end{aligned} \tag{E.17}$$

The first term corresponds to a doubly one-index transformed inactive Fock matrix. The second term is a one-index transformed matrix $P(B)^{[n]}$. The third and fourth terms may be constructed in the AO basis with the matrices multiplying the $\mathscr{P}^{(n)}$ integrals in the contravariant representation.

Appendix F. Expectation Values of One-Index Transformed Hamiltonians

The expectation value of the one-index transformed Hamiltonian can be written in the following alternative ways (Helgaker, 1986)

$$\begin{aligned}\langle(A, H^{[n]})\rangle &= \mathrm{Tr}\, D\{A, h^{(n)}\} + \tfrac{1}{2}\mathrm{Tr}\, d\{A, g^{(n)}\}\\ &= \mathrm{Tr}\{\tilde{A}, D\}h^{(n)} + \tfrac{1}{2}\mathrm{Tr}\{\tilde{A}, d\}g^{(n)}\\ &= 2\mathrm{Tr}\, AF^{[n]}\end{aligned} \tag{F.1}$$

in the MO basis. (In these expressions, the tilde denotes matrix transposition.) The first expression is obtained directly from the definition of the one-index transformed Hamiltonian. The second expression follows from the first by using the identity

$$\mathrm{Tr}\, C\{A, B\} = \mathrm{Tr}\, B\{\tilde{A}, C\} \tag{F.2}$$

which is valid for two- and four-index trace operations and may be proved by simple index manipulations for an arbitrary transformation matrix A. The third expression may be shown by inserting the expression for the Fock matrix [Eq. (E.1)] and rearranging indices.

If the transformation matrix is antisymmetric the Hamiltonian expectation value may be further rewritten as

$$\langle(\kappa, H^{[n]})\rangle = 2\mathrm{Tr}\, \kappa F^{[n]} = \sum_{p>q} \kappa_{pq} f^{[n]}_{pq} = \kappa f^{[n]} \tag{F.3}$$

in terms of the orbital part of the electronic gradient.

In some cases the AO basis is more convenient, in particular

$$\begin{aligned}\langle(A, H^{[n]})\rangle &= \mathrm{Tr}\{\tilde{A}, D\}_{\mathrm{ao}} h^{(n)}_{\mathrm{AO}} + \tfrac{1}{2}\mathrm{Tr}\{\tilde{A}, d\}_{\mathrm{ao}} g^{(n)}_{\mathrm{AO}}\\ &= 2\mathrm{Tr}\, A_{\mathrm{AO}} F^{[n]}_{\mathrm{ao}} = 2\mathrm{Tr}\, A_{\mathrm{ao}} F^{[n]}_{\mathrm{AO}}\end{aligned} \tag{F.4}$$

In the first expression the integrals are in the covariant AO representation (in which they are calculated), and the one-index transformed density elements are in the contravariant representation (obtained from the MO basis in usual one- and two-electron transformations). The second expression is useful whenever the transformation matrix is calculated directly in the covariant AO representation and requires the transformation of the Fock matrix to the contravariant representation. The last expression is convenient when the number of perturbations is large, since it avoids the transformation of the covariant AO Fock matrix to the MO or contravariant AO representations.

Combining Eqs. (F.3) and (F.4) we see that (Rice and Amos, 1985)

$$\sum_{p>q} \kappa_{pq} f_{pq}^{[n]} = 2\mathrm{Tr}\, \kappa_{\mathrm{ao}} F_{\mathrm{AO}}^{[n]} \tag{F.5}$$

which requires the transformation of the antisymmetric matrix κ to the contravariant AO representation and no transformation of the Fock matrix.

Appendix G. Wave Function Relaxation Contributions

Many contributions to molecular energy derivatives have the structure

$$R = \tilde{a}^{(i)} M^{-1} b^{(j)} \tag{G.1}$$

where $a^{(i)}$ and $b^{(j)}$ are vectors that depend on the nuclear displacements to orders i and j, respectively, and M is a matrix which is independent of the geometry. By solving the linear equations associated with $a^{(i)}$ and $b^{(j)}$ (response equations)

$$Mc^{(i)} = a^{(i)} \tag{G.2}$$

$$Md^{(j)} = b^{(j)} \tag{G.3}$$

we can rewrite Eq. (G.1) in two alternative ways

$$R = \tilde{a}^{(i)} d^{(j)} = \tilde{c}^{(i)} b^{(j)} \tag{G.4}$$

In practice one is usually presented with one of the expressions $\tilde{a}^{(i)} d^{(j)}$ or $\tilde{c}^{(i)} b^{(j)}$, and their equivalence is established by means of $\tilde{a}^{(i)} M^{-1} b^{(j)}$. The calculation of R involves either the solution of the equations associated with $a^{(i)}$ to obtain $c^{(i)}$, or the solution of the equations associated with $b^{(j)}$ to obtain $d^{(j)}$. To minimize computational expenses one solves the set of equations with the lower order dependence in the geometry.

In MCSCF calculations the orbital rotational parameters are contained in the variational space, and the solution of the response equations through order n then determines the energy through order $2n + 1$. For example, the first-order response equations are sufficient to determine the Hessian as well as the first anharmonicity.

When the orbital rotational parameters are not contained in the variational space, the orbital responses through order $2n + 1$ formally appear in the equations that determine the energy to order $2n + 1$. However, Handy and Schaefer (1984) pointed out that the orbital responses $d^{(j)}$ for $j > n$ always appear in expressions such as $\tilde{a}^{(i)}d^{(j)}$, where $a^{(i)}$ is some vector whose geometry dependence is of order $i \leq n$. Hence, if one solves the equations associated with $a^{(i)}$ rather than those associated with $b^{(j)}$, one obtains the energy through order $2n + 1$ by solving equations of order no higher than n. For example, the expression for the MRCI gradient contains a term $\tilde{a}^{(0)}d^{(1)}$, where the $d^{(1)}$ are the independent Cartesian orbital responses. By solving the single set of equations associated with $a^{(0)}$ one obtains the MRCI gradient without solving the MCSCF orbital response equations for each independent Cartesian direction.

In practice the response equations [Eqs. (G.2) and (G.3)] are solved iteratively and the exact solutions $c^{(i)}$ and $d^{(j)}$ are not available. Instead the equations are solved to some specified tolerance in the residuals

$$\delta_c^{(i)} = Mc_{\mathrm{app}}^{(i)} - a^{(i)} \tag{G.5}$$

$$\delta_d^{(j)} = Md_{\mathrm{app}}^{(j)} - b^{(j)} \tag{G.6}$$

where $c_{\mathrm{app}}^{(i)}$ and $d_{\mathrm{app}}^{(j)}$ are the approximate solutions to the response equations. If the relaxation contributions in the form $\tilde{a}^{(i)}d^{(j)}$ are calculated using these approximate solutions, we obtain

$$\tilde{a}^{(i)}d_{\mathrm{app}}^{(j)} = R + \tilde{a}^{(i)}M^{-1}\delta_d^{(j)} \tag{G.7}$$

$$\tilde{c}_{\mathrm{app}}^{(i)}b^{(j)} = R + \tilde{\delta}_c^{(i)}M^{-1}b^{(j)} \tag{G.8}$$

where R denotes the exact relaxation contribution. Hence the error in the calculated relaxation contribution is proportional to the norm of the residuals.

The relaxation contribution may be expressed in the alternative form (Sellers, 1986)

$$R = \tilde{a}^{(i)}d^{(j)} + \tilde{c}^{(i)}b^{(j)} - \tilde{c}^{(i)}Md^{(j)} \tag{G.9}$$

If we use this expression to calculate R we obtain

$$\tilde{a}^{(i)}d_{\mathrm{app}}^{(j)} + \tilde{c}_{\mathrm{app}}^{(i)}b^{(j)} - \tilde{c}_{\mathrm{app}}^{(i)}Md_{\mathrm{app}}^{(j)} = R - \tilde{\delta}^{(i)}M^{-1}\delta^{(j)} \tag{G.10}$$

so that the error is proportional to the square of the residuals. Quadratic errors are also obtained from the expressions $\tilde{a}^{(i)}d_{\mathrm{app}}^{(j)}$ or $\tilde{c}_{\mathrm{app}}^{(i)}b^{(j)}$ if the approximate solution vectors $c_{\mathrm{app}}^{(i)}$ and $d_{\mathrm{app}}^{(j)}$ are expanded in a common set of trial vectors in the iterative solution of the response equations.

Quadratic errors were first discussed by Jensen (1986) and Helgaker *et al.* (1986a) in the context of expanding the iterative solutions in a common set of trial vectors. Sellers (1986) independently discussed quadratic errors in the context of the symmetric expression [Eq. (G.9)], and a similar discussion appears in a revised manuscript by King and Komornicki (1986).

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Theoretical Studies of Reaction Mechanisms in Chemistry[1]

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I. Introduction

For many years, main efforts in chemistry have been concentrated on problems of chemical synthesis and on structure elucidation. Underlying these efforts is the basic need to understand principles which govern reactivity of chemical systems. Theoretical and experimental investigation in reaction kinetics has presented, therefore, a very substantial part of research in chemistry. Directly connected with this, studies of reaction mechanisms have played an important role in a deeper and more detailed understanding of rate processes. Modern experimental approaches—molecular beam and novel spectroscopic and laser techniques—have provided during the past two decades a wealth of detailed information on elementary chemical processes, representing a challenge to theories of chemical reactivity and offering more and more stringent tests of them.

It is the purpose of this review to present an outline of both the dynamic and static approaches to theoretical studies of reaction mechanisms. The dynamic approach may be regarded—as far as the physics involved is concerned—as the more sophisticated of the two. However, it has limitations in answering many practical questions which a chemist may ask. The static approach, on the other hand, may seem not to be so sophisticated, but at present it provides answers to everyday chemistry in a variety of fields at different levels of theory.

[1] This work is dedicated to Professor Edgar Heilbronner (University of Basel) on the occasion of his 65th birthday anniversary.

ADVANCES IN QUANTUM CHEMISTRY, VOLUME 19

II. Basic Concepts

A. Equations of Motion

We consider a microscopic polyatomic system consisting of N nuclei and n electrons (*1–4*). Let the positions of the nuclei be described by the radius vectors R_α ($\alpha = 1, \ldots, N$). If the polyatomic system is free of external force, the total linear momentum is conserved and thus its center of mass moves with a constant velocity vector (*5*). Consequently, a new coordinate system with its origin fixed at the center of mass can be introduced (the center-of-mass coordinate system), where the description of the polyatomic system can be simplified. Since the position of the center of mass of the entire polyatomic system practically coincides with the position of the center of mass of the nuclear subsystem, the number of the degrees of freedom, F, of the nuclei in the center-of-mass system can be reduced by 3 due to the translation of the center of mass, and by 3 connected with the overall rotation about the center of mass (in case of a linear polyatomic system, the reduction due to the overall rotation is only by 2) (*5*); i.e., the number of independent nuclear coordinates is $F = 3N - 6$ ($3N - 5$). The radius vectors R_α can be then expressed in terms of F generalized coordinates Q^j (*5*):

$$R_\alpha = R_\alpha(Q^j), \qquad j = 1, \ldots, F \tag{1}$$

The coordinates Q^j generate an F-dimensional vector space (or manifold) M – the configuration space of the nuclei. The positions of the nuclei in the configuration space M are given by a single point, the system point $Q \equiv \{Q^j\}$. Analogously, let the positions of the electrons in the center-of-mass system be given by the coordinates $q \equiv \{q^u\}$, $u = 1, \ldots, 3n$.

These coordinates will be employed as variables in the equations of motion describing the time evolution of the polyatomic system.

The use of the quantum treatment in dealing with processes in polyatomic systems is rather limited (*6,7*). Nevertheless, the quantum formulation implies the most general features of the problem, so that it is convenient to commence our consideration with the quantum equations of motion.

The total wave function $\psi(Q, q, t)$ of the polyatomic system in question satisfies the time-dependent Schrödinger equation (*8*)

$$\hat{H}\psi(Q, q, t) = i\hbar\, \partial/\partial t\, \psi(Q, q, t) \tag{2}$$

where

$$\hat{H} = \hat{T}_{\mathrm{nu}} + \hat{T}_{\mathrm{el}} + \hat{U}(Q, q) \tag{3}$$

is the total Hamiltonian of the system; $\hat{T}_{\mathrm{nu}}$ and $\hat{T}_{\mathrm{el}}$ are the kinetic energy operators of the nuclei and electrons, respectively, and $\hat{U}(Q, q)$ is the operator of all interactions due to internal forces acting in the system.

The Hamiltonian $\hat{H}_{\mathrm{el}} = \hat{T}_{\mathrm{el}} + \hat{U}(Q, q)$ of the electronic subsystem at a fixed nuclear configuration Q' does not depend explicitely on time (*9*). Consequently, the states $\phi(Q', q)$ of the electronic subsystem are stationary at the configuration Q' and they coincide with the eigenstates $\psi_m(Q', q)$ of $\hat{H}_{\mathrm{el}}$:

$$\hat{H}_{\mathrm{el}}\psi_m(Q', q) = W_m(Q')\psi_m(Q', q) \tag{4}$$

$W_m(Q')$ is the corresponding eigenvalue, the energy of the mth electronic state at a configuration Q'. Provided the characteristic problem [Eq. (4)] for the electronic Hamiltonian $\hat{H}_{\mathrm{el}}$ can be solved at any configuration Q of the nuclei, the total wave function $\psi(Q, q, t)$ can be expanded in terms of $\psi_m(Q, q)$ (completeness of the electronic basis set is assumed):

$$\psi(Q, q, t) = \sum_m \chi_m(Q, t)\psi_m(Q, q) \tag{5}$$

The expansion coefficients $\chi_m(Q, t)$ depend on the nuclear configuration and time only.

If the electronic wave function $\phi(Q, q)$ remains stationary during the time evolution of the entire polyatomic system, the expansion [Eq. (5)] of the total wave function reduces to a single term, i.e., the nuclear and electronic motion is separated,

$$\psi(Q, q, t) = \chi_m(Q, t)\psi_m(Q, q) \tag{6}$$

and the expansion coefficient $\chi_m = \chi_m(Q, t)$ acquires the meaning of the wave function of the nuclear subsystem. By substituting the expansion [Eq. (6)] into Eq. (3), the Schrödinger equation for the nuclear motion is obtained (*9*),

$$\{\hat{T}_{\mathrm{nu}} + W_m(Q)\}\chi_{m,v}(Q, t) = i\hbar\, \partial/\partial t\ \chi_{m,v}(Q, t) \tag{7}$$

where the role of the potential is taken over by the energy $W_m(Q)$ of the electronic subsystem. Solutions $\chi_{m,v}$ to Eq. (7) correspond to different nuclear states v at a fixed electronic state m.

Equation (7) represents a crucial result for theoretical chemistry: if the electronic wave function $\phi(Q, q)$ is stationary while the time evolution of the polyatomic system is in progress, the nuclei move in the field of force, the potential of which is equal to the energy of one of the eigenstates of the electronic subsystem. In this connection, the potential function $W_m = W_m(Q)$ is referred to as the potential energy surface (PES) corresponding to the mth electronic state of the polyatomic system (*10–12*).

In the next paragraph we will turn our attention to the examination of conditions implying stationary electronic wave functions $\phi(Q, q)$.

If the potential energy surface is given, the time evolution of the polyatomic system is determined by the nuclear equations of motion, Eq. (7). However, solving the quantum Eq. (7) is extremely difficult even for the simplest realistic systems (*13–15*). Fortunately, if the conjugated momenta P

of the nuclei satisfy the condition (*8,9*)

$$P^2 \gg \hbar|\mathrm{div}\ P| \tag{8}$$

then Eq. (7) turns into the Hamilton–Jacobi equation representing one of the equivalent formulations of the classical laws of motion (*5,9*):

$$H + \partial S/\partial t = 0 \tag{9}$$

H is the Hamilton function of the nuclear subsystem, S is the principal Hamilton function of the nuclei, $S = \int[(\sum_j(\partial Q^j/\partial t)P_j) - H]\,dt$, and the momentum conjugated with the coordinate Q^j is $P_j = \partial S/\partial Q^j$. The solution of the classical equations of motion can be carried out more easily (*6,16*).

For a linear motion, say, along Q^k, the condition [Eq. (8)] takes the form

$$P_k^3 \gg \hbar M|\partial W_m/\partial Q^k| \tag{10}$$

where $P_k = [2M(H - W_m)]^{1/2}$ and M is the mass of the nuclei (*9*). The condition [Eq. (10)] for the classical limit of the quantum description states that the nuclei may be treated classically [i.e., their motion can be described by a trajectory $Q = Q(t)$] if it proceeds with high momenta in a nearly uniform field of force.

Except for localized regions of the configuration space M, condition Eq. (8) is usually well satisfied for nuclear subsystems in the energy region from thermal kinetic energies up to hundreds of electron volts (*17*). Thus, due to the suppression of the wave features of the nuclear subsystem, the classical approach represents a rather general basis for treating time evolution in polyatomic systems (on the potential energy surface, or surfaces; see later). The quantization of nuclear degrees of freedom can be obtained within the classical approach by imposing appropriately chosen boundary conditions on the nuclear trajectories (the boxing procedure) (*18,19*).

B. Stationary States of the Electronic Subsystem

In this section we will examine conditions implying stationary states of the electronic subsystem during the time the evolution of the entire polyatomic system is in progress. The nuclear motion will be treated classically (*20,21*).

Let the evolution of the nuclear subsystem be given by a trajectory $Q = Q(t)$. Consequently, the electronic Hamiltonian $\hat{H}_{\mathrm{el}}$ becomes time dependent [through $Q(t)$], and the state $\phi(Q(t), q)$ of the electronic subsystem is, in general, nonstationary; $\phi(Q(t), q)$ obeys the time-dependent Schrödinger equation (*20*)

$$\hat{H}_{\mathrm{el}}\phi(Q(t), q) = i\hbar\ \partial/\partial t\ \phi(Q(t), q) \tag{11}$$

Let us assume that an electronic basis set $\varphi_m(Q', q)$ at any point Q' of M is given and that the following matrix element is defined:

$$W_{mk}(Q') = \langle \varphi_m(Q', q) | \hat{H}_{\mathrm{el}}(Q', q) | \varphi_k(Q', q) \rangle \tag{12}$$

As a result of the linearity of Eq. (11), the solution $\phi(Q(t), q)$ can be written in the form

$$\phi(Q(t), q) = \sum_m A_m(t) \varphi_m(Q, q) \exp\left\{ (i\hbar)^{-1} \int W_m(Q)\, dt \right\} \tag{13}$$

where $A_m(t)$ are time-dependent expansion coefficients and $W_m \equiv W_{mm}$.

Our problem of seeking electronic stationary states corresponding to the evolution of the nuclear subsystem turned out to be identical with the problem of finding stationary solutions to Eq. (11), or of establishing conditions implying time independence of the expansion coefficients $A_m(t)$ in Eq. (13).

By substituting for $\phi(Q(t), q)$ from Eq. (13) to Eq. (11), the time derivative $\dot{A}_m \equiv dA_m/dt$ of the expansion coefficient $A_m(t)$ is obtained:

$$\begin{aligned} \dot{A}_m(t) = (i\hbar)^{-1} \sum_{k \neq m} A_k(t) \{ W_{mk} - i\hbar \langle \varphi_m | \, \partial/\partial t \; \varphi_k \rangle \} \\ \times \exp\left\{ (i\hbar)^{-1} \int (W_k - W_m)\, dt \right\} \end{aligned} \tag{14}$$

On the grounds of Eq. (14) the adiabatic and diabatic electronic basis sets can be defined (*22–24*). An electronic basis set is said to be adiabatic, φ_m^a, if for any configuration Q the matrix W^a [cf. Eq. (12)] is diagonal:

$$W_{mk}^a = W_{mk} \delta_{mk} \tag{15}$$

Then,

$$\dot{A}_m^a = - \sum_{k \neq m} A_k^a(t) \langle \varphi_m^a | \, \partial/\partial t \; \varphi_k^a \rangle \exp\left\{ (i\hbar)^{-1} \int (W_k^a - W_m^a)\, dt \right\} \tag{16}$$

Obviously, $\dot{A}_m^a = 0$ in those regions of M where the matrix elements $\langle \varphi_m^a | \, \partial/\partial t \; \varphi_k^a \rangle = 0$. The definition [Eq. (15)] of the adiabatic basis set implies that the adiabatic electronic wave functions φ_m^a are eigenfunctions of the electronic Hamiltonian $\hat{H}_{\mathrm{el}}$, $\varphi_m^a \equiv \psi_m$ [cf. Eq. (4)]. Since the nonadiabatic coupling elements $\langle \varphi_m^a | \, \partial/\partial t \; \varphi_k^a \rangle$ result from the motion of the nuclear subsystem, the coupling is referred to as dynamic coupling. It attains its maximum value in regions of M where the energy difference between the coupled (interacting) potential energy surfaces is minimal (*25*).

An electronic basis set is said to be diabatic, φ_m^{d}, if at any configuration $\mathbf{Q}$ the matrix elements $\langle \varphi_m^{\mathrm{d}} | \partial/\partial t \; \varphi_k^{\mathrm{d}} \rangle$ vanish:

$$\langle \varphi_m^{\mathrm{d}} | \, \partial/\partial t \; \varphi_k^{\mathrm{d}} \rangle = 0 \tag{17}$$

Then,

$$\dot{A}^{\mathrm{d}}_m = (i\hbar)^{-1} \sum_{k \neq m} A^{\mathrm{d}}_k(t) W^{\mathrm{d}}_{mk} \exp\left\{(i\hbar)^{-1} \int (W^{\mathrm{d}}_k - W^{\mathrm{d}}_m)\, dt\right\} \tag{18}$$

It is obvious that $\dot{A}^{\mathrm{d}}_m = 0$ in those regions of M where the matrix W^d is diagonal: $W^d_{mk} = W_{mk}\delta_{mk}$. The coupling between diabatic states (adiabatic coupling) takes place in consequence of the fact that the diabatic electronic wave functions φ^{d}_m are not eigenfunctions of $\hat{H}_{\mathrm{el}}$; since the adiabatic coupling is connected with the nature of the electronic Hamiltonian, it is referred to as static coupling, and it is supposed to be roughly constant and small throughout M (*25*).

If simultaneously $W^{\mathrm{d}}_{mk} = 0$ and $\langle \varphi^{\mathrm{a}}_m | \, \partial/\partial t \; \varphi^{\mathrm{a}}_k \rangle = 0$ in a region of M, then the nuclei move in the field of force the potential of which is given by the energy W_m of a single state of the electronic subsystem and there is no difference between the description of the electronic subsystem in the adiabatic or diabatic basis sets, i.e., $W^{\mathrm{a}}_m = W^{\mathrm{d}}_m$. The corresponding behavior of the polyatomic system is referred to as electronically adiabatic:

$$\phi^{\mathrm{a,d}}(Q(t), q) \cong \varphi^{\mathrm{a,d}}_m \exp\left\{(i\hbar)^{-1} \int W^{\mathrm{a,d}}_m \, dt\right\}. \tag{19}$$

Generally, Eq. (19) holds in reactant and product asymptotic regions only (see later).

C. Electronic Transitions

The physical idea underlying the concept of adiabatic behavior of polyatomic systems is based on the fact that the electron mass is much smaller than the nuclear mass (at least by three orders of magnitude); consequently, for a slow evolution of the polyatomic system, the velocity of the electrons is much larger than the velocity of the nuclei and thus there is sufficient time for the electronic subsystem to adjust to the evolving nuclear configurations. In this way, the state of the electronic subsystem remains unchanged (though the respective function describing it changes noticeably). The approximate treatment of a polyatomic system based on the idea of a slow (adiabatic) change of the nuclear configurations is referred to as the Born–Oppenheimer (adiabatic)[2] approximation (*26–29*). The Born–Oppenheimer electronic wave function can be identified with the stationary electronic wave function within both the adiabatic or diabatic basis sets, Eq. (19).

In those regions of the configuration space where the adiabatic approximation breaks down (i.e., the dynamic coupling cannot be neglected),

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[2] Some authors also include in the notion of adiabatic approximation the case, where, in addition, all diagonal terms of the coupling matrix are considered.

nonadiabatic transitions may be induced as the system point proceeds through *M*. Processes where the adiabatic approximation breaks down are referred to as electronically nonadiabatic (*30,31*). The collapse of the adiabatic approximation means that the nuclear and electronic subsystems are no longer independent, i.e., the state of the electronic subsystem becomes a function of the nuclear configuration and the velocities of the nuclei. The passage of the system point trajectory through the region of nonadiabatic behavior can thus cause the nuclear subsystem to pass into a field of force determined by a different potential energy surface; this means that in the case of nonadiabatic processes the nuclear subsystem may be consecutively subjected to several fields of force. The field of force which determines the nuclear motion after the passage through the region of nonadiabatic behavior depends on the probability of the nonadiabatic transition (*17,32–34*), which in turn depends on the nature of the coupling between the interacting potential energy surfaces and on the kinematics of the motion in the region of nonadiabatic behavior (*17,25,35*).

However, if the region of nonadiabatic behavior is well localized in *M*, the classical treatment of the nuclear subsystem can be preserved and the evolution of the polyatomic system in the nonadiabatic region (where no potential energy surface is defined!) is to be described by special means.

From the analysis of symmetry properties of polyatomic systems general rules can be derived determining the maximum dimension of the intersection between two interacting potential energy surfaces—the noncrossing rules (*10,36–38*). The noncrossing rules together with the selection rules (*16,32,39,39a*) for processes in polyatomic systems provide a starting point in elucidating the nonadiabatic behavior.

For potential energy surfaces in the adiabatic basis there are the following noncrossing rules[3] ($\dim M = F$): (1) two potential energy surfaces of different symmetry may have ($F - 1$)-dimensional intersections; (2) if the spin-orbit interaction can be neglected, two potential energy surfaces of the same symmetry may have ($F - 2$)-dimensional intersections; (3) if the spin-orbit interaction cannot be neglected, two potential energy surfaces of the same symmetry may have either (a) ($F - 2$)-dimensional intersections when the number of electrons is even or (b) ($F - 3$)-dimensional intersections when the number of electrons is odd.

The dimension of the intersections of potential energy surfaces in the diabatic basis set may be larger than or equal to that of the adiabatic surfaces.

A certain electronic transition in a polyatomic system can be equally described either within the adiabatic or within the diabatic basis set: as the transitions can be induced either by the dynamic or by the static coupling,

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[3] In the case of no "hidden" symmetry (*17*).

respectively, a nonadiabatic transition in the adiabatic set corresponds to diabatic behavior and vice versa [cf. Eq. (14)]. Consequently, the nonadiabatic transition probability P^{a}_{mk} between the adiabatic energy levels V^{a}_{m} and V^{a}_{k} is complementary with the transition probability P^{d}_{mk} between the diabatic energy levels V^{d}_{m} and V^{d}_{k}. To illustrate this in a more particular way, let us consider a polyatomic system where only two potential energy surfaces are coupled, V_1 and V_2. The transition probability P^{a}_{12} between the adiabatic states V^{a}_{1} (at $t = t_1$) and V^{a}_{2} (at $t = t_2$) is given by the square of the amplitude $A^{\mathrm{a}}_{2}(t_2)$ [assuming that $A^{\mathrm{a}}_{1}(t_1) = 1$ and $A^{\mathrm{a}}_{2}(t_1) = 0$]:

$$P^{\mathrm{a}}_{12} = |A^{\mathrm{a}}_{2}(t_2)|^2 \tag{20}$$

The amplitude $A^{\mathrm{a}}_{m}(t)$ can be obtained by solving the set of relations, Eq. (16). Analogously, we have for the probability P^{d}_{12} of this nonadiabatic transition between the diabatic states V^{d}_{1} (at t_1) and V^{d}_{2} (at t_2) [provided $A^{\mathrm{d}}_{1}(t_1) = 1$ and $A^{\mathrm{d}}_{2}(t_1) = 0$]:

$$P^{\mathrm{d}}_{12} = |A^{\mathrm{d}}_{2}(t_2)|^2 \tag{21}$$

The amplitude $A^{\mathrm{d}}_{m}(t)$ results from the set of relations, Eq. (18). As the transition interchanges the indices of the adiabatic and diabatic electronic states, it is obvious that

$$P^{\mathrm{a}}_{12} = 1 - P^{\mathrm{d}}_{12} \tag{22}$$

It should be noted that the condition of the adiabatic approximation, although inherent to the classical treatment of the nuclei, may contradict the condition for the classical limit of quantum mechanics [generally, the condition of slow nuclear motion, $P \sim 0$, and the condition, Eq. (8), may not be fulfilled simultaneously].

The treatment of polyatomic systems based on the classical description of the nuclear motion will be referred to as quasiclassical (*16,17*).

D. Elementary Processes

The notion of the system point $Q \equiv \{Q^j\}$ in the configuration space M of the nuclei makes it possible to express in a concise form the structure (*40*) (i.e., the spatial arrangement of the nuclei) of the entire polyatomic system in question, the structures of its components (such as molecules, ions, radicals, and clusters), and their mutual positions. Any change in the polyatomic system resulting in a variation of a coordinate can be traced throughout M by the system point; thus a space curve in M corresponds to such a change (*41,42*).

Regions in M where interactions between reactants entering a process, or products resulting from a process, are negligible can be defined by values of the coordinates specifying the distance between reactants or products. These regions of M are referred to as asymptotic regions related to the process in question. Definition of an elementary process among the components of the polyatomic system in question can now be given by using the concept of a space curve in M with its end points located in the reactant and product asymptotic regions, respectively: an elementary process in M is characterized by a single passage of space curves from the reactant to the product asymptotic region; i.e., a space curve corresponding to an elementary process leaves only once the reactant asymptote and only once arrives in the product asymptote.

In real systems, this definition of an elementary process fits best the gas phase where the asymptotic regions can be reached.

However, not all space curves singly connecting reactant and product asymptotes correspond to a realistic time evolution describing an elementary process. Such evolution is determined by the equations of motion; within the quasiclassical approach the space curves can be interpreted as system point trajectories in M with their end points located in the reactant and product asymptotes (*43,44*); a trajectory $Q = Q(t)$ is then determined by the classical equations of motion [i.e., within some of the equivalent formulations of classical mechanics tantamount to Eq. (9)].

The degrees of freedom of a polyatomic system can be classified according to the various modes of motion concerned: internal (rotational, vibrational, and electronic) and external (translational) degrees of freedom are distinguished (note that only modes related to the motion of the center of mass are relevant). An elementary process is said to be elastic (*45*) if both structure and energy in any of the degrees of freedom remain unaffected. If only the structure of reactants is conserved, then the corresponding elementary process is referred to as inelastic (*46*) (rotationally, vibrationally, electronically, or a combination of these). In case of a reactive (chemical) elementary process, the structure of the reactants is also subjected to a change (i.e., formation, decay, or rearrangement of chemical bonds takes place).

In general, more than one product asymptotic region can be reached from a single reactant asymptote, i.e., certain reactants may undergo several elementary processes, the so-called channels. Within a channel, processes leading from specific reactant states to specific product states can be distinguished (state-to-state elementary processes).

Thus in the case of a nonreactive (i.e., elastic or inelastic) channel the reactant and product asymptotes coincide; an elastic channel is characterized, in addition, by the identity of the product and reactant internal states.

The way in which reactant change into products in an elementary process will be regarded as the microscopic collision mechanism of the elementary process in question. It is determined within the quasiclassical approach by the characteristics of the system point trajectories.

The notion of mechanism has been used in reaction kinetics in a different sense, too. It means a sequence of elementary processes leading to a certain set of products. The term (macroscopic) reaction mechanism will be used in this sense.

III. Dynamic Approach

A. Quasiclassical Dynamics

1. *Adiabatic Processes*

Within the quasiclassical approach the nuclei are considered to be subject to a classical motion in the field of force, the potential of which is given by the energy pertinent to one of the eigenstates of the electronic subsystem. In the case of electronically adiabatic processes, the field of force for the nuclear motion is determined by a single potential energy surface (pertinent to a single electronic state).

By eliminating the variables describing the motion of the center of mass and the overall rotation, the kinetic energy T of the nuclei assumes a homogeneous quadratic form in the generalized velocities $\dot{Q}^j \equiv dQ^j/dt$ (*5*),

$$T = \frac{1}{2}\sum_{j,k} g_{jk}\dot{Q}^j\dot{Q}^k; \qquad j, k = 1, \ldots, F \tag{23}$$

The metric tensor[4] g_{jk} on the tangent space $T_Q(M)$ to the configuration space M takes the form (*5,41,42*)

$$g_{jk} = \sum_{\alpha} M_\alpha(\partial R_\alpha/\partial Q^j)(\partial R_\alpha/\partial Q^k) \tag{24}$$

where M_α is the mass of the αth nucleus. The arc length element ds of a system point trajectory in M is given by

$$ds = \left(\sum_{j,k} g_{jk}\, dQ^j\, dQ^k\right)^{1/2} \tag{25}$$

The tangent bundle $T(M)$ associated with the configuration space M is a set of F-dimensional vector spaces T_Q (fibres) with coordinates (velocities) $\{V^j\}$; each fiber T_Q is a tangent space to the configuration space M at a point Q (*42*). Hence the tangent bundle $T(M)$ is locally described by $2F$ coordinates $(Q, V) = \{Q^i, V^j\}$. Since any transformation of coordinates Q^i in M induces a linear transformation of V^j in T_Q (*42*), the solution to the equations of motion does not depend on the choice of the coordinate system in M.

The classical equations of motion are equivalent to a vector field $X(Q, V)$

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[4] The contravariant metric tensor g^{jk} is known in the theory of small vibrations as Wilson's G matrix (kinematic matrix).

on $T(M)$ (*42*):

$$X(Q, V) = \sum_i V^i \frac{\partial}{\partial Q^i} + \sum_{j,k,m} \left(\Gamma^j_{km} V^k V^m - g^{jm} \frac{\partial W}{\partial Q^m} \right) \frac{\partial}{\partial V^j} \tag{26}$$

where the Christoffel symbol Γ^j_{km} appears for the coordinate dependent metric tensor g_{ij}; the matrix (g^{ij}) is inverse to (g_{km}):

$$\Gamma^j_{km} = \frac{1}{2} \sum_i g^{ij} \left(\frac{\partial g_{ik}}{\partial Q^m} + \frac{\partial g_{im}}{\partial Q^k} - \frac{\partial g_{km}}{\partial Q^i} \right) \tag{27}$$

This means that evolution of any function $w = w(Q, V)$ on $T(M)$, consistent with classical mechanics, is given by $dw/dt = Xw$ and thus the classical equations of motion take the form:

$$\dot{Q}^j = XQ^j, \qquad \dot{V}^j = XV^j \tag{28}$$

The values of coordinates and velocities (or momenta) at some point in the reactant and product asymptote, respectively, can be used to define the boundary conditions for solving the equations of motion describing an elementary process (*18,43*). The coordinates $Q_1 = \{Q^i_1\}$, $Q_2 = \{Q^i_2\}$ and velocities $V_1 = \{V^j_1\}$, $V_2 = \{V^j_2\}$ at the end points refer to both the internal and translational degrees of freedom; the choice of the end points thus determines the channel as well as the internal (quantized) and translational states of reactants and products.

If the end points are defined, the solution to the classical equations of motion corresponding to an elementary process can be sought; the resulting system point trajectories represent the realistic evolution of the polyatomic system from reactants to products on the given potential energy surface $W_m(Q^j)$ at the total energy $H = T + W(Q^j)$. The solutions to the equations of motion can thus be considered as transformations leading from a set of boundary conditions in the reactant asymptote to a set of boundary conditions in the product asymptote.

Although each set of boundary conditions defines a unique trajectory, not all of the $2F$ quantities at each of the end points can be controlled in an experiment (*4,47,48*) these quantities usually have random distributions (impact parameter, vibrational phase, etc.). Consequently, it is useful to choose the values of the uncontrollable boundary conditions randomly. For a sufficiently high number of the randomly chosen values (on a relevant interval), "all" boundary conditions are included and the resulting set of trajectories (related to an elementary process) represents a dynamical picture of the elementary process within the quasiclassical approach (*6,44*).

It should be noted that the classical equations of motion (usually in the Hamilton's canonical form) are solved by various numerical methods and the random values of the uncontrollable quantities are usually generated by a Monte Carlo procedure (*6,44*).

For fixed boundary values of the controllable quantities (internal states of reactants and products, relative translational energy, scattering angle, etc.), the set of trajectories contains information on detailed reaction attributes: partial cross-section of various channels, state-to-state cross-sections, differential cross-sections, product energy distributions, and related quantities. The branching of products in various channels—product internal and translational states, a certain range of scattering angles, etc.—is identified within the quasiclassical trajectory method, with the relative number of trajectories leading to the given channel, product state, scattering angle, etc.

The quasiclassical trajectory method disregards completely the quantum phenomenon of superposition (*13,18,19*); consequently, the method fails in treating the reaction features connected with the interference effects such as rainbow or Stueckelberg-type oscillations in the state-to-state differential cross sections (*13,17,28*). When, however, more averaged characteristics are dealt with (then the interference is quenched), the quasiclassical trajectory method turns out to be a relatively universal and powerful theoretical tool. Total cross-sections (detailed rate constants) of a large variety of microscopic systems can be obtained in a semiquantitative agreement with experiment (*6*).

Thus, as long as the interference phenomena are suppressed, the quasiclassical method yields a reasonable qualitative view of the dynamics of elementary processes. We will adopt this view in the forthcoming discussions; in the next section it will be shown that the quasiclassical trajectory method can be generalized to treat a large class of electronically nonadiabatic processes.

2. *Nonadiabatic Processes*

If the regions of nonadiabatic behavior are well localized in the configuration space M, an $(F - 1)$-dimensional hypersurface can be defined at which the nonadiabatic transitions may take place; this hypersurface is referred to as the crossing seam. The coupled relations, Eq. (14), describing the corresponding nonseparable electronic and nuclear motion, are to be solved at the seam. Elsewhere, the evolution of the polyatomic system can be then treated adiabatically (*49,50*).

However, the treatment of the class of nonadiabatic processes with isolated regions of nonadiabatic behavior differs from the treatment of adiabatic processes in the following (*6*) ways.

1. The seam must be determined. A reasonable approximation is to choose for seams those regions of M where the interacting potential energy surfaces are degenerate, or nearly degenerate (cf. the noncrossing rules).

2. Coordinates and velocities at the new potential energy surface must be established. In the spirit of the Franck–Condon principle, the coordinates can be assumed to be fixed at the instant of the electronic transition. Since energy and angular momentum are conserved, the velocities at the seam must be adjusted to obey these conservation laws.

3. The probabilities of the electronic transitions must be evaluated.

Whenever a seam is encountered, the system point trajectory $Q = Q(t)$ is split into n branches Q_ℓ, each branch evolving under the influence of one of the interacting potential energy surfaces. A system point trajectory connecting the reactant and product asymptotes may arrive at several seams and its splitting may occur at each seam. The electronic transition probabilities $P_l(Q, \dot{Q})$ can be calculated by numerical integration of the relations, Eq. (14), at each seam

$$P_l(Q, \dot{Q}) = |A_l|^2, \qquad l = 1, \dots, n \tag{29}$$

or evaluated according to analytical formulas based on particular models (*17,20,33,51–54*). The transition probability at each seam is conserved:

$$\sum_l P_l = 1 \tag{30}$$

Consequently, the electronic transition probabilities can be interpreted as relative weights of the individual branches of a system point trajectory. The final weights of trajectories terminating in the product asymptote can then serve for calculating the reaction attributes in the same manner as the numbers of trajectories in case of adiabatic processes (*7,49*).

The quasiclassical approach thus enjoys a wide application in treating multisurface processes where the nonadiabatic behavior is well localized. The treatment fails when the regions of nonadiabatic behavior are too close to classical turning points (*17*) [where $V = 0$; cf. condition Eq. (8)] or in classically forbidden regions (*18,55*) of configuration space M (i.e., in regions the passage of which is not consistent with the classical equations of motion, regardless of the energy and momentum disposal in the system).

B. Reaction Paths

The potential energy function $W = W(Q^j)$ can be given in various equivalent representations. The use of special coordinate systems, however, may result in a substantially simplified description of the nuclear motion corresponding to an elementary process. Orthogonal coordinates yield the diagonal form of the kinetic energy matrix T. Moreover, if the mass-weighted Cartesian coordinates $Y^r = M_r^{1/2} R^r$ are employed (R^r are the Cartesian components of the nuclear radius vectors R_α, $r = 1, \dots, 3N$), the mass of the corresponding system point turns out to be unity:

$$\begin{aligned} T &= \frac{1}{2}\sum_r M_r(\partial R^r/\partial Y^s)(\partial R^r/\partial Y^t)\dot{Y}^s\dot{Y}^t \\ &= \frac{1}{2}\sum_r (\dot{Y}^r)^2; \qquad s, t = 1, \ldots, 3N \end{aligned} \tag{31}$$

As a consequence of the vanishing cross-terms in T and the unit mass of the system point, the nuclear motion due to the potential energy surface, $W = W(Y^r)$, can be represented by sliding a mass point on $W(Y^r)$. The analogy with the mechanical motion in the field of gravity allows one to develop experience-based estimates of the solutions to the equations of motion. Hence, given a potential energy surface, the dynamics of an elementary process can be qualitatively understood.

It should be emphasized that particularly for these merits the quasiclassical (or semiclassical) methods of detailed chemical kinetics have become a basis for the present theoretical understanding of the problems of chemical reactivity.

The gradient matrix $(\partial W/\partial Q^j)$ and the force-constant matrix $(\partial^2 W/\partial Q^j \partial Q^k)$ represent the basic characteristics of a potential energy surface (*56,57*). The dimension of the matrices is given by the number of nuclear degrees of freedom, $F = 3N - 6\ (3N - 5)$ [cf. Eq. (1)], i.e., $j, k = 1, \ldots, F$, as previously.

A point $Q_0 = \{Q_0^j\}$ where all gradient matrix elements are equal to zero is referred to as a stationary point:

$$[\partial W/\partial Q^j]_{Q=Q_0} = 0 \tag{32}$$

A classification of stationary points can be introduced, according to the properties of the eigenvalues of the force-constant matrix $(\partial^2 W/\partial Q^j \partial Q^k)$ at $Q = Q_0$ (*58*): (1) if none of the eigenvalues is negative, the stationary point is a minimum; (2) if all eigenvalues are negative, the stationary point is a maximum; and (3) if one (or more) eigenvalue is negative, the stationary point is a first-order saddle point (or a higher order saddle point). First-order saddle points play a particularly important role since they divide regions of stable configurations in M.

Starting at a saddle point, a path of steepest descent can be defined on the potential energy surface by using the gradient function $\partial W/\partial Q^j$; the path of steepest descent is uniquely determined by extremal values of the gradient unless a stationary point is reached (*58*). Besides the minima corresponding to the reactant and product asymptotes, a potential energy surface may exhibit some additional minima due to, e.g., van der Waals (*59*) complexes or intermediates (see later). In such cases, the reactant and product asymptote can be interconnected by several steepest descent paths and the construction of the corresponding space curve on the potential energy surface may require the knowledge of the position of more than one saddle point. The space curve emanating from a saddle point (or saddle points) and tracing the bottoms of the potential energy valleys between the reactant and product asymptote is referred to as the minimum energy path *(60,61)*.

The minimum energy path is determined by the following covariant equation [cf. Eq. (25) *(60)*:

$$dQ^j/ds = -\frac{\sum\limits_k g^{jk}\,\partial W/\partial Q^k}{\left[\sum\limits_{l,k}(\partial W/\partial Q^l)(\partial W/\partial Q^k)g^{lk}\right]^{1/2}} \tag{33}$$

The arc length s, measured along the minimum energy path, is referred to as the reaction coordinate.

Since both sides of Eq. (33) transform as contravariant vectors, the minimum energy path is invariant to any coordinate transformation. From this point of view, the minimum energy path together with the stationary points can be regarded as a fundamental characteristics of an elementary process.

When the minimum energy path is expressed in the mass-weighted cartesian coordinates Y^j. Eq. (33) reduces to a simpler expression

$$dY^j/ds = -\frac{\partial W/\partial Y^j}{\left[\sum\limits_l(\partial W/\partial Y^l)(\partial W/\partial Y^l)\right]^{1/2}} \tag{34}$$

and the corresponding path (along the unit tangential vector $|dY^j/ds| = 1$) is referred to as the reaction path. Its arc length is called the intrinsic reaction coordinate *(62–64)*. The reasons for introducing the concept of the reaction path (as a special case of the minimum energy path) connect mainly with the respective diagonal form of the kinetic energy and, hence, the possibility of understanding the motion in terms of the sliding mass point.

There has been much debate in recent years concerning the invariance properties of the minimum energy path: the steepest descent path *(65–70a)*

$$dQ^j/ds = -\frac{\partial W/\partial Q^j}{\left[\sum\limits_l(\partial W/\partial Q^l)(\partial W/\partial Q^l)\right]^{1/2}} \tag{35}$$

depends, namely, on the coordinate system employed and thus it appears that the minimum energy path is a coordinate-dependent concept. Nevertheless, it should be emphasized that this problem has been overcome by adopting the covariant definition, Eq. (33). The debate originated in disregarding the difference between the definition, Eqs. (35) and (33).

In the configuration space of the nuclei another orthogonal coordinate system can be defined, consisting of $(F-1)$ coordinates Q^v $(v = 1, \ldots, F-1)$ and the reaction coordinate s as its Fth coordinate. Since the Q^v are orthogonal to s, there is $\partial W/\partial Q^v = 0$ along the reaction coordinate. Consequently, the Taylor expansion of the potential function, in terms of the displacements ΔQ^v with respect to the reaction path, does not contain the first-order terms:

$$\begin{aligned} W &= W(Q^1, \ldots, Q^{F-1}, s) \\ &= W_0(s) + \frac{1}{2} \sum_{v,w} (\partial^2 W/\partial Q^v\, \partial Q^w)\, \Delta Q^v\, \Delta Q^w + \cdots \end{aligned} \tag{36}$$

Hence, if the transversal amplitudes ΔQ^v are small, the contributions of the second term can be neglected, and the potential is mainly given by the zero-order term $W_0(s)$, the energy profile along the minimum energy path (or reaction profile). This is important, because then the energy profile can be considered as an approximation to the potential energy determining the translational motion of the polyatomic system along the reaction path.

In general, the reaction path is curved; the centrifugal force acting on the system point moving with a velocity $\dot{s}$ is proportional to the inverse radius of the local curvature *(15)*. The system point motion is thus forced off the designated reaction path, and as a result of this, a transfer of the translational energy into the vibrational degrees of freedom may take place. Consequently, highly curved segments of reaction paths are considered as regions where vibrational excitation may originate.

Recently, a class of methods has been developed circumventing the dimensionality problem in treating dynamics of polyatomic systems by utilizing the idea of reaction path *(71–74)*. The potential energy term in the reaction-path Hamiltonian (or Hamilton's function) is approximated by a harmonic valley about the reaction path; the kinetic energy terms consist of normal-mode vibrations orthogonal to the reaction coordinate and the translation along the reaction path. The reaction-path Hamiltonian methods provide a framework for at least a start in dealing with the dynamics of polyatomic systems and can be considered, from the methodological point of view, as a compromise between the dynamic and the static approaches.

The calculation of reaction profiles is one of the main subjects of the static approach (see later); the relevance of reaction profiles in representing the potential energy determining the course of elementary processes is given by the adequacy of expansion Eq. (36) and of neglecting the second-order term. It is obvious that expansion Eq. (36) tends to be more adequate when the kinetic energy content in the evolving polyatomic system is small.

A question can be asked whether the minimum energy path may be identified with a system point trajectory. The question of the possibility of obtaining Eq. (33) of the minimum energy path from the classical equations of motion, Eq. (28), can be answered positively only in the quadratic neighborhood dQ^j (along the path) of any point in configuration space of the nuclei: by setting the velocity equal to zero at the point (*75*)

$$dQ^j = \dot{Q}^j\, dt + \tfrac{1}{2}\ddot{Q}^j\, dt^2, \qquad \dot{Q}^j = 0 \tag{37}$$

we have

$$ds = \left(\sum_{j,k} g_{jk}\, dQ^j\, dQ^k\right)^{1/2} = \frac{1}{2}\left(\sum_{j,k} \ddot{Q}^j \ddot{Q}^k\, dt^4\, g_{jk}\right)^{1/2} \tag{38}$$

$$\ddot{Q}^j = \frac{d\dot{Q}^j}{dt} = \frac{d}{dt}\left(\sum_k g^{jk} P_k\right) = \sum_k \left[g^{jk} \dot{P}_k + \sum_i P_k \dot{Q}^i \frac{\partial}{\partial Q^i} g^{jk} \right] = \sum_k g^{jk} \dot{P}_k \tag{39}$$

Since the momentum $P_k = \sum_j g_{jk} \dot{Q}^j$ evolves according to the equation of motion $P_k = -\partial W/\partial Q^k$ [cf. Eq. (28)]. Eq. (33a) immediately follows:

$$\begin{aligned} dQ^j/ds &= \frac{-\dfrac{1}{2}\displaystyle\sum_k g^{jk}(\partial W/\partial Q^k)\, \mathrm{dt}^2}{\dfrac{dt^2}{2}\left[\displaystyle\sum_{i,k,l,m} (\partial W/\partial Q^m) g^{mk} (\partial W/\partial Q^i) g^{il} g_{lk}\right]^{1/2}} \\ &= -\frac{\displaystyle\sum_k g^{jk}\, \partial W/\partial Q^k}{\left[\displaystyle\sum_{i,m} (\partial W/\partial Q^m)(\partial W/\partial Q^i) g^{mi}\right]^{1/2}} \end{aligned} \tag{33a}$$

Conditions [Eq. (37)] connect the concepts of minimum energy path and system point trajectory at any point of configuration space M. It should be noted, however, that these conditions do not have the character of constraints because $V^j = 0$ can hold generally only at isolated points of a trajectory. It can be shown that the general impossibility of deriving Eq. (33a) using the classical laws of motion originates from the singular nature of the passage from dt to ds when the velocity V^j is damped to zero (*75*).

Another feature of the minimum energy path should be mentioned. The symmetry group of the polyatomic system (i.e., of its nuclear subsystem) in the course of the steepest descent from the saddle point cannot change unless a stationary point is reached (*58*). Since the symmetry group of the system at a stationary point cannot be lower than at any other point on the steepest descent path, the point group of the configuration corresponding to a saddle point dividing reactant and product minima cannot exceed the largest common symmetry subgroup of reactants and products. Consequently, e.g., linear intermediate configurations may only correlate with linear configurations of reactants and products.

Recently, the properties of the gradient extremals of PES were subjected to the differential analysis (*75a*). In connection with the analysis of reaction paths, bifurcation regions were carefully examined. There exist several prototypes of such regions (*75b*). The finding of potential energy surfaces possessing a bifurcation transition region has prompted an investigation of dynamic behavior on these types of surfaces (*75c*).

C. Collisional Mechanisms

From the point of view of an elementary reactive collisional act, two limiting cases of collisional mechanisms can be distinguished. They are intimately connected with the type of the potential energy surface on which the reaction takes place.

1. Direct-mode mechanisms are characterized by a single passage of a typical trajectory through the critical region of the PES; a characteristic feature of the underlying surface is a barrier or a relative flatness along the reaction path in the interaction region.
2. Complex-mode mechanisms are characterized by a "snarled-type" typical trajectory passing many times through the critical interaction region, where a strongly coupled intermediate complex is formed; the corresponding PES exhibits a well, a potential energy minimum in the interaction region separating the valleys of reactants and products.

Most of our present understanding of the dynamics and of the collisional mechanisms of elementary chemical reactions comes from classical approaches, from simple classical models, and from quasiclassical trajectory studies. More recently, quantum mechanical results on the dynamics of direct-mode reactions have become available.

For direct-mode reactions, classical models have played an important role in interpreting main features of the dynamics of elementary reactions. The spectator stripping model, the sequential impulse model for high-energy collisions, the harpooning model for a large class of electron-transfer reactions, the rebound model, and the optical potential model of elastic scattering may serve as examples of approximate models developed primarily for interpreting experimental findings in the earlier days. More detailed models were required to describe product state distributions; of those the FOTO (forced oscillation of a tightening oscillator) and especially the DIPR (direct interaction with product repulsion) model and its variations deserve mentioning (for a review of classical models see, e.g., Ref. 6).

Quasiclassical trajectory calculations for direct-mode reactions were successfully performed for numerous systems, in particular for reactions occurring on a single potential energy surface. The procedures and results have been reviewed in detail several times (*6,7,11,12,16*). If several surfaces are involved, special procedures have to be used, of which the trajectory-surface-hopping method (*21*) was practically applied to reactions on surfaces with well-defined crossing seams. The trajectory studies pointed out the occurrence of multiple secondary encounters (termed clutching, clouting, or migration) (*11,76*) even for elementary reactions proceeding basically via a direct mechanism. Angular distributions, characterized for direct-mode reactions by prevailing forward or backward peaking, are usually well reproduced by trajectory calculations, though inadequate knowledge of the details of the PES may lead in some cases to disagreement. It has been suggested (*6*) that in these cases a comparison of quasiclassical trajectory calculations of the differential cross-sections with accurate quantum mechanical calculations using the same PES may be more valuable than a comparison with experiment.

An extensive study of dynamic consequences of systematic variation of model surface features was carried out by Polanyi and co-workers (*11,76*). A model LEPS surface was used and the influence of varying the reaction exoergicity, barrier location, barrier height, and reactant mass combination was investigated. Important general conclusions concerning selectivity of reactant initial energy, product angular distribution, and energy partitioning in products were obtained.

Trajectory calculations for complex-mode reactions have been less frequent; they are time consuming and—because of error accumulation—they may easily become meaningless. Nonetheless, several papers have been reported on trajectory calculations of complex formation and its decay for systems of different intricacy (*6,77*). It appears that the existence of a potential well on the surface is not sufficient: the dynamics depends also heavily on the shape of the well, as the complex has to be trapped by centrifugal barriers (*11*). Recently, complex formation in the system $H^+ + H_2$ and its isotopic variants has been subjected to a systematic investigation (*77*). The question of the complex lifetime was examined in regard to dependence on the form of (small) initial reactant energy, and mass combination. It was shown that reactant rotational excitation in general shortens the complex lifetime and that for this simple system there is a minimum time between the first encounter and the time one can speak of a collision complex which has statistical properties and decays exponentially. This time depends on the property one investigates: it increases substantially from vibrational energy equilibration (about 8 minimum-distance exchanges) to the reactant mass effect memory (about 20 minimum-distance exchanges) to the nuclear spin involvement. (*77*).

In general, one can say that very long trajectories tend to provide angular and energy distributions which are statistical in nature and comparable in quality with conclusions of statistical theories.

The statistical theories provide a relatively simple model of chemical reactions, as they bypass the complicated problem of detailed single-particle and quantum mechanical dynamics by introducing probabilistic assumptions. Their applicability is, however, connected with the collisional mechanism of the process in question, too. The statistical "phase space" theories, associated mostly with the work of Light (in Ref. 6) and Nikitin (see Ref. 17), contain the assumption of a long-lived complex formation and are thus best suited for the description of complex-mode processes. On the other hand, direct character of the process is an implicit dynamical assumption of the transition-state theory.

The two approaches were joined together in the unified statistical model of Miller (*78*). The potential energy surface in question is treated as separable into sections by dividing surfaces. For direct-mode reactions the surface has a single saddle point that divides reactants and products, through which no classical trajectory passes more than once (dividing surfaces S_0, Fig. 1a, for a collinear case $A + BC$). For complex-mode reactions the attractive well in the region of ABC interaction is separated from reactants and products by two saddle points (dividing surfaces S_1 and S_2, Fig. 1b). Statistical theories calculate microcanonical fluxes through the dividing surfaces and, with the use of the incident flux through S_a, arrive at the reaction probability and, finally, at the expression for the respective rate constant. The unified model defines the net reaction probability using the probability branching analysis and derives for it the expression

$$P(\mathrm{b} \leftarrow \mathrm{a}) = \frac{P(\mathrm{b} \leftarrow \mathrm{x})P(\mathrm{x} \leftarrow \mathrm{a})}{P(\mathrm{b} \leftarrow \mathrm{x}) + P(\mathrm{a} \leftarrow \mathrm{x}) - P(\mathrm{b} \leftarrow \mathrm{x})P(\mathrm{a} \leftarrow \mathrm{x})} \tag{40}$$

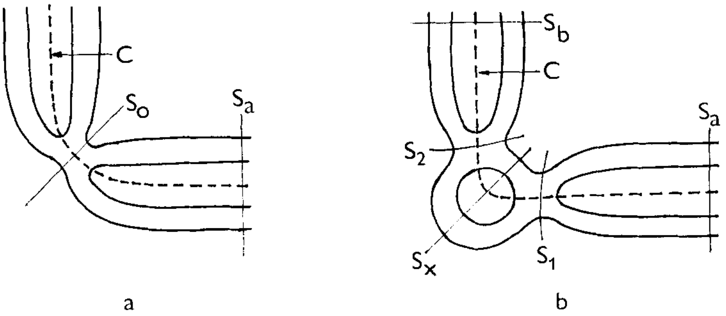


Fig. 1. Schematic view of potential energy surfaces for a collinear $\mathrm{A + BC \rightarrow AB + C}$ reaction, for a direct-mode reaction (a) and a complex-mode reaction (b); S_0, S_1, S_2, S_a, and S_b are dividing surfaces, with S_a and S_b far in the reactant and product regions, respectively. [Adapted from Ref. 79.]

(where the terms have the meaning of probabilities of passing from one dividing surface to the other). The net reaction probability, when expressed by means of the appropriate fluxes through the dividing surfaces, reduces to both the expression for $P(\mathrm{b} \leftarrow \mathrm{a})$ for complex-mode reactions [if $P(\mathrm{a} \leftarrow \mathrm{x})$, $P(\mathrm{b} \leftarrow \mathrm{x}) \ll 1$] and direct-mode reactions [if $P(\mathrm{b} \leftarrow \mathrm{x}) \sim 1$]. The dividing surfaces can be defined in terms of the Keck's variational principle and represent the "bottlenecks" on the PES, i.e., relative minima of the flux in the reactive direction at S_0, S_1, and S_2, respectively. Conservation of angular momentum can be incorporated into the treatment. Also, in this way dividing surfaces for the phenomena of nonadiabatic trapping and of the orbiting model of collision complexes can be described. The unified model was tested on the case of the collinear $H + H_2$ exchange reaction with good results, and its details were further developed (*79*).

IV. Static Approach

In this approach properties of potential energy surfaces are investigated from the point of view of all possible monomolecular transformations of the given reactants. A plausible suggestion concerning the mechanism of the reaction under study is usually made on the basis of reaction barriers or activation energies. Moreover, in some studies, partition functions are evaluated and rate constants are obtained within the framework of the absolute rate theory.

A. Localization of Stationary Points on the Potential Energy Surfaces

Equilibrium configurations of the reactants, products, and activated complexes (for reactions with a barrier separating the reactant and product regions on the PES) are characterized by zero values of the potential energy gradient. The presence of barriers is typical for the majority of organic reactions; dissociation reactions and ion–molecule reactions frequently do not exhibit such barriers. Stationary points characterized by nonnegative eigenvalues of the corresponding matrix of the second derivatives of the energy with respect to the atomic coordinates (also called the force constant matrix or Hessian) are typical for equilibrium configurations of the reactants and products. These points can be easily found by using optimization techniques at almost any level of the quantum chemical calculations (*80–82*).

Great progress has been achieved by introducing analytical expressions for nonempirical calculations of energy gradient components (*83–100*), developed also for methods which include correlation energy. Calculations of energy gradients on the basis of analytical expressions are not only more accurate, but also faster than numerical calculations. However, differences among the individual computer programs are significant. Typically, gradient calculations require up to three times more time than does Hartree–Fock SCF energy calculation. Gradient optimization methods require at least a rough estimate of the Hessian. Classical procedures, e.g., variable metric, Murthagh–Sargent, and conjugate gradient, start with a unit matrix and this matrix is then improved stepwise. A procedure was proposed (*101*) for construction of the approximate Hessian on the basis of estimates of force constants of individual bonds and angles of the molecule under study (this is reminiscent of the methods of molecular mechanics). Moreover, an efficient scheme was devised for updating the Hessian (*102*). Both procedures have been implemented in computer programs of the Gaussian series. On the basis of our experience and in agreement with the proposal made by Schlegel (*102*), it is convenient and economic to compute the Hessian on the basis of SCF runs with small basis sets, and then to exploit it for geometry optimization using the Newton–Raphson algorithms (*103*) in combination with more extensive basis sets. In contrast to the Schlegel method (*101*), this procedure describes more correctly the nondiagonal elements of the Hessian (i.e., the interaction constants) and converges more rapidly.

Analytical expressions are now available for evaluation of the second (*92,100,104–112*) and third (*113–116*) derivatives of energy with respect to the atomic coordinates. Their use for geometry calculations of stationary points is not widespread, although they are not very time consuming. Particularly, the algorithm proposed by Osamura *et al.* (*107*) for calculation of the second derivative matrix (Hessian) requires only 8–65% of the time necessary for energy gradient calculations using the SCF method. The analytical second and third derivatives are employed rather for calculating vibrational characteristics. Extensive use of analytical expressions for evaluating higher energy derivatives when performing the analysis of stationary points, vibrations, and reaction paths is to be expected in the near future.

Results of nonempirical quantum chemical energy and geometry calculations are available in the literature (*117,118*) for hundreds of molecules.

Transition-state configurations for reactions with energy barriers are represented by saddle points on the potential energy surfaces, i.e., by stationary points at which the Hessian has just one negative eigenvalue (cf. Section III,B). The saddle point represents a maximum with respect to the given reaction coordinate and a minimum with respect to all the remaining coordinates. Localization of saddle points is a troublesome task. The majority of methods for the localization of saddle points require repeated calculation of the Hessian or calculations which are similarly time consuming [the Newton–Raphson method (*103*) and methods derived from it (e.g., Refs. 102 and 119), methods which begin from a minimum and proceed uphill towards a saddle point (*120–122*), and a method of minimization of the norm of the gradient introduced by McIver and Komornicki (*123*) (see also Ref. 124)]. Special techniques limited to the investigation of the potential gradient (*125–128*) are useful only in some special cases.

Recently, a technique (*129*) for localization of a point on the crossing seam of two energy surfaces has been suggested, followed by a method of going downhill to the minima on both surfaces, which is equivalent to IRC for single PES reactions.

To predict a reasonable energy and structure of a transition state, an extensive basis set must be used and the correlation energy must be included.

Chemical intuition, which is very useful in the location of minima, usually fails in the search for saddle points. The symmetry of the transition-state structure was discussed and it was shown that many transition states exhibit low symmetry (*130–132*). Some empirical rules have been developed for approximate localization of the transition state. The rule referred to in the literature as the Bell–Evans–Polanyi–Leffler–Hammond rule is well known: the more exoergic the process, the more the transition-state geometry resembles that structure which belongs to a higher energy minimum on the given potential energy surface. This idea has been supported by calculations on S_N2-activated complexes (*133*).

Except for uphill procedures, the initial geometry must lie within the descent region of the transition structure, i.e., the region from which a certain stationary point can be reached. The size of the descent region depends on the method used; however, it is difficult to define it explicitly for a multidimensional surface. There is still another difficulty in the search for saddle points. In systems with possible internal rotations or inversions, saddle points associated with this type of motion are often found instead of the saddle point of the reaction under study (*134,135*). This difficulty can so far be overcome only by forcing the search direction on the basis of rather vague chemical intuition.

A reasonable estimate of transition-state geometries can now be made for S_N2 gas-phase reactions, as shown in an extensive study by Mitchell (*134*).

Although the geometries of numerous activated complexes have been described, semiquantitative rules for estimating transition state structures are still missing.

B. Calculations of Reaction Paths

Obtaining a good potential energy surface is extremely difficult for two main reasons. First, it requires calculations for a huge number of nuclear configurations, and second, these calculations must be performed with nonempirical methods using extended basis sets augmented by one or two sets of polarization functions; it is also necessary to include correlation energy (configuration interaction method or, e.g., the Møller–Plesset type of the perturbation treatment). Thus it is not surprising that frequently less or far less sophisticated calculations are tolerated, and, frequently, only a small part of the PES is taken into account to represent its most important regions, usually the neighborhood of the reaction path. It would be reasonable, however, to emphasize in specific situations that we have obtained, for example, a "4-31G truth", "DZ+P truth" or a "MNDO truth" [4-31G and DZ+P are labels describing the quality of the basis set used; modified neglect of differential overlap (MNDO) is one of the semiempirical methods]. Clearly, in the past few years, a steady shift out of the realm of the semiempirical toward *ab initio* techniques has been observed.

The study of topological energy surfaces is of considerable interest for the elucidation of reaction mechanisms (see, e.g., Refs. 136–139), and studies by Pancíř (*140,141*) and Mezey (*142,143*) have contributed significantly. In some instances the topological studies are based on the graph theory, which has become a new mathematical tool of quantum chemists during the last few years.

1. *Intrinsic Reaction Coordinate*

One of the most useful static methods of microscopic chemical kinetics is based on the definition of the reaction path as introduced by Fukui. This method offers information on reactions in terms of the intrinsic reaction coordinate (*62,144*). A theoretical analysis of the minimum energy path was given in Section III,B. Fukui's definition is equivalent to Eq. (34).

Fukui's reaction path, corresponding to a vibrationless and rotationless trajectory, passes gradually into the normal decomposition mode of the reactants (or products) or into the transition vector of the activated complex. Strictly speaking, Fukui's concept requires the knowledge of an accurately localized saddle point. However, it is also possible to exploit Fukui's procedure for approximately localized saddle points; these points are usually obtained by an independent method. The respective resulting path is then an approximation to the real intrinsic reaction path.

The intrinsic reaction coordinate was transformed into general internal coordinates (i.e., bond lengths, valence angles and other quantities characterizing molecular geometry) by Sana *et al.* (*68*). Thus, for nonlinear molecules, the number of dimensions of the PES is reduced by six (corresponding to translations and rotations of the entire molecule) and, consequently, results in a significant reduction of the computational effort (cf. Section III,B.). Moreover, this transformation allows for the choice of some particularly important internal coordinates. The concept of the intrinsic reaction coordinate can be used for investigation of reaction mechanisms at both the nonempirical (*145–149*) and semiempirical (*150–154*) levels.

Knowledge of the intrinsic reaction coordinate permits theoretical tracing of the change in the geometry along the reaction path; such a procedure is called reaction ergodography (*155*).

Equations for calculation of the intrinsic reaction coordinates have an infinite number of solutions unless passage through a saddle point is required. These solutions are called metaintrinsic reaction coordinates (*144*). All the possible solutions divide the configuration space into cells. The cell structure of the configuration space is essential for the wave-mechanical evaluation of the absolute rate of chemical reactions. Fukui suggested (*144*) a solution of the problem consisting of construction of the Hamiltonian inside a cell and of a time-dependent solution. Because of significant computational difficulties, no numerical calculations have been performed so far using this method.

2. *Intuitive Reaction Path*

The class of these paths possesses a common feature: a geometric parameter (such as the length of the bond which is to be formed or broken, the bond angle, or the distance between the centers of mass of the reacting molecules) is intuitively chosen as a guiding coordinate and the energy is minimized at each step along this coordinate with respect to all, or some, other internal coordinates. This reaction path is sometimes still traditionally called the "minimum energy path" (*156–158*), in contrast to the "steepest descent path." We feel that the term minimum energy path is inadequate because the steepest descent path is also a minimum energy path. Therefore we suggested (*159*) denoting this class of reaction paths as the "intuitive reaction path," as in the title to this section.

Although this type of reaction path corresponds well to chemical intuition, it suffers from a serious drawback: the reaction path from reactants to products generally differs from the path in the opposite direction, i.e., chemical hysteresis may take place (*127*). A saddle point can be reached only in a favorable case. Moreover, it is an expensive procedure because the system under study must be reoptimized in each step.

Nevertheless, when properly used, the intuitive reaction path represents a useful tool for investigating reaction mechanisms, especially in connection with semiempirical methods of quantum chemistry.

3. *Other Types of Reaction Paths*

The so-called least-motion path has been popular for many years. In the original formulation, the elementary reactions that involve the least change in the atomic and electronic configurations are favored (*160,161*). This hypothesis has found numerous applications in organic and inorganic chemistry (*162–167*). However, it is necessary to admit that there exist rather numerous exceptions, primarily due to the fact that the non-least-motion pathway is symmetry allowed while the least-motion path is symmetry forbidden (*168,169*). Dimerization of singlet carbenes is a typical example.

A simple but efficient and useful alternative is represented by the "synchronous transit method" (*125*), where the saddle point region is reached step by step along a path represented by linear and quadratic functions of the distance between the two respective minima. The geometry is optimized in the space orthogonal to the path. Müller has pointed out that the saddle point is not necessarily attained (*127*).

A procedure permitting an uphill walk corresponds well to the chemists' old dream pertaining to the reaction coordinates and studies of reaction mechanisms. A coordinate is introduced (*120*) (see also Ref. 121) with a constraint requiring parallelism between the potential energy gradient and a selected eigenvector of the Hessian, starting from a minimum on the PES, passing exactly through the activated complex and approaching the intrinsic coordinate in the vicinity of the stationary points. When walking uphill in a finite number of steps along the steepest ascent path without correcting them by using the Hessian, a divergent reaction path may result. Even when the Hessian is taken into account, the calculated reaction path oscillates along the real path. The oscillations can be suppressed by minimization in the direction perpendicular to the reaction path (*122*); however, such a calculation is more expensive.

Unfortunately, it turns out that it is relatively easy to follow paths that are of limited chemical interest, e.g., rotation around a single bond or inversion. It is generally much more tedious to investigate paths that are more useful chemically.

4. *Experimental Determination of the Reaction Path: The Chemical Reaction Path*

Information on some parts of a reaction path can be obtained from numerous structural data for a given molecule or molecular fragment located in different environments. This methods, requiring a large set of appropriate crystallographic data, provides a good insight into regions of the reaction path that would be otherwise hardly accessible. Bürgi, Dunitz, and co-workers (*170–172*) investigated a variety of chemical reaction paths for substitution reactions, nucleophilic addition and elimination at the carbonyl group, the ring closure reaction of cycloheptatriene, amide group inversion, and stereoisomerization of the triphenyl phosphine group.

5. *Fragmentary Reaction Profile*

This type of reaction profile corresponds to the graphical representation of the energy values for a set of key structures (stationary points) along the path from the reactants to the products. The individual discrete steps are represented along the coordinate by the structural formulas of the respective species; at each point the corresponding energy value is indicated.

From a practical point of view, reaction profiles are of a value comparable with a complete reaction coordinate (*173,174*), except for special cases such as quantum mechanical tunneling or the description of some dynamic aspects.

The nature of the fragmentary reaction profile allows for the possibility of combining the quantum chemical and experimental data.

In a majority of the works cited in Table I, the reaction mechanism is discussed on the basis of fragmentary reaction profiles. A choice of the most suitable mechanism is intuitively supported by the dominant role of the exponential term in the equations for the evaluation of rate constants. In cases where the activation energies of the two different reaction paths to be compared are close, some care is necessary, not only because of the inaccuracy of quantum chemical calculations. In a study (*206*) of the $H_2CO(S_0) \rightarrow H_2 + CO$ reaction for energies close to the top of the barrier, it was shown that the state with the higher energy reacts more slowly than that with the lower energy. This result contradicts the RRKM theory and has been explained by possible strong mode specifity.

C. Correlation Diagrams

Correlation diagrams are a powerful tool in qualitative studies of chemical reactivity (*207–213*). The majority of types of chemical reactions can be idealized by using highly symmetrized models, where each molecular orbital (MO) can be easily constructed or computed within a simple MO approximation. The EHT method is usually suitable for such a computation.

Predictions can be made about the suitability of different system trajectories on the basis of orbital symmetry conservation rules (*207*). The most suitable trajectory is an approximation to the reaction path of the reaction under study. The rules can also yield information about the possible structure of the activated complex. The correlation diagram technique has been improved in a series of books by Epiotis *et al.* (*214–216*). The method is based on self-consistent field–configuration interaction or valence bond (SCF–CI or VB) (including ionic structures) wave functions. Applications on reactions in the ground states as well as in the excited electronic states are impressive; however, the price to be paid for the predictions seems to be rather high.

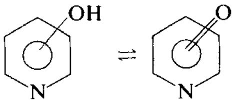
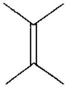
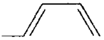
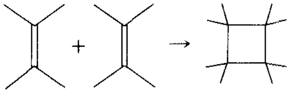
Whether a reaction is forbidden or allowed depends on various factors, including the type and strength of the nonadiabatic coupling (*16*), and need not always be determined by the orbital symmetry conservation rule (*217–219*). However, for most thermal organic reactions in the ground electronic state with sufficiently high energy of excited states, the nonadiabatic coupling is weak and the treatment based on the orbital symmetry conservation rule is well founded.

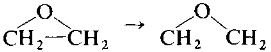
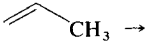
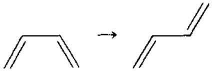
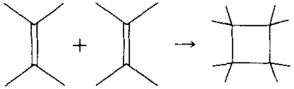
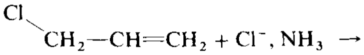
D. Combination of the Dynamic and Static Approaches

An important simplification of the dynamic approach has been introduced by Miller *et al.* (*71,74*). They showed that only a limited region of the entire potential energy surface may be taken into consideration, and thus the

TABLE I

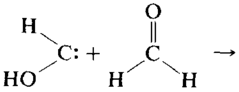
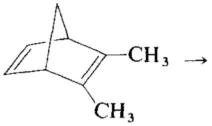
TYPICAL EXAMPLES OF STUDIES OF REACTION MECHANISMS PUBLISHED IN RECENT YEARS

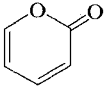
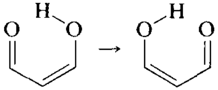
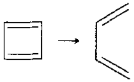
Reaction	Best method of energy calculation// optimization	Notice	Reference
$CHCl_3$, CCl_4 oxidation	MNDO//MNDO	Calculation of relative rate constants	(*175*)
	6-31G**//3-21G	Relative stabilities	(*176*)
$HCOOCH_3 + OH^- + (H_2O)_n \rightarrow$ $HCOO^- + CH_3OH + (H_2O)_n$ ($n = 0, 1, 2$)	MINDO/3//MINDO/3	Water migration from Nu to L, intuitive reaction path	(*177*)
 $+ H_3O^+$	STO-3G//STO-3G	Fragmentary reaction profile	(*178*)
Acrolein + H_3C $\xrightarrow{BF_3}$	MINDO/3//MINDO/3	Study of reactivity and selectivity, intuitive reaction path	(*179*)
	STO-3G//STO-3G	Structure of transition state	(*180*)
$R_2C{=}O + LiBH_4 \rightarrow$ ($R = H, CH_3$)	CI(DZ)//CI(DZ)	Fragmentary reaction profile	(*181*)
cis-HCOOH → *trans*-HCOOH	MCSCF(DZ + P)//—	Energy profile of OH bond rotation	(*182*)

$CH_3^+ + CH_4 \rightarrow$	CI(6-31G)//6-31G	Fragmentary reaction profile	(*183*)
$CH_4^+ + CH_4 \rightarrow$	3-21G//3-21G	Fragmentary reaction profile	(*184*)
$CH_3OH^+ \rightarrow$	6-31G//6-31G	H, H_2 loss, intuitive reaction path	(*185*)
$C_2H_3, C_2H_5 \rightarrow$	CI(6-31G**)//3-21G	H′ migration and dissociation, state correlation diagrams	(*186*)
	CI(4-31G)//4-31G	Stereoselectivity, fragmentary reaction profile	(*187*)
$CH_2{=}C{=}NH + (H_2O)_n \rightarrow$ ($n = 1, 2$)	4-31G//STO-3G	Fragmentary reaction profile	(*188*)
$H_2Fe(CO)_3 +$  $\rightarrow$	EHT//EHT	Structure of complex	(*189*)
$SiH_4 + H^- \rightarrow SiH_5^- \rightarrow$	CI(DZ + dif + 2P)//CI(DZ + dif + 2P)	Intuitive reaction path	(*190*)
	SCF(6-311G**), CI(6-31G*), MP3(6-31G*)//6-311G**	Intuitive reaction path	(*191*)
$CH_3O^{2+} \rightarrow$	MP2(6-31G**)//6-31G	Fragmentary reaction profile	(*192*)
	MCSCF(4-31G)//MCSCF(4-31G)	Analysis of PES	(*193*)
$HX + (M)_n \rightarrow$ (X = F, Cl; M = Mg, Be; $n = 1, 2$)	ACCD(DZ)//ACCD(DZ)	Fragmentary reaction profile	(*194*)
 $ClCH_2{-}CH{=}CH_2 + Cl^-, NH_3 \rightarrow$	4-31G//4-31G	Stereoselectivity of S_N2' reaction, fragmentary reaction profile	(*195*)

(*continues*)

TABLE I (*continued*)

Reaction	Best method of energy calculation// optimization	Notice	Reference
	MP2(6-31G*)//—	Fragmentary reaction profile of different path	(*196*)
$H_2CS \rightarrow H_2 + CS$ $\searrow HCSH$	CI(6-31G**)//6-31G**	IRC, reaction path instability, dynamics	(*197*)
$R\text{—}CH{=}CH_2 + H^{\cdot} \rightarrow$ $(R = H, NH_2, BH_2)$	CI(3-21G)//3-21G	Rate constants by Eyring theory, calculation of correlation energy with small basis set gives generally poor results	(*198*)
$CH_3Cl + Cl^- \rightarrow$	6-31G*//6-31G*	Reaction profile in gas and aqueous (by Monte Carlo method) phases	(*199*)
	MM2//MM2	Fragmentary reaction profile	(*200*)

 + CH_3BeF →	MNDO, STO-3G//MNDO	Fragmentary reaction profile	(*201*)
FCOOH → CO_2 + HF	6-31G**//3-21G	Fragmentary reaction path	(*135*)
	CI(DZ)//DZ	Split of vibrational levels, one-dimensional solution by WKB method	(*202*)
	MCSCF, CI(DZ + P)//TCSCF ("two-configuration SCF") (DZ)	Stationary points for conrotation and disrotation	(*203*)
$SiH_3^+ + H_2 \rightarrow SiH_5^+$ $SiH_4 + H^+ \rightarrow SiH_5^+$	MP4(6-31G**)//SCF(6-31G*)	Reaction enthalpies	(*204*)
$\cdot CH_3 + H_2 \rightarrow CH_4 + H\cdot$	POL-CI(DZ + P)//POL-CI(DZ + P)	Rate constants of isotopically modified reaction by TST	(*205*)

enormous computational effort connected with computation of the whole PES can be greatly reduced. As the relevant region of the PES, the reaction path and its environment are chosen (*220–223*). The environment is approximated by a set of quadratic functions. The coordinate system at any point on the reaction path is divided into two groups: one coordinate along the reaction path, and ($3N - 7$) coordinates—normal modes of harmonic vibrations—perpendicular to the reaction path (N being the number of atoms of the system).

The description of the PES requires quantum chemical calculations of the energy as well as the first and the second derivatives of the energy with respect to the nuclear coordinates at several points on the reaction path. These calculations can be effectively performed by using the recently developed methods (*82–100,104–116*) and programs (*224–226*) for systems consisting of five to six atoms.

Miller's approach is essentially a generalized polyatomic version of a method developed by Hofacker (*227,228*) and Marcus (*229*) for reactions of the $A + BC \rightarrow AB + C$ type.

The first applications (*230–234*) concerned a study of the dependence of the tunneling effect on the curvature of the reaction path, of an energy transfer among different vibrational modes in the course of a reaction, and of the evaluation of microcanonical rate constants for "study-case" reactions, $HCN \rightarrow CNH$, $H_2CO \rightarrow H_2 + CO$, $H_2CC: \rightarrow HC{\equiv}CH$, and proton transfer in malonaldehyde.

A better description of the environment of the reaction path can be taken into consideration when necessary. If, for example, the vibrational modes perpendicular to the reaction path have large amplitudes, the anharmonicity constants of the force field can be included to obtain a more adequate description of the reaction (*74*). This extension of the quadratic environment of the reaction path is, of course, very time consuming.

Construction of the Hamiltonian in cases where the reaction proceeds via different channels has not yet been simply solved. It should be noted that a parallel exit through several channels is for real systems a rule rather than an exception (*74*).

Carrington and Miller (*235*) developed a method called the reaction-surface Hamiltonian for reactions with large amplitudes perpendicular to the reaction path and for some types of reactions with bifurcation of the reaction path. In contrast to the reaction-path Hamiltonian method, in the reaction-surface Hamiltonian method two coordinates are extracted from the complete coordinate set. One coordinate describes motion along the reaction path and the second one describes the large-amplitude motion. Potential energy in space of the remaining $3N - 8$ coordinates perpendicular to the two-dimensional reaction surface is approximated by quadratic functions. It should be noted that the application of the reaction-surface Hamiltonian method requires significantly more computations of the energy and of energy derivatives than the reaction-path Hamiltonian.

The separation of the PES into a part determined by the reaction coordinate and a part described by a quadratic approximation in a subspace of the remaining coordinates has recently often been used, typically with the WKB approximation (*236,237*) Yamashita and Miller (*238*) utilized the reaction-path Hamiltonian method combined with the path-integral method to calculate the rate constant of the reaction of $H + H_2$.

V. Statistical Methods of Chemical Reactivity

Statistical methods are based on a microscopic view of the reacting system. In this respect we consider it reasonable to discuss them briefly in this review. Moreover, the statistical treatment consists of several steps, some of them closely related to the microscopic characteristics of a reacting system.

Statistical methods represent a background for, e.g., the theory of the activated complex (*239*), the RRKM theory of unimolecular decay (*240*), the quasi-equilibrium theory of mass spectra (*241*), and the phase space theory of reaction kinetics (*242*). These theories yield results in terms of the total reaction cross-sections or detailed macroscopic rate constants. The RRKM and the phase space theory can be obtained as special cases of the single adiabatic channel model (SACM) developed by Quack and Troe (*243*). The SACM of unimolecular decay provides information on the distribution of the relative kinetic energy of the products released as well as on their angular distributions.

Generally, the statistical methods assume that in the course of an elementary process a special state of the reacting system is reached where one of the internal degrees of freedom is changed into the translation along the reaction path. Hence, the statistical methods have two features in common.

1. It is assumed that there is a point on the reaction path, the attainment of which leads necessarily to the formation of products. This point on the reaction path from which no backward motion is possible is called the critical configuration; the state of the microscopic system at the critical configuration is referred to as the transition state and the corresponding species is called the activated complex.

2. The rate of the transformation of reactants into products depends on the amount of energy in the different degrees of freedom of the activated complex. However, the distribution of energy is not *a priori* known and it is necessary to make an assumption concerning the energy distribution in the degrees of freedom of the activated complex. From the theory of information

it can be concluded that the least biased assumption is the assumption of equal distribution of the given energy over all the internal degrees of freedom of a given electronic state of the system (*2*). This assumption can be alternatively obtained as a consequence of an equilibrium between the activated complex and the reactants. It should be emphasized, however, that the latter approach is more physical and the conservation laws represent its inherent feature.

In order to be able to describe kinetic phenomena in terms of the statistical methods, the knowledge of the critical configuration on the PES is needed as well as the eigenvalues of all the nonelectronic degrees of freedom of the system in the transition state. As shown in the previous sections, information on the critical configurations is the subject of quantum chemical calculations within the static approach.

The energy levels of the vibrational modes can be predicted with a reasonable accuracy on the basis of the standard Wilson vibrational analysis (*241,244*) (called GF analysis). The vibrational motion of atoms in the polyatomic system is approximated by harmonic oscillations in a quadratic force field. Computations of the force constants are the subject of quantum chemistry.

The energy of rotational motion can be obtained approximately on the basis of the quantum mechanical rigid-rotor model (*9,244*). The system under study is assumed to be rigid in its equilibrium configuration. The computation of the equilibrium geometry is also carried out by quantum chemistry.

It should be noted that, in these approximations [usually referred to as the rigid rotor–harmonic oscillator (RRHO) model], all the kinds of motions—electronic vibrational, and rotational—are strictly separated.

VI. Prospects

At present, it is not possible to solve the problems of chemical reactivity on the basis of the first principles of quantum mechanics.

The purpose of dynamical studies is to find the general features and characteristics of elementary processes. The main effort is focused on the most complete view of the elementary processes as obtained from the experimental as well as theoretical studies of relatively simple model systems, with the aim of obtaining results that allow one to draw general conclusions about the course of elementary processes. Dynamical studies, until recently greatly limited to atom–diatomic reactions, where the potential energy surface can be calculated with high (chemical) accuracy, are now feasible using the promising method developed by Miller and co-workers. This method reduces dramatically the number of necessary computations. A complete description of the PES requires a number of computations of the order 10^{3N-6} (N is number of atoms in the reacting system); Miller's method requires knowledge of the energy and the first and second derivatives of the energy with respect to the nuclear coordinates at several points along the reaction path. Moreover, Miller's method closely relates the static and dynamical approaches and represents a qualitatively satisfactory model for the course of a chemical process. Unfortunately, not all the reacting systems can be modeled in this relatively simple way. Attempts to include additional degrees of freedom, as is done in the reaction-surface Hamiltonian method, are at present limited by the computational capacity. Nevertheless, further development of related methods and their practical applications can be expected.

Statistical methods of calculating the rate (or equilibrium) constants, based on the fragmentary reaction profiles and statistical methods, are now routine and can be used for a broad spectrum of chemical reactions (*245*). Reactivity calculations for systems containing more atoms are usually connected with large computational problems and are very time consuming. In order to comply with the requests of correlating the experimental results, it is necessary to perform SCF runs with extended basis sets and also to include a significant portion of the correlation energy (typically TZ + diffuse functions + P + P′ + MP4 or CI). The treatment of reactions at such a high level could then be used for predicting rate and equilibrium constants even for purposes of chemical engineering.

Semiempirical methods, which are tempting in their economy, often fail. They can, however, be used for preliminary testing of the reaction under study. For this purpose, qualitative methods, based on correlation diagrams, are also very useful.

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β-Decay-Induced Rearrangement of the Molecular Electron Shell and the Problem of Determining the Neutrino Rest Mass

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I. Introduction

The most common type of a radioactive transformation is β decay. Among all the radioactive elements (about 1700), more than 1200 undergo β decay. The nuclear β decay is a transformation of a proton (p) into a neutron (n), and vice versa, accompanied by the emission of an electron (e^-) and a neutrino (ν_e) or their antiparticles (e^+, $\tilde{\nu}_e$) according to the following schemes

$$\beta^- \text{ decay:} \quad \mathrm{n} \rightarrow \mathrm{p} + e^- + \tilde{\nu}_e \tag{1}$$

$$\beta^+ \text{ decay:} \quad \mathrm{p} \rightarrow \mathrm{n} + e^+ + \nu_e \tag{2}$$

Since the nucleus undergoing β decay is usually contained in an atom or a molecule, the β decay is accompanied by rearrangement of the corresponding electron shell. The β^- decay results in the formation of a positive molecular ion in which the initial radioactive nucleus has transformed into a nucleus of the element shifted one square to the right in the periodic table. In the case of β^+ decay, the daughter ion is charged negatively, and the radioactive nucleus is replaced by a nucleus of the element shifted one square to the left in the periodic table.[1] Namely

$$[\mathrm{RA}(Z)] \overset{\beta^-}{\rightarrow} [\mathrm{RA}(Z+1)]^+ + e^- + \tilde{\nu}_e \tag{3}$$

$$[\mathrm{RA}(Z)] \overset{\beta^-}{\rightarrow} [\mathrm{RA}(Z-1)]^- + e^+ + \nu_e \tag{4}$$

---

[1] Similar replacement of a nucleus occurs when the latter captures an electron and undergoes the transformation

$$[\mathrm{RA}(Z)] \xrightarrow[\text{capture}]{\text{electron}} [\mathrm{RA}(Z-1)] + \nu_e$$

in which a neutrino is also emitted.

where A(Z) is a radioactive atom with the charge Z and R is the rest of the molecule (the radical). In these reactions the daughter ion may be formed in different electronic, vibrational, and rotational states. Its further evolution—a traditional problem in radiochemistry—depends both on the specific type of reactions [Eqs. (3) and (4)] and on the type of initial radioactive nucleus, as well as on the chemical structure of the parent molecule. Under certain conditions the daughter ion may be more stable than the parent molecule. This is successfully used for synthesizing the noble gas compounds, for example, xenon trioxide, which is obtained in the β decay of the radioactive iodine: (see review by Nefedov *et al.*, 1981).

$$^{131}\mathrm{I_2O_5} \xrightarrow{\beta^-} \mathrm{IO_2^+} + {}^{131\mathrm{m}}\mathrm{XeO_3}$$

In other cases the daughter nucleus is formed in an excited state, which, via the internal conversion, may lead to the formation of one or more vacancies in the deep electron shells. This usually results in an explosion-type decay of the daughter ion and in the formation of fragments with considerable kinetic energy. The β decay is also used for obtaining radicals with unique properties, namely, the absence of an oppositely charged ion and of a solvate shell, or the fixed initial charge localization. The formation rate of these radicals does not depend on the external conditions (such as temperature, pressure, state of aggregation, etc.) and is determined solely by the rate of the radioactive decay. An example of this is the formation of carbonium ions in the decay of tritium contained in hydrocarbons. However, we will not go further into this wide and well-developed field, and rather refer the interested reader to the numerous reviews (Nefedov *et al.*, 1981; Harbottle and Maddock, 1979; IAEA, 1961, 1965). Let us now consider a new field of application of quantum chemistry—the investigation of the influence that rearrangement of the molecular electron shell has on the β spectrum in connection with the study of neutrino properties. It is to these problems the present review is devoted.

The measurement of the form of the β spectrum near its high-energy edge is presently the most sensitive method of determining the neutrino rest mass. Experiments are carried out with tritium sources, since tritium has the lowest β electron end-point energy, $E_{\beta,\mathrm{max}} = 18.6$ keV, so that the maximum energy resolution can be obtained. In their first paper, Hanna and Pontecorvo (1949) obtained an upper limit of order of 1 keV for the neutrino rest mass, a value corresponding to the energy resolution in their method. The entire subsequent progress in this area of experimental research is due to improvement of the resolution of the measuring instruments. Until recently, the best success in this direction was reached by Bergkvist (1971, 1972). With a magnetic β spectrometer, having at the end point of the tritium β spectrum a resolution ~ 50 eV, the upper limit obtained for the neutrino mass was ~ 55 eV. Bergkvist has reached the resolution energies comparable in magnitude with the electron excitation energies of the helium ions obtained via the β decay of tritium, and has pointed out the need for taking into account the influence of these excitations on the form of the β spectrum in the corresponding data reduction.

In the general case, the tritium atom is contained in a molecule (or a complex), which we denote as RT; we can present β^- decay [Eq. (3)] for tritium-containing molecules in the following form:

$$\mathrm{RT} \xrightarrow{\beta^-} (\mathrm{RHe})^+ + e^- + \tilde{\nu}_e \tag{5}$$

The complex $(\mathrm{RHe})^+$ may be produced in different states, so that the reaction, Eq. (5), corresponds to a multichannel process. From the energy conservation law for the channel $0 \to n$ we obtain the following expression for the kinetic energy of the β electron:

$$E_\beta^{(n)} = \Delta mc^2 - m_e c^2 - E_\nu - E_{\mathrm{rec}} + [E_0(\mathrm{RT}) - E_n(\mathrm{RHe}^+)] \tag{6}$$

where Δm is the nuclear mass defect, i.e., Δmc^2 is the energy released in the β decay of the nucleus, E_ν is the total neutrino energy, E_{rec} is the recoil energy, $E_0(\mathrm{RT})$ is the energy of the ground state of the RT molecule, and $E_n(\mathrm{RHe}^+)$ is the energy of the nth quantum state of the complex $(\mathrm{RHe})^+$. For the maximum kinetic energy of the β electron we obtain

$$E_{\beta,\max}^{(n)} = \Delta mc^2 - m_e c^2 - m_\nu c^2 - E_{\mathrm{rec}} + [E_0(\mathrm{RT}) - E_n(\mathrm{RHe}^+)] \tag{7}$$

To find the average energy transferred to the electronic–vibrational molecular degrees of freedom, it is necessary to know the distribution of the probabilities of formation of the daughter molecule in different final states. This energy is of the same order of magnitude as the expected value of the neutrino rest mass, and at attained energy resolutions must be, naturally, taken into account in the reduction of the experimental β spectrum.

Qualitatively new results concerning the determination of the neutrino rest mass were obtained in 1980, when the data reduction of a set of experiments performed for more than 5 years at the Moscow Institute of Theoretical and Experimental Physics (ITEP) (Lubimov *et al.*, 1980, 1981) for the first time give the lower limit on the neutrino rest mass. The β-electron source was a doubly tritrated amino acid, valine ($C_5H_{11}NO_2$). The early reductions of the results obtained in these experiments have shown that the confidence interval for the neutrino mass substantially depends on the chosen theoretical model. Since the real electron excitation spectrum of the β source was not known, the experimental data were reduced for two model cases:

Case 1. The absence of excitations in the β source (the model of a "bare" nucleus); the 99% confidence interval for the neutrino mass was found to be

$$14 \le m_\nu c^2 \le 26 \quad \mathrm{eV}$$

TABLE I

THE MOST PROBABLE VALUE OF THE NEUTRINO REST MASS[a]

Model	Bare nucleus	T atom	Valine
$m_\nu c^2$ (eV)	6^{+4}_{-12}	27.3 ± 1.2	33 ± 1.1

[a] Obtained by data reduction of the ITEP group experiments using different models (Boris *et al.*, 1983).

Case 2. Atomic tritium in the Bergkvist two-level approximation (Bergkvist, 1972); the interval obtained was

$$24 \leq m_\nu c^2 \leq 46 \quad \text{eV}$$

This raised the problem of finding the probabilities of the excitations of the many-atomic valine molecule (64 electrons) caused by the β decay of a tritium nucleus. Earlier, the influence of the tritium β decay on the electron shell excitations was studied only for the simplest molecules. The most precise calculations were performed for HT by Wolniewicz (1965). However, the considered transitions were only those into the ground and the first excited states of HHe^+. A number of selected electron transitions for molecules OHT, NH_2T, and CH_3T were calculated by Ikuta *et al.* (1977). A consistent analysis of all the aspects of the influence of β decay on the electron shell rearrangement for different types of molecules was performed by Kaplan *et al.*, (1982, 1983), who have also calculated the distribution of excitation probabilities and the β spectrum of the tritium-containing valine.

The results concerning the allowance for the β-source molecular structure (Kaplan *et al.*, 1982, 1983) were used in reduction of the new experimental data obtained by the ITEP group. Table I (Boris *et al.*, 1983) shows the most probable values of the neutrino rest mass obtained by data reduction using the models of a "bare" nucleus, of a tritium atom, and of a real valine molecule. The reduction of the new experimental data within the bare-nucleus model did not lead to a nonzero rest mass of the neutrino. The allowance for the electron structure of valine gives $m_\nu c^2 = 33$ eV.[2] Thus, the quantum chemical calculations proved to be a necessary step in the reduction of the data concerning the properties of an elementary particle.

The question whether the neutrino has or has not a nonzero mass is of fundamental importance not only for elementary particle physics but also for cosmology, since it plays a crucial role in our knowledge of the structure and

[2] The latest data are given in a paper by Boris *et al.* (1985).

the evolution of the universe.[3] This problem is discussed in detail in the reviews by Dolgov and Zel'dovich (1980) and by Zel'dovich and Khlopov (1981). Here we present only the most important consequences.

1. Though the value of m_ν measured by the ITEP group is about 1/15,000 of the electron mass, the average concentration of neutrinos in the universe is so much greater than the average concentration of ordinary matter that more than 90% of the whole mass of the universe is due to neutrinos. So, in a way, we are living in a "neutrino" universe.
2. If the main part of the universe mass is owing to neutrinos, this must have a qualitative effect on the evolution of the universe. If the mass of the neutrino is zero, the observed density of matter in the universe is too small to stop the expansion caused by the "Big Bang." However, if the neutrino mass is not zero, the expansion will eventually stop, and the universe will start shrinking and will collapse in some 20–30 billion years.
3. Our estimations of the age of the universe (or, more exactly, of the time elapsed from the initial explosion) are also altered. For $m_\nu = 0$ the age of the universe is estimated to be 19 billion years, whereas in the case $m_\nu c^2 \approx 30$ eV, the estimate is ~ 12 billion years.
4. The admission that $m_\nu \neq 0$ solves the problem of the "concealed mass." The mass of a galaxy determined by its rotation as a whole considerably exceeds the sum of the observed stellar masses. This difference must be attributed to the unobserved "black holes." However, according to the motion of galaxies, the main part of the concealed mass is distributed along their peripheries. The nonzero mass of the neutrino explains such a distribution of masses.
5. The nonzero mass of the neutrino also can explain why the measured flux of the solar neutrinos is a few times smaller than the one predicted by the theory of thermonuclear generation of solar energy. If $m_\nu \neq 0$, the electron neutrinos may transform into other types of neutrinos[4] that are not recorded by the modern detectors.

We believe that the concepts presented above are more than enough to show the importance of the problems currently being solved with the aid of quantum chemistry.

The problem of the nonzero rest mass of neutrinos cannot be considered as solved at present. The results obtained by the ITEP group are under active

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[3] Thus affording a splendid realization of the laws of dialectics: the properties of an infinitely small particle determine the properties of an infinitely large object.

[4] The existence of such conversions, i.e., neutrino oscillations, cannot be considered completely proved at present.

discussion (Simpson, 1984; Ching Cheng-rui and Ho Iso-hsiu, 1984; Bergkvist, 1985). Independent experiments are necessary, and are being carried out in 16 scientific centers (Vanucci 1985). We should like to stress that quantum chemistry has proved to be necessary not only for m_ν measurement interpretation, but has also acquired status as a new means for investigations covering the whole scope of questions on the effect of nuclear transformations on the molecular structure. It is natural that the knowledge gained in this field is by no means dependent on the final solution of the question on the nonzero rest mass of the neutrino and is significant for quantum chemistry per se.

II. Expression for the Electron Shell Restructuring Probability

A. Initial Formula for the Transition Probability

The method proposed by Fermi (1934) for calculating the β decay of a nucleus is based on the time-dependent perturbation theory. The small value of the weak-interaction constant makes it possible to restrict oneself to the first order in perturbation theory and to use the so-called Fermi Golden Rule

$$P_{\mathrm{if}} = \frac{2\pi}{\hbar} |\langle \Psi^{\mathrm{f}} | H_\beta | \Psi^{\mathrm{i}} \rangle|^2 \, \delta(E_{\mathrm{i}} - E_{\mathrm{f}}) \tag{8}$$

for calculating the probability of the β decay. Here $|\Psi^{\mathrm{i}}\rangle$ is the state vector of the parent nucleus, $|\Psi^{\mathrm{f}}\rangle$ describes the final system of the daughter nucleus and of the emitted β electron and antineutrino, and H_β is the weak-interaction Hamiltonian.

Equation (8) is widely used for calculating the β transitions in nuclei when the influence of the electron shell is disregarded. Under certain limitations this formula is also valid when one does make allowance for the electron shell and for the molecular surrounding of the radioactive nucleus. In this section we present a derivation of the formula for the probability of β decay with due regard for all the molecular degrees of freedom.

The nucleons inside a radioactive nucleus contained in a molecule interact with the electron–neutrino field and undergo the β transition—a transformation of a neutron into a proton accompanied by the emission of a β electron and a neutrino.[5] The weak interaction does not affect the electron shell and the other nuclei of the molecule. For them the β decay is an "instantaneous" change (a jump) in the charge of the radioactive nucleus by unity. Besides this, the nucleus obtains a recoil momentum due to the emission

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[5] Everywhere in the following discussions we will employ the single term "neutrino," making a distinction between the neutrino and the antineutrino (as well as between the β^+ and β^- decays) only in those cases where the difference is essential.

of the β electron and the neutrino. Both of these perturbations are not small with respect to the molecule. Indeed, the typical shift of the molecular levels due to the jump in the charge is $V_{\text{el}} = 5\text{–}20$ eV $\lesssim 0.8$ a.u. (atomic units), i.e., of the same order of magnitude as the distance between the electron levels in a molecule. The perturbation due to the recoil momentum is $V_{\text{rec}} \leq E_{\text{rec, max}} = (m_e/M_{\text{nucl}}) \cdot E_{\beta,\text{max}}$. In the case of tritium, which has the lowest end-point energy $E_{\beta,\text{max}} \approx 18.6$ keV, we find $V_{\text{rec}} \approx 3$ eV ≈ 0.1 a.u. Though these perturbations are not small, the use of the perturbation theory may be based on their "instantaneity," provided the following inequalities are obeyed (Migdal, 1975)

$$V \cdot \tau \ll 1; \qquad \tau \ll \tau_{\text{el}} \tag{9}$$

where V is the perturbation. It is produced within the time τ which must be much shorter than the characteristic times of the internal motions in the molecule $\tau_{\text{el}} < \tau_{\text{vib}} < \tau_{\text{rot}}$. Let us estimate τ. The jump in the charge takes place during the time taken for the β electron to travel through the electron shell of the molecule. Since the "thickness" of the shell is of order of 1 a.u., we have $\tau_{\text{charge}} = 1/v_\beta = (2E_\beta)^{-1/2}$ a.u. The recoil time is determined by the time taken for the β electron to travel through the nucleus, i.e., $\tau_{\text{rec}} = l_{\text{nucl}}/v_\beta \approx 10^{-5} \cdot (2E_\beta)^{-1/2}$ a.u. For the β decay of a tritium nucleus we have $\tau_{\text{charge}} \approx 10^{-18}$ sec. Thus τ_{rec} is about five orders of magnitude smaller, so the second inequality of Eq. (9) is obeyed. Taking $v \cdot \tau = 0.1$ and substituting $V_{\text{el}} \cdot \tau_{\text{charge}}$ and $V_{\text{rec}} \cdot \tau_{\text{rec}}$ into the first inequality of Eq. (9), we see that in both cases Eq. (9) is obeyed when $E_\beta \geq 870$ eV. Thus, Eq. (8) can be used for calculating the probability of the β decay in a molecule in the range of the β-electron energies

$$1 \quad \text{keV} \lesssim E_\beta \leq E_{\beta,\text{max}} \tag{10}$$

i.e., in the very region of the β-electron spectrum that is used for data reduction of the neutrino rest-mass measurements. In this energy region one does not have to consider a number of processes that contribute to the low-energy edge of the β-electron spectrum. These include the direct excitation of the molecular electron shell by the β electron passing through (Batkin and Smirnov, 1980), the exchange of the β electron with molecular electrons (Bahcall, 1963), and others. All these processes are essential at β-electron energies of the order of the binding energy of electrons in the shell, and, thus, may be neglected (Williams and Koonin, 1983) in the high-energy region of the β spectrum. In view of this, we can choose the unperturbed Hamiltonian H_0 in the following form (Cantwell, 1956):

$$H_0 = \sum_{k=1}^{n} H_{\text{nucl},k} + H_{\text{CM, mol}} + H_{\text{mol}} + H_{\text{lept}} \tag{11}$$

Here $H_{\text{nucl},k}$ describes the motion of protons and neutrons (nucleons) of the kth nucleus, $H_{\text{CM},\text{mol}}$ describes the motion of the center of mass of the molecule, H_{mol} is the internal molecular Hamiltonian, and H_{lept} contains the kinetic energy operators of the neutrino and of the β electron (leptons) as well as the term describing the interaction of the latter with the nuclei of the molecule.

In order to use the perturbation theory it is necessary that the state vectors in the matrix element Eq. (8) belong to the spectrum of the unperturbed Hamiltonian H_0 only. However, this is usually not so, since, in β decay, the initial particles are not the same as the final products of the reaction: the initial molecule containing the radioactive atom transforms into a different molecule; besides, the β electron and the neutrino appear. One of the ways to describe the initial and final states using only the H_0 Hamiltonian is to use the isotopic spin formalism for both the nucleons and the leptons (β electron and neutrino). In the appendix (Section V) we present the wave functions of the initial and the final states together with the necessary transformations, which one can use to factorize the initial matrix element Eq. (8) into the intranuclear and the molecular parts. Here we briefly discuss only the approximations necessary for performing such a factorization.

The weak-interaction Hamiltonian H_β in Eq. (8) acts only on the nucleon and the lepton coordinates, leaving the molecular ones unaffected. Consequently, in order to single out the molecular factor in the matrix element Eq. (8), it is necessary that the wave functions of nucleons and leptons be independent of the molecular variables The wave functions describe the motion of the nucleons inside the kth nucleus with respect to its center of mass. The position of the latter is described by the radius vector $\mathbf{R}_k$, and, generally speaking, the wave functions depend both on $\mathbf{R}_k$ and on the internal nucleon coordinates. The wave function of the β electron produced in the final state must also depend on the center-of-mass coordinates of the nuclei.

The nucleons interact with each other by means of nuclear forces (the strong interaction), which leads to the formation of a dense nucleus with the radius $\sim 10^{-13}$ cm. In addition, the nucleons also interact with electrons and other nuclei of the molecule by means of electromagnetic forces, owing to which the nucleus takes part in the vibratory motion of the molecule. Since the electromagnetic forces are considerably weaker than the strong forces, they can only displace the nucleus as a whole but cannot produce any noticeable changes in the shape of the nucleon cloud. This means that the internal wave function of the nucleus depends weakly on the center-of-mass coordinate $\mathbf{R}_k$ and may be calculated for the equilibrium value $\mathbf{R}_k^0$ of the latter.

When performing the integration in the intranuclear matrix element, one should bear in mind that the wave functions of nucleons are limited by the volume of the nucleus ($\sim 10^{-13}$ cm). At such distances the β-electron wave function is practically constant. It is usually assigned the value it has at the boundary of the nucleus and is taken outside the integral, thereby it is supposed that the dynamics of the β transition are totally determined by the nucleon wave functions. After this, the intranuclear matrix element is no longer dependent on the center-of-mass coordainte, and the factorization is easily performed.

As is shown in the appendix (Section V), the matrix element determining the probability of β decay is factorized in the following way:

$$\langle \Psi^{\mathrm{f}} | H_\beta | \Psi^{\mathrm{i}} \rangle = M_{\mathrm{nucl},n}(\mathbf{p}_\nu, \mathbf{p}_\beta) \cdot M_{\mathrm{mol}}(\mathbf{p}_\nu + \mathbf{p}_\beta) \tag{12}$$

Since $\mathbf{P}_{\mathrm{rec}} = \mathbf{p}_\nu + \mathbf{p}_\beta$, we have

$$M_{\mathrm{mol}}(\mathbf{P}_{\mathrm{rec}}) = \langle \Psi^{\mathrm{f}}_{\mathrm{mol}} | \exp[-i\mathbf{P}_{\mathrm{rec}} \cdot \mathbf{R}_n] | \Psi^{\mathrm{i}}_{\mathrm{mol}} \rangle \tag{13}$$

Here $M_{\mathrm{nucl},n}$ is the internal matrix element of the radioactive nucleus which we have supplied with the index n; M_{mol} is the molecular matrix element; $\mathbf{p}_\nu$, $\mathbf{p}_\beta$, and $\mathbf{P}_{\mathrm{rec}}$ are, respectively, the neutrino, the β-electron, and the recoil momenta; $\Psi^{\mathrm{f}}_{\mathrm{mol}}$ and $\Psi^{\mathrm{i}}_{\mathrm{mol}}$ are the wave functions of the daughter and the parent molecules which describe the electronic, vibrational, and rotational molecular degrees of freedom.

B. Factorization of the Molecular Matrix Element

In this section we study more closely the molecular matrix element [Eq. (13)]. The β decay in a molecule may lead to the excitation of all the degrees of freedom—electronic, vibrational, and rotational. Let us first show that the recoil of the radioactive nucleus does not excite the electronic degrees of freedom. To this end we introduce the relative coordinates using the Jakobi transformation and, in order to simplify the calculations, consider a diatomic molecule with N electrons.

Let $\mathbf{R}_1$ and $\mathbf{R}_2$ be the coordinates of the nuclei and $\mathbf{r}_1, \ldots, \mathbf{r}_N$ be the coordinates of the electrons. If $\mathbf{R}$ and ξ denote the corresponding relative cooredinates, and $\mathbf{R}_c$ is the coordinate of the center of mass of the whole system, the Jakobi transformation has the form

$$\begin{aligned}
\mathbf{R} &= \frac{M_1\mathbf{R}_1}{M_1} - \mathbf{R}_2 = \mathbf{R}_1 - \mathbf{R}_2 \\
\xi_1 &= \frac{M_1\mathbf{R}_1 + M_2\mathbf{R}_2}{M_1 + M_2} - \mathbf{r}_1 \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\xi_i &= \frac{M_1\mathbf{R}_1 + M_2\mathbf{R}_2 + m_e\mathbf{r}_1 + m_e\mathbf{r}_2 + \cdots + m_e\mathbf{r}_{i-1}}{M_1 + M_2 + (i-1)\cdot m_e} - \mathbf{r}_i \\
\mathbf{R}_c &= \frac{M_1\mathbf{R}_1 + M_2\mathbf{R}_2 + m_e\mathbf{r}_1 + \cdots + m_e\mathbf{r}_N}{M_1 + M_2 + N\cdot m_e}
\end{aligned} \tag{14}$$

Let us consider nucleus 2 to be the radioactive one and express its radius vector $\mathbf{R}_2$ in terms of the relative coordinates and the coordinate of the center of mass. Assuming that the latter coincides with the center of mass of the nuclei and bearing in mind that in H_{mol} the coordinates of electrons and nuclei are determined with respect to the center of mass of the molecule, we obtain

$$\begin{aligned} &M_{nm}^{\text{mol}}(\mathbf{P}_{\text{rec}}) \\ &\quad = \langle \Psi_{\text{mol},n}^{\text{f}}(\cdots \mathbf{r}_i s_i \cdots ; \mathbf{R}_1, \mathbf{R}_2) | e^{i\mathbf{P}_{\text{rec}}\mathbf{R}_2} | \Psi_{\text{mol},m}^{\text{i}}(\cdots \mathbf{r}_i s_i \cdots ; \mathbf{R}_1, \mathbf{R}_2) \rangle \\ &\quad = \langle \Psi_{\text{mol},n}^{\text{f}}(\cdots \xi_i s_i \cdots ; \mathbf{R}) | e^{i(M_1/M)\mathbf{P}_{\text{rec}}\mathbf{R}} \cdot e^{-i(m_e/M)\mathbf{P}_{\text{rec}} \cdot \Sigma_i^N \boldsymbol{\xi}_i} | \Psi_{\text{mol},m}^{\text{i}}(\cdots \xi_i s_i \cdots ; \mathbf{R}) \rangle \end{aligned} \tag{15}$$

where M_1 is the mass of the first nucleus, $M = M_1 + M_2$ is the mass of the whole molecule, and m_e is the electron mass. The second exponent in the operator describes the influence of the recoil on the motions of electrons. Since the ratio m_e/M of the electron mass to the mass of the molecule is small, we can neglect the effect of the recoil of the radioactive nucleus on the excitation of electrons of the daughter molecule:

$$M_{nm}^{\text{mol}}(\mathbf{P}_{\text{rec}}) = \langle \Psi_{\text{mol},n}^{\text{f}}(\cdots \xi_i s_i \cdots ; \mathbf{R}) | e^{i(M_1/M)\mathbf{P}_{\text{rec}}\mathbf{R}} | \Psi_{\text{mol},m}^{\text{i}}(\cdots \xi_i s_i \cdots ; \mathbf{R}) \rangle \tag{16}$$

The recoil operator in Eq. (16) acts only on the relative coordinates of the nuclei. This reasoning holds also in the case of a multiatomic molecule.

Let us consider the electron–vibrational matrix element. As is usually done, we consider two coordinate systems, the origins of which are located at the center of mass of the molecule. The first coordinate system is fixed in space, while the second system (the rotational one) is fixed to the molecule. For describing the orientation of the rotational system with respect to the fixed frame we use the Eulerian angles $\theta \equiv \{\alpha, \beta, \gamma\}$. In the Born–Oppenheimer approximation, the motion of nuclei may be decomposed into the vibrations of the nuclei about their equilibrium position and the rotation of the molecule as a whole. Accordingly, the wave function of the nuclei $\mathrm{X}_{n,w}(\mathbf{R})$ is presented as a product of the vibrational wave function $\Lambda_{nv}(\mathrm{Q})$ and the rotational wave function $\Theta_{MK}^{J}(\theta)$:

$$\mathrm{X}_{n,w}(\mathbf{R}) = \Lambda_{nv}(Q) \cdot \Theta_{MK}^{J}(\theta) \tag{17}$$

Here n and μ are, respectively, the electron and the vibrational quantum numbers; J is the angular momentum quantum number; M and K are the quantum numbers of projections of J on the Z axis of the fixed system and on the Z' axis of the rotational system, respectively; $Q = \mathbf{R} - \mathbf{R}_0^{\text{n}}$ is the displacement of the nuclei with respect to their equilibrium position; and $w \equiv \{\mu, J, M, K\}$. The total wave function of the molecule is

$$\Psi_{\text{mol},n} = \Psi_n(\xi_1 \cdots \xi_N; \mathbf{R}) \cdot \Lambda_{n\mu}(Q) \cdot \Theta_{MK}^{J}(\theta) \tag{18}$$

The arguments of the electron wave function Ψ_n are given in the rotational coordinate system.

Substituting wave functions of Eq. (18) into the matrix element Eq. (16) and isolating the electron–vibrational matrix element $M_{n\mu,mv}$, we get

$$\begin{aligned}
M_{nm}^{\text{mol}}(\mathbf{P}_{\text{rec}})
&= \langle \Psi_n^{\text{f}}(\xi, \mathbf{R}) \cdot \Lambda_{n\mu}^{\text{f}}(Q) \cdot \Theta_{MK}^{J}(\theta) | e^{i(M_1/M)\mathbf{P}_{\text{rec}}\mathbf{R}} | \Psi_m^{i}(\xi, \mathbf{R}) \Lambda_{mv}(Q) \Theta_{M'K'}^{J'}(\theta) \rangle \\
&= \langle \Theta_{MK}^{J}(\theta) | M_{n\mu,mv}(\theta) | \Theta_{M'K'}^{J'}(\theta) \rangle \qquad (19)
\end{aligned}$$

Let us single out the electron part of the electron–vibrational matrix element. To this end let us consider its integrand versus the distance between the nuclei **R**:

$$M_{n\mu,mv} = \langle \Psi_n^{\text{f}}(\xi, \mathbf{R}) \Lambda_{n\mu}^{\text{f}}(\mathbf{R} - \mathbf{R}_0^{\text{f},n}) | e^{i(M_1/M)\mathbf{P}_{\text{rec}}\mathbf{R}} | \Psi_m^{\text{i}}(\xi, \mathbf{R}) \cdot \Lambda_{mv}^{\text{i}}(\mathbf{R} - \mathbf{R}_0^{\text{i},m}) \rangle \qquad (20)$$

$\mathbf{R}_0^{\text{i},m}$ and $\mathbf{R}_0^{\text{f},n}$ are the equilibrium configurations of the nuclei of the parent molecule (RT) in the electron state m and of the daughter molecule $(\text{RHe})^+$ in the electron state n, respectively. Shown in Fig. 1 are the electron terms and the vibrational wave functions of the parent and the daughter molecules together with the transition nuclear density function

$$F_{n\mu,m0}(\mathbf{R}) = \Lambda_{n\mu}^{\text{f}}(\mathbf{R} - \mathbf{R}_0^{\text{f},n}) \cdot \Lambda_{m,0}^{\text{i}}(\mathbf{R} - \mathbf{R}_0^{\text{i},m}) \qquad (21)$$

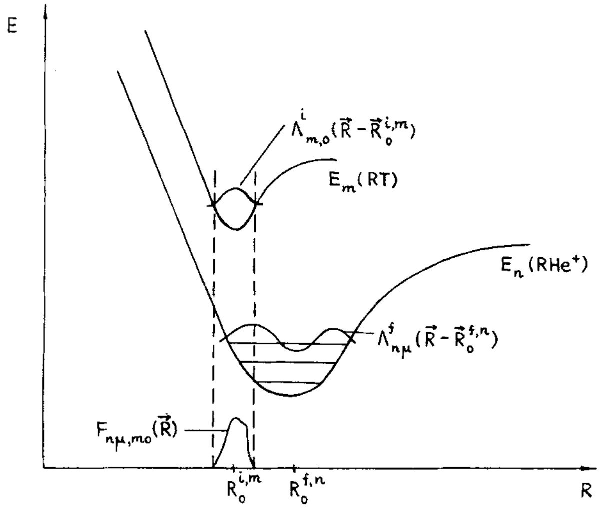


Fig. 1. Scheme of the electronic terms and vibrational wave functions of parent (RT) and daughter $(\text{RHe})^+$ molecules.

From the analysis of the matrix element [Eq. (20)] the following statements hold:

1. The integrand [and consequently the whole matrix element Eq. (20)] is nonzero only in the range of definition of the transition nuclear density function $F_{n\mu,m0}(\mathbf{R})$. Since at room temperatures the β transition occurs from the lowest vibrational states, the range of definition of the vibrational wave function of the initial state $\Lambda^{\mathrm{i}}_{m\nu}(\mathbf{R} - \mathbf{R}_0^{\mathrm{i},m})$ is quite narrow. Thus, $F_{n\mu,m0}(\mathbf{R})$ must be nonzero near the equilibrium distance of the initial molecule $\mathbf{R}_0^{\mathrm{i},m}$.

2. Naturally, the range of definition of $F_{n\mu,m0}(\mathbf{R})$ is not wider than that of the initial vibrational wave function $\Lambda^{\mathrm{i}}_{m,0}(\mathbf{R} - \mathbf{R}_0^{\mathrm{i},m})$. In this region, the electron wave functions vary only slightly. Thus, we may use the Condon approximation and take these functions out of the matrix element Eq. (20), assigning them the values they have at a fixed coordinate $\mathbf{R} = \mathbf{R}_0^{\mathrm{i},m}$. Let us note that the wave functions of the initial and of the final states are taken outside the matrix element Eq. (20), having the values corresponding to the same equilibrium distance $\mathbf{R}_0^{\mathrm{i},m}$ of the parent molecule:

$$\begin{aligned} M_{n\mu,m\nu} &= \langle \Psi^{\mathrm{f}}_n(\xi, \mathbf{R}_0^{\mathrm{i},m}) \,|\, \Psi^{\mathrm{i}}_m(\xi, \mathbf{R}_0^{\mathrm{i},m}) \rangle \\ &\quad \cdot \langle \Lambda^{\mathrm{f}}_{n,\mu}(\mathbf{R} - \mathbf{R}_0^{\mathrm{f},n}) | e^{i(M_1/M)\mathbf{P}_{\mathrm{rec}}\mathbf{R}} | \Lambda^{\mathrm{i}}_{m\nu}(\mathbf{R} - \mathbf{R}_0^{i,m}) \rangle \\ &\equiv M^{\mathrm{el}}_{n,m}(\mathbf{R}_0^{\mathrm{i},m}) \cdot M_{\mu\nu}(\mathbf{P}_{\mathrm{rec}}) \end{aligned} \tag{22}$$

Here $M^{\mathrm{el}}_{n,m}(\mathbf{R}_0^{\mathrm{i},m})$ and $M_{\mu\nu}$ are, respectively, the electron and the vibrational matrix elements. Substituting Eq. (22) into Eq. (19), we get

$$M^{\mathrm{mol}}_{n,m}(\mathbf{P}_{\mathrm{rec}}) = M^{\mathrm{el}}_{n,m}(\mathbf{R}_0^{i,m}) \cdot \langle \Theta^{J}_{MK}(\theta) | M_{\mu\nu}(\mathbf{P}_{\mathrm{rec}}) | \Theta^{J'}_{M'K'}(\theta) \rangle \tag{23}$$

Thus, the molecular matrix element Eq. (13) is factorized into electron and vibrational–rotational matrix elements. The electron matrix element is independent of the recoil momentum, and, consequently, the electron degrees of freedom are excited only by the jump in the charge of the radioactive nucleus, whereas the excitation of vibrations and rotations is due to both the jump in the charge and the recoil of the radioactive nucleus.

Let us note that the electron matrix element should be calculated for the equilibrium configuration of the nuclei of the initial molecule only in the case when the low vibrational states are occupied. At sufficiently high temperatures, when the highly excited vibrational states are occupied with noticeable probability, the electron matrix element must be calculated at an intermediate distance between the nuclei:

$$M^{\mathrm{el}}_{n,m}(\tilde{\mathbf{R}}_0) = \langle \Psi^{\mathrm{f}}_n(\xi, \tilde{\mathbf{R}}_0) \,|\, \Psi^{\mathrm{i}}_{\mathrm{m}}(\xi, \tilde{\mathbf{R}}_0) \rangle \tag{24}$$

If one is interested only in the molecular electron excitations induced by β decay, and sums up the squared modulus of the molecular matrix element Eq. (19) over the final vibrational and rotational quantum numbers and averages it over the initial ones, then, in any case, the electron matrix element is calculated at the equilibrium distance of the parent molecule $\mathbf{R}_0^{\mathrm{i},m}$ [see Eqs. (25–27)].

C. Formula for the Electron Excitation Probability

1. *General Expression*

In order to find the relative probability of the molecule being excited into the nth electronic state it is sufficient to consider only the molecular part of the total matrix element [Eq. (12)], to sum the squared modulus of the molecular matrix element [Eq. (13)] over the quantum numbers of nuclear motion of the final state, and the average it over the quantum numbers of the initial state

$$\begin{aligned} W_{mn} &= \sum_{w,w'} P_w |M_{\mathrm{mol}}(\mathbf{P}_{\mathrm{rec}})|^2 \\ &= \sum_{w,w'} P_w \langle \Psi_n^{\mathrm{f}}(\xi, \mathbf{R}) \mathrm{X}_{nw'}^{\mathrm{f}}(\mathbf{R}) | e^{i(M_1/M)\mathbf{P}_{\mathrm{rec}}\mathbf{R}} | \Psi_m^{\mathrm{i}}(\xi, \mathbf{R}) \mathrm{X}_{mw}^{\mathrm{i}}(\mathbf{R}) \rangle^* \\ &\quad \cdot \langle \Psi_n^{\mathrm{f}}(\xi', \mathbf{R}') \mathrm{X}_{nw'}^{\mathrm{f}}(\mathbf{R}') | e^{i(M_1/M)\mathbf{P}_{\mathrm{rec}}\mathbf{R}'} | \Psi_m^{\mathrm{i}}(\xi', \mathbf{R}') \mathrm{X}_{mw}^{\mathrm{i}}(\mathbf{R}') \rangle \\ &= \sum_{w} P_w \langle \mathrm{X}_{mw}^{\mathrm{i}}(\mathbf{R}) | \langle \Psi_m^{\mathrm{i}}(\xi, \mathbf{R}) | e^{-i(M_1/M)\mathbf{P}_{\mathrm{rec}}\mathbf{R}} | \Psi_n^{\mathrm{f}}(\xi, \mathbf{R}) \rangle \sum_{w'} | \mathrm{X}_{nw'}^{\mathrm{f}}(\mathbf{R}) \rangle \langle \mathrm{X}_{nw'}^{\mathrm{f}}(\mathbf{R}') | \\ &\quad \cdot \langle \Psi_n^{\mathrm{f}}(\xi', \mathbf{R}') | e^{i(M_1/M)\mathbf{P}_{\mathrm{rec}}\mathbf{R}'} | \Psi_m^{\mathrm{i}}(\xi', \mathbf{R}') \rangle | \mathrm{X}_{mw}^{\mathrm{i}}(\mathbf{R}') \rangle \end{aligned} \tag{25}$$

Let us use the relation

$$\sum_{w'} | \mathrm{X}_{nw'}^{\mathrm{f}}(\mathbf{R}) \rangle \langle \mathrm{X}_{nw'}^{\mathrm{f}}(\mathbf{R}') | = \delta(\mathbf{R} - \mathbf{R}') \tag{26}$$

which follows from the requirement that the set of the wave functions describing the motion of the nuclei be complete, and from the fact that, due to the weak dependence of the electron wave function on the nuclear coordinates, it may be taken at a fixed value $\mathbf{R} = \mathbf{R}_0^{\mathrm{i},m}$; this allows us to factorize the matrix element (the Condon approximation). As a result, the product of the conjugate complex exponents and the sum of the probabilities P_w both give unity, and we obtain the following simple formula

$$\begin{aligned} W_{mn} &= |\langle \Psi_n^{\mathrm{f}}(\xi, \mathbf{R}_0^{\mathrm{i},m}) | \Psi_m^{\mathrm{i}}(\xi, \mathbf{R}_0^{\mathrm{i},m}) \rangle|^2 \\ &\quad \cdot \sum_{w} P_w \langle \mathrm{X}_{mw}^{\mathrm{i}}(\mathbf{R}) \,|\, \mathrm{X}_{mw}^{\mathrm{i}}(\mathbf{R}) \rangle \\ &= |\langle \Psi_n^{\mathrm{f}}(\xi, \mathbf{R}_0^{\mathrm{i},m}) | \Psi_m^{\mathrm{i}}(\xi, \mathbf{R}_0^{\mathrm{i},m}) \rangle|^2 \end{aligned} \tag{27}$$

A nontrivial result with respect to the well-known formula of Migdal (1941) for the probability of the β-decay-induced excitation of an atom is the justification in the above derivation for taking the electron wave functions at the equilibrium nuclear configuration of the parent molecule, as well as the justification for the neglect of the influence of the recoil momentum on the value of W_{mn}.

2. *Choice of the Calculation Method*

Since the exact wave functions of a multielectron system cannot be determined, one is faced with the problem of choosing an approximation. From the very beginning one must give up the semiempirical methods, since they cannot be used for studying the β decay in tritium-containing molecules, because there are no empirical parameters for helium-containing daughter complexes. In order for Eq. (27) to give the excitation probability it is necessary and sufficient that the wave function Ψ^{i}_m be normalized to unity, while the functions Ψ^{f}_n $(0 \leq n < \infty)$ belong to a complete orthonormal set of eigenfunctions.

The greater the number of functions Ψ^{f}_n belonging to the orthonormal set, the more completely and in more detail the spectrum of the β-decay-induced excitations of a molecule can be calculated. Consequently, the method for calculating the wave functions of the daughter ion must be such that at a reasonable volume of calculation we would be able to construct a sufficiently large number of multielectron wave functions of excited states. The Hartree–Fock method allows one to construct the wave functions of excited states as the combinations of determinants symmetrized in a certain way. Within this method the excitation is considered to be a transition of an electron from an occupied Hartree–Fock molecular orbital into a vacant one.

However, the vacant Hartree–Fock molecular orbital (MO) obtained as a by-product of the ground-state calculations are of little use for describing the excited states of a molecule. This is due to the fact that the vacant Hartree–Fock MOs correspond to the motion of an excited electron in the potential field of all N electrons rather than of $N - 1$ electrons, as must be the case (Slater, 1963). Hunt and Goddard (HG) (1963) have proposed modifying the Hartree–Fock operator in such a way that it would be possible to describe the motion of an excited electron in the potential V_{N-1}:

$$F_i^{\mathrm{HG}} = h + \sum_j^{N/2}(2J_j - K_j) + aJ_i + bK_i; \qquad 1 \leq i \leq N/2 \tag{28}$$

For singlet excitations $a = -1$ and $b = 2$; for tritlet excitations $a = -1, b = 0$; h, J, and K are, respectively, the one-electron, the Coulomb, and the exchange operators. They have the same meaning as in the usual Hartree–Fock operator. Here F_i^{HG} is the N-electron operator with the hole in the ith occupied MO. Thus, Hunt and Goddard have replaced a single Hartree–Fock operator by a whole set of operators [Eq. (28)] differing in the position of the vacancy. The spectrum of each of these operators is an orthonormal set of MOs:

$$F_i^{\mathrm{HG}}\varphi_n^{(i)} = \varepsilon_n^{(i)}\varphi_n^{(i)}; \qquad \langle\varphi_n^{(i)}\,|\,\varphi_m^{(i)}\rangle = \delta_{nm} \tag{29}$$

However, the MOs belonging to spectra of different operators of the set are not mutually orthogonal

$$\langle \varphi_n^{(i)} \mid \varphi_m^{(j)} \rangle = S_{nm}^{(ij)} \tag{30}$$

This fact does not allow one to construct an orthogonal set of determinant wave functions corresponding to the configurations

$$\Psi_{i\to v}^{\mathrm{HG}} = A \cdot \det[\varphi_{1\alpha}^{(i)}, \varphi_{1\beta}^{(i)}, \ldots, \varphi_{i\alpha}^{(i)}, \varphi_{v\beta}^{(i)}, \ldots]$$

$$\langle \Psi_{i\to v}^{\mathrm{HG}} | \Psi_{j\to w}^{\mathrm{HG}} \rangle = \begin{cases} \delta_{v,w} & \text{for} \quad i = j \\ \mathrm{S}_{v,w} & \text{for} \quad i \neq j \end{cases} \tag{31}$$

Many attempts have been made to alter the Hunt–Goddard procedure in such a way that it would give an orthonormal set of states. Bhattacharyya and Banerjee (1980) have proposed to average the set of operators F_i^{HG} over the position of the hole and, thus, to obtain a single operator with an "average" hole and a single one-electron spectrum. However, such an average hole makes it difficult to classify the excited configurations. In our works (Kaplan *et al.*, 1982, 1983) we have used the Hazinaga version [Huzinaga and Arnau (HA) 1971]. Like Hunt and Goddard, Huzinaga has constructed a set of operators, each with a hole in an occupied MO. However, the correction to the Hartree–Fock operator was projected onto the subspace of vacant orbitals

$$F_i^{\mathrm{HA}} = h + \sum_j^{N/2} (2J_j - K_j) + (1 - P)(aJ_i + bK_i)(1 - P); \qquad 1 \leq i \leq N/2 \tag{32}$$

where a and b have the same values as in Eq. (28); $P = \Sigma_{i=1}^{\mathrm{occ}} |\varphi_i\rangle\langle\varphi_i|$. The one-electron spectra of the operators F_i^{HA} corresponding to different positions of the hole i are not orthogonal to each other. However, all these spectra have a mutual part—the subset of occupied MOs which coincides with the set of occupied MOs for the Hartree–Fock operator. This proved to be sufficient for the determinant wave functions corresponding to different excited configurations to be mutually orthogonal, in contrast to Eq. (31),

$$\Psi_{i\to v}^{\mathrm{HA}} = A \cdot \det[\varphi_{1\alpha}, \varphi_{1\beta}, \ldots, \varphi_{i\alpha}, \varphi_{v\beta}^{(i)}, \ldots] \tag{33}$$

$$F_i^{\mathrm{HA}} \varphi_v^{(i)} = \varepsilon_v^{(i)} \varphi_v^{(i)} \tag{34}$$

$$\langle \Psi_{i\to v}^{\mathrm{HA}} \mid \Psi_{j\to w}^{\mathrm{HA}} \rangle = \delta_{v,w} \delta_{i,j} \tag{35}$$

where φ_i is the Hartree–Fock MO from which the electron is excited.

Thus, as an MO basis for constructing the multielectron wave functions of configurations given by Eq. (33), we will use the Hartree–Fock MO for the occupied one-electron states and the Huzinaga MO [Eq. (34)] for the excited ones. An advantage of the Huzinaga MOs is the simplicity of the way they are obtained, since Eq. (34) is an equation with constant coefficients and one does not have to use the iteration method. Moreover, when one uses the Huzinaga

MO, the configuration interaction (CI) calculations converge more rapidly (Huzinaga *et al.*, 1973). Amus'ya *et al.* (1971) have shown that the wave functions obtained by the $(N - 1)$-electron potential methods, to which the Huzinaga method belongs, partially take account of electron correlation. This corresponds to the summation of a certain subset of terms in the series of the random-phase approximation method. A shortcoming of the Huzinaga method is that it does not take account of the relaxation of the core following the excitation of electrons.

The $(N - 1)$-electron potential method has been used many times for calculating the excited states of molecules and has exhibited a good agreement with experiment. For example, Goddard and Hunt (1974) have calculated 32 excited states of H_2O molecule and have compared the calculated excitation energies with eight experimental values obtained from the electron and photon spectroscopy measurements. They have noted that the average discrepancy between the calculated and experimental values is about 1 eV. The introduction of a scale factor reduces this discrepancy to about 0.1 eV.

3. *Formula for the Probability of Electron Excitation in the MO LCAO Approximation*

Let us consider the parent molecule RT to be in the ground electron state with a closed electron shell, i.e., with the total electron spin $S = 0$.

$$\Psi^i_0(\mathrm{RT}) = (N!)^{-1/2} \det[\varphi_1 \cdot \alpha, \varphi_1 \cdot \beta, \ldots, \varphi_i \cdot \alpha, \varphi_i \cdot \beta, \ldots, \varphi_{N/2} \cdot \alpha, \varphi_{N/2} \cdot \beta] \tag{36}$$

where the φ_i are the RT moleculer orbitals occupied in the ground state. From Eq. (27) for the probability of electron transition it follows that the electron excitations do not lead to a change in the total spin of the molecule, and, consequently, the wave functions of excited states of the daughter molecule $(\mathrm{RHe})^+$ should be taken as singlet. In this discussion we will not take into account the two- and multielectron excitations, since taking them into account in calculations which do not make allowance for the electron correlation gives results that are far from reality

$$\Psi^{\mathrm{f}}_{\mathrm{n}}(\mathrm{RHe}^+) = (2)^{-1/2}\{\Psi^{i\to v}_{\alpha}(\mathrm{RHe}^+) + \Psi^{i\to v}_{\beta}(\mathrm{RHe}^+)\} \tag{37}$$

$$\psi^{i\to v}_{\beta}(\mathrm{RHe}^+) = (N!)^{-1/2} \det[\psi_1 \cdot \alpha, \psi_1 \cdot \beta, \ldots, \psi_i \cdot \alpha, \psi^{(i)}_v \cdot \beta, \ldots, \psi_{N/2} \cdot \alpha, \psi_{N/2} \cdot \beta] \tag{38}$$

$$\psi^{i\to v}_{\alpha}(\mathrm{RHe}^+) = (N!)^{-1/2} \det[\psi_1 \cdot \alpha, \psi_1 \cdot \beta, \ldots, \psi^{(i)}_v \cdot \alpha, \psi_i \cdot \beta, \ldots, \psi_{N/2} \cdot \alpha, \psi_{N/2} \cdot \beta] \tag{39}$$

Here the ψ_i are the RHe^+ molecular orbitals occupied in the ground state, and the $\psi^{(i)}_v$ are the MOs obtained by the Huzinaga–Arnau method in the case when the hole is in the *i*th electron shell and the electron has made a transition into the *v*th vacant orbital.

Substituting wave functions given by Eqs. (36) and (37) into Eq. (27) for the transition probability, and using the formulas of Kaplan and Rodimova (1973), we obtain

$$
\begin{aligned}
W_{0n} \equiv W_{0,\,i\to v} = {}& \Bigg| \frac{1}{\sqrt{2}\cdot N!} \int \{\det[\ldots, \psi_i\cdot\alpha, \psi_v^{(i)}\cdot\beta, \ldots] \\
&+ \det[\ldots, \psi_v^{(i)}\cdot\alpha, \psi_i\cdot\beta, \ldots]\} \\
&\times \det[\ldots, \varphi_i\cdot\alpha, \varphi_i\cdot\beta, \ldots]\, d\mathbf{r}_1, \ldots, d\mathbf{r}_N\cdot ds_1, \ldots, ds_N \Bigg|^2 \\
={}& \left| \frac{1}{\sqrt{2}} \left\{ \begin{vmatrix}
S_{1\alpha 1\alpha}S_{1\alpha 1\beta}S_{1\alpha 2\alpha}S_{1\alpha 2\beta}\cdots & S_{1\alpha(N/2)\beta} \\
S_{1\beta 1\alpha}S_{1\beta 1\beta}S_{1\beta 2\alpha}S_{1\beta 2\beta}\cdots & S_{1\beta(N/2)\beta} \\
\cdots\cdots\cdots\cdots\cdots\cdots & \cdots\cdots \\
S_{i\alpha 1\alpha}S_{i\alpha 1\beta}S_{i\alpha 2\alpha}S_{i\alpha 2\beta}\cdots & S_{i\alpha(N/2)\beta} \\
S^{(i)}_{v\beta 1\alpha}S^{(i)}_{v\beta 1\beta}S^{(i)}_{v\beta 2\alpha}S^{(i)}_{v\beta 2\beta}\cdots & S^{(i)}_{v\beta(N/2)\beta} \\
\cdots\cdots\cdots\cdots\cdots\cdots & \cdots\cdots \\
S_{(N/2)\beta 1\alpha}S_{(N/2)\beta 1\beta}S_{(N/2)\beta 2\alpha}S_{(N/2)\beta 2\beta}\cdots & S_{(N/2)\beta(N/2)\beta}
\end{vmatrix} \right.\right. \\
&\left.\left. + \begin{vmatrix}
S_{1\alpha 1\alpha}S_{1\alpha 1\beta}S_{1\alpha 2\alpha}S_{1\alpha 2\beta}\cdots & S_{1\alpha(N/2)\beta} \\
S_{1\beta 1\alpha}S_{1\beta 1\beta}S_{1\beta 2\alpha}S_{1\beta 2\beta}\cdots & S_{1\beta(N/2)\beta} \\
\cdots\cdots\cdots\cdots\cdots\cdots & \cdots\cdots \\
S^{(i)}_{v\alpha 1\alpha}S^{(i)}_{v\alpha 1\beta}S^{(i)}_{v\alpha 2\alpha}S^{(i)}_{v\alpha 2\beta}\cdots & S^{(i)}_{v\alpha(N/2)\beta} \\
S_{i\beta 1\alpha}S_{i\beta 1\beta}S_{i\beta 2\alpha}S_{i\beta 2\beta}\cdots & S_{i\beta(N/2)\beta} \\
\cdots\cdots\cdots\cdots\cdots\cdots & \cdots\cdots \\
S_{(N/2)\beta 1\alpha}S_{(N/2)\beta 1\beta}S_{(N/2)\beta 2\alpha}S_{(N/2)\beta 2\beta}\cdots & S_{(N/2)\beta(N/2)\beta}
\end{vmatrix} \right\} \right|^2
\end{aligned} \tag{40}
$$

Here ds_i stands for the integration over the spin of the *i*th electron

$$
\begin{aligned}
S_{\kappa\alpha l\beta} &= \int \psi_\kappa^*(\mathbf{r})\cdot\alpha(s)\cdot\varphi_l(\mathbf{r})\cdot\beta(s) = d\mathbf{r}\cdot ds = \delta_{\alpha\beta}\cdot S_{kl} \\
S^{(i)}_{v\alpha l\beta} &= \int \psi_v^{(i)*}(\mathbf{r})\cdot\alpha(s)\cdot\varphi_l(\mathbf{r})\cdot\beta(s)\cdot d\mathbf{r}\cdot ds = \delta_{\alpha\beta}\cdot S^{(i)}_{vl}
\end{aligned} \tag{41}
$$

Performing the integration over the spin variables in the last two determinants in Eq. (40) and permutating the columns and rows, we obtain the following expression

$$W_{0,\,i\to v} = 2(D_{i\to v}\cdot D)^2 \tag{42}$$

Here D is the determinant of the matrix, the elements of which are the overlap integrals of the MO of the parent and the daughter molecules occupied in the ground state:

$$S_{kl} = \langle \psi_k | \varphi_l \rangle \tag{43}$$

The difference between the determinants D and $D_{i \to v}$ is that in the latter the ith row of overlap integrals S_{il} $(1 \leq l \leq N/2)$ is replaced by the row $S_{vl}^{(i)} = \langle \psi_v^{(i)} | \varphi_l \rangle$ $(1 \leq l \leq N/2)$.

Similarly, for the probability of the daughter molecule remaining in the ground electron state we obtain

$$W_{00} = D^4 \tag{44}$$

Equations (42) and (44) were obtained under the assumption that the perturbation is sudden, i.e., that the perturbation time is much less than the characteristic electron times of the initial and the final molecules. However, the perturbation itself may not be small. If we do consider the perturbation to be small, then we can neglect the nondiagonal elements [Eq. (43)] in the matrix D and leave only the diagonal ones. In the case of an atom

$$W_{00} = \prod_{\substack{i=1 \\ \text{occ}}}^{N} \left| \int \psi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) \, d\mathbf{r} \right|^2 \tag{45}$$

gives the probability that all the electrons remain in slightly relaxed atom orbitals with the same quantum numbers as for the initial atom. The probability that at least one of the electrons undergoes a transition into an excited state is given by the formula

$$P = 1 - \prod_{\substack{i=1 \\ \text{occ}}}^{N} \left| \int \psi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) \, d\mathbf{r} \right|^2 \tag{46}$$

(see, e.g., Fano and Cooper, 1968). Similar formulas have often been used for calculating the excitation probabilities of atoms due to the shake-up induced by β decay, by photoionization of inner shells, etc. For example, Carlson and collaborators (1968), using an approximation similar to Eq. (46), have calculated the probability of the shake-up for atoms of elements with $Z = 2 \div 92$. For elements with small Z, Eq. (46) must be less accurate.

In the general case, it is incorrect to use the approximation [Eqs. (45) and (46)] for molecules. Since an atom is a symmetric system, the jump in the charge of the nucleus changes the atomic orbitals without changing the symmetry of the atom shell. Under such conditions the excitation may be small, especially for inner shells of heavy atoms, and, consequently, it is possible to restrict oneself only to the diagonal elements of the matrix D in Eq. (44). In molecules, besides changing the orbitals, the jump in the charge of one of the nuclei usually changes the symmetry of the orbitals as well. For example, in the β decay of tritium contained in a molecule

$$\mathrm{CH_3T} \xrightarrow{\beta} (\mathrm{CH_3He})^+$$

the symmetry T_d of the parent molecule is reduced to C_{3v} for the daughter molecule, and the triply degenerate level splits up into a doublet and a singlet with $\Delta E \approx 7$ eV. As a result, the overlap integrals of the MO of the daughter and parent molecules are not small: for all the decays we have considered, the matrix D contained a large number of nondiagonal elements comparable in magnitude with the diagonal ones, and could not be reduced to the diagonal form, Eq. (45). The molecules with a heavy radioactive atom at the center may be a possible exception.

4. *Probability of Electron Excitation with Allowance for the Electron Correlation*

In order to make allowance for the influence of electron correlation on the probability of the β-decay-induced excitation of a molecule, let us use the configuration interaction method. We will consider the configurations that take account only of the single and double electron excitations into the virtual excited orbitals. For the latter we will use the orbitals obtained by the Huzinaga–Arnau method (see above). The wave function of the ground state of the parent molecule is

$$\Psi_0(\mathrm{RT}) = A_0^0\Phi(K_0) + \sum_{i,v} A_{i,v}^0\Phi(K_i^v) + \sum_{ij,vw} A_{ij,vw}^0\Phi(K_{ij}^{vw}) \tag{47}$$

and for the daughter molecule is

$$\Psi_n(\mathrm{RHe}^+) = B_0^n\Psi(K_0) + \sum_{i',v'} B_{i',v'}^n\Psi(K_{i'}^{v'}) + \sum_{i'j',v'w'} B_{i'j',v'w'}^n\Psi(K_{i'j'}^{v'w'}) \tag{48}$$

Here $\Phi(K_0)$ and $\Psi(K_0)$ are the Slater determinants for the ground state configuration K_0 of the parent and the daughter molecules, respectively. K_i^v is the configuration of molecular orbitals which is obtained from K_0 by replacing the ith MO occupied in the ground state by the vth excited MO. The doubly excited configuration K_{ij}^{vw} is obtained in a similar way. Indices i, j, i', and j' take the values corresponding to the MO occupied in the ground state; indices v, w, v', and w' take the values corresponding to excited orbitals. The wave functions $\Phi(K_i^v)$, $\Phi(K_{ij}^{vw})$, $\Psi(K_{i'}^{v'})$, and $\Psi(K_{i'j'}^{v'w'})$ are linear combinations of Slater determinants corresponding to a definite spin state. For the singlet spin state, $S = 0$, $M_s = 0$, they are

$$\Phi(K_i^v) = \frac{1}{\sqrt{2}}(\det[\ldots,\varphi_i\cdot\alpha,\varphi_v\cdot\beta,\ldots] + \det[\ldots,\varphi_v\cdot\alpha,\varphi_i\cdot\beta,\ldots]) \tag{49}$$

$$\Phi(K_{ii}^{vv}) = \det[\ldots,\varphi_{i-1}\cdot\beta,\varphi_v\cdot\alpha,\varphi_v\cdot\beta,\varphi_{i+1}\cdot\alpha,\ldots] \tag{50}$$

$$\Phi(K_{ii}^{vw}) = \frac{1}{\sqrt{2}}(\det[\ldots, \varphi_{i-1}\cdot\beta, \varphi_v\cdot\alpha, \varphi_w\cdot\beta, \varphi_{i+1}\cdot\alpha, \ldots] + \det[\ldots, \varphi_{i-1}\cdot\beta, \varphi_w\cdot\alpha, \varphi_v\cdot\beta, \varphi_{i+1}\cdot\alpha, \ldots]) \tag{51}$$

$$\Phi(K_{ij}^{vv}) = \frac{1}{\sqrt{2}}(\det[\ldots, \varphi_i\cdot\alpha, \varphi_v\cdot\beta, \ldots, \varphi_v\cdot\alpha, \varphi_j\cdot\beta, \ldots] + \det[\ldots, \varphi_v\cdot\alpha, \varphi_i\cdot\beta, \ldots, \varphi_j\cdot\alpha, \varphi_v\cdot\beta, \ldots]) \tag{52}$$

$$\begin{aligned}\Phi(K_{ij}^{vw}) = \frac{1}{2}(&\det[\ldots, \varphi_i\cdot\alpha, \varphi_v\cdot\beta, \ldots, \varphi_j\cdot\alpha, \varphi_w\cdot\beta, \ldots]\\ &+ \det[\ldots, \varphi_v\cdot\alpha, \varphi_i\cdot\beta, \ldots, \varphi_j\cdot\alpha, \varphi_w\cdot\beta, \ldots]\\ &+ \det[\ldots, \varphi_i\cdot\alpha, \varphi_v\cdot\beta, \ldots, \varphi_w\cdot\alpha, \varphi_j\cdot\beta, \ldots]\\ &+ \det[\ldots, \varphi_v\cdot\alpha, \varphi_i\cdot\beta, \ldots, \varphi_w\cdot\alpha, \varphi_j\cdot\beta, \ldots])\end{aligned} \tag{53}$$

$$\begin{aligned}\Phi(K_{ij}^{wv}) = \frac{1}{2}(&\det[\ldots, \varphi_i\cdot\alpha, \varphi_w\cdot\beta, \ldots, \varphi_j\cdot\alpha, \varphi_v\cdot\beta, \ldots]\\ &+ \det[\ldots, \varphi_w\cdot\alpha, \varphi_i\cdot\beta, \ldots, \varphi_j\cdot\alpha, \varphi_v\cdot\beta, \ldots]\\ &+ \det[\ldots, \varphi_i\cdot\alpha, \varphi_w\cdot\beta, \ldots, \varphi_v\cdot\alpha, \varphi_j\cdot\beta, \ldots]\\ &+ \det[\ldots, \varphi_w\cdot\alpha, \varphi_i\cdot\beta, \ldots, \varphi_v\cdot\alpha, \varphi_j\cdot\beta, \ldots])\end{aligned} \tag{54}$$

The functions $\Psi(K_{i'}^{v'})$, $\Psi(K_{i'i'}^{v'v'})$, etc., for the daughter molecule are of similar form. Functions given by Eqs. (49)–(53) are mutually orthogonal. However, Eq. (53) is not orthogonal to Eq. (54), so instead of the latter, one uses the combination of functions given by Eqs. (53) and (54), which together are orthogonal to Eq. (53). The coefficients A and B in the expansions, Eqs. (47) and (48), are determined by solving the secular equation of the CI method

$$\sum_K A(K)[\langle\Psi(K')|\hat{H}|\Psi(K)\rangle - E\langle\Psi(K')|\Psi(K)\rangle] = 0 \tag{55}$$

The summation is performed over all the configurations K entering Eqs. (47) and (48). Substituting wave functions Eqs. (47) and (48) into the matrix element Eq. (27), we get

$$\begin{aligned}W_{\text{on}} = |\langle\Psi_n(\text{RHe}^+)|\Psi_0(\text{RT})\rangle|^2 = |&B_0^n A_0^0\langle\Psi(K_0)|\Phi(K_0)\rangle\\ &+ A_0^0\sum_{i',v'} B_{i'v'}^n\langle\Psi(K_{i'}^{v'})|\Phi(K_0)\rangle + B_0^n\sum_{i,v} A_{i,v}^0\langle\Psi(K_0)|\Phi(K_i^v)\rangle\\ &+ A_0^0\sum_{i'j',v'w'} B_{i'j',v'w'}^n\langle\Psi(K_{i'j'}^{v'w'})|\Phi(K_0)\rangle + B_0^n\sum_{ij,vw} A_{ij,vw}^0\langle\Psi(K_0)|\Phi(K_{ij}^{vw})\rangle\\ &+ \sum_{ii'vv'} B_{i',v'}^n\cdot A_{i,v}^0\langle\Psi(K_{i'}^{v'})|\Phi(K_i^v)\rangle + \sum_{ii'j',vv'w'} B_{i'j',v'w'}^n\cdot A_{i,v}^0\langle\Psi(K_{i'j'}^{v'w'})|\Phi(K_i^v)\rangle\end{aligned}$$

$$+ \sum_{ii'j,vv'w} B^{n}_{i'v'} \cdot A^{0}_{ij,vw} \langle \Psi(K^{v'}_{i'}) | \Phi(K^{vw}_{ij}) \rangle$$

$$+ \sum_{ii'jj',vv'ww'} B^{n}_{i'j',v'w'} \cdot A^{0}_{ij,vw} \langle \Psi(K^{v'w'}_{i'j'}) | \Phi(K^{vw}_{ij}) \rangle |^{2} \tag{56}$$

The matrix elements between functions $\Psi(K)$ and $\Phi(K)$ are once again expressed in terms of the overlap integrals of the MO of the parent and the daughter molecules. These matrix elements are easily calculated using the mathematics developed in the paper by Kaplan and Rodimova (1973). However, since a few dozen of such elements arise, we do not present the corresponding expressions here. Let us write down only one of them:

$$\langle \Psi(K^{v'}_{i'}) | \Phi(K^{v}_{i}) \rangle = D \cdot D^{i \to v}_{i' \to v'} + D_{i' \to v'} \cdot D^{i \to v} \tag{57}$$

Here D and $D_{i' \to v'}$ are the determinants introduced above [see Eq. (42) and the following explanation]. $D^{i \to v}$ is obtained from D by replacing the ith column $S_{li} = \langle \psi_l | \varphi_i \rangle (i \leq l \leq N/2)$ by the column of overlap integrals $S^{(i)}_{lv} = \langle \psi_l | \varphi^{(i)}_{v} \rangle (1 \leq l \leq N/2)$. $\varphi^{(i)}_{v}$ is the excited MO of the parent molecule into which the electron makes the virtual transition, leaving a hole in the ith occupied orbital. In the matrix of the determinant $D^{i \to v}_{i' \to v'}$ the ith column and the i'th row are replaced in the same way as in the matrices $D^{i \to v}$ and $D_{i' \to v'}$, respectively; besides this, the matrix element $S_{i'i}$ is replaced by the element $S^{(i'i)}_{v'v} = \langle \Psi^{(i')}_{v'} | \varphi^{(i)}_{v} \rangle$.

D. Conclusions

Let us briefly summarize the main results of this section.

1. At the β-electron energies greater than 1 keV, the first-order perturbation theory given by Eq. (8) may be used for calculating the β decay of a nucleus contained in a molecule. In this approximation we did not take account of the direct excitations of electrons of the molecular shell by the β electron passing through and the exchange of the β electron with the electrons of the shell. However, in the considered region of energies these processes are inessential.

2. The β-decay matrix element is factorized into an intranuclear matrix element and a molecular matrix element. The former describes the β transition in the radioactive nucleus, whereas the latter describes the excitation of molecular degrees of freedom induced by the β decay.

3. The vibrations and rotations of the daughter molecule may be excited owing both to the jump in the charge of the radioactive nucleus and to the recoil momentum of the latter. The electron excitations are due only to the jump in the charge.

4. In the Condon approximation the molecular matrix element is factorized into electron and vibrational-rotational matrix elements. In this case the

electron wave functions of both the parent and the daughter molecules are calculated for the equilibrium geometry of the parent molecule.

5. The excitation probabilities are expressed in terms of determinants of the overlap integrals of molecular orbitals of the parent and the daughter molecules. One must take into account all the elements of the determinant, since the nondiagonal matrix elements are comparable in magnitude with the diagonal ones.

III. Effect of β Decay on the Molecular Electron Shell

In this chapter we study the influence of the β decay of one of the molecular nuclei on the rearrangement and excitation of the electron shell. As an object of study we have chosen the organic molecules (hydrocarbons with different degrees of saturation of the C–C bond and molecules containing the amino group, including valine) and metal hydrides. The latter are of interest from the point of view of the influence the degree of ionicity of the chemical bond has on the electron shell restructuring.

Let us first consider the rearrangement of the electron shell in helium-substituted molecular ions with respect to the parent molecules. This information will allow us to understand the influence of the molecular structure on the probability of electron excitations in a molecule.

A. Electron Shell Rearrangement under β Decay

1. Redistribution of Electron Density

In order to perform a qualitative analysis of the β-decay-induced redistribution of electron density it is sufficient to calculate the molecular electron states in the MO LCAO approximation, i.e., not taking into account the correlation of electrons. Below we present the calculation data for a number of molecules, which we have obtained using the "Gaussian-70" program with the basis of s and p functions. We have used the extended atomic basis 4-31G, which contains about twice as many atomic functions as the minimal one (Ditchfield *et al.*, 1971).

The electron density distribution was calculated according to Mulliken (1955; see also Herzberg, 1966). In the MO LCAO approximation the ith molecular orbital is

$$\psi_i = \sum_{a,\rho} c^i_{a\rho}\phi_{a\rho} \tag{58}$$

where $\phi_{a\rho}$ is the basis atomic function, a is the number of the atom, and ρ is the type of the atomic orbital. According to the general principles of quantum mechanics, the electron density of the ith MO containing N_i electrons is

$$\rho_i = N_i\psi_i^2 = N_i\left[\sum_{a,\rho}(c^i_{a\rho})^2(\phi_{a\rho})^2 + 2\sum_{a\rho<a'\rho'} c^i_{a\rho}\cdot c^i_{a'\rho'}\phi_{a\rho}\phi_{a'\rho'}\right] \tag{59}$$

(the molecular orbitals are assumed to be real). Integrating over the whole space and considering the normalization of ψ_i and $\phi_{a\rho}$, we obtain

$$\int \rho_i(\mathbf{r})dV = N_i = N_i\left[\sum_{a\rho}(c^i_{a\rho})^2 + 2\sum_{a\rho<a'\rho'} c^i_{a\rho}\cdot c^i_{a'\rho'}s_{a\rho a'\rho'}\right] \qquad (60)$$

where $s_{a\rho',a'\rho'}$ are the overlap integrals of atomic orbitals.

Among the different types of populations which one can obtain using Eq. (60), we will need only two. The first one is the total joint population of the ath atom in the molecule

$$N_a = \sum_i\sum_\rho N_i[(c^i_{a\rho})^2 + c^i_{a\rho}c^i_{a'\rho'}s_{a\rho a'\rho'}] \qquad (61)$$

This population is also called the charge on the ath atom. Equation (61) is obtained from the general expression Eq. (60) by arbitrarily dividing the electron density of the interatomic bond equally between the two involved atoms. The second one is the partial atomic population

$$n^i_\rho(a) = N_i(c^i_{a\rho})^2 \qquad (62)$$

which corresponds to the contribution of the ρ-type orbital of the atom a to the electron density of the ith MO.

Figure 2a shows the data of our calculations for three molecules: methane (CH_3T), ethane (C_2H_5T), and ethylamine ($NH_2C_2H_4T$).

The produced heilum nucleus draws to itself additional electron density, which in the case of the C–H bond equals 0.91–0.96. This occurs mainly at the expense of the nearest surrounding atoms, though the changes in the electron density also involve the more remote atoms. For comparison, in Fig. 2b we present the redistributions of charges on the atoms of three organic molecules (CH_4, C_2H_6, and C_3H_8) induced by the transformation $^{14}C \rightarrow {}^{14}N^+$. They were calculated by Raadschelders-Buijze *et al.* (1973) using the wave functions of the INDO method. As one can see from Fig. 2b, the formed nitrogen. nucleus draws additionally about 1.1–1.3 of the electron charge. Similar to the redistribution of the charge in tritium-containing molecules, the main part of the charge is transferred to the nitrogen nucleus from the atoms immediately surrounding it; the peripheral atoms are involved in the redistribution of electron density to a smaller extent.

Despite the similarity of the electron density redistributions for tritium-containing and ^{14}C-containing molecules, the subsequent effects of the β decay are different. The β decay in a molecule is a multichannel process. All the channels permitted by the energy conservation law are open. Thus, since the energy released in β decay is much greater than the characteristic molecular energies, the channels leading to a given scheme of decay of the molecule into its parts (dissociation, transition into unbound states, etc.) are always available. The molecules containing a central radioactive atom prove to lead

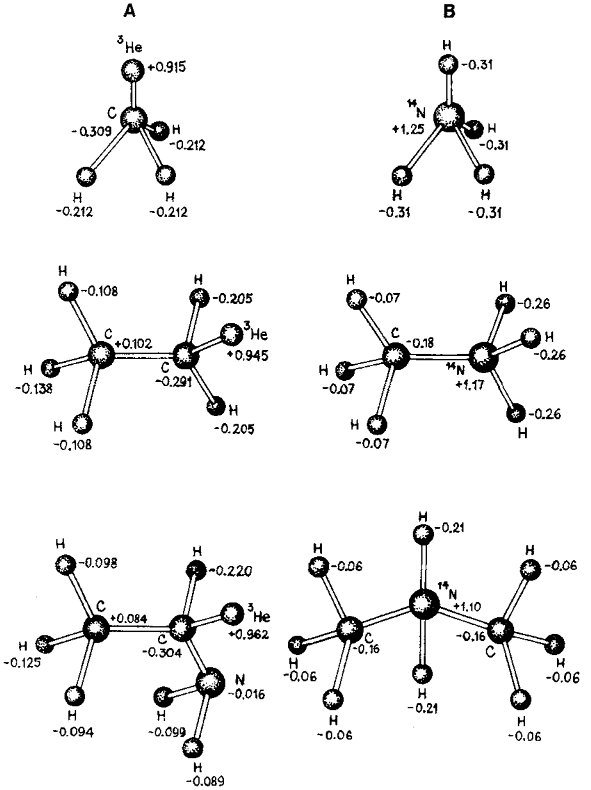


Fig. 2. The β-induced differential electronic densities on atoms for the ground state of the daughter molecular ions: (a) T → He^+ transformations; (b) $^{14}C \rightarrow {}^{14}N^+$. [From Raadschelders-Buijze *et al.* (1973).]

to more stable daughter complexes than the parent molecules themselves (see, e.g., Nefedov *et al.*, 1981). For example, the decoupling energy of a hydrogen atom for the NH_4^+ ion is greater than that for CH_4 by about 1 eV.

On the contrary, in tritium-containing molecules the helium nucleus produced in β decay gathers about 1.8 of the electron charge, i.e., an almost closed shell is formed. This means that for the helium atom, the ground electron state of the daughter molecule is unbound, and as a result the neutral helium atom decouples from the daughter molecule. The only exception is $(HHe)^+$, for which a number of states are bound (Michels, 1966). The decoupling of the helium atom was studied by Ikuta *et al.* (1977) in the case of β decay in methane (CH_3T), water (OHT), and ammonia (NH_2T). Ikuta *et al* calculated the potential energy surfaces and have shown that in the ground electron state of the daughter molecule $(CH_3He)^+$, the surface has no minimum corresponding to the binding of the helium atom with the rest of the molecule. Though the potential surfaces of the daughter molecules $(OHHe)^+$ and $(NH_2He)^+$ have shallow minima along the bonds O—He and N—He, the latter are easily broken, since the repulsive energy of the nuclei for their nonequilibrium configuration, which is formed immediately after the decay and corresponds to the equilibrium configuration of the parent nuclei, exceeds the small binding energies. As was shown by Ikuta *et al.*, in all three cases the decoupled helium atom is neutral.

2. *Nature of Changes in Molecular Orbitals under the Transformation $T \rightarrow He^+$*

The study of the rearrangement of molecular orbitals under the transformation $T \rightarrow He^+$ allows one to understand qualitatively the relation between the excitation spectrum of the daughter ion and the features of its chemical structure. If the MOs of the daughter and the parent molecules coincided, the probability [Eq. (44)] of transition into the ground state would be unity, and the excitation probability would be zero. In the sudden-perturbation approximation, it is to the difference in the orbitals of the initial and the final molecules that the excitation of the latter is due.

Let us analyze the daughter molecule MO for molecules CH_3T and $NH_2C_2H_4T$. In Table II we present the data concerning the MOs occupied in the ground state of the parent RT and the daughter $(RHe)^+$ molecules. Here, $\sum_\rho n_\rho^i(\mathrm{He})$ is the partial population of the ith MO coming from the helium atom; $\sum_a n_\rho^i(a)$ is the sum of contributions of the ρ-type atomic orbitals to the ith MO which goes over the group of atoms having the ρth orbital. Each ground-state MO contains the electron density equal to 2. The numerical data presented in the fourth and fifth columns show what fraction of this density is due to the considered atoms. In the last column of the table we present the arbitrary names of molecular MO groups: "K shell" is the group of MOs constructed mainly of atomic K shells; correspondingly, "L shell" denotes the MOs consisting mainly of the 2*s* states of heavy atoms of molecules.

Analyzing the results presented in Table II, one can see that the replacement of the tritium atom by a helium ion, resulting from the β decay, lowers the energies of all MOs, but by different amounts for different MO groups. In relatively heavy molecules (e.g., in $NH_2C_2H_4T$) such a replacement lowers the energy of the valent MO by 7–9 eV. For the "L shell" and "K shell" MOs the energy is lowered, respectively, by 11–14 and by 7–12.5 eV. In lighter molecules, such as CH_4, the lowering of energy is more pronounced: 10 eV for the valent, 17–19 eV for the "L shell", and 11 eV for the "K shell" orbitals. Thus, the MOs most sensitive to the replacement $T \rightarrow He^+$ are the MOs of the "L shell". This should be expected since it is this group of MOs that has the energy closest to the binding energy of an electron in the He^+ ion

TABLE II

ENERGY, POPULATION, AND EXCITATION PROBABILITIES[a]

RT		(RHe)$^+$				
i_{MO}	E_{MO} (eV)	E_{MO} (eV)	$\sum_{\rho} n_{\rho}^{i}(\text{He})$	$\sum_{a} n_{\rho}^{i}(a)$	W_i (%)[b]	Arbitrary name of MO group
				CH_3T (methane)		
1	14.7	24.7	$8.0\ 10^{-15}$	—	1.1	Valence shells
2	14.7	24.7	$9.3\ 10^{-7}$	—	1.2	
3	14.7	31.7	0.394	$0.78_{2s_c} + \cdots$	8.6	"L shells"
4	25.6	44.6	1.380	$0.15_{2s_c} + \cdots$	21.4	
5	304.4	316.1	$8.0\ 10^{-7}$	$1.98_{1s_c} + \cdots$	0	"K shell"
				$NH_2C_2H_4T$ (ethylamine)		
1	8.4	16.0	$9.3\ 10^{-3}$	—	0.5	Valence shells
2	12.4	20.4	$5.2\ 10^{-4}$	—	0.4	
3	12.8	21.2	0.022	—	0.9	
4	14.0	22.3	0.015	—	0.7	
5	14.5	22.8	0.022	—	1.3	
6	15.5	24.2	0.034	—	1.5	
7	17.2	28.1	0.105	$0.44_{2s_{c1}} + 0.04_{2s_N} + 0.14_{2s_{c2}} + \cdots$	2.9	"L shells"
8	21.6	33.1	0.095	$0.12_{2s_{c1}} + 0.17_{2s_N} + 0.58_{2s_{c2}} + \cdots$	2.2	
9	25.9	37.6	0.227	$0.08_{2s_{c1}} + 0.85_{2s_N} + 0.02_{2s_{c2}} + \cdots$	4.6	
10	30.6	44.3	1.11	$0.18_{2s_{c1}} + 0.03_{2s_N} + 0.00007_{2s_{c2}} + \cdots$	17.7	
11	300.4	307.9	$1.2\ 10^{-7}$	$1.97_{1s_{c2}} + \cdots$	0	"K shells"
12	301.4	313.7	$7.3\ 10^{-5}$	$1.97_{1s_{c1}} + \cdots$	0	
13	416.2	424.4	$2.8\ 10^{-7}$	$1.97_{1s_N} + \cdots$	0	

[a] Data for molecular orbitals of molecules CH_3T and $NH_2C_2H_4T$ for transformation T → He^+.

[b] Probability of electron transition from ith MO to all the unoccupied MOs. Note: helium is bound to carbon atom C_1.

(54.4 eV). The analysis of populations $\sum_\rho n_\rho^i(\mathrm{He})$ presented in the table shows that the maximum contribution to the "L shell" MO is given by the helium ion, and that the "L shell" MO with the lowest energy consists, by more than half, of the electron density given by the helium ion. The contribution of the helium ion to the electron density of the valent MOs, especially to MOs of the "K shell", is small.

In the sixth column of the table we present the summary values of the probability of an electron being excited from the *i*th MO into all the MOs vacant in the ground state (see the next section). According to calculations, as a result of β decay, the most probable states of the daughter molecule are those which correspond to the excitation of an electron from the most distorted (with respect to the parent molecule) MO (from the "L shell") into the first vacant ones. The maximum probability corresponds to the state into which the electron is excited from the most distorted MO of the "L shell" (with the lowest energy). It is easy to understand this qualitatively: if the transformation $T \rightarrow He^+$, which induces the transition from the ground state of RT into the ground state of $(RHe)^+$, did not distort the electron shell, the projection of $\Psi_0(RT)$ onto $\Psi_0(RHe^+)$ would be unity, since, as was noted in the beginning of this section, it is the distortions of the electron shell of (RHe^+) with respect to the electron shell of RT that lead to a decrease of the probability of transition into the ground state, and, consequently, to an increase of the excitation probability.

B. Results of Calculation of the Excitation Probabilities for Different Types of Molecules

1. *Calculations in the MOO LCAO Approximation*

In this section we present the results of calculations, performed according to Eqs. (42) and (44), of the probabilities of excitation of electron states in a number of molecules, using the method described in Section II,C,2. As occupied MOs we have used the MOs obtained according to the Gaussian-70 procedure; the vacant orbitals were found using a specially designed program on the basis of the Huzinaga–Arnau (1971) method. The wave functions of the RHe^+ complex are given by Eqs. (37)–(39).

In order to study the effect of the basis length on the accuracy of calculations, the latter were done for the minimal basis of *s* and *p* Slater functions and for the extended basis 4-31G (Ditchfield *et al.,* 1971). The increase of the basis length also permits one to study a greater number of excited states and to determine the shape of the excitation spectrum with more confidence. Since the basis 4-31G for the small metal hydride molecules contains a relatively small number of functions, for these molecules we have taken a wider basis containing 18 *s* and *p* functions.

In Table III we present the calculated probabilities W_{00} of formation of

TABLE III

PROBABILITY OF FORMATION OF DAUGHTER MOLECULES IN GROUND AND IN EXCITED ELECTRONIC STATES

		Minimal basis			Double basis		
No.	Parent molecule	W_{00}	$\sum_{n\neq 0}^{K} W_{0n}$ [a]	K [b]	W_{00}	$\sum_{n\neq 0}^{K} W_{0n}$ [a]	K [b]
1	Atom T	—	—		0.7023	0.2715	5
2	AlT	—	—	—	0.4965[c]	—	—
3	NaT	—	—	—	0.4010[c]	—	—
4	BT	—	—	—	0.5440[c]	—	—
5	LiT	0.4659	0.4214	8	0.4336[c]	0.4390	32
6	LiOT	0.6099	0.3017	30	0.6152	0.3172	66
7	CH_3T	0.6650	0.2736	20	0.6160	0.3230	55
8	C_2H_3T	0.6650	—	—	0.6006	0.3296	136
9	C_2H_5T	0.6510	—	—	0.6105	0.3170	180
10	CH_3-CHT-CH_3	0.6492	0.2798	130	0.6030	0.3292	377
11	NH_2-CH_2T	0.6543	0.2568	54	0.6095	0.3268	162
12	NH_2-C_2H_4T	0.6495	0.2833	117	0.6079	0.3270	351

[a] Only discrete excitations.

[b] Here K is the number of excitations taken into account.

[c] The basis is longer than the double one (see text).

helium-containing ions in the ground electron state and the summary probabilities $\sum_{n\neq 0} W_{0n}$ that these ions would be excited into discrete states. Also shown in the table are the numbers of excited states taken into account in the calculation. From the presented data it follows that the increase of the basis by two times—and for metal hydrides by more than twice—changes the probabilities only slightly. For all the molecules except LiOT, the increase of the basis lowers the probability W_{00} of remaining in the ground state by 3–5% and increases the excitation probability by approximately the same amount. The effect of the basis length on the results for LiOT is even smaller.

The data show that the molecular surroundings of the tritium atom lower the probability of remaining in the ground state, with respect to the case of an isolated tritium atom, by 8–10% for organic molecules and LiOT and by 16–30% for hydrides of light metals. At the same time the summary probability of being excited into discrete states increases for organic molecules and LiOT by 2.3–3.6% and for LiT by 14.5%. For the rest of the metal hydrides the increase is apparently somewhat greater than it is for organic molecules.

The value $W_{00} = 0.6103$ for CH_3T given by Ikuta *et al.* (1977) is in good agreement with our value, 0.6160. For the other two molecules studied by Ikuta *et al.* (OHT and NH_2T) the values of W_{00} are 0.6235 and 0.6120, respectively. The value for OHT correlates with our value $W_{00} = 0.6152$ for LiOT, in which the radioactive tritium is also bound directly to the oxygen atom.

Let us also note that for organic molecules and for LiOT the probability for excitation into all discrete states is about half the probability of remaining in the ground state. For hydrides of metals belonging to the first group of the periodic table (i.e., for LiT and NaT), the probability of remaining in the ground state and the probability of being excited into all bound states are approximately the same. The distribution of probabilities for hydrides of metals of the third group (BT and AlT) is apparently intermediate between the distributions for organic molecules and for LiT.

Due to the difficulty of calculating the wave functions of an unbound electron in the field of a molecular frame, we did not calculate the probabilities of the daughter ion $(RHe)^+$ being excited into the continuous spectrum. However, the fact that we have taken into account a large number of excitations (see Table III), as well as the fact that the nonzero contribution to the sum of probabilities of discrete excitations is given only by a small number of transitions into the first vacant MO, allows us to suppose that our account of the probability of discrete excitations is sufficiently complete. Consequently, the remaining part of the probability, $1 - W_{00} - \sum_{n \neq 0} W_{0n}$, may be considered as the probability of excitation into the continuous spectrum. For organic molecules and LiOT this probability amounts to 6–8%. For LiT the probability of transition into the continuous spectrum is somewhat greater (~12%).

In the organic molecules we have considered, radioactive tritium atom is directly bound to the carbon atom. The proximity of the obtained values of probabilities for the organic molecules shows that the nature of excitation does not depend on the group of atoms (CH_2 or CH_3) to which the tritium atom belongs, or on the degree of saturation of molecular bonds, or on the size of the molecule. This allows us to conclude that the character of molecular excitations induced by the β decay of tritium is affected mainly by the atom to which tritium is directly bound.

The same conclusion is drawn by Raadschelders-Buijze *et al.* (1973). They have carried out calculations for 13 hydrocarbons of different structure containing ^{14}C. The probability of remaining in the ground electron state after the transition $^{14}C \xrightarrow{\beta} {}^{14}N^+$ is presented in Table IV, which we have taken from the cited paper. The authors have analyzed the connection between the probability values and the structure of MOs and have noted that the electrons of inner shells give a small contribution to the probability. The main contribution comes from the rearrangement of the valent electrons, the contribution of the valent molecular orbitals being proportional to the degree of its mixing with the orbitals of the daughter atom formed after the decay.

TABLE IV

CALCULATED TRANSITION PROBABILITIES W_{00} FOR THE TRANSFORMATION $^{14}C \rightarrow {}^{14}N$ IN SINGLY REPLACED ORGANIC MOLECULES[a]

Parent molecule	W_{00}
^{14}C	0.6610
$^{14}CH_4$	0.6553
C_2H_6	0.6319
C_2H_4	0.6421
C_2H_2	0.6614
$^{14}C_2$	0.6286
C_3H_8[b]	0.6099
C_3H_8[c]	0.6299
C_3H_6	0.6270
C_6H_6	0.6105
C_6H_{12}	0.6023
$C_{10}H_8$	0.5919
$C_{10}H_{12}$[d]	0.5805
$C_{10}H_{12}$[d]	0.5704
CO_2	0.6715

[a] From Raadschelders-Buijze *et al.*, 1973.

[b] The radioactive atom is in the CH_3 group.

[c] The radioactive atom is in the CH_2 group.

[d] The radioactive atom is positioned differently in the benzene ring.

As was discussed above (see Table II and the corresponding comments), the excitation probability is indeed proportional to the amount of the electron density given to the MO of the daughter complex $(RHe)^+$ by helium orbitals. In the case of tritium-containing molecules, the orbitals of He are added mainly to the lowest valent shell of the molecule, which we have arbitrarily named the "L shell".

In view of the fact that the probability of the molecular electron shell restructuring is due solely to the atom nearest to the radioactive one, in Fig. 3 we show the dependence of the probability W_{00} (of remaining in the ground state) on the ionization potential I_i for the shell of the atom nearest to He which is most distorted by the transition $T \rightarrow He^+$. As follows from Fig. 3, for metal hydrides there is a linear dependence on the potential I_i. For nonmetals (C, O, or F) the probability is independent of I_i. Apparently, the obtained dependence on I_i is an illustration of the degree of ionicity of the chemical bond. As a whole, the problem of the influence of properties of an immediate neighbor of the radioactive atom on the β-decay-induced excitations of the molecule requires further study.

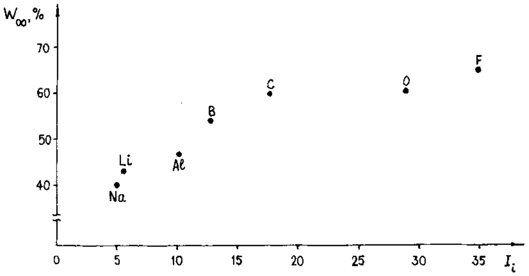


Fig. 3. The daughter ion probability W_{00} for different tritium neighbor atoms via atomic ionization potential I_i.

The distributions of discrete excitations of daughter molecules versus the excitation energy, $W_{0n} = W_{0n}(\Delta E^*_{0n})$, are presented in Fig. 4. The excitation energy was calculated according to the well-known formula of Roothaan (1951) for the energy difference of two singlet states

$$\Delta E^*_{0n} \equiv E_n(K^v_i) - E_0(K_0) = \varepsilon_i - \varepsilon_v - J_{iv} + 2K_{iv} \tag{63}$$

If we assume the Fock operator to have the modified Huzinaga–Arnau form [Eq. (32)], we obtain

$$\Delta E^*_{0n} = \varepsilon_i - \varepsilon^{\mathrm{HA}}_v \tag{64}$$

i.e., the excitation energy is equal to the difference between the energy ε_i of the orbital from which the electron is excited and the energy $\varepsilon^{\mathrm{HA}}_v$ of the orbital into which the electron makes the transition. The excitation spectra are presented as probability distributions in the energy intervals with a step of 5 eV. The probabilities of different transitions within a given interval were simply added. The loss of detailed information allows one to distinguish the general features of excitation spectra of different molecules. The excitation distributions were calculated using the 4-31G basis of atomic functions. For comparison, the distributions calculated for the minimal basis of Slater orbitals are plotted by dashed lines. As follows from Fig. 4, the increase of the basis by approximately two times leads to an insignificant redistribution of the probabilities in the excitation spectrum. Within the MO LCAO approximaton we have disregarded the double-electron excitations. Taking account of the latter with no allowance for electron correlation seems to be unreliable. In the following section we will take into account the double-electron excitations in the framework of the CI method.

The excitation spectra of all organic molecules are similar. They consist of a main maximum which absorbs about half the probability of all excitations (14–20%) and has the energy, about 35–40 eV. This excitation maximum

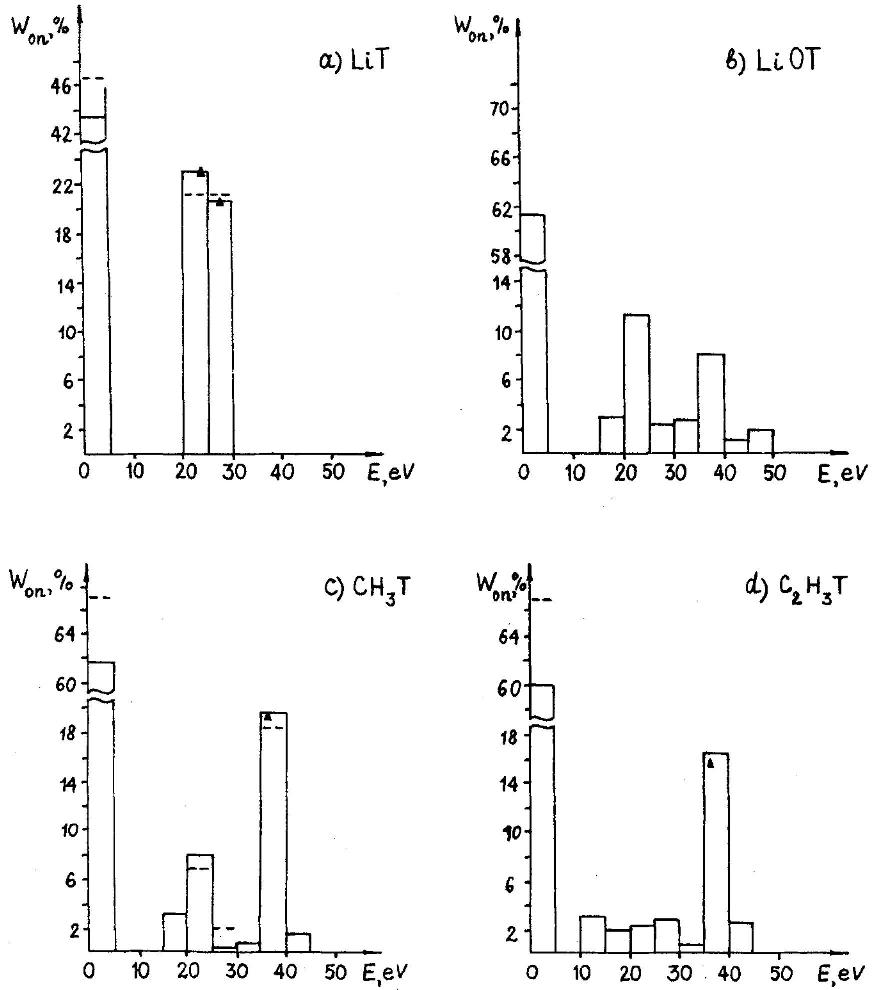


Fig. 4. Distributions of integral probabilities of electron excitations to the energy ranges of $[5n, 5(n + 1)]$ eV in β decay of (a) LiT, (b) LiOT, (c) CH_3T, (d) C_2H_3T, (e) C_2H_5T, (f) C_3H_7T, (g) NH_2–C_2HT, and (h) NH_2–C_2H_4T in the SCF approximation.

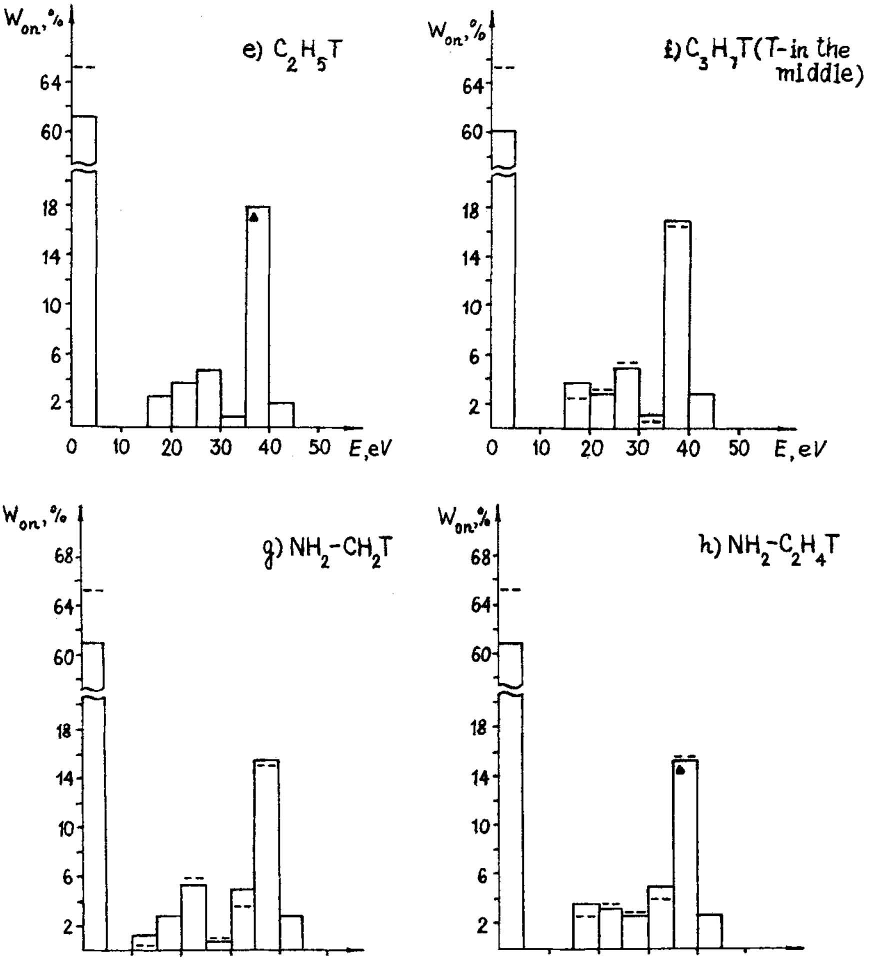


Fig. 4. (*continued*)

corresponds to the transition of electrons from the lowest energy "L shell" MO (see Table II) formed mainly by the helium atom orbitals and the 2*s* orbitals of the carbon atom, to which the helium atom is directly bound. This transition is made into the first vacant molecular orbital. If the transition to the latter is forbidden by selection rules, as is the case for metal hydride molecules, the principal transition is made into the nearest vacant MO not forbidden by selection rules. The remaining excitations represent about 10–15% of the probability. These excitations mainly correspond to transitions from the MOs belonging to the "L shells." The valent molecular electrons are weakly excited. In this connection, let us note that the representation that in the shake-up produced by the β decay it is easiest to excite the least bound valent electrons does not correspond to reality.

The excitation spectrum of $(LiOHe)^+$ is similar to those of organic molecules. The main maximum is shifted toward the smaller energies. The excitation spectrum of $(LiHe)^+$ is poorer than the spectra of other molecules. This is due to the fact that, in LiT, there are only two MOs occupied in the ground state. All the excitations of this molecule correspond to transitions of electrons from external occupied MOs into the vacant ones.

In the LiT molecule, as well as in other tritium-containing molecules, the K-shell electrons are not excited by the β decay.

Ikuta *et al.* (1977) have presented a table of excitations induced by the β decay in molecules $(OHHe)^+$, $(NH_2He)^+$, and $(CH_3He)^+$. There is a good qualitative agreement with our results. A majority of the transitions occur from the groups of MOs that we have named the "L shells". For $(OHHe)^+$ this amounts to 20.4% of the probability; for $(NH_2He)^+$ and $(CH_3He)^+$ we have, respectively, 20.4 and 23.3%. The probabilities of valent excitations for all three molecules are small.

2. *Allowance for the Influence of Electron Correlation on Excitation Probabilities*

In the previous section we calculated the rearrangement of a molecular electron shell induced by β decay using the Hartree–Fock approximation, i.e., making no allowance for the electron correlation. In the present section we estimate the influence of electron correlation on the shape of the excitation spectrum. The account of the correlation by the CI method allows one to make correct allowance for the double excitations, the calculation of which, within the one-determinant approximation, seems unreliable. The CI method allows one to take into account all possible two-electron processes, such as those similar to the appearance of satellites in the X-ray photoelectron spectra.

Estimations of the influence of electron correlation on the β-decay-induced molecular excitations were done by a number of authors in the case of the simplest β-decay system, $HT \rightarrow HHe^+$.

Using the James–Coolidge functions, Schwartz (1955) has calculated the probability of the daughter ion HHe^+ being produced in the ground electron state and has obtained the value $W_{00} = 0.93$. For the parent molecule HT he has used the 10-term function calculated by James and Coolidge (1933) and a similar function obtained by Toh (1940) for the daughter molecule HHe^+. Cantwell (1956) has calculated the probability W_{00} for HHe^+ using a James–

Coolidge function of smaller size. With monomial functions, containing only the exponential factor, for both HT and HHe^+ Cantwell obtained the value $W_{00} = 0.73$, whereas for binomial functions he has obtained $W_{00} = 0.58$. Such a high sensitivity of the probability W_{00} to the types of wave functions of daughter and parent molecules impelled Wolniewicz (1965) to perform a precision calculation of the probabilities of formation of ion HHe^+ in the ground (W_{00}) and in first excited (W_{01}) states. He used a 54-term James–Coolidge wave function for the HT molecule and a 64-term one for the ion HHe^+. The results ($W_{00} = 0.572$ and $W_{01} = 0.178$) proved to be unexpectedly close to those obtained by Cantwell with a rather rough function.

Up to now such a large spread of W_{00} values compels a number of authors (see, e.g., Chengrui *et al.*, 1981) to suppose that an adequate calculation of the β decay in molecules larger than HT is not possible at all, since the wave functions used for large molecules are less accurate than the James–Coolidge functions.

However, as was shown by Michels (1966), the calculations of Toh (1940) contain a numerical error, so the result of Schwartz, $W_{00} = 0.93$, which was based on these calculations, should not be taken into account. The rest of the results show that improvement of the James–Coolidge functions does not change the value of W_{00} so drastically: the calculations with binomial and polynomial James–Coolidge functions give very close reults—0.572 and 0.58, respectively.

When considering the influence of electron correlation one should bear in mind that though the increase of the number of terms in the James–Coolidge wave function undoubtedly improves the allowance for electron correlation, within this approach there is no starting point, since the state corresponding to the absence of electron correlation is not determined. However, according to the adopted definition of Löwdin (1959), by electron correlation one means not the whole correlation but the part of it which is not taken into account by the Hartree–Fock method. Within the latter method the electron correlation is partially taken into account for electrons with parallel spin orientations. Thus, in order to distinguish the electron correlation effects, one must first perform calculations in the Hartree–Fock approximation (as was done in the previous section) and then, using the Hartree–Fock MOs, make allowance for electron correlation either by the variational CI method or using the perturbation theory.

We have performed such calculations in collaboration with G. V. Smelov (Kaplan *et al.*, 1984) for molecules of different types. However, before we present the results, let us discuss the allowance for the influence of electron correlation on the probability of the ion HHe^+ being formed in the ground electron state (Kaplan *et al.*, 1983).

In the work cited above, the probability W_{00} was calculated with wave functions, each of which was a superposition of a certain number of configurations that may be performed as a result of an electron transition from the occupied shell of the ground state into the vacant orbitals. The employed basis was H: 1*s*, 1*s*′; He: 1*s*, 1*s*′, 1*s*″ made up of the Gaussian functions [2*s*] (for H) and [3*s*] (for He) contracted according to Dunning (1970) with scale factors 1 (for H) and 2 (for He). The results are presented in Table V. The maximum error due to the neglect of electron correlation proved to be less than 3.5%. The deviation from the most precise calculation of Wolniewicz (1965) amounts only to 1.4%. The performed calculations confirm the results of Ikuta *et al.* (1977) concerning the small contribution of electron correlation to the probability of the ion HHe^+ being formed in the ground electron state and, consequently, owing to normalization, to the summary excitation probability.

Let us stress, however, that the influence of electron correlation may be manifest in noticeable changes of the excitation spectrum, which are due to the redistribution of excitations between separate transitions. A study of the influence of electron correlation on the shape of the spectrum of molecular excitations induced by the β decay of tritium was performed by Kaplan *et al.* (1984). All the calculations were done using the configuration interaction method. The wave functions of the CI method were chosen as linear combinations of the Slater determinants corresponding to singlet-spin states. The configurations taken into account were those which are obtained in one- and two-electron excitations from the occupied ground-state orbitals into the virtual molecular orbitals that were calculated by the Huzinaga–Arnau (1971) method.

TABLE V

INFLUENCE OF THE ELECTRON CORRELATION ON THE PROBABILITY THAT THE ION $(HHe)^+$ WILL REMAIN IN THE ELECTRON GROUND STATE

	Number of configurations taken into account	
W_{00}	HT	HHe^+
0.6183	1	1
0.6115	3	3
0.6141	3	6
0.6030	3	10
0.5896	6	10
0.5875	10	10
0.5860	10	10

In calculations of excitation probabilities by the Hartree–Fock method, the determinant wave functions of excited states, which correspond to the transition of an electron from the ith occupied MO of the daughter molecule into the virtual one, contained the Huzinaga virtual MO obtained separately for each position of the hole ($1 \leq i \leq N/2$, where N is the number of electrons; see Section II,C,3). For constructing the determinants of excited configurations we have used the spectrum of the virtual Huzinaga MO, which was calculated for each molecule only once, placing the vacancy i in the occupied MO from which the electron is excited under β decay with the greatest probability. As was shown in the previous section, this orbital is the lowest energy MO of the "L shell" (see Table II). If the set of MOs contains a large number of Huzinaga orbitals, and the CI expansion [Eqs. (47) and (48)] is sufficiently wide, the error within such an approach is insignificant, vanishing in the limit of an infinite CI expansion. On the other hand, this approach has allowed us to avoid the cumbersome expressions for the matrix elements of the secular matrix, which are due to the fact that the Huzinaga MOs calculated for different positions of the vacancy are not mutually orthogonal. Furthermore, there is no need to construct the Huzinaga procedure when instead of one vacancy there are two.

The selection of the most essential configurations is a very important problem. Since it is necessary to take into account the configurations for which the transitions are the most probable, the selection criterion was the value of the overlap integral for the ground-state wave function of the parent molecule RT and the wave function of the excited configuration of the daughter molecule RHe^+. On the other hand, the CI functions, which are superpositions of the functions of excited configurations, must give the right value of the excitation energy for the molecule $(RHe)^+$. Because of this, to those configurations which give a large value of the overlap intergral, we have added some others, depending on their contribution to the energy of the excited state in the second order of the perturbation theory (Whitten and Hackmeyer, 1969).

Let us first dwell on the results of calculations for the reaction $HT \xrightarrow{\beta} HHe^+$. For calculating the ground state of HT we have used a wave function constructed out of 21 configurations; the wave functions for calculating the ground and excited states of the daughter ion $(HHe)^+$ consisted of 35 configurations. The basis of atomic functions for HT contained three s and six p functions of the Slater type for each hydrogen atom. The exponent indices of these functions have been obtained by variation of the ground-state energy of H_2 in the CI calculations performed by McLean *et al.* (1960). The atomic basis for HHe^+ was the one used by Peyerimoff (1965) obtained in calculations of the ground state by the MO LCAO method by variation of the Slater orbital indices. In order to describe the excited states of (HHe^+)

with sufficient accuracy, we have supplemented the Peyerimoff basis by two 1*s* and two 2*s* Slater functions. In the preliminary CI calculation we have varied the exponent indices of these functions in such a way that the energy of the first excited state of $(HHe)^+$ would be as close as possible to the sufficiently accurate value obtained by Wolniewicz (1965).

The energy of the first excited transition turned out to be $\Delta E_1 = 27.27$ eV [according to Wolniewicz (1965), $\Delta E_1 = 27.43$ eV]. The results of the calculations are presented in the second line of Table VI; the distribution of electron excitations is presented in Fig. 5. We have calculated the transitions into 35 excited states of the daughter ion; only 7 of them have a probability greater than 0.5%. The main transitions are made into the two lowest vacant orbitals. Accounting for electron correlation has reduced the probability of the ion $(HHe)^+$ remaining in the ground electron state by 0.039. The probability of transition into the first excited state is $W_{01} = 0.159$ [according to Wolniewicz (1965), $W_{01} = 0.178$]. The principal two-electron excitations are located in the region of 60–70 eV and have the total probability 0.12.

The wave function for the molecules LiT and $(LiHe)^+$ contained 45 configurations each, while each wave function for NaT, $(NaHe)^+$, CH_3T, and $(CH_3He)^+$ consisted of the 50 most important configurations. The results of the calculations are presented in Table VI and in Fig. 5. For comparison, the data for the T atom are also presented.

As follows from Table VI, the allowance for electron correlation leads to a small decrease in the probability W_{00} of the complex $(RHe)^+$ being formed in the ground electron state for molecules with covalent-type chemical bonds—e.g., by only 0.01 for CH_3T. However, for molecules with ionic-type chemical bonds these changes are more significant—0.05 for LiT and 0.07 for

TABLE VI

PROBABILITIES OF FORMATION OF DAUGHTER MOLECULES IN GROUND AND IN EXCITED ELECTRONIC STATES WITH ALLOWANCE FOR ELECTRON CORRELATION

Molecule	W_{00}	$\sum_{n\neq 0} W_{0n}$ [a]
T	0.7023	0.2715
HT	0.5769	0.4172
LiT	0.3832	0.5319
NaT	0.3308	0.5741
CH_3T	0.6056	0.3547
Valine	0.6122	0.2815

[a] Only discrete excitations.

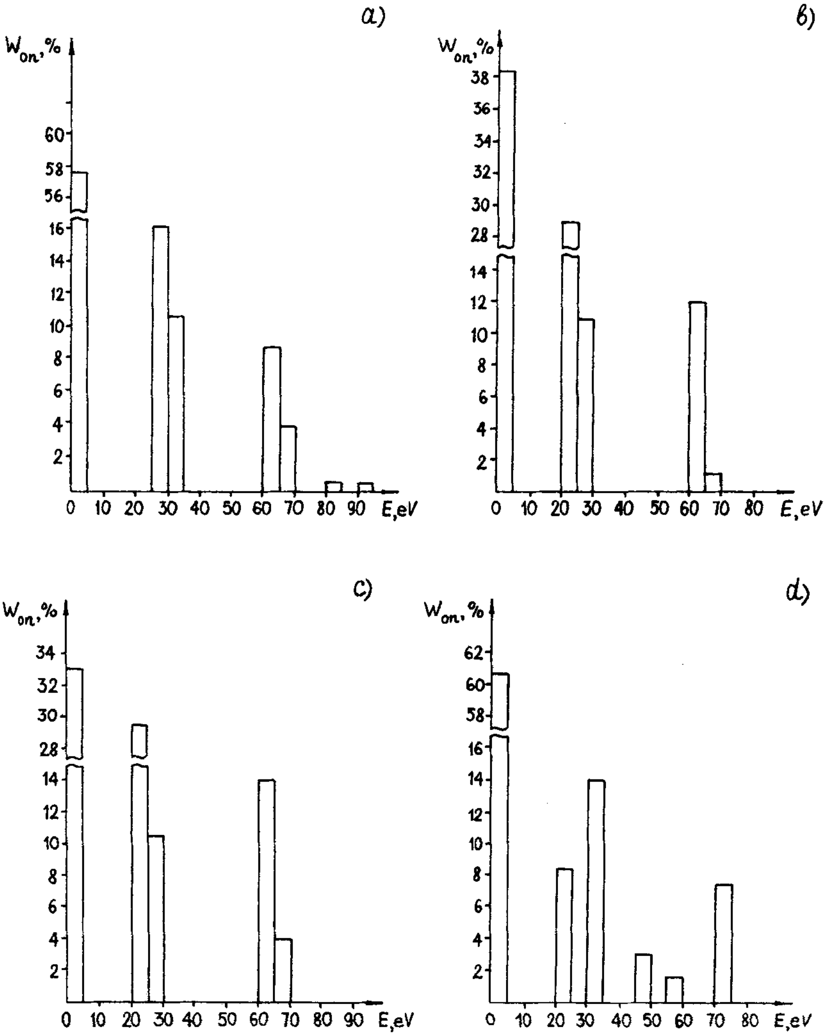


Fig. 5. Distributions of integral probabilities of electron excitations to the energy ranges of $[5n, 5(n + 1)$ eV in β decay of (a) HT, (b) LiT, (c) NaT, and (d) CH_3T, with allowance for the electron correlation.

NaT. For the latter type of molecule the changes in the summary excitation probability are even greater; for LiT it increases by 0.093, whereas for compounds with covalent bonds the changes in $\sum_{n\neq 0} W_{0n}$ are considerably smaller—for CH_3T they amount to 0.032.

In contrast to the probability distributions calculated in the MO LCAO approximation (see Fig. 4), the distributions in Fig. 5 were calculated taking account of the probability of two-electron excitations. Analyzing the influence of electron correlation on the distributions obtained, one can see that the summary probability of one-electron excitations becomes smaller, while the energy of the most probable one-electron excitations changes insignificantly. As in calculations in the Hartree–Fock approximation, the largest contribution to the one-electron excitations is given by the configurations corresponding to the transition of an electron into the first vacant (and not forbidden by selection rules) orbitals from those molecular orbitals that change the most under the transformation $T \rightarrow He^+$. This holds also for the two-electron transitions. The β decay of tritium does not lead to the excitation of K electrons. The probability of excitation of the valent electrons also does not increase; these excitations make a small contribution to the summary excitation probability.

C. Conclusions

Let us briefly summarize the main results of this section, which were obtained on the basis of the analysis of the β decay in the atoms ^3H and ^{14}C contained in molecules.

1. To a considerable extent the redistribution of electron density induced by the β decay in a molecule is due to the gathering of the negative charge on the newly formed atom. The main portion of the charge is transferred from the atoms in the immediate vicinity of the radioactive atom, though the peripheral atoms also take part in the redistribution of electron density.
2. The rearrangement of molecular orbitals induced by the β decay distorts the most the lowest orbitals of the valent shell, which we have named the "L shell." The transitions of electrons from these orbitals give the largest contribution to the excitation probability of the molecule.
3. The features of the molecular excitation spectra are independent of the size and structure of the molecule and are mainly determined by the radioactive atom and its nearest neighbors directly bound to it.
4. In the case of the tritium β decay, all excitation spectra of daughter molecules are similar. They consist of a principal maximum located in the region of 20–40 eV. This maximum accumulates about half the summary probability of all excitations and corresponds to the one-electron transitions from the "L shell" into the lower vacant MO. In addition, the spectra

contain a maximum corresponding to the two-electron transitions, which are also made from the "L shell" transitions into the lower vacant orbitals. The latter maximum is located in the region of 60–75 eV and corresponds to about 5–15% of the probability. The valent electrons are excited only weakly; the K electrons are not excited at all.

5. The allowance for electron correlation leads to an insignificant lowering of the probability of the daughter molecule being formed in the ground electron state for molecules with covalent-type chemical bonds. In the case of ionic bonds the lowering is greater and may be as large as 7%. The probability of one-electron excitations becomes somewhat less when we take into account the two-electron excitation channel. These changes are more pronounced for ionic molecules than they are for covalent molecules.

IV. Influence of Molecular Structure on the Shape of the Tritium β Spectrum and the Problem of Determining the Neutrino Rest Mass

A. β Spectrum and Energy Relations in the Presence of Electron Shell

The spectrum of β decay, or the β spectrum, is a distribution of ejection probabilities for the β electron versus its kinetic energy. As an initial formula for deriviing an expression for the β spectrum we will use Eq. (8). As was mentioned above, the β decay in a molecule is a multichannel process owing to the fact that both the parent and the daughter molecules may be in different electronic, vibrational, and rotational states. Thus, Eq. (8) should be employed for each channel of the reaction. Using the energy conservation law and the factorization of the matrix element, Eq. (12), we obtain the following expression for the probability of β decay in the channel $0 \to n$:

$$P_{0\to n} = (2\pi/\hbar)|M_{\text{nucl}}(\mathbf{p}_\nu, \mathbf{p}_\beta)|^2 \cdot |M_{0n}^{\text{mol}}(\mathbf{P}_{\text{rec}})|^2 \times \delta\{\Delta mc^2 - m_e c^2 - E_\beta - E_\nu - E_{\text{rec}} + [E_0(\text{RT}) - E_n(\text{RHe})^+] \tag{65}$$

The existence of a molecular surrounding leads to an additional term in the energy conservation law (in comparison with the case of a "bare" nucleus), which we have named (Kaplan *et al.*, 1982) the chemical shift

$$\Delta E_{0n} = E_0(\text{RT}) - E_n(\text{RHe}^+) \tag{66}$$

$E_0(\text{RT})$ is the total energy of the parent molecule, including the electronic, vibrational, and rotational energies. Here $E_n(\text{RHe}^+)$ is the energy of the nth state of the daughter molecule. The vibrational and rotational energies of a molecule are of order of 10^{-1}–10^{-2} eV. Both these energies lie well below the resolution limit of the modern β spectrometers (20–50 eV), so at the present experimental level it is impossible to notice the influence of vibrational and

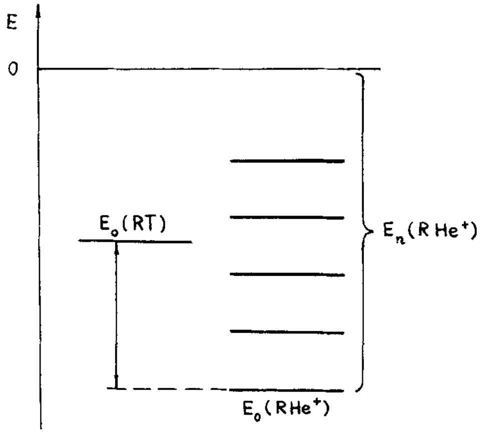


Fig. 6. Relative arrangement scheme of the electronic state energies of the parent (RT) and daughter $(\mathrm{RHe})^+$ molecules.

rotational excitations on the shape of the β spectrum. Because of this, we will suppose that the value of the chemical shift [Eq. (66)] is determined solely by the difference between the electron energies of the parent and the daughter molecules in the considered channel at an equilibrium position of the nuclei.

The ground-state energy $E_0(\mathrm{RHe}^+)$ of the ion $(\mathrm{RHe})^+$ is always below the ground-state energy $E_0(\mathrm{RT})$ of the parent molecule RT, isoelectronic with the ion $(\mathrm{RHe})^+$ (see Fig. 6). Thus, the chemical shift in the $0 \to 0$ channel and in the channels with close energies is always positive. This means that the restructuring of the molecule results in the release of an additional energy, with respect to the case of a bare nucleus, which is equal to the chemical shift in the given channel. This increases the kinetic energies of the β electron and the neutrino. In channels with high excitation energies of $(\mathrm{RHe})^+$ the chemical shift may be negative. In this case the kinetic energy of the β electron may be smaller than in the case of a bare nucleus. This means that the energy spent on excitation is greater than the gain in energy due to the difference between the ground-state energies of RT and $(\mathrm{RHe})^+$.

Since the β-decay energy is sufficiently high, and, consequently, all the decay channels are open, the additional β-electron kinetic energy is determined by the chemical shift averaged over all the channels

$$\overline{\Delta E} = E_0(\mathrm{RT}) - \overline{E_n(\mathrm{RHe}^+)} \qquad (67)$$

As will be shown below, the average chemical shift is always positive. It is convenient to calculate $\overline{\Delta E}$ using Migdal's (1941) theory of sudden perturbations. According to this theory, the electron wave function does not manage to change within the β-decay time, and so the average chemical shift must be calculated using the electron wave functions of the initial molecule:

$$\begin{aligned}\overline{\Delta E} &= \langle \Psi_0(\mathrm{RT}) | H(\mathrm{RT}) - H(\mathrm{RHe}^+) | \Psi_0(\mathrm{RT}) \rangle \\ &= E_0(\mathrm{RT}) - \langle \Psi_0(\mathrm{RT}) | H(\mathrm{RHe}^+) | \Psi_0(\mathrm{RT}) \rangle \end{aligned} \tag{68}$$

Here $H(\mathrm{RT})$ and $H(\mathrm{RHe}^+)$ are the Hamiltonians of the initial and the final molecules, respectively.

Considering that the average excitation energy of the daughter molecule $\overline{\Delta E^*(\mathrm{RHe}^+)}$ is determined as

$$\overline{\Delta E^*(\mathrm{RHe}^+)} = \langle \Psi_0(\mathrm{RT}) | H(\mathrm{RHe}^+) | \Psi_0(\mathrm{RT}) \rangle - E_0(\mathrm{RHe}^+) \tag{69}$$

we find the following connection between $\overline{\Delta E}$ and $\overline{\Delta E^*(\mathrm{RHe}^+)}$:

$$\overline{\Delta E} = E_0(\mathrm{RT}) - E_0(\mathrm{RHe}^+) - \overline{\Delta E^*(\mathrm{RHe}^+)} \tag{70}$$

where $\overline{\Delta E^*}$ includes excitations with transition of (RHe^+) into states with both discrete and continuous spectra, i.e.,

$$\begin{aligned}\overline{\Delta E^*(\mathrm{RHe}^+)} &= \overline{\Delta E^*(\mathrm{RHe}^+)}_{\mathrm{diser}} + \overline{\Delta E^*(\mathrm{RHe}^+)}_{\mathrm{ion}} \\ &= \sum_{n=1}^{\infty} W_{0n}[E_n(\mathrm{RHe}^+) - E_0(\mathrm{RHe}^+)] + \int_{I_1}^{\infty} W_{0E_i} E_i \, dE_i \end{aligned} \tag{71}$$

Here $\overline{\Delta E^*_{\mathrm{discr}}}$ and $\overline{\Delta E^*_{\mathrm{ion}}}$ are, respectively, the average energies of all the transitions into the discrete and continuous spectra; E_i is the energy of the transition into the continuous spectrum; and I_1 is the first ionization potential. The sudden-perturbation theory Eqs. (68) and (69) especially convenient for calculating $\overline{\Delta E}$ and $\overline{\Delta E^*}$, since they involve only the ground-state wave function, allowing one to avoid the calculation of the spectrum of exited states.

Now, let us show how the existence of different electron excitation channels affects the shape of the β spectrum. Since the difference in energy between the channels is no more than 10–15 eV [the energy distance between the excitation levels of the ion $(\mathrm{RHe})^+$], the separate channels are not distinguishable in the experiment, and the resulting β-decay curve is a weighted average over the electron channels. Thus, in order to find the shape of the β spectrum, it is necessary to average Eq. (65) over the quantum numbers of the initial state; to perform the integrations over the neutrino momentum $d\mathbf{p}_\nu = p_\nu^2 \, dp_\nu \, d\Omega_\nu$, over the recoil momentum $d\mathbf{P}_{\mathrm{rec}}$, and over the ejection angels of the β electron $d\Omega_\beta$; and to perform the summation over the final states of the daughter molecule

$$\begin{aligned} dP_\beta = \frac{2\pi}{\hbar} p_\beta \, dp_\beta \int d\Omega_\beta \int p_\nu^2 \, dp_\nu \, d\Omega_\nu |M_{\mathrm{nucl}}(\vec{p}_\nu, \vec{p}_\beta)|^2 \\ \times \mathrm{Av} \sum_n |\mathbf{M}_{0n}^{\mathrm{mol}}(\mathbf{P}_{\mathrm{rec}})|^2 \cdot \delta(\Delta mc^2 - m_e c^2 - E_\beta - E_\nu - E_{\mathrm{rec}} + \Delta E_{0n}) \end{aligned} \tag{72}$$

Here Av stands for the averaging over the vibrational and rotational quantum numbers of the parent molecule RT. The averaging over the electronic quantum numbers of the parent molecule is not performed, since under the existing conditions of experiments using β spectrometers, the excited electron states of the parent molecules belonging to the β source are not occupied. As was shown above [see Eq. (66) and the following discussion], one can disregard the dependence of ΔE_{0n} on the vibrational and rotational quantum numbers of the parent and the daughter molecules. After the squared modulus of the molecular matrix element $M_{0n}^{\mathrm{mol}}(\mathbf{P}_{\mathrm{rec}})$ [Eq. (19)] is summed up over the vibrational and rotational quantum numbers of the daughter molecule, it becomes independent of $\mathbf{P}_{\mathrm{rec}}$ and of the vibrational and rotational quantum numbers of the parent molecule [see Eqs. (25)–(27)]. So there is no need for the averaging, Av; the squared modulus of the molecular matrix element is replaced by the electron excitation probability W_{0n} [Eq. (27)].

In order to perform the integration in Eq. (72), let us neglect the small recoil energy E_{rec} in the energy conservation law and perform the integration over the recoil momentum $\mathbf{P}_{\mathrm{rec}}$. Let us single out the kinematic factor in M_{nucl} (Zel'dovich, 1955):

$$M_{\mathrm{nucl}}(\mathbf{p}_\beta, \mathbf{p}_\nu) = M'_{\mathrm{nucl}}[1 + \alpha(v_\beta/c)\,\mathrm{Cos}(\widehat{\mathbf{p}_\nu, \mathbf{p}_\beta})] \tag{73}$$

here M'_{nucl} is independent of $\mathbf{p}_\beta$ and $\mathbf{p}_\nu$ and contains the Fermi factor $F(E_\beta)$, which takes account of the influence of the molecular field on the motion of the β electron (Rose, 1955). Performing the change of variables

$$p_\nu^2\, dp_\nu = c^{-3}(E_\nu^2 - m_\nu^2 c^4)^{1/2}\, E_\nu\, dE_\nu$$

and substituting

$$p_\beta^2\, dp_\beta = c^{-2} p_\beta (E_\beta + m_e c^2)\, dE_\beta$$

we obtain

$$\begin{aligned} dP(p_\beta) = \sum_n W_{0n}\{A \cdot p_\beta(E_\beta + m_e c^2)|M'_{\mathrm{nucl}}(m_\nu, E_\beta)|^2[(\Delta mc^2 - E_\beta - m_e c^2 \\ + \Delta E_{0n})^2 - m_\nu^2 c^4]^{1/2} \cdot (\Delta mc^2 - E_\beta - m_e c^2 + \Delta E_{0n}) \cdot \Theta_n\}\, dE_\beta \end{aligned} \tag{74}$$

where A is a numerical factor; Θ_n is the step function, which equals unity when, for the given channel n, the expression in the square brackets of Eq. (74) is greater than zero, and equals zero in the opposite case. The summation over n implies also the integration in the channels with a continuous spectrum of the daughter ion excitations. The expression in the curly brackets differs from the β spectrum for the bare nucleus in the presence of the chemical shift ΔE_{0n} in each channel. In the presence of an electron shell, the β spectrum is a weighted sum of such shifted spectra, with weights equal to the probabilities of electron shell excitations.

Far from the end point of the β spectrum one can neglect the quantity $m_\nu^2 c^4$ in the square brackets of Eq. (74). In place of Eq. (74) we obtain

$$dP(p_\beta) = \sum_n W_{0n}\{A \cdot p_\beta \cdot (E_\beta + m_e c^2)|M'_{\text{nucl}}(m_\nu, E_\beta)|^2 \times [\Delta mc^2 - E_\beta - m_e c^2 + \Delta E_{0n}]^2\}\, dE_\beta \tag{75}$$

Equation (75) may be expressed in terms of the chemical shift averaged over all the channels $\overline{\Delta E}$ [Eq. (68)] and the mean-square chemical shift $\overline{\Delta E^2}$:

$$\overline{\Delta E} = \sum_{n=0}^{\infty} W_{0n}\, \Delta E_{0n}, \qquad \overline{\Delta E^2} = \sum_{n=0}^{\infty} W_{0n}\, \Delta E_{0n}^2 \tag{76}$$

namely

$$dP(p_\beta) = A \cdot p_\beta \cdot (E_\beta + m_e c^2)|M'_{\text{nucl}}|^2[(\Delta mc^2 - E_\beta - m_e c^2)^2 + 2(\Delta mc^2 - E_\beta - m_e c^2) \cdot \overline{\Delta E} + \overline{\Delta E^2}]\, dE_\beta \tag{77}$$

The β spectrum is conventionally presented in the Fermi coordinates (Y, E_β), where $Y = [P(p_\beta)/p_\beta^2 \cdot |M'_{\text{nucl}}|^2]^{1/2}$, since in this case the β spectrum for the bare nucleus and for each channel is a straight line called the Kurie plot. Figure 7 shows the Kurie plots which we have calculated for the molecule LiT. At $m_\nu = 0$ we can use Eq. (75) in the whole range of the energy E_β, provided we supplement it with the step function Θ_n in order to cut short the spectra of separate channels when they cross the abscissa axis, as is done in Eq. (74). According to Eqs. (74) and (75), the spectra of separate channels are shifted with respect to the bare nucleus spectrum by an amount equal to the chemical shift ΔE_{0n} for the given channel; in Fig. 7a we show the shift for the channel $0 \to 0$. In terms of the Fermi coordinates, the weight-average spectrum [Eq. (75)] is given by the thick-line curve plotted in Fig. 7a. The end point of the weight average coincides with the end point of the spectrum in the $0 \to 0$ channel. As follows from Eq. (77), when E_β is far from the spectrum end points of separate channels, the weight-average spectrum may be also approximated with accuracy by the straight line

$$\left(\frac{dP(p_\beta)}{A \cdot p_\beta(E_\beta + m_e c^2)|M'_{\text{nucl}}|^2}\right)^{1/2} = (\Delta mc^2 - m_e c^2 - E_\beta) + \overline{\Delta E} + O\left[\frac{\overline{\Delta E^2}}{2(\Delta mc^2 - m_e c^2 - E_\beta)}\right] \tag{78}$$

shifted with respect to the bare nucleus spectrum by an amount equal to the average chemical shift [Eq. (67)]. Here $O[\cdots]$ stands for the corrections to the straight line, which become essential only near the end points of the channel spectra.

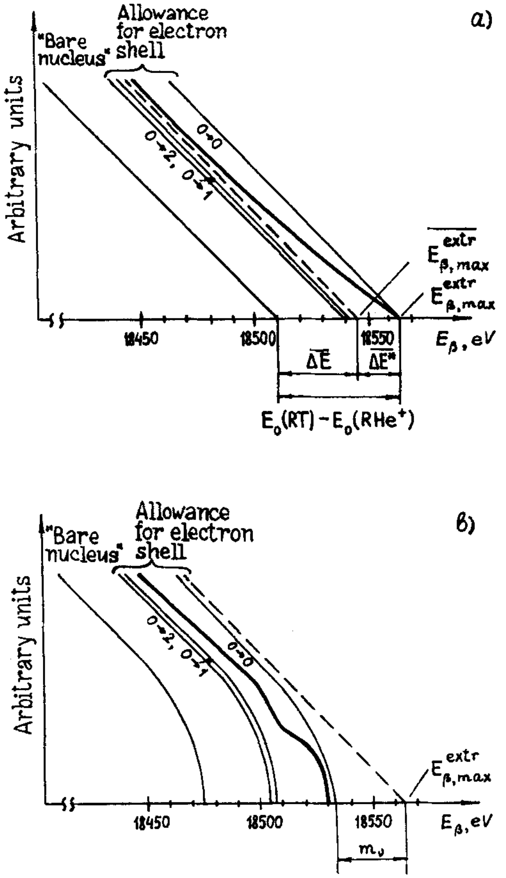


Fig. 7. The β spectrum of LiT: (a) $m_\nu = 0$; (b) $m_\nu = 35$ eV. The thin lines are the β spectra in the electron channels $0 \rightarrow n$; the thick line is the summary spectrum; the dashed line is the extrapolated spectrum; $Y = (P_n/p_\beta^2|M_{\text{nucl}}|^2)^{1/2}$.

If the neutrino rest mass is nonzero, the Kurie plots of the bare nucleus and of separate channels exhibit a parabolic bend approaching the abscissa, as is shown in Fig. 7b. The weight-average spectrum [Eq. (74)] bends as well on approaching the abscissa, though it may have a more complicated form owing to the existence of the different channels, which is manifest in Fig. 7b in the appearance of inflection of the curve of the weight-average spectrum.

One might estimate the value of the neutrino rest mass by the changes in the β spectrum. However, the direct measurements are not possible, since at the high-energy edge of the β spectrum, where the effect of the nonzero m_ν is manifest, the intensity of the spectrum is very low and is well below the level of the apparatus noise. Such experiments require a highly sensitive technique and a fine statistical processing with parametrized values of the neutrino rest mass, of the end point of the β spectrum, and of a number of other quantities (Lubimov *et al.*, 1981).

It should be noted that the end point of the β spectrum may be defined in different ways. For example, Bergkvist (1972) has defined the β-spectrum end point by extrapolating the highest part of the weight-average spectrum [Eq. (78)] to its intersection with the abscissa, as is shown by the dashed line in Fig. 7a [see Eq. (7) of the cited paper and the relevant text]. We will denote the thus-defined end point as $\overline{E^{\text{extr}}_{\beta,\text{max}}}$. In the experiments of the ITEP group (Lubimov *et al.*, 1980, 1981) the end point of the β spectrum E_0 was taken to be the maximum β-electron energy, provided $m_\nu = 0$ (the point $E^{\text{extr}}_{\beta,\text{max}}$ shown in Fig. 7). It is easy to demonstrate that

$$E^{\text{extr}}_{\beta,\text{max}} \equiv E^{(0)}_{\beta,\text{max}} + m_\nu c^2 = \Delta mc^2 - m_e c^2 - E_{\text{rec}} + [E_0(\text{RT}) - E_0(\text{RHe}^+)] \tag{79}$$

Here $E^{(0)}_{\beta,\text{max}}$ is the maximum energy in the channel $0 \to 0$ (see Fig. 7b). The two β-spectrum end-point energies are related in the following way

$$\overline{E^{\text{extr}}_{\beta,\text{max}}} = E^{\text{extr}}_{\beta,\text{max}} - \overline{\Delta E^*}(\text{RHe}^+) = \Delta mc^2 - m_e c^2 + \overline{\Delta E} - E_{\text{rec}} \tag{80}$$

In Table VII we present the chemical shift ΔE_{00} in the $0 \to 0$ channel, the average chemical shift $\overline{\Delta E}$, the average excitation energy of the daughter ion $\overline{\Delta E^*}$, and the end point of the β spectrum $\overline{E^{\text{extr}}_{\beta,\text{max}}}$ for a number of molecules.

TABLE VII

ENERGY CHARACTERISTICS OF THE β DECAY IN MOLECULES (eV)

	In the MO LCAO approximation				With allowance for electron correlation			
Molecule	ΔE_{00}	$\overline{\Delta E}$	$\overline{\Delta E^*}$	$\overline{E^{\text{extr}}_{\beta,\text{max}}}$	ΔE_{00}	$\overline{\Delta E}$	$\overline{\Delta E^*}$	$\overline{E^{\text{extra}}_{\beta,\text{max}}}$
Bare nucleus	—	—	—	18,531 ± 3	—	—	—	—
T	40.82	27.21	13.605	18,558 ± 3	—	—	—	—
HT	—	—	—	—	49.11	29.27	19.83	18,560 ± 4
LiT	57.13	33.74	23.39	18,564 ± 4	56.70	32.00	24.70	18,563 ± 4
BT	50.90	30.28	20.62	18,561 ± 4	—	—	—	—
NaT	57.96	32.92	25.04	18,564 ± 4	57.73	30.96	26.77	18,562 ± 4
AlT	55.93	33.84	22.09	18,564 ± 4	—	—	—	—
LiOT	47.15	29.08	18.07	18,560 ± 4	—	—	—	—
CH_3T	48.62	29.96	18.66	18,560 ± 4	48.82	30.30	18.51	18,561 ± 4
C_2H_3T	48.47	29.54	18.93	18,560 ± 4	—	—	—	—
C_2H_5T	49.15	30.23	18.92	18,561 ± 4	—	—	—	—
CH_3–CHT–CH_3	49.59	30.35	19.24	18,561 ± 4	—	—	—	—
NH_2–CH_2T	48.69	29.85	18.84	18,560 ± 4	—	—	—	—
NH_2–C_2H_4T	49.09	30.00	19.09	18,561 ± 4	—	—	—	—

We have calculated the data presented in the table in collaboration with G. V. Smeloy (Kaplan *et al.*, 1983, 1985). In the MO LCAO approximation we have used the same bases of atomic functions as in calculations of the excitation probabilities of the corresponding molecules (see Section III,B,1). Allowing for electron correlation, calculations of the number of CI configurations and the atomic bases were the same as those given in Section III,B,2.

As follows from Table VII, the average chemical shift is positive for all molecules. This means that the presence of the electron shell always increases the energy of the β electron with respect to the β decay of a bare nucleus. The chemical shift for molecules is greater than it is for an isolated atom: by 2–3 eV for organic molecules and by a somewhat greater shift for the considered metal hydrides. Since $\overline{\Delta E}$ was calculated according to Eq. (68), which takes into account the whole excitation spectrum, including the continuous one, the fact that $\overline{\Delta E}$ is positive means that the probability of excitations with energies higher than $\Delta E_{00} \approx 40$–60 eV is small [see Fig. 6 and the text preceding Eq. (67)]. This gives us assurance that the distributions presented in Figs. 4 and 5 take into account the majority of excitations, as well as assurance that the probability of transitions into continuous spectrum is small.

The existence of electron excitation channels is the cause of the physical broadening of the β spectrum (Bergkvist, 1971). The average excitation energy $\overline{\Delta E}^*(\mathrm{RHe}^+)$ may serve as a measure of this broadening. According to Table VII, the average excitation energies of molecules exceed the average excitation energy of the T atom by 7–12 eV for metal hydrides and by 5–6 eV for organic molecules. Thus, the presence of a molecular surrounding increases the physical broadening of the β spectrum with respect to an isolated T atom. In the experiment, the physical broadening should be manifest only in the vicinity of the end point of the β spectrum in a larger spread of experimental values. Far from this point, the measured resultant β-decay curve is a weighted average over the electron channels [Eq. (78)].

For calculating the values of $\overline{E^{\mathrm{extr}}_{\beta,\mathrm{max}}}$ presented in Table VII, we have used the nuclear mass defect evaluated from the experimental data on the atomic defect (Lippmaa *et al.*, 1985). We have taken the recoil energy to have the value 3 eV, which corresponds to the recoil of a free helium nucleus. In our earlier work (Kaplan *et al.*, 1982, 1983), for calculating $\overline{E^{\mathrm{extr}}_{\beta,\mathrm{max}}}$ we have used the value of the atomic mass defect measured by Smith *et al.* (1981).

B. Allowance for Molecular Structure in Data Processing of the Neutrino Rest Mass Measurements

In Section I we made a brief excursion into the history of studies devoted to the estimation of the neutrino rest mass; in this regard we pointed out the importance of the problem, first raised by Bergkvist (1971, 1972), of taking into account the β-source electron excitations in reduction of the corresponding experimental data. The effect of electron excitations of the β source on the β spectrum is comparable in magnitude with the expected value of the neutrino rest mass, manifesting itself in the region most sensitive to the nonzero m_ν.

In this section we present the calculation (Kaplan *et al.*, 1982, 1983, 1985) of parameters describing the excitations of the β source used by the ITEP group in a series of experiments for measuring the neutrino rest mass. The results of these calculations were used by the ITEP group for data reduction and estimation of m_ν.

From 1976 to 1983, the ITEP group carried out 35 sets of experiments (Tretjakov *et al.*, 1976; Lubimov *et al.*, 1980, 1981; Boris *et al.*, 1983), in which the rest mass of the neutrino was measured by a unique nonferrous spectrometer designed by Tretjakov (1975). This spectrometer has an energy resolution of 45 eV at the end of the tritium β spectrum, and the background level is 15 times smaller than it is in the spectrometer designed by Bergkvist (1972). In 1980 the ITEP group improved their spectrometer and reached a resolution of 20 eV; the background level was lowered by 20 times (Boris *et al.*, 1983). In all 35 sets of experiments the measurements were carried out with the same source of β-electrons, tritiated valine.

In each set of experiments we measured the intensity of the β-electron flux near the high-energy edge of the β spectrum. The theoretical curve of the β spectrum was fitted to the experimental one by the method of least squares. The fitting parameters were the neutrino rest mass m_ν, the end-point energy of the β spectrum $E^{\text{extr}}_{\beta,\,\text{max}}$, and a number of others. Each of the 35 sets was reduced independently; as a result, for each parameter, including m_ν, 35 values were obtained, which formed a certain distribution. This distribution is presented in Fig. 8, which we have taken from Boris *et al.* (1983). The numbers in the boxes denote the numbers of sets. One can see that the most probable value of m_ν is within 25–35 eV. Further statistical processing of these distributions gives a more precise value of m_ν.

The working substance of the ITEP-group β source was a doubly tritiated crystalline amino acid, DL-valine (Mallikarjunan and Rao, 1969), which is a molecular crystal. As a result of decay, during the time $\sim 10^{-18}$ sec the valine molecule transforms into the corresponding helium-containing ion $(\text{RHe})^+$. Since the translational symmetry of the crystal is disturbed, no exciton states are produced, and only molecular states of the complex $(\text{RHe})^+$ are excited. Since in molecular crystals the intermolecular interactions are considerably weaker than the intramolecular ones, one can neglect the influence of the valine crystalline surrounding on the β-decay process and consider only an isolated valine molecule.

Let us note that it is impossible in principle to determine the spectrum of

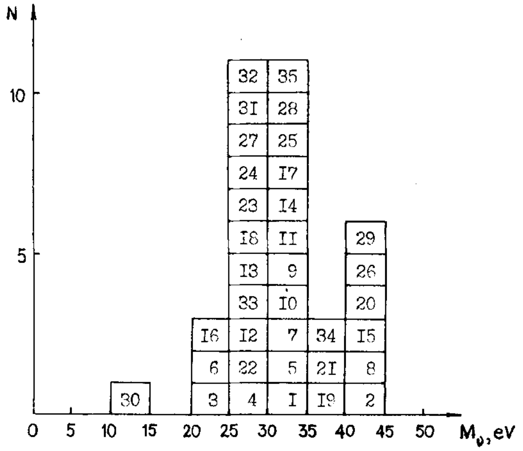
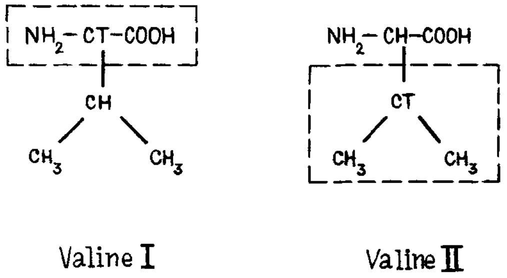


Fig. 8. Histogram of the M_ν values for 35 series of measurements. [From Boris *et al.* (1983).]

the β-decay-induced excitations of the multiatomic valine molecule from its luminescence spectra. This is due to the fact that during the time 10^{-13}–10^{-11} sec, the upper excited states of a molecule transfer the energy to lower excited states in a nonradiative manner, and it is from those levels the luminescence transition occurs. Besides, the valine molecule has no luminescence at all, so it is impossible to determine even the total number of excited molecules. Thus, the spectrum of the β-decay-induced excitations of valine can only be found theoretically.

Following the publication of the papers by the ITEP group (Kozik *et al.*, 1980; Lubimov *et al.*, 1981) a number of attempts were reported (Fukugita and Kubodeva, 1981; Law, 1981; Chengrui *et al.*, 1981) that take into account the influence of the β-decay energy outflow into the electron channel on the neutrino rest mass obtained by reducing the experimental β-spectrum data. Since the authors of all the cited papers have assumed that the spectrum of the working medium used in the experiments (Kozik *et al.*, 1980; Lubimov *et al.*, 1981) cannot be calculated, they started out with models. In papers by Fukugita and Kubodeva (1981) and Law (1981) the source model was atomic tritium. Fukugita and Kubodeva showed that exact allowance for the continuous spectrum has practically no influence on the obtained neutrino rest mass. Allowance for the molecular surrounding was reduced to a change in the parameter of the screening of the atomic 1*s* function (Law, 1981), and it was concluded that an exact molecular calculation is essential for final deductions. In the paper by Chengrui *et al.* (1981) the authors compared the reduction of the experimental data (Kozik *et al.*, 1980; Lubimov *et al.*, 1981) in the atomic-model approximation, on the one hand, with the reduction for



Valine I Valine II

Fig. 9. Location of decaying atom T valine I and valine II.

the HT molecule, on the other, and reached the conclusion that the atomic model overestimates the obtained value of the mass. We note in this connection that our approach, similar to that of Chengrui *et al.*, (1981), but with LiT rather than the HT molecule, did not confirm this overestimate. Reduction by the ITEP group of the experimental data, using the valine spectrum calculated by us, pointed to an opposite tendency [see Table I].

Rigorous approach to the calculation of valine excitations is a difficult task, since the valine molecule contains 19 atoms and 64 electrons. Because, in the ITEP β source, each molecule contained two tritium atoms, the calculations of the excitation spectrum had to be performed for each of the two positions of the radioactive atom separately (the decays of two tritium atoms are not correlated). The two valine molecules differing in the position of the tritium atom experiencing β decay were arbitrarily named valine I and valine II (see Fig. 9).

In view of the large size of the valine molecule, our calculations (Kaplan *et al.*, 1983) were carried out on a minimal basis of 51 Slater orbitals in the MO LCAO approximation using the method described in Sections II, C, and III, B, 1. We have taken into account 608 singly excited states of the ion $(\text{valine–He})^+$. The results of calculations for valine on a minimal basis were corrected with regard to the results of calculation of the influence of the basis length on the excitation probabilities of the fragments that are shown enclosed in boxes in Fig. 9 (the rest of the molecule was replaced by a hydrogen atom).

For all excitation energies, the correction did not exceed 4.5%, its average value amounting to $\sim$0.7%. The energy characteristics were corrected in a similar manner. The data obtained are presented in Table VIII and in Fig. 10.

Comparison of the data in Tables III and VIII shows that the probability of remaining in the ground state is approximately 3% higher for the valine molecule than for related organic molecules. The reason for this is the distortion of the equilibrium geometry of the valine molecule by the crystalline field.

TABLE VIII

PROBABILITIES OF RESTRUCTURING ELECTRON SHELL AND ENERGY CHARACTERISTICS OF THE VALINE β SPECTRUM

Molecule	W_{00}	$\sum_{n \neq 0} W_{0n}$[a]	ΔE_{00} (eV)	$\overline{\Delta E}$ (eV)	$\overline{E^{*}}$[b] (eV)	$\overline{E^{\text{extr}}_{\beta,\max}}$ (eV)
Valine I	0.6512	0.3007	46.79	28.20	18.59	18559 ± 4
Valine II	0.6291	0.3099	48.25	29.37	18.88	18560 ± 4
	(0.6122)[c]	(0.2815)	(48.93)	(30.12)	(18.80)	(18561 ± 4)

[a] Only the discrete spectrum.

[b] Average energy going both to discrete excitations and to ionization.

[c] Numbers in parentheses were obtained using the CI method.

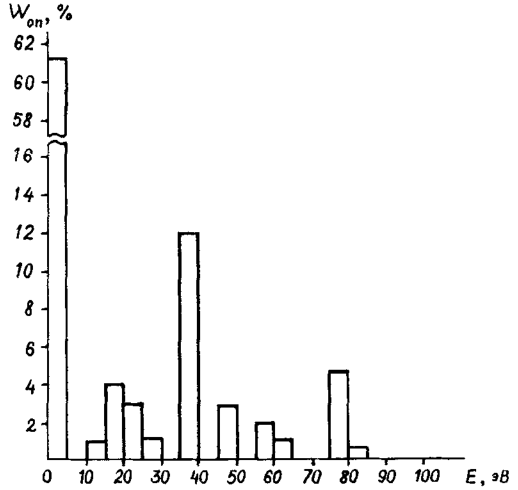


Fig. 10. Distribution of integral probabilities of electron excitations to the energy ranges [5*n*, 5(*n* + 1) eV in β decay of valine.

The most probable excitations in the valine β decay correspond to transitions—of an electron from the MO made up of the 2*s* carbon atom orbitals and the nearly orbitals of the hetero atoms, and of the 1*s* orbitals of helium—into the lower vacant MO, and they have an energy of ~40 eV.

The summary probability of discrete transitions, $W_{00} + \sum_{n \neq 0} W_{0n}$, amounts to 0.952 for valine I and 0.939 for valine II. From this, for the ionization probability we obtain the values 0.048 and 0.061, respectively.

In work by Kaplan *et al.* (1984) the β decay in a valine molecule was calculated with allowance for electron correlation. The method of calculation is presented in Section II,C,4. We have taken 50 configurations which give the largest contribution to the excitation probabilities. The results of calculations for valine II are presented in Table VIII (the numbers in parentheses) and in the histogram of Fig. 10. These results have been used by the ITEP group (Boris et al., 1983) in data reduction of their latest series of experiments. (The obtained values of the neutrino rest mass m_ν are presented in Table I.)

As was discussed in Section IV,A, the quantum chemical calculations allow us to compute the end point of the β spectrum, provided we know the value of the mass defect of the radioactive nucleus. In later experiments of the ITEP group (Boris *et al.*, 1983) the attained energy resolution of ~ 20 eV made it possible to determine the end point of the β spectrum $E^{\text{extr}}_{\beta,\max}$ (E_0 in notations of the ITEP group). The fitting was done within the energy interval 40–50 eV away from the expected edge of the β spectrum. The value obtained was $E_0 = 18{,}579 \pm 2.1$ eV.

The expression for $E^{\text{extr}}_{b,\max}$ is given by Eq. (79). Using the value of Δm obtained by Lippmaa *et al.* (1985), we get $E^{\text{extr}}_{\beta,\max} \equiv E_0 = 18{,}580 \pm 4$ eV. The agreement with the experimental value is more than good.

C. Conclusions

Let us summarize the results of this section:

1. The presence of the electron shell leads to an increase of the kinetic energy of both the β electron and the neutrino, owing to the gain in the energy of the electron–nuclear interaction that is due to the increase of the charge of the radioactive nucleus.

2. The average chemical shift is positive. In the case of the β decay of tritium contained in organic molecules and in molecules of light-metal hydrides, it amounts to 29–34 eV, which is somewhat greater than the chemical shift of atomic tritium, $\Delta E(\mathrm{T}) = 27.21$ eV.

3. For molecules, the average excitation energy $\overline{\Delta E^*}$ of the daughter helium-containing complex is also higher (~ 18–25 eV) than it is for atomic tritium (13.605 eV).

4. The effect of electron excitations of the β source is comparable in magnitude with the expected value of the neutrino rest mass and is manifested in the region most sensitive to the nonzero m_ν. The allowance for the molecular structure of the β source in reduction of the experimental data of the ITEP group has led to the most probable value of the neutrino rest mass $m_\nu = 33$ eV (Boris *et al.*, 1983).

Appendix. Modification of the Molecular Hamiltonian and Factorization of the Matrix Element

As was mentioned in Section II,A, the unperturbed Hamiltonian H_0 [Eq. (11)] must describe both the initial and the final sets of particles involved in the β decay of a nucleus in a molecule. However, the sets of particles in the initial and the final states do not coincide. One can overcome this difficulty by using the isotopic spin formalism (Blatt and Weiskopf, 1952).

One can disregard the electromagnetic interaction of nucleons in comparison with their strong interaction. In this case the proton and the neutron—which may be formally considered as two different states of a single particle, the nucleon—have equal energies and differ only in the projection of the isospin $\tau = 1/2$, just as in the absence of a magnetic field the electron states are degenerate with respect to the spin, differing only in the projection of the spin momentum. The wave function of the nucleus contains the spatial $\mathbf{r}_i$ and the spin s_i coordinates of each nucleon, and also contains their charge coordinates q_i, which, similar to the spin coordinates, may have two values. In the isospin formalism, the charge (isospin) wave function w_{nucl} is singled out as an independent factor

$$\Psi_{\text{nucl}}(\mathbf{r}_1, s_1, q_1; \mathbf{r}_2, s_2, q_2, \ldots) = \bar{\Psi}_{\text{nucl}}(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2, \ldots) \cdot w_{\text{nucl}}(q_1, q_2, \ldots) \tag{A.1}$$

The choice of the nucleus wave function in the form given by Eq. (A.1) makes it possible to describe the eigenfunctions of the Hamiltonian $H_{\text{nucl},k}$ [see Eq. (11)] before and after the β decay by simply varying the set of charge variables in accordance with the number of protons and neutrons in the initial and final states. For obtaining the charge Z of the nucleus it is necessary to apply the charge operator

$$\hat{Z} = (A/2 + \hat{T}_3) \tag{A.2}$$

to the charge wave function w_{nucl} of the nucleus. Here A is the number of nucleons in the nucleus and $\hat{T}_3$ is the projection of the nucleus isospin operator. The latter is constructed similarly to the projection of the total spin operator $\hat{S}_Z$

$$\hat{Z} w_{\text{nucl}}(q_1, q_2, \ldots) = Z w_{\text{nucl}}(q_1, q_2, \ldots) \tag{A.3}$$

The eigenvalue Z in Eq. (A.3) is just the charge of the nucleus.

In β decay, the initial and final molecules are different. However, if we replace the charge Z in the molecular part H_{mol} of the Hamiltonian H_0 [see Eq. (11), Section II] by the charge operator [Eq. (A.2)], the eigenfunctions of

H_{mol} can describe both these molecules:

$$H_{\text{mol}} = T_e + T_n - \sum_{i=1}^{N} \sum_{K=1}^{n} \frac{\hat{Z}_K e^2}{|\mathbf{r}_i - \mathbf{R}_K|} + \frac{1}{2} \sum_{K,K'=1}^{n} \frac{\hat{Z}_K \hat{Z}_{K'} e^2}{|\mathbf{R}_K - \mathbf{R}_{K'}|} + \frac{1}{2} \sum_{i,j=1}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{A.4}$$

Here T_e and T_n are the kinetic energy operators of electrons and nuclei, respectively. The other terms describe the interaction of the nuclei with electrons and the interactions between the nuclei and between the electrons.

The eigenfunctions of H_{mol} [Eq. (A.4)] depend on the charges of nuclei as parameters, and for a given set $\{Z_i\}_1^n$ of charges, form a complete orthonormal system

$$H_{\text{mol}}(\{Z_i\}_1^n)\Psi_{\text{mol},m}(\{Z_i\}_1^n = E_m(\{Z_i\}_1^n)\Psi_{\text{mol},m}(\{Z_i\}_1^n)$$

$$\langle \Psi_{\text{mol},m}(\{Z_i\}_1^n) \,|\, \Psi_{\text{mol},m'}(\{Z_i\}_1^n)\rangle = \delta_{m,m'} \tag{A.5}$$

However, if the sets of charges $\{Z_i\}_1^n$ and $\{Z_i'\}_1^n$ do not coincide, as in the case of β decay, the spectra of Hamiltonians $H_{\text{mol}}(\{Z_i\}_1^n)$ and $H_{\text{mol}}(\{Z_i'\}_1^n)$ are not mutually orthogonal

$$\langle \Psi_{\text{mol},m}(\{Z_i\}_1^n) | \Psi_{\text{mol},m'}(\{Z_i'\}_1^n)\rangle = S_{m,m'}(\{Z_i\}_1^n, \{Z_i'\}_1^n) \tag{A.6}$$

As was shown in Section II, the squared modulus of the overlap integral [Eq. (A.6)] for the parent and the daughter molecules gives the probability of molecular excitations induced by β decay.

The leptonic part H_{lept} of the unperturbed Hamiltonian H_0 describes the motion of the β electron and the neutrino, which are also interpreted as different charge (isospin) states of a single particle, the lepton:

$$H_{\text{lept}} = T_{\text{lept}} + \frac{e^2 Z_n q_{\text{lept}}}{|\mathbf{R}_n - \mathbf{r}_{\text{lept}}|} \tag{A.7}$$

T_{lept} is the lepton kinetic energy. The second term corresponds to the interaction of the β electron with the radioactive nucleus, which we have supplied with the index n (for simplicity, we neglect the interaction of the β electron with all the nuclei of the molecule except the radioactive one). Here Z_n is the charge of the radioactive nucleus and q_{lept} is the charge coordinate of the lepton. For the β electron $q_{\text{lept}}(\beta) = 1$, for the neutrino $q_{\text{lept}}(\nu) = 0$, so Eq. (A.7) contains no term corresponding to the interaction of the neutrino with the nucleus.

A wave function of the Hamiltoniam H_0, Eq. (11), may be presented as a product of the wave functions corresponding to separate terms. For convenience, let us use the fact, known from the field theory (Konopinski, 1966), that the emission of a particle may be interpreted as an absorption of its antiparticle with the opposite spin and an energy of opposite sign, i.e., Eq. (3) (see Section I) may be interpreted as

$$\nu_e + [\mathrm{RA}(Z)] \rightarrow [\mathrm{RA}(Z+1)]^+ + e^- \tag{A.8}$$

The latter statement means that the matrix elements of Eqs. (3) and (A.8) coincide. However, Eq. (A.8) has a more symmetrical form: on the right and on the left there is a single molecule and a single lepton. This is convenient for writing down the wave functions and matrix elements of β decay.

Following Cantwell (1956), let us present the wave functions of the initial Ψ^{i} and the final Ψ^{f} states in the form

$$\Psi^{\mathrm{i}} = \prod_{K=1}^{\mathrm{n}} \Psi^{\mathrm{i}}_{\mathrm{nucl},\ K} \cdot e^{\mathrm{i}\mathbf{P}^{\mathrm{i}}_{\mathrm{c}}\tilde{\mathbf{R}}_{\mathrm{c}}} \cdot \Psi^{\mathrm{i}}_{\mathrm{mol}}(\ldots, \mathbf{r}, s, \ldots; , \ldots, \mathbf{R}, \ldots) \cdot U^{\mathrm{i}}_{\mathrm{lept}} \tag{A.9}$$

$$\Psi^{\mathrm{f}} = \prod_{K=1}^{\mathrm{n}} \Psi^{\mathrm{f}}_{\mathrm{nucl},\ K} \cdot e^{\mathrm{i}\vec{\mathbf{P}}^{\mathrm{f}}_{\mathrm{c}}\vec{\tilde{\mathbf{R}}}_{\mathrm{c}}} \cdot \Psi^{\mathrm{f}}_{\mathrm{mol}}(\ldots, \vec{\mathbf{r}}, s, \ldots; \ldots, \vec{\mathbf{R}}, \ldots) \cdot U^{\mathrm{f}}_{\mathrm{lept}} \tag{A.10}$$

$\mathbf{P}^{\mathrm{i}}_{\mathrm{c}}$ and $\mathbf{P}^{\mathrm{f}}_{\mathrm{c}}$ are the center-of-mass momenta of the parent and the daughter molecules, respectively; $\mathbf{R}_{\mathrm{c}}$ is the coordinate of the center of mass. The tilde denotes the radius vectors given in the laboratory coordinate system (LCS); other radius vectors are given in a coordinate system, the origin of which is located at the center of mass of the molecule (CSM)

$$U^{\mathrm{i}}_{\mathrm{lept}} = \frac{1}{(2\pi)^{3/2}} \cdot e^{-\mathrm{i}\mathbf{p}_\nu\tilde{\mathbf{r}}_{\mathrm{lept}}} \cdot v_\nu(s_{\mathrm{lept}}) \cdot w_\nu(q_{\mathrm{lept}}) \tag{A.11}$$

Here $\mathbf{p}_\nu$ is the neutrino wave number, $v_\nu(s_{\mathrm{lept}})$ is the Dirac 4-spinor for the neutrino, and $w_\nu(q_{\mathrm{lept}})$ is the neutrino charge wave function. If we express $\tilde{\mathbf{r}}_{\mathrm{lept}}$(the neutrino coordinate in the LCS) in terms of the coordinates of the center of mass $\mathbf{R}_{\mathrm{c}}$, of the radioactive nucleus $\mathbf{R}_{\mathrm{n}}$, and of the neutrino $\mathbf{r}_{\mathrm{lept}}$, all given in the CSM, there will be additional factors in the wave function [Eq. (A.11)]:

$$U^{\mathrm{i}}_{\mathrm{lept}} = \frac{1}{(2\bar{\pi})^{3/2}}\, e^{-\mathrm{i}\mathbf{p}_\nu\tilde{\mathbf{R}}_{\mathrm{e}}} e^{-\mathbf{p}_\nu\mathbf{R}_{\mathrm{n}}} e^{-\mathbf{p}_\nu(\mathbf{r}_{\mathrm{lept}} - \mathbf{R}_{\mathrm{n}})} \cdot v_\nu(s_{\mathrm{lept}}) \cdot w_\nu(q_{\mathrm{lept}}) \tag{A.12}$$

The wave function of the β electron may be presented in a similar way (Cantwell, 1956):

$$U^{\mathrm{f}}_{\mathrm{lept}} = e^{\mathrm{i}\mathbf{p}_\beta\tilde{\mathbf{R}}_{\mathrm{e}}} \cdot e^{\mathrm{i}\mathbf{p}_\beta\mathbf{R}_{\mathrm{n}}} \cdot \chi_\beta(\mathbf{r}_{\mathrm{lept}} - \mathbf{R}_{\mathrm{n}}) \cdot w_\beta(q_{\mathrm{lept}}) \tag{A.13}$$

Here χ_β is the Dirac 4-spinor for the β electron and w_β is the β-electron charge function.

Let us substitute wave functions, Eqs. (A.9) and (A.10), taking count of Eqs. (A.11) and (A.12), into the matrix element in the initial expression, Eq. (8) (Section II). The weak-interaction Hamiltonian H_β acts on the charge (isospin) wave functions of the leptons and of the radioactive nucleus n, as well as on the spinor indices of the neutrino and β-electron 4-spinors [the explicit form of H_β is presented in Cantwell (1956)]. Taking all this into account, we obtain the following expression for the matrix element of H_β

$$\begin{aligned}\langle\Psi^{\mathrm{f}}|H_\beta|\Psi^{\mathrm{i}}\rangle = {} & \langle\Psi^{\mathrm{f}}_{\mathrm{nucl},n}\cdot\Psi^{\mathrm{f}}_{\mathrm{mol}}(\ldots,\mathbf{r}_{\mathrm{i}},s_{\mathrm{i}};\mathbf{R}_1,\ldots,\mathbf{R}_{\mathrm{n}})\cdot e^{\mathrm{i}\mathbf{p}_\beta\mathbf{R}_{\mathrm{n}}}\chi_\beta(\mathbf{r}_{\mathrm{lept}}-\mathbf{R}_{\mathrm{n}}) \\ & \cdot w_\beta(q_{\mathrm{lept}})|H_\beta||\Psi^{\mathrm{i}}_{\mathrm{nucl},n}\cdot\Psi^{\mathrm{i}}_{\mathrm{mol}}(\ldots,\mathbf{r}_{\mathrm{i}},s_{\mathrm{i}};\mathbf{R}_1,\ldots,\mathbf{R}_n)(2\bar{\pi})^{-3/2} \\ & \times e^{-\mathrm{i}\mathbf{p}_\nu\mathbf{R}_{\mathrm{n}}}e^{-\mathrm{i}\mathbf{p}_\nu(\mathbf{r}_{\mathrm{lept}}-\mathbf{R}_{\mathrm{n}})}v_\nu(s_{\mathrm{lept}})\cdot w_\nu(q_{\mathrm{lept}})\rangle \\ & \times\langle e^{\mathrm{i}\mathbf{P}^{\mathrm{f}}_{\mathrm{c}}\mathbf{R}_{\mathrm{e}}}\cdot e^{\mathrm{i}\mathbf{p}_\beta\tilde{\mathbf{R}}_{\mathrm{e}}}\,\big|\,e^{\mathrm{i}\mathbf{P}^{\mathrm{i}}_{\mathrm{c}}\mathbf{R}_{\mathrm{e}}}e^{-\mathrm{i}\mathbf{p}_\nu\tilde{\mathbf{R}}_{\mathrm{e}}}\rangle \end{aligned} \tag{A.14}$$

At this stage, we have an isolated matrix element which expresses the momentum conservation law. In addition, owing to the normalization, intranuclear wave functions of all nuclei, except the radioactive one and its daughter nucleus, have disappeared. Further factorization of the matrix element, Eq. (A.14), is presented in the main text [see the four paragraphs preceding Eq. (12)]. It leads to the following simplifications in Eq. (A.14): (1) it is possible to compute the wave function of the radioactive nucleus $\Psi_{\mathrm{nucl},n}$ for the equilibrium position of its center of mass $\mathbf{R}_{\mathrm{n}} = \mathbf{R}^0_{\mathrm{n}}$; (2) the wave functions of the leptons may be assigned the values they have on the surface of the radioactive nucleus. This factorizes the matrix element, Eq. (A.14), further:

$$\begin{aligned}\langle\Psi^{\mathrm{f}}|H_\beta|\Psi^{\mathrm{i}}\rangle = {} & \langle\Psi^{\mathrm{f}}_{\mathrm{nucl},n}\chi_\beta(\mathrm{surf})\cdot W_\beta(q_{\mathrm{lept}})|H_\beta|\Psi^{\mathrm{i}}_{\mathrm{nucl},n}(2\bar{\pi})^{-3/2}e^{-\mathrm{i}\mathbf{p}_\nu(\mathrm{surf})}v_\nu(s_{\mathrm{lept}}) \\ & \cdot W_\nu(q_{\mathrm{lept}})\rangle\langle\Psi^{\mathrm{f}}_{\mathrm{mol}}(\ldots,\mathbf{r}_{\mathrm{i}},s_{\mathrm{i}};\mathbf{R}_1,\ldots,\mathbf{R}_{\mathrm{n}})| \\ & \cdot e^{-\mathrm{i}(\mathbf{p}_\beta+\mathbf{p}_\nu)\mathbf{R}_{\mathrm{n}}}|\Psi^{\mathrm{i}}_{\mathrm{mol}}(\ldots,\mathbf{r}_{\mathrm{i}},s_{\mathrm{i}};\mathbf{R}_1,\ldots,\mathbf{R}_{\mathrm{n}})\rangle \\ & \cdot\delta(\mathbf{p}^{\mathrm{i}}_{\mathrm{e}}-\mathbf{p}_\nu-\mathbf{p}_\beta-P^{\mathrm{f}}_{\mathrm{e}}) \equiv M_{\mathrm{nucl},n}(\mathbf{p}_\nu,\mathbf{p}_\beta) \\ & \cdot M_{\mathrm{mol}}(\mathbf{p}_\nu+\mathbf{p}_\beta)\cdot\delta(\mathbf{P}^{\mathrm{i}}_{\mathrm{c}}-\mathbf{p}_\nu-\mathbf{p}_\beta-P^{\mathrm{f}}_{\mathrm{e}}) \end{aligned} \tag{A.15}$$

Addendum

After the manuscript had been sent for publication, we got acquainted with the detailed review by Ching Cheng-rui and Ho Tso-hsiu (1984) includes a discussion of the various types of experiments on the measurement of neutrino mass. Kolos *et al.* (1985a) published the theoretical results of the Florida Quantum Theory Project investigation on β-decay in the TH molecule. At present this is the most precise calculation of HeT^+ excitation. The authors of the present review are quite satisfied that the data on the calculation of HeT^+ excitation probabilities (obtained by the same method as was used for valine) are in good agreement with our calculations of data from Kolos and co-workers [see Table IX]. Besides, we should like to note that data obtained by us for two-electron excitations in the range 60–70 eV (or more exact, at 61.3, 62.7, and 68.9 eV) with total probability of 0.12 practically coincide with the resonance states of 62.0 and 68.5 eV (Kolos *et al.*, 1985b) with the total probability of 0.11.

TABLE IX

ENERGY OF THE SIX LOWEST STATES OF HHe^+ AND THE PROBABILITY OF TRANSITION TO THESE STATES FROM THE HT GROUND STATE[a]

State	Energy[a] (eV)	W_{0n}[a]	Energy[b] (eV)	W_{0n}[b]
1	0	0.58227	0	0.577
2	27.34	0.16813	27.27	0.159
3	33.99	0.07882	33.96	0.104
4	38.07	0.00803	—	—
5	38.91	0.00012	—	—
6	39.89	0.00912	—	—
		E = 0.846		E = 0.840

[a] From Kolos *et al.* (1985a); the Condon approximation. Taking into account effects of vibration (work carried out in the same paper) only slightly changes the results.

[b] From Kaplan *et al.* (1985).

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