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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 fourteenth volume is now being prepared.

The Editor would like to thank the authors for their contributions which give an interesting picture of the current status of selected parts of quantum chemistry. The topics in this volume cover studies on the properties of linear independence of some of the basic sets commonly used in computational quantum chemistry; molecular electron propagator theory; the problems of chemical isomerism; and the use of symmetry rules in modern chemical graph theory.

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.

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Molecular Electron Propagator Theory and Calculations

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I. Introduction

The electron propagator is being employed in molecular theory primarily for the calculation of electron binding energies (ionization potentials and electron affinities) as well as photoionization cross sections and intensities related to various spectrometric processes. Propagator (Linderberg and Öhrn, 1973) or Green's function (Cederbaum and Domcke, 1977) methods have been successful in providing efficient schemes for accurate theoretical determination of photoelectron spectra of arbitrary molecular systems for a variety of photon sources, and with electron binding energies ranging from the deepest core levels to the outer valence regions. The increasing availability of high-quality photoelectron spectra and the need for their accurate interpretation have triggered a number of theoretical investigations (Cederbaum, 1973a,b, 1974, 1975, 1977; Cederbaum and Domcke, 1977; Cederbaum *et al.*, 1975, 1977, 1978) employing these methods. The advantages of propagator methods become particularly evident when a single, consistent and quantitative scheme is sought, flexible enough to be predictive for the entire range of electron binding energies, including ionization–excitation processes (Purvis and Öhrn, 1974, 1975a,b, 1976).

The usefulness of propagator theory is by no means limited to the realm of electron binding energies. All areas of spectrometry can be given a unified treatment (Linderberg and Öhrn, 1973) and the solution of the equation of motion for the appropriate propagator yields a spectral density function and energy differences from which expectation values and spectra (transition moments and transition energies) can be obtained. Most molecular applications have been made within the Born–Oppenheimer approximation for vertical transitions, but theoretical determination of vibrational fine structure of lines in photoelectron spectra has been accomplished (Cederbaum and Domcke, 1977) using propagator techniques.

The polarization propagator (Linderberg and Öhrn, 1973; Jørgensen, 1975) obtained in various approximations can produce (see, e.g., Oddershede and Jørgensen, 1977 and references therein) nuclear spin–spin coupling constants, spectroscopic constants and radiative lifetimes, frequency-dependent polarizabilities, Verdet constants, excitation energies, transition moments, and correlation energies. Recently, Linderberg and Öhrn (1977) and Öhrn and Linderberg (1979) have shown how consistent ground- and excited-state many-electron wave functions can be obtained from the polarization propagator. Goscinski and Weiner (1980) have used algebraic methods and the Gel'Fand–Naimark–Segal (GNS) construction to analyze and extend the results of Linderberg and Öhrn. Novel parametrized models for molecular electronic structure have been derived within propagator theory (Linderberg and Öhrn, 1973) and Green's function techniques have also had a major impact on the theory of electron–atom and electron–molecule scattering (see, e.g., Csanak *et al.*, 1971).

Section II reviews some of the basic definitions and introduces the notations of the electron propagator. The decoupling problem is stated and general methods of approximation are discussed using a spin orbital basis. The direct pole-residue search as described by Csanak *et al.* (1971) and implemented by Purvis and Öhrn (1974) is discussed for the solution of the working equations to produce the spectral representation of the electron propagator. Section III deals with the concept of moment-conserving decoupling proposed by Lukman and Goscinski (1970). The connection with Padé approximants is exploited and illustrative calculations are reported showing the deficiencies connected with this approach to the decoupling problem.

The idea of diagram-conserving decoupling is described in Section IV following the work of Born and Öhrn (1979). Perturbation theory is used to compare the superoperator formalism (Pickup and Goscinski, 1973) and the diagrammatic expansion method. Approximations are introduced and applications are reported to illustrate the theory. In Section V the concept of renormalized decouplings is discussed with diagrammatic analysis and computational applications to molecular ionization energies and electron affinities.

Photoionization intensities, as they relate to the electron propagator, are discussed in Section VI. A completely satisfying theoretical approach should have the capability to deal with multiple-electron detachment (and attachment) processes. Presently, most theoretical efforts struggle with single-electron detachment or attachment and we are here limiting the discussion to such processes. The emphasis is placed on the calculation of relative intensities of lines in photoelectron spectra.

II. Basic Definitions and Notations

A. Spectral Representation and Equation of Motion of the Electron Propagator

The importance of the electron propagator for the study of single-electron attachment and detachment processes is readily appreciated from its spectral form. In a spin orbital basis this form of the electron propagator is a matrix with elements

$$G_{ij}(E) = \sum_{n} \left[\frac{\langle N|a_i|N+1, n\rangle\langle N+1, n|a_j^\dagger|N\rangle}{E - E_n(N+1) + E_0(N) + i\eta} + \frac{\langle N|a_j^\dagger|N-1, n\rangle\langle N-1, n|a_i|N\rangle}{E + E_n(N-1) - E_0(N) - i\eta} \right], \tag{II.1}$$

which have only simple poles in the energy (frequency) plane when the spin orbital basis is discrete and finite. When the convergence parameter $\eta > 0$ approaches 0 the poles are all on the real energy axis and equal to the differences between the stationary-state total energies of the N-electron ground state and the appropriate final ion states. The overlap amplitudes between such states

$$f_n(j) = \langle N+1, n|a_j^\dagger|N\rangle \quad \text{and} \quad g_n(i) = \langle N-1, n|a_i|N\rangle \tag{II.2}$$

involve the electron field operators a_i and $a_j^\dagger$ (of the spin orbital basis) that satisfy the usual anticommutation relations.

$$[a_i, a_j]_+ = [a_i^\dagger, a_j^\dagger]_+ = [a_i, a_j^\dagger]_+ - \delta_{ij} = 0. \tag{II.3}$$

The Hartree–Fock spin orbitals, occupied and unoccupied, for the N-electron ground state will be employed as the spin orbital basis for the applications discussed here. These overlap amplitudes enter the calculations of intensities of photoelectron spectra, as will be shown.

The N-electron ground state $|N\rangle$ and the ion states $|N+1, n\rangle$, $|N-1, n\rangle$ are eigenstates to the many-electron Hamiltonian

$$H = \sum_i \sum_j (i|h|j)a_i^\dagger a_j + \tfrac{1}{4}\sum\sum\sum\sum \langle ij||kl\rangle a_i^\dagger a_j^\dagger a_l a_k, \tag{II.4}$$

where the one-electron terms $(i|h|j)$ consist of the kinetic and potential energies of an electron due to the Coulombic interaction with the nuclear framework and where

$$\langle ij||kl\rangle = \int i^*(1)j^*(2)r_{12}^{-1}(1 - P_{12})k(1)l(2)\, d(1)\, d(2) \tag{II.5}$$

is an antisymmetrized two-electron integral. This Hamiltonian operates in the Fock space spanned by all independent eigenstates of the number operator of the total number of electrons possible to construct with the chosen, finite spin orbital basis.

The fact that the electron propagator depends on the electron field operators a_i, and $a_j^\dagger$ according to Eq. (II.1) justifies the notation of Linderberg and Öhrn (1973)

$$G_{ij}(E) = \langle\langle a_i; a_j^\dagger\rangle\rangle_E. \tag{II.6}$$

The spectral form of the electron propagator can be manipulated using the identities

$$\begin{aligned} &E(E - E_n(N+1) + E_0(N))^{-1} \\ &\quad = 1 + (E_n(N+1) - E_0(N))(E - E_n(N+1) + E_0(N))^{-1}, \end{aligned} \qquad \text{(II.7)}$$

$$\langle N|a_i|N+1, n\rangle(E_n(N+1) - E_0(N)) = \langle N|[a_i, H]_-|N+1, n\rangle, \qquad \text{(II.8)}$$

and similar expressions for the second term in the sum of Eq. (II.1). These algebraic exercises yield

$$E\langle\langle a_i; a_j^\dagger\rangle\rangle_E = \langle N|[a_i, a_j^\dagger]_+|N\rangle + \langle\langle [a_i, H]_-; a_j^\dagger\rangle\rangle_E, \qquad \text{(II.9)}$$

which is the equation of motion for $G_{ij}(E)$. The second term of the right-hand side is a quantity of the same form as $G_{ij}(E)$ in Eq. (II.1), but with the commutator $[a_i, H]_-$ replacing a_i. It can then be seen that iteration of this equation yields N coupled equations relating the electron propagator to many-electron propagators. The approximations and various considerations of consistency that must be introduced in order to terminate this chain of equations at some suitable level is referred to as the decoupling problem.

Superoperators are employed (Pickup and Goscinski, 1973; Purvis and Öhrn, 1977) to recast the commutator and anticommutator algebras resulting from Eq. (II.9) into standard matrix and vector space techniques. One introduces a linear space, the elements of which are fermion-like electron field operators in general expressed as linear combinations of field operator products

$$\{a_k,\ a_k^\dagger a_l a_m \quad (l < m),\quad a_j^\dagger a_k^\dagger a_l a_m a_n \quad (l < m < n, \ldots)\}. \qquad \text{(II.10)}$$

For X and Y being general elements of this linear space, we define a superoperator identity $\hat{I}$, and a superoperator Hamiltonian $\hat{H}$, such that

$$\hat{I}X = X, \qquad \hat{H}X = [X, H]_-, \qquad \text{(II.11)}$$

and a scalar product

$$(X|Y) = \langle N|[Y, X^\dagger]_+|N\rangle. \qquad \text{(II.12)}$$

These definitions permit the identification

$$\langle\langle a_i; a_j^\dagger\rangle\rangle_E = (a_j|(E\hat{I} - \hat{H})^{-1}a_i). \qquad \text{(II.13)}$$

Introducing vector arrays of electron field operators, we can write the matrix relation

$$\mathbf{G}(E) = \langle\langle \mathbf{a}; \mathbf{a}^\dagger\rangle\rangle_E = (\mathbf{a}|(E\hat{I} - \hat{H})^{-1}\mathbf{a}). \qquad \text{(II.14)}$$

This provides the starting point for approximations and different schemes of decoupling.

The idea of inner projections and the techniques of partitioning (Löwdin, 1965) have been employed for systematic approximate treatments (Nehrkorn *et al.*, 1976; Purvis and Öhrn, 1977) of the electron propagator. With an inner projection, the superoperator resolvent becomes a matrix inverse

$$\mathrm{G}(E) = (\mathbf{a}|\mathbf{h})(\mathbf{h}|(E\hat{I} - \hat{H})\mathbf{h})^{-1}(\mathbf{h}|\mathbf{a}), \tag{II.15}$$

where the inner projection manifold **h** consists of elements from the linear space of electron field operators [Eq. (II.10)]. When the manifold **h** spans this entire space, no approximation has been made. Partitioning of the manifold $\mathbf{h} = \{\mathbf{a};\ \mathbf{f}\}$ with the orthogonality condition $(\mathbf{a}|\mathbf{f}) = \mathbf{0}$ leads to the expression of Pickup and Goscinski (1973)

$$\mathrm{G}^{-1}(E) = (\mathbf{a}|(E\hat{I} - \hat{H})\mathbf{a}) - (\mathbf{a}|\hat{H}\mathbf{f})(\mathbf{f}|(E\hat{I} - \hat{H})\mathbf{f})^{-1}(\mathbf{f}|\hat{H}\mathbf{a}). \tag{II.16}$$

Various approximate treatments can now be carried out readily by truncating the manifold **f**, and by different choices of approximate ground states $|N\rangle$ defining the scalar product of Eq. (II.12). Some systematization of these approximations is usually brought about by perturbation theory.

An unperturbed superoperator Hamiltonian $\hat{H}_0$ is chosen and the partitioning $\hat{H} = \hat{H}_0 + \hat{V}$ is obtained with the associated expression $H = H_0 + V$ for the many-electron Hamiltonian of Eq. (II.4). A common starting point for many different approximations is to write

$$H_0 = \sum_k \varepsilon_k a_k^\dagger a_k, \tag{II.17}$$

with

$$\varepsilon_k\ \delta_{kl} = (k|h|l) + \sum_i \sum_j \langle ki||lj\rangle \langle a_i^\dagger a_j \rangle, \tag{II.18}$$

i.e., a spin orbital energy, and thus the spin orbital basis is the Hartree–Fock basis. The N-electron ground state can correspondingly be expressed as

$$|N\rangle = |\mathrm{O}\rangle + |C\rangle, \tag{II.19}$$

with

$$|\mathrm{O}\rangle = a_1^\dagger a_2^\dagger a_3^\dagger \cdots a_N^\dagger|\mathrm{vac}\rangle, \tag{II.20}$$

and $|C\rangle$ denoting the correlation corrections. The vacuum state is labeled $|\mathrm{vac}\rangle$. The inverse of the Hartree–Fock electron propagator is

$$\mathrm{G}_0^{-1}(E) = (\mathbf{a}(E\hat{I} - \hat{H}_0)\mathbf{a}), \tag{II.21}$$

with the average defining the scalar product of Eq. (II.12) being taken with respect to $|\mathrm{O}\rangle$. The Eq. (II.16) can now be expressed as a Dyson equation (Dyson, 1949):

$$\mathrm{G}^{-1}(E) = \mathrm{G}_0^{-1}(E) - \Sigma(E). \tag{II.22}$$

The self-energy $\Sigma(E)$, here defined as the remainder in Eq. (II.16) once the propagator $\mathrm{G}_0(E)$ of uncorrelated processes is chosen, contains the effect of $\hat{V}$ and $|C\rangle$, and the dynamical relaxation and correlation effects.

A number of applications of approximations to $\mathrm{G}(E)$, based on different choices of operator manifolds, have been reported in the literature. Pickup and Goscinski (1973) chose the inner projection manifold to consist of single- and triple-operator products and neglected the effect of V and $|C\rangle$ in the self-energy. This approximation was applied by Purvis and Öhrn (1974) to the helium atom and the nitrogen molecule and was later extended by them to include the effect of the full superoperator Hamiltonian in the self-energy. Redmon *et al.* (1975) have derived an approximation that includes single-, triple-, and quintuple-operator products in $\mathbf{h}$, and applied this to the neon atom. Several approximations involving single- and triple-operator products in the inner projection manifold, in conjunction with correlated reference states $|N\rangle$, have also been reported (Purvis and Öhrn, 1975; Jørgensen and Simons, 1975).

One difficulty with this type of approach is the somewhat unwieldy order analysis in higher orders of electron interaction, since the inclusion of higher operator products should be balanced with the inclusion of correlation corrections in the reference state $|N\rangle$. Another problem has to do with the size of the inverse matrix in the second term of Eq. (II.16), and is mainly a computational difficulty. The inversion of this matrix requires the determination of all its eigenvectors and eigenvalues, and the dimension of the matrix increases rapidly with the size of the spin orbital basis. When $\mathbf{f}$ consists of only triple products, the dimension is roughly proportional to $NM(M - N)$, where N is the number of electrons, and M is the size of the spin orbital basis. The problem of finding all eigenvalues of this very large matrix has forced the investigation of simple diagonal or block diagonal approximations (Purvis and Öhrn, 1976). Some of these show promise but the use of diagonal or near-diagonal approximations with the inclusion of quintuple- and higher operator products has not received much attention although preliminary investigations clearly indicate this could be quite successful. The extension of the inner projection manifold to higher operator products is not simply related to an order-by-order extension of the perturbation analysis. In fact, Redmon *et al.* (1975) have suggested that certain quintuple or even higher products should be included before all triple products and have pointed out that this would be especially important for an adequate description of "shake-up" processes. This observation has recently been confirmed by Herman *et al.* (1980).

Other formal and computational problems might arise from assuming Hermiticity for the superoperator Hamiltonian,

$$(X|\hat{H}Y) = (\hat{H}X|Y) = (Y|\hat{H}X)^* \tag{II.23}$$

which is generally not satisfied for approximate reference states $|N\rangle$. This has been discussed by Nehrkorn *et al.* (1976).

B. Method of Solution

The solution of Eq. (II.16) consists of finding the poles and Feynman–Dyson amplitudes of the electron propagator and writing a spectral representation similar to that of the exact propagator in Eq. (II.1). The procedure for obtaining the spectral representation from the Dyson equation has been discussed by Layzer (1963), Csanak *et al.* (1971), and Purvis and Öhrn (1974). It begins with a solution to the energy-dependent eigenvalue problem:

$$\mathrm{L}(E)\boldsymbol{\phi}(E) = \boldsymbol{\phi}(E)\mathrm{W}(E), \tag{II.24}$$

where

$$\mathrm{L}(E) = (\mathbf{a}|\hat{H}\mathbf{a}) + \boldsymbol{\Sigma}(E), \tag{II.25}$$

$$\boldsymbol{\phi}(E)\boldsymbol{\phi}^{\dagger}(E^*) = \mathbf{1}, \tag{II.26}$$

and $\mathrm{W}(E)$ is a diagonal eigenvalue matrix. Expanding in terms of the eigenfunctions, $\boldsymbol{\phi}(E)$, $\mathrm{G}(E)$ assumes the form

$$\mathrm{G}(E) = \boldsymbol{\phi}(E)[E\mathbf{1} - \mathrm{W}(E)]^{-1}\,\boldsymbol{\phi}^{\dagger}(E), \tag{II.27}$$

and the poles are those values of E satisfying the equation

$$E_k = W_k(E_k). \tag{II.28}$$

The energy dependence of the eigenvalues, $W_k(E)$, is sketched in Fig. 1, which shows that the poles occur at the intersections of these curves with a line of unit slope passing through the origin. When the inner projection manifold is energy independent, the slope of the $W_k(E)$ curves is always negative since

$$d\boldsymbol{\Sigma}(E)/dE = -(\mathbf{a}|\hat{H}\mathbf{f})(\mathbf{f}|(E\hat{I} - \hat{H})\mathbf{f})^{-2}(\mathbf{f}|\hat{H}\mathbf{a}), \tag{II.29}$$

and the number of propagator poles between any pair of self-energy poles is equal to the number of basis functions in that symmetry (Purvis and Öhrn, 1974).

From the spectral representation, it was noted that the exact propagator has only simple poles, and it is easily shown that the residues at the poles are precisely the Feynman–Dyson amplitudes. Assuming that the approximate propagator in Eq. (II.16) also has only simple poles, the residues can be obtained from elementary residue calculus as

$$\lim_{E\to E_k} (E - E_k)G_{ij}(E) = \Gamma_k\phi_{ik}(E_k)\phi_{jk}^*(E_k) \tag{II.30}$$

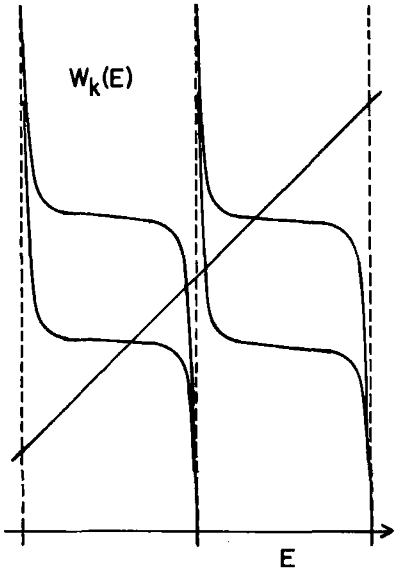

Fig. 1. A sketch of the energy dependence of the function $W_k(E)$ between self-energy poles (indicated by vertical dashed lines). Propagator poles occur at the intersections of these curves with a line of unit slope.

where

$$\Gamma_k^{-1} = \{1 - [dW_k(E)/dE]\}_{E=E_k}. \tag{II.31}$$

According to the Mittag-Leffler theorem (Mittag-Leffler, 1880), the electron propagator can now be written as

$$G_{ij}(E) = \sum_k \frac{\Gamma_k \phi_{ik}(E_k)\phi_{jk}^*(E_k)}{E - E_k} \tag{II.32}$$

which has the form of the spectral representation.

III. Moment-Conserving Decouplings

A. Padé Approximants and the Extended Series of Stieltjes

The evaluation of special functions assumes a central role in applied mathematics. A large number of these functions, from the simple trigonometric and exponential functions to the more complex, hypergeometric and Green's functions, have power series expansions. Their evaluation, therefore, consists of summing the corresponding series expansion. When the series is slowly convergent or when only a limited number of expansion coefficients are known (e.g., through perturbation theory), it may not be practical, or even possible, to evaluate the series term by term until a desired accuracy has been achieved. In these cases, optimal approximations based on a limited number of expansion coefficients are sought. This general problem was first studied by Tchebychev (1874) and Stieltjes (1894) for the series that bear their names and is referred to as the problem of moments. (For more recent reviews of this problem see, e.g., Wall, 1948; Shohat and Tamarkin, 1963; or Vorobyev, 1965.) A general solution of this problem was given by Padé (1892) and is known as the Padé approximant method (Baker, 1975).

Given a function $f(z)$ (z complex) that admits the formal, but not necessarily convergent, power series expansion

$$f(z) = \sum_{k+0}^{\infty} a_k z^k, \tag{III.1}$$

the $[N, M]$ Padé approximant is defined as a rational fraction of the form $P(z)/Q(z)$, where $P(z)$ is a polynomial of degree M and $Q(z)$ is a polynomial of degree N. The coefficients of these polynomials are uniquely determined by equating like powers of z in the equation

$$f(z)Q(z) - P(z) = 0 \text{ (through order } z^{N+M}) \tag{III.2}$$

with the auxiliary condition $Q(0) = 1$. The expansion of $P(z)/Q(z)$, therefore, coincides with Eq. (III.1) through the $(N + M)$th power of z and provides an approximation to the remaining terms.

The term-by-term convergence of Eq. (III.1) is replaced by the convergence of sequences of approximants (such as $[N, N]$, $N = 1, 2, 3, \ldots$) in the Padé approximant method, and although general convergence theorems are difficult to prove for arbitrary series, there exist several extensive special cases for which convergence has been proven. For these series, the Padé approximant can often be shown to extend the natural region of convergence (Baker, 1970) and may be viewed as a method of approximate analytic continuation. A sequence of Padé approximants, therefore, may converge rapidly when the original series expansion converges slowly or not at all.

Two series that have been extensively studied in the problem of moments and for which sequences of Padé approximants have been proven to converge are the series of Stieltjes (1894) and the extended series of Stieltjes (Hamburger, 1920, 1921a,b; also known as the Hamburger moment problem). A series is of the Stieltjes type if and only if the coefficients a_k in Eq. (III.1) can be identified as moments of a distribution

$$a_k = \int_0^{\infty} x^k \, d\psi(x) \tag{III.3}$$

where $\psi(x)$ is a bounded, nondecreasing function with infinitely many points of increase in the interval $(0, \infty)$. The extended series of Stieltjes is defined similarly for the extended interval $(-\infty, \infty)$.

The extended series of Stieltjes has particular significance owing to its intimate relationship with resolvents of Hermitian operators. For any operator A we can define the operator function

$$R(zA) = (1 - zA)^{-1} \tag{III.4}$$

which is trivially related to the resolvent of A. When A is Hermitian, the spectral theorem (Riesz and Sz.-Nagy, 1955) ensures a unique integral representation of $R(zA)$ having the form

$$R(zA) = \int_{-\infty}^{\infty} \frac{dE(\lambda)}{1 - z\lambda}. \tag{III.5}$$

The operator $E(\lambda)$ is called an orthogonal resolution of the identity, and when A has only a discrete spectrum, it can be written

$$E(\lambda) = \sum_k \Theta(\lambda - a_k)|\phi_k\rangle\langle\phi_k|, \tag{III.6}$$

where a_n and ϕ_n are the eigenvalues and eigenfunctions of A. For any vector f in the domain of A^n for all n, the function

$$\langle f|R(zA)f\rangle = R_f(z) = \int_{-\infty}^{\infty} \frac{dE_f(\lambda)}{1 - z\lambda} \tag{III.7}$$

represents either an extended series of Stieltjes or a rational fraction depending on whether $E_f(\lambda)$ has an infinite or finite number of points of increase (Masson, 1970).

In view of possible applications of the Padé approximant method to the superoperator resolvent, we state the content of two theorems regarding the extended series of Stieltjes and discuss some properties of two particular sequences of Padé approximants to these series. Wall (1948) proves that the necessary and sufficient condition for $f(z)$ to be an extended series of Stieltjes is

$$\det\begin{pmatrix} a_0 & a_1 & \cdots & a_n \\ a_1 & a_2 & \cdots & a_{n+1} \\ & & \vdots & \\ a_n & a_{n+1} & \cdots & a_{2n} \end{pmatrix} > 0; \qquad n = 0, 1, 2, \ldots . \tag{III.8}$$

It is also of interest to us to note that (Masson, 1970) if $f(z)$ is an extended series of Stieltjes and the associated moment problem is determinant,[1] then, for fixed $j = 0, \pm 1, \pm 2, \ldots, m$, the sequence $[N, N + 2j + 1]$ of Padé approximants converges to $f(z)$ for $\mathrm{Im}(z) \neq 0$. The convergence is uniform, i.e.,

$$\lim_{N\to\infty} \|[N, N + 2j + 1] - f(z)\| = 0, \qquad \text{(III.9)}$$

with respect to z in any compact region in the upper or lower z half-plane.

In addition to being uniformly convergent, sequences of $[N, N]$ and $[N, N - 1]$ Padé approximants to extended series of Stieltjes have two other features that make them particularly attractive for computational applications. First, these approximants are closely related to variational methods (Nuttall, 1970, 1973). When the operator $R(zA)$ [defined in Eq. (III.5)] is positive definite, the $[N, N]$ and $[N, N - 1)$ approximants provide the following bounds to $R_f(z)$ (Goscinski and Brändas, 1971):

$$[N, N] \geqq R_f(z) \geqq [N, N - 1]. \qquad \text{(III.10)}$$

For resolvent operators such as the superoperator resolvent that are indefinite, bounding properties are more difficult to establish. Vorobyev (1965) has shown, however, that the poles of the $[N, N - 1]$ approximant to $R_f(z)$ are equivalent to the eigenvalues obtained from the usual Rayleigh–Ritz variational problem

$$\mathrm{extr}(\langle\psi|A|\psi\rangle/\langle\psi|\psi\rangle) \qquad \text{(III.11)}$$

where $\psi = c_0 f + c_1 Af + \cdots + c_{N-1}A^{N-1}f$, and the coefficients $\{c_i\}$ are variationally determined. In this sense, the poles of $[N, N - 1]$ to $R_f(z)$ are variationally optimum, but they have no definite bounding properties.

The second attractive feature of the $[N, N]$ and $[N, N - 1]$ approximants is the ease with which they may be computed. Rather than solving Eq. (III.2) to obtain the coefficients of the polynomials $P(z)$ and $Q(z)$, these approximants may be expressed directly in terms of the series coefficients $\{a_k\}$ using matrix formulae derived by Nuttall (1967) and Goscinski and Brändas (1971). For the $[N, N - 1]$ approximant, we have

$$[N, N - 1] = \mathbf{a}_0^\dagger[\mathbf{A}_0 - z\mathbf{A}_1]^{-1}\mathbf{a}_0, \qquad \text{(III.12)}$$

where, in general, $\mathbf{a}_i$ is a column vector with the elements $a_i, a_{i+1}, \ldots, a_{i+N-1}$, and $\mathbf{A}_i$ is an $N \times N$ square matrix with the columns $\mathbf{a}_i, \mathbf{a}_{i+1}, \ldots,$

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[1] The moment problem is said to be determinant if there is a unique, bounded, nondecreasing function $\psi(x)$ satisfying the moment conditions in Eq. (III.3) and the supplementary conditions $\psi(-\infty) = 0$ and

$$\psi(x) = \lim_{\varepsilon\to 0} \tfrac{1}{2}\{\psi(x + \varepsilon) + \psi(x - \varepsilon)\}.$$

$\mathbf{a}_{i+N-1}$. Similarly for the $[N, N]$ approximant we can write

$$[N, N] = a_0 + z\mathbf{a}_1^\dagger[\mathbf{A}_1 - z\mathbf{A}_2]^{-1}\mathbf{a}_1. \tag{III.13}$$

B. Moment-Conserving Decoupling

Expanding the superoperator resolvent in Eq. (II.14) and multiplying both sides of the equation by E, the electron propagator can be expressed as the moment expansion

$$E\mathbf{G}(E) = \sum_{k=0}^{\infty} E^{-k}(\mathbf{a}|\hat{H}^k\mathbf{a}). \tag{III.14}$$

Before the Padé approximant method may be applied to this equation, however, the conventional definition of the Padé approximant must be generalized to matrix Padé approximants (Baker, 1975). This generalization is achieved by replacing the moment coefficients by the corresponding moment matrices and noting that these matrices do not commute when performing subsequent algebraic manipulations. Using Eq. (III.12) to represent the $[N, N - 1]$ approximant to $E\mathbf{G}(E)$, we obtain

$$E\mathbf{G}(E) = \mathbf{m}_0^\dagger(\mathbf{M}_0 - E^{-1}\mathbf{M}_1)^{-1}\mathbf{m}_0, \tag{III.15}$$

or multiplying each side of this equation by E^{-1}, Eq. (III.15) becomes

$$\mathbf{G}(E) = \mathbf{m}_0^\dagger(E\mathbf{M}_0 - \mathbf{M}_1)^{-1}\mathbf{m}_0, \tag{III.16}$$

where $\mathbf{m}_0$ is now a column matrix with block elements

$$\mathbf{m}_0 = \begin{pmatrix} \mathbf{c}_0 \\ \mathbf{c}_1 \\ \vdots \\ \mathbf{c}_{N-1} \end{pmatrix}; \qquad \mathbf{c}_i = (\mathbf{a}|\hat{H}^i\mathbf{a}). \tag{III.17}$$

If $\mathbf{c}_i$ has the dimensions $M \times M$, $\mathbf{M}_i$ is an $NM \times NM$ square matrix with columns $\mathbf{m}_i, \mathbf{m}_{i+1}, \ldots, \mathbf{m}_{i+N-1}$.

There is a close relationship between Eq. (III.16) and the inner projection of the superoperator resolvent

$$\mathbf{G}(E) = (\mathbf{a}|\mathbf{h})(\mathbf{h}|(E\hat{I} - \hat{H})\mathbf{h})^{-1}(\mathbf{h}|\mathbf{a}). \tag{III.18}$$

Goscinski and Lukman (1970) have shown that if the inner projection manifold is chosen to consist of

$$\mathbf{h} = \{a_k\}U\{\hat{H}a_k\}U \cdots U\{\hat{H}^{N-1}a_k\}, \tag{III.19}$$

the inner projection and the $[N, N - 1]$ Padé approximant are equal.

Since in general the $[N, M]$ Padé approximant conserves the first $N + M + 1$ moments in the moment expansion, this choice of inner projection manifolds for the superoperator resolvent is called a moment-conserving decoupling of the equation of motion.

An examination of the $[N, N - 1]$ approximant to the electron propagator shows that its poles are given by the eigenvalues of

$$\mathbf{M}_1\mathbf{c} = \mathbf{M}_0\mathbf{c}d. \tag{III.20}$$

The matrix $\mathbf{M}_0$ is the metric matrix and, by virtue of the operator scalar product, is always positive definite

$$\mathbf{M}_0 = (\mathbf{h}|\mathbf{h}) = \mathrm{Tr}\{\rho[\mathbf{h}\mathbf{h}^\dagger + \mathbf{h}^\dagger\mathbf{h}]\} > 0. \tag{III.21}$$

The determinants of the metric matrices corresponding to various truncations of the moment-conserving inner projection manifold, i.e.,

$$\det(\mathbf{h}_0|\mathbf{h}_0) > 0, \qquad \mathbf{h}_0 = \{\mathbf{a}\}, \tag{III.22}$$

$$\det(\mathbf{h}_1|\mathbf{h}_1) > 0, \qquad \mathbf{h}_1 = \{\mathbf{a}\}U\{\hat{H}\mathbf{a}\}, \tag{III.23}$$

$$\vdots$$

provide the necessary and sufficient conditions to prove that the electron propagator is an extended series of Stieltjes. Consequently, the sequence of $[N, N - 1]$ Padé approximants to the electron propagator should be uniformly convergent and should have variationally optimum properties.

The spectral representation of the electron propagator [Eq. (II.1)] consists of two summations: one that has poles in the lower half of the complex E plane corresponding to electron detachment energies and one which has poles in the upper half-plane corresponding to electron attachment energies. Based on the physical argument that the removal of an electron from a stable atomic or molecular system always requires energy, we obtain a separation of the superoperator resolvent yielding a negative definite operator for electron detachment processes. The poles of the $[N, N - 1]$ approximants are then upper bounds to the exact ionization energies obtainable with a given basis. No formal proof has been put forth for this but an overwhelming amount of numerical data seem to substantiate this conjecture. In particular, the $[1, 0]$ approximant, which is easily verified to be the Hartree–Fock propagator, generally yields poles larger in absolute value than experimental ionization energies. Possible numerical exceptions to this rule may be pointed out, e.g., the near Hartree–Fock limit calculation of Cade *et al.* (1966) on diatomic nitrogen. In this calculation, the magnitude of the $1\pi_u$ orbital energy is slightly (0.2 eV) smaller than the experimental $1\pi_u$ ionization energy. If, on the other hand, the $X^2\Pi_u$ ion state was fortuitously better described than the ground state with the extended basis used, this result would still be an upper bound to the exact ionization energy *in that basis.*

Relaxation and correlation corrections are incorporated in any $[N, N-1]$ Padé approximant beyond the $[1, 0]$ or Hartree–Fock approximant. In particular, we have studied that $[2, 1]$ approximant in some detail. This approximant corresponds to the truncation

$$\mathbf{h} = \{\mathbf{a}\}U\{\hat{H}\mathbf{a}\} \tag{III.24}$$

of the inner projection manifold and conserves the first four moment matrices. The operators $\{f_i | f_i = \hat{H}a_i\}$ consist of a sum over all triple products of simple field operators with each operator product in the sum weighted by an antisymmetrized, two-electron integral. These linear combinations provide a significant reduction in the subspace of triple operators, thus overcoming one major limitation of the operator product decoupling.

Another type of moment-conserving decoupling of the electron propagator equations of motion has been analyzed by Babu and Ratner (1972). This decoupling is achieved by truncating the moment expansion after the mth moment and replacing the mth moment matrix with

$$\mathbf{c}_m = \mathbf{c}_m\mathrm{G}(E). \tag{III.25}$$

Solving the truncated moment expansion for $\mathrm{G}(E)$ yields

$$(E^{m+1}\mathbf{1} - \mathbf{c}_m)\mathrm{G}(E) = \sum_{k=0}^{m-1} E^{m-k}\mathbf{c}_k \tag{III.26}$$

or

$$\mathrm{G}(E) = (E^{m+1}\mathbf{1} - \mathbf{c}_m)^{-1} \sum_{k=0}^{m-1} E^{m-k}\mathbf{c}_k. \tag{III.27}$$

These rational approximants formally conserve m moments but are not of the Padé type (as Babu and Ratner incorrectly identify them) since the auxiliary equation $Q(0) = 1$ is not satisfied, i.e.,

$$\mathrm{Q}(0) = -\mathbf{c}_m \neq 1. \tag{III.28}$$

The auxiliary equation guarantees the uniqueness of the Padé approximants: only one $[N, N-1]$ Padé approximant will conserve exactly m moments. The nonuniqueness of this decoupling scheme is easily demonstrated by replacing Eq. (III.25) with

$$\sum_{k=n}^{m} E^{-k}\mathbf{c}_k = \sum_{k=n}^{m} E^{-k}\mathbf{c}_k\mathrm{G}(E), \qquad 0 < n \leq m. \tag{III.29}$$

Solving for $\mathrm{G}(E)$,

$$\left[E\mathbf{1} - \sum_{k=n}^{m} E^{-k}\mathbf{c}_k\right] \mathrm{G}(E) = \sum_{l=0}^{n-1} E^{-l}\mathbf{c}_l \tag{III.30}$$

$$\mathrm{G}(E) = \left[E^{m}\mathbf{1} - \sum_{k=n}^{m} E^{m-k}\mathbf{c}_k\right]^{-1} \sum_{l=0}^{n-1} E^{m-l}\mathbf{c}_l, \tag{III.31}$$

we obtain m rational approximants ($n = 1, \ldots, m$) that formally conserve m moments.

C. Method of Solution

The first step in obtaining the spectral representation of the electron propagator with the moment-conserving decoupling is the evaluation of the necessary moment matrices. The first four moment matrices that are necessary to construct the [2, 1] approximant have been evaluated by Redmon (1975) using the grand canonical density operator [Eq. (II.44)]. The result for the matrix elements of $(\mathbf{a}|\hat{H}^3\mathbf{a})$ appears in Appendix 2 and corrects an error in the original derivation (L. T. Redmon, private communication, 1977).

Once the moment matrices have been evaluated, the matrices $\mathbf{M}_0$ and $\mathbf{M}_1$ are constructed and the corresponding eigenvalue problem, Eq. (III.20), must be solved. In general, the dimension of the eigenvalue problem increases linearly with the size of the inner projection manifold, i.e., the $[N, N - 1]$ approximant presents an eigenvalue problem of dimension NM, where M is the size of the spin orbital basis. For the [2, 1] approximant, therefore, the dimension of this problem is only twice the size of the spin orbital basis. This means that for even rather large basis sets, standard matrix eigenvalues techniques may be employed to solve this problem in nonpartitioned form. As a consequence, all the poles and the spectral density of the electron propagator are obtained from a single matrix diagonalization, thus avoiding the energy-dependent pole search.

Denoting the eigenvectors by $\mathbf{c}$, where

$$\mathbf{c}\mathbf{c}^{\dagger} = \mathbf{M}_0^{-1}, \tag{III.32}$$

and the eigenvalues by the diagonal matrix $\mathbf{d}$, the spectral representation of the electron propagator can be derived,

$$\mathrm{G}(E) = \mathbf{m}_0^{\dagger}\mathbf{c}\mathbf{c}^{-1}[E\mathbf{M}_0 - \mathbf{M}_1]^{-1}\mathbf{M}_0\mathbf{c}\mathbf{c}^{-1}\mathbf{M}_0^{-1}\mathbf{m}_0 \tag{III.33}$$

$$= \mathbf{m}_0^{\dagger}\mathbf{c}[E\mathbf{1} - \mathbf{d}]^{-1}\mathbf{c}^{-1}\mathbf{M}_0^{-1}\mathbf{m}_0. \tag{III.34}$$

Defining the matrix

$$\mathbf{x} = \mathbf{m}_0^{\dagger}\mathbf{c}, \tag{III.35}$$

which is rectangular with the dimensions $M \times NM$, Eq. (III.34) becomes

$$\mathbf{G}(E) = \mathbf{x}(E\mathbf{1} - \mathbf{d})^{-1}\mathbf{x}^{\dagger}. \tag{III.36}$$

This equation conserves the first $2N$ moment matrices of the moment expansion, which implies, in particular,

$$\mathbf{x}\mathbf{x}^{\dagger} = (\mathbf{a}|\mathbf{a}) = \mathbf{1} \tag{III.37}$$

from the conservation of the first moment.

The complete solution of the electron propagator that is conveniently obtained with this decoupling can be used to determine a self-consistent, single-particle reduced density matrix (1-matrix). The i,jth element of the 1-matrix can be computed from the contour integral (Linderberg and Öhrn, 1973)

$$\langle a_i^{\dagger} a_j \rangle = (2\pi i)^{-1} \int_c G(E)_{ij}\, dE. \tag{III.38}$$

The contour c runs from $-\infty$ to ∞ along the real axis and encloses only poles of $G(E)_{ij}$ that lie below the chemical potential (μ) when finally closed in the upper half of the complex E plane. The integral is evaluated to be

$$\langle a_i^{\dagger} a_j \rangle = \sum_{k \leq \mu} \lim_{E \to d_k} (E - d_k) G(E)_{ij} \tag{III.39}$$

$$= \sum_{k \leq \mu} x_{ik} x_{jk}^{*}. \tag{III.40}$$

Owing to the orthonormality of the spectral density elements [Eq. (III.37)]

$$\sum_{k \leq \mu} x_{ik} x_{jk}^{*} = \delta_{ij} |x_{ij}|^2, \tag{III.41}$$

it follows that the 1-matrix is diagonal with occupation numbers determined by

$$\langle n_i \rangle = \sum_{k \leq \mu} |x_{ik}|^2. \tag{III.42}$$

Using pure state occupation numbers of zero and one in the grand canonical density operator (Linderberg and Öhrn, 1973) for the initial computation of G(E), then occupation numbers determined from Eq. (III.42) on subsequent computations, a self-consistent set of occupation numbers can be sought.

D. Computational Considerations and Applications

The most time-consuming step in the construction of the [2, 1] Padé approximant to the electron propagator is the construction of the moment matrices. The fourth moment matrix (given in Appendix 2) is particularly difficult since it involves five unrestricted orbital summations plus another two symmetry-restricted orbital summations of two-electron integrals. Using direct summation techniques, the time needed to construct this matrix is roughly proportional to N^7. This is a formidable computational problem, but one that must be accepted in favor of the more manageable matrix dimensions.

Fortunately, the N^7 problem is not as intimidating as it might seem on first appearance. The "brute-force" summation of two-electron integrals in the moment matrices resums certain partial sums that may appear in more than one term or matrix element. These redundant summations can be avoided with considerable savings in computer time by computing the partial sums once and reusing them. Two specific partial sums we have employed are

$$[ij|kl] = \sum_{s,s'} \langle ij\|ss'\rangle\langle ss'\|kl\rangle, \tag{III.43}$$

$$\{ij|kl\} = \sum_{s,s'} \langle is\|js'\rangle\langle ks'\|ls\rangle. \tag{III.44}$$

Since these partial sums contain a double summation that is performed only once, the original N^7 problem is effectively reduced to N^5. The construction of the moment matrices is now comparable in difficulty to the transformation of the two-electron integrals from the primitive basis to the computational (usually Hartree–Fock) basis, which is also roughly proportional to N^5.

When the number of two-electron integrals is too large to be held in core, their random access from peripheral storage becomes relatively time consuming. The partial sums are much more efficiently constructed from ordered lists of two-electron integrals that can be read into primary (core) storage when needed. For the partial sums defined above, the two-electron integrals must be sorted into ordered lists of the type $\langle ij|**\rangle$ and $\langle i*|j*\rangle$, where * indicates all orbital indices that yield a nonzero integral for the corresponding i,jth distribution.

The integral sorts are performed using the Yoshimine sorting technique (Yoshimine, 1973). Briefly summarized, this technique involves a partition of available core into a number of buffers. Each buffer holds integrals corresponding to a specific i,j distribution, e.g., $\langle ij|**\rangle$. (When the number of distributions is large, several may be held in each buffer.) Reading through the two-electron integral list, integrals are then sorted into the appropriate buffers. As each buffer fills, it is written to direct-access, peripheral storage and assigned a record number. All record numbers corresponding to integrals from the same buffer are saved in a "chaining" array for that buffer. After the entire integral list has been processed and all buffers have been dumped, it is then possible to chain back through the direct-access records, copying integrals of the same distribution back into core. These integrals may then be further sorted within distributions, e.g., $k < l$ for each i,j, and finally saved sequentially on a peripheral storage device.

Diatomic nitrogen was the first molecule to be studied with the [2, 1] Padé approximant. It is an ideal test case for calculating ionization energies from a correlated, many-electron formalism such as propagator theory since both the Hartree–Fock and ΔE(SCF) approximations incorrectly predict the order of the $3\sigma_g$ and $1\pi_u$ ionizations (Cade *et al.*, 1966). Only when correlation corrections are included is the correct ordering obtained (Cederbaum and Domcke, 1977, and references therein).

A double zeta, contracted basis of Gaussian-type orbitals (GTOs) was employed in this calculation. This basis consisted of Huzinaga's 9s, 5p set of primitive orbitals (Huzinaga, 1965), which was contracted to 4s, 2p (Dunning, 1970). This basis has been optimized by Dunning on the nitrogen atom and is listed in Table I. The corresponding one- and two-electron integrals were calculated at the experimental internuclear separation, R = 2.068 a.u. (Herzberg, 1955), using the MOLECULE integral program (Almlöf, 1974).

The Hartree–Fock calculation and the two-electron integral transformation were performed with the program GRNFNC (Purvis, 1973). The Hartree–Fock total energy with this basis was E(HF) = −108.8782 a.u., which is about 3 eV higher than the result of Cade *et al.* (1966). There is

TABLE I

CONTRACTED GAUSSIAN BASIS FOR NITROGEN

s Orbitals		p Orbitals	
Exponents	Contraction coefficients	Exponents	Contraction coefficients
5909.4400	0.002001	26.7860	0.018257
887.4510	0.015310	5.9564	0.116407
204.7490	0.074293	1.7074	0.390111
59.8376	0.253364	0.5314	0.637221
19.9981	0.600576	0.1654	1.000000
2.6860	0.245111		
7.1927	1.000000		
0.7000	1.000000		
0.2133	1.000000		

TABLE II

Principal Ionization Energies for the Nitrogen Molecule Resulting from the [1, 0] and [2, 1] Propagator Approximants[a]

Orbital	[1, 0]	[2, 1]	Experiment[b]
$1\sigma_g$	427.7	472.4	409.9
$2\sigma_g$	41.6	46.5	37.3
$3\sigma_g$	17.0	30.4	15.5
$1\pi_u$	17.0	23.1	16.8
$1\sigma_u$	427.6	478.8	409.9
$2\sigma_u$	21.0	30.9	18.6

[a] $E(\mathrm{HF}) = -108.8782$ H.

[b] Siegbahn *et al.* (1969).

also a discrepancy in the Hartree–Fock orbital energies. While the calculation of Cade *et al.* predicted the $1\pi_u$ orbital energy to be 0.53 eV below the $3\alpha_g$, this calculation predicts the $1\pi_u$ energy to be 0.05 eV higher. The correct ordering of the $3\alpha_g$ and $1\pi_u$ ionizations with this basis is merely fortuitous, since based on a total energy criterion, the basis of Cade *et al.* is more accurate.

The next step of the calculation involved the integral sorts, partial summations, and the construction of the moment matrices. The poles and spectral density were finally computed as outlined in the previous section and are presented along with the [1, 0] results in Table II. The ionization energies of both approximants seem to be upper bounds to the experimental results of Siegbahn *et al.* (1969), but without exception the results of the [2, 1] approximant are worse than the [1, 0] approximant. In an attempt to incorporate some ground-state correlation into the grand canonical density operator, new occupation numbers were computed from the spectral density and the [2, 1] approximant was recalculated. This calculation, however, yielded no significant improvements in the ionization energies.

In order to ascertain whether the poor results from the [2, 1] approximant for nitrogen are representative of other calculations or just the consequence of a pathological test case, the water molecule was chosen for a second application. Similarly to the calculation for nitrogen, a double zeta contracted basis of GTOs was also employed in this calculation. Huzinaga's 9s, 5p primitive basis for oxygen and 4s primitive basis for hydrogen were contracted with Dunning's coefficients to 4s, 2p and 2s, respectively. The orbital exponents for the hydrogen atoms were scaled

TABLE III

CONTRACTED GAUSSIAN BASIS FOR WATER

Hydrogen s sets		Oxygen s sets		Oxygen p sets	
Exponents	Contraction coefficients	Exponents	Contraction coefficients	Exponents	Contraction coefficients
13.3615	0.032828	7816.5400	0.002031	35.1832	0.019580
2.0133	0.231208	1175.8200	0.015436	7.9040	0.124189
0.4538	0.817238	273.1880	0.073771	2.3051	0.394727
0.1233	1.000000	81.1696	0.247606	0.7171	0.627375
		27.1836	0.611832	0.2137	1.000000
		3.4136	0.241205		
		9.5322	1.000000		
		0.9398	1.000000		
		0.2846	1.000000		

by 1.14 to more realistically represent the effective nuclear charge in the molecule, and the final basis appears in Table III. Again, the integrals were computed with the MOLECULE program at the equilibrium internuclear geometry, $R(\mathrm{OH}) = 1.809$ a.u., angle HOH = 104.5° (Benedict *et al.*, 1956). A total energy of $E(\mathrm{HF}) = -76.0082$ a.u. was computed with the Hartree–Fock portion of GRNFNC and was followed by the two-electron integral transformation. Finally, the integral sorts and partial sums were performed, the moment matrices constructed, and the poles and spectral density obtained for the [2, 1] approximant. The results for both the [1, 0] and [2, 1] approximants are presented in Table IV and

TABLE IV

PRINCIPAL IONIZATION ENERGIES FOR WATER RESULTING FROM THE [1, 0] AND [2, 1] PROPAGATOR APPROXIMANTS[a]

Orbital	[1, 0]	[2, 1]	Experiment[b]
$1a_1$	559.4	619.2	540.2
$2a_1$	37.0	44.7	32.2
$3a_1$	15.4	29.7	14.7
$1b_1$	13.8	32.6	12.6
$1b_2$	19.5	29.6	18.6

[a] $E(\mathrm{HF}) = -76.0082$ H.

[b] Siegbahn *et al.* (1969).

appear to be upper bounds to the experimental ionization energies. Once more, the [2, 1] results are consistently worse than the [1, 0] results. A few iterations on the occupation numbers yielded no significant improvements.

E. Evaluation of the Moment-Conserving Decoupling

Formally, the moment-conserving decoupling is an attractive decoupling procedure. Being closely related to the Padé approximant method, this decoupling allows the application of numerous results from the classical moment problem to propagator theory. In particular, it was proven that the sequence of $[N, N - 1]$ approximants converges uniformly to the exact electron propagator in a given basis, and it was shown that these approximants represent a variationally optimum choice of the inner projection manifold. Why then are the results of the [2, 1] approximant so much worse than the results of the [1, 0] approximant? To answer this question, it is necessary to investigate the approximations introduced in terms of basis quality, density operator, and decoupling procedure.

First of all, since computational economy and not high accuracy was the criterion for the test calculations of nitrogen and water, diffuse basis functions were not included in the basis sets. Such functions are most important for the virtual orbitals and are important in describing electron relaxation and correlation (Purvis and Öhrn, 1974; Cederbaum and Domcke, 1977). Further studies with such diffuse properly augmented basis sets should be carried out.

Second, it is possible that significant ground-state correlation may have been neglected with our choice of Hartree–Fock reference state. Rather than explicitly correlating the reference state (e.g., through perturbation theory), an attempt was made to estimate the effect of correlation through the self-consistent determination of the occupation numbers as described in Section III,C. This procedure was not pursued to true self-consistency since each iteration required a complete recalculation of the [2, 1] approximant. It was obvious, however, after the first few iterations that no significant improvements had been obtained.

Based on the preceding implications, the third approximation—the inner projection manifold truncation—seems to be primarily responsible for the poor numerical results. Owing to the complicated operator sums in this manifold, an order analysis is not readily possible. Consequently, it is extremely difficult to identify the problem with this decoupling procedure. It can only be concluded that the number of moments conserved is not a useful criterion for decoupling.[2] This conclusion is consistent with the

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[2] Babu and Ratner (1972) reported the same conclusion, which was based on an application of their rational approximants to the Hubbard model.

uniform convergence of the $[N, N-1]$ sequence since uniform convergence is not necessarily monotonic, but it suggests that more accurate decouplings require the incorporation of more information about the moment expansion than just the moment matrices. The additional information needed is indeed available, and in the next section, we will demonstrate how it may be extracted using perturbation theory.

IV. Diagram-Conserving Decouplings

A. The Diagrammatic Expansion Method

The decoupling problem that can be formulated as different levels of linearization of the propagator equations of motion as suggested by Linderberg and Öhrn (1967) can be efficiently formulated via the superoperator formalism. Other procedures involve the method of functional derivatives (see, e.g., Csanak *et al.*, 1971) and the diagrammatic expansion method (see, e.g., Mattuck, 1967; Fetter and Walecka, 1971; Cederbaum and Domcke, 1977).

The diagrammatic expansion of the electron propagator is usually derived using time-dependent perturbation theory. The N-electron Hamiltonian is partitioned into an unperturbed part plus a time-dependent perturbation

$$H = H_0 + \exp(-\varepsilon|t|)V, \tag{IV.1}$$

where ε is a small positive quantity. The unperturbed Hamiltonian H_0 is chosen to yield an exactly solvable, eigenvalue problem

$$H_0|\Phi_0\rangle = E_0|\Phi_0\rangle, \tag{IV.2}$$

and the time dependence of the unperturbed eigenstates is given by

$$|\Phi_0(t)\rangle = \exp(-iH_0t)|\Phi_0\rangle. \tag{IV.3}$$

In order to simplify the remaining problem of finding the fully perturbed eigenstates $|\psi(t)\rangle$, it is convenient to introduce the "interaction representation" (Fetter and Walecka, 1971) by the transformation

$$|\Psi_1(t)\rangle = \exp(iH_0t)|\Psi(t)\rangle. \tag{IV.4}$$

In this representation, the Schrödinger equation has the form

$$i[\partial|\Psi_1(t)\rangle/\partial t] = \exp(-\varepsilon|t|)V(t)|\Psi_1(t)\rangle, \tag{IV.5}$$

where

$$V(t) = \exp(iH_0t)V\exp(-iH_0t). \tag{IV.6}$$

The time dependence of the interaction eigenstates can be expressed as

$$|\Psi_I(t)\rangle = U_\varepsilon(t, t_0)|\Psi_I(t_0)\rangle, \tag{IV.7}$$

where $U_\varepsilon(t, t_0)$ is the time-evolution operator. Substituting Eq. (IV.7) into Eq. (IV.5), the evolution operator is found to satisfy the differential equation

$$i[\partial U_\varepsilon(t, t_0)/\partial t] = \exp(-\varepsilon|t|)V(t)U_\varepsilon(t, t_0) \tag{IV.8}$$

with the initial condition

$$U_\varepsilon(t_0, t_0) = 1. \tag{IV.9}$$

It is more convenient to solve for $U_\varepsilon(t, t_0)$ by first transforming Eq. (IV.8) into an integral equation

$$U_\varepsilon(t, t_0) = 1 - i\int_{t_0}^{t} dt_1 \exp(-\varepsilon|t|)V(t_1)U_\varepsilon(t_1, t_0). \tag{IV.10}$$

This integral equation has the form of the Volterra equation of the second kind (Löwdin, 1967) and is solved iteratively to yield

$$\begin{aligned} U_\varepsilon(t, t_0) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n \\ \times \exp\{-\varepsilon(|t_1| + |t_2| + \cdots + |t_n|)\} \\ \times T[V(t_1)V(t_2)\cdots V(t_n)]. \end{aligned} \tag{IV.11}$$

The time ordering operator T rearranges the product of perturbation operators such that the left-most term is the latest in chronological order.

The perturbed eigenstates $|\Psi_I(t_0)\rangle$ can now be expressed in terms of the unperturbed eigenstates by noting that as $t_0 \to \infty$, $|\Psi_I(t_0)\rangle \to |\Phi_0\rangle$, and as t_0 increases from $-\infty$ to 0, the perturbation is "adiabatically switched on"

$$|\Psi_I(0)\rangle = U_\varepsilon(0, -\infty)|\Psi_0\rangle. \tag{IV.12}$$

According to a theorem of Gell-Mann and Low (1951), if

$$\lim_{\varepsilon\to 0} \frac{U\varepsilon(0, -\infty)|\Phi_0\rangle}{\langle\Phi_0|U_\varepsilon(0, -\infty)|\Phi_0\rangle} \equiv \frac{|\Psi_I(0)\rangle}{\langle\Phi_0|\Psi_I(0)\rangle} \tag{IV.13}$$

exists, then it is an eigenstate of H

$$\frac{H|\Psi_I(0)\rangle}{\langle\Phi_0|\Psi_I(0)\rangle} = \frac{E|\Psi_I(0)\rangle}{\langle\Phi_0|\Psi_I(0)\rangle}. \tag{IV.14}$$

These results can now be used to determine the electron propagator. In Section II, the propagator was defined as the ground-state average of a time-ordered product of field operators in the Heisenberg representation

$$iG_{ij}(t) = \frac{\langle\Psi_{\mathrm{H}}|T[a_i(t)a_j^{\dagger}(0)]|\Psi_{\mathrm{H}}\rangle}{\langle\Psi_{\mathrm{H}}|\Psi_{\mathrm{H}}\rangle}. \tag{IV.15}$$

Using Eq. (IV.13) and the fact that $|\Psi_{\mathrm{H}}\rangle = |\Psi_{\mathrm{I}}(0)\rangle$, this average can be expressed in the interaction representation as

$$iG_{ij}(t) = \frac{\langle\Phi_0 U_\varepsilon(\infty,\, t)T[a_i(t)a_j^{\dagger}(0)]U_\varepsilon(t,\, -\infty)|\Phi_0\rangle}{\langle\Phi_0|U_\varepsilon(-\infty,\, \infty)|\Phi_o\rangle}. \tag{IV.16}$$

Using the expansion of the evolution operator [Eq. (IV.11)] and taking the limit $\varepsilon \to 0$, it can be shown (Fetter and Walecka, 1971) that

$$\begin{aligned} iG_{ij}(t) &= \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n \\ &\times \frac{\langle\Phi_0|T[V(t_1)\cdots V(t_n)a_i(t)a_j^{\dagger}(0)]|\Phi_0\rangle}{\langle\Phi_0|U(-\infty,\, \infty)|\Phi_0\rangle}. \end{aligned} \tag{IV.17}$$

The final step in the diagrammatic expansion method is to expand the numerators of each term in Eq. (IV.17) using Wick's theorem (Wick, 1950; Linderberg and Öhrn, 1973) and to represent them diagrammatically (e.g., Fetter and Walecka, 1971). The denominator of Eq. (IV.17) must also be expanded and diagrammed, and when this is done, all unlinked or disconnected diagrams arising from the expansion of the numerator will cancel (Abrikosov *et al.*, 1965).

Formally, the diagrammatic expansion method and the superoperator formalism appear strikingly dissimilar. The diagrammatic method is formulated in the causal representation while the superoperator formalism utilizes the energy representation. The diagrammatic method employs a pictorial representation of the algebraic structure while the superoperator formalism emphasizes the algebraic structure directly. The content of the resulting equations is the same using either method, therefore, the two formalisms are inherently equivalent. In this section we explicitly demonstrate the equivalence between these two formalisms and re-examine the superoperator decoupling approximations in terms of a diagrammatic analysis.

B. Perturbation Theory

The unifying feature of the diagrammatic expansion method and the superoperator formalism is perturbation theory (Born and Öhrn, 1978). Since the commutator product is distributive with respect to addition, we can define a partitioning of the superoperator Hamiltonian into an unperturbed part plus a perturbation,

$$\hat{H} = \hat{H}_0 + \hat{V}. \tag{IV.18}$$

One convenient partitioning, which will be shown to readily yield the Hartree–Fock propagator as the unperturbed electron propagator, is the Møller–Plesset partitioning (Møller and Plesset, 1934). With this partitioning, H_0 has the form

2780

$$\sum_{r} \varepsilon_r a_r^\dagger a_r - \tfrac{1}{2} \sum_{r,r'} \langle rr' \| rr' \rangle \langle n_r \rangle \langle n_{r'} \rangle \tag{IV.19}$$

and the perturbation is expressed as

$$\begin{aligned} V = \sum_{r,r',s,s'} & \langle rr' \| ss' \rangle [\tfrac{1}{4} a_r^\dagger a_{r'}^\dagger a_{s'} a_s - \delta_{r's'} \langle n_{r'} \rangle a_r^\dagger a_s] \\ & + \tfrac{1}{2} \sum_{r,r'} \langle rr' \| rr' \rangle \langle n_r \rangle \langle n_{r'} \rangle . \end{aligned} \tag{IV.20}$$

Of course, when the commutator product is formed for the superoperators, the constant term in these definitions will cancel.

Other partitionings of the Hamiltonian may also be assumed and may lead to superior convergence properties (Claverie *et al.*, 1967). One alternative partitioning that has been employed in the perturbation calculation of correlation corrections to the total energy is the Epstein–Nesbet partitioning (Epstein, 1926; Nesbet, 1955a,b). In propagator applications, the work of Kurtz and Öhrn (1978) may be roughly interpreted in terms of a partitioning in which the unperturbed Hamiltonian incorporates all relaxation contributions to the ionization energy. It is less obvious how to define this unperturbed Hamiltonian explicitly, but it formally satisfies the eigenvalue equation

$$\hat{H}_0' a_k = \Delta E_k(\mathrm{SCF}) a_k \tag{IV.21}$$

in contrast to

$$\hat{H}_0 a_k = \varepsilon_k a_k \tag{IV.22}$$

for the Møller–Plesset partitioning. The method of Kurtz and Öhrn yields excellent ionization energies and electron affinities with a simple second-order self-energy. It has not been formally analyzed in detail.

Corresponding to the partitioning of the superoperator Hamiltonian, we can introduce a partitioning of the operator space defined by the projection superoperators $\hat{O}$ and $\hat{P}$,

$$\hat{O} = \sum_{k} |a_k)(a_k| = |\mathbf{a})(\mathbf{a}|, \tag{IV.23}$$

$$\hat{P} = \hat{I} - \hat{O}. \tag{IV.24}$$

These superoperators operate on elements of the operator space through the relations

$$\hat{O}X_i = \sum_k |a_k)(a_k|X_i), \tag{IV.25}$$

$$\hat{P}X_i = X_i - \hat{O}X_i \tag{IV.26}$$

and are idempotent ($\hat{O}^2 = \hat{O}$, $\hat{P}^2 = \hat{P}$), self-adjoint ($\hat{O}^\dagger = \hat{O}$, $\hat{P}^\dagger = \hat{P}$), and mutually exclusive ($\hat{O}\hat{P} = \hat{P}\hat{O} = 0$). The superoperator $\hat{O}$ projects from an arbitrary operator product the part that lies in the model subspace, i.e., the part that is spanned by the eigenelements of $\hat{H}_0$. The superoperator $\hat{P}$ projects onto the orthogonal complement of the model subspace, i.e., the part that we have no *a priori* knowledge about.

To obtain a perturbation expansion of the superoperator resolvent, we consider its outer projection (Löwdin, 1965) onto the model subspace,

$$\hat{G}(E) = \hat{O}(E\hat{I} - \hat{H})^{-1}\hat{O} \tag{IV.27}$$

$$= \hat{O}(E\hat{I} - \hat{H}_0 - \hat{V})^{-1}\hat{O}. \tag{IV.28}$$

By iterating the identity

$$(A - B)^{-1} = A^{-1} + A^{-1}B(A - B)^{-1}, \tag{IV.29}$$

the inverse in Eq. (IV.28) can be expanded as

$$\hat{G}(E) = (E\hat{I} - \hat{H}_0)^{-1}\hat{O} + (E\hat{I} - \hat{H}_0)^{-1}\hat{O}\hat{V}(E\hat{I} - \hat{H}_0)^{-1}\hat{O}$$
$$+ (E\hat{I} - \hat{H}_0)^{-1}\hat{O}\hat{V}(E\hat{I} - \hat{H}_0)^{-1}\hat{V}(E\hat{I} - \hat{H}_0)^{-1}O + \cdots, \tag{IV.30}$$

where the property

$$[\hat{H}_0, \hat{O}]_- = 0 \tag{IV.31}$$

has been used. Now since $\hat{O}$ plus $\hat{P}$ form a resolution of the identity, each resolvent of $\hat{H}_0$ occurring between perturbation superoperators $\hat{V}$ can be rewritten as a sum of its projections on the model subspace and the orthogonal complement:

$$(E\hat{I} - \hat{H}_0)^{-1} = (E\hat{I} - \hat{H}_0)^{-1}\hat{O} + (E\hat{I} - \hat{H}_0)^{-1}\hat{P} \tag{IV.32}$$

$$= \hat{G}_0(E) + \hat{T}_0(E). \tag{IV.33}$$

With this notation, Eq. (IV.30) becomes

$$\hat{G}(E) = \hat{G}_0(E) + \hat{G}_0(E)\hat{V}\hat{G}_0(E) + \hat{G}_0(E)\hat{V}[\hat{G}_0(E) + \hat{T}_0(E)]\hat{V}\hat{G}_0(E)$$
$$+ \hat{G}_0(E)\hat{V}[\hat{G}_0(E) + \hat{T}_0(E)]\hat{V}[\hat{G}_0(E) + \hat{T}_0(E)]\hat{V}\hat{G}_0(E) + \cdots \tag{IV.34}$$

and can be resummed to yield

$$\hat{G}(E) = \hat{G}_0(E) + \hat{G}_0(E)[\hat{V} + \hat{V}\hat{T}_0(E)\hat{V} + \hat{V}\hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V}$$
$$+ \cdots]\hat{G}(E). \tag{IV.35}$$

Defining the reduced resolvent of the full superoperator Hamiltonian as

$$\hat{T}(E) = \hat{P}[\alpha\hat{O} + \hat{P}(E\hat{I} - \hat{H})\hat{P}]^{-1}\hat{P} \qquad (\alpha \neq 0) \tag{IV.36}$$

$$= \hat{T}_0(E) + \hat{T}_0(E)\hat{V}\hat{T}(E), \tag{IV.37}$$

Eq. (IV.35) can be written in closed form

$$\hat{G}(E) = \hat{G}_0(E) + \hat{G}_0(E)[\hat{V} + \hat{V}\hat{T}(E)\hat{V}]\hat{G}(E). \tag{IV.38}$$

Alternatively, we can define wave and reaction superoperators through the equations (cf. Löwdin, 1962, or Brandow, 1967)

$$\hat{W}(E) = \hat{I} + \hat{T}(E)\hat{V}, \tag{IV.39}$$

$$\hat{t}(E) = \hat{V}\hat{W}(E). \tag{IV.40}$$

The reduced resolvent, wave, and reaction superoperators introduced in this section are functions of the superoperators $\hat{I}$, $\hat{H}_0$, and $\hat{V}$ and as a consequence, operate in a more complicated way. To apply a superoperator function to an operator in the operator space, it must first be expanded in terms of the superoperators $\hat{I}$, $\hat{H}_0$, and $\hat{V}$, which are then successively applied to the operator according to Eq. (II.11). For example,

$$\hat{W}(E)X_i = [\hat{I} + \hat{T}(E)\hat{V}]X_i \tag{IV.41}$$

$$= [\hat{I} + \hat{T}_0(E)\hat{V} + \hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V} + \cdots]X_i, \tag{IV.42}$$

where

$$\hat{T}_0(E)\hat{V}\hat{X}_i = [E^{-1}\hat{I} + E^{-2}\hat{H}_0 + E^{-3}\hat{H}_0^2 + \cdots]\hat{P}\hat{V}X_i, \text{ etc.} \tag{IV.43}$$

C. Equivalence of the Superoperator Formalism and the Diagrammatic Expansion Method

Equations (IV.35) and (IV.38) represent the superoperator form of the Dyson equation and the reaction superoperator [Eq. (IV.40)] can be identified as the self-energy. To demonstrate that Eq. (IV.35) corresponds term by term with the diagrammatic propagator expansion, we must first form the operator average of $\hat{G}(E)$ to obtain the matrix Dyson equation, then evaluate all necessary operator averages, and finally diagram the resulting algebraic formulae. Owing to the complicated operator averages that must be evaluated in third and higher orders of the perturbation superoperator, the equivalence between these two formalisms has only been explicitly demonstrated through third order and is assumed in all higher orders.

The matrix Dyson equation is obtained by forming the operator average of $G(E)$ with respect to the basis elements of our model subspace

$$\mathbf{G}(E) = (\mathbf{a}|\hat{G}(E)\mathbf{a}) \tag{IV.44}$$

$$= \mathbf{G}_0(E) + \mathbf{G}_0(E)\boldsymbol{\Sigma}(E)\mathbf{G}(E), \tag{IV.45}$$

where

$$\Sigma(E) = (\mathbf{a}|\hat{V}\mathbf{a}) + (\mathbf{a}|\hat{V}\hat{T}_0(E)\hat{V}\mathbf{a}) + (\mathbf{a}|\hat{V}\hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V}\mathbf{a}) + \cdots . \tag{IV.46}$$

Since $\hat{H}_0$ was chosen to be the Fock superoperator, the appropriate density operator to employ in the evaluation of the operator averages is the Hartree–Fock density operator. Realizing that the grand canonical density operator reduces to the Hartree–Fock density operator when pure state occupation numbers of zero or one are chosen, we shall employ this density operator.

Beginning with the evaluation of matrix elements for the unperturbed propagator, $\mathrm{G}_0(E)$, the Hartree–Fock propagator is easily obtained (cf. Section II,C)

$$G_0(E)_{ij} = (a_j|(E\hat{I} - \hat{H}_0)^{-1}a_i) \tag{IV.47}$$

$$= E^{-1}(a_j|a_i) + E^{-2}(a_j|H_0 a_i) + E^{-3}(a_j|\hat{H}_0^2 a_i) + \cdots \tag{IV.48}$$

$$= E^{-1}\,\delta_{ij} + E^{-2}\varepsilon_i\,\delta_{ij} + E^{-3}\varepsilon_i^2\,\delta_{ij} + \cdots \tag{IV.49}$$

$$= (E - \varepsilon_i)^{-1}\,\delta_{ij}. \tag{IV.50}$$

The evaluation of each term in the self-energy expansion requires the initial evaluation of $\hat{V}a_i$,

$$\hat{V}a_i = \tfrac{1}{4}\sum_{r,r',s,s'} \langle rr'\|ss'\rangle[a_i, a_r^\dagger a_{r'}^\dagger a_{s'} a_s]_- - \sum_{r,s,s'} \langle rs'\|ss'\rangle[a_i, a_r^\dagger a_s]_- \langle n_{s'}\rangle \tag{IV.51}$$

$$= \tfrac{1}{2}\sum_{r,s,s'} \langle ir\|ss'\rangle a_r^\dagger a_{s'} a_s - \sum_{s,s'} \langle is'\|ss'\rangle \langle n_{s'}\rangle a_s. \tag{IV.52}$$

With this result, the first-order term $(a_j|\hat{V}a_i)$ is obtained without much additional effort

$$\Sigma^{(1)}(E)_{ij} = (a_j|\hat{V}a_i) \tag{IV.53}$$

$$= \tfrac{1}{2}\sum_{r,s,s'} \langle ir\|ss'\rangle \operatorname{Tr}\{\rho[a_r^\dagger a_{s'} a_s, a_j^\dagger]_+\} - \sum_{s,s'} \langle is'\|ss'\rangle \langle n_{s'}\rangle \operatorname{Tr}\{\rho[a_s, a_j^\dagger]_+\} \tag{IV.54}$$

$$= \sum_{r,s} \langle ir\|js'\rangle \langle n_{s'}\rangle\,\delta_{rs'} - \sum_{s} \langle is'\|js'\rangle \langle n_{s'}\rangle \tag{IV.55}$$

$$= 0. \tag{IV.56}$$

When the effective, single-particle potential used in the unperturbed problem is the Hartree–Fock self-consistent field potential, all single-particle corrections vanish (Bartlett and Silver, 1975a).

The evaluation of the second- and higher-order self-energy matrices requires the evaluation of $\hat{T}_0(E)\hat{V}a_i$ and $\hat{V}\hat{T}_0(E)\hat{V}a_i$. The first of these quantities can be expanded as

$$\hat{T}_0(E)\hat{V}a_i = (E\hat{I} - \hat{H}_0)^{-1}\hat{P}\hat{V}a_i \tag{IV.57}$$

$$= (E\hat{I} - \hat{H}_0)^{-1}\hat{V}a_i - \sum_k (E\hat{I} - \hat{H}_0)^{-1}|a_k)(a_k|\hat{V}a_i) \tag{IV.58}$$

using Eq. (IV.24). It follows from the previous result for $(a_j|\hat{V}a_i)$ that the second term in Eq. (IV.58) vanishes. The first term can now be evaluated by expanding the resolvent of $\hat{H}_0$ and realizing that any operator product is an eigenelement to $\hat{H}_0$, i.e.,

$$-\hat{H}_0 a_r^\dagger a_{s'} a_s = (\varepsilon_r - \varepsilon_{s'} - \varepsilon_s) a_r^\dagger a_{s'} a_s. \tag{IV.59}$$

Consequently, we obtain

$$\hat{T}_0(E)\hat{V}a_i = \tfrac{1}{2}\sum_{r,s,s'} (E + \varepsilon_r - \varepsilon_s - \varepsilon_{s'})^{-1}\langle ir\|ss'\rangle a_r^\dagger a_{s'} a_s - \sum_{s,s'} (E - \varepsilon_s)^{-1}\langle is'\|ss'\rangle\langle n_{s'}\rangle a_s \tag{IV.60}$$

with the help of Eq. (IV.43). The remaining application of $\hat{V}$ and the average value evaluation is straightforward and yields

$$\Sigma^{(2)}(E)_{ij} = (a_j|\hat{V}\hat{T}_0(E)\hat{V}a_i) \tag{IV.61}$$

$$= \sum_{r,s,s'} \frac{\langle ir\|ss'\rangle\langle ss'\|jr\rangle}{(E + \varepsilon_r - \varepsilon_s - \varepsilon_{s'})} \times [\tfrac{1}{2}\langle n_r\rangle + \tfrac{1}{2}\langle n_s\rangle\langle n_{s'}\rangle - \langle n_r\rangle\langle n_{s'}\rangle] \tag{IV.62}$$

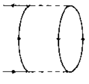
for the matrix elements of the second-order self-energy.

The Hartree–Fock average is now obtained by choosing occupation numbers of zero and one. An examination of the occupation number factor in Eq. (IV.62) reveals that with this restriction, it will be nonvanishing only when the summation index r runs over occupied spin orbitals and s and s' run over unoccupied spin orbitals or when r runs over unoccupied spin orbitals and s and s' run over occupied spin orbitals. Denoting $a, b, c, \ldots$ as summation indices over occupied spin orbitals; $p, q, r, \ldots$ for unoccupied spin orbitals; and $i, j, k, \ldots$ for unspecified spin orbitals, Eq. (IV.62) can now be written as two terms that involve restricted spin orbital summations

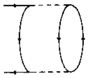
$$\Sigma^{(2)}(E)_{ij} = \frac{1}{2}\sum_{a,p,q} \frac{\langle ia\|pq\rangle\langle pq\|ja\rangle}{(E + \varepsilon_a - \varepsilon_p - \varepsilon_q)} + \frac{1}{2}\sum_{p,a,b} \frac{\langle ip\|ab\rangle\langle ab\|jp\rangle}{(E + \varepsilon_p - \varepsilon_a - \varepsilon_b)}. \tag{IV.63}$$

The conversion of Eq. (IV.63) into diagrams is a straightforward procedure for which we shall use the rules and diagram convention of Brandow (1967) and Bartlett and Silver (1975b). This convention represents the synthesis of the antisymmetrized vertices of the Hugenholtz (1957) or Abrikosov *et al.* (1965) diagrams with the extended interaction lines of the Goldstone (1957) diagrams. The application of these rules to the terms in Eq. (IV.63) yields the following diagrams:

$$\frac{1}{2}\sum_{a,p,q}\frac{\langle ia\|pq\rangle\langle pq\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)} \tag{IV.64}$$



$$\frac{1}{2}\sum_{p,a,b}\frac{\langle ip\|ab\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)} \tag{IV.65}$$



These diagrams are precisely the same as those obtained in the second-order diagrammatic expansion after a Fourier transformation into the energy representation (Cederbaum and Domcke, 1977).

The evaluation of the third-order self-energy matrix is similar to the second-order matrix but much more tedious and the result is presented in Appendix 3. As was done for the second-order expression, the occupation numbers must again be restricted to zero and one to obtain the Hartree–Fock average. When this restriction is made, the unrestricted spin orbital summations in Appendix 3 will reduce to summations involving occupied, unoccupied, and unspecified spin orbitals. Using the algebraic identity

$$\frac{A}{(E-a)(E-b)}=\frac{A}{(a-b)}\left[\frac{1}{(E-a)}-\frac{1}{(E-b)}\right] \tag{IV.66}$$

it is possible to combine terms in such a way that expressions involving only occupied and unoccupied spin orbital summations are obtained. These expressions are presented in Appendix 1. The corresponding diagrams in Appendix 1 again are precisely those occurring in the third-order, diagrammatic self-energy expansion.

D. Diagram-Conserving Decoupling

The wave and reaction superoperators identified with the help of perturbation theory in Section IV,B have special importance in the development of decoupling approximations for the electron propagator. As we have already seen, the reaction superoperator generates the diagrammatic self-energy expansion. A truncation of this expansion offers one viable decoupling scheme. The wave superoperator, on the other hand, has the property of generating eigenelements of the unperturbed superoperator Hamiltonian

$$(E\hat{I}-\hat{H})\hat{W}(E)\mathrm{a}=0. \tag{IV.67}$$

This property is easily proven by first using Eq. (IV.39) to expand $\hat{W}(E)$ and then premultiplying both sides of Eq. (IV.67) by $\hat{P}$

$$(E\hat{I} - \hat{H})\hat{W}(E)\mathbf{a} = (E\hat{I} - \hat{H})\mathbf{a} + (E\hat{I} - \hat{H})\hat{T}(E)\hat{V}\mathbf{a}, \tag{IV.68}$$

$$\hat{P}(E\hat{I} - \hat{H})\hat{W}(E)\mathbf{a} = \hat{P}(E\hat{I} - \hat{H})\mathbf{a} + \hat{P}(E\hat{I} - \hat{H})\hat{T}(E)\hat{V}\mathbf{a}. \tag{IV.69}$$

Using the identity

$$\hat{P}(E\hat{I} - \hat{H})\hat{T}(E) = \hat{P} \tag{IV.70}$$

and the property $\hat{P}\mathbf{a} = 0$, Eq. (IV.69) simplifies to

$$\hat{P}(E\hat{I} - \hat{H})\hat{W}(E)\mathbf{a} = -\hat{P}\hat{V}\mathbf{a} + \hat{P}\hat{V}\mathbf{a} = 0, \tag{IV.71}$$

which implies the validity of Eq. (IV.67).

It is of interest at this point to show a connection between the superoperator formalism and the equations of motion (EOM) method for determining ionization energies (Simons and Smith, 1973). In this method, one seeks solutions of the equation

$$[H, Q]_- = \omega Q \tag{IV.72}$$

which is precisely Eq. (IV.67). Here the operator Q is interpreted as a correlated ionization operator that generates, in principle, the exact $(N - 1)$-electron ion states from the exact N-electron reference state. One approach to solving Eq. (IV.72) involves the application of Rayleigh–Schrödinger perturbation theory (Purvis and Öhrn, 1976; Dalgaard and Simons, 1977). By partitioning the Hamiltonian operator, expanding both the ionization operator Q and the ionization energy ω in terms of a perturbation parameter, and collecting terms of the same order, a set of perturbation theory equations is obtained. The solution of these equations yields an expansion for Q that is analogous to the superoperator equation

$$\mathbf{h} = \hat{W}(E)\mathbf{a}. \tag{IV.73}$$

The only difference is that E is replaced by ω_0, which is a consequence of using Rayleigh–Schrödinger rather than Brillioun–Wigner perturbation theory.

Returning now to the inner projection of the superoperator resolvent

$$\mathbf{G}(E) = (\mathbf{a}|\mathbf{h})(\mathbf{h}|(E\hat{I} - \hat{H})\mathbf{h}^{-1}(\mathbf{h}|\mathbf{a}), \tag{IV.74}$$

we may view Eq. (IV.73) as an alternative prescription for choosing the inner projection operator manifold. Recalling from Section II that since the density operator describing the unperturbed (model) problem does not commute with the full Hamiltonian, the operator scalar product will not in general exhibit Hermitian symmetry. Consequently, we define

$$(\mathbf{h}| = (\mathbf{a}|\hat{W}^{\dagger}(E) \tag{IV.75}$$

and note that

$$(\mathbf{a}|\hat{W}^{\dagger}(E) \neq (\hat{W}(E)\mathbf{a}|. \tag{IV.76}$$

Approximate electron propagator decouplings can now be obtained by truncating the expansion of the wave superoperator,

$$\hat{W}(E) = \hat{I} + \hat{T}_0(E)\hat{V} + \hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V} + \cdots . \tag{IV.77}$$

Truncation of this expansion after the superoperator identity trivially yields the Hartree–Fock propagator, therefore we next consider

$$\hat{W}(E) = \hat{I} + \hat{T}_0(E)\hat{V}. \tag{IV.78}$$

Noting that the subspaces $\{a_k\}$ and $\{f_k \,|\, f_k = \hat{T}_0(E)\hat{V}a_k\}$ are mutually orthogonal, Eq. (IV.74) can be readily solved for $\mathbf{G}^{-1}(E)$:

$$\mathbf{G}^{-1}(E) = \mathbf{G}_0^{-1}(E) - \mathbf{\Sigma}(E), \tag{IV.79}$$

where

$$\mathbf{\Sigma}(E) = (\mathbf{a}|\hat{V}\hat{T}_0(E)\hat{V}\mathbf{a})(\mathbf{a}|\hat{V}\hat{T}_0(E)(E\hat{I} - \hat{H})\hat{T}_0(E)\hat{V}\mathbf{a})^{-1}(\mathbf{a}|\hat{V}\hat{T}_0(E)\hat{V}\mathbf{a}). \tag{IV.80}$$

Making the following identifications from Section IV,C:

$$(\mathbf{a}|\hat{V}\hat{T}_0(E)\hat{V}\mathbf{a}) = \mathbf{\Sigma}^{(2)}(E), \tag{IV.81}$$

$$(\mathbf{a}|\hat{V}\hat{T}_0(E)(E\hat{I} - \hat{H}_0)\hat{T}_0(E)\hat{V}\mathbf{a}) = \mathbf{\Sigma}^{(2)}(E), \tag{IV.82}$$

$$(\mathbf{a}|\hat{V}\hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V}\mathbf{a}) = \mathbf{\Sigma}^{(3)}(E), \tag{IV.83}$$

Eq. (IV.82) can be rewritten

$$\mathbf{\Sigma}(E) = \mathbf{\Sigma}^{(2)}(E)[\mathbf{\Sigma}^{(2)}(E) - \mathbf{\Sigma}^{(3)}(E)]^{-1}\mathbf{\Sigma}^{(2)}(E). \tag{IV.84}$$

Expanding the inverse of Eq. (IV.84), we easily see that this self-energy approximant coincides with the diagrammatic expansion through third order but additionally yields contributions to all higher orders. If the exact self-energy is rewritten as a moment expansion in terms of a perturbation parameter λ,

$$\lambda^{-1}\mathbf{\Sigma}(E) = \sum_{k=0}^{\infty} \lambda^{k}(\mathbf{a}|\hat{V}(\hat{T}_0(E)\hat{V})^{k}\mathbf{a}), \tag{IV.85}$$

we see that Eq. (IV.84) represents the [1, 1] Padé approximant to this expansion. Owing to the close connection between Padé approximants and the inner projection technique as demonstrated in Section III, this result is not surprising. These Padé approximants to the self-energy, however, will have entirely different convergence properties than those studied in Section II.

E. Approximations and Applications

Computational applications of the [1, 1] Padé approximant to the self-energy require the evaluation of the second- and third-order self-energy matrices. The second-order matrix is relatively easy to evaluate. The third-order matrix, on the other hand, is exceedingly more difficult and can presently be only approximately calculated without excessive computational effort. An examination of the formulae in Appendix 3 reveals that unlike the fourth moment matrix in the moment-conserving decoupling, the third-order self-energy matrix is energy dependent. This additional complication makes the partial summation technique used in the moment-conserving decoupling ineffectual since the third-order self-energy matrix will generally need to be resummed with different values of E hundreds of times in the search for poles of the propagator.

The first approximation that we will examine is the complete neglect of the third-order self-energy matrix. With this approximation, the [1, 1] approximant in Eq. (IV.86) reduces to a second-order truncation of the diagrammatic self-energy expansion,

$$\mathbf{\Sigma}(E) = \mathbf{\Sigma}^{(2)}(E). \tag{IV.86}$$

This second-order self-energy approximation is interesting not only because it contains the lowest-order relaxation and correlation corrections to Koopman's theorem, but also because it exhibits the same analytic form as the exact self-energy (Hedin and Lundqvist, 1969; Cederbaum and Domcke, 1977). Furthermore, since several second-order, ionization energy calculations have been reported in the literature, this approximation will afford both a convenient check of new computer code and the computational experience necessary to implement more refined approximations.

The first computational application of this decoupling approximation was to the water molecule using the same basis and internuclear geometry as described in Section III,D. The results of this calculation are presented in Table V along with the Koopmans' theorem, ΔE(SCF), and experimental values for the ionization energies. Two ionization energies have been tabulated for the $2a_1$ ionization with their corresponding pole strength [Γ_k of Eq. (II.31)] in parentheses. The occurence of two relatively strong propagator poles for this ionization represents a breakdown in the quasiparticle description of inner valence ionizations (Cederbaum, 1977) and

TABLE V

PRINCIPAL IONIZATION ENERGIES OF WATER COMPUTED WITH THE 14 CGTO BASIS

Orbital	Koopmans	$\Delta E(\mathrm{SCF})^a$	$\Sigma^{(2)}_{(E)}$	Experiment^b
$1a_1$	559.4	540.8	539.4	540.2
$2a_1$	37.0	34.6	34.0(0.61) 32.6(0.28)	32.2
$3a_1$	15.4	13.0	12.9	14.7
$1b_1$	13.8	11.0	10.8	12.6
$1b_2$	19.5	17.8	18.1	18.6

[a] Goscinski *et al.* (1975).
[b] Siegbahn *et al.* (1969).

makes assignments of principal and shake-up ionizations ambiguous.[3] In general, the second-order ionization energies are quite encouraging and represent significant improvements to each of the Koopmans' values. Furthermore, these results are comparable in accuracy to the ΔE(SCF) results but possess the convenience of being obtained in a single calculation whereas the ΔE(SCF) results required six separate Hartree–Fock calculations.

The relatively poor agreement of the $3a_1$ and $1b_1$ ionization energies with the experimental values in Table V seems attributable to basis incompleteness. Despite the lack of polarization functions, this suspicion is supported by the facts that the $3a_1$ orbital is the highest occupied orbital in that symmetry and that this basis contains only two contracted Gaussian orbitals of b_1 symmetry. In order to study the basis dependence of the second-order self-energy approximation, two additional calculations were performed with larger basis sets. The first of these calculations employed a 26-contracted-orbital basis that augmented the original 14 orbitals (Table III) with a set of p orbitals on the hydrogen atoms and a set of d orbitals on oxygen—all with unit exponents. The Hartree–Fock total energy obtained with this basis was $E(\mathrm{HF}) = -76.0459$ H. The second calculation employed a 38-contracted-orbital basis that included all of the orbitals in the 26-orbital basis plus an additional set of diffuse p orbitals on the hydrogen atoms ($\alpha = 0.25$) and a set of diffuse d orbitals on oxygen ($\alpha = 0.40$). This basis yielded a Hartree–Fock total energy of $E(\mathrm{HF}) = -76.0507$ H.

[3] The ESCA spectrum of the water molecule (Siegbahn *et al.*, 1969) substantiates this phenomenon since the $2a_1$ peak is quite broad and asymmetric. Experimentally, it appears that the lower-energy ionization should have a larger pole strength (in contrast with the results of Table V) since the peak is skewed to higher binding energies.

TABLE VI

BASIS SET EFFECTS ON THE IONIZATION ENERGIES OF WATER COMPUTED WITH A SECOND-ORDER SELF-ENERGY APPROXIMATION

Symmetry	14 CGTOs	26 CGTOs	38 CGTOs	Cederbaum (1973a)
a_1	36.5(0.005)	37.1(0.003)		
	34.0(0.607)	33.4(0.288)	33.2(0.231)	
	32.6(0.279)	32.1(0.592)	31.9(0.628)	32.9
	12.9(0.913)	13.4(0.908)	13.5(0.903)	13.2
b_1	34.9(0.005)	35.1(0.005)		
	10.8(0.909)	11.1(0.904)	11.2(0.900)	10.9
b_2	40.6(0.003)	40.8(0.004)		
	18.1(0.931)	18.0(0.922)	18.0(0.919)	17.7
E(HF)	−76.0082	−76.0459	−76.0507	−76.0419

The most significant propagator poles calculated in the valence region (0 ~ 40 eV) with each of the three water basis sets are presented in Table VI along with the second-order results of Cederbaum (1973a). The inclusion of polarization functions not only improves the $3a_1$ and $1b_1$ ionization energies, it also reverses the relative pole strengths of the two dominant $2a_1$ poles, bringing the theoretical results into better agreement with experimental observations (see footnote on page 35). Cederbaum's second-order results were obtained with a basis comparable in size and quality to the 26-orbital basis in Table VI. He deletes several virtual orbitals from this basis before computing the ionization energies, however. This approximation may account for the small discrepancies between his results and those reported here.

The formaldehyde molecule was chosen for a second application of the second-order self-energy approximation. Ionization energies were calculated using two basis sets. The first consisted of Huzinaga's 9s, 5p primitive basis sets for oxygen and carbon (Huzinaga, 1965) contracted to 4s and 2p functions with Dunning's contraction coefficients (Dunning, 1970). The orbital exponents of Huzinaga's 4s primitive basis for hydrogen were scaled by a factor of 1.2, and the resultant orbitals were contracted to 2s functions as recommended by Dunning. The complete basis appears in Table VII. The second basis augmented the first by the addition of one set of p orbitals on the hydrogen atoms and one set of d orbitals on both the oxygen and carbon atoms. Unit exponents were chosen for the p orbitals on hydrogen while exponents of 0.8 were chosen for the d orbitals. One- and two-electron integrals were computed with the MOLECULE program (Almlöf, 1974) at the experimental equilibrium geometry: R(CO) =

TABLE VII

CONTRACTED GAUSSIAN BASIS FOR FORMALDEHYDE

Carbon s sets		Oxygen s sets		Carbon p sets		Oxygen p sets		Hydrogen s sets	
Exponents	Contraction coefficients	Exponents	Contraction coefficients	Exponents	Contraction coefficients	Exponents	Contraction coefficients	Exponents	Contraction coefficients
4232.6100	0.002029	7816.5400	0.002031	18.1557	0.018534	35.1832	0.019580	19.2406	0.032828
634.8820	0.015535	1175.8200	0.015436	3.9864	0.115442	7.9040	0.124189	2.8992	0.231208
146.0970	0.075411	273.1880	0.073771	1.1429	0.386206	2.3051	0.394727	0.6535	0.817238
42.4974	0.257121	81.1696	0.247606	0.3594	0.640089	0.7171	0.627375	0.1776	1.000000
14.1892	0.596555	27.1836	0.611832	0.1146	1.000000	0.2137	1.000000		
1.9666	0.242517	3.4136	0.241205						
5.1477	1.000000	9.5322	1.000000						
0.4962	1.000000	0.9398	1.000000						
0.1533	1.000000	0.2846	1.000000						

TABLE VIII

PRINCIPAL IONIZATION ENERGIES FOR FORMALDEHYDE

	24		42			
Orbital	Koopmans	$\Sigma^{(2)}_{(E)}$	Koopmans	$\Sigma^{(2)}_{(E)}$	Theory[a]	Experiment
$1a_1$	560.12	538.93	559.81	538.62	—	539.43[b]
$2a_1$	309.09	297.27	308.87	296.90	—	294.21[b]
$3a_1$	38.94	33.66	38.18	32.56	—	34.2[c]
$4a_1$	23.39	20.97	23.30	21.03	—	21.15[c]
$5a_1$	17.29	13.98	17.38	14.38	14.42	16.2[d]
$1b_1$	14.56	13.83	14.45	13.72	13.50	14.5[d]
$1b_2$	19.47	17.16	19.08	17.07	16.63	17.0[d]
$2b_2$	12.06	9.04	11.93	9.30	9.25	10.9[d]
E(HF)	−113.8257		−113.8901		−113.9012	

[a] Second-order results of Cederbaum *et al.* (1975).

[b] Jolly and Schaaf (1976).

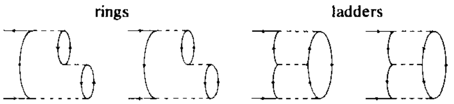
[c] Hood *et al.* (1976).

[d] Estimated center of gravity (Cederbaum and Domcke, 1977) from spectrum of Turner *et al.* (1970).

2.2825 a.u., R(CH) = 2.1090 a.u., and angle HCH = 116.52° (Oka, 1960; Takagi and Oka, 1963), and the Hartree–Fock calculations and two-electron integral transformations were performed with GRNFNC (Purvis, 1973). The Hartree–Fock total energy for the smaller, 24-orbital basis (no polarization) was $E(\mathrm{HF}) = -113.8257$ H, and for the larger, 42-orbital basis (with polarization) $E(\mathrm{HF}) = -114.8901$ H. The Hartree–Fock orbital energies and second-order self-energy results for both basis sets are presented in Table VIII for the principal ionizations along with the second-order results of Cederbaum *et al.* (1975) and the experimental values.

The results in Table VIII typify two general features of ionization energy calculations. The first is that Koopmans' theorem yields values that are usually higher than experimental ionization energies. Second, the inclusion of second-order relaxation and correlation corrections generally over-corrects the Koopmans' estimate and yields values that are usually lower than experiment. For several ionizations in Table VIII, the second-order deviations from experiment are as large as the Koopmans' values, but opposite in sign. Although it is possible that the larger polarized basis used in the second calculation may still lack adequate polarization functions, the rather large discrepancies between the second-order results and experiment more probably indicate that third- (and higher) order self-energy corrections are now sizable. The general conclusion that a second-order self-energy approximation is inadequate for an accurate calculation of ionization energies has been previously concluded by Cederbaum (1973b) and necessitates a re-examination of the approximation made in Eq. (IV.86).

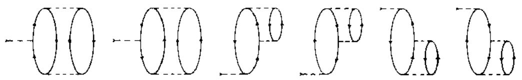
Rather than completely neglecting the third-order self-energy matrix, let us now consider an approximation that includes at least part of these contributions. Which third-order self-energy diagrams should be included? There are two well-established results that are relevant to this question: Studies of the electron gas model have shown that in the limit of high electron density, the so-called ring diagrams dominate the self-energy expansion (Pines, 1961), while in the limit of low electron density, the so-called ladder diagrams dominate (Galitskii, 1958). In order to determine whether atomic and molecular self-energies can be approximated by specific third-order diagrams (e.g., rings or ladders), we need to evaluate all third-order diagrams for some representative systems. Cederbaum (1975) has done this for several simple systems and has found that both ring *and* ladder diagrams dominate the third-order self-energy. This result implies that atoms and molecules lie somewhere between the high and low density extremes. It is therefore essential to include both ring and ladder diagrams in any third-order self-energy approximation. These diagrams are



(IV.87)

and correspond to the algebraic expressions labeled A–D in Appendix 1.

We include six additional diagrams in our third-order self-energy approximation because of the computational efficiency with which they are evaluated. These diagrams are the energy-independent diagrams



(IV.88)

corresponding to expressions M–R in Appendix 1. For these six diagrams, it is feasible to employ the partial summation technique since they must be evaluated only once.

Approximating the full third-order self-energy matrix by only ring, ladder, and constant-energy diagrams, let us now consider the solution of the Dyson equation with the [1, 1] Padé approximant to the self-energy expansion. Owing to the fact that the inner projection manifold from which the [1, 1] approximant was derived is energy dependent [Eq. (IV.73)], the simple analytic form of the self-energy eigenvalues, illustrated in Fig. 1, is lost. Furthermore, the self-energy poles are now given by

$$\det(\Sigma^{(2)}(E) - \Sigma^{(3)}(E)) = 0 \qquad \text{(IV.89)}$$

rather than by an eigenvalue problem and are consequently more difficult to obtain. For these reasons, the pole search described in Section II and used with the second-order self-energy approximation is no longer an efficient or reliable procedure. An alternative method of solution employed in the following applications uses the Hartree–Fock orbital energy as an initial guess to the propagator pole and iterates Eq. (II.28) to convergence. When convergent, this procedure invariably yields a principal propagator pole and its corresponding pole strength. Although the [1, 1] self-energy approximant does not guarantee a positive pole strength, this was never a problem in any of the calculations reported here.

The principal ionization energies for the water molecule were calculated using both the 14 and 26 CGTO basis sets in order to evaluate the [1, 1] Padé approximant to the self-energy expansion, and the results appear in Table IX. The most significant feature of these results is that each ionization energy has been shifted from its second-order value to higher energy and is now in better agreement with the experimental value. It is further noticed that the valence ionization energies are still smaller than the experimental values while the $1a_1$ (core) ionization energy is now larger than experiment. Apparently, the diagrams included in the third-order self-energy matrix overestimate the actual relaxation and correlation effects for this ionization.

TABLE IX

COMPARISON OF PRINCIPAL IONIZATION ENERGIES FOR WATER OBTAINED WITH THE SECOND-ORDER AND THE [1, 1] SELF-ENERGIES USING THE 14- AND 26-CGTO BASIS SETS

	14		26		
Orbital	$\Sigma^{(2)}_{(E)}$	[1, 1]	$\Sigma^{(2)}_{(E)}$	[1, 1]	Experiment[a]
$1a_1$	539.4	541.6	539.2	540.9	540.2
$2a_1$	34.0(0.607) 32.6(0.279)	[b]	32.1	32.2	32.2
$3a_1$	12.9	13.4	13.4	13.6	14.7
$1b_1$	10.8	11.1	11.1	11.3	12.6
$1b_2$	18.1	18.4	18.0	[c]	18.6

[a] Siegbahn *et al.* (1969).

[b] No convergence (see text).

[c] No results.

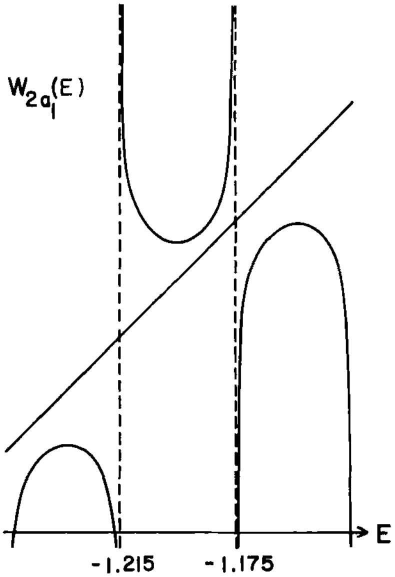


Fig. 2. A sketch of W_{2a_1} in the energy region of the $2a_1$ ionization obtained with the [1, 1] self-energy approximant using the 14-CGTO basis.

Convergence difficulty was experienced for the $2a_1$ ionization energy using the 14-orbital basis. A schematic plot of $W_{2a_1}(E)$ is presented in Fig. 2 and reveals that there are not propagator poles in this energy region. This anomaly is no doubt a consequence of an inadequate basis since the 26-orbital basis yields a very accurate $2a_1$ ionization energy.

F. Evaluation of the Diagram-Conserving Decoupling

The algebraic structure of the superoperator formalism has been successfully exploited in this section to yield several new insights into the decoupling problem. The application of perturbation theory has demonstrated that the electron propagator equation of motion can be resummed to yield the equivalent of the diagrammatic expansion. This resummation also allows the identification of wave and reaction superoperators that have special importance in decoupling approximations. We have shown that when the inner projection manifold of the superoperator resolvent is chosen to consist of the first-order truncation of the wave superoperator, a [1, 1] Padé approximant to the self-energy expansion is obtained. This approximant is correct through third order and contains a geometric approximation to all higher orders. In general, the Nth-order truncation of the wave superoperator will yield an $[N, N]$ Padé approximant that is correct through the $(2N + 1)$th order in the self-energy expansion. One final insight afforded by this decoupling is the realization that electron correlation can be described exclusively in the operator space. We argued in Section II that when the propagator was defined as a single-time Green's function, the density operator was arbitrary. We have now demonstrated in this section that any desired order in the self-energy expansion may be obtained using as a specific choice, the uncorrelated, Hartree–Fock density operator.

These computational applications of the diagram-conserving decoupling are encouraging and demonstrate that it is important, if not essential, that third-order ring and ladder diagrams be included in any self-energy approximation although the errors arising from basis incompleteness may be of equal magnitude and hence cannot be ignored. The inclusion of the third-order ring, ladder, and constant-energy diagrams in the [1, 1] self-energy approximant has succeeded in improving the second-order results but even these results are not consistently in better agreement with experiment than the Koopmans' theorem values.

One important feature of the [1, 1] self-energy approximant is that even though it is constructed from only the second- and third-order self-energy matrices, it contains a geometric approximation of all higher orders in the self-energy expansion. Certainly, some fourth- or higher-order terms may be just as important as third-order terms; therefore, in this sense this approximation is reasonable. The fourth- and higher-order terms arising from the [1, 1] self-energy approximant, however, are not readily analyzed diagrammatically. In fact, being a purely algebraic approximation, the [1, 1] approximant may not yield any valid fourth- or higher-order diagrams. Since the ring and ladder diagrams dominate the third-order self-energy matrix, one can argue that they may be most important also in higher orders of the self-energy expansion. An appropriate modification of this decoupling would then be to allow the summation of these specific diagrams in all orders. Approximations of this type are referred to as renormalized decouplings and are examined within the superoperator formalism in the next section.

V. Renormalized Decouplings

A. Renormalization Theory

In Section IV, we tacitly assumed that the application of perturbation theory to the calculation of ionization energies and electron affinities was valid and that the resulting self-energy expansion was convergent. Historically, however, it was discovered that in both the nuclear many-body problem and the electron gas model, the simple self-energy expansions are divergent. In order to remove these divergences, it is necessary to sum certain appropriate classes of diagrams to all orders. This method of partial summations is known as renormalization theory (see, e.g., Kumar, 1962; Mattuck, 1967) and may be viewed as an analytic continuation of the perturbation expansion. Although a variety of renormalization procedures exist, such as propagator, interaction, and vertex renormalizations, the distinctions mainly depend on the types of diagrams included in the partial summation and are not particularly important for our consideration.

One renormalization that we are already familiar with is that [1, 1] self-energy approximant derived in Section IV. In fact, any rational self-energy approximant may be regarded as a renormalization since its geometric expansion will approximate all orders of the perturbation expansion. One problem encountered with the [1, 1] approximant and that occurs in general for rational approximants derived via purely algebraic considerations is that their geometric expansions may contain no readily identifiable diagrams (at least beyond the lowest orders). Since specific diagrams often dominate the self-energy expansion (such as ring and ladder diagrams for atoms and molecules) it is valuable to investigate whether the superoperator formalism can be adapted to yield renormalized self-energy expressions that sum specific diagrams. The solution, as we shall see, is rather simple and involves a restriction in the types of operator products allowed to span the orthogonal complement of the model subspace. As a specific example, the two particle–one hole Tamm–Dancoff approximation (2p–h TDA) (Schuck *et al.*, 1973; Schirmer and Cederbaum, 1978) is derived from an effective interaction that is logically obtained by a projection of the perturbation superoperator onto the subspace spanned by 2p–h type operators (Born and Öhrn, 1979). Finally, the diagonal approximation to the full 2p–h TDA self-energy previously derived and applied to the calculation of ionization energies is shown to neglect terms that are, in fact, diagonal and necessary to prevent an overcounting of all diagrams containing diagonal ladder parts.

B. Derivation of the 2p–h TDA and Diagonal 2p–h TDA Equations

Recalling some of the results of Section IV, we had obtained the matrix Dyson equation

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\boldsymbol{\Sigma}(E)\mathbf{G}(E), \tag{V.1}$$

where the self-energy matrix $\boldsymbol{\Sigma}(E)$ had the following expansion

$$\boldsymbol{\Sigma}(E) = [\mathbf{a}|(\hat{V} + \hat{V}\hat{T}_0(E)\hat{V} + \hat{V}\hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V} + \cdots)\mathbf{a}]. \tag{V.2}$$

Introducing the reduced resolvent of the full superoperator Hamiltonian, $\hat{T}(E)$, which is just a projection of the superoperator resolvent on the orthogonal complement

$$\hat{T}(E) = \hat{P}[\alpha\hat{O} + (E\hat{I} - \hat{H}_0)\hat{P} - \hat{P}\hat{V}\hat{P}]^{-1}\hat{P}, \tag{V.3}$$

the self-energy expansion was written in closed form

$$\boldsymbol{\Sigma}(E) = (\mathbf{a}|\hat{V}\mathbf{a}) + (\mathbf{a}|\hat{V}\hat{T}(E)\hat{V}\mathbf{a}). \tag{V.4}$$

It was further shown that when the grand canonical density operator is used to evaluate the operator averages, the first-order term vanishes.

When $\hat{P}$ is the exact projector of the orthogonal complement,

$$\hat{P} = \hat{1} - \hat{O}, \tag{V.5}$$

the term $\hat{P}\hat{V}\hat{P}$ in Eq. (V.3) is responsible for generating the operator products that span this subspace. The expansion of this term from the inverse and its repeated application in each order of the perturbation expansion yields larger and larger operator products that are only limited by the number of electrons in the reference state. If instead of allowing all possible operator products, we restrict them to some simple types that occur in each order, it may be possible to identify and sum specific diagrams in all orders of the perturbation expansion.

The restriction of the operator products in the orthogonal complement is achieved by approximating the orthogonal projector as

$$\hat{P} = |\mathbf{f})(\mathbf{f}| \tag{V.6}$$

where the manifold $\{\mathbf{f}\}$ contains the desired operator products. The projector $\hat{P}$ now has the effect of projecting from the perturbation expansion only those operator products that lie in the subspace spanned by $\{\mathbf{f}\}$. The approximation to $\hat{P}$ in Eq. (V.6) must, of course, preserve the properties of the exact projector and should be idempotent, self-adjoint, and orthogonal to $\hat{O}$.

Our previous experience with the operator product decouplings suggests that the set of triple operator products $\{a_k^\dagger a_l a_m\}$ be chosen as a first approximation to $\hat{P}$. There is a stronger motivation for using this operator product, however. If the third-order ring and ladder diagrams in Eq. (IV.87) are examined, it can be seen that between any two interaction lines there occurs only two particle lines (upgoing) and one hole line (downgoing) or vice versa. This implies that the intermediate or virtual states that are represented by these diagrams consist of only 2p–h or 2h–p excitations of the reference state. Both of these excitations are described with the triple-operator products.

The set of triple products $\{a_k^\dagger a_l a_m\}$ is not orthogonal to the simple operators of the model subspace, hence these two subspaces must be orthogonalized. Using the Gram–Schmidt orthogonalization procedure (see, e.g., Löwdin, 1956), we define

$$f_{klm} = N_{klm}^{-1/2}\left[a_k^\dagger a_l a_m - \sum_n (a_n|a_k^\dagger a_l a_m)a_n \right] \tag{V.7}$$

$$= N_{klm}^{-1/2}[a_k^\dagger a_l a_m + \delta_{km}\langle n_k\rangle a_l - \delta_{kl}\langle n_k\rangle a_m], \tag{V.8}$$

where

$$N_{klm} = \langle n_k \rangle - \langle n_k \rangle \langle n_l \rangle - \langle n_k \rangle \langle n_m \rangle + \langle n_l \rangle \langle n_m \rangle. \tag{V.9}$$

The projector

$$\hat{P} = \sum_{k,l,m} |f_{klm})(f_{klm}|, \qquad l < m, \tag{V.10}$$

is now indempotent, self-adjoint, and orthogonal to $\hat{O}$. The projection of the perturbation superoperator on the 2p–h subspace $\hat{P}\hat{V}\hat{P}$ that occurs in Eq. (V.3) can now be regarded as an effective interaction. The expansion of Eq. (V.3) with $\hat{P}$ defined as in Eq. (V.10) should yield all diagrams containing 2p–h and 2h–p excitations of the reference state.

The necessary operator averages needed to evaluate $\hat{P}\hat{V}\hat{P}$ are

$$(a^{\dagger}_{k'}a_{l'}a_{m'}|\hat{V}a_l) = (a_l|\hat{V}a^{\dagger}_{k'}a_{l'}a_{m'})^* = N_{k'l'm'}\langle lk'\|m'l'\rangle \tag{V.11}$$

$$\begin{aligned}(a^{\dagger}_{k'}a_{l'}a_{m'}|\hat{V}a^{\dagger}_{k}a_{l}a_{m}) = {} & N_{k'l'm'}\{\langle ml\|m'l'\rangle\,\delta_{kk'}(1 - \langle n_m\rangle - \langle n_l\rangle) \\ & - \langle k'm\|km'\rangle\,\delta_{ll'}(\langle n_k\rangle - \langle n_m\rangle) - \langle k'l\|kl'\rangle\,\delta_{mm'}(\langle n_k\rangle - \langle n_l\rangle) \\ & + \langle k'm\|kl'\rangle\,\delta_{m'l}(\langle n_k\rangle - \langle n_m\rangle) + \langle k'l\|km'\rangle\,\delta_{ml'}(\langle n_k\rangle - \langle n_l\rangle) \\ & + \langle k'm\|l'm'\rangle\,\delta_{kl}\langle n_k\rangle + \langle k'l\|m'l'\rangle\,\delta_{km}\langle n_k\rangle\} \\ & + N_{klm}\{\langle ml\|kl'\rangle\,\delta_{m'k'}\langle n_{m'}\rangle + \langle ml\|m'k\rangle\,\delta_{l'k'}\langle n_{l'}\rangle\}\end{aligned} \tag{V.12}$$

Substituting these expressions and performing some cancellation yields

$$\begin{aligned}\hat{P}\hat{V}\hat{P} = {} & \sum_{\substack{k,l,m \\ l<m}} \sum_{\substack{k',l',m' \\ l'<m}} N_{klm}^{-1/2} N_{k'l'm'}^{1/2} \langle ml\|m'l'\rangle \\ & \times \delta_{kk'}(1 - \langle n_m\rangle - \langle n_l\rangle)|f_{k'l'm'})(f_{klm}| \\ & - \sum_{\substack{k,l,m \\ l<m}} \sum_{\substack{k',l',m' \\ l'<m'}} N_{klm}^{-1/2} N_{k'l'm'}^{1/2} \langle k'm\|km'\rangle \\ & \times \delta_{ll'}(\langle n_k\rangle - \langle n_m\rangle)|f_{k'l'm'})(f_{klm}| \\ & - \sum_{\substack{k,l,m \\ l<m}} \sum_{\substack{k',l',m' \\ l'<m'}} N_{klm}^{-1/2} N_{k'l'm'}^{1/2} \langle k'l\|kl'\rangle \\ & \times \delta_{mm'}(\langle n_k\rangle - \langle n_l\rangle)|f_{k'l'm'})(f_{klm}| \\ & + \sum_{\substack{k,l,m \\ l<m}} \sum_{\substack{k',l',m' \\ l'<m'}} N_{klm}^{-1/2} N_{k'l'm'}^{1/2} \langle k'm\|kl'\rangle \\ & \times \delta_{lm'}(\langle n_k\rangle - \langle n_m\rangle)|f_{k'l'm'})(f_{klm}| \\ & + \sum_{\substack{k,l,m \\ l<m}} \sum_{\substack{k',l',m' \\ l'<m'}} N_{klm}^{-1/2} N_{k'l'm'}^{1/2} \langle k'l\|km'\rangle \\ & \times \delta_{ml'}(\langle n_k\rangle - \langle n_l\rangle)|f_{k'l'm'})(f_{klm}|.\end{aligned} \tag{V.13}$$

Additional simplification can be achieved at this point by transposing the operators $a_{l'}$ and $a_{m'}$ in $|f_{k'l'm'})$ of the last two terms in Eq. (V.13) with the appropriate change of sign,

$$|f_{k'l'm'}) = -|f_{k'm'l'}). \tag{V.14}$$

After interchanging dummy indices $l' \leftrightarrow m'$, the fourth and fifth terms become equal to the second and third terms, respectively, and since the diagonal terms $l' = m'$ vanish, the summations with $l' < m'$ and $l' > m'$ can be combined as unrestricted summations over l' and m'. Since the first term in Eq. (V.13) is obviously symmetric in l' and m', the restriction $l' < m'$ in that term may be removed by multiplying the sum by a factor of $\frac{1}{2}$. The remaining restriction, $l < m$, may also be removed by introducing another factor of $\frac{1}{2}$ since

$$\begin{aligned}\hat{P}\hat{V}\hat{P} = \sum_{\substack{k,l,m\\ l<m}} \sum_{k',l',m'} & N_{klm}^{-1/2} N_{k'l'm'}^{1/2} \{\tfrac{1}{2}\langle ml\|m'l'\rangle\, \delta_{kk'}(1 - \langle n_m\rangle - \langle n_l\rangle) \\ & - \langle k'm\|km'\rangle\, \delta_{ll'}(\langle n_k\rangle - \langle n_m\rangle) - \langle k'l\|kl'\rangle \\ & \times \delta_{mm'}(\langle n_k\rangle - \langle n_l\rangle)\}|f_{k'l'm'})(f_{klm}|\end{aligned} \tag{V.15}$$

is symmetric in these indices, as can be verified by interchanging $l \leftrightarrow m$ and relabeling dummy indices $l' \leftrightarrow m'$. Expanding the ket-bra superoperator

$$\tfrac{1}{2} \sum_{k,l,m} \sum_{k',l',m'} |f_{k'l'm'})(f_{klm}| \tag{V.16}$$

out of the inverse, evaluating the remaining operator averages, and resumming the expansion yields the 2p–h TDA self-energy

$$\begin{aligned}\Sigma(E)_{ij} = \tfrac{1}{2} \sum_{k,l,m} \sum_{k',l',m'} & N_{klm}^{1/2} N_{k'l'm'}^{1/2} \langle ik\|lm\rangle \\ & \times \{(\mathbf{f}|(E\hat{I} - \hat{H}_0)\mathbf{f}) - (\mathbf{f}|\hat{V}\mathbf{f})\}^{-1}_{klm,k'l'm'} \langle l'm'\|jk'\rangle,\end{aligned} \tag{V.17}$$

where

$$\begin{aligned}(f_{k'l'm'}|(E\hat{I} - \hat{H}_0)f_{klm}) &= (E + \varepsilon_k - \varepsilon_l - \varepsilon_m)\, \delta_{kk'}\, \delta_{ll'}\, \delta_{mm'}, \\ (f_{k'l'm'}|\hat{V}f_{klm}) &= N_{klm}^{-1/2} N_{k'l'm'}^{1/2} \{\tfrac{1}{2}\langle ml\|m'l'\rangle\, \delta_{kk'}(1 - \langle n_m\rangle - \langle n_l\rangle) \\ &\quad - \langle k'm\|km'\rangle\, \delta_{ll'}(\langle n_k\rangle - \langle n_m\rangle) - \langle k'l\|kl'\rangle \\ &\quad \times \delta_{mm'}(\langle n_k\rangle - \langle n_l\rangle)\}.\end{aligned} \tag{V.18}$$

Although different in appearance, this self-energy expression is formally the same as that obtained by Purvis and Öhrn (1975a), using the operator product decoupling, and by Cederbaum (1975) and Schirmer and Cederbaum (1978), using the diagrammatic method. The present derivation clearly illuminates the parallelism between the two formalisms.

Owing to the large dimension of the $\{f_{klm}\}$ operator subspace and the associated difficulty in diagonalizing $(\mathbf{f}|\hat{V}\mathbf{f})$, computational applications of the 2p–h TDA have usually involved additional approximations. One approximation that has facilitated computational applications is known alternatively as the shifted Born collision (SBC) approximation (Purvis and Öhrn, 1974, 1975a) or the diagonal 2p–h TDA (Cederbaum, 1974, 1975; Cederbaum and Domcke, 1977). This "diagonal" approximation restricts the spin orbital summation indices in Eq. (V.13) to $k' = k, l' = l$, and $m' = m$, thereby neglecting the last two summations and yielding the following self-energy expression:

$$\overset{\text{2p-h TDA}}{\Sigma(E)_{ij}} = \frac{1}{2}\sum_{k,l,m} N_{klm}\frac{\langle ik\|lm\rangle\langle lm\|jk\rangle}{(E+\varepsilon_k-\varepsilon_l-\varepsilon_m)-\Delta}, \tag{V.19}$$

where

$$\Delta = \langle ml\|ml\rangle(1-\langle n_m\rangle-\langle n_l\rangle)-\langle km\|km\rangle(\langle n_k\rangle - \langle n_m\rangle)-\langle kl\|kl\rangle(\langle n_k\rangle-\langle n_l\rangle). \tag{V.20}$$

By neglecting the last two summations in Eq. (V.13), however, this approximation actually neglects some diagonal contributions to $(f_{k'l'm'}|\hat{V}f_{klm})$. As we have explicitly demonstrated in the derivation of Eqs. (V.17) and (V.18), the 2p–h TDA self-energy sums are symmetric in both l, m and l', m'; consequently, the last two summations in Eq. (V.13) contain precisely the same contributions as the second and third summations, respectively. If the diagonal approximation ($k' = k$, $l' = l$, $m' = m$) is made in Eqs. (V.17) and (V.18), this symmetry is properly accounted for and the resulting self-energy expression is

$$\overset{\text{2p-h TDA}}{\Sigma(E)_{ij}} = \frac{1}{2}\sum_{k,l,m} N_{klm}\frac{\langle ik\|lm\rangle\langle lm\|jk\rangle}{(E+\varepsilon_k-\varepsilon_l-\varepsilon_m)-\Delta}, \tag{V.21}$$

where

$$\Delta = \tfrac{1}{2}\langle ml\|ml\rangle(1-\langle n_m\rangle-\langle n_l\rangle)-\langle km\|km\rangle(\langle n_k\rangle - \langle n_m\rangle)-\langle kl\|kl\rangle(\langle n_k\rangle-\langle n_l\rangle). \tag{V.22}$$

Equation (V.22) differs from Eq. (V.20) by the factor of $\frac{1}{2}$ in the first term. The inclusion of this factor in the diagonal 2p–h TDA is necessary to prevent an overcounting of diagrams with diagonal ladder parts (see next section) and can shift ionization energies 0.3–0.4 eV higher in energy (Born and Öhrn, 1979).

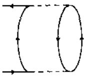
C. Diagrammatic Analysis

In order to determine precisely which self-energy diagrams are included in the 2p–h TDA self-energy, it is necessary to expand the effective interaction matrix $(\mathbf{f}|\hat{V}\mathbf{f})$ from the inverse in Eq. (V.17) and diagram the resulting algebraic expressions in each order. The expansion of Eq. (V.17) yields the following terms in lowest orders:

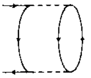
$$\begin{aligned}
&\overset{\text{2p-h TDA}}{\Sigma(E)_{ij}}\\
&\quad = \tfrac{1}{2} \sum_{k,l,m} \sum_{k',l',m'} N^{1/2}_{klm} N^{1/2}_{k'l'm'} \langle ik \| lm \rangle \Bigg\{ \frac{\delta_{kk'}\delta_{ll'}\delta_{mm'}}{(E + \varepsilon_k - \varepsilon_l - \varepsilon_m)} \\
&\quad + \frac{(f_{k'l'm'} | \hat{V} f_{klm})}{(E + \varepsilon_k - \varepsilon_l - \varepsilon_m)(E + \varepsilon_{k'} - \varepsilon_{l'} - \varepsilon_{m'})} \\
&\quad + \sum_{\kappa,\lambda,\mu} \frac{(f_{k'l'm'} | \hat{V} f_{\kappa\lambda\mu})(f_{\kappa\lambda\mu} | \hat{V} f_{klm})}{(E + \varepsilon_k - \varepsilon_l - \varepsilon_m)(E + \varepsilon_\kappa - \varepsilon_\lambda - \varepsilon_\mu)(E + \varepsilon_{k'} - \varepsilon_{l'} - \varepsilon_{m'})} \\
&\quad + \cdots \Bigg\} \langle l'm' \| jk' \rangle.
\end{aligned} \tag{V.23}$$

As was done in Section IV,C, the terms in Eq. (V.23) can be simplified by first restricting the summations over all spin orbitals to summations over occupied or unoccupied spin orbitals such that the occupation number factor $N^{1/2}_{klm} N^{1/2}_{k'l'm'}$ is nonvanishing. Doing this in the first term of Eq. (V.23) and then summing over the delta functions yields

$$\frac{1}{2} \sum_{a,p,q} \frac{\langle ia \| pq \rangle \langle pq \| ja \rangle}{(E + \varepsilon_a - \varepsilon_p - \varepsilon_q)} \tag{V.24}$$



$$+ \frac{1}{2} \sum_{p,a,b} \frac{\langle ip \| ab \rangle \langle ab \| jp \rangle}{(E + \varepsilon_p - \varepsilon_a - \varepsilon_b)} \tag{V.25}$$



which are the same second-order self-energy diagrams as obtained in Eqs. (IV.64) and (IV.65).

Restricting the spin orbital summations in the second term of Eq. (V.23) yields the following expressions:

$$\frac{1}{2} \sum_{a,p,q} \sum_{b,r,s} \frac{\langle ia \| pq \rangle}{(E + \varepsilon_a - \varepsilon_p - \varepsilon_q)} (f_{brs} | \hat{V} f_{apq}) \frac{\langle rs \| jb \rangle}{(E + \varepsilon_b - \varepsilon_r - \varepsilon_s)} \tag{V.26}$$

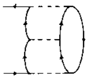
$$+ \frac{1}{2} \sum_{a,p,q} \sum_{r,b,c} \frac{\langle ia \| pq \rangle}{(E + \varepsilon_a - \varepsilon_p - \varepsilon_q)} (f_{rbc} | \hat{V} f_{apq}) \frac{\langle bc \| jr \rangle}{(E + \varepsilon_r - \varepsilon_b - \varepsilon_c)} \tag{V.27}$$

$$+ \frac{1}{2} \sum_{p,a,b} \sum_{d,q,r} \frac{\langle ip \| ab \rangle}{(E + \varepsilon_p - \varepsilon_a - \varepsilon_b)} (f_{cqr} | \hat{V} f_{pab}) \frac{\langle qr \| jc \rangle}{(E + \varepsilon_c - \varepsilon_q - \varepsilon_r)} \tag{V.28}$$

$$+ \frac{1}{2} \sum_{p,a,b} \sum_{q,c,d} \frac{\langle ip \| ab \rangle}{(E + \varepsilon_p - \varepsilon_a - \varepsilon_b)} (f_{qcd} | \hat{V} f_{pab}) \frac{\langle cd \| jq \rangle}{(E + \varepsilon_q - \varepsilon_c - \varepsilon_d)} \tag{V.29}$$

Now substituting Eq. (V.18) for the effective interaction matrices, we find that the delta functions in Eq. (V.18) further restrict the spin orbital summations in such a way that only expressions (V.26) and (V.29) are nonvanishing. After some simplification, the nonvanishing contributions are found to be

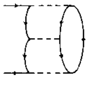
$$\frac{1}{4}\sum_{a}\sum_{p,q,r,s}\frac{\langle is\|pq\rangle\langle qp\|sr\rangle\langle rs\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)(E+\varepsilon_a-\varepsilon_r-\varepsilon_s)} \tag{V.30}$$



$$-\frac{1}{2}\sum_{a,b}\sum_{p,q,r}\frac{\langle ia\|pq\rangle\langle bq\|ar\rangle\langle pr\|jb\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)(E+\varepsilon_b-\varepsilon_p-\varepsilon_r)} \tag{V.31}$$

$$-\frac{1}{2}\sum_{a,b}\sum_{p,q,r}\frac{\langle ia\|pq\rangle\langle bp\|ar\rangle\langle rq\|jb\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)(E+\varepsilon_b-\varepsilon_r-\varepsilon_q)} \tag{V.32}$$

$$-\frac{1}{4}\sum_{a,b,c,d}\sum_{p}\frac{\langle ip\|ab\rangle\langle ba\|dc\rangle\langle cd\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(E+\varepsilon_p-\varepsilon_c-\varepsilon_d)} \tag{V.33}$$

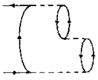


$$+\frac{1}{2}\sum_{a,b,c}\sum_{p,q}\frac{\langle ip\|ab\rangle\langle qb\|pc\rangle\langle ac\|jq\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(E+\varepsilon_q-\varepsilon_a-\varepsilon_c)} \tag{V.34}$$

$$+\frac{1}{2}\sum_{a,b,c}\sum_{p,q}\frac{\langle ip\|ab\rangle\langle qa\|pc\rangle\langle cb\|jq\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(E+\varepsilon_q-\varepsilon_b-\varepsilon_c)} \tag{V.35}$$

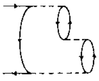
Expressions (V.30) and (V.33) are the only ones that represent valid third-order diagrams as written, however, by interchanging dummy indices $p \leftrightarrow q$ in Eq. (V.32) and $a \leftrightarrow b$ in Eq. (V.35), expressions (V.31) and (V.32) can be combined to yield

$$-\sum_{a,b}\sum_{p,q,r}\frac{\langle ia\|pq\rangle\langle bq\|ar\rangle\langle pr\|jb\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)(E+\varepsilon_b-\varepsilon_p-\varepsilon_r)} \tag{V.36}$$



and expressions (V.34) and (V.35) can be combined to yield

$$\sum_{a,b,c}\sum_{p,q}\frac{\langle ip\|ab\rangle\langle qb\|pc\rangle\langle ac\|jq\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(E+\varepsilon_q-\varepsilon_a-\varepsilon_c)} \tag{V.37}$$



which now correspond to the two third-order ring diagrams as indicated. These results verify that one of our original objectives, which was to include all third-order ring and ladder diagrams, has been achieved.

The diagrammatic analysis of the third term in Eq. (V.23) proceeds in the same way as that of the first two terms, but since the effective interaction matrix appears twice, it involves considerably more algebra. For this reason, we simply display the resulting diagrams in Fig. 3. It is significant to realize that the fourth-order diagrams in Fig. 3 include not only ring and ladder diagrams but also mixed diagrams that consist of both ring and ladder parts. In the third-order analysis, the first term in Eq. (V.18) was responsible for yielding the ladder diagrams while the second and third

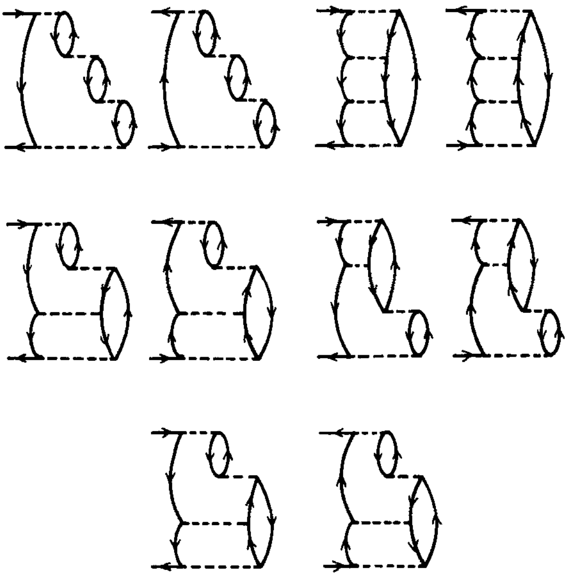
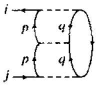


Fig. 3. Fourth-order self-energy diagrams arising from the 2p–h TDA.

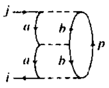
terms yielded the ring diagrams. Therefore if we denote the first term as a ladder part and the second and third terms as ring parts, the mixed diagrams in fourth order are found to arise from the product of a ladder part and a ring part. Inducing the results of the fourth-order analysis to higher orders, we conclude that our second objective, which was to sum all ring and ladder diagrams in all orders of the self-energy expansion, has been exceeded: not only are all ring and ladder diagrams included in the 2p–h TDA self-energy, but also the mixed diagrams that exhibit both ring and ladder parts.

The diagonal 2p–h TDA self-energy may also be analyzed diagrammatically. This analysis is even simpler than for the full 2p–h TDA since the denominator shifts are now scalars rather than matrices. A comparison of diagrams obtained with the denominator shift in Eq. (V.30) versus that in Eq. (V.22) will reveal the significance of the factor of $\frac{1}{2}$. Considering the approximation in Eqs. (V.21) and (V.22) first, we obtain the following third-order expressions:

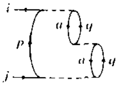
$$\frac{1}{4}\sum_{a,p,q}\frac{\langle ia\|pq\rangle\langle pq\|pq\rangle\langle pq\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)^2} \tag{V.38}$$



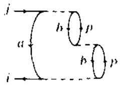
$$-\frac{1}{4}\sum_{a,b,p}\frac{\langle ip\|ab\rangle\langle ab\|ab\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)^2} \tag{V.39}$$



$$-\sum_{a,p,q}\frac{\langle ia\|pq\rangle\langle ap\|ap\rangle\langle pq\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)^2} \tag{V.40}$$



$$+\sum_{a,b,p}\frac{\langle ip\|ab\rangle\langle pb\|pb\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)^2} \tag{V.41}$$



The only difference between these diagrams and the third-order diagrams of the full, 2p–h TDA is that the incoming lines on the middle interaction line have the same labels as the outgoing lines. Now analyzing the approximation in Eqs. (V.19) and (V.20), we obtain the following third-order expressions:

$$\frac{1}{2}\sum_{a,p,q}\frac{\langle ia\|pq\rangle\langle pq\|pq\rangle\langle pq\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)^2} \tag{V.42}$$

$$-\frac{1}{2}\sum_{a,b,p}\frac{\langle ip\|ab\rangle\langle ab\|ab\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)^2} \tag{V.43}$$

$$-\sum_{a,p,q}\frac{\langle ia\|pa\rangle\langle ap\|ap\rangle\langle pq\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)^2} \tag{V.44}$$

$$+\sum_{a,b,p}\frac{\langle ip\|ab\rangle\langle pb\|pb\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)^2} \tag{V.45}$$

Expressions (V.44) and (V.45) are identical to (V.40) and (V.41), respectively, however, expressions (V.42) and (V.43) both differ by a factor of $\frac{1}{2}$ from (V.38) and (V.39). This discrepancy is a direct consequence of the missing factor in the denominator shift, Eq. (V.20), and leads to an overcounting of these third-order diagonal ladder diagrams since there should be a factor of $\frac{1}{2}$ for *each pair* of equivalent lines. Similarly, it is rather easy to show that this approximation overcounts all higher-order diagrams containing this diagonal ladder part.

D. Computational Applications and Evaluation of the Diagonal 2p–h TDA Self-Energy

The main attraction of the diagonal 2p–h TDA self-energy for the calculation of ionization energies and electron affinities is its pseudo second-order structure. Computational experience with the diagram-conserving decouplings has taught us that the second-order self-energy approximant is both easily constructed and evaluated. The diagonal 2p–h TDA requires only the additional evaluation of Eq. (V.22), which merely shifts the second-order self-energy poles. As a consequence the diagonal 2p–h TDA self-energy mimics the exact self-energy by possessing only simple poles. Another consequence of the pseudo second-order structure is that the energy dependence will have the simple analytic form illustrated in Fig. 1. This property, which was absent in the [1, 1] self-energy approximant, simplifies the pole search for the electron propagator. In spite of the simplicity of its pseudo second-order structure, however, the diagonal 2p–h TDA self-energy incorporates diagonal ring, ladder, and mixed diagrams in all orders of the self-energy expansion as was shown in the previous section. This property encourages speculation that significantly more relaxation and correlation will be accounted for in this decoupling than with the second-order decoupling, but the accuracy of the corresponding ionization energies or electron affinities can only be evaluated via actual computational applications. As was done with the diagram-conserving decouplings, ionization energies for the water and formaldehyde molecules were computed using the diagonal 2p–h TDA self-energy.

For the water molecule, calculations were performed with both the 14- and 26-contracted-Gaussian-orbital basis sets described in Sections III,D and IV,E. The principal ionization energies computed with the diagonal 2p–h TDA and the diagonal 2p–h TDA plus third-order constant-energy diagrams [denoted $\Sigma(E)^{(2)}_{\mathrm{SHIFT}}$ and $\Sigma(E)^{(2)}_{\mathrm{SHIFT}} + \Sigma(\infty)^{(3)}$] are presented in Table X. Comparing these results with those in Table VIII for the second-order and [1, 1] self-energy approximants reveals that each ionization has been shifted to higher energy. This shift has led to a significant improvement in the valence ionization energies ($3a_1$, $1b_1$, and $1b_2$), which are now within approximately 0.5 eV of the experimental results. For the inner valence ($2a_1$) and core ($1a_1$) ionizations, however, this energy shift leads to worse agreement. In addition, the diagonal 2p–h TDA results for the $1a_1$ ionization exhibit an enormous basis dependence. The addition of polarization functions in the 26-orbital basis has yielded nearly 13 eV in additional relaxation. The most probable explanation for this basis dependence is that the 2p–h TDA self-energy poles are determined by Hartree–Fock orbital energies and two-electron integrals rather than by orbital energies alone as with the second-order self-energy. The orbital energies are rather insensitive to basis changes, whereas the two-electron integrals are not.

Calculations for the formaldehyde molecule were performed with the 24- and 42-orbital basis sets described in Section IV,E. Ionization energies were computed using the diagonal 2p–h TDA and are presented in Table XI. The third-order constant-energy diagrams were not evaluated for this molecule. Similar to the water results, the diagonal 2p–h TDA results for formaldehyde are also consistently higher in energy than the second-order results (Table VIII). This shift considerably improves the valence ionization energies, however, the average deviation from the experimental re-

TABLE X

WATER RESULTS OBTAINED WITH THE DIAGONAL 2p–h TDA AND DIAGONAL 2p–h TDA PLUS CONSTANT THIRD-ORDER SELF-ENERGIES

	14 CGTOs			26 CGTOs			
	Koopmans	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}} + \Sigma^{(3)}_{(\infty)}$	Koopmans	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}} + \Sigma^{(3)}_{(\infty)}$	Experiment[a]
$1a_1$	559.45	554.91	556.04	559.40	542.78	543.51	540.2
$2a_1$	37.04	34.62	35.00	36.62	33.69	33.93	32.2
$3a_1$	15.43	13.61	13.95	15.66	14.12	14.31	14.7
$1b_1$	13.78	11.64	11.97	13.67	11.83	12.00	12.6
$1b_2$	19.52	18.51	18.80	19.34	18.46	18.61	18.6

[a] Siegbahn *et al.* (1969).

TABLE XI

FORMALDEHYDE RESULTS OBTAINED WITH THE DIAGONAL 2p–h TDA SELF-ENERGY

	24 CGTOs		42 CGTOs		
	Koopmans	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	Koopmans	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	Experiment
$1a_1$	560.12	542.86	559.81	542.09	539.43[a]
$2a_1$	309.09	299.82	308.87	299.31	294.21[a]
$3a_1$	38.94	35.60	38.18	34.31	34.2[b]
$4a_1$	23.39	21.75	23.30	21.79	21.15[b]
$5a_1$	17.29	14.99	17.38	15.33	16.2[c]
$1b_1$	14.56	14.11	14.45	14.03	14.5[c,d]
$1b_2$	19.47	17.91	19.08	17.77	17.0[c]
$2b_2$	12.06	9.92	11.93	10.11	10.9[c]

[a] Jolly and Schaaf (1976).

[b] Hood *et al.* (1976).

[c] Estimated center of gravity (Cederbaum and Domcke, 1977) from spectrum of Turner *et al.* (1970).

[d] 14.38(8) VIP (Turner *et al.*, 1970).

sults remains approximately 0.8 eV. The core ionizations within the diagonal 2p–h TDA suffer a small deterioration in accuracy but do not exhibit the extreme basis dependence that was observed in the water calculations. Part of the discrepancies between the diagonal 2p–h TDA and the experimental results can certainly be eliminated by further basis saturation; however, in the next section, we will propose that even ionization energies of 1.0 eV accuracy are usually sufficient to unambiguously interpret photoelectron spectra if combined with a calculation of relative photoionization intensities.

Cederbaum and co-workers (1977, 1978; Schirmer *et al.*, 1977, 1978) have recently developed computer programs that implement the full, nondiagonal 2p–h TDA to the self-energy and have reported several molecular applications. In these calculations, they claim only a 1.0 eV accuracy and rely heavily on vibrational analyses to assist with the interpretation of photoelectron spectra. The off-diagonal matrix elements seem to have little importance in the valence region because the propagator poles are relatively well separated. In the inner valence and core regions, however, where principal ionization poles and shake-up poles overlap and interact, level shifts and intensity changes are observed. In these regions, even the nondiagonal 2p–h TDA is not fully satisfactory since ion-state relaxation and hole–hole interactions, neither of which are described by this self-energy approximation, may also be important (Wendin, 1979). Implementations (Cederbaum *et al.*, 1978) of the full 2p–h TDA has involved truncations of the orbital basis for handling of the inverse matrix problem of the self-energy. This can lead to quite misleading results if not examined critically, as shown by Mishra and Öhrn (1980).

The fact that the self-energy can be separated into a relaxation part $\Sigma^{\mathrm{R}}(E)$ and a correlation part $\Sigma^{\mathrm{C}}(E)$, as shown by Born *et al.* (1978), was utilized by Kurtz and Öhrn (1978) to calculate the poles of the electron propagator as

$$E = -I_i(\Delta\mathrm{SCF}) + \Sigma^{\mathrm{C}}_{ii}(E). \tag{V.46}$$

The ΔSCF energy difference $-I_i(\Delta\mathrm{SCF})$ for the hole-state labeled by Hartree–Fock spin orbital

$$-I_i(\Delta\mathrm{SCF}) = \varepsilon_i + \Sigma^{\mathrm{R}}_{ii}(\varepsilon_i) \tag{V.47}$$

represents the relaxation contributions to all orders. It is most readily calculated as the difference of the total Hartree–Fock energies of the ground state and the appropriate ion state. The correlation part Σ^{C}_{ii} of the self-energy is in lowest order

$$\begin{aligned}\Sigma^{\mathrm{C}(2)}_{ii}(E) &= \frac{1}{2}\sum_{a\neq i}\sum_{p}\sum_{q}\frac{|\langle pq\|ia\rangle|^2}{E+\varepsilon_a-\varepsilon_p-\varepsilon_q}\\ &\quad+\frac{1}{2}\sum_{a\neq i}\sum_{b\neq i}\sum_{p}\frac{|\langle ab\|ip\rangle|^2}{E+\varepsilon_p-\varepsilon_a-\varepsilon_b}.\end{aligned} \tag{V.48}$$

For an electron propagator pole corresponding to an electron attachment energy, i refers to a particle state, and the restricted summations in Eq. (V.48) have to be changed to the unoccupied orbitals. These correlation terms can be obtained in any order of perturbation theory (Born *et al.*, 1978). The multiple summations involved means that actual calculations become prohibitive in higher orders. One possible way out is to use renormalization ideas to obtain an approximate form for $\Sigma^{\mathrm{C}}_{ii}(E)$ that has the correct behavior and is not too complex. Ortiz and Öhrn (1980) have investigated the use of the diagonal 2p–h TDA form

$$\begin{aligned}\Sigma^{\text{2p}-\text{h TDA}}_{ii}(E) &= \frac{1}{2}\sum_{a\neq i}\sum_{p}\sum_{q}\frac{|\langle pq\|ia\rangle|^2}{E+\varepsilon_a-\varepsilon_p-\varepsilon_q-\Delta_{apq}}\\ &\quad+\frac{1}{2}\sum_{a\neq i}\sum_{b\neq i}\sum_{p}\frac{|\langle ab\|ip\rangle|^2}{E+\varepsilon_p-\varepsilon_a-\varepsilon_b+\Delta_{pab}}\end{aligned} \tag{V.49}$$

with $\Delta_{apq} = \frac{1}{2}\langle pq\|pq\rangle - \langle ap\|ap\rangle - \langle aq\|aq\rangle$, for the calculation of electron affinities. In Eq. (V.49) the restricted summations would again be applied to the unoccupied orbital labels when an electron attachment energy is considered. The results for the Cl_2 molecule are given in Table XIII with the different basis sets identified in Table XII. The importance of

TABLE XII

Cl_2 AND Cl_2^- CGTO BASIS

Type	Exponent	Coefficient	Basis	Type	Exponent	Coefficient	Basis
s	40850	0.002532	E, F, J	p	240.8	0.014595	E, F, J
	6179	0.019207			56.56	0.099047	
	1425	0.095257			17.85	0.330562	
	409.2	0.345589			6.350	0.682874	
	135.5	0.636401					
				p	6.350	1.0	E, F, J
s	135.5	0.120956					
	50.13	0.648511	E, F, J	p	2.403	1.0	E, F, J
	20.21	0.275487					
				p	0.6410	1.0	E, F, J
s	6.283	1.0	E, F, J				
				p	0.1838	1.0	E, F, J
s	2.460	1.0	E, F, J				
				p	0.064	1.0	F, J
s	0.5271	1.0	E, F, J				
s	0.1884	1.0	E, F, J				
				d	0.6	1.0	J
s	0.082	1.0	J				

TABLE XIII

ADIABATIC ELECTRON AFFINITY OF Cl_2 (eV)

Basis	$R(Cl_2)$	$F(Cl_2^-)$	Vertical[a]	$V(Cl_2^-)^b$ −	$D(Cl_2)^c$ =	EA(adiabatic)
E	4.1	5.1	Eq. (12)	3.08	1.24	1.84
			Eq. (13)	2.62		1.38
F	4.1	5.1	Eq. (12)	3.60	1.29	2.31
			Eq. (13)	3.19		1.90
J	3.8	5.0	Eq. (12)	4.00	1.98	2.02
			Eq. (13)	3.74		1.76

[a] Equation (12) means that $V(Cl_2^-)$ is calculated as $-I + \Sigma^{C(2)}$; Equation (13) means that $V(Cl_2^-)$ is calculated as $-I + \Sigma^{2p\text{-}h\ \mathrm{TDA}}$.

[b] $V(Cl_2^-)$ is the vertical detachment energy of $X^2\ \Sigma_u^+ \to X^1\ \Sigma_g^+$ at $R = 5.0$ bohrs.

[c] $D(Cl_2)$ is the difference in energy between the points $R = 3.8$ and 5.0 bohrs on the $X^1\ \Sigma_g^+$ potential energy curve.

working with "saturated" basis sets is stressed by Ortiz and Öhrn (1980). It cannot be stressed enough that basis set effects can be very large and one must devise systematic steps for improving the computational basis. The inclusion of a sufficiently large set of diffuse basis functions seems to be most important.

VI. Photoionization Intensities

A. Introduction

The evaluation of each decoupling approximation in the preceding sections was based on the comparison of propagator poles to experimental ionization energies. This criterion represents a particular bias since it does not reflect the quality of the Feynman–Dyson amplitudes (defined in Section II,A). The Feynman–Dyson amplitudes determine the spectral density function (Linderberg and Öhrn, 1973)

$$A(x, x'; E) = \begin{cases} \sum_k f_k(x) f_k^*(x')\delta(E - E_k) & \text{for} \quad E > \mu, \\ \sum_k g_k(x) g_k^*(x')\delta(E - E_k) & \text{for} \quad E \leq \mu, \end{cases} \tag{VI.1}$$

where the parameter μ is the ground-state Fermi energy. The function $A(x, x'; E)$ contains a plethora of useful information. This is evidenced by the relation of the spectral density to the single-particle, reduced density matrix (Linderberg and Öhrn, 1973)

$$\gamma(x, x') = \int_C A(x, x'; E)\, dE \tag{VI.2}$$

for the N-electron ground state. It is important, therefore, to choose a decoupling approximation that not only yields accurate ionization energies but also an accurate spectral density. In order to evaluate the quality of the spectral density function one can compare averages of specific one-electron operators, as calculated from the reduced density matrix, with experimental results. Another procedure that is more closely related to our goal of interpreting photoelectron spectra is the calculation of photoionization intensities or cross sections. A theoretical prediction of relative photoionization intensities can simplify orbital assignments when the ionization energies are not accurately given. A theoretically predicted variation in relative intensities with photon energy is particularly useful if photoelectron spectra are available with different ionization sources (Katrib *et al.*, 1973). In the following sections, we derive computational expressions that relate the Feynman–Dyson amplitudes to the total photoionization cross section, discuss the major approximations assumed, and then present several applications.

B. Derivation of Computational Formulas for the Total Photoionization Cross Section

The differential cross section for photoionization derived from first-order, time-dependent perturbation theory using a semiclassical model for the interaction of radiation and matter is (Bethe and Salpeter, 1957; Kaplan and Markin, 1968; Smith, 1971)

$$\frac{d\sigma_{\mathrm{s}}}{d\Omega_{\mathrm{f}}} = \frac{4\pi^2|\mathbf{k}_{\mathrm{f}}|}{c|A_0|^2\omega}\left|\left\langle N, s\left|\sum_k \mathbf{A}_k\cdot\boldsymbol{\nabla}_k\right|N\right\rangle\right|^2. \tag{VI.3}$$

In this equation, $\mathbf{k}_{\mathrm{f}}$ is the momentum of the ejected photoelectron and $\mathbf{A} = \Sigma_k\mathbf{A}_k$ is the vector potential. For a closed-shell system, the initial state $|N\rangle$ can be represented by an antisymmetrized N-electron wavefunction

$$|N\rangle = \Phi_0(x_1, x_2, \ldots, x_N) \tag{VI.4}$$

and the final state $|N, s\rangle$ is represented by

$$\begin{aligned}|N, s\rangle = (N/2)^{1/2}O_{\mathrm{AS}}[&v(\mathbf{k}_{\mathrm{f}}, \mathbf{r})\alpha(\zeta)\Phi_{\mathrm{s}\beta}(x, x_2, \ldots, x_{N-1})\\ &-v(\mathbf{k}_{\mathrm{f}}, \mathbf{r})\beta(\zeta)\Phi_{\mathrm{s}\alpha}(x_1, x_2, \ldots, x_{N-1})].\end{aligned} \tag{VI.5}$$

Here $\Phi_{\mathrm{s}\alpha}$ and $\Phi_{\mathrm{s}\beta}$ are the two doublet spin components of the $(N-1)$-electron ion, $v(\mathbf{k}_{\mathrm{f}}, \mathbf{r})$ denotes the wavefunction of the photoelectron, and O_{AS} is an antisymmetrizer

$$O_{\mathrm{AS}} = N^{-1}\left[1 - \sum_{k=1}^{N-1} P_{kN}\right]. \tag{VI.6}$$

The form of Eq. (VI.5) guarantees that the singlet spin symmetry of the system is preserved.

Evaluating the matrix element in Eq. (VI.3) yields (Purvis and Öhrn, 1975a)

$$\left\langle N, s \middle| \sum_k \mathbf{A}_k \cdot \boldsymbol{\nabla}_k \middle| N \right\rangle = \sqrt{2} \int v^*(\mathbf{k}_f, \mathbf{r})\mathbf{A}_s \cdot \boldsymbol{\nabla} g_s(\mathbf{r})\, d\mathbf{r} + \sqrt{2} \int v^*(\mathbf{k}_f, \mathbf{r})\mathbf{p}_s(\mathbf{r})\, d\mathbf{r} \qquad \text{(VI.7)}$$

where

$$N^{-1/2} g_s(\mathbf{r})\chi(\zeta) = \int \Phi_s^*(x_1, \ldots, x_{N-1})\, \Phi_0(x_1, \ldots, x_{N-1}; \mathbf{r}, \chi(\zeta)) \times dx_1 \cdots dx_{N-1} \qquad \text{(VI.8)}$$

$$N^{-1/2} \mathbf{p}_s(\mathbf{r})\chi(\zeta) = (N-1) \int \Phi_s^*(x_1, \ldots, x_{N-1})\mathbf{A}_1 \cdot \boldsymbol{\nabla}_1 \Phi_0(x_1, \cdots x_{N-1}; \mathbf{r}, \chi(\zeta))\, dx_1 \cdots dx_{N-1}. \qquad \text{(VI.9)}$$

The first term in Eq. (VI.7) relates the Feynman–Dyson amplitude $g_s(\mathbf{r})$ to the photoionization cross section and the second term arises from the nonorthogonality of $v(\mathbf{k}_f, \mathbf{r})$ and Φ_0. When $v(\mathbf{k}_f, \mathbf{r})$ is strongly orthogonal to Φ_0, this term vanishes. Even when $v(\mathbf{k}_f, \mathbf{r})$ is not strongly orthogonal to Φ_0, the first term in Eq. (VI.7) will dominate if the kinetic energy of the photoelectron is much greater than its binding energy (Rabalais *et al.*, 1974), therefore we shall neglect this term:

$$\frac{d\sigma_s}{d\Omega_f} = \frac{8\pi^2|\mathbf{k}_f|}{c|A_0|^2\omega} \left| \int v^*(\mathbf{k}_f, \mathbf{r})\mathbf{A}_s \cdot \boldsymbol{\nabla} g_s(\mathbf{r})\, d\mathbf{r} \right|^2 . \qquad \text{(VI.10)}$$

Further simplification can be obtained by neglecting retardation of the photoelectron momentum by the photon momentum (also called the dipole approximation in analogy with photon-induced transitions in the discrete spectrum; Bethe and Salpeter, 1957; Steinfeld, 1974). The vector potential $\mathbf{A}_s$ has the following plane wave decomposition in terms of the incident photon momentum $\mathbf{k}_\omega$ and polarization $\mathbf{n}$

$$\mathbf{A}_s = |\mathbf{A}_0| \exp(i\mathbf{k}_\omega \cdot \mathbf{r}_s)\mathbf{n}. \qquad \text{(VI.11)}$$

If the wavelength of the incident photon is large compared with molecular dimensions, the exponential may be approximated by unity.

$$\mathbf{A}_s \simeq |A_0|\mathbf{n}. \qquad \text{(VI.12)}$$

With this approximation, the differential photoionization cross section becomes

$$d\sigma_s/d\Omega_f = (8\pi^2|\mathbf{k}_f|/c\omega)|\mathbf{n} \cdot \mathbf{P}|^2, \qquad \text{(VI.13)}$$

where

$$\mathbf{P} \equiv \int v^*(\mathbf{k}_f, \mathbf{r})\, \nabla g_s(\mathbf{r})\, d\mathbf{r}. \qquad \text{(VI.14)}$$

Owing to the random orientation of molecules in a gaseous sample, the experimentally observed photoionization intensities in the molecular reference frame represent an average over all incident-photon directions. Furthermore, if the incident photon beam is unpolarized, we must also average over photon polarizations. Making the appropriate averages in Eq. (VI.13) (Smith, 1971), we obtain

$$\begin{aligned} d\sigma_s/d\Omega_f = (8\pi^2|\mathbf{k}_f|/c\omega)(4\pi)^{-1} \int \tfrac{1}{2}\{|\mathbf{n}_1\cdot\mathbf{P}|^2 \\ + |\mathbf{n}_2\cdot\mathbf{P}|^2\}\, d\Omega_\omega. \end{aligned} \qquad \text{(VI.15)}$$

Since the two polarization directions $\mathbf{n}_1$ and $\mathbf{n}_2$ and the incident-photon direction $\mathbf{k}_\omega/|\mathbf{k}_\omega|$ form a right-handed system of axes, we can write

$$|\mathbf{P}|^2 = |\mathbf{n}_1\cdot\mathbf{P}|^2 + |\mathbf{n}_2\cdot\mathbf{P}|^2 + |\mathbf{k}_\omega\cdot\mathbf{P}|^2/|\mathbf{k}_\omega|^2, \qquad \text{(VI.16)}$$

and Eq. (VI.15) becomes

$$\begin{aligned} d\sigma_s/d\Omega_f &= (8\pi^2|\mathbf{k}_f|/c\omega)\tfrac{1}{8} \int \{|\mathbf{P}|^2 - |\mathbf{k}_\omega\cdot\mathbf{P}|^2/|\mathbf{k}_\omega|^2\}\, d\Omega_\omega && \text{(VI.17)} \\ &= (8\pi^2|\mathbf{k}_f|/c\omega)|\mathbf{P}|^2(8\pi)^{-1} \int \{1 - \cos^2\theta_\omega\}\, d\Omega_\omega && \text{(VI.18)} \\ &= (8\pi^2|\mathbf{k}_f|/3c\omega)|\mathbf{P}|^2. && \text{(VI.19)} \end{aligned}$$

In order to evaluate $|\mathbf{P}|^2$, some form for the photoelectron wavefunction $v(\mathbf{k}_f, \mathbf{r})$ must now be chosen. In principle, the photoelectron wavefunction could be obtained by the solution of the Bethe–Salpeter equation for the polarization propagator, where the superoperator resolvent has been modified to include the time-dependent interaction of the radiation and matter fields (see, e.g., Csanak *et al.*, 1971). A solution of this type would require the use of continuum functions as well as discrete functions in the basis and is not yet feasible for general molecular systems. Alternatively, we seek a simple but accurate, analytic representation of the photoelectron wavefunction. For photoionization of atoms or molecules with high (tetrahedral or octahedral) symmetry, the electronic potential of the ion is nearly spherically symmetric, and $v(\mathbf{k}_f, \mathbf{r})$ may be asymptotically represented by a plane wave plus incoming Coulomb waves (see, e.g., Smith, 1971). For molecules with lower symmetry, distortions of the electronic potential enormously complicate the nature of the incoming waves. We assume in this derivation that the photoelectron is simply represented by the plane wave part

$$v(\mathbf{k}_f, \mathbf{r}) = (2\pi)^{-3/2} \exp(i\mathbf{k}_f \cdot \mathbf{r}). \tag{VI.20}$$

The applicability and implications of this approximation will be discussed in the following section. With this choice, Eq. (VI.14) can be integrated by parts and yields

$$\mathbf{P} = -(2\pi)^{-3/2} \int g_s(\mathbf{r})\, \nabla \exp(-i\mathbf{k}_f \cdot \mathbf{r})\, d\mathbf{r} \tag{VI.21}$$

$$= i\mathbf{k}_f(2\pi)^{-3/2} \int \exp(-i\mathbf{k}_f \cdot \mathbf{r}) g_s(\mathbf{r})\, d\mathbf{r}. \tag{VI.22}$$

In our computational scheme, the Feynman–Dyson amplitudes in Eq. (VI.22) are represented by a linear combination of Hartree–Fock orbitals. The Hartree–Fock orbitals can be decomposed into contracted Cartesian Gaussian functions on each atomic center, and each contracted Gaussian function can be further decomposed into a sum of primitive Gaussian functions. Therefore, ultimately the Feynman–Dyson amplitudes can be represented as some linear combination of primitive Gaussian functions on each atomic center

$$g_s(\mathbf{r}) = \sum_{\alpha,k} C^s_{\alpha k} \phi_{\alpha k}(\mathbf{r} - \mathbf{R}_\alpha). \tag{VI.23}$$

Here α represents the sum over atomic centers and k the sum over primitive Gaussian functions on each center. Transforming the photoelectron position vector to the coordinate frames of each atomic center by the substitution $\mathbf{r}' = \mathbf{r} - \mathbf{R}_\alpha$, Eq. (VI.22) can be re-expressed in terms of the primitive computational basis

$$\mathbf{P} = i\mathbf{k}_f(2\pi)^{-3/2} \sum_{\alpha,k} \exp(-i\mathbf{k}_f \cdot \mathbf{R}_\alpha) c^s_{\alpha k} \int \exp(-i\mathbf{k}_f \cdot \mathbf{r}') \phi_{\alpha k}(\mathbf{r}')\, d\mathbf{r}'. \tag{VI.24}$$

The integral over $\mathbf{r}$ in Eq. (VI.24) represents a Fourier transform of each primitive Gaussian function, and formulas for its evaluation are derived by Kaijser and Smith (1977).

The final step in this derivation is to integrate the differential photoionization cross section [Eq. (VI.19)] over all photoelectron directions in the solid angle $d\Omega_f$

$$\sigma_s = (8\pi^2 k_f / 3c\omega) \int |\mathbf{P}|^2\, d\Omega_f. \tag{VI.25}$$

Since $\mathbf{P}$ involves a sum over atomic centers, Eq. (VI.25) will contain both one- and two-center contributions (Schweig and Thiel, 1974)

$$\sigma_s = (8\pi^2 k_f^3 / 3c\omega) \sum_{\alpha,k} \sum_{\beta,l} c^s_{\alpha k} c^s_{\beta l} Q^s_{\alpha k,\beta l}. \tag{VI.26}$$

The one-center terms ($\alpha = \beta$) have the form

$$Q^{\mathrm{s}}_{\alpha k,\alpha l} = \int \Phi^{*}_{\alpha k}(\mathbf{k}_{\mathrm{f}})\Phi_{\alpha l}(\mathbf{k}_{\mathrm{f}})\, d\Omega_{\mathrm{f}}, \tag{VI.27}$$

where $\phi_{\alpha k}(\mathbf{k}_{\mathrm{f}})$ represents the Fourier transform

$$\Phi_{\alpha k})\mathbf{k}_{\mathrm{f}}) = (2\pi)^{-3/2} \int \exp(-i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{r}')\phi_{\alpha k}(\mathbf{r}')\, d\mathbf{r}' \tag{VI.28}$$

and the two-center terms ($\alpha \neq \beta$) are given by

$$Q^{\mathrm{s}}_{\alpha k,\beta l} = \int \Phi^{*}_{\alpha k}(\mathbf{k}_{\mathrm{f}})\Phi_{\beta l}(\mathbf{k}_{\mathrm{f}}) \exp(-i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{R}_{\alpha\beta})\, d\Omega_{\mathrm{f}}, \tag{VI.29}$$

where $\mathbf{R}_{\alpha\beta} = \mathbf{R}_{\alpha} - \mathbf{R}_{\beta}$. Owing to the orthogonality of the spherical harmonics that describe the angular dependence of the Fourier transforms, the one-center terms are easily evaluated. The two-center terms are complicated slightly by the exponential factor, but these too can be evaluated analytically. For this purpose, it is convenient to define the integral

$$I(l_1m_1, l_2m_2) = \int \mathcal{Y}_{l_1m_1}(\theta_{\mathrm{f}}, \phi_{\mathrm{f}})\mathcal{Y}_{l_2m_2}(\theta_{\mathrm{f}}, \phi_{\mathrm{f}}) \exp(-i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{R}_{\alpha\beta})\, d\Omega_{\mathrm{f}}, \tag{VI.30}$$

where $\mathcal{Y}_{l_1m_1}$ and $\mathcal{Y}_{l_2m_2}$ are real spherical harmonics (Harris, 1973) representing the angular dependence of the transforms $\Phi^{*}_{\alpha k}$ and $\Phi_{\beta l}$, respectively. Using the expansion

$$\exp(\pm i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{R}_{\alpha\beta}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (\pm i)^{l} j_l(k_{\mathrm{f}}R_{\alpha\beta})\mathcal{Y}_{lm}(\theta_{\mathrm{f}}, \phi_{\mathrm{f}})\mathcal{Y}_{lm}(\theta, \phi), \tag{VI.31}$$

Eq. (VI.30) becomes

$$I(l_1m_1, l_2m_2) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-i)^{l} j_l(k_{\mathrm{f}}R_{\alpha\beta})C^{m_1m_2m}_{l_1l_2l}\mathcal{Y}_{lm}(\theta, \phi). \tag{VI.32}$$

In these equations, $(\theta_{\mathrm{f}}, \phi_{\mathrm{f}})$ represents the photoelectron direction in the atomic reference frame, (θ, ϕ) represents the direction of $\mathbf{R}_{\alpha\beta}$ in the molecular frame, $j_l(k_{\mathrm{f}}R_{\alpha\beta})$ is a spherical Bessel function of lth order, and $C^{m_1m_2m}_{l_1l_2l}$ is a Clebsh–Gordan coefficient defined by (Harris, 1973)

$$C^{m_1m_2m}_{l_1l_2l} = \int \mathcal{Y}_{l_1m_1}(\theta_{\mathrm{f}}, \phi_{\mathrm{f}})\mathcal{Y}_{l_2m_2}(\theta_{\mathrm{f}}, \phi_{\mathrm{f}})\mathcal{Y}_{lm}(\theta_{\mathrm{f}}, \phi_{\mathrm{f}})\, d\Omega_{\mathrm{f}}. \tag{VI.33}$$

When the distance $\mathbf{R}_{\alpha\beta}$ coincides with the molecular z axis, the expansion in Eq. (VI.31) simplifies to

$$\exp(\pm i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{R}_{\alpha\beta}) = (4\pi)^{1/2} \sum_{l} (\pm i)^{l}(2l + 1)^{1/2} j_l(k_{\mathrm{f}}R_{\alpha\beta})\mathcal{Y}_{l0}(\theta_{\mathrm{f}}, \phi_{\mathrm{f}}) \tag{VI.34}$$

and Eq. (VI.30) becomes

$$I(l_1m_1,\ l_2m_2)$$

$$= (4\pi)^{1/2}\,\delta_{m_1m_2} \sum_{l=|l_1-l_2|}^{|l_1+l_2|} (-i)^l(2l+1)^{1/2} C_{l_1l_2l}^{m_1m_20} j_l(k_{\mathrm{f}}R_{\alpha\beta}). \qquad \text{(VI.35)}$$

For arbitrary directions of $\mathbf{R}_{\alpha\beta}$ that do not coincide with the molecular z axis, a new coordinate frame can be defined in which $\mathbf{R}_{\alpha\beta}$ does coincide with this axis, and the spherical harmonics can be transformed to this coordinate frame using the familiar rotation matrices (Schweig and Thiel, 1974). In this way, Eq. (VI.35) can be used to evaluate all two-center integrals arising from any molecular geometry.

Another simple representation of the photoelectron wavefunction is an orthogonalized plane wave (OPW) (see Ellison, 1974; Lohr, 1972)

$$v(\mathbf{k}_{\mathrm{f}}, \mathbf{r}) = N\left[1 - \sum_{\alpha k} |\phi_{\alpha k}(\mathbf{r} - \mathbf{R}_\alpha)\rangle\langle\phi_{\alpha k}(\mathbf{r} - \mathbf{R}_\alpha)|\right] \exp(i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{r}), \qquad \text{(VI.36)}$$

i.e., the plane wave is orthogonalized to all bound-state basis functions. This choice guarantees the orthogonality of the upper (continuum) N-electron state to the N-electron ground state.

The normalization constant

$$N = \left[1 - 2\sum_{\alpha k} |\Phi_{\alpha k}(\mathbf{k}_f)|^2 + \sum_{\alpha k}\sum_{\beta l} \Phi_{\alpha k}(\mathbf{k}_f)\Phi^*_{\beta l}(\mathbf{k}_f)\langle\Phi_{\alpha k}|\Phi_{\beta l}\rangle\right]^{-1/2} \qquad \text{(VI.37)}$$

will differ significantly from unity only close to threshold for ionization processes.

Substituting the expression (VI.36) into Eq. (VI.14) results in the following expression for the differential cross section of Eq. (VI.19):

$$\frac{d\sigma_{\mathrm{s}}(\mathbf{k}_{\mathrm{f}})}{d\Omega_{\mathrm{f}}} = \frac{8\pi^2|\mathbf{k}_{\mathrm{f}}|}{3c\omega}\left[\sum_{\alpha k}\sum_{\beta l}\{|\mathbf{k}_{\mathrm{f}}|^2 C^{\mathrm{s}}_{\alpha k}C^{\mathrm{s}}_{\beta l} + \mathbf{m}_{\alpha k}\cdot\mathbf{m}_{\beta l}\}\exp(-i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{R}_{\alpha\beta})\right.$$
$$\times\ \Phi_{\alpha k}(\mathbf{k}_f)\Phi^*_{\beta l}(\mathbf{k}_f) - 2\,\mathrm{Im}\sum_{\alpha k}\sum_{\beta l}\mathbf{k}_{\mathrm{f}}\cdot\mathbf{m}_{\alpha k}C^{\mathrm{s}}_{\beta l}\exp(-i\mathbf{k}_{\mathrm{f}}\cdot\mathbf{R}_{\alpha\beta})$$
$$\left.\times\ \Phi_{\alpha k}(\mathbf{k}_f)\Phi^*_{\beta l}(\mathbf{k}_{\mathrm{f}})\right], \qquad \text{(VI.38)}$$

where

$$\mathbf{m}_{\alpha k} = \sum_{\beta l} \langle\Phi_{\alpha k}(\mathbf{r} - \mathbf{R}_\alpha)|\nabla|\Phi_{\beta l}(\mathbf{r} - \mathbf{R}_\beta)\rangle C^{\mathrm{s}}_{\beta l}, \qquad \mathbf{k}_{\mathrm{f}}\cdot\mathbf{m}_{\alpha k} = |\mathbf{k}_{\mathrm{f}}||\mathbf{m}_{\alpha k}|\cos\theta;$$

using the addition theorem for spherical harmonics

$$P_l(\cos\theta) = [4\pi/(2l+1)] \sum_{m=-l}^{l} \mathcal{Y}_{lm}(\theta', \phi')\mathcal{Y}_{lm}(\theta'', \phi''),$$

θ being the angle between the directions defined by (θ', ϕ') and (θ'', ϕ'')

$$\cos\theta = P_1(\cos\theta) = \tfrac{1}{3}(4\pi)\sum_{m=-1}^{1} \mathcal{Y}_{1m}(\theta_\mathrm{f}, \phi_\mathrm{f})\mathcal{Y}_{1m}(\theta_{\mathbf{m}_{\alpha k}}, \phi_{\mathbf{m}_{\alpha k}}),$$

where

$$\theta_{m_{\alpha k}} = \cos^{-1}(m^z_{\alpha k}/|m_{\alpha k}|), \qquad \phi_{m_{\alpha k}} = \tan^{-1}(m^y_{\alpha k}/m^x_{\alpha k}).$$

The superscripts denote the appropriate components of the vector $\mathbf{m}_{\alpha k}$. Finally, averaging over all photoelectron directions yields

$$\begin{aligned}\sigma_\mathrm{s} = \frac{8\pi^2|\mathbf{k}_\mathrm{f}|}{3c\omega}\Big[&\sum_{\alpha k}\sum_{\beta l}\{|\mathbf{k}_\mathrm{f}|^2 C^\mathrm{s}_{\alpha k}C^\mathrm{s}_{\beta l} + \mathbf{m}_{\alpha k}\cdot\mathbf{m}_{\beta l}\}Q_{\alpha k,\beta l}\\ &- (16/3)\pi^{3/2}\,\mathrm{Im}\sum_{\alpha k}\sum_{\beta l}\sum_{i}\sum_{j}\sum_{L=|l_i-l_j|}^{l_i+l_j}\sum_{l=|L-1|}^{L+1}\mathbf{m}_{\alpha k}\\ &\times|\mathbf{k}_\mathrm{f}|f_{\alpha k}(k_\mathrm{f})f^*_{\beta l}(k_\mathrm{f})(-i)^l j_l(k_\mathrm{f}R_{\alpha\beta})(2l+1)^{1/2}C_i^{\alpha k}C_j^{\beta l}\\ &\times\sum_{n=-1}^{1}\mathcal{Y}_{1n}(\theta_{\mathbf{m}_{\alpha k}}, \phi_{\mathbf{m}_{\alpha k}})C^{nn0}_{L1l}C^{nm_im_j}_{Ll_il_j})\end{aligned} \tag{VI.39}$$

for linear molecules. In Eq. (VI.39) $f_{\alpha k}$ and $f_{\beta l}$ are the radial portions of the Fourier transforms $\Phi_{\alpha k}(\mathbf{k}_\mathrm{f})$ and $\Phi_{\beta l}(\mathbf{k}_\mathrm{f})$, respectively (Kaijser and Smith, 1977):

$$\Phi_{\alpha k}(\mathbf{k}_\mathrm{f}) = f_{\alpha k}(k_\mathrm{f})\sum_i C_i^{\alpha k}\mathcal{Y}_{l_i,m_i}(\theta_\mathrm{f}, \phi_\mathrm{f}), \tag{VI.40}$$

$$\Phi_{\beta l}(\mathbf{k}_\mathrm{f}) = f_{\beta l}(k_\mathrm{f})\sum_j C_j^{\beta l}\mathcal{Y}_{l_j,m_j}(\theta_\mathrm{f}, \phi_\mathrm{f}). \tag{VI.41}$$

For nonlinear molecules, similar expressions apply employing appropriate rotation matrices.

C. Discussion of Approximations

Relatively little work has been devoted to the theoretical calculation of photoionization cross sections for molecules compared with that for atoms (see, e.g., Marr, 1967; Stewart, 1967; Kelly, 1976). The major impediments until recently have been a lack of sufficiently accurate molecular wave functions and an absence of accurate analytic representations for the photoelectron wave function (Kaplan and Markin, 1968; Schweig and Thiel, 1974). With the development of efficient molecular integral and Hartree–Fock programs, Hartree–Fock wavefunctions are now readily available for a large number of molecules. This availability in turn has stimulated several theoretical calculations of molecular photoionization cross sections using the frozen orbital approximation (Rabalais *et al.*, 1974; Dewar *et al.*, 1975; Allison and Cavell, 1978; Cavell and Allison, 1978).

In the frozen orbital approximation, the N-electron reference state is assumed to be the Hartree–Fock ground state, and the ion states are constructed by removing the orbital corresponding to the ionized electron. This approximation neglects both correlation corrections in the ground and ion states and ion-state relaxation. Following Purvis and Öhrn (1975a), we have replaced the frozen orbital approximation by a many-electron treatment that incorporates both relaxation and correlation corrections. This treatment derives from the use of the Feynman–Dyson amplitudes obtained from the electron propagator to compute the photoionization cross section.

The form of the photoelectron wave function is still a major problem in the calculation of molecular photoionization cross sections and represents the most critical step in our derivation. The plane wave approximation was chosen for its simplicity, however, it has several serious limitations. The most serious limitation is its failure to correctly predict experimentally observed angular distributions (Bethe and Salpeter, 1957; Schweig and Thiel, 1974). This deficiency is not readily apparent when the differential cross section is averaged over all photoelectron directions, and in our computational applications, we compute only spherically averaged, total cross sections. Lohr (1972) has shown that by retaining the second term in Eq. (VI.7), qualitatively correct angular distributions may be obtained. The retention of this term is equivalent to the orthogonalized plane wave (OPW) approximation.

A second limitation of the plane wave approximation is the implicit neglect of electrostatic interactions between the photoelectron and the molecular ion. For ionization processes near threshold where the photoelectron leaves with low kinetic energy, these interactions are especially important, and the wavefunction of the photoelectron exhibits a decrease in wavelength as $\mathbf{r} \rightarrow \mathbf{0}$. The OPW approximation again partially corrects this deficiency (Lohr, 1972) but exhibits a rather abrupt change in wavelength that is more characteristic of a short-range potential rather than the long-range Coulomb potential. Other representations of low-energy photoelectrons, e.g., multicentered Coulomb wave expansions, have also been proposed (Tuckwell, 1970). As the kinetic energy of the photoelectron tends to higher energies, the effect of electrostatic interactions on the total cross section becomes negligible, and the plane wave approximation becomes sufficiently accurate (Bethe and Salpeter, 1957).

Unfortunately, as the plane wave approximation becomes more suitable at high photoelectron energies, the dipole approximation [Eq. (VI.12)] deteriorates and must be re-examined. Bethe and Salpeter (1957) have shown that when retardation effects are included in the calculation of differential photoionization cross sections, the lowest-order correction is proportional to ($|\mathbf{v}|/c$), where v is the photoelectron velocity. This correction, however, only affects the angular distribution and vanishes when the differential cross section is averaged over all incident-photon directions. Higher-order corrections for retardation are proportional to ($|\mathbf{v}|/c)^2$ as are the relativistic corrections, but these are usually negligible even when the photon wavelength is comparable to the molecular dimensions.

D. Computational Applications

In this section, the relative photoionization intensities for the water and acetylene molecules are computed using the Feynman–Dyson amplitudes obtained in the second-order diagram-conserving and the diagonal 2p–h TDA renormalized decoupling approximations. Comparative calculations corresponding to a Mg K_α photon source ($\hbar\omega = 1253.6$ eV), for which the plane wave approximation is expected to be good, and a He (II) photon source ($\hbar\omega = 40.81$ eV), for which the plane wave approximation is expected to be less accurate, are presented. These results are further compared with intensities obtained using the frozen orbital approximation in order to assess the magnitude of many-electron correlation and relaxation corrections. For acetylene, the dependence of intensity on photon energy for the valence orbitals is plotted, and orbital and density difference plots are presented and discussed.

The relative photoionization intensities for water corresponding to a Mg K_α photon source and a He (II) photon source are presented in Tables XIV and XV, respectively. These results were obtained using the 26-contracted-Gaussian-orbital basis at the experimentally determined equilibrium geometry as described in detail in Section IV,E and are scaled relative to the $3a_1$ intensity. As expected, the relative intensities computed for the Mg K_α source in Table XIV compare reasonably well with those obtained experimentally (Rabalais *et al.*, 1974). The orthogonalized plane

TABLE XIV

RELATIVE PHOTOIONIZATION INTENSITIES FOR WATER EXCITED BY Mg K_α (1253.6 eV)

Orbital	FO[a]	$\Sigma^{(2)}_{(E)}$	$\Sigma^{(2)}_{(E)_{\text{SHIFT}}} + \Sigma^{(3)}_{(\infty)}$	OPW[b]	Experiment[b]
$2a_1$	4.69	1.32 2.57	4.15	4.50	3.84
$3a_1$	1.00	1.00	1.00	1.00	1.00
$1b_1$	0.62	0.52	0.55	0.18	0.36
$1b_2$	0.40	0.35	0.37	0.09	0.31

[a] Frozen orbital approximation.

[b] Rabalais *et al.* (1974).

TABLE XV

RELATIVE PHOTOIONIZATION INTENSITIES FOR WATER EXCITED BY He(II) (40.81 eV)

Orbital	FO[a]	$\Sigma^{(2)}_{(E)}$	$\Sigma^{(2)}_{(E)_{\mathrm{SHIFT}}} + \Sigma^{(3)}_{(\infty)}$	OPW[b]	Experiment[c]
$2a_1$	0.55	0.28 0.66	0.84	0.26	[d]
$3a_1$	1.00	1.00	1.00	1.00	1.00
$1b_1$	1.16	1.15	1.15	0.86	0.96
$1b_2$	0.83	0.84	0.83	1.10	0.80

[a] Frozen orbital approximation.
[b] Rabalais *et al.* (1975).
[c] Rabalais *et al.* (1974).
[d] Not observed.

wave results of Rabalais *et al.* (1975) are presented for comparison and also correctly order the relative intensities. It is interesting to note the larger discrepancy between the $1b_1$ and $1b_2$ intensities in our calculations compared to Rabalais *et al.* than in the $2a_1$ and $3a_1$ intensities. Since for X-ray photons the OPW corrections are not expected to be large, this discrepancy is most likely a basis set effect. Our basis contained d-type polarization functions on oxygen as well as p-type polarization functions on the hydrogen atoms, whereas Rabalais *et al.* have used only a minimal basis.

The relative intensities presented in Table XV do not correctly match the experimentally observed intensities. This is not particularly surprising owing to the inadequacy of the plane wave approximation at low photon energies. It is more surprising that the OPW results also yield an incorrect ordering of the intensities. The failure of the OPW approximation indicates the necessity for a more accurate photoelectron wavefunction.

Many-electron correlation and relaxation corrections appear negligible in the intensities of both Tables XIV and XV. The deviations between the frozen orbital approximation (FO), the second-order self-energy approximation ($\Sigma(E)^{(2)}$), and the diagonal 2p–h TDA with third-order constant energy diagrams ($\Sigma(E)^{(2)}_{\mathrm{SHIFT}} + \Sigma(\infty)^{(3)}$), are small and may be attributed to differences in the photoelectron momenta. Different ionization energies obtained with different decoupling approximations were used to compute the photoelectron momenta from the conservation of total energy

$$|\mathbf{k}_f| = [2(\omega - \mathrm{IP})]^{1/2}, \qquad \text{(VI.42)}$$

(in atomic units), consequently, deviations in the IPs result in deviations in $|\mathbf{k}_f|$.

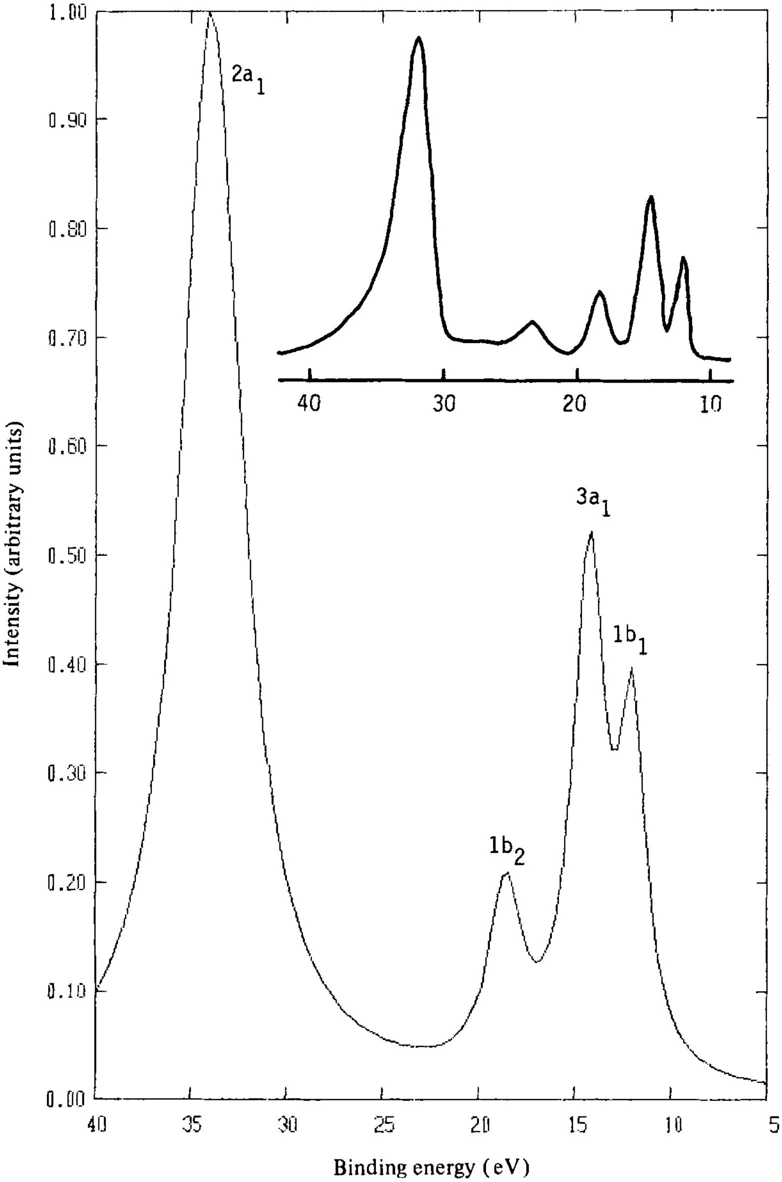


Fig. 4. A plot of the theoretical ESCA spectrum for the valence ionizations of water. The experimental spectrum of Siegbahn *et al.* (1969) is sketched in the insert.

The relative intensities computed with the diagonal 2p–h TDA plus third-order constant energy diagrams for the Mg K_{α} photon source are plotted in Fig. 4. In order to compare the theoretical spectrum to the experimental ESCA (electron spectroscopy for chemical analysis) spectrum (Siegbahn *et al.*, 1969), which is sketched as an insert, the ionization lines were given a Lorentzian width estimated from the experimental spectrum. The major features of the experimental spectrum are well reproduced with the exception of the peak at approximately 23 eV. This peak has been attributed to the ionization of $2a_1$ electrons by the Mg $K_{\alpha 3,4}$ satellite in the photon source (Siegbahn *et al.*, 1969) and therefore should not appear in the theoretical spectrum since the calculations assumed a purely monochromatic source.

A recent experimental study of relative photoionization intensities of acetylene with various photon sources (Cavell and Allison, 1978) motivated our examination of this molecule. As preparatory steps to the calculation of relative intensities, Hartree–Fock and electron propagator calculations were performed at the experimental equilibrium geometry, $R(\mathrm{CC}) = 2.279$ a.u. and $R(\mathrm{CH}) = 2.005$ a.u. (Buenker *et al.*, 1967), with two different basis sets. The first basis consisted of Huzinaga's 9s, 5p primitive basis for carbon and 4s basis (unscaled) for hydrogen (Huzinaga, 1965) contracted with Dunning's coefficients (Dunning, 1970) to 4s, 2p on carbon and 2s on hydrogen (see Table VII). The complete molecular basis consisted of 24 contracted Gaussian orbitals and yielded a Hartree–Fock total energy of $E(\mathrm{HF}) = -76.7948$ H. The second basis augmented the first by the addition of a set of d functions on each carbon atom ($\alpha_d = 0.60$) and a set of p functions on each hydrogen atom ($\alpha_p = 0.75$). The addition of these diffuse, polarization functions brought the size of the basis to 42 contracted Gaussian orbitals and yielded a Hartree–Fock total energy of $E(\mathrm{HF}) = -76.8267$ H.

Valence ionization energies were computed with the second-order self-energy approximation and the diagonal 2p–h TDA for each basis. The results for the 24 orbital basis are presented in Table XVI and the results for the 42 orbital basis appear in Table XVII. In each table the full nondiagonal 2p–h TDA results of Cederbaum *et al.* (1978) and the experimental results of Cavell and Allison (1978) are included for comparison. In contrast to previous calculations reported here, the ionization energies obtained for acetylene are larger (with the exception of the $1\pi_u$ ionization) than the experimental values. A breakdown in the quasi-particle picture for the $2\sigma_g$ ionization, which is evidenced by the shake-up pole, may account for the particularly poor results for these ionizations. The off-diagonal 2p–h TDA contributions considerably improve these two ioniza-

TABLE XVI

VALENCE IONIZATION ENERGIES FOR ACETYLENE (24 CGTOs)

Orbital	Koopmans	$\Sigma^{(2)}_{(E)}$	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	Theory[a]	Experiment[b]
$2\sigma_g$ Shake-up	—	38.29	—	28.9	27.6
$2\sigma_g$	28.42	25.47	26.48	23.9	23.5
$3\sigma_g$	18.55	16.39	17.08	16.4	16.8
$1\pi_u$	11.32	11.20	11.29	10.8	11.4
$2\sigma_u$	20.81	18.21	19.12	18.0	18.7

[a] Cederbaum *et al.* (1978).
[b] Cavell and Allison (1978).

tion energies (Cederbaum *et al.*, 1978), however, the shake-up energy still disagrees with the experimental value by more than an electron volt.

Relative photoionization intensities for acetylene are presented in Table XVIII for a Mg K_α photon source and in Table XIX for a He (II) photon source. In both tables the intensities were scaled relative to the $1\pi_u$ intensity. As for water, the intensities corresponding to the Mg K_α source are in reasonable agreement with experimental intensities and show only a slight diminuation when correlation and relaxation effects are included. The OPW result of Cavell and Allison (1978) for the $2\sigma_g$ ionization in Table XVIII seems inexplicably high, and the $3\sigma_g$ ionization is not observed experimentally.

The relative intensities for acetylene computed with the He (II) source exhibit better agreement with the experimental results than do the water

TABLE XVII

VALENCE IONIZATION ENERGIES FOR ACETYLENE (42 CGTOs)

Orbital	Koopmans	$\Sigma^{(2)}_{(E)}$	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	Theory[a]	Experiment[b]
$2\sigma_g$ Shake-up	—	38.20	34.45	28.9	27.6
$2\sigma_g$	28.07	24.56	25.73	23.9	23.5
$3\sigma_g$	18.46	16.56	17.24	16.4	16.8
$1\pi_u$	11.16	11.13	11.24	10.8	11.4
$2\sigma_u$	20.90	[c]	19.47	18.0	18.7

[a] Cederbaum *et al.* (1978).
[b] Cavell and Allison (1978).
[c] No results.

TABLE XVIII

RELATIVE PHOTOIONIZATION INTENSITIES FOR ACETYLENE EXCITED BY Mg K_α (1253.6 eV)

Orbital	FO[a]	$\Sigma^{(2)}_{(E)}$	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	OPW[b]	Experiment[b]
$2\sigma_g$	18.90	17.75	17.79	26.86	13.3
$3\sigma_g$	0.51	0.48	0.48	0.65	[c]
$1\pi_u$	1.00	1.00	1.00	1.00	1.00
$2\sigma_u$	7.74	—	7.50	11.18	9.5

[a] Frozen orbital approximation.
[b] Cavell and Allison (1978).
[c] Not observed.

results. Here, only the relative intensities of the two weakest ionizations, the $2\sigma_g$ and $2\sigma_u$, were reversed. The OPW results predict the correct ordering but attribute a much weaker intensity to the $2\sigma_g$ ionization than is observed experimentally.

The relative intensities in Table XVIII computed with the diagonal 2p–h TDA and Mg K_α source have been plotted in Fig. 5. As in Fig. 4, the lines have been given Lorentzian widths and the experimental spectrum appears as an insert. The most striking difference between these two spectra is the absence of the intense shake-up in the theoretical spectrum. Not only was this peak predicted to lie 7 eV higher than the experimental peak in energy, it also yielded a relative intensity several orders of magnitude smaller than the $2\sigma_g$ intensity (at 23.4 eV). The weak experimental peak at about 14.5 eV arises from the ionization of $2\sigma_g$ electrons by Mg $K_{\alpha 3,4}$ radiation (Cavell and Allison, 1978) and is absent in the theoretical spectrum. The $3\sigma_g$ peak that should occur at 16.8 eV is not observed

TABLE XIX

RELATIVE PHOTOIONIZATION INTENSITIES FOR ACETYLENE EXCITED BY He(II) (40.81 eV)

Orbital	FO[a]	$\Sigma^{(2)}_{(E)}$	$\Sigma^{(2)}_{(E)\mathrm{SHIFT}}$	OPW[b]	Experiment[b]
$2\sigma_g$	0.45	0.36	0.72	0.09	0.26
$3\sigma_g$	0.45	0.44	0.87	0.77	0.68
$1\pi_u$	1.00	1.00	1.00	1.00	1.00
$2\sigma_u$	0.29	—	0.50	0.41	0.29

[a] Frozen orbital approximation.
[b] Cavell and Allison (1978).

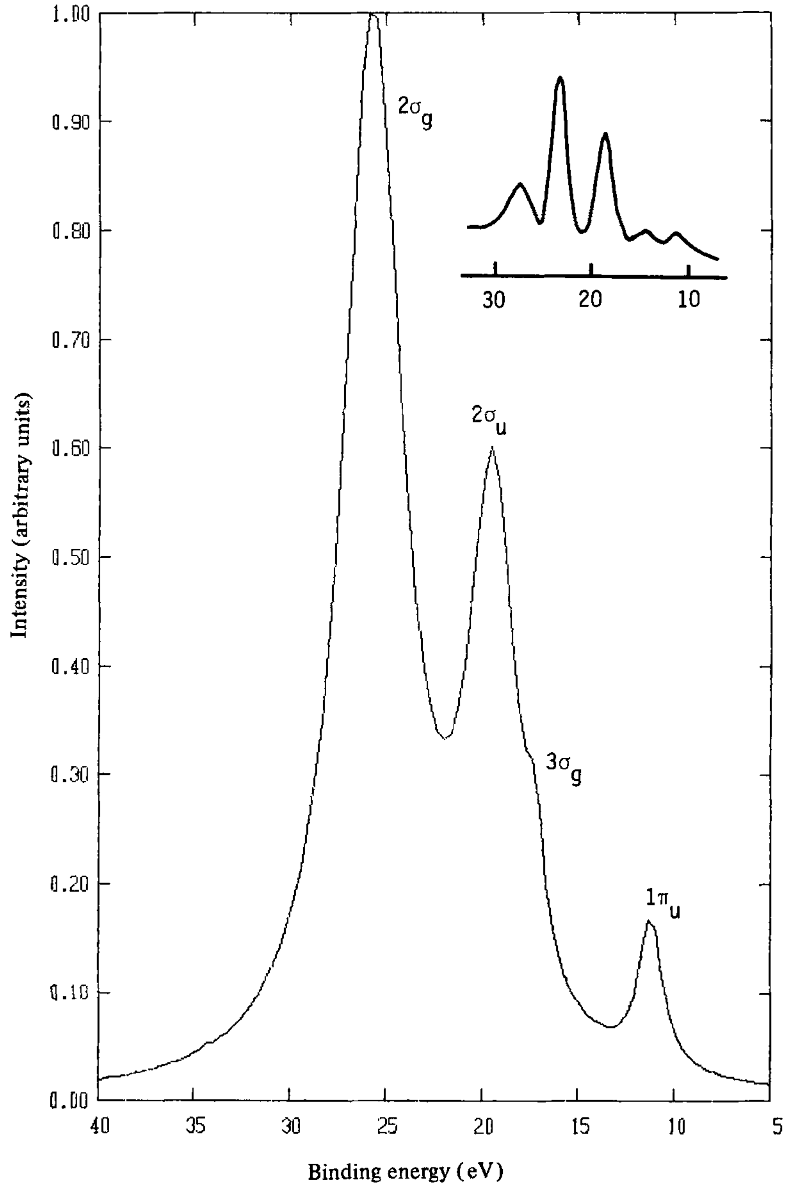


Fig. 5. A plot of the theoretical ESCA spectrum for the valence ionizations of acetylene. The experimental spectrum of Cavell and Allison (1978) is sketched in the insert.

experimentally but can be identified as a shoulder on the $2\sigma_u$ peak in the theoretical spectrum.

Figure 6 shows the dependence of the photoionization cross section on photon energy for 0–200 eV. Over this energy range, ionization from the $1\pi_u$ orbital is predicted to be most probable, and this is verified by the experimental data of Cavell and Allison (1978) obtained at 21.2 eV [He (I)], 40.8 eV [He (II)], and 151.4 eV [Zr M_ζ]. Another interesting feature of this figure is the slight minimum exhibited by the $2\sigma_g$ curve around 125 eV. Minima of this type in the photoionization cross section were first predicted by Cooper (1962) and are referred to as Cooper minima. Cooper minima have been observed in the cross sections for a number of atoms by means of X-ray and ultraviolet absorption spectroscopy (see, e.g., Codling, 1976), however, at present there are no photoelectron spectroscopic data of this type owing to the limitation of available photon sources. The application of synchrotron radiation to photoelectron spectroscopy should soon offer a means of studying the energy dependence of the orbital cross sections in a continuous energy interval from 0 to about 200 eV (Codling, 1973).

Orbital plots are presented for the $2\sigma_u$, $3\sigma_g$, and $1\pi_u$ Feynman–Dyson amplitudes in Fig. 7. Since the dominant component in each of these amplitudes is the corresponding Hartree–Fock orbital (i.e., $2\sigma_u$, $3\sigma_g$, and $1\pi_u$, respectively) the correlation and relaxation corrections are not readily observable. In order to examine these many-electron contributions more readily, density difference plots between the amplitudes of Fig. 7 and their corresponding Hartree–Fock orbital were made and are presented in Figs. 8–10. Since the Feynman–Dyson amplitudes are not normalized, it is necessary to normalize them before computing the density difference. In all of these plots, the Hartree–Fock density is negative, which means any positive distortions imply density enhancement in the propagator amplitude while negative distortions imply density diminution. Figure 8 shows a density diminution for $3\sigma_g$ in both the C—C and C—H bonding regions with a density enhancement in the antibonding region. Figure 9 ($1\pi_u$) shows an enhancement in the C—C pi bonding, and Fig. 10 ($2\sigma_u$) shows an enhancement in the C—H bonding with a slight diminution of antibonding character.

It is apparent from the numerical results presented in this section that the calculated relative photoionization intensities, at least within the plane wave approximation, are not very sensitive to improvements in the Feynman–Dyson amplitudes. It is likely that more accurate photoelectron wavefunctions will improve the sensitivity of these quantities but not at the orthogonalized plane wave level. Although the OPW approximation is more justifiable formally, the results of Rabalais *et al.* (1974) and Cavell

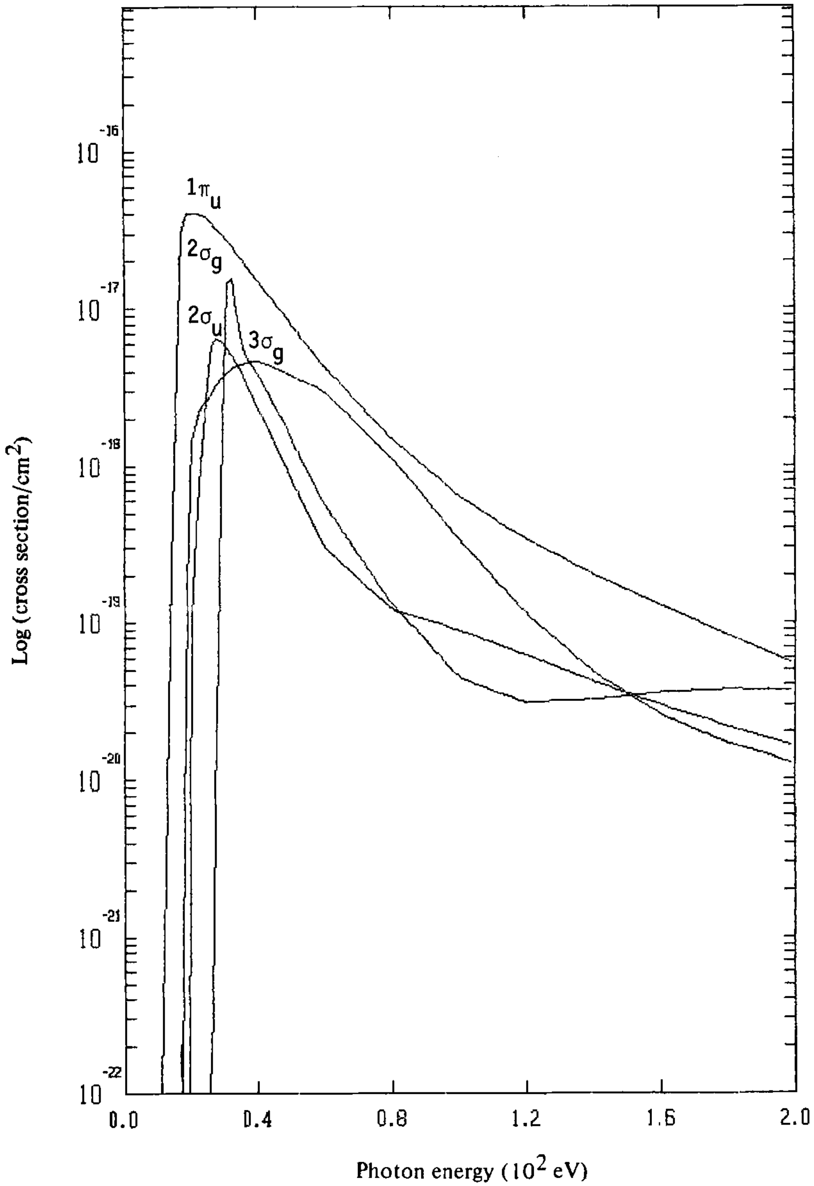


Fig. 6. A plot of the photoionization cross-sections versus photon energy for the valence orbitals of acetylene in the region 0–200 eV.

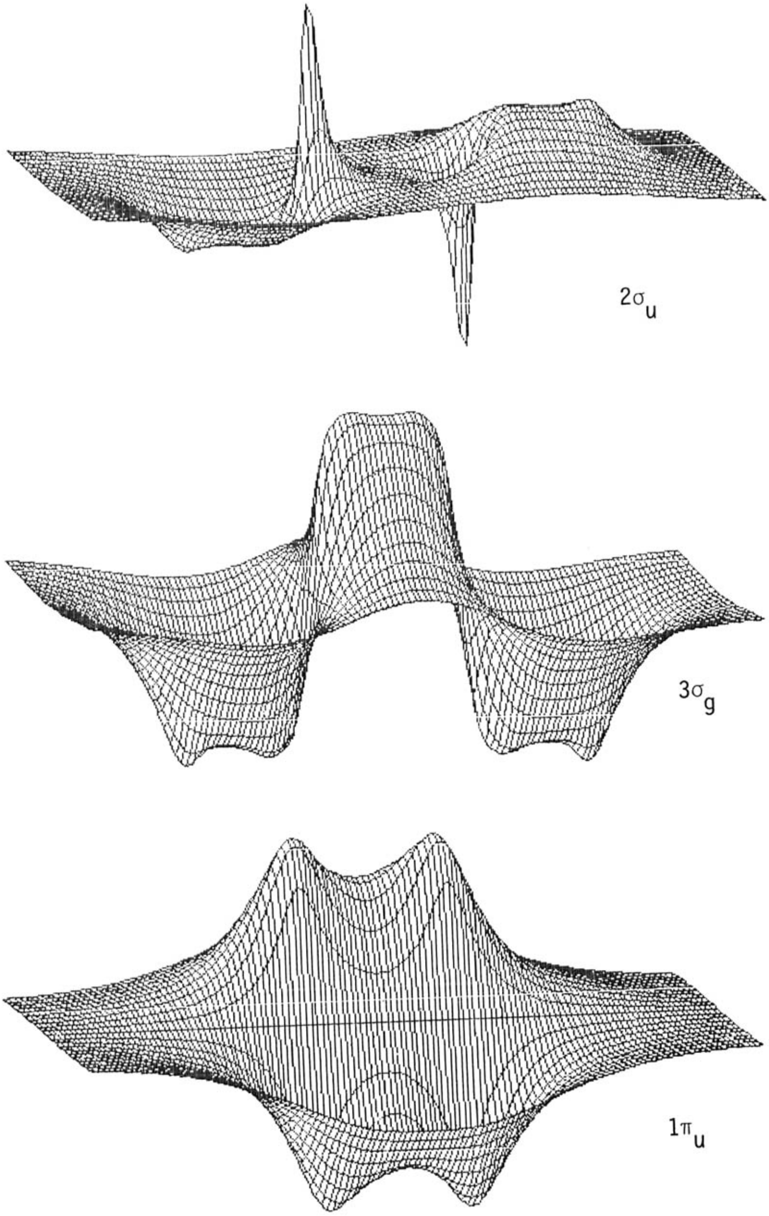


Fig. 7. Orbital plots for the $2\sigma_u$, $3\sigma_g$, and $1\pi_u$ Feynman–Dyson amplitudes of acetylene.

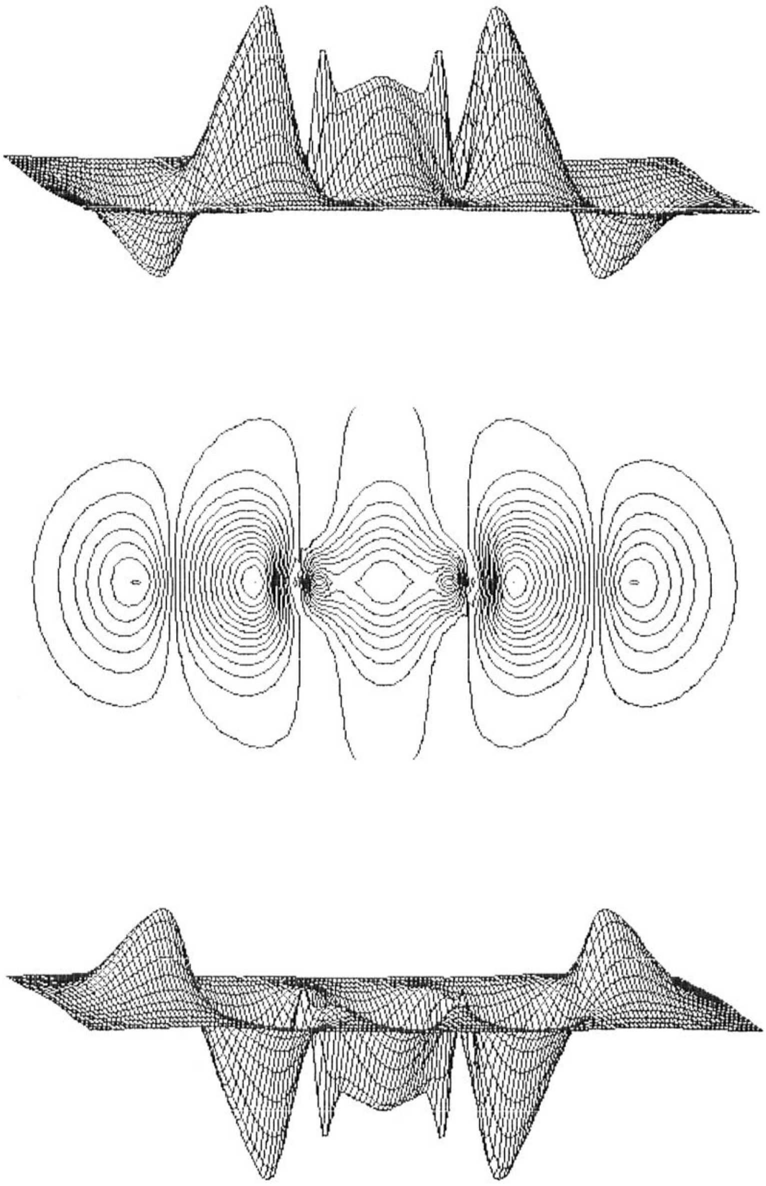


Fig. 8. A density difference plot between the $3\sigma_g$ Feynman–Dyson amplitude and the $3\sigma_g$ Hartree–Fock orbital of acetylene. Each contour represents a density increment of about 1.5 × 10^{-4} a.u.

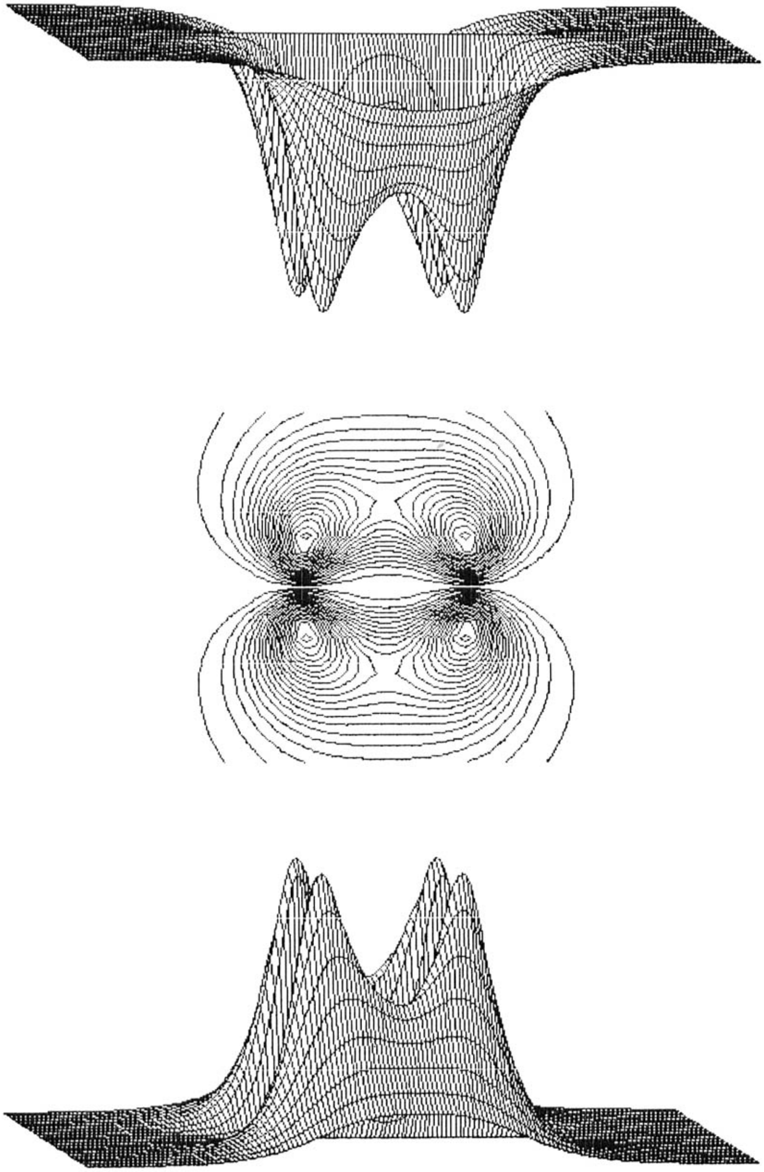


Fig. 9. A density difference plot between the $1\pi_u$ Feynman–Dyson amplitude and the $1\pi_u$ Hartree–Fock orbital of acetylene. Each contour represents a density increment of about 3.6 × 10^{-3} a.u.

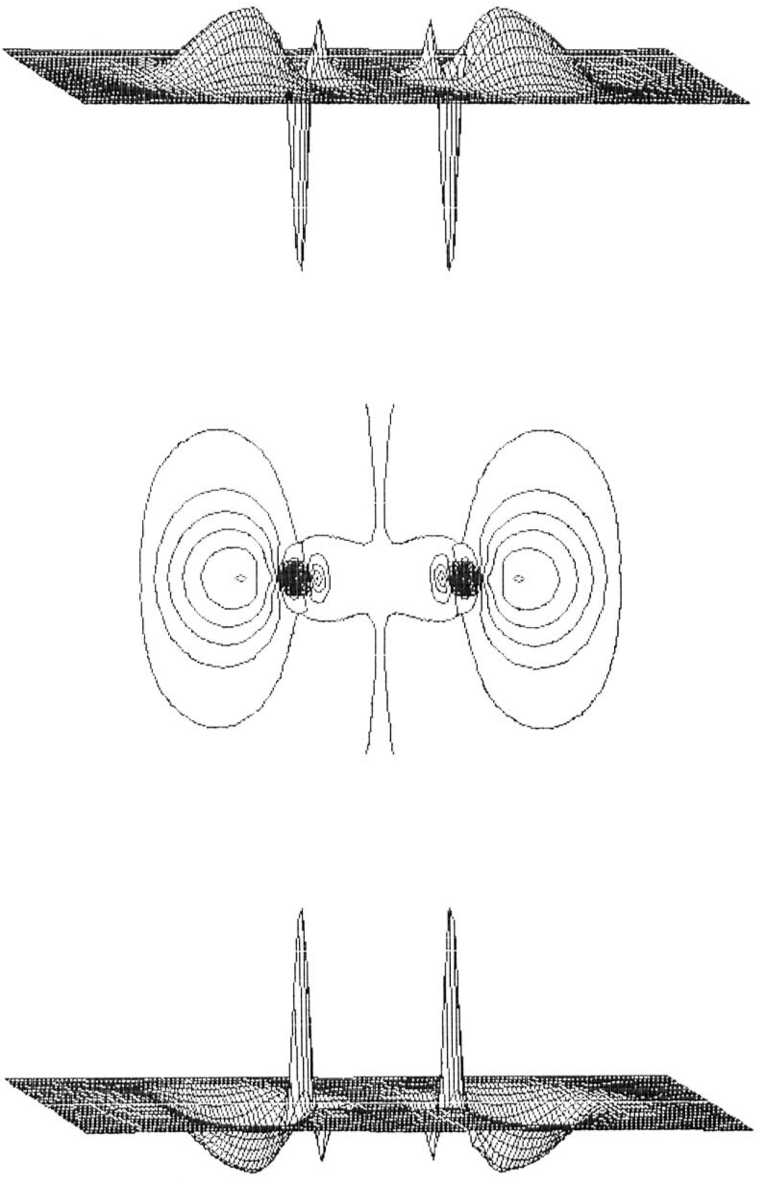


Fig. 10. A density difference plot between the $2\sigma_u$ Feynman–Dyson amplitude and the $2\sigma_u$ Hartree–Fock orbital of acetylene. Each contour represents a density increment of about 4.4×10^{-4} a.u.

and Allison (1978) do not exhibit any marked improvements to the plane wave results in the two molecules studied here. Qualitative changes in the propagator amplitudes may be observed via density difference plots, however, more quantitative comparisons must await other computational applications.

VII. Conclusions

In a self-consistent determination of the electron propagator the decoupling procedure must necessarily interrelate the approximations of ground-state averages and the truncations of electron field operator manifolds. In a perturbation treatment progressing by analysis of terms in orders of the electron interaction it is possible to proceed by systematic improvement of either the reference state or the projection manifolds of electron field operators (or a combination of both) (Dalgaard and Simons, 1977). We have chosen to examine the decoupling approximation while maintaining a Hartree–Fock reference state. This has several advantages since this reference state has a simple representation with a clear-cut division of the orbital space into an occupied and an unoccupied set and since this state is efficiently generated by a number of available computer programs.

The superoperator formalism that was originally introduced as a notational convenience has a rich algebraic structure that has been largely unexploited. As we demonstrated in Section IV, the superoperator Hamiltonian may be partitioned and a perturbation theory may be developed in the operator space. The perturbation expansion of the superoperator resolvent readily yields the Dyson equation and allows an identification of wave and reaction superoperators. The definition of these auxiliary superoperators elucidates the parallelism between the superoperator formalism and the diagrammatic expansion method and permits a unified conceptual framework.

When the superoperator resolvent is approximated by an inner projection, various choices of the inner projection manifold that correspond to different decouplings may be viewed as different approximations to the wave superoperator in the following equation (Born and Öhrn, 1977)

$$|\mathbf{h}) = \hat{W}(E)|\mathbf{a}).$$

In particular, the operator product decoupling corresponds to the choice

$$\hat{W} = \hat{I} + \{a_k^\dagger a_l\}, \qquad \hat{W} = \hat{I} + \{a_k^\dagger a_l\} + \{a_k^\dagger a_l^\dagger a_m a_n\}, \ \ldots,$$

the moment-conserving decoupling corresponds to

$$\hat{W} = \hat{I} + \hat{H}, \qquad \hat{W} = \hat{I} + \hat{H} + \hat{H}^2, \ \ldots,$$

and the diagram-conserving decoupling of the Padé type corresponds to

$$\hat{W}(E) = \hat{I} + \hat{T}_0(E)\hat{V}, \qquad \hat{W}(E) = \hat{I} + \hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V}, \ldots .$$

Alternatively, the superoperator resolvent may be approximated by an outer projection, in which case decoupling approximations correspond to various approximations to the reaction (or self-energy) superoperator. Two decouplings of this type that have been presented are the simple diagram-conserving decoupling that corresponds to

$$\hat{t}(E) = \hat{V} + \hat{V}\hat{T}(E)\hat{V}$$

with

$$\hat{T}(E) = \hat{T}_0(E), \qquad \hat{T}(E) = \hat{T}_0(E) + \hat{T}_0(E)\hat{V}\hat{T}_0(E), \ldots ,$$

and a renormalized decoupling corresponding to

$$\hat{t}(E) = \hat{V} + \hat{V}\hat{T}(E)\hat{V} \qquad \text{with} \quad \hat{T}(E) = \hat{T}_0(E) + \hat{T}_0(E)\hat{M}\hat{T}(E)$$

and where $\hat{M}$ is an effective potential obtained by projecting the perturbation superoperator onto a subspace of the orthogonal complement. When this subspace is chosen to consist of simple operator products, this decoupling is formally equivalent to the operator product decoupling, however, other approximations may be envisioned.

Each of the above-mentioned decoupling approximations have been studied in detail computationally and have been evaluated on the basis of a comparison of the propagator poles with experimental ionization energies. The moment-conserving decouplings discussed in Section III were found to yield unacceptably poor numerical results. It is plausible that since the moment matrices involve averages of various powers of the full superoperator Hamiltonian, the moment expansion may not be convergent anywhere in the complex plane. If this is the case, analytic continuation cannot be performed, and the Padé approximant method will not improve convergence. In any event, it may be generally concluded that the number of conserved moments is no indication of the accuracy of this decoupling.

A more successful approach is the diagram-conserving decouplings presented in Section IV. A simple second-order self-energy truncation was found to overcorrect the Hartree–Fock orbital energy estimate of the ionization energy and yielded results that were generally too small. The inclusion of third-order diagrams, particularly rings and ladders, is necessary to obtain reasonable agreement with experiment. Energy shifts resulting from the addition of diffuse polarization functions to the computational basis were observed to be of nearly the same magnitude as the shifts obtained from third-order ring and ladder diagrams, hence care must be taken to insure basis saturation.

The renormalized 2p–h TDA decoupling was found to have several desirable features. Although only a diagonal approximation was implemented, principal ionization energies accurate to within an electron volt were generally obtained. Shake-up energies were less accurately described owing to the neglect of ion state relaxation and hole–hole correlation in the 2p–h TDA.

The numerical results of Section VI indicate that the calculation of relative photoionization intensities using a plane wave approximation for the photoelectron is not a sensitive reflection of the quality of the Feynman–Dyson amplitudes. The severity of the plane wave approximation most likely obliterates the many-electron relaxation and correlation corrections. More accurate photoelectron representations such as orthogonalized plane waves or Coulomb waves should afford a more accurate evaluation of the Feynman–Dyson amplitudes, or alternatively, one-electron properties may be computed using the single-particle reduced density matrix obtained from the spectral density.

There are several possible directions that the work described here can take. It is obviously quite possible to apply these decoupling ideas to the polarization propagator. Currently, decouplings of this propagator have been based on operator products. The odd or fermion-like operator products in the electron propagator theory must be replaced by even or boson-like operator products to account for the particle-conserving nature of the polarization propagator theory, but with this minor modification, the application of the diagram-conserving and renormalized decouplings also seems feasible.

More accurate decouplings are still needed for the electron propagator in order to better describe shake-up energies. With this goal in mind, Cederbaum and co-workers and Mishra and Öhrn (1980) have recently implemented the full nondiagonal 2p–h TDA by exploiting spin and orbital symmetry to reduce the dimension of the 2p–h operator subspace. Preliminary results indicate that this approximation provides some improvement but is still inadequate and quite costly. It has proven to be necessary to reduce drastically the orbital basis sets in the calculation of the self-energy in order to make the full 2p–h TDA tractable. This can often be a less than satisfactory procedure, as pointed out by Mishra and Öhrn (1980). The need for higher operator products, particularly quintuple products, is indicated by the CI studies of Bagus and Viinikka (1977) and may necessitate the implementation of a 3p–2h renormalization.

Another attractive avenue for extension is a combination of the 2p–h TDA renormalization with the Hamiltonian partitioning of Kurtz and Öhrn (1978). Work along this line for electron affinities by Ortiz and Öhrn (1980) has given very encouraging results.

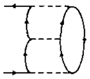
Finally, the problem of open-shell reference states has not been considered here. The retention of a restricted Hartree–Fock reference state in this regard will be a tremendous simplification, and the various spin and orbital symmetry couplings between the reference state and operator manifold may be treated with the theory of tensor operators.

Particularly interesting in this connection is the recent work by Born and Shavitt (1980), which uses appropriately normalized Wigner operators of the unitary group $U(n)$ (n is the size of the orbital basis) in place of the electron creation and annihilation operators. The many-electron spin eigenfunctions are represented in terms of the Gel'fand–Zetlin basis (see, e.g., Paldus, 1976). Much of this development is inspired by the work of Biedenharn and Louck (1968).

Appendix 1

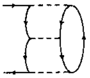
$$\Sigma_{ij}^{(3)}(E) =$$

$$\frac{1}{4}\sum_a\sum_p\sum_q\sum_r\sum_s \frac{\langle ia\|pq\rangle\langle pq\|rs\rangle\langle rs\|ja\rangle}{(E+\varepsilon_a-\varepsilon_r-\varepsilon_s)(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)}$$



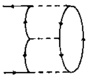
(A)

$$-\frac{1}{4}\sum_a\sum_b\sum_c\sum_d\sum_p \frac{\langle ip\|ab\rangle\langle ab\|cd\rangle\langle cd\|jp\rangle}{(E+\varepsilon_p-\varepsilon_c-\varepsilon_d)(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)}$$



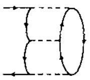
(B)

$$-\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ib\|rq\rangle\langle ra\|pb\rangle\langle pq\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)(E+\varepsilon_b-\varepsilon_q-\varepsilon_r)}$$



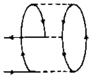
(C)

$$+\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle iq\|cb\rangle\langle cp\|aq\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(E+\varepsilon_q-\varepsilon_b-\varepsilon_c)}$$



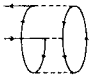
(D)

$$+\frac{1}{4}\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle ic\|ab\rangle\langle ab\|pq\rangle\langle pq\|jc\rangle}{(E+\varepsilon_c-\varepsilon_p-\varepsilon_q)(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q)}$$



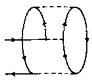
(E)

$$+\frac{1}{4}\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle ia\|pq\rangle\langle pq\|bc\rangle\langle bc\|ja\rangle}{(E+\varepsilon_a-\varepsilon_p-\varepsilon_q)(\varepsilon_b+\varepsilon_c-\varepsilon_p-\varepsilon_q)}$$



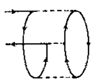
(F)

$$+\frac{1}{4}\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ip\|ab\rangle\langle ab\|qr\rangle\langle qr\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(\varepsilon_a+\varepsilon_b-\varepsilon_q-\varepsilon_r)}$$



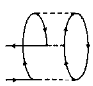
(G)

$$+\frac{1}{4}\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ip\|qr\rangle\langle qr\|ab\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(\varepsilon_a+\varepsilon_b-\varepsilon_q-\varepsilon_r)}$$



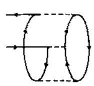
(H)

$$-\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ir\|aq\rangle\langle ab\|pr\rangle\langle pq\|jb\rangle}{(E+\varepsilon_b-\varepsilon_p-\varepsilon_q)(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_r)}$$



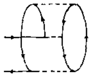
(I)

$$-\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ib\|pr\rangle\langle pq\|ab\rangle\langle ar\|jq\rangle}{(E+\varepsilon_b-\varepsilon_p-\varepsilon_r)(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q)}$$

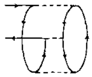


(J)

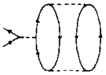
$$-\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle iq\|ac\rangle\langle ab\|pq\rangle\langle pc\|jb\rangle}{(E+\varepsilon_q-\varepsilon_a-\varepsilon_c)(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q)}$$


(K)

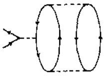
$$-\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle ic\|qb\rangle\langle qp\|ac\rangle\langle ab\|jp\rangle}{(E+\varepsilon_p-\varepsilon_a-\varepsilon_b)(\varepsilon_a+\varepsilon_c-\varepsilon_p-\varepsilon_q)}$$


(L)

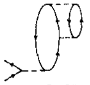
$$+\frac{1}{2}\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ir\|jp\rangle\langle ab\|rq\rangle\langle pq\|ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q)(\varepsilon_a+\varepsilon_b-\varepsilon_q-\varepsilon_r)}$$


(M)

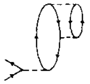
$$-\frac{1}{2}\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle ia\|jc\rangle\langle cb\|pq\rangle\langle pq\|ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q)(\varepsilon_b+\varepsilon_c-\varepsilon_p-\varepsilon_q)}$$


(N)

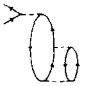
$$+\frac{1}{2}\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ip\|ja\rangle\langle ab\|qr\rangle\langle qr\|pb\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_q-\varepsilon_r)(\varepsilon_a-\varepsilon_p)}$$


(O)

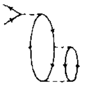
$$-\frac{1}{2}\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle ip\|ja\rangle\langle bc\|pq\rangle\langle aq\|bc\rangle}{(\varepsilon_b+\varepsilon_c-\varepsilon_p-\varepsilon_q)(\varepsilon_a-\varepsilon_p)}$$


(P)

$$+\frac{1}{2}\sum_a\sum_b\sum_p\sum_q\sum_r \frac{\langle ia\|jr\rangle\langle rb\|pq\rangle\langle pq\|ab\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q)(\varepsilon_a-\varepsilon_r)}$$


(Q)

$$-\frac{1}{2}\sum_a\sum_b\sum_c\sum_p\sum_q \frac{\langle ic\|jp\rangle\langle pq\|ab\rangle\langle ab\|cq\rangle}{(\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q)(\varepsilon_c-\varepsilon_p)}.$$


(R)

Appendix 2

$$\begin{aligned}
(\mathbf{a}|H^3\mathbf{a})_{ij} = {} & \varepsilon_i^3\ \delta_{ij} \\
& + \sum_{r,s,s'} (\varepsilon_i+\varepsilon_j+\varepsilon_s+\varepsilon_{s'}-\varepsilon_r)\langle ir\|ss'\rangle\langle ss'\|jr\rangle \\
& \times [\tfrac{1}{2}\langle n_r\rangle + \tfrac{1}{2}\langle n_s\rangle\langle n_{s'}\rangle - \langle n_r\rangle\langle n_s\rangle] \\
& + \sum_{r,s,s',l,l'} \langle ir\|ss'\rangle\langle ss'\|ll'\rangle\langle ll'\|jr\rangle \\
& \times [\tfrac{1}{4}\langle n_r\rangle - \tfrac{1}{2}\langle n_r\rangle\langle n_l\rangle + \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle - \tfrac{1}{2}\langle n_r\rangle\langle n_s\rangle \\
& + \langle n_r\rangle\langle n_s\rangle\langle n_{l'}\rangle - \langle n_l\rangle\langle n_{l'}\rangle\langle n_s\rangle - \tfrac{1}{4}\langle n_s\rangle\langle n_{s'}\rangle \\
& + \tfrac{1}{2}\langle n_s\rangle\langle n_{s'}\rangle\langle n_l\rangle] \\
& + \sum_{r,s,s',l,l'} \langle ir\|ss'\rangle\langle s'l\|rl'\rangle\langle l's\|jl\rangle \\
& \times [2\langle n_l\rangle\langle n_{s'}\rangle + \langle n_r\rangle\langle n_l\rangle\langle n_s\rangle - \langle n_r\rangle\langle n_l\rangle - \langle n_r\rangle\langle n_{l'}\rangle \\
& + \langle n_r\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle + 2\langle n_r\rangle\langle n_l\rangle\langle n_{l'}\rangle - \langle n_l\rangle\langle n_{s'}\rangle\langle n_r\rangle \\
& - \langle n_{l'}\rangle\langle n_s\rangle\langle n_r\rangle - 2\langle n_l\rangle\langle n_{s'}\rangle\langle n_{l'}\rangle - \langle n_l\rangle\langle n_{s'}\rangle\langle n_s\rangle
\end{aligned}$$

$$+ \langle n_s\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle]$$

$$+ \sum_{r,s,s',l,l'} \langle ir\|js\rangle\langle ss'\|ll'\rangle\langle ll'\|rs'\rangle$$

$$\times [\tfrac{1}{2}\langle n_r\rangle\langle n_{s'}\rangle - \langle n_l\rangle\langle n_{l'}\rangle - \langle n_r\rangle\langle n_{s'}\rangle\langle n_{l'}\rangle$$

$$+ \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_r\rangle + \langle n_l\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle + \tfrac{1}{2}\langle n_s\rangle\langle n_{s'}\rangle$$

$$+ \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_s\rangle - \langle n_s\rangle\langle n_{s'}\rangle\langle n_l\rangle]$$

Appendix 3

$$(\mathbf{a}|\hat{V}\hat{T}_0(E)\hat{V}\hat{T}_0(E)\hat{V}\mathbf{a})_{ij}$$

$$= \sum_{r,s,s',l,l'} \frac{\langle ir\|ss'\rangle\langle ss'\|ll'\rangle\langle ll'\|jr\rangle}{(E + \varepsilon_r - \varepsilon_s - \varepsilon_{s'})(E + \varepsilon_r - \varepsilon_l - \varepsilon_{l'})}$$

$$\times [\tfrac{1}{4}\langle n_r\rangle - \tfrac{1}{2}\langle n_r\rangle\langle n_l\rangle + \tfrac{1}{4}\langle n_l\rangle\langle n_{l'}\rangle - \tfrac{1}{2}\langle n_r\rangle\langle n_s\rangle + \langle n_r\rangle\langle n_s\rangle\langle n_{l'}\rangle$$

$$- \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_s\rangle]$$

$$+ \sum_{r,s,s',l,l'} \frac{\langle ir\|ss'\rangle\langle ss'\|ll'\rangle\langle ll'\|jr\rangle}{(E + \varepsilon_r - \varepsilon_s - \varepsilon_{s'})(E - \varepsilon_j + \varepsilon_l + \varepsilon_{l'} - \varepsilon_s - \varepsilon_{s'})}$$

$$\times [\tfrac{1}{4}\langle n_l\rangle\langle n_{l'}\rangle - \tfrac{1}{4}\langle n_s\rangle\langle n_{s'}\rangle - \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle + \tfrac{1}{2}\langle n_s\rangle\langle n_{s'}\rangle\langle n_l\rangle]$$

$$+ \sum_{r,s,s',l,l'} \frac{\langle ir\|js\rangle\langle ss'\|ll'\rangle\langle ll'\|rs'\rangle}{(E - \varepsilon_j + \varepsilon_r - \varepsilon_s)(E - \varepsilon_j + \varepsilon_r + \varepsilon_{s'} - \varepsilon_{l'} - \varepsilon_l)}$$

$$\times [\tfrac{1}{2}\langle n_r\rangle\langle n_{s'}\rangle - \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle - \langle n_r\rangle\langle n_{s'}\rangle\langle n_{l'}\rangle + \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_r\rangle$$

$$+ \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle]$$

$$+ \sum_{r,s,s',l,l'} \frac{\langle ir\|js\rangle\langle ss'\|ll'\rangle\langle ll'\|rs'\rangle}{(E - \varepsilon_j + \varepsilon_r - \varepsilon_s)(E - \varepsilon_j + \varepsilon_l + \varepsilon_{l'} - \varepsilon_s - \varepsilon_{s'})}$$

$$\times [\tfrac{1}{2}\langle n_s\rangle\langle n_{s'}\rangle - \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle + \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle + \tfrac{1}{2}\langle n_l\rangle\langle n_{l'}\rangle\langle n_s\rangle$$

$$- \langle n_s\rangle\langle n_{s'}\rangle\langle n_l\rangle]$$

$$+ \sum_{r,s,s',l,l'} \frac{\langle ir\|ss'\rangle\langle s'l\|rl'\rangle\langle l's\|jl\rangle}{(E + \varepsilon_r - \varepsilon_s - \varepsilon_{s'})(E + \varepsilon_l - \varepsilon_s - \varepsilon_{l'})}$$

$$\times [\langle n_l\rangle\langle n_{s'}\rangle - \langle n_r\rangle\langle n_l\rangle + \langle n_r\rangle\langle n_l\rangle\langle n_s\rangle + \langle n_r\rangle\langle n_l\rangle\langle n_{l'}\rangle - \langle n_{l'}\rangle\langle n_s\rangle\langle n_r\rangle$$

$$- \langle n_l\rangle\langle n_{s'}\rangle\langle n_{l'}\rangle - \langle n_l\rangle\langle n_s\rangle\langle n_{s'}\rangle + \langle n_s\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle]$$

$$+ \sum_{r,s,s',l,l'} \frac{\langle ir\|ss'\rangle\langle s'l\|rl'\rangle\langle l's\|jl\rangle}{(E + \varepsilon_r - \varepsilon_s - \varepsilon_{s'})(E - \varepsilon_j + \varepsilon_r + \varepsilon_{l'} - \varepsilon_{s'} - \varepsilon_l)}$$

$$\times [\langle n_l\rangle\langle n_{s'}\rangle - \langle n_r\rangle\langle n_{l'}\rangle + \langle n_r\rangle\langle n_{l'}\rangle\langle n_{s'}\rangle + \langle n_r\rangle\langle n_{l'}\rangle\langle n_l\rangle$$

$$- \langle n_l\rangle\langle n_{s'}\rangle\langle n_r\rangle - \langle n_l\rangle\langle n_{s'}\rangle\langle n_{l'}\rangle]$$

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Chemical Isomerism and Its Contemporary Theoretical Description*

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I. Introduction

The concept of isomerism is very old—in chemistry the first, in principle, albeit still valid definition of isomers as "compounds possessing the same chemical constitution and molecular weight but differing properties" was formulated 150 years ago (Berzelius, 1830). Moreover, according to Snelders (1964) the origins of the concept of isomerism may be traced back to antiquity, in the ideas of the Greek atomists Leucippos and Democritos, reported by Aristotle in his Metaphysics (e.g., the 1960s edition). From the very beginning, the interpretation of chemical isomerism has been intimately connected with the concept of molecular

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* Dedicated to the 150th anniversary of the designation of the phenomenon of chemical isomerism by Berzelius (1830).

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structure and its development. Isomerism in organic chemistry seemed, at the outset, to be well defined. However, difficulties began to arise after the introduction of the new, short-time physical techniques that enabled differentiation of structures undergoing rapid interconversion. Stereochemically nonrigid molecules (Muetterties, 1965) represent an objective example of difficulties involving the concepts both of structure and of isomerism. It has been accepted that a definition of isomerism cannot be given in the absence of defined experimental criteria of the conditions and methods of observation (Eliel, 1977; Mislow and Bickart, 1977). This requirement is met (although in rather implicit form) by the following definition (Mislow, 1966; Rouvray, 1974): Isomers are individual chemical species with identical molecular formulae that display at least some differing physicochemical properties, and that are stable for long periods of time in comparison with those during which measurements of their properties are made. There is an immense abundance of accumulated experimental information about isomers. New types of isomerism have been continuously recognized in both inorganic (e.g., Gažo, 1974) and organic (e.g., Mislow, 1976) chemistry.

Study of the phenomenon of isomerism has always been considered as an organic part of theoretical chemistry. Various schemes classifying over 30 recognized varieties of isomerism have arisen from this study (Rouvray, 1974). However, Wheland (1960) feels that the proposed schemes are often rather cumbersome. Moreover, the distinctions they are based on are frequently not very important. The scheme proposed by Jennen (1954, 1955) may serve as a relatively complete phenomenological classification. Recently this problem has been solved from a more abstract point of view using algebraic methods. Ege (1971) treated the relationships between isomers in terms of set theory. The use of group theory is summarized by Mead (1974). Finally, Mislow (1977) studied the classification of pairwise relationships between isomeric structures by graph theory.

Algebraic methods were the first theoretical tools to yield a significant result in the study of isomerism. The first serious attempts at algebraic isomer enumeration were made in 1874 (for a review, see Rouvray, 1975). In spite of their abstract character, the algebraic methods permit not only rationalization of isomeric relationships, but can even lead to prediction of new reactions. Automerizations proceeding through six-membered transition states (Balaban, 1967) are a classical example.

Later two further powerful theoretical tools were employed in addition to this algebraic approach: the methods of quantum chemistry and statistical mechanics. With the quantum-chemical approach, the individual isomers and the relationships between them are treated as minima and their interrelations, respectively, on the corresponding potential energy hypersurface or hypersurfaces. Statistical mechanics enables the temperature and entropy to be treated properly. Quantum chemistry can serve as a generator of information for statistical-mechanical treatments. Linking of the two fields—traditionally somewhat distant—has been demonstrated several times at the computational level (e.g., Daudel, 1973; Slanina, 1975c; Clementi, 1976a). Moreover, recently Löwdin (1977) presented a unification of quantum mechanics, quantum statistics, classical thermodynamics and (to some extent) classical mechanics using trace algebra. In this way, a correct physical basis was provided for the contemporary theory of chemical reactivity.

Theoretical study of isomerism is, at present, being carried out vigorously along all the lines mentioned above. In this article, the present concept of isomerism will be sketched in both the conventional quantum-chemical and the rigorous quantum-mechanical approaches. Quantum-chemical and algebraic techniques for the study of isomers will be discussed and illustrated; special attention will be devoted to the overlap between them. Finally, the recently formed field of chemical-reactivity theory will be described, viz., the evaluation of the reaction characteristics of chemical processes (both equilibrium and rate) whose components have been shown by theoretical analysis to be mixtures of isomers.

II. Quantum-Chemical Picture of Isomerism

Separation of electronic and nuclear motion (Born and Oppenheimer, 1927) underlies many of our present chemical concepts and has always been regarded as a *sine qua non* of quantum chemistry (Woolley, 1978a). The primary consequence of the Born–Oppenheimer approximation is the concept of a potential energy hypersurface. Bond lengths and bond angles, force constants, energy barriers, frequencies of vibrational and rotational motions, etc., are expressed in terms of the properties of the potential energy hypersurface. The proposition that all experiments involving molecules can be explained in terms of molecular structure has become the central dogma of molecular science (Woolley and Sutcliffe, 1977).

Within the Born–Oppenheimer approach, solution of the time-independent Schrödinger equation

$$\hat{H}_{\mathrm{T}}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}) \tag{1}$$

for a system of electrons (described by the set of electronic coordinates $\mathbf{r}$) and nuclei (described by the set of nuclear coordinates $\mathbf{R}$) in the absence of external fields with the total nonrelativistic Hamiltonian $\hat{H}_{\mathrm{T}}$ is facilitated by approximating the total wave function $\Psi(\mathbf{r}, \mathbf{R})$ by only one term in the following expansion:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{n,m} \Phi_n(\mathbf{r}, \mathbf{R})\, \chi_{nm}(\mathbf{R}). \tag{2}$$

The electronic wave function $\Phi_n(\mathbf{r}, \mathbf{R})$ can be obtained by solving the electronic Schrödinger equation

$$\hat{H}_{\text{elec}} \Phi_n(\mathbf{r}, \mathbf{R}) = U_n(\mathbf{R}) \Phi_n(\mathbf{r}, \mathbf{R}) \tag{3}$$

for a fixed nuclear configuration. The solution of Eq. (3) for all spatial arrangements of the nuclei will generate the potential energy hypersurface $U_n(\mathbf{R})$, which governs the motion of the nuclei. The nuclear wave function $\chi_{nm}(\mathbf{R})$ follows from the solution of the nuclear eigenvalue problem using either the Born–Oppenheimer (clamped nuclei) potential $U_n(\mathbf{R})$ or the more sophisticated adiabatic potential (Born, 1951; Born and Huang, 1954).

The Born–Oppenheimer or the adiabatic approximation enable every electronic state of any molecule to be connected with the potential energy hypersurface depending on the nuclear coordinates $\mathbf{R}$. Let us suppose that the potential energy $U(\mathbf{R})$ has a minimum U_0 at some nuclear configuration $\mathbf{R}_e$. In classical mechanics it is natural to denote configuration $\mathbf{R}_e$ as an equilibrium configuration (the nuclei lie at time-independent positions). According to quantum mechanics, however, this state cannot actually be realized because the uncertainty principle precludes the simultaneous specification of the position and momentum variables. However, there is a state of nuclear motion with the lowest energy that is compatible with the uncertainty relations. This state corresponds to certain zero-point vibrations leading to a quantum correction due to the zero-point motion Δ_0. Thus the quantum ground state energy is obtained.

$$E_0 = U_0 + \Delta_0. \tag{4}$$

The equilibrium structure parameters are yielded directly by quantum-chemical calculations but their experimental determination can be performed only for several of the simplest molecules. In routine practice, a number of different definitions of molecular structure are used (sometimes even without well-defined physical significance). Instead of equilibrium structure, various average structures are used for representation of molecular geometry. In electron-diffraction experiments the molecular geometry is obtained in terms of the average r_a and r_g parameters. The differences between equilibrium parameters and parameters r_a or r_g may be substantially greater than the experimental error (Hedberg, 1974). Similarly, structural parameters can be obtained from rotational spectra in terms of various average parameters, e.g., r_m, r_s, r_0, and r_z (Schwendeman, 1974). Moreover, none of these techniques of structure determination is entirely experimental—each requires a certain theoretical model within which the structure can be adjusted to fit the experiment. It is clear that none of the structures mentioned above may be considered as the true structure. As Wilson (1979) recently emphasized, molecular structure is a concept involving a convention, an agreement upon definition.

A given set of electrons and nuclei can often yield a potential energy hypersurface with more than one minimum. If the minima correspond to one compound each (and not to several infinitely separated smaller compounds), we deal with the phenomenon of isomerism in its common form. Ideally, the relationships within such a system of isomers should be treated in terms of the whole potential energy hypersurface comprising all the possible configurations (Liehr, 1963). However, at the present state of numerical quantum chemistry, the following extent of information (Bauer, 1970) has to be considered as the upper computational limit: (*i*) precise location of the minima on the relevant hypersurface for each set of electronic quantum numbers, (*ii*) determination of the curvatures of the hypersurface at each minimum, and (*iii*) evaluation of the barrier heights that separate adjacent minima. Moreover, for the estimation of the transition possibilities between the minima, quantum-mechanical tunneling should be considered as well as, if necessary, the transition probability between different hypersurfaces.

If transitions between the minima can occur at the given temperature to a significant extent, nonrigid molecules are involved. Experimental research has revealed a large number of systems that are described by a set of nuclear configurations (for a review, see Spiridonov *et al.*, 1978; Bastiansen *et al.*, 1979). The technique of dynamic NMR spectroscopy (e.g., Sergeyev, 1973; Steigel, 1978) represents an especially powerful tool in this study. Bullvalene (Fig. 1) is a classical example of a stereochemically nonrigid (or fluxional—see, e.g., Cotton, 1968) molecule. If the atoms of bullvalene were labeled, it would be possible to distinguish 1,209,600 structures, all of which interconvert very rapidly at room temperature (von Doering and Roth, 1963a,b).

From the experimental point of view, it is important to determine whether two species are distinguishable or not. In addition to the Muetterties (1965) criterion mentioned above, several others were suggested in which the energy barrier ΔU separating the adjacent minima appears explicitly. According to Eliel (1977), two species can be considered identical if ΔU is less than RT (where R is the gas constant). Bersuker (1976) has included tunneling effect and considers configurations as in principle indistinguishable for which:

$$\Delta U < 2h\omega, \tag{5}$$

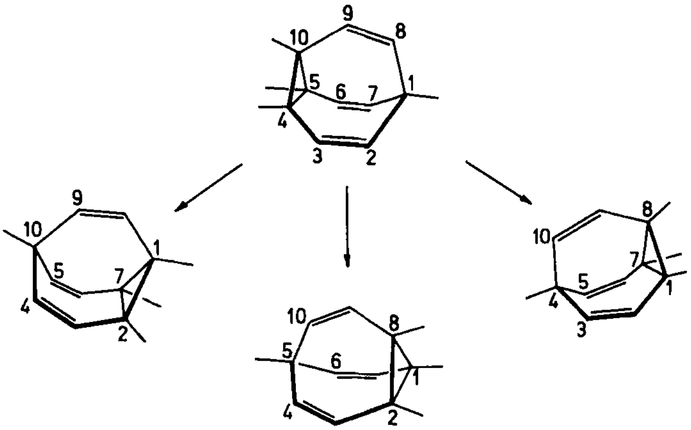


Fig. 1. An example of a fluxional molecule—bullvalene. Indicated are 4 of 1,209,600 equivalent structures (von Doering and Roth, 1963a,b) together with interconversions. At higher temperatures, the interconversions are so fast that the corresponding NMR spectrum consists of a single, sharp band.

where ω is the vibrational frequency of the motion involved in the interconversion. With very low energy barriers separating flat minima, the static concept of equilibrium structures becomes unsuitable at moderately high temperatures and it is necessary to employ the dynamic model of quasi-free particles (Boldyrev *et al.*, 1976, 1977).

It should finally be mentioned that the description of the symmetry properties of a system exhibiting several potential energy minima separated by surmountable energy barriers requires the use of the permutation-inversion group (Longuet-Higgins, 1963) of the total Hamiltonian. In order to further characterize a chemical isomer, the way in which this isomer removes some of the symmetry properties of the Hamiltonian must be defined. The symmetry is reduced by forbidding some of the permutations and/or space inversion and is described by a group of feasible operations (a subgroup of the group describing completely the internal symmetry of the total Hamiltonian). The feasible operations chosen should correspond to a path on the potential energy hypersurface that involves only points with low potential energy. This so-called feasibility concept has recently been replaced by a rigorous mathematical definition in the isometric group approach (e.g., Frei *et al.*, 1979).

A potential energy hypersurface is the starting point for the quantum-chemical study of isomerism. This hypersurface can be characterized at three different levels: (*i*) representation of the hypersurface using its critical points, (*ii*) mapping of the hypersurface by curves linking the points from (*i*) and, finally, (*iii*) evaluation of the whole hypersurface.

A. Location and Identification of Stationary Points

It is well known that all chemically interesting points on a potential energy hypersurface (points representing reactants, products, and transition states) are stationary with respect to a variation of the nuclear coordinates (e.g., McIver and Komornicki, 1972; Mezey, 1977). Thus the gradient vector g vanishes at these points, termed stationary points:

$$g = \nabla U(\mathbf{R}) = 0. \tag{6}$$

Such stationary points are characterized by calculating and diagonalizing the matrix of the second partial derivatives of the potential energy (the force constant matrix) F. The eigenvalues of F measure the curvature of the potential energy hypersurface along each of the principal directions corresponding to the eigenvectors of F. From the point of view of chemical reactivity, three kinds of stationary points can be distinguished: local minima, transition states, and higher types of stationary point, their F matrices having zero, one, and two or more negative eigenvalues, respectively. Representation of the hypersurface by its stationary points is, for the majority of chemically interesting systems, the upper feasibility limit in quantum-chemical study at present. One of many examples of representing hypersurfaces by stationary points is depicted in Fig. 2.

Over the past decade, considerable progress has been made in stationary point location and identification. Since the pioneer works of Pulay (1969, 1970, 1971) and of McIver and Komornicki (1971) efficient geometry optimization procedures have been worked out for various quantum-chemical methods including those at the *ab initio* MC SCF level (Kato and Morokuma, 1979; Goddard *et al.*, 1979). Efficient search for stationary points has been significantly facilitated by the introduction of analytic calculation of the energy gradient. Selected examples of such optimization procedures are presented in Table I. Let us note, however, for the sake of thoroughness, that in certain cases even mere numerical construction of the energy gradient is satisfactorily efficient (e.g., Poppinger, 1975; Collins *et al.*, 1976; Payne, 1976; De Tar, 1977; Lauer *et al.*, 1979; Havlas and Maloň, 1980).

Generally, the application of the optimization technique in theoretical chemistry is nothing new—see, e.g., the review by Garton and Sutcliffe (1974). Moreover the same scheme as that used later with quantum-chemical methods was used earlier in the optimization of molecular structures within the framework of the consistent force field method (Lifson and Warshel, 1968). This scheme can commonly be divided into two steps: (*i*) construction of the potential energy gradient from the analytic formulae at any point on the hypersurface, and (*ii*) generation of the improved coordinates by the iterative optimization technique chosen according to the character of the problem. Provided that we limit the study

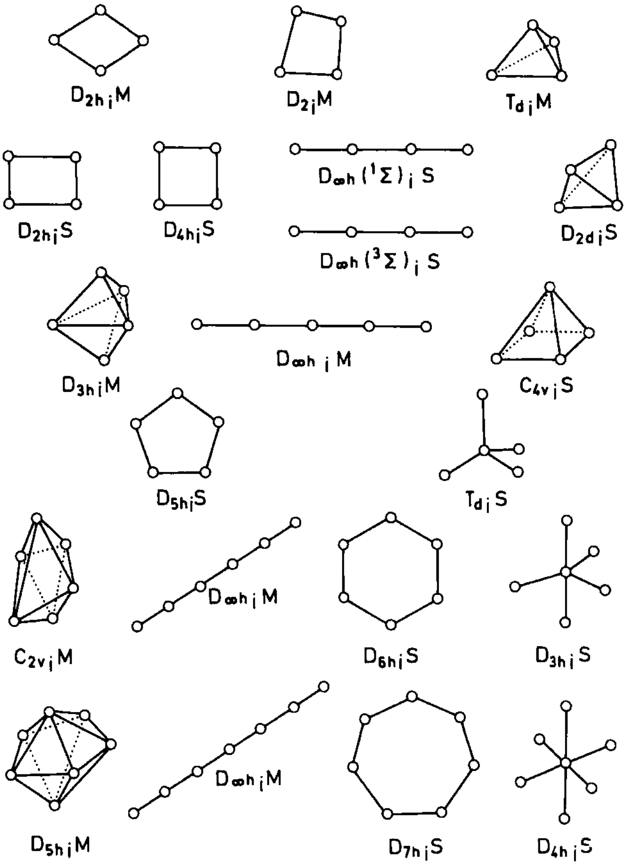


Fig. 2. Schemes of stationary points found (Slanina and Zahradník, 1977) on the MINDO/2 potential energy hypersurfaces of C_n (n = 4–7); M is a minimum, S a saddle point (transition state or higher type of stationary point). (Reprinted with permission from *J. Phys. Chem.* Copyright © 1977 American Chemical Society.)

to the location of minima, the optimization can be carried out as an energy minimization procedure. For the other stationary points, the latter technique may be of limited utility unless the symmetry properties can be applied (McIver and Komornicki, 1972; Ermer, 1975). However, McIver and Komornicki (1972) proved that the minimization of scalar quantity $\mathscr{G}$ (the Euclidean norm of the gradient):

$$\mathscr{G} = \mathbf{g} \cdot \mathbf{g} \tag{7}$$

is generally applicable.

For a single-determinant LCAO molecular orbital wave function, the

TABLE I

SELECTED EXAMPLES OF AUTOMATIC GEOMETRY OPTIMIZATION TECHNIQUES WITH ANALYTIC EVALUATION OF ENERGY GRADIENT

Methodical level of $U(\mathbf{R})$	References
Empirical	Lifson and Warshel (1968); Niketić and Rasmussen (1977)[a]; Ferguson and Beckel (1973); Slanina *et al.* (1978)
Semiempirical	McIver and Komornicki (1971); Zeiss and Whitehead (1971); Rinaldi and Rivail (1972); Pulay and Török (1973); Pancíř (1973); Grimmer and Heidrich (1973); Rinaldi (1976); Dewar and Komornicki (1977); Khalil and Shanshal (1977); Scharfenberg (1978); Dewar and Yamaguchi (1978); Leška *et al.* (1979)
Ab initio SCF	Pulay (1969, 1977[a], 1979); Schlegel *et al.* (1975); Huber *et al.* (1976); Komornicki *et al.* (1977); Dupuis and King (1978); Pople *et al.* (1978)
Ab initio SCF CI	Tachibana *et al.* (1978); Yamashita *et al.* (1980)
Ab initio MC SCF	Kato and Morokuma (1979); Goddard *et al.* (1979)

[a] Comprehensive review.

energy gradient can be determined analytically in a rather simple manner. If the wave function is determined variationally, the energy is stationary with respect to the LCAO expansion coefficients and the terms arising from the derivatives of the expansion coefficients vanish. This useful property of such variational functions, recognized by Hurley (1954), was further explored for evaluating the analytic first derivatives of the energy with respect to a nonlinear parameter (Bratož, 1958; Moccia, 1967; Gerratt and Mills, 1968a; Fletcher, 1970). The resultant derivatives of the atomic integrals are expanded as a sum of integrals involving the derivatives of the basis functions. The derivatives of Gaussian functions with respect to the nuclear coordinates were described by Boys (1950). Similar formulae for Slater orbitals were given by Gerratt and Mills (1968b) and in a quite general form by Beran *et al.* (1978). It is worth mentioning that the evaluation of the gradient does not reduce to a simple scheme if the wave function is not variationally optimized (Komornicki *et al.*, 1977). This is true for CI wave functions as only the CI coefficients are variationally determined (in contrast to the energy gradient in the MC SCF formalism—see Goddard *et al.*, 1979; Kato and Morokuma, 1979).

The Hellmann–Feynman theorem may be quite useful for evaluating the energy gradient, although it is rigorously satisfied only by exact wave functions or by certain types of approximate wave functions (e.g., Schutte, 1971; Deb, 1973). A proper analytic formula for the gradient of the CI potential energy, based on application of the Hellmann–Feynman theorem to the CI matrix operator, was given by Tachibana *et al.* (1978). Huber (1979) employed the Hellmann–Feynman force as a time-saving tool for approximation of the energy gradient in the first few iterations of a geometry optimization.

When the analytic energy gradient at any point of the hypersurface is available the realization of step (*ii*) can be discussed. The scheme generally used for optimizations of molecular structure can be expressed as follows:

$$\mathbf{R}_{i+1} = \mathbf{R}_i - H_i\mathbf{g}_i, \tag{8}$$

where $\mathbf{g}_i$ is the gradient evaluated in the *i*th iteration, H_i is a symmetric matrix whose adjustment characterizes a particular algorithm, and $\mathbf{R}_{i+1}$ is the $(i + 1)$th approximation of the geometry used as the starting point in the next iteration. The algorithm described by Fletcher and Powell (1963), following from an earlier suggestion by Davidon (1959), and especially the version of Murtagh and Sargent (1970) are most widely used. For minimizing scalar (7), the efficient generalized least squares method of Powell (1965) has been employed (McIver and Komornicki, 1972).

Once the stationary point of the potential energy hypersurface is located, diagonalization of the force constant matrix provides a conclusive test characterizing a particular structure. Three levels of force constant matrix evaluation can be distinguished: (*i*) double numerical differentiation, (*ii*) analytic differentiation followed by numerical differentiation, and (*iii*) double analytic differentiation. In approach (*i*) a systematic variation of the nuclear configuration is accompanied by quantum-chemical calculations for each configuration (e.g., Baran and Kołos, 1962; McLean, 1964; Paldus and Hrabě, 1968; Dewar and Metiu, 1972; Nelander and Ribbegård, 1974; Smit and Roos, 1978). At level (*iii*), the expression for the energy is differentiated twice to obtain an analytic formula for the force constants (e.g., Bratož, 1958; Bishop and Randić, 1966; Gerratt and Mills, 1968a; Bishop and Macias, 1969, 1970, 1971; Swanstrøm *et al.*, 1971; Bloemer and Bruner, 1972; Yde *et al.*, 1972; Thomsen and Swanstrøm, 1973a,b; Pople *et al.*, 1979). Applicability of the Hellmann–Feynman theorem has been discussed and tested several times in this connection (Kern and Karplus, 1964; Gerratt and Mills, 1968a,b; Schutte, 1971; Swanstrøm *et al.*, 1971; Yde *et al.*, 1972). At present the most widely used treatment for a quantum-chemical construction of matrix *F* is (*ii*) developed by Pulay (1969, 1970, 1971). Of the many works using this approach, only the recent ones will be mentioned (Kanakavel *et al.*, 1976; Dewar and Komornicki, 1977; Schlegel *et al.*, 1977; Al-Jiburi *et al.*, 1979; Yamashita *et al.*, 1980).

B. Curves on the Potential Energy Hypersurface

Mapping of the potential energy hypersurface by curves interconnecting two minima represents a link between description through location of the stationary points and (hypothetical) exhaustive numerical point-by-point definition. This concept of the reaction path supplies more detailed knowledge of the shape and behavior of the hypersurface than can be ascertained from the characteristics of stationary points alone. Curves with minimal energy barriers are particularly important. Generally, there is not necessarily a relationship between a reaction path and the dynamics of the chemical reaction. Nevertheless, it seems reasonable to assume that a real chemical process can be approximated by one particular reaction path (i.e., by one curve on the hypersurface), at least at low temperatures (Baskin *et al.,* 1974; Mezey, 1980).

There are many different ways in which reaction paths can be obtained. Traditionally, the path is constructed by successive incrementing of a selected internal coordinate (called the reaction coordinate or mapping parameter; e.g., Empedocles, 1969; Ermer, 1976, respectively) between the path-limiting values. The remaining degrees of freedom are reoptimized in each step. However, reaction paths constructed in this way are by no means unique and exhibit further serious imperfections. A given choice of reaction coordinate can produce different paths, depending on whether one starts from the reactants or from the products (phenomenon called chemical hysteresis) (Dewar and Kirschner, 1971a). It was also shown that these paths (or at least the reaction path derivative) may be discontinuous (Dewar and Kirschner, 1971a; Baskin *et al.,* 1974; Komornicki and McIver, 1974; McCullough and Silver, 1975; Bauschlicher *et al.,* 1976). Moreover, the reaction path may fail to contain the transition state (Dewar and Kirschner, 1971b) and/or to yield a stable product (Dewar and Kirschner, 1971a).

As an alternative to these methods, minimum-energy paths leading from saddle points to the adjoining potential energy minima have been proposed by Fukui (1970). This sort of path is a curve that connects two minima, passes through a transition state, and is orthogonal to the energy equipotential contour surface, i.e., it follows the negative energy gradient everywhere (i.e., the path of steepest descent) except in the transition state where the initial direction is determined by the direction of the principal axis of negative curvature. A method for calculation of the steepest-descent path that avoids evaluation of gradients or second-derivative matrices has recently been proposed (Müller and Brown, 1979).

The definition given by Fukui (1970) guarantees a unique reaction path within a given coordinate system. However, the minimum-energy path still depends on the choice of coordinates used for description of the system (Pearson *et al.*, 1975; Stanton and McIver, 1975). If the kinetic energy T in the chosen coordinate system can be expressed in terms of conjugate linear momentum P_j as follows:

$$T = \tfrac{1}{2} \sum_j P_j^2, \tag{9}$$

the path of the steepest descent on the corresponding hypersurface represents a special solution of the classical equations of motion (Fukui *et al.*, 1975; Schaefer, 1975; Ishida *et al.*, 1977)—a hypothetical trajectory proceeding under the conditions of infinitely slow nuclear motion and continuous dissipation of the nuclear kinetic energy. With this clear physical meaning, this "intrinsic reaction coordinate" is independent of the coordinate system. Its initial direction at the transition state given by the vibrational normal coordinate that has a negative eigenvalue (Murrell and Laidler, 1968) is especially important. This normal mode can be used for identifying the reactants and products that are associated with the transition state (even without evaluation of the whole intrinsic reaction coordinate).

Mass-weighted Cartesian coordinates are an example of systems complying with Eq. (9). This coordinate system has been used by Ishida *et al.* (1977) in the calculation of the intrinsic reaction coordinate at the *ab initio* SCF level. Quite recently, the concept of intrinsic reaction coordinate has been further generalized and worked out in detail (Tachibana and Fukui, 1978, 1979a,b; Mezey, 1980).

C. Calculation of the Potential Energy Hypersurface as a Whole

Rigorously speaking, the potential energy hypersurface could be generated by solving the electronic Schrödinger equation (3) for all spatial arrangements of the nuclei. It is generally known that, apart from simple models, the potential energy $U_n(\mathbf{R})$ cannot be obtained directly in an analytic form. Consequently, Eq. (3) can be solved at a given quantum-chemical level for only a finite number of discrete nuclear configurations. The range of these configurations and their number depend on the purpose for which the hypersurface is generated. This point-by-point mapping is followed by an analytic fitting procedure. The results obtained by quantum-chemical generation of potential energy hypersurfaces have been reviewed several times (e.g., Eyring and Lin, 1974; Bader and Gangi, 1975; Devaquet, 1975; Murrell, 1977; Nikitin and Zülicke, 1978).

There is no general instruction for the choice of the function form employed in the fitting procedure. Provided we are only interested in the region of relatively small displacements from the equilibrium configuration, the representation of the potential energy hypersurface as a power series expansion in displacement coordinates will be sufficient (i.e., the usual approach in determination of the hypersurfaces from vibration–rotation data—see, e.g., Mills, 1977). However, such representations suffer from several imperfections with large displacements from equilibrium (Simons, 1974). Simons *et al.* (1973) introduced new expansion coordinates with the form $\rho = (R - R_e)/R$ that have recently been demonstrated to offer distinct advantages as a vehicle for the analytic representation of quantum-chemical potential hypersurfaces (Diab and Simons, 1977). In the field of weak intermolecular interactions, an expansion in terms of radial functions and Legendre polynomials has been used (e.g., Gallup, 1977a).

The work of Clementi and co-workers (for a survey, see Clementi, 1976b) on the water dimer and the solvation of biomolecules is the most extensive quantum-chemical calculation of potential energy hypersurfaces carried out so far. It has been shown (Popkie *et al.*, 1973) for $(H_2O)_2$ that the analytic formula that best combines numerical accuracy with mathematical simplicity is that found from H_2O charge distribution calculations, similar to that already proposed by Bernal and Fowler (1933). Description of the interaction between water and biomolecules was based on a Lennard-Jones type potential (Clementi *et al.*, 1977).

Sorbie and Murrell (1975) have described a method for constructing analytical functions of potential surfaces with small polyatomic molecules. The resultant hypersurfaces have correct asymptotic behavior on dissociation and reproduce the known spectroscopic constants of the molecule. The potentials were based mostly on the spectroscopic constants of the equilibrium structure; however, quantum-chemical and kinetic data related to other features of the hypersurface were also included (e.g., Murrell *et al.*, 1976; Farantos *et al.*, 1977; Varandas and Murrell, 1977; Carter *et al.*, 1980).

Once the analytic form of potential hypersurface based on point-by-point quantum-chemical calculations is obtained, a comprehensive search for the stationary points can be carried out as described in Section II,A. However, evaluation of the energy gradient is considerably easier and faster here. Solution of the water dimer isomerism problem (Slanina, 1980) based on the powerful *ab initio* SCF CI hypersurface of Matsuoka *et al.* (1976) is an example of this approach. Farantos *et al.* (1977) succeeded in elucidating the isomeric relationships for two triatomic molecules, i.e., SO_2 (OSO versus SOO) and ClO_2 (OClO versus ClOO). The study was performed using the analytic potentials derived according to Sorbie and Murrell (1975).

The relationships between the individual stationary points on the mul-

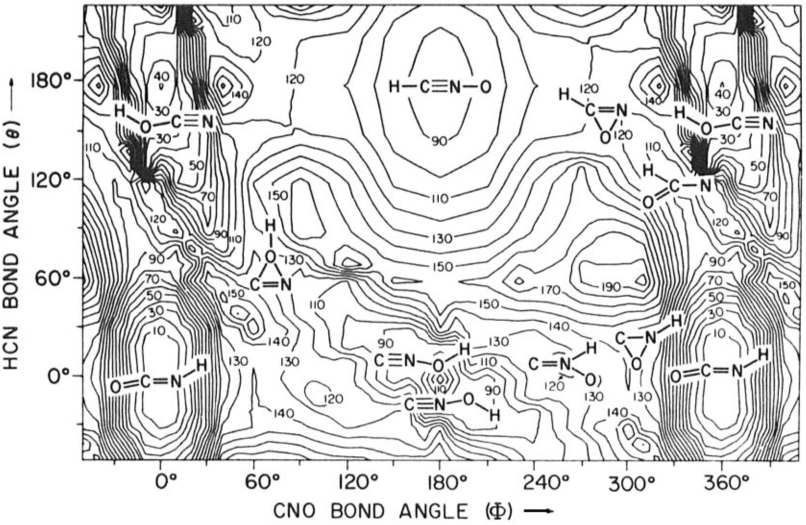


Fig. 3. Visualization of the six-dimensional 4-31G potential energy hypersurface of CHNO by two-variable mapping in terms of bond angles θ = HCN angle and Φ = CNO angle (Poppinger *et al.*, 1977). Contour labels are in kilocalories per mole with respect to the lowest calculated point on the hypersurface ($\theta = \Phi = 0°$). (Reprinted with permission from *J. Am. Chem. Soc.* Copyright © 1977 American Chemical Society.)

tidimensional hypersurface may become evident from visualization by two-variable mapping. For illustration, the 4-31G conformational energy contour map for the CHNO system (Poppinger *et al.*, 1977) is presented in Fig. 3. The plot is described in terms of two bond angles assuming that each point on which the map is based is a minimum with respect to the four remaining variables.

III. Quantum Theory and Isomerism

In recent years there has been an increasing interest in the capabilities and limitations of the Born–Oppenheimer and adiabatic approximations. In fact, the breakdown of the Born–Oppenheimer approximation in cases of degeneracy or near degeneracy of the electronic states was known from the early days of quantum chemistry (Renner, 1934; Jahn and Teller, 1937). Recently, theoretical discussions of the adiabatic hypothesis and of general features of the potential hypersurfaces indicated that regions of nuclear configuration space must exist where the adiabatic hypothesis may fail completely (Longuet-Higgins, 1975; Aronowitz, 1976; Stone, 1976; Davidson, 1977). Moreover, it has been argued that there is no consistent manner according to which an expansion in the set of adiabatic functions [Eq. (2)] can be chosen to represent a true eigenfunction of the total Hamiltonian (Woolley and Sutcliffe, 1977; Aronowitz, 1978). A new derivation for the separation of electronic and nuclear motion was also given (Essén, 1977) showing that the form of the interaction between the particles is responsible for the separation.

During the discussion of the validity of the Born–Oppenheimer approximation special attention has been paid to the classical concept of molecular structure. This concept has been criticized as being inconsistent with the requirements of quantum theory (Woolley, 1976, 1977, 1978a,b; Woolley and Sutcliffe, 1977). To obtain the conventional picture of molecular physics from quantum mechanics it was recommended that the notion of structure be added to the quantum theory as a postulate of equal status (Woolley, 1978b).

A. Extension of the Concept of Molecular Structure

Wilson (1979) recently showed how the classical definition of molecular structure can be generalized to include nonadiabatic wave functions. This extension is based on probability interpretation of wave functions. The overall wave function $\Psi(\mathbf{r}, \mathbf{R})$ introduced in Eq. (1) determines the probability $P(\mathbf{r}, \mathbf{R})\, d\mathbf{r}\, d\mathbf{R}$ of finding the electrons in $d\mathbf{r}$ at $\mathbf{r}$ and the nuclei in $d\mathbf{R}$ at $\mathbf{R}$:

$$P(\mathbf{r}, \mathbf{R})\, d\mathbf{r}\, d\mathbf{R} = |\Psi(\mathbf{r}, \mathbf{R})|^2\, d\mathbf{r}\, d\mathbf{R}. \tag{10}$$

The probability $P(\mathbf{R})\, d\mathbf{R}$ of the nuclei being in $d\mathbf{R}$ at $\mathbf{R}$ regardless of the positions of the electrons is obviously given by

$$P(\mathbf{R})\, d\mathbf{R} = d\mathbf{R} \int |\Psi(\mathbf{r}, \mathbf{R})|^2\, d\mathbf{r}. \tag{11}$$

Let us now consider $P_{\mathbf{R}}(\mathbf{r})\, d\mathbf{r}$ denoting the probability of electrons being in $d\mathbf{r}$ at $\mathbf{r}$ when the nuclei are localized at $\mathbf{R}$. Probability reasoning gives the following relationship:

$$P_{\mathbf{R}}(\mathbf{r}) = \frac{|\Psi(\mathbf{r}, \mathbf{R})|^2}{\int |\Psi(\mathbf{r}, \mathbf{R})|^2\, d\mathbf{r}}, \tag{12}$$

where the denominator merely renormalizes the distribution. Distribution (12) enables evaluation of the expectation value $E_{\text{elec}}(\mathbf{R})$ of the electronic energy:

$$E_{\text{elec}}(\mathbf{R}) = \frac{\int \Psi^*(\mathbf{r}, \mathbf{R}) \hat{H}_{\text{elec}}\, \Psi(\mathbf{r}, \mathbf{R})\, d\mathbf{r}}{\int |\Psi(\mathbf{r}, \mathbf{R})|^2\, d\mathbf{r}}, \tag{13}$$

where the electronic Hamiltonian $\hat{H}_{\text{elec}}$ was already introduced in Eq. (3).

Let us now pass from the nonadiabatic level to the Born–Oppenheimer

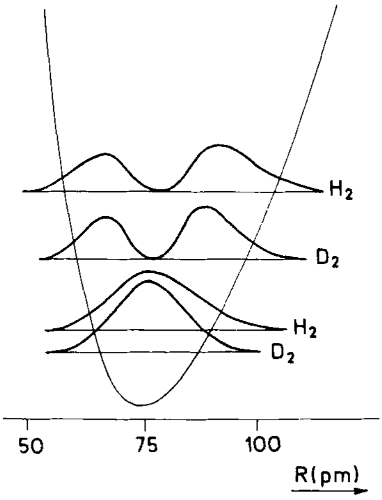


Fig. 4. Probability distributions $P(R) = R^2 \int |\Psi(r, R)|^2 \, dr$ for the two lowest vibrational states of H_2 and D_2 (Kołos and Wolniewicz, 1964) computed in a nonadiabatic approach (the potential energy curve has only formal significance).

approximation. Using Eq. (3) it can easily be shown that function (13) reduces to the conventional Born–Oppenheimer energy hypersurface $U_n(\mathbf{R})$. In other words, function (13) represents the hypersurface extended beyond the Born–Oppenheimer hypersurface and permits generalization of the conventional molecular structure notion in terms of $E_{\mathrm{elec}}(\mathbf{R})$. While the usual equilibrium molecular structure is independent of the vibrational or rotational state, the generalized definition based on hypersurface (13) may depend on all the quantum numbers. Wilson (1979) also noted an interesting relationship to the uncertainty principle. Operator $\hat{H}_{\mathrm{elec}}$ commutes with the nuclear coordinates $\mathbf{R}$ and consequently the electronic energy and the nuclear coordinates could be measured simultaneously in the Born–Oppenheimer concept.

The introduction of hypersurface (13) is one approach to the extension of molecular structure definition. An alternative represents the most probable structure, i.e., the set of nuclear coordinate values $\mathbf{R}$ maximizing the probability density $P(\mathbf{R})$ introduced by Eq. (11). Probability distributions for the two lowest vibrational states of H_2 and D_2 given by Kołos and Wolniewicz (1964) are shown in Fig. 4. As can be seen in this figure, such a structure definition has a drawback. The structure will change considerably for higher vibrational states and there will be several configurations of nearly equal probability. Other definitions of molecular structure may be suggested; e.g., the expectation values of some operators connected with nuclear coordinates. The choice of the appropriate definition depends on its further application.

B. Molecular Wave Function and Isomerism

Each member of the set of all chemical species comprising the same number and kind of nuclei as well as the same number of electrons is described by the same total (molecular) Hamiltonian. The molecular Hamiltonian does not describe a particular chemical species. The formal definition of a molecule as a quantum-mechanical system does not distinguish between isomers. On the other hand, chemistry has supplied us with an enormous number of well-defined distinct pairs (or even series) of isomers, each of them exhibiting apparent uniqueness. In order to interpret this fact, Woolley (1976) supposed that the stationary states of different isomeric structures correspond to different subsets of states of the Hilbert space spanned by the molecular Hamiltonian and that there are selection rules that prevent transitions between these different subsets of states.

This question was recently discussed in detail by Aronowitz (1978). He concluded that the molecular Hamiltonian spans a single coherent Hilbert space rather than a series of coherent subspaces. Moreover, it was pointed out that no expansion in terms of the product of electronic and nuclear functions for only a single chemical species can yield a true eigenfunction of the total Hamiltonian and can span the full Hilbert space. The assignment of various eigenfunctions of the molecular Hamiltonian to distinct chemical species can be considered only as an approximation. Various situations can, however, occur, e.g., the lowest Ψ can have a negligible amplitude everywhere outside a certain domain of the nuclear configuration space or can also have a noticeable amplitude in other regions. However, there is in any case a certain unity among isomeric chemical compounds, even seemingly distinct ones—the more closely we examine them, the less unique these species become. Uniqueness is, nevertheless, sometimes a good approximation because of the relative isolation of one stability domain from another. Aronowitz (1978) hypothesized that direct transformation from one isomeric species to another can occur only when two species are in states that are mutually degenerate. As a consequence of this assumption, the interconversion is governed by symmetry rules and orthogonality requirements. Moreover, it was shown that any two stability regions having no degeneracies in common must exhibit pathways leading to a common region (otherwise the space spanned by the molecular Hamiltonian would be divided into coherent subspaces). Thus, in principle, all the stability regions should be accessible to each other.

Wilson (1979) recently analyzed the problem of whether it is necessary for Ψ to be a stationary state function (i.e., independent of time). He argued that observations of true stationary states were never made, among other things, because the chemical preparation generates the system in a certain geometry rather than in a precise energy state (as the properties important in separation depend largely on structure). Thus, the chemically prepared compound is initially localized and therefore cannot be in a stationary state. The resulting state is generally time dependent, however its change with time may be slow or even negligible. For example, transition of one isomeric form into another by tunneling may take years or even much longer (Löwdin, 1965). Clearly, such times permit accurate total energy measurements without disturbing the geometry. It is evident that, from the point of view of nonstationary states, the uniqueness of certain isomers is a well-founded concept.

Let us mention finally that our present understanding of isomerism in terms of the molecular wave function is sketched only in a rough form in the literature and that further progress can be expected.

IV. The Algebraic Aspects of Isomerism

Quantitative description by numerical quantum chemistry methods is one possible theoretical approach to the study of isomerism. Algebraic nonnumerical treatment is another. This treatment enables direct insight into the intrinsic logical structure underlying the isomerism problem. For example, algebraic methods have been employed in the study of chemical chirality (e.g., Mead, 1974, 1980; Dugundji *et al.*, 1978; Keller *et al.*, 1978). However, in our context the algebraic approaches to the evaluation of stationary points on a given potential energy hypersurface are especially important. Even if there is no rigorous procedure that would permit us to say, *a priori,* how many stationary points occur on a given hypersurface, two purely algebraic techniques were developed that may be at least partially helpful in solution of this problem: the method of topological reduction and characterization of the hypersurface, and isomer enumeration methods. In addition to these methods, the extended concept of isomerism based on the algebraic approach will also be briefly discussed in this section.

A. Topological Reduction and Characterization of Hypersurfaces

This approach, introduced and developed by Krivoshey (1969) and by Krivoshey and Sleta (1976), enables suitably defined topology to represent a hypersurface by its one-dimensional image. In such a representation, all the differential properties of the hypersurface are ignored and only the

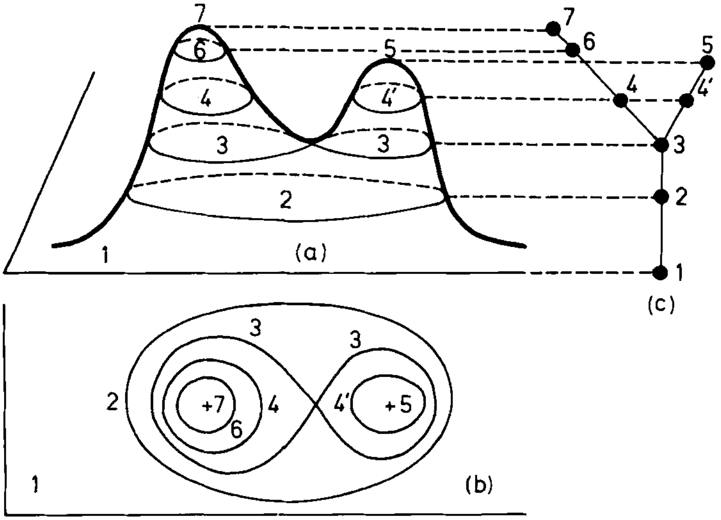


Fig. 5. Process of mapping a two-dimensional surface (a) by tree representation (c) (Krivoshey and Sleta, 1976); (b) the surface contour plot.

topological properties are considered. This method is based on Kronrod's (1950) mathematical treatment of the one-dimensional properties of functions of many variables.

Let us start with a simple example of a function of two variables that exhibits two local maxima and one saddle point (Fig. 5). An equipotential level of the surface consists of one or two components; let us represent each component by a single point on a plane. These points are ordered with respect to the function values. If the function is single-valued and continuous, then, according to Kronrod (1950), the constructed set of points will result in a special kind of a graph, viz., a tree—a connected graph containing no polygons (see, e.g., Essam and Fisher, 1970). Local maxima are represented by its end vertices 5 and 7, the saddle point by branch vertex 3. In a similar way we can construct such a tree for a multidimensional hypersurface. Again, each separate contour of an equipotential level on the hypersurface is ascribed a point in the one-dimensional representation, and the points are ordered according to the function values (i.e., energy). The result is again a tree. Its vertices represent the stationary points and its edges (branches) map the interrelations between them. Local minima and maxima correspond to end vertices with a vertex degree of 1; saddle points are represented by branch vertices with a vertex degree ≥3. On passing a branch vertex the number of components of the level set changes. In this manner the topological properties of

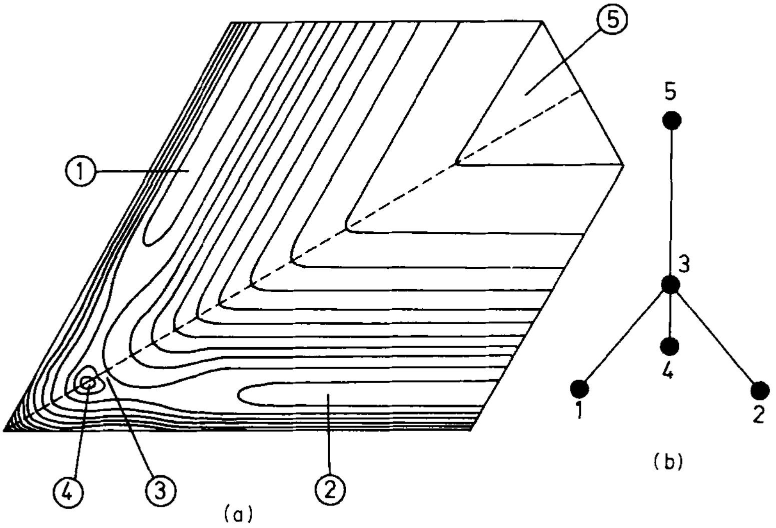


Fig. 6. Tree representation (b) of the potential energy surface (Eyring *et al.*, 1935) of the linear H_3 molecule (a).

the hypersurface that determine the number, type, and mutual position of the stationary points are apparent from the corresponding tree at a glance.

The construction of the tree is quite easy if the hypersurface is described by a contour plot. This is illustrated by the linear H_3 molecule (Eyring *et al.*, 1935), whose familiar energy contour map is depicted in Fig. 6 together with the corresponding tree. The valleys of the reactants and products are represented by end vertices 1 and 2, the local maximum (complete dissociation into three separate hydrogen atoms) by end vertex 5, and the activated complex by branch vertex 3. End vertex 4 corresponds to a small depression near the saddle point (the basin is, in fact, an artifact of the method—see, e.g., Laidler, 1969). However, the most common quantum-chemical output is a table of energies corresponding to various nuclear configurations. Zhuravlev *et al.* (1975) proposed a useful algorithm for constructing the tree in such a case, based on set theory. The tree representation was further extended to cover a set of hypersurfaces (Krivoshey and Sleta, 1976). In addition, topological reduction of hypersurfaces to trees enables study of the general hypersurface properties. For example, it was shown that the trees of n-dimensional hypersurfaces ($n > 2$) have only two kinds of branch vertices (Krivoshey, 1976). This finding could facilitate both stationary point location on a hypersurface and the construction of the tree.

It is evident that every path along the potential energy hypersurface has an image in a tree representation (i.e., the path from one tree vertex to another). Moreover, the tree representation enables ready discovery of relationships between these paths and stationary points that are not directly apparent from the table of energy–geometry data (Fraga *et al.*, 1978). The fact that topological reduction of a hypersurface results in a connected graph containing no polygons may sometimes facilitate complete stationary point location.

B. Isomer Enumeration Methods

Isomer enumeration is one of the oldest applications of graph theory to chemistry; the first use of graphs in a chemical context was depiction of molecules. In graph theory, enumeration means counting of nonisomorphic graphs. Reducing an isomer enumeration problem to the purely graphical enumeration, the tools of graph theory and combinatorial theory can be widely employed. The field of isomer enumeration has been reviewed comprehensively by Rouvray (1974, 1975).

The powerful enumeration theorem of Pólya (1935) represents the most important enumeration result. Pólya's enumerative theory is considered (Biggs *et al.*, 1976) a milestone, not only in graph theory and chemical enumeration, but in mathematics as a whole. The theorem was foreseen in certain respects in the works of Redfield (1927) and of Lunn and Senior (1929). Pólya (1935) fruitfully combined the method of generating functions and some results from the theory of permutation groups. Generating functions are power series whose coefficients correspond to the solution of an enumeration problem. For example, the coefficient of x^k in the polynomial

$$F(x) = 1 + x + 3x^2 + 3x^3 + 3x^4 + x^5 + x^6 \qquad (14)$$

gives the number of positional isomers formed when benzene is substituted by k identical univalent groups $*$ (see Fig. 7). Let A be a permutation group containing n permutations that represent the symmetry of object set X having p elements (for benzene $X \equiv \{1, \ldots, 6\}$). The cycle index $Z(A)$ of A is introduced as a polynomial series in the variables $s_1, \ldots, s_p$:

$$Z(A) = \frac{1}{n} \sum H_{j_1, \ldots, j_p} s_1^{j_1} \cdots s_p^{j_p}, \qquad (15)$$

where $H_{j_1,\ldots,j_p}$ denotes the number of permutations with j_1 1-cycles, $\ldots, j_p$ p-cycles and the sum includes all possible choices of j_i for permutations in the group. Let us now consider a set Y of elements called figures (for substituted benzenes $Y \equiv \{\mathrm{H}, *\}$) and introduce the notion of a configuration that results from assigning the figure to each element of object

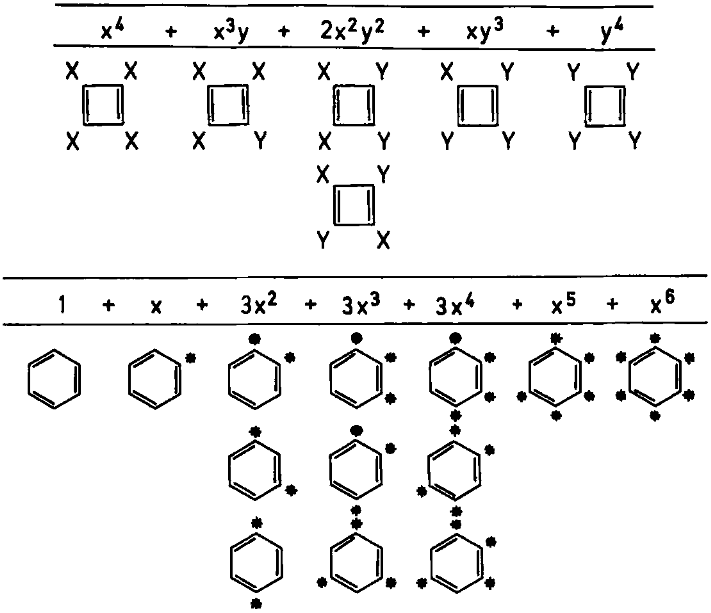


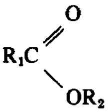
Fig. 7. Representation of the solution of an enumeration problem by a generating function for cyclobutadiene fully substituted by two kinds of univalent substituents (X, Y) and for benzene successively substituted by one kind of univalent group (*).

set X. The figures are enumerated by figure generating function $c(x)$ [for substituted benzenes $c(x) = 1 + x$]. Two configurations are considered equivalent if they are related to by symmetry. The task is to find generating function $C(x)$ for the set of nonequivalent configurations (i.e., for equivalence classes of configurations). Pólya's enumeration theorem (1935) states that generating function $C(x)$ will be obtained by substituting $c(x^r)$ for s_r in the cycle index. Pólya supplemented his general theorem by an account of its applications to isomer enumeration (1936) and by discussion of its many mathematical aspects (1937).

Pólya's Hauptsatz has proved to be an extremely powerful tool in determining isomer counts. However, there is another method of isomer enumeration (though less sophisticated) that should also be considered, i.e., the iterative approach. This straightforward technique introduced by Henze and Blair (1931a,b) is based on setting up recursion formulae giving the number of isomers for any member of a series provided that all the preceding members were evaluated. Using computers, the scope of the iterative approach has been extended considerably in recent years (for a review, see Rouvray, 1974).

TABLE II

ISOMER ENUMERATION RESULTS IN SOME ACYCLIC SERIES[a,b]

n (carbon atom content)	1	2	3	4	5	10	15	20	25
$C_nH_{2n+1}^-$	1	1	2	4	8	507	48865	5622109	712566567
	1	1	2	5	11	1553	328092	82300275	22688455980
C_nH_{2n+2}	1	1	1	2	3	75	4347	366319	36797588
	1	1	1	2	3	136	18127	3396844	749329719
RCH_2OH	1	1	1	2	4	211	19241	2156010	269010485
	1	1	1	2	5	551	110500	27012286	7333282754
R_1R_2CHOH			1	1	3	194	19181	2216862	281593237
			1	2	5	768	162672	40807290	11247841224
$R_1R_2R_3COH$				1	1	102	10443	1249237	161962845
				1	1	234	54920	14480699	4107332002
 $R_1C(=O)OR_2$		1	2	4	9	599	57564	6589734	832193902
		1	2	4	10	1319	273172	67819576	18581123978
$R_1R_2C{=}CR_3R_4$		1	1	3	5	377	36564	4224993	536113477
		1	1	4	6	895	185310	46244031	12704949506

[a] According to Henze and Blair (1931a,b), Pólya (1936), and Read (1976); the numbers of structural isomers are given in the upper line, the numbers of stereoisomers in the lower.

[b] R, R_i denote an alkyl radical or hydrogen atom; R_1, R_2, R_3, for secondary and tertiary alcohols, and R_2, for esters, are alkyl radicals.

Enumeration studies have been carried out in a series of very varied types of molecules, both acyclic (e.g., Read, 1976) and cyclic (e.g., Balaban, 1976). Illustrative results on acyclic compounds are given in Table II. An immense increase in the isomer counts with an increasing content of carbon atoms is clearly evident from these data. From the point of view of the present theory of chemical reactivity, based on the stationary points of potential energy hypersurface, a key question is how to relate the results of enumeration studies with the stationary points. Clearly, a one-to-one correspondence need not necessarily exist: each structure considered in the enumeration need not have a corresponding stationary point and, at the same time, one enumerating configuration can be realized by more than one stationary point. Nevertheless, we can suppose that the enumeration results present a reasonable indication for estimation of the order of magnitude of the number of stationary points.

Suitable choice of the permutation group for the isomer enumeration enables inclusion of some forms of stereoisomerism (Read, 1976) or even molecular nonrigidity (Leonard *et al.*, 1975; Leonard, 1977; Balasubramanian, 1979a,b). In fact, Pólya (1937) considered three types of permutation groups with enumeration of a given series. Evaluation of isomer counts for nonrigid molecules requires that the permutation group also contain the feasible permutations induced by the internal degrees of freedom. For this purpose, a generalized wreath product method was developed (Balasubramanian, 1979a,b). Cyclohexane is an interesting example of nonrigid molecule enumeration (Leonard *et al.*, 1975; Flurry, 1976; Leonard, 1977). The Pólya theorem employing the point group of chair form of cyclohexane (D_{3d}) yields an erroneous cyclohexane isomer number. The correct number is obtained by combining the ring-flip-rotation operation with the D_{3d} point group (the nonrigid molecular symmetry group obtained is isomorphic with the D_{6h} point group).

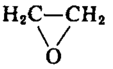
C. Extended Concept of Isomerism

For the design of syntheses, an extension of the concept of isomerism has been proposed (Ugi and Gillespie, 1971a), leading from molecules to ensembles of molecules. Let A be a given set of atoms. For an ensemble of molecules that has the total empirical formula A, any compound or collection of chemical species is taken that is formed from A using each atom exactly once. The family of isomeric ensembles of molecules of A is the set of all ensembles of molecules that have empirical formula A. Table III shows an example—the family of isomeric ensembles of molecules that have the empirical formula C_2H_6O. The extended concept of isomerism corresponds well to the quantum-mechanical description of isomerism. Like conventional isomers, all members of a family of isomeric ensembles of molecules are described by one total Hamiltonian. Similarly, within the Born–Oppenheimer case more member ensembles of molecules are incorporated into the potential energy hypersurface as the infinite region of the dissociation products.

Isomerism has been interpreted as an equivalence relation (Ege, 1971;

TABLE III

FAMILY OF ISOMERIC ENSEMBLES OF MOLECULES WITH EMPIRICAL FORMULA C_2H_6O[a]

$2C + 6H + O$; $CH_3—CH_2—OH$; $CH_3—O—CH_3$; $CH_3—CHO + H_2$; $CH_4 + CH_2O$;
$CH_3OH + CH_2$;  $H_2C—CH_2$ (with O bridging) $+ H_2$; $CH_2{=}CH_2 + H_2O$; $H_2C{=}CHOH + H_2$;
$CO + CH_4 + H_2$; $CH_2 + CH_2O + H_2$; $H_2C{=}C{=}O + 2H_2$; $HC{\equiv}C—OH + 2H_2$;
$HC{\equiv}CH + H_2O + H_2$; $CO + CH_2 + 2H_2$; $2CH_2 + H_2O$

---

[a] Only conceivable neutral components are considered (Dugundji *et al.*, 1976).

Ugi and Gillespie, 1971a; Ugi *et al.*, 1972); the same holds for isomerism in its extended form. Dugundji *et al.* (1976) pointed out that the analysis of chemical systems requires the generation of models that represent certain equivalence classes of states rather than the states themselves.

The family of isomeric ensembles of molecules of A contains the whole chemistry of collection A of atoms. Chemical processes are interconversions of ensembles of molecules; the left and right sides of chemical equations refer to isomeric ensembles of molecules. The apparatus of isomeric ensembles of molecules has been used in analyzing the logical structure of chemistry (Dugundji *et al.*, 1976) and in nonempirical and semiempirical designing syntheses (Ugi and Gillespie, 1971b; Ugi *et al.*, 1972, 1979). Nonempirical, topological computer programs for the design of syntheses based on the mathematical model of constitutional chemistry have been developed (Blair *et al.*, 1974; Weise, 1975; Gasteiger and Jochum, 1978).

V. Isomerism and the Theory of Chemical Reactivity

Systematic investigation of a potential energy hypersurface often reveals several different minima (each corresponding to only one compound) and/or several different saddle points representing activated complexes in a single rate process. Energy (or other) criteria can sometimes eliminate all but one structure that plays an important role under the given experimental conditions. Explicit considerations of isomerism in such a case would be only of formal value. However, it may also happen that two or more structures of comparable stability coexist and are indistinguishable experimentally. Then any structure-dependent observable can be considered as an average value resulting from contributions of all the isomers in question. Recently, special attention has been paid to the quantum-chemical evaluation of reaction characteristics (both standard and activation) of chemical processes whose components have been shown by theoretical analysis to be mixtures of isomers.

The need for such a weighting can be illustrated by a recent example. C_4 aggregates were studied using the MINDO/2 method (Slanina and Zahradník, 1977). Three C_4 isomers with symmetry groups D_{2h}, D_2, and T_d were found (Fig. 2). The conventional treatment accounts primarily for the thermodynamic characteristics (e.g., standard enthalpy and entropy changes) of the following partial reactions:

$$4C(s) \rightleftharpoons C_4(g;\ D_{2h}), \tag{16}$$

$$4C(s) \rightleftharpoons C_4(g;\ D_2), \tag{17}$$

$$4C(s) \rightleftharpoons C_4(g;\ T_d). \tag{18}$$

However, the experimental mass-spectrometric values (Drowart *et al.*, 1959) do not correspond to any of processes (16)–(18) but to the total equilibrium:

$$4C(s) \rightleftharpoons C_4(g). \tag{19}$$

Correct comparison of the theoretical outputs with the observables requires carrying out of a weighting of the contributions of partial processes (16)–(18) to overall process (19).

A. Usefulness of the Theory of Chemical Reactivity in Contemporary Quantum Chemistry

Before outlining the isomerism of chemical process components and its consequences regarding evaluation of the chemical reactivity characteristics, the present state of quantum-chemical calculations of the equilibrium and rate constants themselves should be surveyed briefly (i.e., theoretical calculations of the reaction characteristics of processes not exhibiting isomerism of their components).

1. *Calculations of Equilibrium Thermodynamic Characteristics*

Statistical mechanics has enabled relation of bulk macroscopic properties to molecular characteristics—all the thermodynamic functions can be expressed in terms of partition functions involving molecular energy levels. The procedures for calculating thermodynamic properties of gases from spectroscopic data were worked out in principle in the 1930s (e.g., Rodebush, 1931; Kassel, 1936; Wilson, 1940), although those for higher approximations of molecular motions (vibrational anharmonicity, rotational–vibrational coupling, internal rotation, etc.) were developed later (e.g., Godnew, 1956; Woolley, 1956; Frankiss and Green, 1973; Hollenstein *et al.,* 1980). At present, perfectly measured and analyzed rotational–vibrational spectra are available only for a few polyatomic molecules. Consequently, the thermodynamic functions of polyatomic molecules are generally evaluated assuming a rigid rotator and harmonic oscillator (RRHO). It is therefore desirable to know the error in thermodynamic functions evaluated using the RRHO approximation. The comparisons performed with more sophisticated models (e.g., McBride and Gordon, 1961; Bron and Wolfsberg, 1972; Frankiss and Green, 1973) or with experiments (e.g., Frankiss and Green, 1973; Slanina and Zahradník, 1974) indicate a reasonable exploitation of the RRHO partition functions. An illustrative example (Scott *et al.,* 1962) is given in Table IV.

Substitution of quantum-chemical generation of molecular parameters for their spectroscopic (and/or other, e.g., calorimetric) determination enables elimination of any dependence on experimental information. Thus

TABLE IV

CONTRIBUTIONS OF INDIVIDUAL MOTIONS TO THE ENTROPY S°_T (IN J/K/mol) OF TOLUENE[a,b]

Contribution(s)	S°_T T = 298.15 K	S°_T T = 1000 K
Translation	165.16	190.31
Rigid rotation	107.08	122.18
Harmonic vibration	33.62	209.04
Internal rotation	14.80	19.83
Vibrational anharmonicity[c]	0.01	1.89
Total calculated	320.67	543.25
Observed	321.21	—

[a] See Scott *et al.* (1962); Frankiss and Green (1973).
[b] Standard state—ideal gas at 101,325 Pa pressure.
[c] Empirical estimation of the anharmonicity contributions.

thermodynamic functions become obtainable directly from first principles (masses, fundamental constants, and Coulomb's law being the only input information). In fact, the serviceability of each quantum-chemical method for generation of molecular information for the construction of partition functions should be proved first. This step was carried out comprehensively at the CNDO/2, INDO, and MINDO/2 (Slanina *et al.*, 1977) and MINDO/3 (Dewar and Ford, 1977) levels. Illustrative data (Slanina *et al.*, 1977) in Table V on the NH_3 molecule show the quality of the CNDO/2 partition functions. These studies proved that (especially at moderate temperatures) even semiempirical quantum-chemical calculations may assist in evaluating the thermodynamic functions of species whose molecular constants cannot be determined experimentally. On the nonempirical level hitherto only the quality of the enthalpy term was tested (e.g., Hurley, 1973; Karlström *et al.*, 1978a). With respect to the good quality of the semiempirical entropy term there is no need to repeat the tests on the *ab initio* level. There are several processes whose equilibrium constants were evaluated using various quantum-chemical methods; Table VI gives selected examples of such studies. Only one calculation was carried out using higher than the RRHO approximation, the study of *o–p* hydrogen conversion (Kosloff *et al.*, 1974). However recent interest in quantum-chemical description of vibrational anharmonicity (e.g., Almlöf, 1972; Pecul and Janoschek, 1974; Støgård *et al.*, 1975; Jönsson and Nelander, 1977; Botschwina, 1979; Bouteiller *et al.*, 1980) may soon help to improve the quality of the theoretical partition functions of polyatomic molecules.

TABLE V

COMPARISON OF PARTITION FUNCTIONS Q OF $NH_3(g)$ CALCULATED USING EXPERIMENTAL (NRAO[a], RRHO[b]) AND CNDO/2[c] MOLECULAR CONSTANTS[d]

T (K)	$\log Q^{(\mathrm{NRAO})} - \log Q^{(\mathrm{RRHO})}$	$\log Q^{(\mathrm{RRHO})} - \log Q^{(\mathrm{CNDO/2})}$
298.15	0.005	−0.058
500	0.006	−0.038
1000	0.015	0.030
2000	0.035	0.166

[a] NRAO—partition functions of nonrigid rotator and of anharmonic oscillators.

[b] RRHO—partition functions of rigid rotator and of harmonic oscillators.

[c] RRHO approximation of partition functions.

[d] See Slanina *et al.* (1977).

2. *Calculations of Rate Characteristics*

At present the activated-complex (or the transition-state) theory of Eyring (1935) and Evans and Polanyi (1935) represents the only treatment effectively applicable to the calculation of rate constants of chemically interesting processes. Golden (1979) has declared this approach an invaluable tool in rate constant evaluation. Similar to equilibrium processes, the linking up with quantum-chemical methods removes any need of empirical assessment of input information. From the point of view of computational quantum chemistry, there is no appreciable difference in generating parameters for the calculation of standard thermodynamic functions and for treatment within the activated-complex theory.

Here it should be noted that the use of the activated-complex theory has received a tremendous impetus from the fact that recently reported comparisons (e.g., Truhlar and Kuppermann, 1971; Baer *et al.*, 1974; Essén *et al.*, 1976; Miller, 1976; Truhlar *et al.*, 1976; Connor *et al.*, 1979; Truhlar, 1979) of the values of rate characteristics obtained on the basis of the activated-complex theory with the results of exact quantum-mechanical calculations showed a surprisingly good agreement (for very simple reaction systems). Table VII gives a typical example (Essén *et al.*, 1976; Truhlar *et al.*, 1976). The low temperature region is an exception. At these temperatures the contribution of quantum-mechanical tunneling may become significant. Its evaluation within one-dimensional barriers (e.g., barriers by Eckart, 1930, or Wigner, 1932) is straightforward and can be carried out with the amount of information ordinarily afforded by

TABLE VI. SELECTED EXAMPLES OF QUANTUM-CHEMICAL CALCULATIONS OF EQUILIBRIUM CONSTANTS

Equilibrium process[a]	Generating quantum-chemical method	Reference
$2LiCl_2 \rightleftharpoons (LiCl)_2$	Empirical potential	Berkowitz (1958)
$n\,C(s) \rightleftharpoons C_n;\ n = 1-17$	Simple MO method	Pitzer and Clementi (1959)
$H_2^+ + H_2 \rightleftharpoons H_3^+ + H$	*Ab initio* SCF CI	Schwartz and Schaad (1967)
$K^+ + H_2O \rightleftharpoons KH_2O^+$	Empirical potential	Searles and Kebarle (1969)
$2LiH \rightleftharpoons (LiH)_2$	*Ab initio* SCF	Kollman *et al.* (1972)
$HCN \rightleftharpoons HNC$	*Ab initio* SCF	Booth and Murrell (1972)
$o\text{-}H_2 \rightleftharpoons p\text{-}H_2$	Exact solution	Kosloff *et al.* (1974)
$2H_2O \rightleftharpoons (H_2O)_2$	*Ab initio* SCF	Braun and Leidecker (1974)
$2X \rightleftharpoons X_2;\ X = CH_3, NH_2, HCO$	MINDO/2	Zahradník *et al.* (1974)
$2X_2 \rightleftharpoons (X_2)_2;\ X = N, O, Br, I$	Empirical potential	Slanina *et al.* (1974)
$H_2 + H_3^+ \rightleftharpoons H_5^+$	CNDO/2	Slanina (1975c)
$n\,H_2O \rightleftharpoons (H_2O)_n;\ n = 2-5$	Empirical potential	Owicki *et al.* (1975)
$C_2H_2 + OH^- \rightleftharpoons C_2H^- + H_2O$	*Ab initio* SCF	Čársky *et al.* (1976)
$Li + H_2O \rightleftharpoons LiOH + H$		
$2NF_2 \rightleftharpoons N_2F_4$	CNDO/2	Slanina *et al.* (1976)
$n\,C(s) \rightleftharpoons C_n;\ n = 4-7$	MINDO/2	Slanina and Zahradník (1977)
$cis\text{-}N_2F_2 \rightleftharpoons trans\text{-}N_2F_2$	CNDO/2	Slanina (1977c)
$CH_3OH + n\,H_2O \rightleftharpoons CH_3OH \cdot n\,H_2O;\ n = 1, 3, 6$	PCILO	Hobza *et al.* (1978)
$2NO \rightleftharpoons (NO)_2$	*Ab initio* SCF	Slanina (1978a)
Equilibria containing AH_2, AH_3, and AH_4 and their cations; A = N, O	*Ab initio* SCF	Kellö *et al.* (1978)
$C_2H_5^+ + H_2 \rightleftharpoons C_2H_7^+$	MINDO/3; *ab initio* SCF and CEPA PNO	Köhler and Lischka (1978)
$2HF \rightleftharpoons (HF)_2$	*Ab initio* SCF	Hobza *et al.* (1979)
$2HCl \rightleftharpoons (HCl)_2$		
Lactam–lactim tautomeric equilibria	MINDO/3	Krebs *et al.* (1980)
$2H_2O \rightleftharpoons (H_2O)_2$	*Ab initio* SCF CI	Slanina (1980)

[a] Gas-phase processes.

TABLE VII

COMPARISON OF QUANTUM-MECHANICAL (QM) AND TRANSITION-STATE-THEORY (TST) ONE-DIMENSIONAL RATE CONSTANTS k (IN cm/sec) FOR THE COLLINEAR REACTION $H + Cl_2 \rightarrow HCl + Cl$

	k		
T (K)	QM	TST-Q[a]	TST
200[b]	2.10×10^2	—	9.74×10^1
300[c]	1.8×10^3	1.89×10^3	1.23×10^3
500[c]	9.0×10^3	8.75×10^3	7.85×10^3
1000[c]	3.3×10^4	3.76×10^4	3.70×10^4

[a] Correction to tunneling according to Wigner (1932) included.
[b] See Essén *et al.* (1976).
[c] See Truhlar *et al.* (1976).

the RRHO quantum-chemical description of stationary points (e.g., Stern and Weston, 1974; Jakubetz, 1979).

So far the most comprehensive quantum-chemical calculation of activation parameters using transition-state theory is the MINDO/3 study of Dewar and Ford (1977). Their results concerning rather large molecules (see Table VIII), even nonrigid ones, are promising, especially as substantial experimental uncertainties have to be considered in some cases. Table IX surveys other selected examples of quantum-chemical calculations of rate constants. Again, the RRHO approximation was used for all the reactions in Tables VIII and IX.

B. General Equilibrium Isomeric Problem

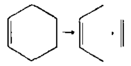
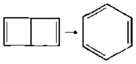
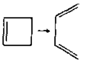
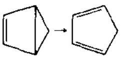
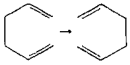
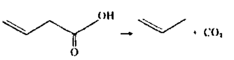
All interesting aspects of consequences on isomerism as far as the evaluation of standard or activation characteristics is concerned can be treated in the following unified manner. A general equilibrium process should be considered:

$$\sum_{k=1}^{n} \nu_k A_k = 0 \qquad (20)$$

between n reaction components A_k with stoichiometric coefficients ν_k in the ideal gas phase. Equilibrium (20) is accompanied by standard enthalpy change ΔH°_T, standard entropy change ΔS°_T, standard Gibbs energy change ΔG°_T, etc. Let us assume that, in addition, there is isomerism of the components, i.e., any component A_k is an equilibrium mixture of j_k isomers $A_k^{(1)}$, $A_k^{(2)}$, . . . , $A_k^{(j_k)}$. Without a loss of generality it is possible

TABLE VIII

COMPARISON OF MINDO/3 AND OBSERVED ACTIVATION ENTROPIES $\Delta S^{\ddagger}_{\mathrm{T}}$ (IN J/K/mol)[a]

		$\Delta S^{\ddagger}_{\mathrm{T}}$	
Rate process[b]	T (K)	MINDO/3	Observed[c]
	600	37.7	33.7
	321	6.2	-20.9 ± 29.3[d]
	423	3.2	0.4 ± 3.8
	350	6.7	17.9 ± 12.4
	523	-71.1	-57.7 ± 4.2
	650	-58.2	-42.7 ± 10.5

[a] See Dewar and Ford (1977).
[b] Gas-phase processes.
[c] For sources of the observed values, see Dewar and Ford (1977).
[d] Measurements in solution.

to suppose the $A_k^{(1)}$ isomer to have the lowest energy. Under conditions of full thermodynamic equilibrium the overall process (20) becomes a superposition of all possible partial equilibria. We shall limit ourselves to the following set of $\prod_{k=1}^{n} j_k$ partial processes:

$$\sum_{k=1}^{n} \nu_k A_k^{(i_k)} = 0 \qquad (i_k = 1, 2, \ldots, j_k). \tag{21}$$

Let the reaction characteristics $\Delta H^\circ_{1,1,\ldots,1}$, $\Delta S^\circ_{1,1,\ldots,1}$, and $\Delta G^\circ_{1,1,\ldots,1}$ accompany process (21) for the choice $i_1 = i_2 = \cdots = i_n = 1$. Moreover, isomerizations within each group of isomers will be considered, i.e., processes

$$A_k^{(1)} = A_k^{(i_k)} \qquad (k = 1, 2, \ldots, n; \quad i_k = 1, 2, \ldots, j_k) \tag{22}$$

TABLE IX

SELECTED EXAMPLES OF QUANTUM-CHEMICAL CALCULATIONS OF RATE CONSTANTS WITHIN THE ACTIVATED-COMPLEX THEORY

Rate process[a]	Generating quantum-chemical method	Reference
$H + H_2 \rightarrow H_2 + H$	*Ab initio* SCF CI	Shavitt (1968)
Cyclohexane inversion	MINDO/2	Komornicki and McIver (1973)
1,3,5-Hexatriene cyclization	MINDO/2	Komornicki and McIver (1974)
Ethyl-cation inversion	CNDO/2	Heidrich and Stromeyer (1976)
cis-$N_2F_2 \rightarrow$ *trans*-N_2F_2	CNDO/2	Slanina (1977c; 1978b)
$A + BC \rightarrow AB + C$	*Ab initio* SCF	Čársky and Zahradník (1979)
$(HF)_2 \rightarrow (HF)_2$ $(HCl)_2 \rightarrow (HCl)_2$	*Ab initio* SCF	Hobza *et al.* (1979)
$H_2CCH_2F \rightarrow H_2CCHF + H$	*Ab initio* SCF	Kato and Morokuma (1980)[b]
$OH + H_2 \rightarrow H_2O + H$	*Ab initio* SCF CI	Schatz and Walch (1980)
$(H_2O)_2 \rightarrow (H_2O)_2$	*Ab initio* SCF CI	Slanina (1981)

[a] Gas-phase processes.

[b] The RRKM theory of unimolecular reactions was used.

described by the standard values $\Delta H^\circ_{1\rightarrow i_k}$, $\Delta S^\circ_{1\rightarrow i_k}$, and $\Delta G^\circ_{1\rightarrow i_k}$, and by the corresponding equilibrium constant of isomerization $K_{1\rightarrow i_k}$. Then the following relationships hold (Slanina, 1975a):

$$\Delta H^\circ_T = \Delta H^\circ_{1,1,\ldots,1} + \sum_{k=1}^{n} \sum_{i_k=1}^{j_k} \nu_k w_{i_k} \Delta H^\circ_{1\rightarrow i_k}, \tag{23}$$

$$\Delta S^\circ_T = \Delta S^\circ_{1,1,\ldots,1} + \sum_{k=1}^{n} \sum_{i_k=1}^{j_k} \nu_k w_{i_k} (\Delta S^\circ_{1\rightarrow i_k} - R \ln w_{i_k}), \tag{24}$$

$$\Delta G^\circ_T = \Delta G^\circ_{1,1,\ldots,1} + \sum_{k=1}^{n} \sum_{i_k=1}^{j_k} \nu_k w_{i_k} (\Delta G^\circ_{1\rightarrow i_k} + RT \ln w_{i_k}), \tag{25}$$

where the weight factors w_{i_k} (independent of the choice of standard state) are given by

$$w_{i_k} = K_{1\rightarrow i_k} \Big/ \sum_{i_k=1}^{j_k} K_{1\rightarrow i_k}. \tag{26}$$

Clearly, the right sides of Eqs. (23)–(25) contain quantities corresponding to the individual isomers, the quantities which are obtainable primarily from the theoretical treatment. The left sides then yield the total effective values of characteristics resulting from the experimental data without considering the reaction component isomerism. Contributions of any energetically less stable isomers to the total value can be considered as corrections to the quantity describing process (21) realized by the energetically most stable isomers. Weighting relations (23)–(26) can mainly be used for comparison of the experimental and theoretical outputs in case of processes, where the isomerism of the reaction components was revealed theoretically or (though known) could not be treated properly (or even eliminated) in the experiment. However, the weighting treatment assumes complying with the conditions of thermodynamic equilibrium, i.e., the existence of equilibrium mixtures of isomers. In any particular case it must be considered whether these conditions were attained in the experiment. This demands an investigation of kinetic processes establishing the total equilibrium, i.e., consideration of the corresponding energy barriers (including the possible catalytic activity). Chemistry prefers to operate with individual well-defined isomers. However in the gas phase at elevated temperatures it may be difficult to assure such specificity. Nevertheless, even in such a case specific generation of isomers (e.g., DePuy *et al.*, 1979) or preferential formation of less stable isomers (e.g., Chang *et al.*, 1979) may occur. We shall concentrate only on cases where realization of full equilibrium conditions is ensured.

For the sake of completeness it should be mentioned that several special cases of the general equilibrium isomeric problem have been considered in the past. However, an effective exploitation of special or even general isomeric schemes is possible only after introduction of quantum-chemical methods as sources of reliable information on individual isomers. Experimental techniques have only rarely been able to replace them and alternative determination of the characteristics of isomers from empirical potential functions or from an assessment could be misleading. Hitherto various cases of isomers linked by hindered internal rotation were treated most frequently (Aston *et al.*, 1946; Beckett *et al.*, 1947; McCullough *et al.*, 1954; Lielmezs and Bondi, 1965; Scott and Crowder, 1967; Heatley, 1972; Frankiss, 1974; Compton, 1977), especially in description of macromolecules (the rotational isomeric state model—see, e.g., Volkenshtein, 1959; Flory, 1969). Consequences of isomerism in the formation of charge-transfer complexes were discussed by Orgel and Mulliken (1957); an analogous problem with microclusters was studied recently by Hoare (1979). Consideration of isomerism in biomolecules (especially of polypeptides) has also been carried out (e.g., Gō and Scheraga, 1969; Lewis *et al.*, 1973; Hagler *et al.*, 1979), in some cases also considering environmental effects (Hopfinger, 1971; E. J. Brändas, L. L. Combs, and L. J. Dunne, unpublished results, 1979).

C. Chemical Equilibria with Isomerism of the Reaction Component

Nowadays nearly every issue of a theoretical journal contains at least one article indicating the existence of several different minima on the energy hypersurface of a system (frequently a very simple one). A comprehensive description of current results alone would require a separate article. Therefore only several representative examples will be mentioned. Studying the singlet hypersurface of the CHNO system (Fig. 3), Poppinger *et al.* (1977) located nine or seven minima, depending on the basis set used. Since the theoretical discovery of cyclic ozone (Wright, 1973), the existence of this isomer was demonstrated at different levels of approximation, including the MC SCF level (Karlström *et al.*, 1978b). Moreover, four energy minima were found on the singlet hypersurface of protonated ozone (Kausch and von Schleyer, 1980). Findings on simple stable enols are of great chemical interest (Bouma *et al.*, 1977; Bouma and Radom, 1978). Theoretical studies of less stable isomers have often been inspired by observations in interstellar space (e.g., Green and Herbst, 1979[1]). The HCN/HNC pair serves as a classical example (e.g., Booth and Murrell, 1972; Ishida *et al.*, 1977; Redmon *et al.*, 1980). New pieces of information on various isomers and relationships between them have continuously been reported at both the semiempirical (e.g., Herndon *et al.*, 1968; Cowley *et al.*, 1969; Favini *et al.*, 1977; Cetina *et al.*, 1978; Zielinski and Rein, 1978; Czermiński *et al.*, 1979; Dougherty and Mislow, 1979; Niemeyer, 1979; Slanina and Grabowski, 1979; Loos and Leška, 1980)[2] and the nonempirical (e.g., Pearson *et al.*, 1974; Talaty *et al.*, 1975; Karlström *et al.*, 1976; Kao, 1977; Niemeyer, 1978; Redmon *et al.*, 1978; Barthelat *et al.*, 1979; Moffat, 1979; Noack, 1979; van den Berg and den Boer, 1979)[2] levels. Rotational isomers are especially easy to study theoretically (e.g., Radom and Pople, 1970; Pople, 1974[1]; Moffat, 1976; Epiotis *et al.*, 1977[1]; Baraldi *et al.*, 1977; Binkley and Pople, 1977; Radom *et al.*, 1978; Olsen, 1979a,b; Olsen and Howell, 1979).[2] Quantum-chemical calculations have become increasingly helpful in solving gas-phase ion chemistry structure problems (e.g., Bowen and Williams, 1977; Dewar and Rzepa, 1977; Dits *et al.*, 1977; Goetz *et al.*, 1977; Hehre, 1977[1]; Bouma *et al.*, 1979; Jefford *et al.*, 1979; Köhler and Lischka, 1979; Wenke and Lenoir, 1979; Lipkowitz *et al.*, 1980).[2] Theoretical studies of this kind yield good examples of ample isomerism (see, e.g., Fig. 8). Electronic excited states stand for another class of isomers frequently described theoretically (e.g., Hehre *et al.*, 1976; Dykstra *et al.*, 1977; Lucchese and Schaefer, 1977; Roos and Siegbahn, 1977; Gustav *et al.*, 1978; Hood and Schaefer, 1978; Kapur *et al.*, 1978; Laidig and Schaefer, 1978; van Lenthe

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[1] Comprehensive review.

[2] Only ten selected examples are given for each kind of computation.

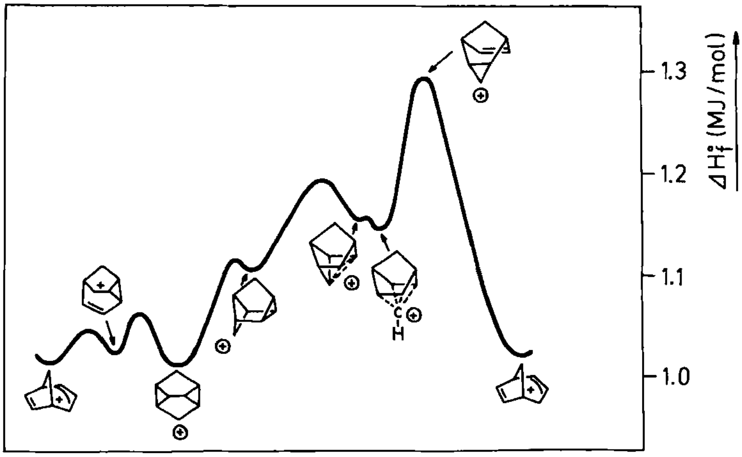


Fig. 8. The connectivity and the magnitude of the barriers (MINDO/3 results—Jefford *et al.*, 1979) between selected C_8H_9 cations. (Reprinted with permission from *J. Am. Chem. Soc.* Copyright © 1979 American Chemical Society.)

and Ruttink, 1978; Wetmore and Schaefer, 1978).[2] In addition to the discovery of gas-phase isomerism, quantum-chemical studies can also predict such phenomena in gas–solid phase interactions, viz., isomerism of the adsorption complex (e.g., Muetterties and Stein, 1979; Slanina *et al.*, 1979) and isomerism of model clusters (e.g., Burton, 1973; Anderson, 1976; Fantucci and Balzarini, 1978; Martin, 1978; Muetterties *et al.*, 1979[1]). Finally, numerous examples of isomerism predicted by molecular mechanics calculations should be mentioned (e.g., Gö and Scheraga, 1973; Lewis *et al.*, 1973; Allinger *et al.*, 1976; Niketić and Rasmussen, 1977[1]; White and Morrow, 1977; Dougherty *et al.*, 1978; Dunfield *et al.*, 1978; Hald and Rasmussen, 1978; White and Morrow, 1979; Jeffrey and Taylor, 1980).[2]

Results of the afore-mentioned studies convincingly indicate (in spite of the fact of having been carried out in most cases only in terms of geometry and potential energy) that at least some reaction components in a chemical equilibrium are commonly mixtures of individual isomeric structures exhibiting comparable stability. In fact, each chemical equilibrium can (at least formally) be treated using the general equilibrium isomeric formulation provided that electronic excited states of each reaction component are taken into account. However, the following special case of process (21), viz.:

$$\sum_{k=1}^{r} \eta_k B_k = C^{(i)} \qquad (i = 1, 2, \ldots, m) \tag{27}$$

is mostly pertinent to the present theoretical study of equilibrium processes. Now several aspects of association equilibrium (27) exhibiting isomerism only in product *C* will be considered.

1. *Interpretation at the Microscopic Level*

For simplicity the standard thermodynamic characteristics of partial processes (27) will be designated ΔH_i°, ΔS_i°, and ΔG_i° (instead of the general designation $\Delta X^\circ_{1,1,\ldots,1,i}$). Then Eqs. (23)--(25) are simplified to

$$\Delta H^\circ_{\mathrm{T}} = \sum_{i=1}^{m} w_i \, \Delta H_i^\circ, \tag{28}$$

$$\Delta S^\circ_{\mathrm{T}} = \sum_{i=1}^{m} w_i(\Delta S_i^\circ - R \ln w_i), \tag{29}$$

$$\Delta G^\circ_{\mathrm{T}} = \sum_{i=1}^{m} w_i(\Delta G_i^\circ + RT \ln w_i). \tag{30}$$

As described in Section V,A,1, any of the partial characteristics ΔX_i° can be obtained in terms of partition functions and ground-state energies [Eq. (4)]. Similarly, weights w_i can be expressed in these molecular terms (Slanina, 1979b):

$$w_i = \frac{q_i \exp[-(e_0^{(i)} - e_0)/kT]}{\sum_{j=1}^{m} q_j \exp[-(e_0^{(j)} - e_0)/kT]}, \tag{31}$$

where q_k is the partition function of the k-th partial product $C^{(k)}$:

$$q_k = \sum_{j} \exp\left\{ - \frac{[e_j^{(k)} - e_0^{(k)}]}{kT} \right\}, \tag{32}$$

where the sum is taken over all the eigenstates of $C^{(k)}$, and the $e_j^{(k)}$ denote their energies; $e_0^{(k)}$ is the ground-state energy of $C^{(k)}$ (the lowest value of the $e_0^{(k)}$ set is designated e_0). The characteristics of individual $C^{(k)}$ structures used for generating the partial ΔX_i° values are all that is needed for evaluating w_i. Only one presumption underlies the weighting treatment, i.e., the postulate of full separability of the motion of individual isomers.

The following inequalities (Slanina, 1979a) may help us in understanding the relationships between the partial and summary characteristics:

$$\Delta H^\circ_{\mathrm{min}} \leq \Delta H^\circ_{\mathrm{T}} \leq \Delta H^\circ_{\mathrm{max}}, \tag{33}$$

$$\Delta S^\circ_{\mathrm{min}} < \Delta S^\circ_{\mathrm{T}} \leq \Delta S^\circ_{\mathrm{max}} + R \ln m \qquad (m > 1). \tag{34}$$

Indices min and max denote the minimum and maximum, respectively, in the set of the partial ΔX_i° values. Relationships (33) and (34) enable useful assessment of the magnitude of the total effective ΔX_T° values regardless

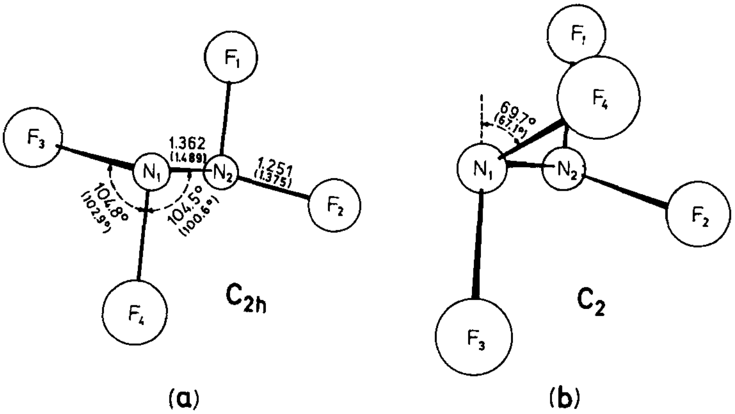


Fig. 9. CNDO/2 structures (Slanina *et al.*, 1976) of *trans*- (a) and *gauche*-N_2F_4 (b) [bond lengths in 10^{-10} m; experimental values of Cardillo and Bauer (1969) in parentheses; for complete structural characteristics see the quoted articles].

of the magnitude of weighting factors w_i. Generally, the summary entropy term can be expected to be influenced more by the phenomenon of reaction component isomerism than the summary enthalpy term.

2. *Examples of Quantum-Chemical Studies*

The CNDO/2 study (Slanina *et al.*, 1976) of difluoroamino radical dimerization

$$2NF_2(g) \rightleftharpoons N_2F_4(g) \tag{35}$$

reproduced the experimental finding (Colburn *et al.*, 1965) that N_2F_4 is a mixture of two rotamers (*gauche* and *trans*—see Fig. 9), the *gauche*-N_2F_4 rotamer also consisting of a pair of d,l-enantiomers. The results of the weighting treatment are demonstrated in Table X and, for a broader tem-

TABLE X

STANDARD ENTHALPY ΔH_T° AND ENTROPY ΔS_T° TERMS FOR THE PARTIAL AND OVERALL DIMERIZATIONS OF NF_2 AT TEMPERATURE $T = 423.15$ K GIVEN BY CNDO/2 CALCULATIONS[a]

Process	ΔH_T° (kJ/mol)[b]	ΔS_T° (J/K/mol)[b]
$2NF_2(g) \rightleftharpoons$ *trans*-$N_2F_4(g)$[c]	−90.08	−183.6
$2NF_2(g) \rightleftharpoons$ *gauche*-$N_2F_4(g)$[c]	−94.65	−179.4
$2NF_2(g) \rightleftharpoons N_2F_4$(g; total)	−94.00	−176.6

[a] See Slanina *et al.* (1976).

[b] Standard state—ideal gas at 101,325 Pa pressure.

[c] See Fig. 9.

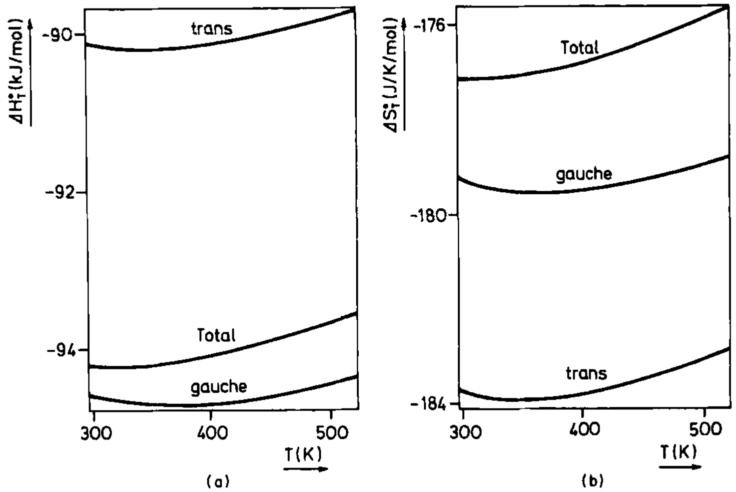


Fig. 10. Temperature dependences of CNDO/2 standard enthalpy ΔH_T° (a) and entropy ΔS_T° (b) terms (Slanina *et al.*, 1976) for the partial and overall (total) dimerizations of NF_2.

perature interval, also in Fig. 10. The ΔH_T° term is predominantly connected with the formation of *gauche*-N_2F_4 (due to the relation between both the partial enthalpy terms). With the ΔS_T° term the effect of the isomerism is stronger; the difference between the summary and any of the partial terms is significant in the whole temperature range studied.

The isomerism of the C_4–C_7 aggregates was properly taken into account in the MINDO/2 evaluation of the standard thermodynamic characteristics of formation of these aggregates (Slanina and Zahradník, 1977). Table XI gives a numerical illustration of equilibria (16)–(19). The difference between the total value and the partial one corresponding to the most stable structure (D_{2h}) at the temperature of the experiment (Drowart *et al.*, 1959) is by no means negligible with both the enthalpy and entropy terms. The total entropy term coincides circumstantially with that of D_2 isomer formation; this demonstrates the qualitative variety of weighting-treatment results. It is also evident (and will further be documented in detail) that mere approximation of the characteristics of the overall process using those of the most stable structure (as is common in contemporary quantum-chemical practice) may be quite misleading.

3. *Inverse Problem*

The weighting treatment can be used not only for the determination of total characteristics from partial results but also vice versa. This modification has been suggested (Slanina, 1975a) as a generalization of the third

TABLE XI

PARTIAL AND TOTAL MINDO/2 STANDARD ENTHALPY ΔH_T° AND ENTROPY ΔS_T° TERMS OF $4C(s) \rightleftharpoons C_4(g)$ EQUILIBRIUM AT $T = 2400$ K[a]

Process	ΔH_T° (kJ/mol)[b]	ΔS_T° (J/K/mol)[b]
$4C(s) \rightleftharpoons C_4(g; D_{2h})$[c]	904.1	210.2
$4C(s) \rightleftharpoons C_4(g; D_2)$[c]	952.2	213.6
$4C(s) \rightleftharpoons C_4(g; T_d)$[c]	1301.5	205.5
$4C(s) \rightleftharpoons C_4(g; \text{total})$	909.9	213.6

[a] See Slanina and Zahradník (1977).
[b] Standard state—ideal gas at 101,325 Pa pressure.
[c] See Fig. 2.

law analysis. In particular, standard enthalpy changes $\Delta H_{i,0}^\circ$ of processes (27) at absolute zero are determined from the experimental temperature dependence of the corresponding summary equilibrium constant K of the total process (27) by optimizing the expression

$$\Delta = \sum_T \left[K - \sum_{i=1}^{m} \exp\left(\frac{\Delta\Phi_i^\circ}{R} - \frac{\Delta H_{i,0}^\circ}{RT} \right) \right]^2, \tag{36}$$

i.e., by solving the equations

$$\partial\Delta / \partial \Delta H_{i,0}^\circ = 0 \qquad (i = 1, 2, \ldots, m). \tag{37}$$

In Eq. (36) $\Delta\Phi_i^\circ$ denote the changes in the standard thermodynamic potential associated with partial processes (27) and the summation runs over temperatures at which K was measured. Terms $\Delta\Phi_i^\circ$ are fully described by partition functions that may be constructed on the basis of molecular constants originating from spectral measurements or from quantum-chemical calculations. Application of the inverse problem in conjunction with those quantum-chemical methods that fail to provide a satisfactory account of energies but give molecular constants accurate enough for calculation of the entropy (Slanina, 1977d) is especially useful. The inverse scheme based on experimental molecular constants was also employed (Slanina, 1975b) in determining the energetics of the partial processes (35).

D. Rate Processes with Isomerism of the Activated Complex

The phenomenon of isomerism should not be considered only for equilibrium processes. The original concept of the activated-complex theory assumes that the transformation of reactants into products passes

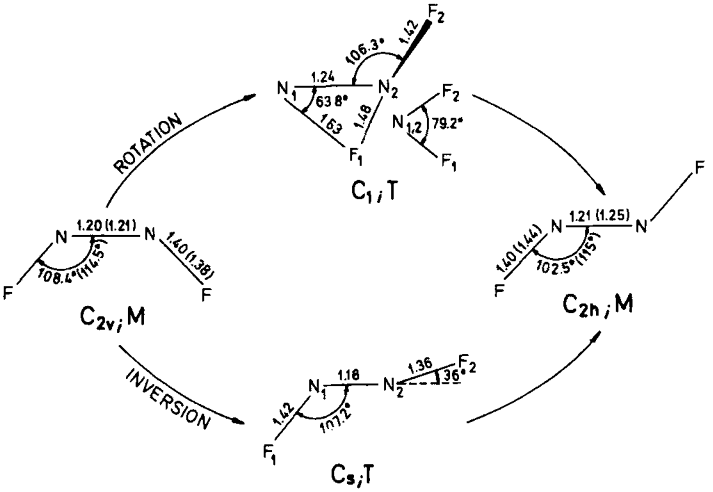


Fig. 11. Structure of four stationary points found (Slanina, 1977c) on the CNDO/2 potential energy hypersurface of N_2F_2; M is a minimum, T a transition state [bond lengths in 10^{-10} m; experimental values taken from Stull and Prophet (1971) in parentheses].

through a single activated complex. However, several quantum-chemical studies have recently indicated the existence of more than one saddle point meeting the requirements for an activated complex of the given rate process. A common example is *cis–trans* interconversion around the —N═N— bond, which is realized by both the inversion and the rotation mechanisms (Fig. 11). The corresponding activated complexes are different in structure but have similar activation barriers (e.g., Gordon and Fischer, 1968; Howell and Kirschenbaum, 1976; Favini and Todeschini, 1978). The activated-complex isomerism has also been indicated in other theoretical studies of both unimolecular (Valko and Kovařík, 1976; Seeger *et al.*, 1977; Cimiraglia *et al.*, 1978; Penkovsky, 1978; Peterson and Csizmadia, 1979) and bimolecular (Schleker and Fleischhauer, 1979) reactions. The concept of activated-complex isomerism thus supposes two or more different activated complexes existing between one common set of reactants and one common set of products. It should be noted that this concept does not necessarily overlap with the Curtin–Hammett principle (e.g., Hammett, 1976). The latter is concerned with processes leading to different sets of products. Let us mention finally that it would be possible to introduce a more general concept of activated-complex isomerism also covering the quantum-chemical description of various multistep reactions (Figuera *et al.*, 1976; Dewar *et al.*, 1977).

Whereas theoretical calculation simply allows separate evaluation of partial rate constants that describe the transitions through individual activated complexes (the partial characteristics are primary theoretical outputs), in an experiment such exact differentiation is hardly possible. Generally it must be expected that, in cases where isomerism of activated complex has been detected theoretically, an experiment will produce only the total value of the rate constant. Correct confrontation of theoretical and experimental values again requires (as in equilibrium processes) carrying out an appropriate weighting of the contributions of particular activated complexes. In fact, the equilibrium hypothesis on which the activated-complex theory is based (i.e., the thermodynamical basis of this theory) enables straightforward application of the formalism of the general equilibrium isomeric problem. One can ask whether a passing of different activated complexes from one to the other through a higher type of stationary point would interfere in this scheme. However, such a transition lies beyond the original framework of the activated-complex theory as the latter postulates only one direction for the activated complexes (transition from reactants to products). Nevertheless, let us admit the existence of interconversions of different activated complexes (in spite of their possibly negligible probabilities in comparison with the probabilities of the ordinary process), it then follows from the equilibrium hypothesis that the activated complexes should be in equilibrium, not only with the reactants, but also mutually. Consequently, the flux of the activated complexes in both directions of the interconversion process (i.e., the flux of activated complexes from reactants not to products but into the region of the other activated complex) is equal.

The weighting for the rate process displaying isomerism of the activated complex can be summarized as follows (Slanina, 1977a). A rate process should be considered that is accomplished by $n^{\ddagger}$ different pathways from reactants to products, each of them going through a single activated complex $Y_i^{\ddagger}$ ($i = 1, 2, \ldots, n^{\ddagger}$), the i-th partial activation process being described by the partial activation enthalpy and entropy $\Delta H_i^{\ddagger}$ and $\Delta S_i^{\ddagger}$, respectively. Due consideration of activation-process thermodynamics leads to the following relationships between the total rate characteristics $\Delta H_T^{\ddagger}$ and $\Delta S_T^{\ddagger}$ (obtained in the experiment) and the partial ones:

$$\Delta H_T^{\ddagger} = \sum_{i=1}^{n^{\ddagger}} w_i^{\ddagger} \, \Delta H_i^{\ddagger} \tag{38}$$

$$\Delta S_T^{\ddagger} = \sum_{i=1}^{n^{\ddagger}} w_i^{\ddagger}(\Delta S_i^{\ddagger} - R \ln w_i^{\ddagger}), \tag{39}$$

where the weighting factors $w_i^{\ddagger}$ can be expressed in a similar way as in equilibria [Eq. (31)]. Equations (38) and (39) were also converted into the

TABLE XII

PARTIAL AND TOTAL CNDO/2 ACTIVATION ENTHALPY $\Delta H_T^\ddagger$ AND ENTROPY $\Delta S_T^\ddagger$ OF ISOMERIZATION *cis*-$N_2F_2(g) \rightarrow$ *trans*-$N_2F_2(g)$ AT $T = 2000$ K[a]

Rate process	$\Delta H_T^\ddagger$ (kJ/mol)	$\Delta S_T^\ddagger$ (J/K/mol)
Through the activated complex of C_s symmetry[b]	309.0	−5.81
Through the activated complex of C_1 symmetry[b]	272.5	−13.82
Overall process	280.7	−7.56

[a] See Slanina (1978b).
[b] See Fig. 11.

forms with the Arrhenius frequency factor and the activation energy on the left side (Slanina, 1977a).

This weighting scheme has so far been applied to the theoretical description of three rate processes exhibiting activated-complex isomerism (Slanina, 1977a, 1978b, 1981). The first illustrative example concerns the rate process:

$$cis\text{-}N_2F_2(g) \rightarrow trans\text{-}N_2F_2(g). \tag{40}$$

This process was fully described within the activated-complex theory using the CNDO/2 method (Slanina, 1977a,c). The consequences of activated-complex isomerism (Fig. 11) can be seen in Table XII and for a broad temperature interval in Fig. 12. It is evident that consideration of both activated-complex structures is essential at higher temperatures.

With process (40) the influence of isomerism on evaluation of the tunnel effect was also studied. The overall tunnel-effect correction Γ and the partial corrections Γ_i are related simply by (Slanina, 1978b):

$$\Gamma = \sum_{i=1}^{n^\ddagger} w_i^\ddagger \Gamma_i. \tag{41}$$

In spite of tunnel-effect insignificance for process (40) itself, an interesting feature was found for summary correction Γ (Fig. 13). This function exhibits an unusual increase in the studied temperature interval.

The second example is the chair-boat isomerization of cyclohexane:

$$C_6H_{12}(g;\ D_{3d}) \rightarrow C_6H_{12}(g;\ D_2) \tag{42}$$

which according to the MINDO/2 study of Komornicki and McIver (1973) proceeds via an activated complex of C_s or of C_2 symmetry. Table XIII illuminates the corresponding weighting conditions. The $\Delta H_i^\ddagger$ terms are similar, the existence of the isomerism is pronounced only for the entropy.

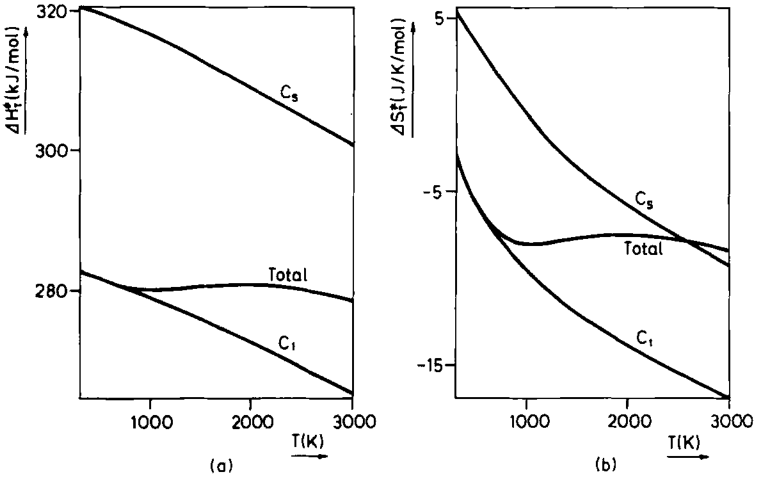


Fig. 12. Temperature dependences of CNDO/2 (Slanina, 1978b) activation enthalpy $\Delta H^\ddagger_T$ (a) and entropy $\Delta S^\ddagger_T$ (b) of the *cis–trans* isomerization of $N_2F_2(g)$ for C_s and C_1 activated complexes and for the overall activation process (total).

E. Isomerism of Multimolecular Clusters

Recently, a considerable amount of work has been done using the cluster concept (Frank and Wen, 1957; Némethy and Scheraga, 1962a,b; Hagler *et al.*, 1972; Lentz *et al.*, 1974; Hoare, 1979) for the description of real gases and of the liquid state by quantum-chemical methods as a source of information on clusters (for a review, see Clementi, 1976b;

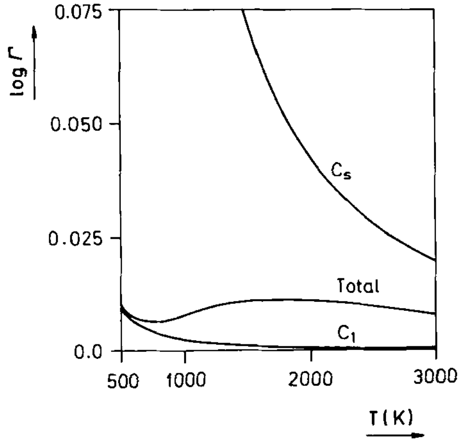


Fig. 13. Temperature dependences of tunnel-effect corrections Γ for the C_s and C_1 activated complexes and for the overall activation process (total) in *cis–trans* isomerization of $N_2F_2(g)$ based on CNDO/2 calculations (Slanina, 1978b).

TABLE XIII

PARTIAL AND TOTAL MINDO/2 ACTIVATION ENTHALPY $\Delta H^{\ddagger}_{T}$ AND ENTROPY $\Delta S^{\ddagger}_{T}$ OF CYCLOHEXANE ISOMERIZATION $C_6H_{12}(g; D_{3d}) \rightarrow C_6H_{12}(g; D_2)$ AT $T = 298$ K

Rate process	$\Delta H^{\ddagger}_{T}$ (kJ/mol)	$\Delta S^{\ddagger}_{T}$ (J/K/mol)
Through the activated complex of C_s symmetry[a]	26.36	25.02
Through the activated complex of C_2 symmetry[a]	26.78	28.62
Overall process[b]	26.60	32.75

[a] See Komornicki and McIver (1973).
[b] See Slanina (1977a).

Hobza and Zahradník, 1980). This field of vigorous quantum-chemical activity is of special interest also for the concept of reaction component isomerism. Five facts contribute to the significance of this isomerism: (*i*) numerous cases of isomerism of multimolecular clusters are frequently discovered theoretically, (*ii*) comparable stability of individual isomers is to be expected in rather broad temperature ranges for at least some of the structures, (*iii*) interchange in the stability order of individual isomers may occur at different temperatures, (*iv*) easy establishing of full interisomeric thermodynamic equilibrium is expectable and, finally, (*v*) at present, experiments can generally yield only the total effective values of the cluster characteristics. Figure 14 illustrates items (*i*)–(*iii*) using the weights within the $(H_2)_2$ system. This cluster system is assumed to be a mixture of four structures (Kochanski *et al.*, 1973; Jaszuński *et al.*, 1977), each with a different symmetry. Other dimer clusters with isomerism are $(NO)_2$ (Skaarup *et al.*, 1976), $(Cl_2)_2$ (Prissette and Kochanski, 1978), $(CO_2)_2$ (Brigot *et al.*, 1977), $(H_2CO)_2$ and $(CH_3COCH_3)_2$ (Frurip *et al.*, 1978), and $(CF_3CH_2OH)_2$ (Curtiss, 1977a). Heteromolecular clusters also exhibit the isomerism discovered theoretically (Slanina, 1974; Jönsson *et al.*, 1975; Prissette *et al.*, 1978). Isomerism of clusters consisting of more members should be considerably greater as is indicated by studies of water- (Kistenmacher *et al.*, 1974; Clementi, 1976b) and of methanol-oligomers (Curtiss, 1977b). For instance, according to Owicki *et al.* (1975) the water tetramer occurs in at least the three different forms depicted in Fig. 15. Moreover, two water pentamers found (Fig. 16) are supposed to represent only a minority of the $(H_2O)_5$ energy minima. The study of clusters based on empirical potentials (e.g., Hoare and Pal, 1971a,b, 1972; Kaelberer *et al.*, 1976) is sometimes considered to lie on the periphery of quantum-

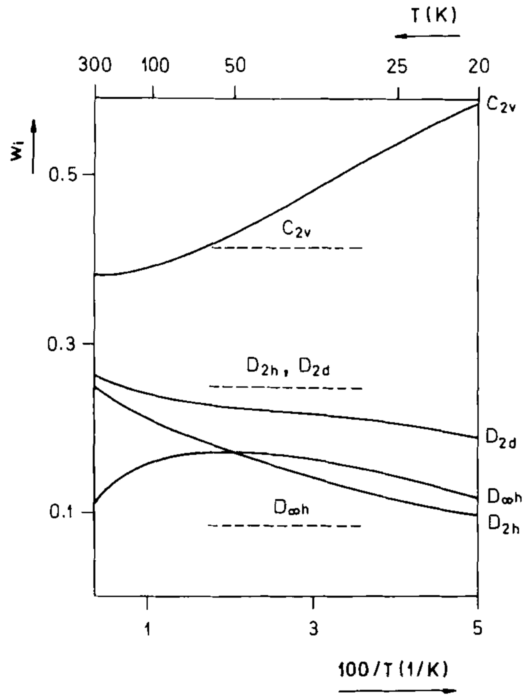


Fig. 14. Temperature dependences (Slanina, 1979a) of weights w_i of $(H_2)_2$ with D_{2h}, $D_{\infty h}$, C_{2v}, and D_{2d} symmetries; approximate temperature-independent weights from Evett and Margenau (1953) are also indicated (dashed lines).

chemical investigations; however, it has supplied us with very good instructive examples of cluster isomerism. For example, 13 particles governed by the Lennard-Jones or Morse potentials form 988 or 36 distinct energy minima, respectively (Hoare, 1979).

As in ordinary chemical equilibria, the RRHO description represents the upper limit of computational studies of multimolecular clusters. The only exception is the study of two-atom clusters (e.g., He_2—Poulat *et al.*, 1975). The results for the highly anharmonic molecule Xe_2 have shown, however, that the partition function based on the harmonic-oscillator model and that obtained for the anharmonic oscillator are of the same order of magnitude (Shin, 1977; le Roy, 1979). However, even harmonic force fields of molecular clusters are obtained very rarely (mostly only for the intermolecular degrees of freedom); consequently, reliable differentiation of local minima and other kinds of stationary points on a cluster hypersurface cannot, as a rule, be carried out. When the force constant matrix is not known, vibrational partition function q_v must be neglected,

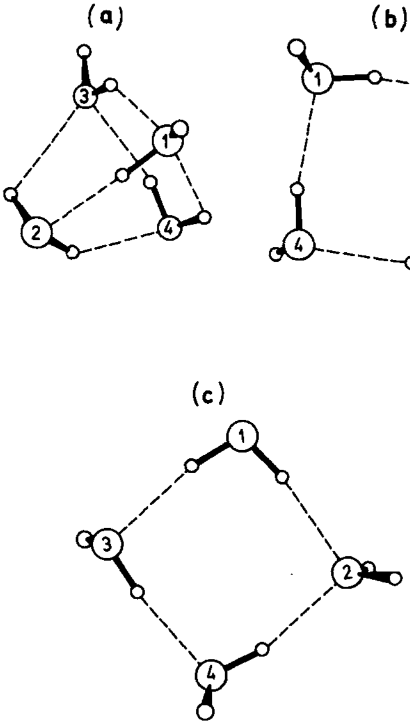


Fig. 15. Minimum-energy water tetramers (according to Owicki *et al.*, 1975): (a) pyramid, (b) S_4 cyclic, (c) asymmetric cyclic. (Reprinted with permission from *J. Phys. Chem.* Copyright © 1975 American Chemical Society.)

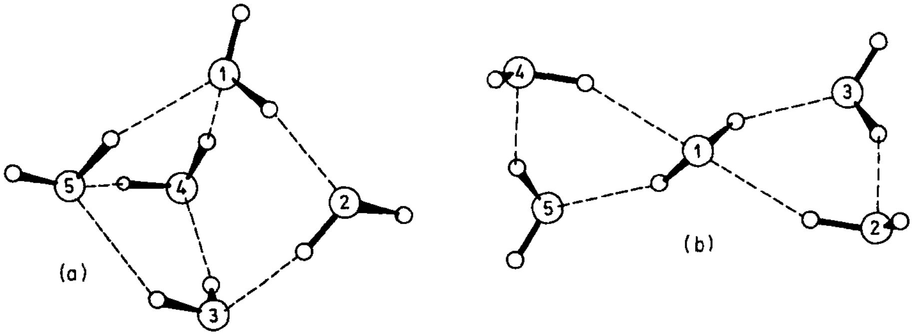


Fig. 16. Minimum-energy water pentamers (according to Owicki *et al.*, 1975): (a) cage, (b) C_2. (Reprinted with permission from *J. Phys. Chem.* Copyright © 1975 American Chemical Society.)

TABLE XIV

TEMPERATURE DEPENDENCE[a] OF THE WEIGHT w_{trans} OF *trans*-$(NO)_2$ IN AN EQUILIBRIUM MIXTURE WITH *cis*-$(NO)_2$ FOR VARIOUS APPROXIMATIONS[b] OF VIBRATIONAL MOTION

T (K)	w_{trans}		
	"Exact"	$q_v = 1$	$q_v = 1;\ \Delta_0 = 0$
20	0.89	0.89	0.0004
50	0.69	0.68	0.04
100	0.61	0.58	0.16
200	0.60	0.52	0.29
500	0.63	0.49	0.39

[a] See Slanina (1979b).

[b] "Exact" means values obtained using vibrational partition function q_v and quantum correction Δ_0 for the zero-point motion, both in the harmonic-oscillator approach.

i.e., set equal to 1. Nevertheless, this approximation need not always have drastic consequences for evaluation of weights w_i for the following reasons: (*i*) the form of Eq. (31) permits significant canceling out in the numerator and denominator and (*ii*) the temperatures important for the existence of clusters are often so low that it is reasonable to expect q_v itself to be close to 1. However, if vibrational frequencies for construction of q_v are not available, the quantum correction due to the zero-point motion Δ_0 should also be neglected [Eq. (4)]. As can be seen from Table XIV the latter approximation may lead to serious deviations, especially in low temperature region (Slanina, 1979b).

It is reasonable to suppose that w_i behavior for larger clusters will be quite varied. This is supported by the figures in Table XV concerning the

TABLE XV

TEMPERATURE DEPENDENCES[a] OF WEIGHTS w_P, w_{S_4}, AND w_A OF PYRAMID[b] (P), S_4 CYCLIC[b] (S_4) AND ASYMMETRIC CYCLIC[b] (A) WATER TETRAMERS

T (K)	w_P	w_{S_4}	w_A
100	0.997	0.003	1×10^{-8}
400	0.62	0.30	0.08
700	0.33	0.27	0.40

[a] See Slanina (1979a).

[b] See Fig. 15.

water tetramers (Fig. 15). Whereas at the beginning of this temperature range the weight of the asymmetric cyclic tetramer is least important, at the end of the range it becomes the highest of all the three weight values (Owicki *et al.*, 1975; Slanina, 1979a). Let us note finally that approximate approaches to w_i evaluation based on geometrical considerations have also been suggested (Evett and Margenau, 1953; Gallup, 1977a,b). It is evident from Fig. 14 that these temperature-independent weights are rather approximate.

If weights w_i and the values of the partial characteristics are available, the weighting treatment leading to the total effective values of these characteristics can be carried out. Comparisons of the most-stable-structure values and overall thermodynamic functions show that marked differences may occur that increase with increasing temperature (Slanina, 1978a, 1979a,b; Hoare, 1979). Crucial factors determining these differences are as follows: the potential-energy gap between the ground-state and higher isomers, quantum corrections Δ_0, the individual components of partition functions, and the partial values of the characteristics themselves. For example, interplay between these factors for water tetramers leads to considerable changes in both the overall enthalpy and entropy terms compared with those for the most stable isomer (Owicki *et al.*, 1975; Slanina, 1979a) beginning at temperatures below the normal boiling point of water (Table XVI). To obtain comparable effects for the thermodynamic characteristics of water pentamers the temperature has to be increased further (Table XVII). The announced results of Hoare and McInnes (Hoare, 1979) on the Lennard-Jones minimal sets of up to 13 particles should provide even more pronounced manifestation of

TABLE XVI

STANDARD ENTHALPY ΔH°_T AND ENTROPY ΔS°_T TERMS FOR THE PARTIAL[a] AND OVERALL[b] WATER TETRAMERIZATION AT $T = 400$ K

Process	ΔH°_T (kJ/mol)[c]	ΔS°_T (J/K/mol)[c]
$4H_2O(g) \rightleftharpoons (H_2O)_4(g;\ P)$[d]	−77.36	−335.1
$4H_2O(g) \rightleftharpoons (H_2O)_4(g;\ S_4)$[d]	−73.01	−330.1
$4H_2O(g) \rightleftharpoons (H_2O)_4(g;\ A)$[d]	−59.79	−308.4
$4H_2O(g) \rightleftharpoons (H_2O)_4(g;\ \text{total})$	−74.69	−324.4

[a] See Owicki *et al.* (1975).

[b] See Slanina (1979a).

[c] Standard state—ideal gas at 101,325 Pa.

[d] P—pyramid, S_4—S_4 cyclic, A—asymmetric cyclic tetramer; see Fig. 15.

TABLE XVII

STANDARD ENTHALPY ΔH°_T AND ENTROPY ΔS°_T TERMS FOR THE PARTIAL[a] AND OVERALL[b] WATER PENTAMERIZATION AT $T = 700$ K

Process	ΔH°_T (kJ/mol)[c]	ΔS°_T (J/K/mol)[c]
$5H_2O(g) \rightleftharpoons (H_2O)_5(g;\ C)$[d]	−94.73	−436.0
$5H_2O(g) \rightleftharpoons (H_2O)_5(g;\ C_2)$[d]	−70.29	−402.9
$5H_2O(g) \rightleftharpoons (H_2O)_5(g;\ \text{total})$	−83.99	−415.8

[a] See Owicki *et al.* (1975).

[b] See Slanina (1979b).

[c] Standard state—ideal gas at 101,325 Pa.

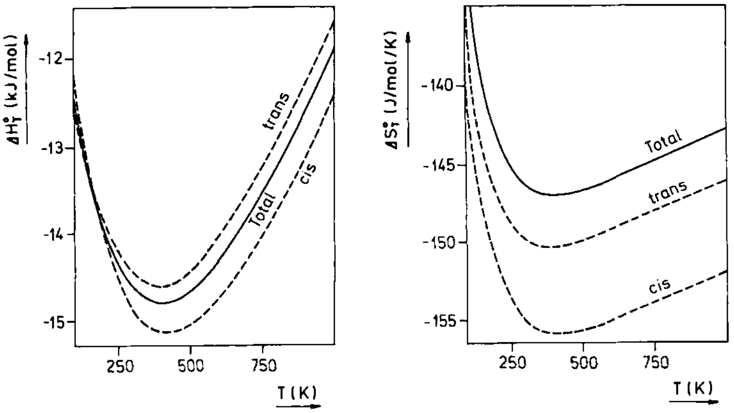
[d] C and C_2 means the cage and C_2 pentamer, respectively—see Fig. 16.

multiple-configuration thermodynamic consequences. The common belief that the ground-state isomer alone can sufficiently represent the isomeric-cluster set is thrown into serious doubt by these results. The concept of the most stable structure itself becomes rather indefinite as the most stable structure determination may differ depending on whether the potential energy scale, the $\Delta H^\circ_{i,0}$ scale [Eq. (36)], or the w_i scale (i.e., the Gibbs energy scale) is used, the latter moreover being temperature dependent (Slanina, 1978a).

The inverse problem may be considered potentially advantageous in refining quantum-chemical information on isomeric clusters. The energetics of the dimerization equilibrium

$$2NO(g) \rightleftharpoons (NO)_2(g) \tag{43}$$

is an example (Slanina, 1977d). According to the *ab initio* SCF study of Skaarup *et al.* (1976) $(NO)_2$ is formed by two structures, viz., the *cis* and *trans* species. The fact that the correlation effects were not considered in this study should not influence the quality of the molecular geometries and force fields found. However, the degree of the energy information uncertainty precludes establishing which of the two forms is energetically more stable. Combining the *ab initio* SCF molecular parameters of both isomers of $(NO)_2$ with the experimental temperature dependence (Billingsley and Callear, 1971) of the equilibrium constant of the overall process (43) within the framework of the inverse problem enabled complete thermodynamic description of the partial and overall equilibria (43). Figure 17 gives the temperature dependences of the corresponding ΔH°_T and ΔS°_T terms (Slanina, 1978a). Again, simulation of the thermodynamic functions of the overall process (43) by those belonging to either of the partial



(a) (b)

Fig. 17. Temperature dependences of refined *ab initio* SCF standard enthalpy ΔH°_T (a) and entropy ΔS°_T (b) terms (Slanina, 1978a) for the partial and overall (total) dimerizations of NO.

equilibria might be quite misleading (in terms of potential energy the *cis* isomer is more stable).

Virial coefficients B_n are an important source of information on real gas-phase nonideality. The overall B_n terms can be decomposed into three components, one of which is determined by the formation of two- to n-particle clusters. Interpretation of the latter contribution to B_n in terms of the equilibrium constants for the formation of individual isomers of two- to n-molecule clusters has been given (Slanina, 1977b). In fact, the comparable role of individual isomeric clusters in evaluation of B_2 of nitric oxide seen from illustrative Table XVIII is a straightforward consequence of the closeness of their weights w_i.

TABLE XVIII

CONTRIBUTIONS[a] OF THE FORMATION OF $(NO)_2$ CLUSTERS TO THE SECOND VIRIAL COEFFICIENT B_2 (IN cm^3/mol) OF NITRIC OXIDE AT T = 121.72 K[b]

	B_2		
Source	*trans*-$(NO)_2$	*cis*-$(NO)_2$	total-$(NO)_2$
Refined *ab initio* SCF	−131.1	−87.8	−218.9
Observed[c]	—	—	−224.4

[a] Slanina (1978a).

[b] The normal boiling point of nitric oxide is[c] 121.36 K.

[c] For references, see Slanina (1978a).

In addition to the real gas phase, multimolecular clusters also represent a model that seems to correspond most adequately to the present state of computational quantum chemistry for the purposes of liquid-state studies. The concept of cluster isomerism was modified within the cavity approach (Eley, 1939) for the dissolution of a gas in a liquid (cavity isomerism) and used for the PCILO study (Hobza *et al.*, 1978) of the hydration process:

$$CH_3OH(g) \rightleftharpoons CH_3OH(H_2O(l)). \qquad (44)$$

The cavities were modeled by the water shells of the $CH_3OH \cdot nH_2O$ clusters ($n = 1, 3, 6$) and their variety was properly considered in evaluation of hydration quantities (Table XIX). In spite of the rather small role of isomerism in this special case, cavity isomerism may generally be significant.

The water dimer represents perhaps the most thoroughly theoretically studied molecular complex. In studying $(H_2O)_2$ a number of possible structures have been considered. Whereas the determination of the trans near-linear dimer as most stable can be taken for granted, there is confusion in the literature concerning the existence of the less stable isomers. Quite recently, a comprehensive search for stationary points on the *ab initio* SCF CI potential energy hypersurfaces (Matsuoka *et al.*, 1976) was carried out (Slanina, 1980). Of the six stationary points found (Fig. 18) only one was identified as a minimum. This negation of water-dimer isomerism (with respect to equilibrium problems) was supported by evaluation of the standard entropy. At the same time, the study disclosed activated-complex isomerism (see Fig. 18b–d) in the interconversion (Slanina, 1981):

$$(H_2O)_2(g) \rightarrow (H_2O)_2(g). \qquad (45)$$

TABLE XIX

PARTIAL AND TOTAL PCILO STANDARD HYDRATION ENTHALPY $\Delta H^\circ_{h,T}$ AND ENTROPY $\Delta S^\circ_{h,T}$ AT $T = 298.15$ K[a]

Model process[b]	$\Delta H^\circ_{h,T}$ (kJ/mol)[c]	$\Delta S^\circ_{h,T}$ (J/K/mol)[c]
$n = 1$	2.93	−118.0
$n = 3$	−29.97	−118.0
$n = 6$	−41.87	−118.0
Total	−41.78	−117.6

[a] See Hobza *et al.* (1978).

[b] The cavity was modeled by the water shell in the cluster $CH_3OH \cdot n\,H_2O$.

[c] Gas standard state—ideal gas at 101,325 Pa; solution standard state—solution at unit mole fraction.

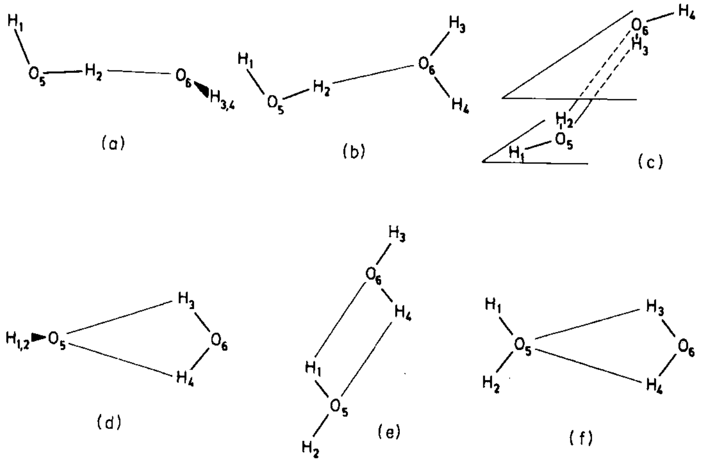


Fig. 18. Schemes of the stationary points found (Slanina, 1980) on *ab initio* SCF CI hypersurfaces (Matsuoka *et al.*, 1976) of $(H_2O)_2$; M is a minimum, T a transition state, H a higher type of stationary point: (a) C_s, M; (b) C_s, T; (c) S_2, T; (d) C_{2v}, T; (e) C_{2h}, H; (f) C_{2v}, H.

The temperature dependence of the weights $w_i^\ddagger$ of three different activated complexes involved in the process (45) shows features typical for isomeric clusters: in the low temperature region one structure is completely predominant while at higher temperatures all the three isomers considered become equally significant, this being connected with a change in the order of magnitude of two weights (Table XX). The behavior of partial and

TABLE XX

TEMPERATURE DEPENDENCES[a] OF WEIGHTS $w_i^\ddagger$ OF THE ACTIVATED COMPLEXES[b] IN WATER DIMER INTERCONVERSION

	$w_i^\ddagger$		
T (K)	C_s	S_2	C_{2v}
200	0.93	0.06	0.01
500	0.66	0.19	0.15
800	0.53	0.22	0.25

[a] Based on *ab initio* SCF calculations including the intermolecular correlation contribution (Matsuoka *et al.*, 1976).

[b] See Fig. 18b–d.

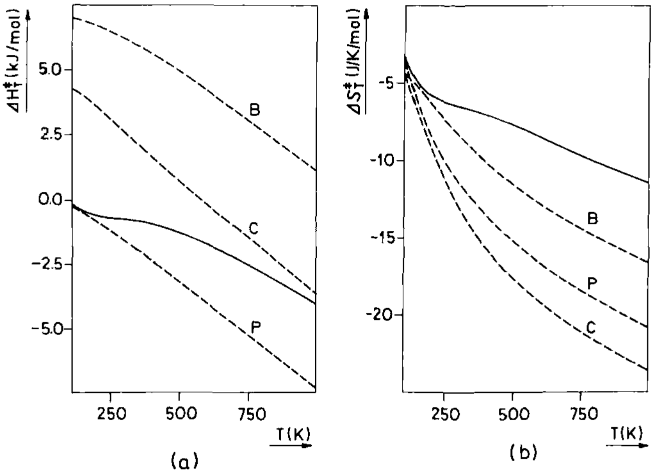


Fig. 19. Temperature dependences of activation enthalpy $\Delta H^{\ddagger}_{T}$ (a) and entropy $\Delta S^{\ddagger}_{T}$ (b) of water-dimer interconversion for C_s planar-linear (P), S_2 closed (C), and C_{2v} bifurcated (B) activated complexes and for the overall activation process (solid line).

total activation parameters describing rate process (45) also confirms the marked differences between the total characteristics and those of the most stable (or any other) activated complex (Fig. 19) at elevated temperatures. It is also apparent that the presence of hydrogen atoms and of low barriers for interconversion favors the possibility of quantum-mechanical tunneling at low temperatures. In contrast to rate process (40) the summary tunnel-effect correction for the overall rate process (45) does not exhibit a paradoxical increase (Fig. 13) but instead decreases smoothly with increasing temperature (Fig. 20).

For the sake of completeness, the relationship of this approach to the Monte Carlo simulations can be mentioned (for a review, see, e.g., Lal, 1971; Wood and Erpenbeck, 1976); the latter technique has rarely been employed in connection with quantum-chemical interaction potentials (because of tediousness of their generation) (Abraham, 1974; Clementi, 1976b; Lie *et al.*, 1976; Mruzik, 1977; Owicki and Scheraga, 1977; Jorgensen, 1979). In fact, the use of an artificial potential having the form of isolated minima separated by infinitely high barriers would practically reduce the Monte Carlo method to our weighting treatment. However, in contrast to the usual Monte Carlo calculations, the above approach takes into account rotational–vibrational motions. From this point of view weights (31) could be considered more sophisticated than the Monte Carlo values. Thus both approaches should be considered in parallel rather than hierarchically.

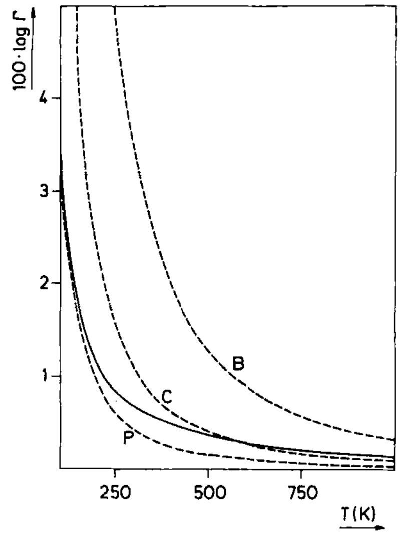


Fig. 20. Temperature dependences of tunnel-effect corrections Γ for the P, C, and B (see description of Fig. 19) activated complexes and for the overall activation process (solid line) in water-dimer interconversion.

VI. Concluding Remarks

In this article we have attempted to show how the phenomenon of chemical isomerism as a general feature of chemical systems (i.e., a fact already established by experiment) can be further emphasized and elaborated by various relevant theoretical means, especially with systems hardly amenable to detailed observations. It has been indicated that further theoretical progress would be desirable in the development of several topics. Within the Born–Oppenheimer approach, the development of mathematical means ensuring complete location of stationary points on the hypersurface, improvement of the quality of descriptions of rotational–vibrational motions (both individual within an isolated isomer and collective interconnecting single structures) and subsequently innovation of partition functions and, finally, replacement of potential energy hypersurfaces by Gibbs energy ones, seem to be especially important problems. Solution of all these tasks would also contribute to the construction of a generalized theory of chemical reactivity within which any component of a chemical process could display isomerism, for (as we have tried to show) the simulation of multiple-isomer characteristics by those of (any single) individual structure should no longer be generally considered

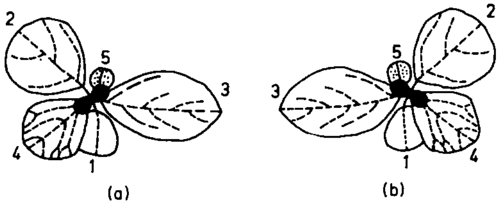


Fig. 21. An example of biological isomerism—enantiomorphism of tobacco; the numbers indicate the order of leaf budding (according to Kasinov, 1973).

acceptable. The rigorous quantum-mechanical description of isomerism should be extended so that it could cover not only chemical but also atomic (see, e.g., Polikanov, 1977) and perhaps even biological (see, e.g., Kasinov, 1973, and Fig. 21) isomerism in a unified concept. Then, the idea of the Greek atomists that is nearly 25 centuries old would become well-founded at a microscopic level.

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Note Added in Proof

During the preparation of this article, several interesting papers appeared which have a close relation to problems discussed here. The present state of molecular structure calculations has been evaluated (P.-O. Löwdin, *Advan. Quantum Chem.* **12,** 263, 1980) and importance of the density matrix approach emphasized. The latter technique has been applied to the study of relaxation of optical isomers (R. A. Harris, and L. Stodolsky, *J. Chem. Phys.* **74,** 2145, 1981). R. S. Berry has surveyed general phenomenology of nonrigid clusters [*in* "Quantum Dynamics of Molecules" (R. G. Woolley, ed.), p. 143. Plenum, New York, 1980]. Redfield's (1927) enumeration theory has been shown to incorporate some of the recent developments in molecular combinatorics (R. A. Davidson, *J. Am. Chem. Soc.* **103,** 312, 1981).

Further examples illustrating multiconfiguration thermodynamics have been given by the author (*Chem. Phys. Lett.*, in press), including applications to molecular catalysis (*Zh. Fiz. Khim.*, in press; *Chem. Phys. Lett.*, in press).

Review of the Linear Independence Properties of Infinite Sets of Functions Used in Quantum Chemistry

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I. Introduction

In order to construct a sequence of approximate wave functions Ψ_N for an explicitly unknown eigenstate Ψ of a given Hamiltonian, one may

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choose an *infinite* set of basis functions $\{\phi_n\}_{n=1}^{\infty}$, write Ψ_N as a linear combination of the first N functions:

$$\Psi_N = \sum_{n=1}^{N} c_n^N \phi_n, \tag{1}$$

and determine the expansion coefficients c_n^N by an adequate variational calculation. However, as is well known, the c_n^N depend on the number of basis functions N itself, as indicated by the superscript, and must therefore be recalculated all over again if N is increased. Naturally, these coefficients also depend on the special method of calculation, i.e., for any N a Rayleigh–Ritz method leads to a *different* set $\{c_n^N\}_{n=1}^{N}$ than a variance minimization (see Section III,D), and the best approximation of the exact eigenstate, defined in Eq. (17), gives still other coefficients. These statements are true, even if $\{\phi_n\}_{n=1}^{\infty}$ is an *orthonormal* set.

Thus, Eq. (1) does by no means show the first N terms of an *expansion* for the state Ψ, so that one may ask, whether the expansion coefficients c_n^N do have any physical meaning at all. One may expect that this is the case for $N \to \infty$. However, as our considerations will show, one must be careful with such a conclusion.

All the following investigations will be performed in a separable *Hilbert* space **H**, endowed with the norm $\|\cdot\|$ and the scalar product $(\cdot\,,\cdot)$. In the applications, **H** will be specified to be $L^2(\mathbf{R}^s)$ and related spaces or one of the *Sobolev* spaces[1] ($c > 0$, $r = 0, 1, 2, \ldots$)

$$W_2^{(r)}(\mathbf{R}^s){:} = \{f \in L^2(\mathbf{R}^s) \,|\, (c + \mathbf{p}^2)^{r/2}\hat{f}(\mathbf{p}) \in L^2(\mathbf{R}^s)\}, \tag{2}$$

with $\hat{f}(\mathbf{p})$ denoting the Fourier transform of f. These fulfill the inclusion relation

$$W_2^{(r+1)}(\mathbf{R}^s) \subset W_2^{(r)}(\mathbf{R}^s) \subset L^2(\mathbf{R}^s), \qquad r = 1, 2, 3, \ldots, \tag{3}$$

and are endowed with stronger norms than L^2.

Let our basis set[2] $\{\phi_n\}_{n=1}^{\infty}$ now be *complete* in **H**. Then, the c_n^N can obviously be determined such that

$$\|\Psi_N - \Psi\| \to 0 \qquad (N \to \infty) \tag{4}$$

is valid. This can, for instance, be achieved by the Rayleigh–Ritz method. Especially, with respect to eigenstates Ψ of nonrelativistic electronic molecular Hamiltonians, if $\{\phi_n\}_{n=1}^{\infty}$ is complete in $\mathbf{H} = W_2^{(1)}$, then the coeffi-

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[1] For a recent discussion of Sobolev spaces and their properties see the books of Adams (1975), Weidmann (1976, especially p. 276), and Reed and Simon (1975, especially p. 50). Note that different values $c > 0$ in Eq. (2) induce different but equivalent normalizations of the same space $W_2^{(r)}$. Moreover, especially for $r = 0$ we have $W_2^{(0)} = L^2$.

[2] The notation "basis set" is used for "set of functions"; it should not be confused with the concept of a "(Schauder) basis", which is considered in Section III,J.

cients c_n^N, obtained from the secular equations, lead to approximations Ψ_N, which fulfill Eq. (4) with $\| \cdot \|$ denoting the norm of $W_2^{(1)}$ (for details, see Klahn and Bingel, 1977a). Thus, the problem of *approximating* Ψ can be solved by a *completeness argument* alone.

But the *behavior of the coefficients* c_n^N as $N \to \infty$ and the problem of *representing* Ψ by an expansion are quite different questions. These can be answered by special *linear independence* properties of the basis set.

A. The Problems

The problems that are covered by linear independence properties are best summarized by listing the following questions:

(1) Does the convergence of the expansion coefficients c_n^N in N to some *final* c_n already follow from Eq. (4), *independent* of the method, by which the c_n^N are determined:

$$\lim_{N\to\infty} c_n^N = c_n \qquad (n = 1, 2, 3, \ldots)? \tag{5}$$

If this question can positively be answered, we will say that Ψ has the *formal expansion*[3]

$$\Psi \sim \sum_{n=1}^{\infty} c_n \phi_n. \tag{6}$$

Moreover, can the limiting values c_n in Eq. (5) depend on the method of calculation?

(2) Does the formal expansion (6) *represent* Ψ in the sense

$$\left\| \sum_{n=1}^{N} c_n \phi_n - \Psi \right\| \to 0 \qquad (N \to \infty), \tag{7a}$$

such that we may write

$$\Psi = \sum_{n=1}^{\infty} c_n \phi_n \tag{7b}$$

instead of Eq. (6)? One could additionally ask the same question in the case that the limiting values c_n in Eq. (5) depend on the special approximation, a problem that is touched upon only marginally (Sections III,B and III,C,2).

(3) Are the coefficients c_n of an expansion according to Eq. (7b) always *uniquely* determined by Ψ?

(4) Is the element Ψ *uniquely* determined by the coefficients c_n de-

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[3] This definition of a formal expansion is equivalent with the concept of a (formal) *biorthonormal* expansion, defined in Eq. (25). Other definitions of formal expansions are also possible, however, these are not used in this article.

fined in Eq. (5), or, in other words, do two different elements Ψ and Ψ' always have different formal expansions?

The answers to these questions are summarized in Section III,K.

One should note the decisive difference between Eqs. (4) and (7): In Eq. (4), the number N occurs in *two* places [cf. Eq. (1)], namely as the number of basis functions used for the approximation Ψ_N and as a parameter in c_n^N, whereas Eq. (7) only makes use of the *final* coefficients c_n, which do *not* depend on N. Equation (7) may be *violated*, even if Eqs. (4) and (6) are fulfilled. This is extensively demonstrated in Section III,I, showing the *pathological* properties of formal expansions.

As is well known, in *finite-dimensional unitary spaces* the problem of unique expansions can be answered by *linear independence* arguments (see Section II). With respect to our questions (1)–(4), this suggests to investigate linear independence properties of *infinite* basis sets in Hilbert spaces **H**. This was already done in an earlier article (Klahn and Bingel, 1977b), however, in the meantime it turned out that the theory given there can be considerably improved.

Different from unitary spaces, in **H** no standard definition of linear independence can be given; instead of this we get a *hierarchy* of *non* equivalent criteria (see Fig. 2), each of which may answer our questions (1)–(4) to some extent. These criteria are as follows: finitely linear independence (Section III,A), ω-linear independence (Section III,B), minimality (Section III,C), uniform minimality (Section III,J), the Bessel (Section III,F) and Riesz properties (Section III,L), which reflect special properties of the *overlap matrix*, γ-linear independence (Section III,M), which is based on the value of *Gram's determinant*, and orthonormality. Some further concepts are also discussed for completeness: Hilbertian sets (Section III,G), the asymptotic dimension (Section III,N), and a linear independence property given by Eq. (70).

Most of these criteria can be studied in the mathematical literature (see Singer, 1970). One could even define additional ones and refine Fig. 2 in this way. However, there seems to be no comprehensive treatment that collates all of them, especially for Hilbert spaces, and also presents examples that are interesting in quantum chemistry. Moreover, since the language of a mathematician and a quantum chemist is sometimes quite different, this article may also contribute to a unification of notations.

B. Overcompleteness

Whereas linear dependence of a basis set in a *finite*-dimensional space can very simply be avoided by suitable deletion of some elements, in an *infinite*-dimensional space this is by no means trivial. This fact can be easiest seen from the possible occurrence of *overcompleteness* (see Löwdin, 1956; Klahn and Bingel, 1977b).

We call a complete set $\{\phi_n\}_{n=1}^{\infty}$ of **H** *over*complete if at least one element ϕ_k can be left out, but $\{\phi_n\}_{n=1, n\neq k}^{\infty}$ is still complete, nevertheless. We call the complete set $\{\phi_n\}_{n=1}^{\infty}$ *exactly* complete if it becomes *in*complete by omission of a single arbitrarily chosen element.

Overcompleteness will turn out to be a "marriage" of completeness and a special form of linear dependence, the *nonminimality* (see Section III,C,1), which generally cannot be overcome by deleting some functions—different from the situation in finite-dimensional spaces. A simple example, well known as the *theorem of Müntz and Szász,* may illustrate this.

The set of exponential-type functions $\{\exp(-\zeta_n x)\}_{n=1}^{\infty}$, where ζ_n ($n = 1, 2, 3, \ldots$) are mutually different positive orbital exponents, is complete in $\mathbf{H} = L^2(\mathbf{R}^+)$ if and only if

$$\sum_{n=1}^{\infty} \zeta_n/(1 + \zeta_n^2) = \infty \tag{8}$$

is fulfilled. The proof of this theorem was given by Müntz (1914) and Szász (1916) and is also contained in subsequent articles and textbooks (e.g., Paley and Wiener, 1934; Crum, 1956; Schönhage, 1971; Higgins, 1977, p. 95).

If Eq. (8) is fulfilled, then the completeness of $\{\exp(-\zeta_n x)\}_{n=1}^{\infty}$ is preserved by deleting a *finite* (or, provided that the elements are suitably chosen, even an *infinite*) number of functions, since the divergence of the sum (8) is not affected. Thus, these exponential-type functions, if they are complete at all, are overcomplete to a high degree.

As a simple consequence of overcompleteness, Eq. (5) need *not* be fulfilled, even if Eq. (4) is: At least one function ϕ_k of an overcomplete set can be approximated by the others $\{\phi_n\}_{n=1, n\neq k}^{\infty}$ with arbitrary accuracy. Thus the coefficients c_k^N ($N = k, k + 1, \ldots$) for the approximation of any given $\Psi \in \mathbf{H}$ can be chosen *arbitrarily* and Eq. (4) can be satisfied, nevertheless; or in other words, in the case of an overcomplete basis set the coefficients c_n of Eq. (5) depend on the special approximation. A numerical demonstration for the violation of Eq. (5) in a *variational calculation* is given in Table I. So it is not surprising that an element $\Psi \in \mathbf{H}$ can generally not be expanded in terms of overcomplete sets.

II. Expansions in Finite-Dimensional Unitary Spaces

In order to get a better insight in the linear independence properties of a Hilbert space, a discussion of the *finite*-dimensional case is very useful. The accordances and differences in both cases become more evident in this way, especially with respect to the concept of *biorthonormality.*

Let $\mathbf{H}_M$ be an M-dimensional complex unitary space with the scalar product $(\cdot, \cdot)$, let $\{\phi_n\}_{n=1}^N$ be a set of functions in $\mathbf{H}_M$, and let $[\phi_n]_{n=1}^N$ denote the linear span of $\{\phi_n\}_{n=1}^N$. Then, any $\Psi \in [\phi_n]_{n=1}^N$ has an expansion

$$\Psi = \sum_{n=1}^{N} c_n \phi_n \tag{9}$$

with suitable complex numbers c_n ($n = 1, \ldots, N$). Furthermore, if $\{\phi_n\}_{n=1}^N$ is *complete* in $\mathbf{H}_M$, i.e., if

$$\mathbf{H}_M = [\phi_n]_{n=1}^N, \tag{10}$$

then any $\Psi \in \mathbf{H}_M$ has an expansion like (9). However, the expansion coefficients c_n need not be *unique*. Uniqueness is only obtained if the system $\{\phi_n\}_{n=1}^N$ is *linearly independent*. Complete sets are obviously linearly independent if and only if $N = M$.

According to the definition of exact and overcompleteness in $\mathbf{H}$ (see Section I,B), we call a complete set $\{\phi_n\}_{n=1}^N$ *exactly* complete in $\mathbf{H}_M$ if it is linearly independent, and *over*complete if it is linearly dependent. Thus, the exactly complete basis sets of $\mathbf{H}_M$ allow *unique* expansions for all $\Psi \in \mathbf{H}_M$, whereas overcomplete sets do not.

Linear independence in $\mathbf{H}_M$ can be characterized by different criteria, which are all equivalent (see Gantmacher, 1977, especially Chapter IX):

(a) The equation $\sum_{n=1}^N c_n \phi_n = \theta$, where $c_n (n = 1, \ldots, N)$ are arbitrary complex numbers and θ denotes the zero element of $\mathbf{H}_M$, implies $c_n = 0$ ($n = 1, \ldots, N$). (This is the original definition of linear independence in a vector space.)

(b) There exists a *biorthonormal sequence* (BOS) $\{\phi_n^*\}_{n=1}^N$ in $\mathbf{H}_M$, i.e., a set of elements ϕ_n^* with the property $(\phi_n, \phi_m^*) = \delta_{nm}$. *Note:* A BOS is *uniquely* determined if and only if $\{\phi_n\}_{n=1}^N$ is *complete* in $\mathbf{H}_M$. If $\{\phi_n\}_{n=1}^N$ is *in*complete, then uniqueness of $\{\phi_n^*\}_{n=1}^N$ can be enforced by the subsidiary condition $\phi_n^* \in [\phi_n]_{n=1}^N$, which can always be fulfilled. Such a unique BOS will be called *the* BOS (see Fig. 1). In the special case of an orthonormal set $\{\phi_n\}_{n=1}^N$ *the* BOS is given by $\phi_n^* = \phi_n (n = 1, \ldots, N)$.

(c) Let $\mathbf{S}^{(N)}(\phi_1, \ldots, \phi_N) = ((\phi_n, \phi_m))_{n,m=1}^N$ denote the *overlap* matrix or *Gram's* matrix having the lowest eigenvalue $\mu_1^N(\phi_1, \ldots, \phi_N)$. Then μ_1^N is positive [cf. also Eq. (49)].

(d) *Gram's determinant* $\gamma_N(\phi_1, \ldots, \phi_N) = \det \mathbf{S}^{(N)}(\phi_1, \ldots, \phi_N)$ is a positive number.

A complete set is therefore exactly complete in $\mathbf{H}_M$, *iff (if and only if) it has a BOS, and it is overcomplete, iff it does not.* This statement holds also in the infinite-dimensional case (cf., Section III,C,1).

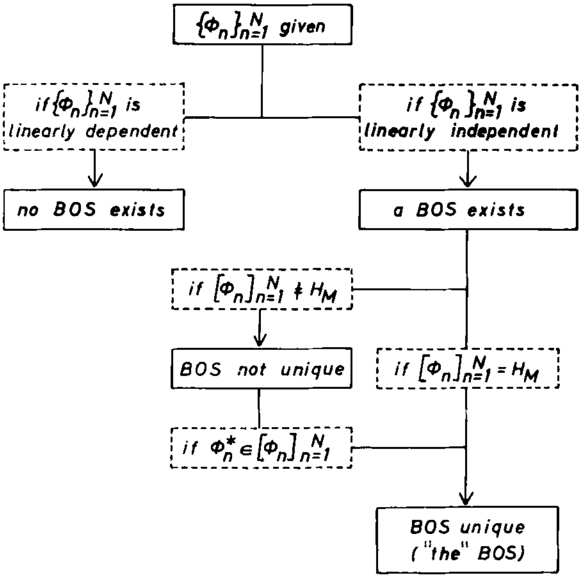

Fig. 1. The existence of a BOS (biorthonormal sequence) and conditions for its uniqueness in the case of a given finite basis set $\{\phi_n\}_{n=1}^N$. The scheme is also valid for $N = M = \infty$, provided that "linear independence" is substituted by "minimality" and $[\phi_n]_{n=1}^N$ by $\overline{[\phi_n]}$.

The BOS of a linearly independent set can obviously be constructed very easily:

$$\phi_n^* = \sum_{k=1}^{N} T_{nk}^{(N)} \phi_k \qquad (n = 1, \ldots, N). \tag{11}$$

Here, $T^{(N)}(\phi_1, \ldots, \phi_N)$ is the inverse of the overlap matrix $S^{(N)}(\phi_1, \ldots, \phi_N)$. Another characterization of $T^{(N)}$ is obtained from Eq. (11):

$$T_{nm}^{(N)} = (\phi_n^*, \phi_m^*) = S_{nm}^{(N)}(\phi_1^*, \ldots, \phi_N^*) \tag{12a}$$

or, equivalently

$$\begin{aligned} T^{(N)}(\phi_1, \ldots, \phi_N) &:= [S^{(N)}(\phi_1, \ldots, \phi_N)]^{-1} \\ &= S^{(N)}(\phi_1^*, \ldots, \phi_N^*), \end{aligned} \tag{12b}$$

i.e., $T^{(N)}$, or $(S^{(N)})^{-1}$, respectively, is the overlap matrix of *the* BOS, a relation that in an *infinite*-dimensional Hilbert space is much more critical [cf., Eq. (95)]. Since $T^{(N)}$ is a nonsingular matrix, Eq. (11) shows furthermore that

$$[\phi_n]_{n=1}^N = [\phi_n^*]_{n=1}^N, \tag{13}$$

i.e., *the* BOS subtends always $[\phi_n]_{n=1}^N$, quite *different* from the infinite-dimensional case (see Section III,H). It follows especially that the BOS of an exactly complete set in H_M exists, is unique, and is also (exactly) complete.

The knowledge of a BOS allows a very elegant calculation of the expansion coefficients c_n in Eq. (9): These can be written in the form of a scalar product [cf. Eqs. (9) and (11)][4]

$$c_n = (\Psi, \phi_n^*) = \left(\Psi, \sum_{k=1}^{N} \mathbf{T}_{nk}^{(N)}\phi_k\right), \qquad n = 1, \ldots, N, \tag{14}$$

such that any exactly complete set $\{\phi_n\}_{n=1}^{N}$ leads to the unique expansion

$$\Psi = \sum_{n=1}^{N} (\Psi, \phi_n^*)\phi_n, \qquad \forall \quad \Psi \in \mathbf{H}. \tag{15a}$$

Since the BOS $\{\phi_n^*\}_{n=1}^{N}$ is also exactly complete, we have additionally

$$\Psi = \sum_{n=1}^{N} (\Psi, \phi_n)\phi_n^*, \qquad \forall \quad \Psi \in \mathbf{H}, \tag{15b}$$

showing that both $\{\phi_n\}_{n=1}^{N}$ and $\{\phi_n^*\}_{n=1}^{N}$ are *bases* of $\mathbf{H}_M$. In the special case of an *orthonormal* system $\{\phi_n\}_{n=1}^{N}$, the representations (15a) and (15b) of Ψ coincide and the coefficients are the well-known generalized *Fourier*-expansion coefficients.

In a three-dimensional unitary space $\mathbf{H}_3$, a geometrical interpretation of biorthonormality is well known: The elements $\{\phi_n\}_{n=1}^{3}$ and $\{\phi_n^*\}_{n=1}^{3}$ behave just like the vectors of a lattice and its reciprocal lattice, since these are biorthogonal to each other too. Furthermore, $\{\phi_n\}_{n=1}^{N}$ and $\{\phi_n^*\}_{n=1}^{N}$ can be considered as a *covariant* and *contravariant* basis of $\mathbf{H}_N$.

So far, the concept of biorthonormality did not play an important role in quantum chemistry. The concept was introduced by Des Cloizeaux (1960) and was used with respect to linked cluster expansions (Brandow, 1967), second quantization formalism (Moshinsky and Seligman, 1971), valence bond calculations (Norbeck and McWeeny, 1975; Schubert *et al.*, 1977), and Rayleigh–Schrödinger perturbation theory with applications to intermolecular interactions (Gouyet, 1973a,b, 1974; Kochanski and Gouyet, 1975); Dahl (1978) discussed the use of biorthonormal orbital basis sets for intermolecular interactions between one-electron atoms.

III. Criteria of Linear Independence in Infinite-Dimensional Hilbert Spaces

If $[\phi_n]$ now denotes the linear span of an *infinite* set of functions $\{\phi_n\}_{n=1}^{\infty}$ in an *infinite*-dimensional Hilbert space $\mathbf{H}$ and if $\overline{[\phi_n]}$ denotes the

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[4] As can be seen from Eq. (9) by scalar multiplication, the coefficients c_n do not depend on the special choice of the BOS.

appertaining closure in H, then any $\Psi \in \overline{[\phi_n]}$ can obviously be approximated by $\{\phi_n\}_{n=1}^{\infty}$ according to Eq. (4). However, since it is normally difficult to check whether an element $\Psi \in \mathbf{H}$ is even an element of $\overline{[\phi_n]}$, it is reasonable to require the *completeness*[5] of $\{\phi_n\}_{n=1}^{\infty}$ in H, such that

$$\mathbf{H} = \overline{[\phi_n]} \tag{16}$$

in complete analogy to Eq. (10). But with respect to the expansion problem [see Eqs. (5)–(7)] of a special function Ψ, which lies in $\overline{[\phi_n]}$, the knowledge of completeness does not help at all.

In order to attack this problem, we now present a series of criteria of linear independence, which are summarized and related to each other in Fig. 2.[6] Most of these criteria can be defined also in *Banach* spaces (see Singer, 1970), where only a norm and no scalar product is available; however, this is not the subject of this article.

A. Finitely Linear Independence

For nearly all considerations concerning infinite basis sets $\{\phi_n\}_{n=1}^{\infty}$, it is a minimum requirement that any *finite* subset $\{\phi_n\}_{n=1}^{N} (N = 1, 2, 3, \ldots)$ is linearly independent in the sense of finite-dimensional vector spaces. This weakest form of linear independence is called *finitely linear independence* (see Singer, 1970, p. 50). Sometimes, a finitely linearly independent set $\{\phi_n\}_{n=1}^{\infty}$ is also called a *linear basis,* an *algebraic basis,* or a *Hamel basis* (Kiesewetter, 1973, p. 31).

None of the questions posed in Section I,A can be answered in terms of finitely linear independence. However, a Hamel basis allows unique expansions in the *finite*-dimensional subspaces $[\phi_n]_{n=1}^{N}$ of H. For example, the *orthogonal projection*[7] $\Psi_N^{(\mathrm{BA})}$ of an arbitrary element $\Psi \in \mathbf{H}$ onto $[\phi_n]_{n=1}^{N}$ has an expansion that is given by Eq. (15a):

$$\Psi_N^{(\mathrm{BA})} = \sum_{n=1}^{N} (\Psi_N^{(\mathrm{BA})}, \phi_n^*(N))\phi_n = \sum_{n=1}^{N} (\Psi, \phi_n^*(N))\phi_n. \tag{17}$$

In Eq. (17), $\phi_n^*(N)$ denotes the BOS of $\{\phi_n\}_{n=1}^{N}$ in $[\phi_n]_{n=1}^{N}$, is uniquely defined by Eq. (11), and depends on N itself; the right-hand side of Eq. (17) follows from the *orthogonal projection theorem* (Kato, 1966, p. 252). $\Psi_N^{(\mathrm{BA})}$ is nothing else than the *best approximation* of Ψ in the finite basis $\{\phi_n\}_{n=1}^{N}$ (see Singer, 1970, p. 174; Achieser and Glassmann, 1968, p. 21),

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[5] For the definition of completeness and related concepts see Higgins (1977, especially p. 14), and Achieser and Glasmann (1968, p. 23).

[6] If one reverses all arrows in Fig. 2, one obtains the relations between the *dependence* properties.

[7] The superscript BA in $\Psi_N^{(\mathrm{BA})}$ stands for "Best Approximation."

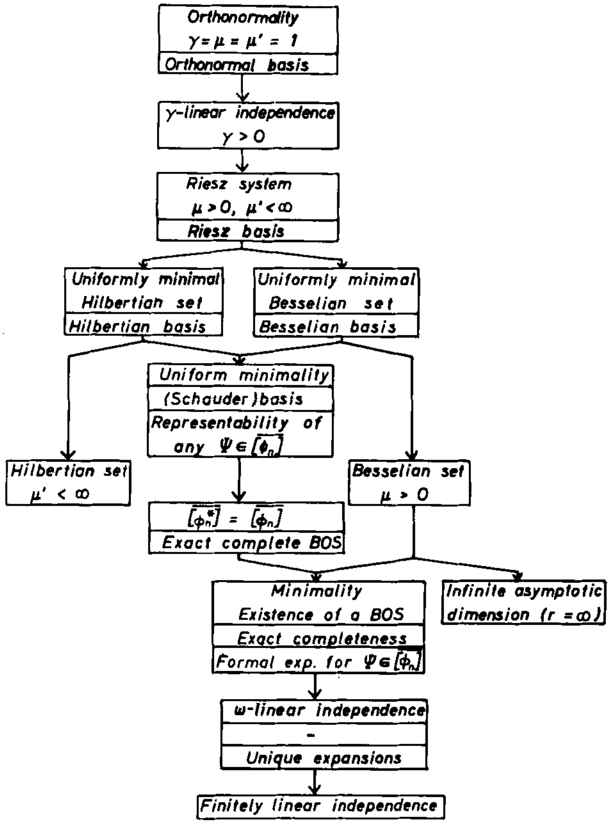

Fig. 2. The criteria of linear independence for infinite bases sets in a Hilbert space and their relations among each other. The top line of each box denotes the criterion, the second line the notation for complete sets, and the bottom line shows, if at all, a characteristic property of the criterion.

i.e., the expansion coefficients in Eq. (17) are chosen such that the norm (4) takes its minimum value, the so-called *distance*. The distance can also be written in terms of Gram's determinant γ_N (Gantmacher, 1977, p. 250; Achieser and Glasmann, 1968, p. 16):

$$\begin{aligned}\delta^{(N)}(\Psi;\phi_1,\ldots,\phi_N) &:= \min_{c_n\in\mathbf{C}}\left\|\Psi-\sum_{n=1}^{N}c_n\phi_n\right\|\\ &= \left\|\Psi-\sum_{n=1}^{N}(\Psi,\phi_n^*(N))\phi_n\right\|\\ &= \left[\frac{\gamma_{N+1}(\Psi,\phi_1,\ldots,\phi_N)}{\gamma_N(\phi_1,\ldots,\phi_N)}\right]^{1/2}. \qquad (18)\end{aligned}$$

It goes to zero as $N \to \infty$ for any $\Psi \in \mathbf{H}$ *if* the basis set is complete in **H**. However, without any further information on the basis set $\{\phi_n\}_{n=1}^{\infty}$, no conclusions are possible with respect to the behavior of the expansion coefficients $(\Psi, \phi_n^*(N))$ as $N \to \infty$.

B. ω-Linear Independence

The direct analog of the original form of linear independence, as defined for a finite-dimensional vector space [see Section II, characterization (a) of linear independence], is the ω-linear independence.

A basis set $\{\phi_n\}_{n=1}^{\infty}$ is called *ω-linearly independent* (see Singer, 1970, p. 50; Kato, 1966, p. 265; Higgins, 1977, p. 73) if the relation $\|\sum_{n=1}^{N} c_n \phi_n\| \to 0$ $(N \to \infty)$, where $c_n \in \mathbf{C}$ $(n = 1, 2, 3, \ldots)$ implies $c_n = 0$ $(n = 1, 2, 3, \ldots)$.

Obviously, ω-linear independence implies finitely linear independence. But the opposite is *not* true (see Fig. 2). This is shown by the following example: Let $\{\phi_n\}_{n=2}^{\infty}$ be a complete orthonormal set and $\phi_1 \in \mathbf{H}$ with $\phi_1 \notin [\phi_n]_{n=2}^{\infty}$. Then, $\{\phi_n\}_{n=1}^{\infty}$ is finitely linearly independent, but ω-linearly dependent, because the nonzero coefficients $c_1 = -1$ and $c_n = (\phi_1, \phi_n)$ for $n \geq 2$ lead to $\|\sum_{n=1}^{N} c_n \phi_n\| \to 0$ $(N \to \infty)$. Therefore, as another example, a basis set consisting of two orthonormal complete subsystems at different atomic centers is also finitely linearly independent, but ω-linearly dependent.

Examples of ω-linearly *in*dependent systems in $\mathbf{H} = L^2$ are[8] $(\zeta > 0, p = 1, 2)$:

(a) $\{x^{n-1}\}_{n=1}^{\infty}$ in $L^2(a, b)$ with $a, b \in \mathbf{R}$ (Nikolskii, 1954);
(b) $\{x^k \exp(-\zeta n x^p)\}_{n=1}^{\infty}$ with fixed $k = 0, 1, 2, \ldots$ in $L^2(\mathbf{R}^+)$;
(c) $\{x^{n-1} \exp(-\zeta x^p)\}_{n=1}^{\infty}$ in $L^2(\mathbf{R}^+)$;
(d) $\{r^l \exp(-\zeta n r^p) Y_{lm}\}_{n=1,\, l=0,\, m=-l}^{\infty\ \ \infty\ \ \ l}$ in $L^2(\mathbf{R}^3)$ with Y_{lm} the spherical harmonics (see, e.g., Landau and Lifschitz, 1965);
(e) $\{r^{n+l-1} \exp(-\zeta r^p) Y_{lm}\}_{n=1,\, l=0,\, m=-l}^{\infty\ \ \infty\ \ \ l}$ in $L^2(\mathbf{R}^3)$.

The examples show that ω-linear independence does not prevent overcompleteness; e.g., $\{\exp(-nx)\}_{n=1}^{\infty}$ is ω-linearly independent by example (b), however, it is overcomplete in $L^2(\mathbf{R}^+)$ by the theorem of Müntz and Szász [see Eq. (8)].

Since, by the definition of ω-linear independence, the zero element has only the zero representation, we get as an immediate consequence an answer to question (3) of Section I,A: *Provided that an element* $\Psi \in \mathbf{H}$ *has an expansion in terms of* $\{\phi_n\}_{n=1}^{\infty}$ *according to Eq. (7), then the expansion*

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[8] For the proofs, which are not shown here, among other techniques extensive use has been made of the invariance properties of ω-linear independence, which are discussed in Sections IV,C and D.

TABLE I

RAYLEIGH–RITZ ENERGIES E_0^N AND EXPANSION COEFFICIENTS c_n^N FOR THE GROUND STATE OF THE HYDROGEN ATOM AND THE MEASURE OF LINEAR INDEPENDENCE μ_1^N FOR INCREASING N[a]

N	$-E_0^N$	c_1^N	c_2^N	c_3^N	c_4^N	μ_1^N
2	0.47558	1.7685	−0.81329			0.305-01
3	0.49249	2.7908	−2.8474	1.0239		0.986-03
4	0.49717	4.0438	−6.8102	5.3453	−1.6028	0.341-04
5	0.49879	5.5121	−13.500	17.212	−11.110	0.122-05
6	0.49943	7.1856	−23.814	43.555	−45.141	0.442-07
7	0.49971	9.0579	−38.749	94.799	−139.58	0.160-08
8	0.49985	11.125	−59.406	185.78	−362.83	0.578-10
10	0.49995	15.835	−122.82	574.48	−1751.1	0.739-13

[a] Performed with the basis set of Eq. (19) using an 18-digit precision. The coefficients are normalized according to $(\mathbf{c}^N)^\dagger \mathbf{S}^{(N)} \mathbf{c}^N = 1$.

coefficients c_n of this element are uniquely determined if and only if $\{\phi_n\}_{n=1}^\infty$ is ω-linearly independent. However, ω-linear independence does not guarantee that a given $\Psi \in \mathbf{H}$ has an expansion at all.

Now, let us approximate an element $\Psi \in \mathbf{H}$ with an ω-linearly *dependent* basis set, where Ψ is assumed to have an expansion. Then it is not surprising that the limiting values c_n depend on the special method of approximation, since the expansion of Ψ itself is not unique.

However, even if the expansion coefficients c_n of Ψ are uniquely determined, i.e., if $\{\phi_n\}_{n=1}^\infty$ is ω-linearly *in*dependent, the coefficients c_n^N need generally *not* converge to these c_n as $N \to \infty$, since $\{\phi_n\}_{n=1}^\infty$ may be overcomplete (see Section I,B). This is also clear from the analysis of linear independence properties alone: ω-linear independence does *not* say that $\|\sum_{n=1}^N c_n \phi_n\| \to 0$ implies $c_n^N \to 0$ as $N \to \infty$, as minimality does [see characterization (d) of minimality in Section III,C,1]. Thus the expansion coefficients of two different approximations Ψ_N and Ψ_N' of the same Ψ may have different limiting values for $N \to \infty$.

Indeed, the coefficients c_n^N of some $\Psi \in \mathbf{H}$ need not converge at all as $N \to \infty$, e.g., one may have $c_n^N \to \infty$ $(N \to \infty)$ for some n. Such a behavior of c_n^N is demonstrated in Table I: The *Rayleigh–Ritz* energies E_0^N and expansion coefficients c_n^N have been computed numerically for the electronic ground state of the hydrogen atom $\Psi_0 = \pi^{-1/2} \exp(-r)$, using the basis set

$$\{\pi^{-1/2}(1 + n/2)^{3/2} \exp[-(1 + n/2)r]\}_{n=1}^N, \tag{19}$$

TABLE II[a]

N	$-E_0^N$	c_1^N	c_2^N	c_3^N	c_4^N	μ_1^N
2	0.458333	1.7321	−1.0000			0.134-00
3	0.489357	2.2986	−2.4071	0.9859		0.173-01
4	0.497850	2.6135	−3.5680	2.6622	−0.8783	0.220-02
5	0.499627	2.7483	−4.2609	4.2327	−2.5800	0.278-03
6	0.499941	2.7992	−4.6109	5.3372	−4.4263	0.347-04
8	0.499999	2.8246	−4.8463	6.3629	−6.9795	0.524-06
10	0.500000	2.8279	−4.8902	6.6350	−7.9859	0.767-08
∞	0.5	$2\sqrt{2}$ $= 2.8284$	$-2\sqrt{6}$ $= -4.8990$	$3\sqrt{5}$ $= 6.7082$	$-\sqrt{70}$ $= -8.3666$	0.0

[a] See the legend of Table I, where Eq. (19) has to be replaced by Eq. (20). The limiting values of c_n^N as $N \to \infty$, $c_n = 4(-1)^{n-1}2^{-n}[(n-1)!]^{-1}[(2n)!]^{1/2}$, $n = 1, 2, 3, \ldots$, are obtained from the Taylor expansion of $\exp(-r/2)$. $\mu_1^N \to 0$ $(N \to \infty)$ follows from the overcompleteness of the set (20).

which is ω-linearly independent for $N \to \infty$ by example (d), but overcomplete (essentially) by the theorem of Müntz and Szász. Obviously, the energy values converge to the correct ground state energy, which is −0.5 a.u., whereas the expansion coefficients become absolutely larger and larger for all n.

As can be seen from the value μ_1^N ["measure of linear independence," see Eq. (49)], this divergent behavior of the c_n^N is not based on numerical instabilities of the calculation, due to an "almost linear dependence" (see Section III,F) of the finite basis set, but it is a pure analytic effect, based on the *over*completeness of (18) for $N \to \infty$.

Of course, there are also cases, where convergence of the c_n^N as $N \to \infty$ is obtained, even if the basis set is *over*complete: Doing the analogous calculation as before with the basis set[9]

$$\{[4\pi(2n)!]^{-1/2} r^{n-1} \exp(-r/2)\}_{n=1}^{N} \tag{20}$$

instead of (19), we get convergence with respect to both the Rayleigh–Ritz energies E_0^N and coefficients c_n^N as $N \to \infty$ (see Table II). The convergence of the coefficients, however, is based on the special element $\Psi \in \mathbf{H}$ under consideration and, above all, on the *procedure* of their determination.

By these two examples it seems that especially the *Rayleigh–Ritz* method, performed in an ω-linearly independent basis set, fulfills Eq. (5) if the eigenstate Ψ has an expansion as given by Eq. (7) at all. However, to

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[9] The *over*completeness of (2) for $N \to \infty$ follows from the completeness of $\{x^n \exp(-x/2)\}_{n=n'}^{\infty}$ in $L^2(\mathbf{R}^+)$ for any fixed $n' = 0, 1, 2, \ldots$ (see Klahn and Bingel, 1977a,b; Kinoshita, 1957, especially the footnote No. 29).

the author's knowledge such a statement has not been proved so far. For overcomplete, but ω-linearly independent basis sets, it is therefore presumably meaningless to investigate the validity of Eq. (7) using coefficients c_n, which are different from those obtained by means of Eq. (5) with the Rayleigh–Ritz method.

The criterion of ω-linear independence is of special interest in some theorems that prove the Schauder basis property by "stability" arguments (see Singer, 1970, p. 94; Kato, 1966, p. 265; Higgins, 1977, p. 73). This fact explains the importance of this criterion in the theory of bases.

C. Minimality

1. *Exact Completeness and Overcompleteness*

The variety of possibilities with respect to the behavior of c_n^N as $N \to \infty$, as described in Section III,B, does not occur if the basis set is assumed to fulfill a stronger criterion of linear independence: This criterion is the *minimality* or *strongly linear independence* (see Markushevich, 1943), which was introduced by Kaczmarz and Steinhaus (1951, pp. 53 and 263). It allows also a sharp characterization of exact completeness and overcompleteness.

A basis set $\{\phi_n\}_{n=1}^{\infty}$ is called minimal or strongly linearly independent in **H** if $\phi_k \notin \overline{[\phi_1, \ldots, \phi_{k-1}, \phi_{k+1}, \ldots]}$ holds for $k = 1, 2, 3, \ldots$.

This definition says that no element ϕ_k of a minimal set can be approximated by the others with arbitrary accuracy. Thus, if $\{\phi_n\}_{n=1}^{\infty}$ is complete and *minimal* in **H**, then $\{\phi_n\}_{n=1, n\neq k}^{\infty}$ is *in*complete for all k, i.e., $\{\phi_n\}_{n=1}^{\infty}$ is *exactly* complete. On the other hand, if a complete set is *nonminimal*, then there exists at least one element ϕ_k such that $\phi_k \in \overline{[\phi_1, \ldots, \phi_{k-1}, \phi_{k+1}, \ldots]}$ with the consequence that $\{\phi_n\}_{n=1, n\neq k}^{\infty}$ is still complete, i.e., $\{\phi_n\}_{n=1}^{\infty}$ is *over*complete. Thus we have the interesting characterization:

A complete set $\{\phi_n\}_{n=1}^{\infty}$ is exactly complete in **H** iff (if and only if) it is minimal, and is overcomplete iff it is nonminimal, or, in a more suggestive notation:

exact completeness = *completeness* + *minimality*
overcompleteness = *completeness* + *nonminimality*

Since the minimality of a basis set may be difficult to show by means of the original definition and also in order to clear up the relations to finite-dimensional unitary spaces, it is very useful to have the following *equivalent characterizations* of minimality:

(a) $\{\phi_n\}_{n=1}^{\infty}$ is minimal in **H**.
(b) The distance [see Eq. (18)]

$$\delta_k = \lim_{N\to\infty} \delta^{(N-1)}(\phi_k; \phi_1, \ldots, \phi_{k-1}, \phi_{k+1}, \ldots, \phi_N) \tag{21}$$

is a positive number for all $k = 1, 2, 3, \ldots$.

(c) There exists a *biorthonormal sequence* (BOS) $\{\phi_n^*\}_{n=1}^{\infty}$ in **H**, i.e., a set of elements ϕ_n^* with the property $(\phi_n, \phi_m^*) = \delta_{nm}$. *Note:* A BOS is *uniquely* determined if and only if $\{\phi_n\}_{n=1}^{\infty}$ is *complete* in **H**. If $\{\phi_n\}_{n=1}^{\infty}$ is *in*complete, then uniqueness of $\{\phi_n^*\}_{n=1}^{\infty}$ can be enforced by the subsidiary condition $\phi_n^* \in \overline{[\phi_n]}$, which can always be fulfilled. Such a unique BOS will be called *the* BOS (see Fig. 1). In the special case of an orthonormal set $\{\phi_n\}_{n=1}^{\infty}$ *the* BOS is given by $\phi_n^* = \phi_n$ $(n = 1, 2, 3, \ldots)$.

(d) The relation $\|\sum_{n=1}^{N} c_n^N \phi_n\| \to 0$ $(N \to \infty)$, where $c_n^N \in \mathbf{C}$ $(n = 1, 2, 3, \ldots)$ implies $c_n^N \to 0$ $(N \to \infty)$ for all $n = 1, 2, 3, \ldots$. (For comparison see the definition of ω-linear independence!)

(e) For all positive integers N there exist constants C_N with $1 \leq C_N < \infty$ such that we have

$$\left\| \sum_{n=1}^{N} c_n \phi_n \right\| \leq C_N \left\| \sum_{n=1}^{N+M} c_n \phi_n \right\| \tag{22}$$

for all positive integers M and all complex c_n $(n = 1, \ldots, N + M)$.

The proofs of equivalence are contained in the mathematical literature (Singer, 1970, p. 54; Achieser and Glasmann, 1968, p. 34; Kaczmarz and Steinhaus, 1951, p. 264; Markushevich, 1943).

Using the characterization (c) of minimality, instead of an earlier statement we now get a corollary, which reads just as for unitary spaces (see Section II): *A complete set* $\{\phi_n\}_{n=1}^{\infty}$ *is exactly complete iff it has a BOS, and is overcomplete iff it does not.*

Besides, characterization (c) shows that minimal sets are always ω-linearly independent: Let $\sum_{n=1}^{\infty} c_n \phi_n = \theta$, where $c_n \in \mathbf{C}$ $(n = 1, 2, 3, \ldots)$, then $c_k = 0$ $(k = 1, 2, 3, \ldots)$ obtains from scalar multiplication with the elements ϕ_k^* of the BOS, showing the ω-linear independence of $\{\phi_n\}_{n=1}^{\infty}$. But ω-linearly independent sets need not be minimal, as can be seen from the overcomplete and thus nonminimal set $\{\exp(-nx)\}_{n=1}^{\infty}$ in $L^2(\mathbf{R}^+)$ [see Section III,B, example (b)].

2. *Formal Biorthonormal Expansions*

From characterization (d) of minimality we expect that the expansion coefficients of approximations with a minimal basis set have a *stable* convergence behavior as $N \to \infty$, as indicated by Eq. (5). Indeed, since a minimal set has a BOS, the expansion coefficients c_n^N can be written as

$$c_n^N = \left(\sum_{k=1}^{N} c_k^N \phi_k, \phi_n^* \right) = (\Psi_N, \phi_n^*), \tag{23}$$

where the right-hand side does not depend on the special choice of $\{\phi_n^*\}_{n=1}^{\infty}$. Thus Eq. (4) implies unique limiting values of c_n^N

$$\lim_{N \to \infty} c_n^N = c_n = (\Psi, \phi_n^*) \tag{24a}$$

for all $n = 1, 2, 3, \ldots$, which are quite independent of how the c_n^N have been calculated. Furthermore, as is shown in a book of Kiesewetter (1973, p. 33), the *rate* of convergence is given by

$$|c_n^N - (\Psi, \phi_n^*)| \leq \delta_n^{-1} \|\Psi_N - \Psi\| \qquad (n = 1, 2, 3, \ldots). \qquad \text{(24b)}$$

If now $\{\phi_n\}_{n=1}^{\infty}$ is an *exactly complete* and thus minimal basis set, the terms of the sum

$$\Psi \sim \sum_{n=1}^{\infty} (\Psi, \phi_n^*)\phi_n \qquad (25)$$

are well-defined for all $\Psi \in \mathbf{H}$. Equation (25) is called the *formal biorthonormal* expansion of Ψ. If $\{\phi_n\}_{n=1}^{\infty}$ is assumed to be minimal and *incomplete* instead of exactly complete, then the basis set allows also formal expansions, however, only for all $\Psi \in \overline{[\phi_n]}$, of course.

Because of Eq. (24a) this formal expansion is the same as that defined in Eq. (6), i.e., question (1) of Section I,A can positively be answered for all $\Psi \in \overline{[\phi_n]}$ iff $\{\phi_n\}_{n=1}^{\infty}$ is minimal in $\mathbf{H}$. [The stronger "iff" instead of "if" is explained by the characterization (d) of minimality in Section III,C,1.]

It should be stressed that the right-hand side of Eq. (25) need *not* represent Ψ in the sense of Eq. (7) (see Section III,I). That is why we always speak of a *formal* expansion. However, *if* Ψ has an expansion according to Eq. (7), then the coefficients c_k are just given by the formal expansion coefficients (Ψ, ϕ_k^*), a fact that is immediately seen by scalar multiplication of Eq. (7b) with ϕ_k^*.

In this article, the questions of formal expansions and of representing Ψ are only treated for exactly complete basis sets. Since expansions in terms of *over*complete sets are also of some importance [see Eq. (20) and Table II, or the Kinoshita expansion of the helium wavefunction (Kinoshita, 1957)], this is an essential restriction. However, the reasons are as follows:

(a) With respect to overcomplete sets, formal expansions, as defined in Section I,A, do not at all exist for any $\Psi \in \mathbf{H}$. Nevertheless, one could try to define generalized formal expansions so that Eq. (5) holds at least for *special* approximations, e.g., the Rayleigh–Ritz method or the best approximation. But it is by no means self-evident that the limit (5) exists for all $n = 1, 2, 3, \ldots$ (see Table I).

(b) There is no theory in terms of basis set properties alone that assures convergence of such a generalized formal expansion of Ψ, i.e., the proof that Eq. (7) holds needs tools that are due to the basis set *and* to properties of the function Ψ under consideration.

In the special case of an *orthonormal* basis set, the formal expansion (25) is just the generalized *Fourier* expansion of Ψ, which represents Ψ in the sense of Eq. (7), as is well known.

There is furthermore a simple relation between the finite BOSs and the infinite BOS of a minimal set $\{\phi_n\}_{n=1}^{\infty}$: If $\{\phi_n^*(N)\}_{n=1}^{N}$ and $\{\phi_n^*\}_{n=1}^{\infty}$ denote *the* BOSs of $\{\phi_n\}_{n=1}^{N}$ and $\{\phi_n\}_{n=1}^{\infty}$, respectively, then Eqs. (18) and (24a) give as $N \to \infty$

$$(\Psi, \phi_n^*(N)) \to (\Psi, \phi_n^*), \qquad \forall \quad \Psi \in \overline{[\phi_n]}, \tag{26}$$

i.e., we have a *weak* convergence of $\phi_n^*(N)$ to ϕ_n^* for $n = 1, 2, 3, \ldots$ in $\overline{[\phi_n]}$.

In this context one should also note: With the exception of orthonormal basis sets, the finite truncation $\{\phi_n^*\}_{n=1}^{N}$ of the infinite BOS contrary to $\{\phi_n^*(N)\}_{n=1}^{N}$, is *not* a BOS of $\{\phi_n\}_{n=1}^{N}$ for all N, although the biorthonormality relation $(\phi_n, \phi_m^*) = \delta_{nm}$ is fulfilled. The reason is that $\phi_k^* \notin [\phi_n]_{n=1}^{N}$ for at least one $k \in \{1, \ldots, N\}$ if N is sufficiently large, whereas $\phi_k^*(N) \in [\phi_n]_{n=1}^{N}$ for all $k \in \{1, \ldots, N\}$ by Eq. (11).

D. Minimality and Variational Methods

As can be seen from Tables I and II, the expansion coefficients c_n^N for eigenstates of nonrelativistic molecular systems, obtained from the secular equations of a Rayleigh–Ritz calculation, *can* converge to limits c_n as $N \to \infty$, but they *need* not. However, from Eq. (24a), a simple condition results that guarantees Eq. (5): We assume that the basis set is *exactly complete in* $W_2^{(1)}(\mathbf{R}^{3M})$, with M denoting the number of electrons, i.e., $\{\phi_n\}_{n=1}^{\infty}$ is complete in $W_2^{(1)}$ and minimal in $W_2^{(1)}$. Then the approximate Rayleigh–Ritz energies converge to the eigenvalues of the molecule and, provided that Ψ is a nondegenerate state, the appertaining functions Ψ_N converge to the exact eigenstate Ψ within the norm of $W_2^{(1)}$ (see Klahn and Bingel, 1977a). Therefore, the c_n^N converge to the values of Eq. (24a), i.e., the Rayleigh–Ritz method constructs a formal expansion of Ψ for $N \to \infty$.

Analogously, if the c_n^N are obtained from minimizing the *variance*

$$R(E, \Psi_N) = \|(H - E)\Psi_N\|^2/\|\Psi_N\|^2 \tag{27}$$

(see Preuss, 1962; Kleindienst and Altmann, 1976) with respect to E and c_n^N, where H denotes the Hamiltonian, one can show that $\{\phi_n\}_{n=1}^{\infty}$ has to be exactly complete in $W_2^{(2)}(\mathbf{R}^{3M})$ instead of in $W_2^{(1)}(\mathbf{R}^{3M})$. Under this condition one gets also convergence with respect to energies, coefficients [Eq. (5)], and wave functions [Eq. (4)] within the $W_2^{(2)}$ norm.

As shown in Section IV (see Table V), the condition of minimality in $W_2^{(1)}$ or $W_2^{(2)}$ can in practical applications be substituted by the stronger condition that $\{\phi_n\}_{n=1}^{\infty}$ is minimal in L^2. If the basis set is indeed minimal in L^2, the formal expansion coefficients can also be obtained as scalar products of Ψ and the L^2-BOS in L^2, instead of doing all calculations in $W_2^{(1)}$. It is interesting to note that the *final* coefficients c_n do *not* depend on whether they are determined in L^2, $W_2^{(1)}$ or $W_2^{(2)}$, whereas the coefficients c_n^N, obtained by different methods, do, of course.

E. Examples of Minimal Basis Sets

As an illustration of the concepts of minimality, biorthonormality, exact completeness, and overcompleteness numerous examples can be given, among them basis sets that are of special interest in quantum chemistry like the *Hylleraas* and *Pekeris basis sets* [cf. Eqs. (32), (37), (41)]. A representative example of a minimal set was first discussed by Kaczmarz and Steinhaus (1951, Chapter VIII): With $\{\chi_n\}_{n=1}^{\infty}$ denoting an arbitrary orthonormal set in **H**,

$$\{\phi_n = 2^{-1/2}(\chi_{n+1} - \chi_n)\}_{n=1}^{\infty} \tag{28}$$

is a minimal set in **H** having *the* BOS

$$\left\{\phi_n^* = -\sqrt{2}\sum_{k=1}^{n}\chi_k\right\}_{n=1}^{\infty}. \tag{29}$$

Moreover, if $\{\chi_n\}_{n=1}^{\infty}$ is complete in **H**, then so is the set (28) (see Kaczmarz and Steinhaus, 1951, p. 273), i.e., (28) is exactly complete. All the other properties of (28) discussed below are summarized in Table III.

1. *The Modified Hydrogen Eigenfunctions*

As a special example of (28), we consider Laguerre's orthonormal functions (see Courant and Hilbert, 1953, p. 93)

$$\chi_n(x) = [(n-1)!]^{-1}\exp(-x/2)L_{n-1}(x), \qquad n = 1, 2, 3, \ldots, \tag{30}$$

which form a complete orthonormal set in $\mathbf{H} = L^2(\mathbf{R}^+)$. By Eq. (28) we get the special minimal and thus exactly complete set

$$\left\{\phi_n = (\sqrt{2}nn!)^{-1}\exp\left(-\frac{x}{2}\right)x\,\frac{dL_n(x)}{dx}\right\}_{n=1}^{\infty}. \tag{31}$$

This corresponds to the spherically symmetric *modified* hydrogen eigenfunctions in $L^2(\mathbf{R}^+)$, first used by Hylleraas (1928, 1964).

The full set of modified hydrogen eigenfunctions in $\mathbf{H} = L^2(\mathbf{R}^3)$, which were introduced by Hylleraas (1928) as a basis set for variational calculations in order to have a *complete*[10] set in $L^2(\mathbf{R}^3)$, is

$$\{\phi_{nlm}(\mathbf{r}) = R_{nl}(\zeta, r)\; Y_{lm}(\vartheta, \varphi)\}_{n>l, l\geq 0, m\leq l}, \tag{32}$$

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[10] It is well known that the discrete hydrogen eigenfunctions do not form a complete set.

with $\mathbf{r} = (r, \vartheta, \varphi)$ the spherical coordinates, $Y_{lm}(\vartheta, \varphi)$ the spherical harmonics, and $(\zeta > 0)$

$$R_{nl}(\zeta, r) = \left[\frac{(n - l - 1)!\zeta}{2n[(n + l)!]^3}\right]^{1/2} \left(\frac{r}{\zeta}\right)^l \exp\left(-\frac{\zeta r}{2}\right) \frac{d^{2l+1}}{dr^{2l+1}} L_{n+l}(\zeta r). \tag{33}$$

The comparison of (32) and (33) with the hydrogen eigenfunctions shows that the latter differ from the modified ones (32) by an orbital exponent $\zeta(n) = 2/n$, varying with n. This has the consequence that the set (32) is not orthogonal in the usual sense, but orthogonal with a weight factor r^{-1}:

$$(\phi_{nlm}, r^{-1}\phi_{n'l'm'}) = (\zeta/2n)\delta_{nn'}\delta_{ll'}\delta_{mm'}. \tag{34}$$

Equation (34) shows that

$$\{\phi^*_{nlm} = (2n/\zeta r)\phi_{nlm}\}_{n>l,\, l\geq 0,\, |m|\leq l} \tag{35}$$

is the BOS of (32) in $L^2(\mathbf{R}^3)$, and since (32) is complete in $L^2(\mathbf{R}^3)$ (see Klahn and Bingel, 1977a), (32) is an exactly complete set in $L^2(\mathbf{R}^3)$. Therefore, any $\Psi \in L^2(\mathbf{R}^3)$ has a formal expansion in terms of (32), according to Eq. (25).

But what about the properties of (32) in *Sobolev* spaces [cf. Eq. (2)]? The completeness of (32) in $W_2^{(1)}(\mathbf{R}^3)$ and $W_2^{(1)}$ is well known (see Klahn and Bingel, 1977a). Now, minimality in L^2 implies minimality in $W_2^{(1)}$ and in $W_2^{(2)}$ (see Table V). Thus, (32) is also exactly complete in $W_2^{(1)}(\mathbf{R}^3)$ and $W_2^{(2)}(\mathbf{R}^3)$.

One can furthermore simply verify that

$$\left(\frac{2}{\zeta}\phi_{nlm}, \left(\frac{1}{8}\zeta^2 - \frac{1}{2}\nabla^2\right)\frac{2}{\zeta}\phi_{n'l'm'}\right) = \delta_{nn'}\delta_{ll'}\delta_{mm'} \tag{36}$$

with ∇ the gradient operator. This equation says that $\{2\zeta^{-1}\phi_{nlm}\}$ with $n > l$, $l \geq 0$, and $|m| \leq l$ is an *orthonormal* set in[11] $W_2^{(1)}(\mathbf{R}^3)$. Consequently, the partial sums of the formal expansion of an arbitrary $\Psi \in W_2^{(1)}(\mathbf{R}^3)$ [cf. Eq. (72)] *converge* to Ψ in the sense of Eq. (7), relative to the $W_2^{(1)}$ norm and all the more in the mean. In particular a wave function that fulfills $\Psi \in W_2^{(2)}(\mathbf{R}^3) \subset W_2^{(1)}(\mathbf{R}^3)$, has a formal expansion in terms of (32) representing Ψ in the mean and in $W_2^{(1)}(\mathbf{R}^3)$.

2. *Two-Electron Hylleraas Basis for S-States*

A *two*-electron basis set for S-states, obtained from (32), is[12]

$$\left\{\phi_{nn'l}(r_1, r_2, \vartheta) = \frac{(2l + 1)^{1/2}}{4\pi} R_{nl}(\zeta, r_1)\, R_{n'l}(\zeta, r_2)\, P_l(\cos\vartheta)\right\}_{n,n'>l\geq 0}, \tag{37}$$

---

[11] The number c of Eq. (2) has been chosen as $c = \zeta^2/4$ in Eq. (36). For the case of a different equivalent normalization in $W_2^{(1)}$ see Section III,L.

[12] For the choice of coordinates see Hylleraas (1928, 1964).

with P_l the Legendre polynomials (see Courant and Hilbert, 1953, p. 82) and R_{nl} as defined in Eq. (33). The minimality of (37) in $L^2(\mathbf{R}^6)$ is shown by the existence of the appertaining BOS

$$\left\{ \phi^*_{nn'l} = \frac{4nn'}{\zeta^2 r_1 r_2} \; \phi_{nn'l} \right\}_{n,n'>l\geq 0} . \tag{38}$$

Since (37) is furthermore complete in the spaces[13] S-$L^2(\mathbf{R}^6)$, S-$W_2^{(1)}(\mathbf{R}^6)$, and S-$W_2^{(2)}(\mathbf{R}^6)$ (see Klahn and Bingel, 1977a), the set is exactly complete in these three spaces (see, also Table V) and leads therefore to formal expansions of arbitrary S-states. Similarly, as for the set (32), it can be shown by an orthogonality argument like (36) that the formal expansions of all $\Psi \in$ S-$W_2^{(2)}(\mathbf{R}^6)$ in (37) represent Ψ in the $W_2^{(1)}(\mathbf{R}^6)$ norm and thus all the more in the mean [in the sense of Eq. (7)].

3. *The Pekeris Basis*

As a preparation for the comprehension of the minimality properties of the Pekeris basis set, we first consider ($\alpha \geq 0$)

$$\{\phi_n(\alpha, x) = x^\alpha \chi_n(x)\}_{n=1}^\infty \tag{39}$$

in $\mathbf{H} = L^2(\mathbf{R}^+)$, with χ_n again denoting Laguerre's orthonormal functions of Eq. (30). This set, which is well known to be complete for all positive α, and which is obviously orthonormal for $\alpha = 0$, has the curious property of being *exactly* complete (and thus minimal) for all $\alpha < \frac{1}{2}$ and of becoming *over*complete (and thus nonminimal) for $\alpha \geq \frac{1}{2}$. A more detailed investigation shows that the sets

$$\{\phi_n(\alpha, x)\}_{n=1}^\infty \qquad \text{for} \qquad \alpha < \tfrac{1}{2} \tag{40a}$$

$$\{\phi_n(\alpha, x)\}_{n=1, n\neq n(1)}^\infty \qquad \text{for} \quad \tfrac{1}{2} \leq \alpha < \tfrac{3}{2} \tag{40b}$$

$$\{\phi_n(\alpha, x)\}_{n=1, n\neq n(1), n(2)}^\infty \qquad \text{for} \quad \tfrac{3}{2} \leq \alpha < \tfrac{5}{2} \tag{40c}$$

and so forth are each *exactly* complete, where $n\,(1)$ and $n\,(2)$ are arbitrary different positive integers. This means that the *over*completeness, or more precisely the nonminimality, of (39) in the regions $\frac{1}{2} \leq \alpha < \frac{3}{2}$ or $\frac{3}{2} \leq \alpha < \frac{5}{2}$ can be *removed* by the deletion of one or, respectively, two arbitrarily chosen functions. The proof of this remarkable fact for $\alpha < \frac{3}{2}$ is given in Appendix A.

As an application of the special case $\alpha = \frac{1}{2}$, we consider the Pekeris basis set (see Pekeris, 1958, 1959)

$$\{\phi_{nml}(x, y, z) = L_{n-1}(x)\, L_{m-1}(y)\, L_{l-1}(z) \exp[-\tfrac{1}{2}(x + y + z)]\}_{n,m,l=1}^\infty \tag{41}$$

---

[13] S-$L^2(\mathbf{R}^6)$, S-$W_2^{(1)}(\mathbf{R}^6)$, and S-$W_2^{(2)}(\mathbf{R}^6)$ denote the subspaces of all S-functions of $L^2(\mathbf{R}^6)$, $W_2^{(1)}(\mathbf{R}^6)$, and $W_2^{(2)}(\mathbf{R}^6)$.

in S-$L^2(\mathbf{R}^6)$, where x, y, and z denote *perimetric* coordinates. Since S-$L^2(\mathbf{R}^6)$ can in perimetric coordinates be described as the three-dimensional weighted L^2 space $L^2_\rho(\mathbf{R}^{+3})$ with the weight function

$$\rho(x, y, z) = 8\pi^2(x + \tfrac{1}{2}z)(y + \tfrac{1}{2}z)(x + y) \tag{42}$$

(see Hylleraas, 1964, especially p. 22), all completeness and linear independence considerations of (41) can be performed for

$$\{\rho^{1/2}\phi_{nml}\}_{n,m,l=1}^{\infty} \quad \text{in} \quad \mathbf{H} = L^2(\mathbf{R}^{+3}) \tag{43}$$

(see Sections IV,B and D). This shows that the question of the exact and overcompleteness of (41) is essentially answered by the example (39) for $\alpha = \frac{1}{2}$. Indeed, an analogous consideration for (43), as given in Appendix A, shows that the Pekeris basis set (41) is *over*complete in S-$L^2(\mathbf{R}^6)$: One may omit at least one arbitrary element from (41) without destroying its completeness. Therefore, using (41) as a basis set in a variational calculation for He S-states, no conclusion as to the behavior of the expansion coefficients c_n^N as $N \to \infty$ an be drawn so far.

However, (41) is exactly complete in S-$W_2^{(1)}(\mathbf{R}^6)$ and S-$W_2^{(2)}(\mathbf{R}^6)$, i.e., the c_n^N, if they are obtained from a *Rayleigh–Ritz* method or a *variance minimization* (see Section III,D), converge indeed according to Eqs. (5) and (24a): The completeness of (41) in S-$W_2^{(1)}(\mathbf{R}^6)$ and S-$W_2^{(2)}(\mathbf{R}^6)$ was shown by Klahn and Bingel (1977a); the minimality follows from the existence of a BOS in S-$W_2^{(1)}(\mathbf{R}^6)$ (see Appendix B and Table V). Therefore in a Rayleigh–Ritz calculation no single function of (41) can be left out in spite of its overcompleteness in S-$L^2(\mathbf{R}^6)$!

4. *Miscellaneous Basis Sets*

We know that the set $\{\exp(-\zeta_n x)\}_{n=1}^{\infty}$, if it is complete at all, i.e., if Eq. (8) holds, is overcomplete and thus nonminimal. But what happens if the set is incomplete, i.e., if Eq. (8) does not hold? The simple answer, which in a bit different form can be found in mathematical textbooks (e.g., Achieser and Glasmann, 1968, p. 36), is a complement of the theorem of Müntz and Szász:

The set of exponential-type functions $\{\exp(-\zeta_n x)\}_{n=1}^{\infty}$ is *minimal* in $L^2(\mathbf{R}^+)$ if and only if

$$\sum_{n=1}^{\infty} \zeta_n/(1 + \zeta_n^2) < \infty \tag{44}$$

is fulfilled, i.e., if and only if the system is *in*complete in $L^2(\mathbf{R}^+)$.

The next example may again demonstrate that our feeling for exact and overcompleteness in infinite-dimensional spaces is rather restricted: The set

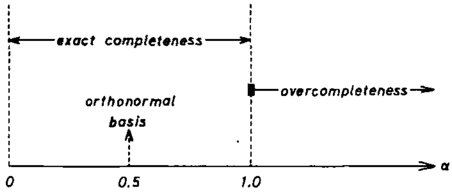

Fig. 3. Minimality properties of the basis set (45) in terms of the parameter α. Overcompleteness means that an arbitrary finite number of functions can be omitted without destroying the completeness.

$$\left\{ \phi_n(\alpha, x) = \frac{H_n(x)\exp(-\alpha x^2)}{(2^n n!\sqrt{\pi})^{1/2}} \right\}_{n=0}^{\infty}, \tag{45}$$

where $H_n(x)$ are Hermite's polynomials (see Courant and Hilbert, 1953, p. 91) and α is a positive number, has the surprising property of being *exactly* complete in $L^2(\mathbf{R})$ if $\alpha < 1$, and *over*complete in $L^2(\mathbf{R})$ if $\alpha \geq 1$ (see Fig. 3), as shown by the following considerations: The completeness of (45) is well known for any $\alpha > 0$ (Achieser and Glasmann, 1968, p. 33). Furthermore, (45) is *orthonormal* for $\alpha = \frac{1}{2}$ and thus

$$\{\phi_n^*(\alpha, x) = \phi_n(1 - \alpha, x)\}_{n=0}^{\infty} \tag{46}$$

is the BOS of (45) if $\alpha < 1$. This proves the exact completeness of (45) for $\alpha < 1$. However, for $\alpha \geq 1$ we have $\{\phi_n^*(\alpha, x)\}_{n=0}^{\infty} \not\subset L^2(\mathbf{R})$ and thus (46) is no longer a BOS of (45). That (45) is indeed overcomplete for $\alpha = 1$ is seen from the fact that the set of Fourier transformed elements[14]

$$\left\{ \hat{\phi}_n(1, p) = i^n \frac{p^n \exp(-p^2/4)}{(2^{n+1} n!\sqrt{\pi})^{1/2}} \right\}_{n=0}^{\infty} \tag{47}$$

forms an overcomplete set in $L^2(\mathbf{R})$: An arbitrary finite number of elements may be deleted from (47) without destroying its completeness (see the last example of this section). Because of the equality

$$\phi_n(\alpha, x) = \exp[-(\alpha - 1)x^2]\phi_n(1, x) \tag{48}$$

nonminimality also obtains for $\alpha > 1$, since this property is preserved under bounded linear transformations (Section IV,C,1).

As a last nice example, we consider $\{x^n \exp(-\alpha x^2)\}_{n=0}^{\infty}$. This set is overcomplete in every Sobolev space $W_2^{(r)}(\mathbf{R})$: Any finite number of functions can be omitted, however, with the exception of the first r functions $\{x^n \exp(-\alpha x^2)\}_{n=0}^{r-1}$, which are indispensable. The proof of this assertion, which should be performed in momentum space, is left to the reader as an exercise.

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[14] Note that unitary transformations preserve both completeness and linear independence properties.

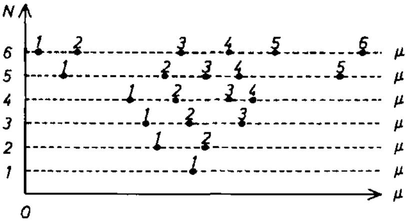

Fig. 4. Schematic illustration for the distribution of the eigenvalues μ_n^N ($n = 1, \ldots, N$) of Gram's matrix $S^{(N)}$ with increasing N, as given by the separation theorem (50). The numbers above the points, marking μ_n^N, denote the index n.

F. Besselian Sets

In numerical calculations the *degree* of linear independence of a *finite* set $\{\phi_n\}_{n=1}^N$ is often measured by the lowest eigenvalue $\mu_1^N(\phi_1, \ldots, \phi_N)$ of the overlap matrix $S^{(N)}$; sometimes, μ_1^N is called the *"measure of linear independence"* (see Courant and Hilbert, 1953, p. 61). However, the behavior of μ_1^N with increasing N is also of interest for analytic investigations.

The measure of linear independence is always a nonnegative number, since it is the minimum of the quadratic form of the overlap matrix[15]

$$\mu_1^N(\phi_1, \ldots, \phi_N) = \min_{c\in C^N} \frac{c^\dagger S^{(N)} c}{c^\dagger c} = \min_{c\in C^N} \frac{\left\| \sum_{n=1}^{N} c_n\phi_n \right\|^2}{\sum_{n=1}^{N} |c_n|^2} \tag{49}$$

and we have $\mu_1^N = 0$ if and only if $\{\phi_n\}_{n=1}^N$ is linearly dependent. Furthermore, $\{\mu_1^N\}_{N=1}^\infty$ forms a *monotonically decreasing* sequence of numbers with increasing N. This follows from the well known *separation theorem* of McDonald (1933) and Davies (1960), which is illustrated in Fig. 4:

$$\mu_n^N \geq \mu_n^{N+1} \qquad (n = 1, \ldots, N) \tag{50a}$$

$$\mu_{n+1}^{N+1} \geq \mu_n^N \qquad (n = 1, \ldots, N), \tag{50b}$$

where μ_n^N ($n = 1, \ldots, N$) denote the eigenvalues of $S^{(N)}$, arranged in order of their size. Thus, the sequence $\{\mu_1^N\}_{N=1}^\infty$ must have a nonnegative limit

$$\mu = \lim_{N\to\infty} \mu_1^N(\phi_1, \ldots, \phi_N) \geq 0. \tag{51}$$

This fact leads to a new definition of linear independence: The set $\{\phi_n\}_{n=1}^\infty$ is called *Besselian* if $\mu > 0$, and *non-Besselian* if $\mu = 0$.

An equivalent definition, preferred by mathematicians (Singer, 1970, p. 337; Kiesewetter, 1973, p. 154; Higgins, 1977, p. 74; Bari, 1951;

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[15] c† denotes the adjoint of c.

Pelczynski and Singer, 1964; Čanturija, 1964; Veic, 1965), which needs only the existence of a *norm* and which is therefore valid even in *Banach* spaces, can easily be obtained from Eq. (49):

The set $\{\phi_n\}_{n=1}^{\infty}$ is Besselian if there exists a positive constant μ, which should be chosen as large as possible,[16] such that

$$\mu \sum_{n=1}^{N} |c_n|^2 \leq \left\| \sum_{n=1}^{N} c_n \phi_n \right\|^2 \tag{52}$$

holds for all sequences $\{c_n\}_{n=1}^{N}$ of complex numbers and all $N = 1, 2, 3, \ldots$.

Thus, for non-Besselian sets, the measure of linear independence goes to zero for increasing N, and the finite set $\{\phi_n\}_{n=1}^{N}$ then is sometimes called *"almost linearly dependent"* for sufficiently large N (see Courant and Hilbert, 1953, p. 63). Such a behavior of μ_1^N is rather often observed in numerical calculations. Well-known examples of this type are the sets $\{\exp(-nx)\}_{n=1}^{N}$ and $\{x^{n-1} \exp(-x)\}_{n=1}^{N}$ in $L^2(\mathbf{R}^+)$ (see Löwdin, 1962, and Tables I and II).

It should be emphasized that the Bessel property may depend on the *normalization* of $\{\phi_n\}_{n=1}^{\infty}$, different from the criteria of linear independence discussed before. For instance, an *orthogonal* system with the property $\|\phi_n\| \to 0$ $(n \to \infty)$ is obviously *non*-Besselian, since in this case

$$\mu_1^N = \min_{1 \leq n \leq N} \|\phi_n\|^2 \to 0 \qquad (N \to \infty), \tag{53}$$

whereas the appertaining ortho*normal* system $\{\|\phi_n\|^{-1}\phi_n\}_{n=1}^{\infty}$ leads to $\mu = 1$ and is therefore Besselian. In order to get a criterion that is invariant against different normalizations, in an earlier article (Klahn and Bingel, 1977b) $\{\phi_n\}_{n=1}^{\infty}$ was called linearly independent if $\{\|\phi_n\|^{-1}\phi_n\}_{n=1}^{\infty}$ is Besselian. However, this is not a conventional definition in the mathematical literature.

One should note that the same problem occurs already in a finite-dimensional space: Almost linear dependence depends also on the normalization of $\{\phi_n\}_{n=1}^{N}$, as can be seen from Eq. (53) for fixed N.

For the special case of a basis set that is normalized to *unity*, there are some extra properties valid for μ_1^N and μ: The trace of the overlap matrix is equal to the number of functions, i.e., we have (see Gantmacher, 1977, p. 87)

$$\sum_{n=1}^{N} \mu_n^N = \operatorname{tr} \mathbf{S}^{(N)} = N \tag{54}$$

---

[16] This additional condition guarantees that μ is equal to the value of Eq. (51).

The case $N = 1$ and Eq. (50a) then imply

$$0 \le \mu \le \mu_1^{N+1} \le \mu_1^N \le 1, \qquad N = 1, 2, 3, \ldots . \tag{55}$$

Moreover, $\mu = 1$ holds if and only if $\{\phi_n\}_{n=1}^{\infty}$ is orthonormal: The implication from orthonormality to $\mu = 1$ is trivial; the reverse assertion follows from Eqs. (54) and (55): $\mu = 1$ implies $\mu_1^N = 1$ by Eq. (55) and thus $\mu_n^N = 1$ $(n = 1, \ldots, N)$ for all N by Eq. (54), which completes the proof.

Now, it follows immediately from Eqs. (18) and (21) that Besselian sets are always minimal, i.e., they always have a BOS (see Fig. 2): Let $\{\mu_n^{N-1,k}\}_{n=1}^{N-1}$ denote the eigenvalues of Gram's matrix for $\{\phi_n\}_{n=1,n\neq k}^{N}$, then the distance between ϕ_k and $[\phi_n]_{n=1,n\neq k}^{N}$ becomes by Eqs. (18) and (104)

$$\begin{aligned}&\delta^{(N-1)}(\phi_k; \phi_1, \ldots, \phi_{k-1}, \phi_{k+1}, \ldots, \phi_N)\\ &\quad = \left[\frac{\mu_1^N \cdot \mu_2^N \cdots \mu_N^N}{\mu_1^{N-1,k} \cdots \mu_{N-1}^{N-1,k}}\right]^{1/2}\end{aligned} \tag{56}$$

Using the separation theorem (50b), we get

$$\delta^{(N-1)}(\phi_k; \phi_1, \ldots, \phi_{k-1}, \phi_{k+1}, \ldots, \phi_N) \ge (\mu_1^N)^{1/2} \ge \mu^{1/2}. \tag{57}$$

Thus, minimality obtains from $\mu > 0$ by characterization (b) of minimality (Section III,C,1).

However, on the other hand, minimality does not imply the Bessel property. For instance, the set (28) is *minimal,* but *non*-Besselian[17]: its overlap matrix is a Jacobi matrix, whose elements read

$$\mathbf{S}_{nm}^{(N)} = \begin{cases} 1 & \text{for} \quad n = m \\ -\frac{1}{2} & \text{for} \quad |n - m| = 1 \\ 0 & \text{otherwise} \end{cases} \tag{58}$$

such that the eigenvalues of $\mathbf{S}^{(N)}$ are (see Zurmühl, 1958, p. 222)

$$\mu_n^N = 1 - \cos[\pi n/(N + 1)] \qquad (n = 1, \ldots, N), \tag{59}$$

i.e., we have $\mu_1^N \to 0$ $(N \to \infty)$. Moreover, we note that the largest eigenvalue μ_N^N is bounded from above:

$$\mu_N^N \le 2. \tag{60}$$

Since the Bessel property is a stronger property of linear independence than minimality, $\mu > 0$ should also imply stronger statements. Indeed, using Eqs. (57), (21), and (24b), we get an estimate for the rate of convergence of the expansion coefficients, which is given by

$$|c_n^N - (\Psi, \phi_n^*)| \le \mu^{-1/2} \|\Psi_N - \Psi\| \tag{61}$$

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[17] As a consequence, the Hylleraas basis sets (31), (32), and (37) are also non-Besselian in L^2.

instead of Eq. (24b). Equation (61) shows a *uniform* convergence[18] of the c_n^N $(N \to \infty)$ with respect to n, because the right-hand side is independent of n.

A simple example of a Besselian set is given by

$$\{\phi_n = 2^{-1/2}(\chi_{n+1} - \chi_1)\}_{n=1}^{\infty} \tag{62}$$

with $\{\chi_n\}_{n=1}^{\infty}$ an arbitrary orthonormal system of **H**. The appertaining Gram matrix is

$$S_{nm}^N = \begin{cases} 1 & \text{for} \quad n = m \\ \frac{1}{2} & \text{for} \quad n \neq m \end{cases} \tag{63}$$

having the eigenvalues

$$\mu_n^N = \begin{cases} \frac{1}{2} & \text{for} \quad n = 1, \ldots, N-1 \\ \frac{1}{2}(N+1) & \text{for} \quad n = N \end{cases} \tag{64}$$

Thus, (62) is Besselian with $\mu = \frac{1}{2}$. Consequently, it is minimal, which can also be seen from the existence of *the* BOS

$$\{\phi_n^* = \sqrt{2}\chi_{n+1}\}_{n=1}^{\infty}. \tag{65}$$

All the properties of (62), discussed here and below, are also summarized in Table III.

Another, more physical example of a Besselian set is the basis set of "*even-tempered* functions," used by Raffenetti (1973) and Bardo and Rüdenberg (1973) for the approximation of atomic SCF orbitals (see also Feller and Rüdenberg, 1979; Schmidt and Rüdenberg 1979; Klahn and Bingel, 1977b). These functions are essentially exponential-type functions, as discussed in the theorem of Müntz and Szász, with orbital exponents, which form a geometric series. For example, with respect to the set $\{\sqrt{2}\zeta^{n/2} \exp(-\zeta^n x\}_{n=1}^{\infty}$, the author could prove its Bessel property in $L^2(\mathbf{R}^+)$ analytically by Eq. (52), at least for $\zeta \in (0, 1/25)$ and $\zeta > 25$. However, better estimates might enlarge this range, possibly up to all $\zeta > 0$ with $\zeta \neq 1$ (cf. also Section III,L).

Also, an infinite set of normalized equal functions, which are centered in the form of a half-infinite linear chain, and which have an overlap $|S| < \frac{1}{2}$ only with next neighbors, is a Besselian set. The analysis is quite the same as for the set (99), if putting $S = -\lambda/(1 + \lambda^2)$, since (99) has the same overlap matrix. Equation (101a) shows that $\mu = 1 - 2|S|$.

---

[18] The Bessel property is only a sufficient, but not a necessary condition for achieving uniform convergence. For instance, as is simple to verify by (58), (18), and (21), we get $\delta_k = \delta > 0$ $(k = 1, 2, 3, \ldots)$ for the set (28), and thus *uniform* convergence for the c_n^N by (24b), although (28) is *non*-Besselian.

TABLE III

THE LINEAR INDEPENDENCE PROPERTIES OF $\{\phi_n\}_{n=1}^{\infty}$, AS DEFINED IN EQ. (28) OR EQ. (62), RESPECTIVELY[a]

Property	Set (28)	Set (62)	If $\overline{[\chi_n]} = \mathbf{H}$
ϕ_n	$2^{-1/2}(\chi_{n+1} - \chi_n)$	$2^{-1/2}(\chi_{n+1} - \chi_1)$	—
$\overline{[\phi_n]} = \overline{[\chi_n]}$?	Yes	Yes	$\{\phi_n\}_{n=1}^{\infty}$ complete
Minimal?	Yes	Yes	
ϕ_n^*	$-\sqrt{2} \sum_{k=1}^{n} \chi_k$	$\sqrt{2}\chi_{n+1}$	$\{\phi_n\}_{n=1}^{\infty}$ is exactly complete
$\overline{[\phi_n^*]} = \overline{[\phi_n]}$?	Yes	No	BOS of (28): complete BOS of (62): incomplete
$\mu_n^N \; (n = 1, \ldots, N)$	$1 - \cos \dfrac{n\pi}{N+1}$	$\frac{1}{2} \; (n \leq N - 1), \quad \dfrac{N+1}{2} \; (n = N)$	—
Besselian?	No ($\mu = 0$)	Yes ($\mu = \frac{1}{2}$)	—
Hilbertian?	Yes ($\mu' = 2$)	No ($\mu' = \infty$)	—
Uniformly minimal?	No	No	$\{\phi_n\}_{n=1}^{\infty}$ no Schauder basis
Eq. (95) holds?	Yes	No	—
Riesz system?	No ($\mu = 0$)	No ($\mu' = \infty$)	—
γ_N	$(N + 1)/2^N$	$(N + 1)/2^N$	—
γ-Independent?	No ($\gamma = 0$)	No ($\gamma = 0$)	—

[a] $\{\chi_n\}_{n=1}^{\infty}$ denotes an arbitrary orthonormal set in **H**.

G. Hilbertian Sets

Instead of the smallest eigenvalue of the overlap matrix, we consider now its largest one μ_N^N. By the separation theorem (50b), this value is *monotonically increasing* with N, and it is always positive, of course. However, the sequence $\{\mu_N^N\}_{N=1}^{\infty}$ may be either bounded or unbounded from above, i.e., the limiting value

$$\mu' = \lim_{N\to\infty} \mu_N^N(\phi_1, \ldots, \phi_N) \tag{66}$$

can be finite or infinite.

The basis set is called *Hilbertian* if $\mu' < \infty$, and *non-Hilbertian* if $\mu' = \infty$. An equivalent definition of Hilbertian sets is that there exists a positive constant μ', which should be chosen as small as possible, such that

$$\left\| \sum_{n=1}^{N} c_n \phi_n \right\|^2 \leq \mu' \sum_{n=1}^{N} |c_n|^2 \tag{67}$$

holds for all sequences $\{c_n\}_{n=1}^{N}$ of complex numbers and all $N = 1, 2, 3, \ldots$ (see Singer, 1970, p. 338; Higgins, 1977, p. 74).

It is by no means self-evident that a basis set is Hilbertian, as seen from the set (62), which is Besselian but non-Hilbertian by Eq. (64). An example of a Hilbertian set is given by the set (28) [see Eq. (60)].

Just as for Besselian sets, the Hilbert property depends on the normalization of the elements ϕ_n, again. Especially for sets that are *normalized to unity,* we have in complete analogy to Eq. (55)

$$1 \leq \mu_N^N \leq \mu_{N+1}^{N+1} \leq \mu' \leq \infty, \qquad N = 1, 2, 3, \ldots, \tag{68}$$

and the case $\mu' = 1$ occurs if and only if $\{\phi_n\}_{n=1}^{\infty}$ is orthonormal. Moreover, since $\mu_1^N \geq 0$, a simple consequence of Eq. (54) is that

$$\mu_N^N \leq N. \tag{69}$$

This tells us that μ_N^N goes to infinity, if at all, rather slowly. [For an example, see Eq. (64).] For comparison, the measure of linear independence μ_1^N may decrease to zero *exponentially* (see Löwdin, 1962; Tables I and II).

The *numerical stability* of a symmetric orthogonalization (see Löwdin, 1956) is mainly governed by the ratio μ_1^N/μ_N^N; in order to get reasonable results, one needs a higher computational accuracy, the less this ratio is. However, Eq. (69) explains why for practical purposes it is sufficient to consider μ_1^N alone as a measure of stability.

Indeed, the Hilbert property by itself is not at all a criterion of linear independence. This is only the case for the Hilbert and Bessel properties together ("Riesz property," see Section III,L). But Besselian and Hilbertian sets have an interesting *duality* property:

The BOS of a Besselian set ($\mu > 0$) is Hilbertian, and *the* BOS of a Hilbertian set ($\mu' < \infty$), if it exists, is Besselian. Moreover, the characteristic values $(\mu')^*$ and μ^* of *the* BOS, defined in Eqs. (66) and (51), are $(\mu')^* = \mu^{-1}$ and $\mu^* = (\mu')^{-1}$, respectively. The proof of this statement makes essential use of Eq. (129). It is also contained in the repeatedly cited book of Singer (1970, p. 338), however, under the additional assumption that $\{\phi_n\}_{n=1}^{\infty}$ is a Schauder basis. Note that the statement becomes wrong if an *arbitrary* BOS instead of *the* BOS is considered, e.g., if $\{\phi_n\}_{n=1}^{\infty}$ is given by Eq. (65) and $\{\phi_n^*\}_{n=1}^{\infty}$ by Eq. (62).

H. Minimal Sets with $\overline{[\phi_n]} = \overline{[\phi_n^*]}$

A BOS of a minimal set can always be chosen such that $\overline{[\phi_n^*]} \subset \overline{[\phi_n]}$ holds. Therefore one may ask whether even

$$\overline{[\phi_n]} = \overline{[\phi_n^*]} \tag{70}$$

is fulfilled. In the case of an exactly complete set $\{\phi_n\}_{n=1}^{\infty}$, Eq. (70) would obviously mean that the BOS is also exactly complete. As is shown by Eq. (13), such a condition is indeed valid in finite-dimensional unitary spaces. However, in Hilbert spaces, Eq. (70) may be *violated:*

For example, let us again consider the set (62) with $\{\chi_n\}_{n=1}^{\infty}$ now being a *complete* orthonormal set in **H**. Then (62) is complete, too (see Higgins, 1977, p. 19), having the unique BOS $\{\sqrt{2}\chi_{n+1}\}_{n=1}^{\infty}$ [Eq. (65)]. But this set is obviously incomplete, since χ_1 is missing. Thus we have[19]

$$\overline{[\phi_n^*]} = \overline{[\chi_{n+1}]} \neq \{\chi_1\} \oplus \overline{[\chi_{n+1}]} = \overline{[\chi_n]} = \overline{[\phi_n]}, \tag{71}$$

i.e., Eq. (70) is violated.

Therefore, Eq. (70) defines a stronger criterion of linear independence than minimality does. It is furthermore an interesting fact that neither is the Bessel property implied by (70) nor do Besselian sets always fulfill Eq. (70); e.g., the sets (28) and (29) fulfill Eq. (70) (see Section IV,B), although (28) is non-Besselian, whereas (62) is a Besselian set, which, however, violates Eq. (70). This fact implies the *extra branch* in Fig. 2 for the property (70).

Now, let our basis set $\{\phi_n\}_{n=1}^{\infty}$ be *exactly complete* such that any $\Psi \in \mathbf{H}$ has a formal expansion (25). Then the independence property (70) answers the question (4) of Section I,A at once: *The formal expansion coefficients* $\{c_n = (\Psi, \phi_n^*)\}_{n=1}^{\infty}$ *of any* $\Psi \in \mathbf{H}$ *determine this* Ψ *uniquely, i.e., there is no second element* $\Psi' \neq \Psi$ *in* **H** *with the same formal expansion coefficients if and only if Eq. (70) is fulfilled.*

The reason is: Only if (70) is violated, i.e., if $\{\phi_n^*\}_{n=1}^{\infty}$ is *in*complete, there exists a nonzero element $\Phi \in \mathbf{H}$ with $(\Phi, \phi_n^*) = 0$ $(n = 1, 2, 3, \ldots)$ such that both elements Ψ and $\Psi + \Phi$ have the same formal expansion.

Just as the previous criteria of linear independence, Eq. (70) does not guarantee that the formal expansion of Ψ fulfills Eq. (7). However, let us *assume* that the formal expansion of Ψ represents some element $\Psi' \in \mathbf{H}$, i.e., that the partial sums

$$s_N(\Psi) = \sum_{n=1}^{N} (\Psi, \phi_n^*)\phi_n \tag{72}$$

converge to Ψ' in the norm of **H**. Then Eq. (70) implies $\Psi' = \Psi$, since

$$(\Psi - \Psi', \phi_n^*) = (s_N(\Psi), \phi_n^*) - (\Psi', \phi_n^*) \rightarrow 0 \qquad (N \rightarrow \infty) \tag{73}$$

for all $n = 1, 2, 3, \ldots$ .Vice versa, if Eq. (70) does not hold, then we have $\Psi' \neq \Psi$ either with respect to Ψ itself or with respect to $\Psi + \Phi$ instead, where Φ is again an element of **H** with $(\Phi, \phi_n^*) = 0$ $(n = 1, 2, 3, \ldots)$.

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[19] Equation (71) holds even if $\{\chi_n\}_{n=1}^{\infty}$ is incomplete in **H**.

Thus, Eq. (70) is the necessary and sufficient condition in order to guarantee that the formal expansions of all $\Psi \in \mathbf{H}$, which represent an element at all, represent just Ψ itself (see also Singer, 1970, p. 32; Banach, 1932, p. 106).

I. Pathological Properties of Formal Expansions

1. *The Pathological Cases*

The formal expansion (25) of an element $\Psi \in \mathbf{H}$ does not normally represent Ψ, even if the basis set is complete in $\mathbf{H}$ (cf. Kaczmarz and Steinhaus, 1951, p. 271). What can happen? The following cases can occur as $N \to \infty$, where $s_N(\Psi)$ denotes again the partial sums of Eq. (72):

(a) The desirable case that (7) is valid, i.e.,

$$\|s_N(\Psi) - \Psi\| \to 0. \tag{74}$$

(b) There exists an element $\Psi' \in \mathbf{H}$ with $\Psi' \neq \Psi$ and[20]

$$\|s_N(\Psi) - \Psi'\| \to 0. \tag{75}$$

(c) There is no element Ψ' as defined in (b), but $s_N(\Psi)$ is norm-bounded:

$$\|s_N(\Psi)\| \leq c < \infty. \tag{76}$$

(d) $s_N(\Psi)$ is not even norm-bounded.

Some examples may illustrate the cases (b)–(d): We choose any complete orthonormal set $\{\chi_n\}_{n=1}^{\infty}$ in $\mathbf{H}$ such that the basis set (62) is exactly complete. Then, the partial sums of $\Psi = \chi_1$ are [see Eqs. (72) and (65)]

$$s_N(\chi_1) = \theta \tag{77}$$

for all N, i.e., we have case (b) with $\Psi' = \theta$. Furthermore, for the element $\Psi = \sum_{n=1}^{\infty} n^{-1}\chi_n$ we get [see Eqs. (72), (62), and (65)]

$$s_N\left(\sum_{n=1}^{\infty} n^{-1}\chi_n\right) = \sum_{n=1}^{N} (n+1)^{-1}(\chi_{n+1} - \chi_1) \tag{78}$$

as an example for case (d), since the orthonormality of $\{\chi_n\}_{n=1}^{\infty}$ leads to

$$\left\| s_N\left(\sum_{n=1}^{\infty} n^{-1}\chi_n\right)\right\|^2 = \sum_{n=1}^{N} (n+1)^{-2} + \left[\sum_{n=1}^{N} (n+1)^{-1}\right]^2, \tag{79}$$

i.e., an expression that diverges as $N \to \infty$. Similar results are obtained for the set[21] (28): For $\Psi = \chi_1$, Eqs. (72) and (29) give immediately

$$s_N(\chi_1) = -\sum_{n=1}^{N} (\chi_{n+1} - \chi_n) = \chi_1 - \chi_{N+1}, \tag{80}$$

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[20] This case does not occur if (70) is fulfilled.

[21] For this set the case (b) cannot occur, since Eq. (70) is fulfilled (see Table III).

which does not converge to any $\Psi' \in \mathbf{H}$, which, however, is norm-bounded with $\|s_N(\chi_1)\| = \sqrt{2}$, i.e., we have case (c). If we choose $\{\chi_n\}_{n=1}^{\infty}$ especially to be Laguerre's orthonormal functions of Eq. (30) in $\mathbf{H} = L^2(\mathbf{R}^+)$, then Eq. (80) reads

$$s_N(\exp(-x/2)) = \exp(-x/2)[1 - (N!)^{-1}L_N(x)]. \tag{81}$$

This sequence does not converge to $\exp(-x/2)$ as $N \to \infty$, but it is norm-bounded. Analogously, the partial sums of $\Psi = \sum_{n=1}^{\infty} n^{-1}\chi_n$, obtained from Eqs. (72), (28), and (29), are

$$s_N\left(\sum_{n=1}^{\infty} n^{-1}\chi_n\right) = \sum_{n=1}^{N} n^{-1}\chi_n - \chi_{N+1}\sum_{k=1}^{N} k^{-1} \tag{82}$$

and illustrate again case (d), since the norm of $s_N(\Psi)$ is given by

$$\left\|s_N\left(\sum_{n=1}^{\infty} n^{-1}\chi_n\right)\right\|^2 = \sum_{n=1}^{N} n^{-2} + \left[\sum_{k=1}^{N} k^{-1}\right]^2 \to \infty \qquad (N \to \infty). \tag{83}$$

2. *Applications to Rayleigh–Ritz Calculations*

One may now ask whether these pathological properties play a role also with respect to the Rayleigh–Ritz method. This is indeed the case. Especially for the hydrogen atom, the basis sets of Rayleigh–Ritz calculations can be chosen such that we get the following curious properties:

(a) The Rayleigh–Ritz energies converge correctly as $N \to \infty$.

(b) The approximate Rayleigh–Ritz wave functions converge to the hydrogen eigenfunctions according to Eq. (4), where $\|\cdot\|$ denotes the $W_2^{(1)}(\mathbf{R}^3)$ norm.

(c) The Rayleigh–Ritz expansion coefficients converge according to Eq. (5), i.e., for $N \to \infty$ a formal expansion of the exact eigenstates is obtained.

(d) But nevertheless, the formal expansions of the ground state are due to the pathological cases (b) or (c) of Section III,I,1.

These properties are yielded when using again the basis sets (62) or (28), respectively, for the variational calculation, where now

$$\begin{aligned}\chi_n(\zeta, r) &= 2\zeta^{-1}\phi_{n00}(r) \\ &= (2\pi\zeta)^{-1/2}(nn!)^{-1}\exp\left(-\frac{\zeta r}{2}\right)\frac{dL_n(\zeta r)}{dr},\end{aligned} \tag{84}$$

i.e., the spherically symmetric *modified* hydrogen eigenfunction of Eq. (32), which form a complete *orthonormal* set in $\mathbf{H} = \text{S-}W_2^{(1)}(\mathbf{R}^3)$ by Eq. (36). Thus, the sets (62) and (28) are exactly complete in $\text{S-}W_2^{(1)}(\mathbf{R}^3)$ (see

Section III,E and Table III), a fact which proves the asserted properties (a)–(c) at once (see Section III,D). Moreover, if[22]

$$a_n = (\Psi, \chi_n)_{\mathrm{H}} = (\Psi, (\tfrac{1}{8}\zeta^2 - \tfrac{1}{2}\nabla^2)\chi_n), \qquad n = 1, 2, 3, \ldots, \tag{85}$$

denote the (generalized) Fourier-expansion coefficients of Ψ with respect to $\{\chi_n\}_{n=1}^{\infty}$, then by Eqs. (24a), (65), and (29) the formal expansion coefficients of Ψ are ($n = 1, 2, 3, \ldots$)

$$c_n(62) = \sqrt{2}\, a_{n+1} \qquad \text{for basis set (62)}, \tag{86a}$$

$$c_n(28) = -\sqrt{2} \sum_{k=1}^{n} a_k \qquad \text{for basis set (28)}. \tag{86b}$$

Because of Eq. (24a), these coefficients are also obtained from the variational calculation as limiting values of c_n^N as $N \to \infty$. Especially, for the hydrogen 1s state $\Psi_{1\mathrm{s}} = \pi^{-1/2}\exp(-r)$ the integration of (85) gives

$$a_n(1\mathrm{s}) = -\frac{2^{1/2}\zeta^{3/2}}{(1 + \frac{1}{2}\zeta)^2}\, n \left(\frac{1 - \frac{1}{2}\zeta}{1 + \frac{1}{2}\zeta}\right)^{n-1} \tag{87}$$

so that (86a) and (86b) yield ($n = 1, 2, 3, \ldots$)

$$c_n(62, 1\mathrm{s}) = -\frac{2\zeta^{3/2}}{(1 + \frac{1}{2}\zeta)^2}(n + 1)\left(\frac{1 - \frac{1}{2}\zeta}{1 + \frac{1}{2}\zeta}\right)^{n} \quad \text{for basis set (62)} \tag{88a}$$

$$c_n(28, 1\mathrm{s}) = 2\zeta^{-1/2}\left\{1 - (n + 1)\left(\frac{1 - \frac{1}{2}\zeta}{1 + \frac{1}{2}\zeta}\right)^{n} + n\left(\frac{1 - \frac{1}{2}\zeta}{1 + \frac{1}{2}\zeta}\right)^{n+1}\right\} \quad \text{for basis set (28)}. \tag{88b}$$

With respect to the basis set (62), the partial sums of the 1s state are

$$\begin{aligned} s_N(\Psi_{1\mathrm{s}}) &= \sum_{n=1}^{N} c_n(62, 1\mathrm{s})2^{-1/2}(\chi_{n+1} - \chi_1) \\ &= \sum_{n=1}^{N} a_{n+1}(1\mathrm{s})(\chi_{n+1} - \chi_1) \\ &= \sum_{n=1}^{N+1} a_n(1\mathrm{s})\chi_n - \chi_1 \sum_{n=1}^{N+1} a_n(1\mathrm{s}) \\ &= \sum_{n=1}^{N+1} a_n(1\mathrm{s})\chi_n + 2^{-1/2}c_{N+1}(28, 1\mathrm{s})\chi_1. \end{aligned} \tag{89}$$

The sum on the right-hand side converges to $\Psi_{1\mathrm{s}}$ in the S-$W_2^{(1)}(\mathbf{R}^3)$ norm, because it is just the truncated *Fourier expansion* of $\Psi_{1\mathrm{s}}$ with respect to $\{\chi_n\}_{n=1}^{N+1}$, and $c_{N+1}(28, 1\mathrm{s}) \to 2\zeta^{-1/2}$ ($N \to \infty$) follows from Eq. (88b). Consequently, Eq. (89) gives

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[22] Different from the notation used so far in this section $(\cdot\,,\cdot)$ denotes the scalar product in $L^2(\mathbf{R}^3)$ and $(\cdot\,,\cdot)_{\mathrm{H}}$ the scalar product in $\mathrm{H} = $ S-$W_2^{(1)}(\mathbf{R}^3)$; $\|\cdot\|_{\mathrm{H}}$ denotes the norm in S-$W_2^{(1)}(\mathbf{R}^3)$.

$$\|s_N(\Psi_{1s}) - \Psi_{1s} - (2/\zeta)^{1/2}\chi_1\|_{\mathbf{H}} \to 0 \qquad (N \to \infty). \tag{90}$$

Thus, the formal expansion of Ψ_{1s} in the basis set (62) represents an element Ψ' in the sense of Eq. (75), where $\mathbf{H} = \text{S-}W_2^{(1)}(\mathbf{R}^3)$. However, this element *differs* from the 1s eigenstate by the function $(2/\zeta)^{1/2}\chi_1 = -\pi^{-1/2} \exp(-\frac{1}{2}\zeta r)$, i.e., we have case (b) of Section III,I,1 as asserted in (d). We note that the special case $\zeta = 2$ corresponds obviously to the example discussed in Eq. (77), since $\Psi_{1s} + \chi_1 = \theta$ for $\zeta = 2$.

Since the formal expansion coefficients (88b) do not go to zero as $n \to \infty$, it is evident that the appertaining formal expansion in the basis set (28) cannot represent any element in $\text{S-}W_2^{(1)}(\mathbf{R}^3)$ (see Singer, 1970, p. 21). A similar but more tedious calculation as done in (89) gives

$$\begin{aligned} s_N(\Psi_{1s}) &= \sum_{n=1}^{N} c_n(28,\ 1\text{s})2^{-1/2}(\chi_{n+1} - \chi_n) \\ &= \sum_{n=1}^{N} a_n(1\text{s})\chi_n + 2^{-1/2}c_N(28,\ 1\text{s})\chi_{N+1}, \end{aligned} \tag{91}$$

showing that $s_N(\Psi_{1s})$ is not strongly convergent in $\mathbf{H} = \text{S-}W_2^{(1)}(\mathbf{R}^3)$. But it is norm-bounded in $\mathbf{H}$ and belongs therefore to case (c) of Section III,I,1:

$$\begin{aligned} \|s_N(\Psi_{1s})\|_{\mathbf{H}}^2 &= \sum_{n=1}^{N} a_n^2(1\text{s}) + \frac{1}{2}c_N^2(28,\ 1\text{s}) \to \|\Psi_{1s}\|_{\mathbf{H}}^2 + \frac{2}{\zeta} \\ &= \frac{1}{2} + \frac{\zeta^2}{8} + \frac{2}{\zeta} \qquad (N \to \infty). \end{aligned} \tag{92}$$

Especially, the case $\zeta = 2$ corresponds to the example (80), as seen from Eq. (88b).

J. Uniform Minimality and Schauder Bases

The possible occurrence of the cases (a)–(d) in Section III,I,1 makes it reasonable to introduce the concept of a *basis* in the true mathematical sense:

> A set $\{\phi_n\}_{n=1}^{\infty}$ is called a basis in $\mathbf{H}$ if all $\Psi \in \mathbf{H}$ have a unique expansion, such that Eq. (7) is fulfilled (Singer, 1970, p. 1; Kato, 1966, p. 265; Achieser and Glasmann, 1968, p. 40).

The notion of a basis was first introduced by Schauder (1927), especially for Banach spaces. Therefore, more precisely, one speaks sometimes of a *Schauder* basis. (For further details of this denomination, see Singer, 1970, p. 151.)

It is a trivial consequence that the sets (28) and (62) are no bases, as shown by Eqs. (77)–(83), whereas, e.g., complete orthonormal systems are always bases. Thus, especially, both Hylleraas basis sets (31) and (32) are not bases in L^2; however, (32) is a basis in $W_2^{(1)}(\mathbf{R}^3)$, nevertheless, because of its orthonormality (36).

By its definition, a basis is always *complete,* and, moreover, it is *minimal,* as can be seen from a theorem of Banach (1932, p. 111), i.e., any basis has a BOS.[23] Thus, a basis is a special exactly complete set, and one may expect that the basis property is—just like exact completeness (see Section III,C,1)—a marriage of completeness and a new form of linear independence, stronger than minimality:

We call a set $\{\phi_n\}_{n=1}^{\infty}$ *uniformly minimal* in **H** if all $\Psi \in \overline{[\phi_n]}$ have a unique expansion in terms of $\{\phi_n\}_{n=1}^{\infty}$ such that Eq. (7) is fulfilled, i.e., if $\{\phi_n\}_{n=1}^{\infty}$ is a basis of $\overline{[\phi_n]}$.[24]

This definition is chosen such that we can say: *A complete set* $\{\phi_n\}_{n=1}^{\infty}$ *is a basis in* **H** *if and only if it is uniformly minimal,* or in a short notation:

(*Schauder*) *basis property* = *completeness* + *uniform minimality.*

Another reason for the definition of uniform minimality is that this property of linear independence is just the exact condition for Eq. (7) to hold in $\overline{[\phi_n]}$. But so far uniform minimality is explained only in terms of a Schauder basis, i.e., by the validity of Eq. (7), and not by intrinsic properties of $\{\phi_n\}_{n=1}^{\infty}$ itself. It can, however, also be tested by using the following equivalent characterization:

The set $\{\phi_n\}_{n=1}^{\infty}$ is uniformly minimal in **H** if and only if there exists a constant C with $1 \leq C < \infty$ such that we have

$$\left\| \sum_{n=1}^{N} c_n \phi_n \right\| \leq C \left\| \sum_{n=1}^{N+M} c_n \phi_n \right\| \tag{93}$$

for all positive integers N and M and all complex c_n ($n = 1, \ldots, N + M$) (see Singer, 1970, p. 58; the assumption of completeness of $\{\phi_n\}_{n=1}^{\infty}$, made in Singer's proof, can be suppressed).

A comparison of Eqs. (93) and (23), where C may depend on N, shows immediately that uniform minimality is a special form of minimality, and explains also why we speak of *uniform* minimality. Moreover, we have now a final answer to question (2) of Section I,A: *Eq.* (*7*) *is valid for all* $\Psi \in \overline{[\phi_n]}$, *if and only if Eq.* (*93*) *holds.*

Let us now look for the correct place of uniform minimality in Fig. 2: Neither does the Bessel property imply uniform minimality,[25] nor does uniform minimality imply the Bessel property (for an example, see Singer,

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[23] For completeness we note that a biorthonormal system $\{\phi_n, \phi_n^*\}_{n=1}^{\infty}$ is called *regular* if $\{\phi_n\}_{n=1}^{\infty}$ is a basis.

[24] Singer (1970, p. 27) calls such a set a *basic sequence* instead.

[25] The set (62) would be a counter-example.

1970, p. 350). Thus, uniform minimality may not be displayed in the branch for Besselian sets of Fig. 2. However, uniform minimality implies always the linear independence property $\overline{[\phi_n]} = \overline{[\phi_n^*]}$ of Eq. (70),[26] as can be seen from the following *duality theorem:*

If $\{\phi_n\}_{n=1}^{\infty}$ is a basis in **H**, then the appertaining BOS $\{\phi_n^*\}_{n=1}^{\infty}$ is also a basis in **H** (see Higgins, 1977, p. 24).

If $\{\phi_n\}_{n=1}^{\infty}$ is not complete in **H**, but only uniformly minimal, then one may restrict the whole space **H** to $\tilde{\mathbf{H}} = \overline{[\phi_n]}$. Of course, the duality theorem is also valid with $\tilde{\mathbf{H}}$ instead of **H**, which proves our assertion. Therefore, uniform minimality is a stronger criterion of linear independence than Eq. (70).

From the duality theorem it follows furthermore that any $\Psi \in \mathbf{H}$ has *two* convergent expansions *if* $\{\phi_n\}_{n=1}^{\infty}$ is a basis:[27]

$$\left\| \Psi - \sum_{n=1}^{N} (\Psi, \phi_n^*)\phi_n \right\| \to 0 \qquad (N \to \infty), \tag{94a}$$

$$\left\| \Psi - \sum_{n=1}^{N} (\Psi, \phi_n)\phi_n^* \right\| \to 0 \qquad (N \to \infty). \tag{94b}$$

These equations are completely analogous to Eqs. (15a) and (15b) in a unitary space. As a consequence of (94), we get another interesting relation: If $\{\phi_n^*\}_{n=1}^{\infty}$ is *the* BOS of a uniformly minimal set $\{\phi_n\}_{n=1}^{\infty}$, then we have[28]

$$\sum_{k=1}^{\infty} (\phi_n, \phi_k)(\phi_k^*, \phi_m^*) = \delta_{nm} \qquad (n, m = 1, 2, 3, \ldots). \tag{95}$$

This equation is the analog of Eq. (12b), i.e., the analog of the fact that the Gram matrices of $\{\phi_n\}_{n=1}^{N}$ and $\{\phi_n^*\}_{n=1}^{N}$ are *inverse* to each other. Whereas this statement in unitary spaces is always correct, provided that $\{\phi_n\}_{n=1}^{N}$ has a BOS, in a Hilbert space the existence of the BOS alone, which is already a rather strong condition, is not sufficient for Eq. (95) to hold.

K. Survey

Now, our questions (1)–(4), posed in the Introduction, have been answered. Let us summarize the results, where the validity of Eq. (4) is always assumed:

(1) Equation (5) holds if the basis set is minimal (or exactly complete) in **H**, i.e., if $\{\phi_n\}_{n=1}^{\infty}$ has a BOS [see Eq. (24a)] such that the formal

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[26] The reverse of this statement is not true, as shown by the set (28).

[27] If $\{\phi_n\}_{n=1}^{\infty}$ is only exactly complete and obeys Eq. (70), but is not a basis, then the curious case can occur that for some $\Psi \in \mathbf{H}$ only one of the two equations is valid.

[28] Uniform minimality is only a sufficient criterion for (95) to hold; e.g., (95) holds for (28), which is nonuniformly minimal, however, it does not hold for (62).

expansion (6) is just the biorthonormal expansion (25). However, minimality is a rather strong condition, since it guarantees Eqs. (5) and (6) for *all* $\Psi \in \mathbf{H}$ and *independent* of the method of approximating Ψ, i.e., independent of the calculation of $\{c_n^N\}_{n=1}^N$ ($N = 1, 2, 3, \ldots$). Therefore, also for nonminimal (or overcomplete) basis sets Eq. (5) *may* hold (see Tables I and II), depending decisively on the function Ψ under consideration and the special method of its approximation. (Of course, by characterization (d) of minimality in Section III,C,1, for any given $\Psi \in \mathbf{H}$ one can choose at least one approximation $\{\Psi_N\}_{N=1}^\infty$ that leads to arbitrary limiting values in Eq. (5) for some n if $\{\phi_n\}_{n=1}^\infty$ is nonminimal.) Sometimes it is useful to look for a suitable Hilbert space $\mathbf{H}$, so that $\{\phi_n\}_{n=1}^\infty$ becomes minimal in $\mathbf{H}$. This was done, for instance, for the Pekeris basis set (41), which is overcomplete in S-$L^2(\mathbf{R}^6)$, but exactly complete in S-$W_2^{(1)}(\mathbf{R}^6)$, nevertheless.

(2) Equation (7) holds, if the basis set is uniformly minimal (or a Schauder basis) in $\mathbf{H}$, i.e., if Eq. (93) holds. However, this condition is also a rather strong condition, since it guarantees Eq. (7) for *all* $\Psi \in \mathbf{H}$, whereas a quantum chemist is normally only interested in the approximation of eigenstates, which have rather special properties. Thus, in many cases, the criterion of uniform minimality will not work. Again, it may sometimes be useful to choose the Hilbert space $\mathbf{H}$ suitably in order that $\{\phi_n\}_{n=1}^\infty$ becomes uniformly minimal, as done for the Hylleraas basis set (32), which is uniformly minimal in $W_2^{(1)}(\mathbf{R}^3)$, but not in $L^2(\mathbf{R}^3)$.

(3) Provided that an element $\Psi \in \mathbf{H}$ has an expansion in the sense of Eq. (7), then uniqueness of the expansion coefficients c_n is assured if and only if $\{\phi_n\}_{n=1}^\infty$ is ω-linearly independent.

(4) All pairs of two different elements Ψ and Ψ' have different formal expansions (25) if and only if the linear independence property (70) holds.

L. Riesz Systems

Let us now assume that our basis set is both Besselian ($\mu > 0$) *and* Hilbertian ($\mu' < \infty$). Such a set is called a *Riesz* system (Higgins, 1977, p. 74; Achieser and Glasmann, 1968, p. 45). If either $\mu = 0$ or $\mu' = \infty$ or both holds, then $\{\phi_n\}_{n=1}^\infty$ is said to be *non-Riesz*. By Eqs. (52) and (67) an equivalent definition is the following:

$\{\phi_n\}_{n=1}^\infty$ is a Riesz system if there are two constants μ and μ' (which should be chosen as large or small, respectively, as possible) such that

$$\mu \sum_{n=1}^N |c_n|^2 \le \left\| \sum_{n=1}^N c_n\phi_n \right\|^2 \le \mu' \sum_{n=1}^N |c_n|^2 \tag{96}$$

holds for all sequences $\{c_n\}_{n=1}^N$ of complex numbers for all $N = 1, 2, 3, \ldots$.

From Eq. (96), it follows at once that

$$\left\| \sum_{n=1}^{N} c_n\phi_n \right\|^2 \le \mu' \sum_{n=1}^{N} |c_n|^2 \le \mu' \sum_{n=1}^{N+M} |c_n|^2 \le \frac{\mu'}{\mu} \left\| \sum_{n=1}^{N+M} c_n\phi_n \right\|^2 \qquad (97)$$

for all positive integers N and M, i.e., Eq. (93) is fulfilled with $C = (\mu'/\mu)^{1/2}$. Thus, *every Riesz system is uniformly minimal* (see Fig. 2). Especially, we get the result (see Achieser and Glasmann, 1968, p. 41) that *any complete Riesz system is a Schauder basis in* **H**; however, a basis need not be a Riesz system, since it need not be Besselian or Hilbertian (Singer, 1970, p. 351). It is a remarkable fact that the basis property in this way may be tested in terms of special properties of the *overlap matrix.*

One can therefore try to show the validity of Eq. (7) for all $\Psi \in$ **H** by calculating the eigenvalues μ_1^N and μ_N^N of the overlap matrix $\mathbf{S}^{(N)}$ for $N \to \infty$. But since the Riesz property is still stronger than uniform minimality, it is clear that Riesz systems form a rather restricted class of basis sets and that consequently the proof of Eq. (7) in this way will often fail.

How strong the Riesz property is, indeed, becomes evident when investigating its *invariance properties* against linear transformations, as done in Section IV,C,2. It turns out that Riesz systems are, so to speak, only *"disguised" orthonormal systems:*

As is well known, any Hilbert space $\overline{[\phi_n]}$ can be endowed with different *equivalent* norms, i.e., if $\|\cdot\|$ is a norm of $\overline{[\phi_n]}$, then $\|\cdot\|'$ obeying

$$c_1\|\Psi\| \le \|\Psi\|' \le c_2\|\Psi\| \qquad \forall \quad \Psi \in \overline{[\phi_n]}; \qquad c_1, c_2 > 0, \qquad (98)$$

is also a norm of $\overline{[\phi_n]}$. If a basis set is a Riesz system with respect to $\|\cdot\|$, one can always choose a second equivalent norm $\|\cdot\|'$ such [see Eq. (131)] that the basis set becomes *orthonormal* with respect to the appertaining scalar product $(\cdot\,,\cdot)'$.

An example of a Riesz basis is the set of modified hydrogen eigenfunctions of Eq. (32) in the Sobolev space $W_2^{(1)}(\mathbf{R}^3)$ if $W_2^{(1)}(\mathbf{R}^3)$ is *arbitrarily* normalized. Only for the special choice of the norm $c = \zeta^2/4$ in Eq. (2) is the set (32) an orthonormal basis. Another example of a Riesz basis are the *nonharmonic Fourier functions* $\{(2\pi)^{-1/2}\exp(\mathrm{i}\zeta_n x)\}_{n=1}^{\infty}$ in $L^2(-\pi, \pi)$ with some restrictive conditions on the complex numbers ζ_n. The properties of this set are summarized in detail in the book of Higgins (1977, pp. 78–83).

Using Eq. (67), one can show that the *even-tempered functions* like $\{\sqrt{2}\zeta^{n/2}\exp(-\zeta^n x)\}_{n=1}^{\infty}$ in $L^2(\mathbf{R}^+)$ or their Gaussian type analogs are Hilbertian for all $\zeta > 0$ with $\zeta \neq 1$. Thus, these functions form also a Riesz system, possibly under some restrictive conditions on ζ (cf., Section III,F). Nevertheless, there are elements of $L^2(\mathbf{R}^+)$ which cannot be expanded in terms of such a Riesz set, because it is *in*complete by the Müntz–Szàsz theorem.

A last interesting example is the following generalization of (28):

$$\{\phi_n = (1 + \lambda^2)^{-1/2}(\chi_{n+1} - \lambda\chi_n)\}_{n=1}^{\infty}; \{\chi_n\}_{n=1}^{\infty} \text{ orthonormal.} \tag{99}$$

This set is a Riesz system for all $\lambda \in \mathbf{R}$ with $\lambda \neq \pm 1$, since the eigenvalues of Gram's matrix are

$$\mu_n^N = 1 - 2\frac{|\lambda|}{1 + \lambda^2}\cos\frac{n\pi}{N + 1} \qquad (n = 1, \ldots, N), \tag{100}$$

so that we get

$$\mu = 1 - 2|\lambda|/(1 + \lambda^2) \tag{101a}$$

$$\mu' = 1 + 2|\lambda|/(1 + \lambda^2) \tag{101b}$$

by Eqs. (51) and (66). Moreover, (99) is simply shown to be complete in $\overline{[\chi_n]}$ if and only if $|\lambda| \geq 1$. Therefore, (99) is a Riesz *basis* in $\overline{[\chi_n]}$ for all $\lambda \in \mathbf{R}$ with $|\lambda| > 1$.

M. γ-Linear Independence

Since the positivity of Gram's determinant γ_N is a criterion of linear independence in a finite-dimensional unitary space (see Section II), let us investigate how to define the determinant of an infinite-dimensional overlap matrix and what such a concept means.

It seems reasonable to define

$$\gamma = \lim_{N\to\infty} \gamma_N(\phi_1, \ldots, \phi_N) \tag{102}$$

as Gram's determinant of the infinite set $\{\phi_n\}_{n=1}^{\infty}$. However, Eq. (102) may be meaningless: If, for instance, $\{\phi_n\}_{n=1}^{\infty}$ is an *orthogonal* set with $\|\phi_{2n-1}\| = n$ and $\|\phi_{2n}\| = n^{-1}$ $(n = 1, 2, 3, \ldots)$, then we have $\gamma_{2N-1} = N^2$ and $\gamma_{2N} = 1$ $(N = 1, 2, 3, \ldots)$, i.e., the limit (102) does not exist at all. In order to avoid such a case, let us assume in the following that the basis set is *normalized to unity.*

Then the general properties of Gram's determinant can be summarized in the inequality

$$0 \leq \gamma \leq \gamma_{N+1} \leq \gamma_N \leq 1 \tag{103}$$

in complete analogy to Eq. (55): The inequality $0 \leq \gamma_{N+1}$ follows from the nonnegativity of μ_1^N [see Eq. (49)] and the product representation for γ_N:

$$\gamma_N = \prod_{n=1}^{N} \mu_n^N. \tag{104}$$

The last part of Eq. (103) ($\gamma_N \leq 1$) is a simple consequence of the so-called *Hadamard inequality* (see Gantmacher, 1977, p. 252), and the monotonical decrease of γ_N follows again from well-known inequalities for Gram determinants (see Gantmacher, 1977, p. 252; Weinhold, 1972). Thus, $\{\gamma_N\}_{N=1}^{\infty}$ is a monotonically decreasing sequence that is bounded from below by zero; therefore the limit (102) exists and obeys $0 \leq \gamma \leq \gamma_N$ for any $N = 1, 2, 3, \ldots$. This fact leads to a further criterion of linear independence:

A set $\{\phi_n\}_{n=1}^{\infty}$ in **H** with $\|\phi_n\| = 1$ $(n = 1, 2, 3, \ldots)$ is called *γ-linearly independent* if $\gamma > 0$, and *γ-linearly dependent* if $\gamma = 0$.

Because of Eq. (103) the special case $\gamma = 1$ occurs if and only if $\{\phi_n\}_{n=1}^{\infty}$ is orthonormal, just as for $\mu = 1$ or $\mu' = 1$, respectively (see Sections III,F and G).

Now, from Eqs. (104) and (54) one can derive the inequality (see Appendix C)

$$\gamma_N \leq \mu_n^N \exp(1 - \mu_n^N) \qquad (n = 1, \ldots, N), \tag{105}$$

which holds for all $N = 1, 2, 3, \ldots$. This implies immediately that *γ-linearly independent sets are always Riesz systems* (see Fig. 2), because we would get $\gamma_N \to 0$ $(N \to \infty)$ by Eq. (105) if either $\mu_1^N \to 0$ or $\mu_N^N \to \infty$ as $N \to \infty$. It is indeed surprising that non-Hilbertian sets, i.e., those with $\mu_N^N \to \infty$, are always γ-linearly dependent $(\gamma = 0)$ in spite of the product representation (104). The reason is the rather restrictive *trace condition* (54).

An example will now demonstrate that on the other side Riesz systems need not be γ-linearly independent: Let $\{\chi_n\}_{n=1}^{\infty}$ denote an orthonormal system and let

$$\left.\begin{aligned} \phi_{2n-1} &= (1/\sqrt{3})(\sqrt{2}\chi_{2n-1} + \chi_{2n}) \\ \phi_{2n} &= (1/\sqrt{3})(\sqrt{2}\chi_{2n-1} - \chi_{2n}) \end{aligned}\right\} \qquad (n = 1, 2, 3, \ldots). \tag{106}$$

Then $\{\phi_n\}_{n=1}^{\infty}$ is a Riesz system, since the overlap matrix of $\{\phi_n\}_{n=1}^{2N}$ has only the two different eigenvalues $\mu_n^{2N} = \frac{2}{3}$ $(n = 1, \ldots, N)$ and $\mu_n^{2N} = \frac{4}{3}$ $(n = N + 1, \ldots, 2N)$. But nevertheless, (106) is γ-linearly dependent with

$$\gamma_{2N} = (\tfrac{8}{9})^N \to 0 \qquad (N \to \infty). \tag{107}$$

This shows that γ-linear independence is a very strong criterion of linear independence, which in practical cases occurs only rather seldom. It is clear that the sets (28) and (62) are also γ-linearly dependent, because they are not even Riesz systems [see Eqs. (59) and (64); Table III]. Their Gram determinants are given by

$$\gamma_N = (N + 1)/2^N \tag{108a}$$

for both sets and go exponentially to zero as $N \to \infty$. The corresponding Gram determinants for (99) are

$$\gamma_N = \left(-\frac{\lambda}{1+\lambda^2}\right)^N U_N\left(-\frac{1+\lambda^2}{2\lambda}\right) = \frac{1-\lambda^{2(N+1)}}{(1-\lambda^2)(1+\lambda^2)^N}, \qquad (108b)$$

a result that is obtained from the fact that γ_N obeys a recursion formula quite similar to the Chebyshev polynomials of the second kind $U_N(\,\cdot\,)$ (see Magnus *et al.*, 1966, p. 256). Equation (108b) reduces obviously to (108a) for $\lambda = 1$ and shows that (99) is also γ-dependent for any real $\lambda \neq 0$.

A γ-linearly *in*dependent basis system is yielded from the set (99) if the parameter λ, which is fixed in Eq. (99), now diverges sufficiently rapidly to infinity as $n \to \infty$ like, e.g.,

$$\lambda_n = a^{n/2} \qquad (a > 2;\ n = 1, 2, 3, \ldots). \qquad (109)$$

The expansion of Gram's determinant γ_N gives the recursion formula ($N = 2, 3, 4, \ldots$)

$$\gamma_1 = 1, \qquad \gamma_2 = 1 - S_1^2, \qquad \gamma_{N+1} = \gamma_N - S_N^2\gamma_{N-1} > \gamma_N - S_N^2, \qquad (110a)$$

where S_n denote the overlap integrals of next neighbors:

$$S_n = (\phi_n, \phi_{n+1}) = -\lambda_{n+1}[(1+\lambda_n^2)(1+\lambda_{n+1}^2)]^{-1/2}. \qquad (110b)$$

A repeated application of the inequality (110a) shows immediately the γ-linear independence for at least $a > 2$:

$$\gamma_{N+1} > 1 - \sum_{n=1}^{N} S_n^2 > 1 - \sum_{n=1}^{N} a^{-n} > \frac{a-2}{a-1} > 0. \qquad (110c)$$

N. Asymptotic Dimension

The concept of the *asymptotic dimension r*, introduced by Courant and Hilbert (1953, p. 63), is another possibility for characterizing infinite systems. However, it is no real criterion of linear independence. Speaking a bit loosely, the value r is the dimension of the linear space that is spanned by $\{\phi_n\}_{n=N}^{\infty}$ for unrestrictedly increasing N. The original definition sounds a bit circumstantial:

> A set $\{\phi_n\}_{n=1}^{\infty}$ has the asymptotic dimension $r = \infty$ if for arbitrary $s = 1, 2, 3, \ldots$ there exist arbitrary large indices $n(1), \ldots, n(s)$ and a positive C_s such that $\mu_1^s(\phi_{n(1)}, \ldots, \phi_{n(s)}) \geq C_s$.

The set has the asymptotic dimension $1 \leq r < \infty$ if such indices exist only for $s \leq r$ and if $\mu_1^{r+1}(\phi_{n(1)}, \ldots, \phi_{n(r+1)})$ converges to zero as $n(1), \ldots, n(r+1) \to \infty$. We have $r = 0$ if $\phi_n \to \theta$ $(n \to \infty)$.

Thus one may differentiate between those sets having finite or infinite asymptotic dimension. This concept was extensively discussed in a recent article (Klahn and Bingel, 1977b) including examples for both cases $r < \infty$ and $r = \infty$ as well as an equivalent definition allowing the determination of r by simple inspection of $\{\phi_n\}_{n=1}^{\infty}$. Moreover, it was shown that Besselian sets always have an infinite asymptotic dimension. With this statement, Fig. 2 is completely explained.

IV. Invariance Properties of Infinite Sets of Functions

It is a well known, but nevertheless curious fact that an *invertible* linear transformation A in a Hilbert space **H** like a *Schmidt orthonormalization* may transform an infinite *over*complete set of functions into an *exactly* complete one. Obviously, the overcomplete set $\{\phi_n\}_{n=1}^{\infty}$, which contains *more* elements than necessary for the approximation of an arbitrary $\Psi \in \mathbf{H}$, in this way becomes a set

$$\{\psi_n = A\phi_n\}_{n=1}^{\infty} \tag{111}$$

having just the "correct number" of functions, since no function can be left out without destroying the completeness of (111). Of course, both systems $\{\phi_n\}_{n=1}^{\infty}$ and $\{\psi_n\}_{n=1}^{\infty}$ are infinite. Thus, one could argue that the curiousness of this fact is only founded in our restricted feeling for infinity. However, one can also try to find a more satisfactory explanation of this phenomenon.

The real question behind this problem is the question for *invariance* properties of infinite basis sets. Since exact completeness or overcompleteness means that a set is complete *and* minimal or nonminimal, respectively (see Section III,C,1), the application of a linear operator A to $\{\phi_n\}_{n=1}^{\infty}$ may preserve or destroy the one or the other property. Therefore, a full comprehension can be obtained from investigating the invariance of completeness and of linear independence, as defined in Section III, against such transformations.

In *finite*-dimensional vector spaces, especially in unitary spaces, a very simple answer can be given: An *invertible* matrix **A** preserves the completeness as well as the linear independence of a finite basis set. Analogously, incompleteness and linear dependence are also preserved by such matrices.[29] In Hilbert spaces, however, the *boundedness* of A or of its inverse A^{-1} plays an important role (see Sections IV,B and C), in order to get sufficient criteria of invariance. Moreover, since there are numerous

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[29] The less interesting case of a *singular* matrix leads to the following result: **A** preserves incompleteness and destroys completeness; it preserves linear dependence and may destroy or preserve linear independence, according to the special vectors under consideration.

different possibilities for defining linear independence, a special kind of linear independence may be changed to another one by a suitable choice of A. Necessary conditions on A for such "changing" transformations are also obtained from the criteria in Section IV,C,1 and are summarized in Table IV.

Another closely related problem is the question for the independence properties of a given basis set in *different* Hilbert spaces like L^2, L^2_ρ with ρ a weight function, or $W_2^{(r)}$. Such a question may arise, when investigating the convergence of an approximation to a wave function within different norms, as especially done for the Rayleigh–Ritz method and the variance minimization (see Section III,D). As a simple application of the theory it is shown which properties of $\{\phi_n\}_{n=1}^{\infty}$ are also valid in $W_2^{(r')}$, if these have already been stated in another Sobolev space $W_2^{(r)}$ (Table V).

A. Properties of the Linear Transformation *A*

In order to clarify the notations, we first summarize some simple properties of linear transformations, which are used subsequently.

Let A be a linear operator in **H** with the domain $D(A) = [\phi_n]$ and the range $W(A) = [A\phi_n]$

$$A : D(A) \rightarrow W(A). \tag{112}$$

If this map is one to one, the inverse of A

$$A^{-1} : D(A^{-1}) = W(A) \rightarrow D(A) \tag{113}$$

is defined in $W(A)$ as the map that sends $A\Psi$ to Ψ. It is not assumed that $D(A)$ or $W(A)$ are dense in **H**, i.e., no assumption is made on the completeness of $\{\phi_n\}_{n=1}^{\infty}$ or $\{A\phi_n\}_{n=1}^{\infty}$. This applies also to the case that A is given by an infinite *matrix*, e.g., a lower triangular matrix as for the Schmidt orthonormalization procedure

$$\psi_n = \sum_{k=1}^{n} A_{nk}\phi_k \qquad (n = 1, 2, 3, \ldots). \tag{114a}$$

The invertibility of A is assured by the condition

$$A_{nn} \neq 0 \qquad (n = 1, 2, 3, \ldots), \tag{114b}$$

which also implies that $D(A) = W(A)$. In the special case of a Schmidt orthonormalization, A_{nn} is given by [see Eq. (18)]

$$A_{nn} = [\delta^{(n-1)}(\phi_n; \phi_1, \ldots, \phi_{n-1})]^{-1}. \tag{114c}$$

Of course, in practical cases $D(A)$ will often not be defined as the linear span of a given basis set; instead of this, $D(A)$ can, for instance, be given by the requirement that A is self-adjoint in **H**.

An important condition for the conservation of linear dependence or independence is the boundedness of A or A^{-1}, respectively:

$$\|A\Psi\| \leq \|A\| \, \|\Psi\| \qquad \forall \quad \Psi \in D(A), \tag{115}$$

$$\|A^{-1}\Phi\| \leq \|A^{-1}\| \, \|\Phi\| \qquad \forall \quad \Phi \in W(A). \tag{116}$$

Putting $\Phi = A\Psi$ into (116), $\|A^{-1}\| < \infty$ yields

$$\|A\Psi\| \geq \|A^{-1}\|^{-1}\|\Psi\| \qquad \forall \quad \Psi \in D(A). \tag{117}$$

Furthermore, the boundedness of A^{-1} in $W(A)$ implies that its adjoint

$$(A^{-1})^* : \overline{D(A)} \to \overline{W(A)}, \tag{118}$$

where $\overline{D(A)}$ and $\overline{W(A)}$ denote the closures of $D(A)$ and $W(A)$ in $\mathbf{H}$, is a closed and bounded operator in $\overline{D(A)}$ with $\|(A^{-1})^*\| = \|A^{-1}\|$ (see Weidmann, 1976, p. 71). Additionally we have (see Weidmann, 1976, p. 90)

$$(A^{-1})^{**} = \overline{A^{-1}}, \tag{119}$$

where $\overline{A^{-1}}$ denotes the closure of A^{-1} mapping from $\overline{W(A)}$ to $\overline{D(A)}$.

A rather important class of operators is given by those with

$$\|A\| < \infty \qquad \textit{and} \qquad \|A^{-1}\| < \infty, \tag{120}$$

the so-called *equivalence* transformations. If A is an equivalence transformation, then the sets $\{\phi_n\}_{n=1}^{\infty}$ and $\{\psi_n = A\phi_n\}_{n=1}^{\infty}$ are called *equivalent* (see Higgins, 1977, p. 74) or sometimes also *strictly equivalent* (see Singer, 1970, p. 68). For example, any unitary transformation is an equivalence transformation.

B. Invariance Properties of Completeness

Whereas completeness in finite-dimensional unitary spaces is invariant under invertible transformations, in Hilbert spaces this is generally not the case; e.g., the differential operator

$$A = 1 - d^2/dx^2 \tag{121}$$

having the domain $D(A) = W_2^{(2)}(\mathbf{R})$ [see Eq. (2)], is a self-adjoint operator in $\mathbf{H} = L^2(\mathbf{R})$, whose inverse A^{-1} is defined in all $\mathbf{H}$. Nevertheless, the completeness of

$$\{\phi_n = x^n \exp(-\tfrac{1}{2}x^2)\}_{n=1}^{\infty} \tag{122}$$

is not preserved under application of the operator (121), for a simple calculation gives

$$(\exp(-|x|), A\phi_n) = 0 \qquad (n = 1, 2, 3, \ldots), \tag{123}$$

showing the *in*completeness of $\{A\phi_n\}_{n=1}^{\infty}$ in $L^2(\mathbf{R})$. Of course, there are sets of functions other than (122), whose completeness in $L^2(\mathbf{R})$ is *not* destroyed by the application of (121), namely exactly those sets that are complete in $W_2^{(2)}(\mathbf{R})$ (see Klahn and Bingel, 1977a). So, the invariance of completeness with respect to this special operator depends decisively on the special basis set under consideration.

However, there are also sufficient criteria on the *operator* in Eq. (111) that guarantee the conservation of completeness for *arbitrary* sets of functions:

(1) If A is a bounded linear operator, whose inverse A^{-1} is densely defined in $\mathbf{H}$, then A preserves completeness (Proof: see Klahn, 1979).

(2) If A is an infinite lower triangular matrix according to Eqs. (114a) and (114b), then it preserves both completeness and incompleteness.

Statement (2) guarantees, for instance, that a Schmidt orthonormalization does not affect the completeness property of a given infinite basis set. Concerning statement (1), the operator (121), for example, does not fulfill the assumptions, since A is unbounded, but its inverse does and therefore preserves completeness in $L^2(\mathbf{R})$.

Statement (1) may also be useful when considering weighted Hilbert spaces such as

$$L_\rho^2 = \{\Psi | (\Psi, \rho\Psi) < \infty\} \tag{124}$$

with $\rho > 0$ (almost everywhere) a weight function. The completeness of $\{\phi_n\}_{n=1}^{\infty}$ in L_ρ^2 is namely equivalent to the completeness of $\{\rho^{1/2}\phi_n\}_{n=1}^{\infty}$ in L^2—a fact that is essentially based on the equalities

$$(\Psi, \Phi)_\rho = (\rho^{1/2}\Psi, \rho^{1/2}\Psi) \qquad \forall \quad \Psi, \Phi \in \mathbf{H} \tag{125a}$$

$$\|\Psi\|_\rho = \|\rho^{1/2}\Psi\| \qquad \forall \quad \Psi \in \mathbf{H}, \tag{125b}$$

with $(\cdot\ ,\ \cdot)_\rho$ denoting the scalar product and $\|\cdot\|_\rho$ the norm of the space L_ρ^2. Consequently, any complete set of L^2 is also complete in L_ρ^2 if the multiplicative operator $A = \rho^{1/2}$ preserves completeness.

As a special application of this result, we consider the Sobolev spaces of order r, defined in Eq. (2), which are weighted L^2 spaces in the *momentum* representation with the weight function $\rho_r = (c + \mathbf{p}^2)^r$: Assuming the completeness of a set $\{\phi_n\}_{n=1}^{\infty}$ in $W_2^{(r)}$, or equivalently the completeness of $\{\rho_r^{1/2}\hat{\phi}_n\}_{n=1}^{\infty}$ in L^2, then completeness of $\{\rho_{r'}^{1/2}\hat{\phi}_n\}_{n=1}^{\infty}$ obtains from statement (1) with

$$A = (\rho_{r'}/\rho_r)^{1/2} = (c + \mathbf{p}^2)^{-(r-r')/2} \tag{125}$$

for all $r' \leq r$. Thus, completeness in $W_2^{(r)}$ implies completeness in $W_2^{(r')}$ if $r' \leq r$ (see Table V)—a result that is already well known (see, e.g., Klahn and Bingel, 1977a).

C. Invariance Properties of Linear Independence

The invariance properties of *linear independence* are quite different from those for completeness. As can be seen rather trivially, a general rule is the following: If a set $\{\phi_n\}_{n=1}^{\infty}$ has one of the properties summarized in Fig. 2, then (with the exception of asymptotic dimension) any *sub*set of $\{\phi_n\}_{n=1}^{\infty}$ has the same property. This is surely a minimum requirement for a reasonable definition of linear independence.

1. *Preserving Transformations*

In order that a linear operator A preserve a special form of linear independence or dependence for *any* basis set, A has to fulfill certain sufficient criteria. The simplest case is the finite linear independence, since the investigations can be performed analogously as for finite-dimensional spaces. Therefore, using the original definition of linear independence in $\mathbf{H}_M$ [see Section II, definition (a)], we get immediately the statement: *An invertible linear operator* [*see Eq.* (*113*)] *preserves finitely linear independence as well as finitely linear dependence.* Vice versa, the existence of A^{-1} in $W(A) = [A\phi_n]$ is also necessary for the conservation of finite linear independence (see Table IV).

However, when considering the stronger criteria of independence, the invertibility of A alone is no longer sufficient; we need the boundedness of A^{-1} or A:

LEMMA. Let A be a linear operator that has a *bounded inverse* [see Eqs. (113) and (116)]. Then the following properties of any given basis set are preserved under the application of A:

(a) ω-linear independence;
(b) minimality, i.e., the existence of a BOS;
(c) the Bessel property; and
(d) the non-Hilbert property.

Contrarily, if A itself is a *bounded* linear operator [see Eqs. (112) and (115)], then it preserves the following properties:

(e) ω-linear dependence;
(f) nonminimality;
(g) the non-Bessel property; and
(h) the Hilbert property.

The complete proof of this lemma is contained in a preprint of this article (Klahn, 1979, Appendices E–G), whereas it is only sketched here:

The parts (a) and (e) are obtained by means of Eqs. (116) and (115), respectively, using the definition of ω-linear independence for $\{\phi_n\}_{n=1}^{\infty}$ as well as for $\{\psi_n = A\phi_n\}_{n=1}^{\infty}$. The proof of (b) is based on the equation

$$\{\psi_n^* = (A^{-1})^*\phi_n^*\}_{n=1}^\infty, \tag{126}$$

where $\{\phi_n^*\}_{n=1}^\infty$ and $\{\psi_n^*\}_{n=1}^\infty$ denote *the* BOSs of $\{\phi_n\}_{n=1}^\infty$ and $\{\Psi_n = A\phi_n\}_{n=1}^\infty$, respectively: Since A^{-1} is bounded by assumption, Eq. (118) shows that $\psi_n^* \in \overline{[\psi_n]}$ for all n, i.e., (126) is *the* BOS of $\{\psi_n\}_{n=1}^\infty$, if it is a BOS at all. The BOS property of $\{\psi_n^*\}_{n=1}^\infty$, however, follows immediately from Eq. (119). The easiest proof of part (f) is obtained, when using the characterization (d) of minimality in Section III,C,1 and Eq. (115).

The validity of the statements (c) and (h) can be directly seen from the inequalities

$$\mu_\psi \geq \mu_\phi \|A^{-1}\|^{-2}, \tag{127a}$$

$$\mu_\psi' \leq \mu_\phi' \|A\|^2, \tag{127b}$$

where μ_ϕ, μ_ψ and μ_ϕ', μ_ψ' denote the values defined in Eqs. (51) and (66) for the sets $\{\phi_n\}_{n=1}^\infty$ and $\{\psi_n\}_{n=1}^\infty$, respectively. Equations (127a) and (127b) follow at once from the combination of Eqs. (117), (52) and (115), (67):

$$\left\| \sum_{n=1}^N c_n A\phi_n \right\|^2 \geq \|A^{-1}\|^{-2} \left\| \sum_{n=1}^N c_n\phi_n \right\|^2 \geq \mu_\phi \|A^{-1}\|^{-2} \sum_{n=1}^N |c_n|^2 \tag{128a}$$

$$\left\| \sum_{n=1}^N c_n A\phi_n \right\|^2 \leq \|A\|^2 \left\| \sum_{n=1}^N c_n\phi_n \right\|^2 \leq \mu_\phi' \|A\|^2 \sum_{n=1}^N |c_n|^2 \tag{128b}$$

Moreover, if $\{\phi_n\}_{n=1}^\infty$ is an orthonormal set, we have $\mu_\phi = \mu_\psi = 1$ and the second inequalities of (128) become an equality, so that we get

$$\mu_\psi = \|A^{-1}\|^{-2}, \qquad \mu_\psi' = \|A\|^2 \tag{129}$$

instead of Eq. (127). The remaining statements (d) and (g) of the lemma can also simply be shown by means of Eqs. (67), (117) and (52), (115).

By this lemma, our starting question of Section IV can now be answered. To that end let us ask: What happens when applying Schmidt's matrix to an *overcomplete* set, i.e., to a complete, nonminimal set. If we assume that the Schmidt matrix represents a *bounded* operator [see Eq. (115)], then it preserves completeness [see Section IV,B, statements (1) and (2)] and nonminimality by statement (f) of the lemma, and thus the transformed set is again overcomplete in direct contradiction to its orthonormality. Consequently, the Schmidt matrix must represent an *unbounded* operator [see also Eq. (114c)], which preserves completeness but destroys nonminimality and thus leads to an exactly complete set. In brief, the explanation to our question is that completeness and nonminimality have quite different invariance properties. If an operator A does not fulfill a condition of boundedness, as required for the statements (a)–(h), then for a given set $\{\phi_n\}_{n=1}^\infty$ the questionable property of independence or dependence may be preserved or not depending on the special set.

2. *Equivalence Transformations*

As another consequence of the lemma, Riesz systems and non-Riesz systems are invariant under *equivalence* transformations.

Of course, all the other linear dependence and independence properties, discussed in Section IV,C,1, are also invariant under equivalence transformations (see the lemma in Section IV,C,1). Thus, equivalence transformations are unable to *change* the special form of linear dependence or independence of a given set, as ω-linear (in)dependence, (non)minimality, the (non-)Bessel property or the (non-)Riesz property. In brief, one could say that a basis set remains in its "class" under equivalence transformations. A class in this context means the set of all systems $\{\phi_n\}_{n=1}^{\infty}$ that are linearly independent due to one definition but linearly dependent due to a stronger one; e.g., being minimal but non-Besselian, or Besselian but non-Riesz (see Fig. 2).

This statement is also true for all the other properties listed in Fig. 2, with the exception of γ-linear independence and orthonormality.[30] For instance, from Eqs. (93), (115), and (116) we get immediately that *uniform minimality and nonuniform minimality are invariant under equivalence transformations.*

Therefore, by statement (1) of Section IV,B *the Schauder basis property is also invariant under equivalence transformations* (see Higgins, 1977, p. 75), provided that the transformations A map from $\mathbf{H}$ *onto* $\mathbf{H}$, i.e., that $\overline{W(A)} = \mathbf{H}$ ("full equivalence," see Singer, 1970, p. 69). This fact serves as an important foundation for testing the Schauder basis property of explicitly given sets of functions by so-called *stability* theorems, e.g., the *Payley–Wiener stability theorem,* and by *nearness* conditions (see Higgins, 1977, p. 71; Singer, 1970, p. 84; Kato, 1966, p. 265).

There is, however, an important difference between the Riesz property and all the other independence properties of Fig. 2: Whereas the equivalence of A is normally only a *sufficient* condition of invariance, with respect to Riesz systems it is also *necessary:*

Let $\{\phi_n\}_{n=1}^{\infty}$ and $\{\psi_n\}_{n=1}^{\infty}$ be two Riesz systems in $\mathbf{H}$ and $\psi_n = A\phi_n$ ($n = 1, 2, 3, \ldots$) with A a linear transformation. Then a suitable combination of the inequalities (96), written down for both sets $\{\phi_n\}_{n=1}^{\infty}$ and $\{\psi_n\}_{n=1}^{\infty}$, shows that A and A^{-1} are bounded in $[\phi_n]$ and $[A\phi_n]$, respectively:

$$\|A\| \leq (\mu'_\psi/\mu_\phi)^{1/2}, \qquad \|A^{-1}\| \leq (\mu'_\phi/\mu_\psi)^{1/2}, \tag{130}$$

i.e., that A is an equivalence transformation [see Eq. (120)].

This statement says that the set of all those Riesz systems in $\mathbf{H}$, con-

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[30] γ-Linear independence and orthonormality are obviously invariant under unitary transformations.

nected by linear[31] transformations, forms an *equivalence class*. Especially, it implies the following consequences:

(a) The Schmidt matrix A, which orthonormalizes a Riesz system, represents an equivalence transformation, or, any Riesz system has an orthonormal system, to which it is equivalent. This statement proves the fact that Riesz systems are "disguised" orthonormal systems: The equivalent norm of Eq. (98) needs only to be chosen as

$$\|\Psi\|' = \|A\Psi\| \qquad \forall \quad \Psi \in \overline{[\phi_n]}. \tag{131}$$

(b) Since the norms of two different Sobolev spaces $W_2^{(r)}$ and $W_2^{(r')}$ $(r' \neq r)$ are nonequivalent, a given set $\{\phi_n\}_{n=1}^{\infty}$ can never be a Riesz system of *both* spaces, e.g., an orthonormal set of L^2 can never be a Riesz system in $W_2^{(r)}$ $(r > 0)$.

3. *Changing Transformations*

After having considered the problem of *conserving* linear independence properties, it is now natural to ask for conditions on A that imply a *change* of linear independence for any set $\{\phi_n\}_{n=1}^{\infty}$. As was already discussed, nonminimality may change to minimality only by *unbounded* operators. Analogously, we obtain corresponding *necessary* conditions on A for the other alterations of linear independence properties by means of the lemma in Section IV,C,1 and Eq. (130):

For example, a minimal set becomes nonminimal only if $\|A^{-1}\| = \infty$, or, a Besselian set that is non-Riesz becomes a Riesz system only if its non-Hilbert property is destroyed, i.e., only if $\|A^{-1}\| = \infty$. Similarly, the necessary conditions for the other cases are established and summarized in Table IV.

There are only two additional entries in Table IV that cannot be explained by the previous investigations: One can show that the transformation from a Besselian (non-Hilbertian) set to a Riesz system is always bounded[32] and that the inverse transformation therefore has a bounded inverse.

Concerning the main diagonal of Table IV, apart from the invertibility there are no necessary criteria in terms of the operator A alone. If either $\|A\| = \infty$ or $\|A^{-1}\| = \infty$, then whether the appertaining form of independence (or dependence) is preserved or not depends decisively on the system $\{\phi_n\}_{n=1}^{\infty}$ itself.

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[31] With respect to nonlinear transformations one has to use a weaker concept of equivalence (see Singer, 1970, pp. 68 and 341).

[32] For the proof one shows easily by Eqs. (52) and (67) that the Schmidt matrix constructed from the Besselian (non-Hilbertian) set represents a bounded operator. The assertion then follows from the statement appertaining to Eq. (130).

TABLE IV

NECESSARY CONDITIONS ON A FOR CHANGING THE INDEPENDENCE PROPERTY[a] OF ANY SET $\{\phi_n\}_{n=1}^{\infty}$

$\{A\phi_n\}_{n=1}^{\infty}$ $\{\phi_n\}_{n=1}^{\infty}$	Finitely linear independence	ω-Linear independence	Minimality (BOS exists)	Bessel property ($\mu > 0$)	Riesz property ($\mu > 0$, $\mu' < \infty$)	ONS
Finitely linear independence	A^{-1} exists in $W(A)$	$\|A\| = \infty$	$\|A\| = \infty$	$\|A\| = \infty$	$\|A\| = \infty$	$\|A\| = \infty$
ω-Linear independence	$\|A^{-1}\| = \infty$	A^{-1} exists in $W(A)$	$\|A\| = \infty$	$\|A\| = \infty$	$\|A\| = \infty$	$\|A\| = \infty$
Minimality (BOS exists)	$\|A^{-1}\| = \infty$	$\|A^{-1}\| = \infty$	A^{-1} exists in $W(A)$	$\|A\| = \infty$	$\|A\| = \infty$	$\|A\| = \infty$
Bessel property	$\|A^{-1}\| = \infty$	$\|A^{-1}\| = \infty$	$\|A^{-1}\| = \infty$	A^{-1} exists in $W(A)$	$\|A^{-1}\| = \infty$, $\|A\| < \infty$	$\|A^{-1}\| = \infty$, $\|A\| < \infty$
Riesz property	$\|A^{-1}\| = \infty$	$\|A^{-1}\| = \infty$	$\|A^{-1}\| = \infty$	$\|A\| = \infty$, $\|A^{-1}\| < \infty$	$\|A^{-1}\| < \infty$, $\|A\| < \infty$	$\|A^{-1}\| < \infty$, $\|A\| < \infty$
ONS	$\|A^{-1}\| = \infty$	$\|A^{-1}\| = \infty$	$\|A^{-1}\| = \infty$	$\|A\| = \infty$, $\|A^{-1}\| < \infty$	$\|A^{-1}\| < \infty$, $\|A\| < \infty$	$A^* = A^{-1}$

[a] The given properties exclude the stronger ones, e.g. "Bessel property" means that the set is non-Riesz. (ONS, orthonormal system.)

D. Applications to Weighted L^2 Spaces and Sobolev Spaces

Whereas linear independence or dependence of a basis set in a finite-dimensional unitary space is not affected when changing the original norm to a weighted one,[33] this is quite different for infinite-dimensional Hilbert spaces. Just as for completeness in weighted Hilbert spaces (see Section IV,B), the question of linear independence in L^2_ρ can be reduced to an investigation in L^2, again by using Eq. (125):

A set $\{\phi_n\}_{n=1}^{\infty} \subset L^2_\rho$ *has one of the properties summarized in Fig. 2 (or the negation of it) if and only if* $\{\rho^{1/2}\phi_n\}_{n=1}^{\infty}$ *has just this property in* L^2 *(weight function theorem).*

The investigation of the transformed set $\{\rho^{1/2}\phi_n\}_{n=1}^{\infty}$ in L^2 can be done, for instance, by using the invariance considerations of Section IV,C with $A = \rho^{1/2}$: If ρ^{-1} is bounded, then, for example, any minimal set of L^2 is also minimal in L^2_ρ (see statement (b) of the lemma in Section IV,C,1). If, however, the inverse weight function ρ^{-1} is unbounded, then the curious case can occur that $\{\phi_n\}_{n=1}^{\infty}$ is minimal in L^2, but nonminimal in L^2_ρ. An example of this kind is given by the set of Hermite's orthonormal func-

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[33] The reason is that the original definition of linear independence in finite-dimensional spaces (see Gantmacher, 1977, p. 51 and Section II of this article) does not make use of any norm.

tions in $L^2(\mathbf{R})$ with $\rho(x) = \exp(-x^2)$ (see Fig. 3), i.e., these functions are exactly complete in L^2, but overcomplete in L^2_ρ.

As a further consequence of the weight function theorem and its analog for completeness (see Section IV,B) we get the simple statement: A set $\{\phi_n\}_{n=1}^\infty$ is exactly complete in L^2_ρ if and only if $\{\rho^{1/2}\phi_n\}_{n=1}^\infty$ is exactly complete in L^2. Of course, the same conclusion is true with respect to the Schauder basis property.

The combination of the weight function theorem and the invariance properties discussed in Section IV,C imply also some interesting results due to *Sobolev* spaces. Let us therefore choose a set $\{\phi_n\}_{n=1}^\infty$ common to $W_2^{(r)}(\mathbf{R}^s)$ and $W_2^{(r')}(\mathbf{R}^s)$ $(r, r' \geq 0)$, i.e., $\phi_n \in W_2^{(r)} \cap W_2^{(r')}$, and ask: What are the linear independence properties of $\{\phi_n\}_{n=1}^\infty$ in $W_2^{(r')}$ if they are known in $W_2^{(r)}$? The answers, summarized in Table V, are as follows:

(1) If $\{\phi_n\}_{n=1}^\infty$ is minimal in $W_2^{(r)}(\mathbf{R}^s)$, then it is also minimal in $W_2^{(r')}(\mathbf{R}^s)$ for $r' \geq r$. Especially, a minimal set of L^2 (i.e., $r = 0$) is minimal in every Sobolev space. Moreover, if $\{\phi^*_{r,n}\}_{n=1}^\infty$ is the BOS of $\{\phi_n\}_{n=1}^\infty$ in $W_2^{(r)}$, then the Fourier-transformed elements of the corresponding BOS in $W_2^{(r')}$ are given by

$$\hat{\phi}^*_{r',n} = (\rho_r/\rho_{r'})\hat{\phi}^*_{r,n}, \qquad \rho_r = (c + \mathbf{p}^2)^r, \tag{132}$$

and therefore we have in position space

$$\phi^*_{r',n} = (c - \nabla^2)^{-(r'-r)}\phi^*_{r,n}, \tag{133}$$

with ∇ the gradient operator in $\mathbf{R}^s$. The proof of these statements runs as follows: Minimality of $\{\phi_n\}_{n=1}^\infty$ in $W_2^{(r)}$ is equivalent to the minimality of $\{\rho_r^{1/2}\hat{\phi}_n\}_{n=1}^\infty$ in L^2 by the weight function theorem. Thus the application of $A = (\rho_{r'}/\rho_r)^{1/2}$, having a bounded inverse for $r' \geq r$ in $L^2(\mathbf{R}^s)$, implies minimality of $\{\rho_{r'}^{1/2}\hat{\phi}_n\}_{n=1}^\infty$ in L^2 by the lemma in Section IV,C,1 and consequently minimality of $\{\phi_n\}_{n=1}^\infty$ in $W_2^{(r')}$ again by the weight function theorem. Equation (132) follows essentially from Eq. (126).

(2) If $\{\phi_n\}_{n=1}^\infty$ is Besselian (Hilbertian) in $W_2^{(r)}$, then it is also Besselian (Hilbertian) in $W_2^{(r')}$ for $r' \geq r$ $(r' \leq r)$. Especially, a Besselian set of L^2 (i.e., $r = 0$) is also Besselian in every Sobolev space, and a Hilbertian set of $W_2^{(r')}$ is always Hilbertian in L^2. The proof runs just as for minimality [statements (c) and (h) of the lemma].

(3) The analogous results for ω-linear independence and finitely linear independence (Table V) are similarly obtained.

As a very simple application of Table V we get the result: Any orthonormal set of functions in L^2 is also Besselian and thus minimal and ω-linearly independent in $W_2^{(r)}$ $(r > 0)$, however, it is non-Riesz and thus non-Hilbertian $(\mu' = \infty)$ in $W_2^{(r)}$.

TABLE V[a]

Property	Sufficient condition
Completeness	$r' \leq r$
Finitely linear independence	Any r'
ω-Linear independence	$r' \geq r$
Minimality	$r' \geq r$
Bessel property	$r' \geq r$
Hilbert property	$r' \leq r$
Riesz property	$r' = r$ (even necessary)

[a] Sufficient conditions (right column) on the indices r and r' of two Sobolev spaces $W_2^{(r)}(\mathbf{R}^s)$ and $W_2^{(r')}(\mathbf{R}^s)$, such that $\{\phi_n\}_{n=1}^{\infty}$ has the property of the left column in $W_2^{(r')}(\mathbf{R}^s)$, provided that $\{\phi_n\}_{n=1}^{\infty}$ has this property in $W_2^{(r)}(\mathbf{R}^s)$. The condition $r' = r$ for the Riesz property is also necessary because of statement (b) in Section IV,C,2.

Of course, in addition to Table V, one could also summarize the corresponding negative properties, such as ω-linear *dependence*. For these, the sufficient conditions on r and r' are obtained from the right column of Table V by interchanging both numbers.

Appendix A. Completeness and Minimality Properties of the Sets (40a) and (40b)

The minimality of (40a) and (40b) is shown by the existence of the appertaining BOSs [χ_n denote Laguerre's orthonormal functions of Eq. (30)]:

$$\{\phi_n^*(\alpha, x) = x^{-\alpha}\chi_n(x)\}_{n=1}^{\infty} \qquad \text{for } \alpha < \tfrac{1}{2}, \tag{133a}$$

$$\{\phi_n^*(\alpha, x) = x^{-\alpha}(\chi_n - \chi_{n(1)})\}_{n=1, n\neq n(1)}^{\infty} \qquad \text{for } \tfrac{1}{2} \leq \alpha < \tfrac{3}{2}. \tag{133b}$$

It remains to show that (40b) is complete in $L^2(\mathbf{R}^+)$, i.e., if $\Phi \in L^2(\mathbf{R}^+)$ is orthogonal to (40b), then $\Phi = \theta$ follows. This is done by determining the biorthonormal expansion of the element ($\alpha \geq \frac{1}{2}$, $0 < \beta < 1$)

$$\Psi = x^{\alpha}\Phi \exp(-\tfrac{1}{2}\beta x) \in L^2(\mathbf{R}^+), \tag{134}$$

in the exactly complete basis set

$$\{\varphi_n = \chi_n \exp(-\tfrac{1}{2}\beta x)\}_{n=1}^{\infty} \tag{135}$$

heaving the *complete* BOS

$$\{\varphi_n^* = \chi_n \exp(+\tfrac{1}{2}\beta x)\}_{n=1}^{\infty}. \tag{136}$$

Since Φ is orthogonal to the set (40b) by assumption, Eqs. (134), (136), and (39) imply

$$(\Psi, \varphi_n^*) = (\Phi, x^{\alpha}\chi_n) = (\Phi, \phi_n(\alpha, x)) = 0 \tag{137}$$

for all $n \neq n(1)$. Thus, the formal biorthonormal expansion (25) of Ψ is given by a single term

$$\Psi \sim (\Phi, \phi_{n(1)}(\alpha, x))\varphi_{n(1)} = \Psi', \tag{138}$$

representing an element $\Psi' \in L^2(\mathbf{R}^+)$. Because (136) is complete in $L^2(\mathbf{R}^+)$, we conclude $\Psi = \Psi'$ [see Section III,H, especially Eq. (73)], so that we get Φ from Eqs. (134), (138), and (135):

$$\Phi = x^{-\alpha}\exp(\tfrac{1}{2}\beta x)\Psi' = (\Phi, \phi_{n(1)}(\alpha, x))x^{-\alpha}\chi_{n(1)}. \tag{139}$$

However, since $\alpha \geq \frac{1}{2}$, the assumption that $\Phi \in L^2(\mathbf{R}^+)$ is only valid if the prefactor $(\Phi, \phi_{n(1)}(\alpha, x)) = 0$, i.e., only if $\Phi = \theta$.

Appendix B. The BOS of the Pekeris Basis Set in S-$W_2^{(1)}(\mathbf{R}^6)$

In order to construct the BOS of the Pekeris basis set (41) in $\mathbf{H} =$ S-$W_2^{(1)}(\mathbf{R}^6)$, we define[34]

$$l_{nml}(\Psi) = (\rho^{-3/4}\phi_{nml}, \rho^{-1/4}\Psi) \qquad \forall \quad \Psi \in \text{S-}W_2^{(1)}(\mathbf{R}^6) \tag{140}$$

with ϕ_{nml} and ρ, as given by Eqs. (41) and (42), and show that $l_{nml}(\Psi)$ is a bounded linear functional in S-$W_2^{(1)}(\mathbf{R}^6)$ for all n, m, and l: Because $\rho^{-3/4}\Phi_{nml} \in$ S-$L^2(\mathbf{R}^6)$, as can be seen by integration, the Schwarz inequality gives

$$|l_{nml}(\Psi)| \leq \|\rho^{-3/4}\phi_{nml}\| \, \|\rho^{-1/4}\Psi\|. \tag{141}$$

Using the more familiar coordinates r_1, r_2, r_{12} instead of the perimetric x, y, z (see Hylleraas, 1964), the inequality

$$\rho^{-1/2} = (2\sqrt{2}\pi)^{-1}(r_1 r_2 r_{12})^{-1/2} \leq (6\sqrt{2}\pi)^{-1}(r_1^{-3/2} + r_2^{-3/2} + r_{12}^{-3/2}) \tag{142}$$

shows that $\rho^{-1/2}$ is infinitesimally form-bounded by $-\nabla^2$ (see Reed and Simon, 1975, p. 170), i.e., there exists a constant c', such that

$$\|\rho^{-1/4}\Psi\|^2 = (\Psi, \rho^{-1/2}\Psi) \leq c'\|\Psi\|_{\mathrm{H}}^2 \qquad \forall \quad \Psi \in \text{S-}W_2^{(1)}(\mathbf{R}^6). \tag{143}$$

Putting $c_{nml} = \sqrt{c'}\|\rho^{-3/4}\phi_{nml}\|$, we obtain from (141) and (143)

$$|l_{nml}(\Psi)| \leq c_{nml}\|\Psi\|_{\mathrm{H}} \qquad \forall \quad \Psi \in \text{S-}W_2^{(1)}(\mathbf{R}^6), \tag{144}$$

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[34] Here, $(\cdot\,,\,\cdot)$ and $(\cdot\,,\,\cdot)_{\mathrm{H}}$ denote the scalar products of S-$L^2(\mathbf{R}^6)$ and $\mathbf{H} =$ S-$W_2^{(1)}(\mathbf{R}^6)$, respectively. The corresponding norms are denoted by $\|\cdot\|$ and $\|\cdot\|_{\mathrm{H}}$.

showing the boundedness of the linear functional l_{nml} in S-$W_2^{(1)}(\mathbf{R}^6)$. Consequently, by the lemma of Riesz–Fréchet (see Reed and Simon, 1972, p. 43) there exists an element $\phi^*_{nml} \in$ S-$W_2^{(1)}(\mathbf{R}^6)$ with

$$l_{nml}(\Psi) = (\Psi, \phi^*_{nml})_{\mathrm{H}} \qquad \forall \quad \Psi \in \text{S-}W_2^{(1)}(\mathbf{R}^6). \tag{145}$$

Now, it follows from Eqs. (145), (140), (41), and the orthonormality of the set (30) that

$$\begin{aligned}(\phi_{nml}, \phi^*_{n'm'l'})_{\mathrm{H}} &= l_{n'm'l'}(\phi_{nml}) \\ &= (\rho^{-3/4}\phi_{n'm'l'}, \rho^{-1/4}\phi_{nml}) \\ &= \delta_{nn'}\delta_{mm'}\delta_{ll'},\end{aligned} \tag{146}$$

showing that $\{\phi^*_{nml}\}^{\infty}_{n,m,l=1}$ is the BOS of (41) in S-$W_2^{(1)}(\mathbf{R}^6)$. From Eq. (146) we see that ϕ^*_{nml} can formally be written as [see also Eq. (132) for $r' = 1$ and $r = 0$]

$$\phi^*_{nml} = (c - \nabla^2)^{-1}\rho^{-1}\phi_{nml}, \tag{147}$$

with c as defined in Eq. (2), and ∇ the six-dimensional gradient operator. However, since $\rho^{-1}\phi_{nml} \notin$ S-$L^2(\mathbf{R}^6)$, the formula (147) has to be justified, as done above.

Appendix C. Proof of Inequality (105)

The inequality (105) gives a bound to Gram's determinant in terms of the eigenvalues μ_n^N of the overlap matrix for any $N = 1, 2, 3, \ldots$. It follows from the product representation of γ_N [Eq. (104)] and the trace condition (54), i.e., from equations that are valid for all Hermitian matrices $\mathbf{S}^{(N)}$ with $S_{nn}^{(N)} = 1$ $(n = 1, \ldots, N)$.

The proof of (105) makes use of the well-known inequality

$$\left(1 - \frac{x}{n-1}\right)^{n-1} \le \left(1 - \frac{x}{n}\right)^{n}, \tag{148}$$

which is valid for $n = 2, 3, 4, \ldots$ if $x \le 0$, and for $n \ge x + 1$ if $x > 0$.

The case $N = 1$ of Eq. (105) is trivial. Now, a product of positive numbers $\{\mu_k^N\}_{k=1,k\neq n}^N$, which have a fixed sum, takes its maximum value if all its factors μ_k^N are equal. Thus, from Eq. (104) we get the estimate $(N \ge 2)$

$$\gamma_N = \mu_n^N \prod_{\substack{k=1\\k\neq n}}^{N} \mu_k^N \le \mu_n^N \left[(N-1)^{-1} \sum_{\substack{k=1\\k\neq n}}^{N} \mu_k^N\right]^{N-1}. \tag{149}$$

Using the trace condition (54), this leads to

$$\gamma_N \le \mu_n^N \left(\frac{N - \mu_n^N}{N-1}\right)^{N-1} = \mu_n^N \left(1 - \frac{\mu_n^N - 1}{N-1}\right)^{N-1}. \tag{150}$$

Putting $x = \mu_n^N - 1$ and using (148) repeatedly, it follows that

$$\gamma_N \leq \mu_n^N \left(1 - \frac{x}{N'}\right)^{N'} \qquad (N' > N - 1). \tag{151}$$

Since the sequence $(1 - x/N')^{N'}$ is monotonically increasing with N' and bounded from above by $\exp(-x)$, Eq. (151) proves (105) for $N = 2, 3, 4, \ldots$.

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Symmetry Rules in the Graph Theory of Molecular Orbitals

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I. Introduction

Every molecule may be represented by a structure formula. If the points correspond to atoms and the lines to chemical bonds, then the molecular graph represented by points (vertices) and lines (edges) may be drawn in correspondence with a structure formula. Graph theory has various applications in chemistry (Balaban, 1976). One hundred years ago, by the method of graph theory, the structures of conjugated molecules were depicted (Crum Brown, 1861, 1864) and the enumeration of the isomers of alkanes was made (Cayley, 1874, 1875, 1881). The use of graph theory for studying problems in quantum chemistry was developed by Coulson and

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Rushbrooke (1940), who first established the well-known pairing theorem of the alternant molecules.

Hückel molecular orbitals (HMO) have had many applications to organic chemistry since it was originated by Hückel (1931a,b), and quantum chemists study HMO in various aspects. Because the molecular graphs of HMO have the most apparent topological properties, great success has been achieved using graph theory to study HMO. The pairing theorem can easily be proved by graph theory (Cvetković, 1969; Rouvray, 1972), stabilities of conjugated molecules can be discussed and the ($4n + 2$) rule can be established (Graovac *et al.*, 1977). The Woodward–Hoffmann conservation rules of orbital symmetry for the concerted reaction (Woodward and Hoffmann, 1970) can also be shown by graph theory (Tang and Jiang, 1977a; Tang and Sun, 1979). There has been much work done on the fundamental concepts and achievements of graph theory applied to quantum chemistry (Gutman and Trinajstić, 1973a; Rouvray, 1976; Trinajstić, 1977a; Graovac *et al.*, 1977), from which readers can obtain useful knowledge and many original references; it is not necessary to discuss them further in this article.

In correspondence with a molecular graph, there can be a characteristic matrix representing the topological properties. The characteristic values of the topological matrix or the characteristic roots of the characteristic equation are also the eigenvalues of the molecule, so it is especially effective to use the method of graph theory in the search for the eigenvalue spectra of a molecule. The present article emphasizes the structural characteristics of the characteristic matrices and the solutions of the characteristic equations of the molecular graphs, especially those of the symmetrical molecular graphs.

II. Characteristic Polynomials $G(x)$

Use of the method of graph theory to deal with HMO eigenvalue problems of conjugated molecules is an important aspect of the application of graph theory to quantum chemistry. In HMO, it is easy to write out the characteristic matrices and their characteristic determinants. In order to obtain the molecular orbitals and their energies, and to analyze their mutual relationships, it is sometimes necessary to expand the characteristic determinants in the form of polynomials. It becomes difficult when the number of atoms and the complexity of the molecular structure increase. Graph theory of molecular orbitals was first established and developed for solving this fundamental problem (Coulson, 1950; Sachs, 1964; Hosoya, 1972). Their achievements were summarized as Sachs theorem (Sachs,

1964) and its applications (Graovac *et al.*, 1972; Gutman and Trinajstić, 1973b; Trinajstić, 1977b).

Another approach, that of expanding the characteristic determinants, might be called the method of $G(x)$ functions (Heilbronner, 1953; Streitwieser, 1961; Schwenk, 1974; Tang and Jiang, 1976; Zhang, 1979), which differs from the method of Sachs theorem. According to this method, it is easier to write out the characteristic polynomial $G(x)$ corresponding to the molecular graph, and to factorize $G(x)$ by means of the symmetries of the molecular graph (Heilbronner, 1954; Tang and Jiang, 1976, 1977a,b; Yan and Wang, 1978a,b,c; Wang and Yan, 1978; Liu, 1978, 1979). All of these methods simplify calculation of the eigenvalues and eigenvectors.

A. Molecular Graphs and Their Characteristic Polynomials

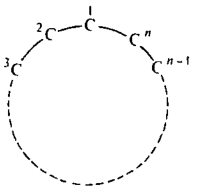
The graph theory of molecular orbitals is built on HMO. In graph theory, every conjugated molecule corresponds to a molecular graph. In the molecular graphs, the atoms in the molecular skeleton are represented by small circles (O) called vertices and the bonds between the bonding atoms are represented by short lines (-) called edges. For example, in correspondence with a conjugated unbranched linear chain of carbon atoms referred to as polyene

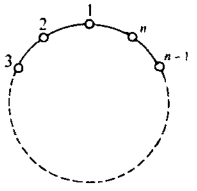
$$\overset{1}{\mathrm{H_2C}}=\overset{2}{\mathrm{CH}}-\overset{3}{\mathrm{CH}}=\overset{4}{\mathrm{CH}}\text{-----------}\overset{n-1}{\mathrm{CH}}=\overset{n}{\mathrm{CH_2}},$$

the molecular graph is

$$\overset{1}{\mathrm{O}}-\overset{2}{\mathrm{O}}-\overset{3}{\mathrm{O}}-\overset{4}{\mathrm{O}}\text{-----------}\overset{n-1}{\mathrm{O}}-\overset{n}{\mathrm{O}}.$$

A cyclic annulene molecule and its corresponding molecular graph are, respectively,





In these molecules and molecular graphs, (1, 2, ---, $n-1$, n) are the numbers of the atoms.

In HMO, if the Coulomb integral α of the carbon atom is defined as zero, and the exchange integral β between the carbon atoms is taken as an energy unit, then the characteristic determinant and the characteristic polynomial of the unbranched linear polyene is

$$g_n(x) \equiv \begin{array}{c|ccccccc|} & 1 & 2 & 3 & \cdots & n-2 & n-1 & n \\ 1 & x & -1 & 0 & \cdots & \cdots & \cdots & 0 \\ 2 & -1 & x & -1 & \ddots & & \bigcirc & \vdots \\ 3 & 0 & -1 & x & \ddots & \ddots & & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \vdots \\ n-2 & \vdots & \bigcirc & & \ddots & x & -1 & 0 \\ n-1 & \vdots & & & & -1 & x & -1 \\ n & 0 & \cdots & \cdots & \cdots & 0 & -1 & x \end{array} = \sum_{r=0}^{[n/2]} (-1)^r \frac{(n-r)!}{r!(n-2r)!} x^{n-2r}, \quad (1)$$

where $(n/2)$ represents the integral part of $n/2$. The characteristic polynomial of the cyclic annulene is

$$g_n^0(x) \equiv \begin{array}{c|ccccccc|} & 1 & 2 & 3 & \cdots & n-2 & n-1 & n \\ 1 & x & -1 & 0 & \cdots & \cdots & 0 & -1 \\ 2 & -1 & x & -1 & \ddots & & \bigcirc & 0 \\ 3 & 0 & -1 & x & \ddots & \ddots & & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \vdots \\ n-2 & \vdots & \bigcirc & & \ddots & x & -1 & 0 \\ n-1 & 0 & & & & -1 & x & -1 \\ n & -1 & 0 & \cdots & \cdots & 0 & -1 & x \end{array} = g_n(x) - g_{n-2}(x) - 2. \quad (2)$$

Hence, $g_n^0(x)$ may also be represented in terms of $g_n(x)$. Equations (1) and (2) are two fundamental relations in the graph theory of molecular orbitals introduced in this article; they are already known from determinant theory (Kowalewski, 1943). When expressions $g_n(x)$ are known, and the characteristic polynomial $G(x)$ of a conjugated molecule is expressed by $g_n(x)$, then the apparent expression of $G(x)$ can be obtained.

From Eq. (1), the first four $g(x)$ may be seen as: $g_0 = 1$, $g_1 = x$, $g_2 = x^2 - 1$, $g_3 = x^3 - 2x$.

When there is a heteroatom at place k in the conjugated molecule, then there is an overdot or an asterisk in the corresponding molecular graph, and the element a_{kk} at the kth row and kth column of the characteristic determinant is

$$a_{kk} = \dot{x} \equiv x - \dot{\delta}, \qquad \dot{\delta} \equiv (\dot{\alpha} - \alpha)/\beta. \quad (3)$$

If place l links with place k, then

$$a_{kl} = a_{lk} = -\dot{\beta}/\beta \equiv -\dot{\eta}. \quad (4)$$

When a heteroatom at place k is linked with a heteroatom at place m, then

$$a_{km} = a_{mk} = -\dot{\beta}^*/\beta \equiv -\dot{\eta}^*. \quad (5)$$

In the above equations, $\dot{\alpha}$, $\dot{\beta}$, and $\dot{\beta}^*$ are the Coulomb integral and exchange integral of the corresponding atoms, respectively. It will be shown in the following sections that the characteristic determinants containing heteroatoms can also be expressed by $g(x)$, so as to be expanded apparently in terms of the powers of x.

B. Two Fundamental Theorems of the Characteristic Polynomials

This section describes two fundamental theorems concerning the expansion characteristic polynomials $G(x)$ (Heilbronner, 1953; Streitwieser, 1961; Schwenk, 1974; Tang and Jiang, 1976; Wang and Yan, 1978; Liu, 1978; Zhang, 1979).

THEOREM 1. Cutting off any one of the bonds in a conjugated molecule containing n atoms, two fragments containing l and m atoms are formed, respectively. If G_n, G_l, and G_m are the characteristic polynomials of the original molecule and its two fragments, respectively, then

$$G_n = G_l G_m + aG_{l-1}G_{m-1} \qquad (n = l + m). \tag{6}$$

In this relation, G may be g, g^0, or the complex characteristic polynomials containing heteroatoms and rings. The meaning of a is as follows:

Cutting off carbon–carbon bond (○—¦—○), $a = -\eta^2 = -1$
Cutting off carbon–heteroatom bond (○—¦—●), $a = -\dot{\eta}^2$
Cutting off heteroatom–heteroatom bond (●—¦—∗), $a = -\dot{\eta}^{*2}$

G_{l-1} and G_{m-1} are, respectively, the corresponding characteristic polynomials of the residual parts of two fragments when the atom adjacent to the cut-off bond is pulled out.

Using the Laplace theorem (Kowalewski, 1943) to expand the determinant of the molecule by means of order k subdeterminants, one finds no difficulty proving Theorem 1.

When Theorem 1 is used, the following points must be noticed:

The place cut-off bond must make the molecule fission the two fragments and not open the ring. When it is done this way, the resultant determinant has the form

$$(\det)_l(\det)_m + a(\det)_{l-1}(\det)_{m-1}.$$

There are no restrictions on the molecular fragments.

Satisfying the above condition, the initial place cut-off bond does not produce different results.

THEOREM 2. For any single ring of conjugated molecules containing heteroatoms, the characteristic polynomial G_n^0 may be given by

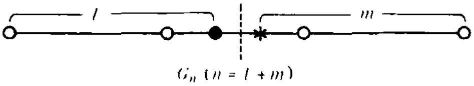
$$G_n^0 = G_n + aG_{n-2} + 2b. \tag{7}$$

G_n is the characteristic polynomial of the conjugated unbranched linear chain formed by the original conjugated single ring by means of cutting off a bond; G_{n-2} is the characteristic polynomial of the conjugated unbranched linear chain formed by the original conjugated single ring by means of pulling out the atoms adjacent to the cut-off bond; a means the same as in Theorem 1; b is $(-b) = \prod \eta_i$, where $\eta = 1$ for the carbon–carbon bond, $\eta = \dot{\eta}$ for the carbon–heteroatom bond, and $\eta = \dot{\eta}^*$ for the heteroatom–heteroatom bond.

Using the Laplace theorem (Kowalewski, 1943) to expand the characteristic determinant of the conjugated single ring containing heteroatoms, there is no difficulty in proving Theorem 2.

Having obtained Theorems 1 and 2, one may utilize the cutting approach to write out easily the characteristic polynomials of any complex conjugated molecules. If there are many different cutting approaches, the final result will be unchanged. Some examples are now cited to illustrate the Theorems 1 and 2.

Example 1. A general conjugated unbranched linear chain molecule containing heteroatoms is represented by



Cutting off the bond (O—*), it becomes

According to Theorem 1, we obtain

$$G_n = \dot{g}_l \overset{*}{g}_m - \overset{\cdot *}{\eta}^2 g_{l-1} g_{m-1},$$

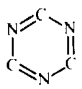
$G_l = \dot{g}_l$ shows that there is a heteroatom at the terminal of the unbranched linear chain. The meaning for $G_m = \overset{*}{g}_m$ is the same as $a = -\overset{*}{\eta}^2$. To express $G_n(x)$ as $g(x)$, one may continue to cut off the graph of the molecular fragments corresponding to $\dot{g}_l$ and $\overset{*}{g}_m$, and finally obtain

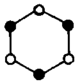
$$\dot{g}_l = g_{l-1}\dot{g}_1 - \dot{\eta}^2 g_{l-2} g_0, \qquad \overset{*}{g}_m = g_{m-1}\overset{*}{g}_1 - \overset{*}{\eta}^2 g_{m-2} g_0.$$

We already know that $\dot{g}_1 = \dot{x} = x - \dot{\delta}$ and $\overset{*}{g}_1 = \overset{*}{x} = x - \overset{*}{\delta}$. Finally, we obtain

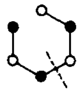
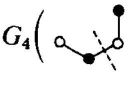
$$\begin{aligned} G_n(x) = {} & [(x - \dot{\delta})g_{l-1} - \dot{\eta}^2 g_{l-2}] \\ & [(x - \overset{*}{\delta})g_{m-1} - \overset{*}{\eta}^2 g_{m-2}] - \overset{\cdot *}{\eta}^2 g_{l-1} g_{m-1}. \end{aligned}$$

Example 2. 1,3,5-Triazine. The structure and the molecular graph are, respectively,





According to Theorem 2, we are ready to write out the characteristic polynomial

$G_6^0 = G_6\Big($  $\Big) - \dot{\eta}^2 G_4\Big($  $\Big) - 2\dot{\eta}^6.$

Once again, according to Theorem 1, we obtain

$$G_6 = g_{\dot{3}}\dot{g}_3 - \dot{\eta}^2\dot{g}_2^2, \qquad G_4 = \dot{g}_2^2 - \dot{\eta}^2\dot{g}_1 g_1,$$

$$g_{\dot{3}} = g_1\dot{g}_2 - \dot{\eta}^2 g_0 g_1, \qquad \dot{g}_3 = \dot{g}_1\dot{g}_2 - \dot{\eta}^2 g_0\dot{g}_1,$$

$$\dot{g}_2 = g_1\dot{g}_1 - \dot{\eta}^2 g_0^2.$$

In these equations, $g_{\dot{3}}$ indicates that there is a heteroatom within the chain, and $\dot{g}_3$ that there is a heteroatom at the terminal of the chain. Finally, we obtain

$$G_6^0 = x^3(x - \dot{\delta})^3 - 6\dot{\eta}^2 x^2(x - \dot{\delta})^2 + 9\dot{\eta}^4 x(x - \dot{\delta}) - 4\dot{\eta}^6.$$

III. Plane Symmetry

In this section, the problem of factorizing the characteristic polynomials of the plane-symmetrical molecules will be discussed.

A. Structural Characteristics of the Characteristic Matrices

For plane-symmetrical molecules, when the atoms are numbered by its symmetrical planes, the characteristic matrix of the molecular graph, namely the Hückel matrix (Rouvray, 1976), is of center symmetry. This is represented as

$$\mathbf{H} = \mathbf{H}[\,\cdot\,], \qquad (\mathbf{H})_{ij} = (\mathbf{H}[\,\cdot\,])_{n+1-i,n+1-j}. \tag{8}$$

where $(\mathbf{H})_{ij}$ represents the ith row and the jth column element of $\mathbf{H}$.

If there is only one symmetrical plane in the molecule, and the symmetrical plane does not pass through the atom, then the characteristic matrix is

$$\mathbf{H}_1 = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}[\cdot] & \mathbf{A}[\cdot] \end{pmatrix}; \tag{9}$$

when the symmetrical plane passes through the atoms, the characteristic matrix is

$$\mathbf{H}_2 = \begin{pmatrix} \mathbf{A} & \mathbf{U} & \mathbf{B} \\ \tilde{\mathbf{U}} & \mathbf{P} & \tilde{\mathbf{U}}[|] \\ \mathbf{B}[\cdot] & \mathbf{U}[—] & \mathbf{A}[\cdot] \end{pmatrix}. \tag{10}$$

In Eqs. (9) and (10), **A** and **B** are matrix blocks, and $[|]$ and $[—]$ are defined as follows:

$(\mathbf{U})_{ij} = (\mathbf{U}[—])_{n+1-i,j}$ (exchanging the symmetrical rows);
$(\tilde{\mathbf{U}})_{ij} = (\mathbf{U}[|])_{i,n+1-j}$ (exchanging the symmetrical columns);

$\tilde{\mathbf{U}}$ and **U** are the row and column matrices, respectively; $\tilde{\mathbf{U}}$ is the transposed matrix of **U**; **P** is a square matrix and its order is equal to the number of atoms on the symmetrical plane.

By means of the fundamental theory of the determinants, it is not difficult to prove the following equations

$$\det \mathbf{H}_1 = |\mathbf{A} + \mathbf{B}[|]| \cdot |\mathbf{A}[\cdot] - \mathbf{B}[-]|, \tag{11}$$

$$\det \mathbf{H}_2 = \begin{vmatrix} \mathbf{A} + \mathbf{B}[|] & \mathbf{U} \\ 2\tilde{\mathbf{U}} & \mathbf{P} \end{vmatrix} \cdot |\mathbf{A}[\cdot] - \mathbf{B}[-]|. \tag{12}$$

In these transformations of the determinants, the following relations have been used

$$\mathbf{A}[\cdot\,|] = \mathbf{A}[—], \qquad \mathbf{A}[—|] = \mathbf{A}[\cdot], \qquad \mathbf{A}[\cdot\,—] = \mathbf{A}[|].$$

If there are two symmetrical planes in the molecule, and the atoms are numbered by its two symmetrical planes, then the characteristic matrix will have a two-step center-symmetrical structure; namely, after factorizing the characteristic determinant for the first time, the matrices obtained,

$$(\mathbf{A} + \mathbf{B}[|]), \qquad (\mathbf{A}[\cdot] - \mathbf{B}[—]), \qquad \begin{pmatrix} \mathbf{A} + \mathbf{B}[|] & \mathbf{U} \\ 2\tilde{\mathbf{U}} & \mathbf{P} \end{pmatrix},$$

are also of the center-symmetrical structure like Eqs. (9) and (10). If the second symmetrical plane does not pass through any atom, the matrix will have a structure like that of Eq. (9); if the second symmetrical plane passes through the atoms, the matrix will have the structure of Eq. (10). Thus, Eq. (11) or (12) may be factorized into four factors. These properties can be extended to the case when there are more than two symmetrical planes perpendicular to each other.

B. Graph Rules

According to the factorizing rules of Section III,A, it is not difficult to prove the following theorem of graph rules dealing with the plane-symmetrical molecules (Tang and Jiang, 1976, 1977b; Wang and Yan, 1978).

THEOREM 3. If there are two symmetrical planes perpendicular to each other in the graph of a conjugated molecule, then two symmetrical planes will cut off the molecular graph into four subgraphs which occupy one quarter of the system of coordinates, respectively. Let G_{++}, G_{-+}, G_{--}, and G_{+-} represent the characteristic polynomials corresponding to first, second, third, and fourth quarter, respectively; then the characteristic polynomial of the whole molecule is

$$G(x) = G_{++}G_{-+}G_{--}G_{+-}. \tag{13}$$

If there is only one symmetrical plane, then Eq. (13) is simplified to

$$G(x) = G_{+}G_{-} \tag{14}$$

In Eq. (13), every $G_{\Delta\Delta}$ (namely, G_{++}, G_{-+}, G_{--}, and G_{+-}) belonging to each quarter has the form:

$$G_{\Delta\Delta} = G_0 + \sum a_i' G_i(\leftarrow\!\phi\!-\!\mathrm{O}) + \sum c_k G_k(\leftarrow\!\mathrm{O}) + \sum a_i' a_j' G_{ij}\begin{pmatrix}\leftarrow\!\phi\!-\!\mathrm{O}\\ |\\ \leftarrow\!\phi\!-\!\mathrm{O}\end{pmatrix} + \sum c_k c_l G_{kl}\begin{pmatrix}\leftarrow\!\mathrm{O}\\ \\ \leftarrow\!\mathrm{O}\end{pmatrix} + \sum a_i' c_k G_{ik}\begin{pmatrix}\leftarrow\!\phi\!-\!\mathrm{O}\\ \\ \leftarrow\!\mathrm{O}\end{pmatrix} + \cdots, \tag{15}$$

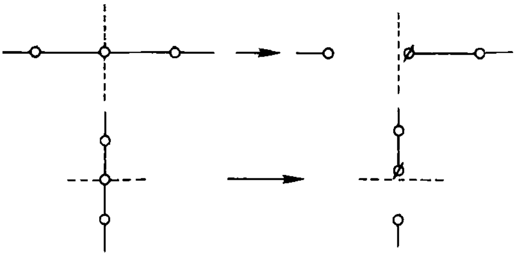
where G_0 represents the characteristic polynomial corresponding to the subgraph which is not to be treated; $G(\leftarrow\!\phi\!-\!\mathrm{O})$ represents the characteristic polynomials of the subgraphs which are residual parts by pulling out the terminal pair of atoms $(\leftarrow\!\phi\!-\!\mathrm{O})$; $G(\leftarrow\!\mathrm{O})$ represents the characteristic polynomials of the subgraphs which are residual parts by pulling out the terminal atom; $G\left(\begin{smallmatrix}\leftarrow\phi-\mathrm{O}\\ \leftarrow\phi-\mathrm{O}\end{smallmatrix}\right)$ represents the characteristic polynomials of the subgraphs which are residual parts by pulling out two terminal pairs of atoms $(\leftarrow\!\phi\!-\!\mathrm{O})$ at the same time. The meanings of other G symbols are similar to those of the previously defined symbols. In Eq. (15),

$a_i' = -1$ when $(\phi\!-\!\mathrm{O})$ is a carbon–carbon bond;
$a_i' = -\eta^2$ when (ϕ—●) or ($\blacklozenge$—O) is a carbon–heteroatom bond;
$c_k = +1$ (or -1) when the direction of pulling out the terminal carbon atom is along the positive (or negative) x axis or y axis;

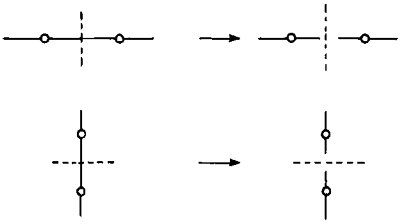
$c_k = +\dot{\eta}$(or $-\dot{\eta}$) when the direction of pulling out the terminal heteroatom is along the positive (or negative) x axis or y axis.

Before using this theorem to deal with concrete problems, the following illustrations to Theorem 3 are given.

(1) When the symmetrical planes pass through the atoms, the atoms cut off by the x axis are assigned to first and second quarters, and the atoms cut off by the y axis are assigned to first and fourth quarters. Both the cut-off atom and its adjacent atom are called the "terminal pair of atoms," and are denoted by (⧲—○), and dealt with by the following rules: The terminal atoms in the third and fourth quarters (cut off by the x axis), and in the second and third quarters (cut off by the y axis), which are adjacent to the atoms cut off by symmetrical planes, do not take part in the following treatments:



When the symmetrical planes pass through the bonds, every cut-off bond is assigned to a half-bond on both of the two subgraphs. The atom adjacent to the cut-off bond is called a "terminal atom," denoted by (—○), and dealt with by the following rules:



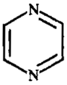
(2) Removing the terminal pair of atoms (⧲—●) and (⧳—○), the factor $-\eta^2$ is added; for (⧳—*), the factor $-\overset{*}{\eta}^2$ is added. Removing the terminal atom adjacent to the cut-off carbon–carbon bond along the positive(negative) x axis or y axis, the factor $+1(-1)$ is added; for the heteroatom–heteroatom bond, the factor $+\dot{\eta}(-\dot{\eta})$ is added.

(3) Every terminal pair of atoms and terminal atom are pulled out once

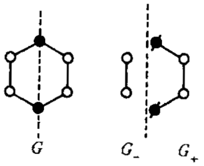
separately, and then every two of these are pulled out together once, and so on. After every removal of the terminal pair of atoms and terminal atoms, the characteristic polynomials corresponding to the residual subgraphs are multiplied by the above factor, and then summed.

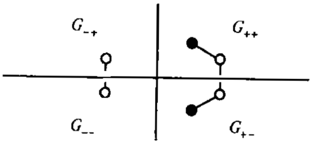
C. Examples

Example 1. Pyrazine

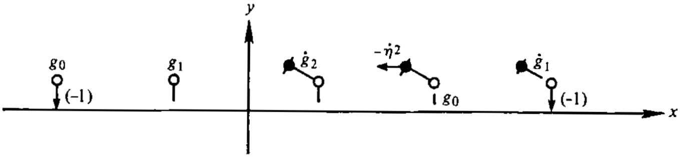


Its graph, the successive subgraphs, and the corresponding characteristic polynomials are





G_{++} and G_{-+} are dealt with as follows (others are dealt with similarly),



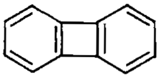
From these successive subgraphs, we may obtain

$$G_{++} = \dot{g}_2 - \dot{\eta}^2 g_0 - \dot{g}_1 = (x - \dot{\delta})g_1 - \dot{\eta} g_0 - \dot{\eta}^2 g_0 - (x - \dot{\delta})$$
$$= x^2 - (\dot{\delta} + 1)x + (\dot{\delta} - 2\dot{\eta}^2),$$
$$G_{-+} = g_1 - g_0 = x - 1, \qquad G_{--} = g_1 + g_0 = x + 1,$$
$$G_{+-} = \dot{g}_2 - \dot{\eta}^2 g_0 + \dot{g}_1 = x^2 - (\dot{\delta} - 1)x - (\dot{\delta} + 2\dot{\eta}^2).$$

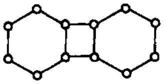
Let $G = G_{++}G_{-+}G_{--}G_{+-} = 0$, then

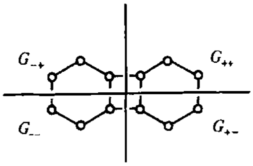
$$x = \tfrac{1}{2}\{(\dot{\delta} + 1) \pm [(\dot{\delta} + 1)^2 - 4(\dot{\delta} - 2\dot{\eta}^2)]^{1/2}\}, \quad 1,$$
$$-1, \quad \tfrac{1}{2}\{(\dot{\delta} - 1) \pm [(\delta - 1)^2 + 4(\dot{\delta} + 2\dot{\eta}^2)]^{1/2}\}.$$

Example 2. Biphenylene

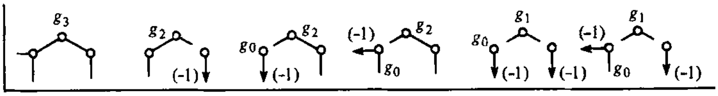


Its molecular graph and subgraphs are





G_{++} is dealt with as follows



The other G's may be dealt with in a similar way according to Theorem 3.

From the above successive subgraphs, we obtain

$$G_{++} = g_3 - 3g_2 + 2g_1 = x^3 - 3x^2 + 3,$$

$$G_{-+} = g_3 - g_2 = x^3 - x^2 - 2x + 1,$$

$$G_{--} = g_3 + 3g_2 + 2g_1 = x^3 + 3x^2 - 3,$$

$$G_{+-} = g_3 + g_2 = x^3 + x^2 - 2x - 1.$$

Solving these equations, we obtain

$$x = \pm(2\cos\tfrac{1}{3}\omega - 1),\quad \pm[2\cos\tfrac{1}{3}(\omega + 2\pi) - 1],\quad \pm[2\cos\tfrac{1}{3}(\omega + 4\pi) - 1],$$

$$\pm\tfrac{1}{3}(2\sqrt{7}\cos\tfrac{1}{3}\omega' - 1),\quad \pm\tfrac{1}{3}[2\sqrt{7}\cos\tfrac{1}{3}(\omega' + 2\pi) - 1],$$

$$\pm\tfrac{1}{3}[2\sqrt{7}\cos\tfrac{1}{3}(\omega' + 4\pi) - 1],$$

where $\omega = \cos^{-1} 1/2$ and $\omega' = \cos^{-1}(2\sqrt{7})^{-1}$.

IV. Axis Symmetry—No Atom on the Symmetry Axis

In this section, the method of factorizing the characteristic polynomials of the axis-symmetric molecules which have no atom on the symmetry axis (Yan and Wang, 1978a; Liu, 1979) will be discussed.

A. Structural Characteristics of the Characteristic Matrices

By analysis of the characteristic matrices of various axis-symmetric molecules with no atom on the axis, we readily see that if the atoms in the molecule are numbered according to the cyclic blocks then the characteristic matrix has the following block-cyclic form

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_0 & \mathbf{H}_1 & \cdots & \mathbf{H}_{n-1} \\ \mathbf{H}_{n-1} & \mathbf{H}_0 & \cdots & \mathbf{H}_{n-2} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{H}_1 & \mathbf{H}_2 & \cdots & \mathbf{H}_0 \end{pmatrix} \tag{16}$$

If there are *m* atoms in the axis-symmetric equivalent fragment, then

$$\mathbf{H}_k = \begin{pmatrix} h_{11}^{(k)} & h_{12}^{(k)} & \cdots & h_{1m}^{(k)} \\ h_{21}^{(k)} & h_{22}^{(k)} & \cdots & h_{2m}^{(k)} \\ \vdots & \vdots & \ddots & \vdots \\ h_{m1}^{(k)} & h_{m2}^{(k)} & \cdots & h_{mm}^{(k)} \end{pmatrix} \quad (k = 0, 1, \ldots, n-1). \tag{17}$$

According to determinant theory, it is not difficult to prove (Yan and Wang, 1978a)

$$\det \mathbf{H} = \prod_{k=0}^{n-1} \left| \sum_{j=0}^{n-1} \omega_k^j \mathbf{H}_j \right|, \qquad \omega_k \equiv \exp\left(i\,\frac{2\pi k}{n}\right). \tag{18}$$

In the HMO case,

$$\mathbf{H}_2 = \mathbf{H}_3 = \cdots \mathbf{H}_{n-2} = 0.$$

From Eq. (18) it is shown that if the characteristic value problems of the axis-symmetric molecules are dealt with by means of this approach, then the characteristic polynomials may be factorized according to axis symmetry.

B. Graph Rules

From the previous section, which discussed the factorizing rule, the theorem of graph rules dealing with the axis-symmetric molecules with no atom on the symmetry axis can be proved.

THEOREM 4. When a conjugated molecular graph containing nm atoms and having n fold symmetric axis is cut off by n spoke lines having equal angle distances, n subgraphs containing m atoms are formed. Let $G_{(k)}(x)$ be the characteristic polynomial corresponding to the kth subgraph. The characteristic polynomial of the whole molecule is then

$$G(x) = \prod_{k=0}^{n-1} G_{(k)}(x) \tag{19}$$

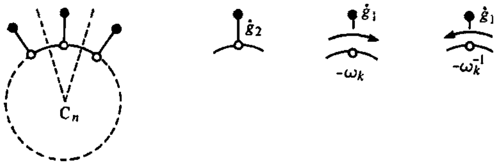
$$\begin{aligned} G_{(k)}(x) &= G_0 + \sum a_l G_l(\leftarrow\!\circ\quad\circ\!\rightarrow) + \sum A_i G_i(\leftarrow\!\circ\!\sim\!\circ\!\rightarrow) \\ &\quad + \sum a_l A_i G_{li}\begin{pmatrix}\leftarrow\!\circ\quad\circ\!\rightarrow \\ \leftarrow\!\circ\!\sim\!\circ\!\rightarrow\end{pmatrix} + \sum A_i A_j G_{ij}\begin{pmatrix}\leftarrow\!\circ\!\sim\!\circ\!\rightarrow \\ \leftarrow\!\circ\!\sim\!\circ\!\rightarrow\end{pmatrix} \\ &\quad + \cdots \end{aligned} \tag{20}$$

In Eq. (20), G_0 is the characteristic polynomial corresponding to the untreated subgraph; $G_l(\leftarrow\!\circ\quad\circ\!\rightarrow)$ is the characteristic polynomial which corresponds to the residual subgraph after two terminal atoms adjacent to the lth atom chain including the cut-off bond are removed; $G_i(\leftarrow\!\circ\!\sim\!\circ\!\rightarrow)$ is the characteristic polynomial corresponding to the residual subgraph after the atom chain including the cut-off bond is drawn out; $G_{li}\begin{pmatrix}\leftarrow\!\circ\quad\circ\!\rightarrow \\ \leftarrow\!\circ\!\sim\!\circ\!\rightarrow\end{pmatrix}$ is the characteristic polynomial which corresponds to the residual subgraph after two atoms adjacent to the lth atom chain including the cut-off bond are removed and the ith atom chain including the cut-off bond is drawn out; $G_{ij}\begin{pmatrix}\leftarrow\!\circ\!\sim\!\circ\!\rightarrow \\ \leftarrow\!\circ\!\sim\!\circ\!\rightarrow\end{pmatrix}$ is the characteristic polynomial which corresponds to the residual subgraph after two nonintersecting ith and jth atom chains including the cut-off bonds are drawn out; $a_l = -1$ when two carbon–carbon terminal atoms are removed, and $a_l = -\dot{\eta}^2$ when the carbon–heteroatom terminal atoms are removed; A_i is related to the direction in which the atom chain is drawn out; $A_i = \omega_k b$ when the atom chain is drawn out clockwise, and $A_i = \omega_k^{-1} b$ when the atom chain is drawn out anticlockwise; $(-b) = \Pi\eta_i$, η_i includes all η in the atom chain, and the two terminal half-bonds become one bond. The removal and the drawing-out actions must be combined in various ways.

C. Examples

Applications of Theorem 4 are illustrated by the following examples.

Example 1. Heteroradialene. There is a C_n axis in the molecule. The molecular graph and its successive subgraphs are:



From these subgraphs, we obtain

$$\begin{aligned} G &= \prod_{k=0}^{n-1} [\dot{g}_2 - (\omega_k + \omega_k^{-1})\dot{g}_1] \\ &= \prod_{k=0}^{n-1} \left[x^2 - \left(2\cos\frac{2\pi k}{n} + \dot{\delta}\right)x - \dot{\eta}^2 + 2\dot{\delta}\cos\frac{2\pi k}{n}\right] = 0, \end{aligned}$$

Solving these equations gives us

$$x = \frac{1}{2}\left\{\left(2\cos\frac{2\pi k}{n} + \delta\right) \pm \left[\left(2\cos\frac{2\pi k}{n} + \delta\right)^2 + 4\left(\eta^2 - 2\delta\cos\frac{2\pi k}{n}\right)\right]^{1/2}\right\}$$

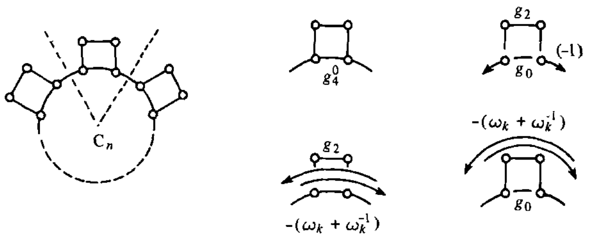
$$k = 0, 1, 2, \ldots, n-1.$$

When the radialene does not contain the heteroatoms, the above equation is transformed to

$$x = \cos\frac{2\pi k}{n} \pm \left(\cos^2\frac{2\pi k}{n} + 1\right)^{1/2} \qquad (k = 0, 1, 2, \ldots, n-1).$$

This result was first obtained by Hess and Schaad (1971) using a finite-difference technique.

Example 2. Butadio annulene. There is a C_n axis in this molecule. The molecular graph and its successive subgraphs are drawn and we obtain



From this graph and the subgraphs, we obtain

$$G = \prod_{k=0}^{n-1} [g_4^0 - (1 + \omega_k + \omega_k^{-1})g_2 - (\omega_k + \omega_k^{-1})].$$

When the concrete forms of g_4^0 and g_2 are substituted into the above equation, we obtain

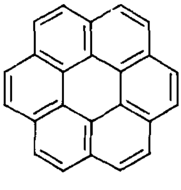
$$x^4 - \left(5 + 2\cos\frac{2\pi k}{n}\right)x^2 + 1 = 0 \qquad (k = 0, 1, 2, \ldots, n-1).$$

Thus,

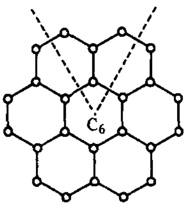
$$x = \pm\frac{1}{\sqrt{2}}\left\{\left(5 + 2\cos\frac{2\pi k}{n}\right) \pm \left[\left(5 + 2\cos\frac{2\pi k}{n}\right)^2 - 4\right]^{1/2}\right\}$$

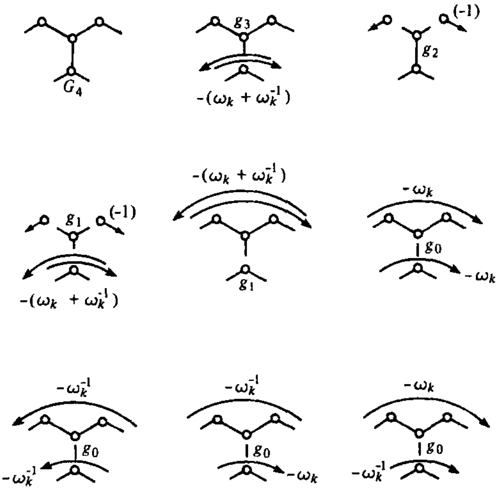
$$k = 0, 1, 2, \cdots, n-1.$$

Example 3. Coronene



This molecule has a C_6 axis. The results of cutting off the molecular graph with spoke lines are given as:





From all of these subgraphs, we obtain

$$G = \prod_{k=0}^{5} [G_4 - (\omega_k + \omega_k^{-1})g_3 - g_2 + 2 + (\omega_k^2 + \omega_k^{-2})].$$

According to Theorem 1,

$$G_4 = g_3 g_1 - g_1^2 = x^4 - 3x^2.$$

Finally, we obtain these results:

$$(x + 1)(x^3 - 3x^3 - x + 5) = 0, \qquad k = 0,$$

$$(x - 1)(x^3 - 4x - 2) = 0, \qquad k = 1, 5,$$

$$(x + 1)(x^3 - 4x + 2) = 0, \qquad k = 2, 4,$$

$$(x - 1)(x^3 + 3x^2 - x - 5) = 0, \qquad k = 3.$$

Example 4. It is interesting to point out that if a bond in the chain molecule and the ring molecule is cut off with C_1 axis, then Theorems 1 and 2 can be proved.

V. Axis Symmetry—Atoms on the Symmetry Axis

The approaches to the treatment of axis-symmetric molecules with atoms on the symmetry axis are discussed in this section (Yan and Wang, 1978b; Liu, 1979).

A. Structural Characteristics of the Characteristic Matrices

If the atoms in the axis-symmetric molecules with atoms on the symmetry axis are numbered according to cyclic blocks, then the characteristic matrices will have the following form

$$\mathbf{H} = \begin{pmatrix} \mathbf{B}_0 & \mathbf{B} & \mathbf{B} & \cdots & \mathbf{B} \\ \tilde{\mathbf{B}} & \mathbf{H}_0 & \mathbf{H}_1 & \cdots & \mathbf{H}_{n-1} \\ \tilde{\mathbf{B}} & \mathbf{H}_{n-1} & \mathbf{H}_0 & \ddots & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \tilde{\mathbf{B}} & \mathbf{H}_1 & \cdots & \cdots & \mathbf{H}_0 \end{pmatrix} \tag{21}$$

In Eq. (21), if the axis only passes through one atom, then $\mathbf{B}_0$ is a one-row and one-column matrix containing one element, $\mathbf{B}$ is a one-row and m-column matrix, and $\tilde{\mathbf{B}}$ is the transposed matrix of $\mathbf{B}$. $\mathbf{H}_k$ ($k = 0, 1, 2, \cdots, n-1$) is of the same form as Eq. (17); m is the number of atoms in a symmetrical fragment. When the axis passes through l atoms, then $\mathbf{B}_0$ will be an order l square matrix.

According to the determinant theory, it can be proved (Yan and Wang, 1978b) that

$$\begin{gathered} \det \mathbf{H} = \begin{vmatrix} \mathbf{B}_0 & n\,\mathbf{B} \\ \tilde{\mathbf{B}} & \mathbf{C}_0 \end{vmatrix} \prod_{k=1}^{n-1} \left| \sum_{j=0}^{n-1} \omega_k^j \mathbf{H}_j \right|, \\ \mathbf{C}_0 = \sum_{j=0}^{n-1} \mathbf{H}_j, \qquad \omega_j \equiv \exp\left(i\,\frac{2\pi k}{n}\right). \end{gathered} \tag{22}$$

Equation (22) is the mathematical basis of the graph theory dealing with the axis-symmetric molecule with atoms on the symmetrical axis.

B. Graph Rules

According to Eq. (22), by factorizing the characteristic determinant, the theorem of the graph rules dealing with the axis-symmetric molecule with atoms on the symmetrical axis can be proved.

THEOREM 5. By taking n spoke lines with equal angle distance to cut off the conjugated molecular graph containing ($nm + 1$) atoms with n fold symmetrical axis, n subgraphs are formed. The central atom is assigned to the zeroth subgraph, and its characteristic polynomial is $G_{(0)}(x)$; the other subgraphs ($k = 1, 2, \cdots, n-1$) contain, respectively, m atoms, and their characteristic polynomials are $G_{(k)}(x)$, respectively. In the kth subgraph ($k = 1, 2, \cdots, n-1$), the cut-off bonds adjacent to the central atom are canceled. Thus, the characteristic polynomial of the whole molecule is

$$G(x) = G_{(0)}(x) \prod_{k=1}^{n-1} G_{(k)}(x) \tag{23}$$

The treatment of the kth subgraph and its $G_{(k)}(x)$ are the same as in Section IV. If there is no relation between the symmetrically equivalent fragments except those adjacent to the center, then the kth fragment ($k = 1, 2, \cdots, n-1$) is seen as an isolated molecule. $G_{(0)}(x)$ is

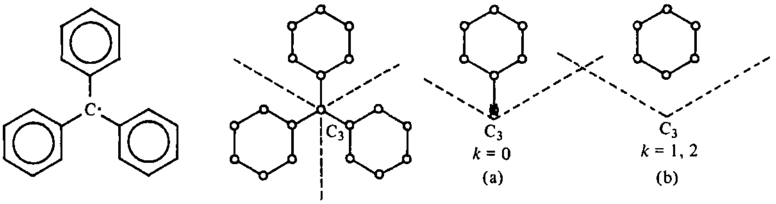
$$\begin{aligned} G_{(0)}(x) = {} & G_1 + (n-1)a'G(\leftarrow\!\otimes\!-\!\circ) + (n-1)\Sigma a'a_lG_l\left(\begin{smallmatrix}\leftarrow\otimes-\circ\\ \leftarrow\circ\quad\circ\rightarrow\end{smallmatrix}\right)\\ & + (n-1)\Sigma a'A_tG_t\left(\begin{smallmatrix}\leftarrow\otimes-\circ\\ \leftarrow\circ\!\sim\!\circ\rightarrow\end{smallmatrix}\right) + \cdots. \end{aligned} \tag{24}$$

In Eq. (24), G_1 is the same as in the case of the molecule with no atom in the center; $G(\leftarrow\!\otimes\!-\!\circ)$ is the polynomial which belongs to the residual subgraph after pulling out the center pair of atoms; a, A, and a' are the same as in the cases of Eqs. (15) and (20).

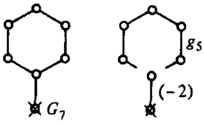
C. Examples

Some examples are now given to illustrate the applications of Theorem 5.

Example 1. Triphenylmethyl. The molecule, the molecular graph, and the circumstance cut off by the spoke lines are:



From the above subgraph (a), we are ready to form the various subgraphs of $G_{(0)}(x)$



Thus, it is obtained that

$$G_{(0)}(x) = G_7 - 2g_5 = g_6^0 g_1 - 3g_5.$$

According to the preceding Theorem 1, one has

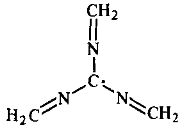
$$g_5 = g_3g_2 - g_2g_1 = (g_2g_1 - g_1g_0)g_2 - g_2g_1 = g_1g_2(g_2 - 2).$$

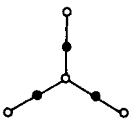
From the preceding Theorem 4, if the benzene is cut off by the spoke lines of the C_3 axis, we then have $g_6^0 = (g_2 - 3)g_2^2$. Finally, we obtain

$$G_{(0)} = g_1g_2[g_2^2 - 3g_2 - 3(g_2 - 2)] = 0, \qquad x = 0, \quad \pm 1, \quad \pm(4 \pm \sqrt{3})^{1/2}.$$

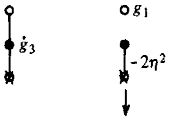
In graph (b), $G_{(k)}(x)$ $(k = 1, 2)$ corresponds to two isolated benzene molecules, hence $G_{(k)}(x) = g_6^0 = 0$ $(k = 1, 2)$, and then $x = \pm 1, \pm 1, \pm 2; \pm 1, \pm 1, \pm 2$.

Example 2. Trimethyleneamino-methyl





The graph and subgraphs corresponding to $k = 0$ are:



From these subgraphs, one obtains that

$$G_{(0)}(x) = g_{\dot{3}} - 2\dot{\eta}^2 g_1 = x^3 - \dot{\delta}x^2 - 4\dot{\eta}^2 x = 0.$$

Solving this equation, one has $x = 0$ and $\frac{1}{2}[\dot{\delta} \pm (\dot{\delta}^2 + 16\dot{\eta}^2)^{1/2}]$. The graph and subgraphs correspnding to $(k = 1, 2)$ are

Thus, we obtained

$$G_{(k)}(x) = \dot{g}_2 = x^2 - \dot{\delta}x - \dot{\eta}^2 = 0, \qquad x = \tfrac{1}{2}(\dot{\delta} \pm \sqrt{\dot{\delta}^2 + 4\dot{\eta}^2}) \quad (k = 1, 2).$$

VI. Center Symmetry

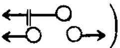
In graph theory, π systems are all considered to have a plane configuration, so center symmetry is in fact equivalent to twofold axis symmetry. For the concrete molecules, there are three cases: (1) the symmetry center is not on atom and bond (this kind of molecule may be treated like the case in Section IV); (2) the symmetry center is on the atom (this kind of molecule may be treated like the case in Section V); and (3) the symmetry center is on the bond (the approach to deal with this kind of molecules is similar to the case of the twofold axis-symmetric molecules.

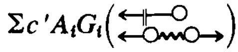
However a treatment for the bond through the symmetry center must be added to the approach).

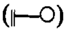
THEOREM 6. The characteristic polynomials $G(x)$ of the center-symmetric molecules may be factorized into two factors by using the following rules

$$G(x) = G_{(0)}(x)G_{(1)}(x). \tag{25}$$

If the symmetry center is not on the atom and bond, it may be dealt with according to Theorem 4; if the symmetry center is on the atom, it may be dealt with according to Theorem 5; if the symmetry center is on the bond, then

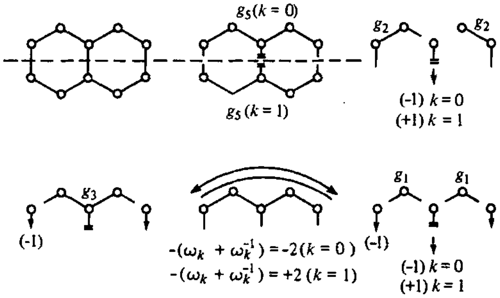
$G_{(k)}(x) = G_1 + c'G($  $) + \Sigma c'a_lG_l($  $)$

$+ \Sigma c'A_lG_l($  $) + \cdots \qquad (k = 0, 1). \qquad (26)$

The meaning of G_1 is the same as in Eq. (24). In the subgraph, each action of pulling out the atom () adjacent to the cut-off bond provides a factor c'. The meaning of c' is that when $k = 0$, $c' = -1$ (carbon) or $-\eta$ (heteroatom); when $k = 1$, $c' = +1$ (carbon) or $+\eta$ (heteroatom). The meanings of other symbols are the same as in the preceding sections.

As an example, naphthalene is taken to illustrate the application of Theorem 6. It ought to be pointed out that there are two symmetry planes perpendicular to each other in the molecule, so that if Theorem 3 is used to treat this molecule, then the factorizing of the characteristic polynomial will be more thorough.

Example 1. Naphthalene. The graph and subgraphs of this molecule are:



From these subgraphs, we obtained

$$\begin{aligned} G_{(0)}(x) &= g_5 - g_2^2 - g_3 - 2 + g_1^2 \\ &= (x - 1)(x^2 + x - 1)(x^2 - x - 3) = 0, \end{aligned}$$

$$\begin{aligned} G_{(1)}(x) &= g_5 + g_2^2 - g_3 + 2 - g_1^2 \\ &= (x + 1)(x^2 - x - 1)(x^2 + x - 3) = 0, \end{aligned}$$

and the solutions are

$$x = \pm 1, \quad \tfrac{1}{2}(-1 \pm \sqrt{5}), \quad \tfrac{1}{2}(1 \pm \sqrt{13}), \quad -1, \quad \tfrac{1}{2}(1 \pm \sqrt{5}), \quad \tfrac{1}{2}(-1 \pm \sqrt{13}).$$

VII. Conjugated Polymers

From a structural viewpoint, the polymer is formed by joining together many similar structural units. The conjugated polymer is a large π system. When the structural units in the polymer are increased, the energy levels are transformed into energy bands. Many optical, electrical, and thermal properties of polymers are determined by energy bands. So, it is very important to calculate energy levels or energy bands of the polymers. In addition to this, some of the conductive solids formed by organic molecules are sometimes molecular crystals of one-dimensional structure, and the approach to dealing with them is the same as that for polymers.

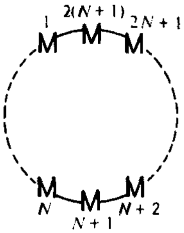
It is not difficult to write out the HMO characteristic determinant of a conjugated polymer, and the rigorous solutions of some concrete molecules have been obtained (Rouvray, 1976). However, the general method for solving the characteristic equations has not been obtained at all. The main difficulty in obtaining general solutions of the HMO characteristic equations for the conjugated polymers is due to the fact that the polymers do not have rigorous translation symmetry, namely there is a terminal effect. Stankevich (1968, 1969a,b, 1972) has more thoroughly investigated these problems and obtained the integral formula calculating the mean value $\bar{\varepsilon}$ of π-electronic energy belonging to each chain unit. Some other authors have also investigated these problems in several ways in the last few years (Tang and Jiang, 1977b; Zhang *et al.*, 1979; Wang and Yan, 1979). When the molecular weight becomes large enough, then the terminal effect may be neglected. In this case, the linear polymer can be seen as a ring polymer; so it is an ideal approach to replace the characteristic value problem of a linear polymer with one of the same-ring polymer, as was done by Bochvar and Stankevich (1967). It is the so called Born–von Karman condition in solid physics (Avery, 1972).

A. Structural Characteristics of the Molecular Graphs

The conjugated molecules may be divided into two types from the viewpoint of graph theory. Let a conjugated molecule have the structural unit M and chain length N, namely,

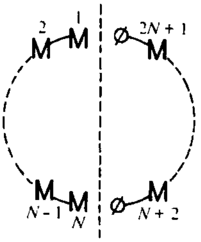
$$\underset{1}{\mathrm{M}}-\underset{2}{\mathrm{M}}-\underset{3}{\mathrm{M}} \cdots \underset{N-2}{\mathrm{M}}-\underset{N-1}{\mathrm{M}}-\underset{N}{\mathrm{M}},$$

where the horizontal lines do not represent single bonds and only represent bonding between two neighboring M's. Take $2(N + 1)$M to form a ring molecule with a $(2N + 1)$fold symmetry axis:



There is one symmetry plane passing through the $(N + 1)$th and $2(N + 1)$th units at least. It may be divided into two cases according to the situation, cutting off the molecular graph into two subgraphs.

(1) When the symmetry plane passes through atoms, and the original graph is cut off as follows



then according to Theorem 3, the characteristic polynomial of the original polymer is a factor of the characteristic polynomial of ring molecule $(\mathbf{M})_{2(N+1)}$.

In addition to this, according to Theorem 4, the characteristic polynomial of ring molecule $(\mathbf{M})_{2(N+1)}$ can be factorized to $2(N + 1)$ factors

$$G_{(\mathrm{M})_{2(N+1)}}(x) = \prod_{k=1}^{2(N+1)} G_{(k)}(x).$$

So, it is easy to see that the characteristic polynomial of the original conjugated polymer $(\mathbf{M})_N$ can be factorized as

$$G_{(\mathrm{M})_N}(x) = \prod_{k=1}^{N} G_{(k)}(x) = \prod_{k=1}^{N} |\mathbf{H} + \mathbf{B}\exp\{i[\pi k/(N + 1)]\} + \tilde{\mathbf{B}}\exp\{-i[\pi k/(N + 1)]\}|, \tag{27}$$

where $\mathbf{H}$ is the Hückel matrix of a structural unit, $\mathbf{B}$ is the matrix which represents the relation between two adjacent structural units, and $\tilde{\mathbf{B}}$ is the transposed matrix of **B**. Each factor $G_{(k)}(x)$ can be obtained according to Theorem 4.

(2) When the symmetry plane does not pass through the atoms, then $G_{(\mathrm{M})_N}(x)$ is not a factor of $G_{(\mathrm{M})_{2(N+1)}}(x)$. In this case, the circumstance is complex, but Stankevich (1968, 1969a,b, 1972) pointed out that $G_{(\mathrm{M})_N}(x)$ may also be factorized as

$$G_{(\mathrm{M})_N}(x) = \prod_{k=1}^{N} G_{(k)}(x) = \prod_{k=1}^{N} \left|\mathbf{H} + \mathbf{B}e^{i\theta_k} + \tilde{\mathbf{B}}e^{-i\theta_k}\right|, \tag{28}$$

where θ_k is not a function of the integer N, and satisfies an inequality

$$[\pi(k - 1)N] < \theta_k < (\pi k/N) \qquad (k = 1, 2, \ldots, N). \tag{29}$$

Thus, the characteristic equations of the conjugated polymers may also be dealt with by means of Theorem 4. In the above descriptions,

$$\theta_k = \pi k/(N + 1) \tag{30}$$

is a particular example of Eq. (29).

B. Graph-Theoretical Method and Its Applications

According to the principle given above, the fundamental theorem dealing with the graphs of the conjugated polymers may now be obtained (Wang and Yan, 1978).

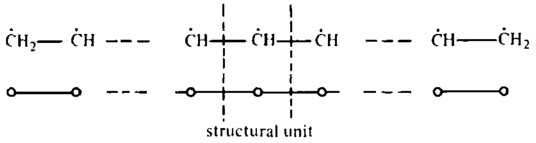
THEOREM 7. Take two perpendicular lines to cut off the polymer containing N units and to pick out one structural unit. The cut-off subgraph is dealt with by the same approaches dealing with the molecular graph with no atom on the symmetry axis (Section IV), except replacing ω_k with ε_k formed by pulling out a chain, where

$$\varepsilon_k = \exp(i\theta_k) \qquad (k = 1, 2, \ldots, N). \tag{31}$$

According to the preceding section (Section VII,A), if the concrete polymer satisfies the first case, θ_k is given by Eq. (30); if the concrete polymer satisfies the second case, θ_k is given by Eq. (29).

Now we take some examples to illustrate the applications of Theorem 7.

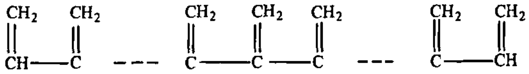
Example 1. Polyene

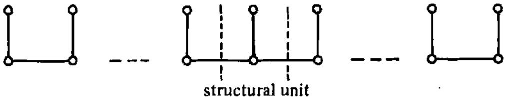


The solutions of this molecular characteristic equation were already obtained many years ago (Rouvray, 1976). It is the simplest conjugated polymer. According to the preceding Theorem 7, the structural unit cut off by two perpendicular lines is an atom with two terminal bonds. When this subgraph is dealt with by Theorem 7, the characteristic polynomial and its solutions are obtained:

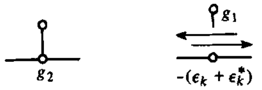
Thus, $g_1 - (\varepsilon_k + \varepsilon_k^*) = 0$, $x = 2\cos[\pi k/(N + 1)]$, where $k = 1, 2, \ldots, N)$.

Example 2. Poly-bimethylene-ethylene. The molecule and its molecular graph are:





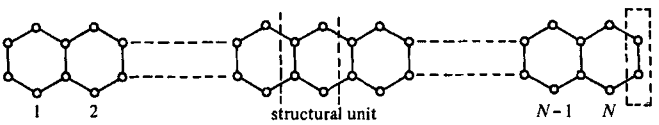
The cut-off graph of the structural unit and its subgraph are



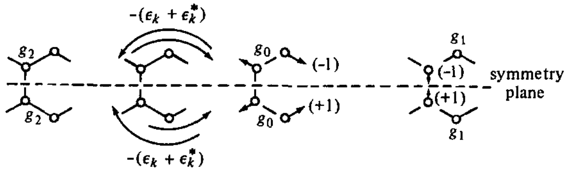
Thus, it is given that $g_2 - (\varepsilon_k + \varepsilon_k^*)g_1 = 0$,

$$x = \cos[\pi k/(N + 1)] \pm \{\cos^2[\pi k/(N + 1)] + 1\}^{1/2}$$
$$(k = 1, 2, \ldots, N).$$

Example 3. Polyacene



This molecule differs slightly from others in that there is a residual ethylene which is shown in a square sash at the terminal, except the repeated structural unit. For this molecule, the cut-off structural unit also has a symmetry plane, and then it may be dealt with by Theorem 3 once again. The actual treatments are

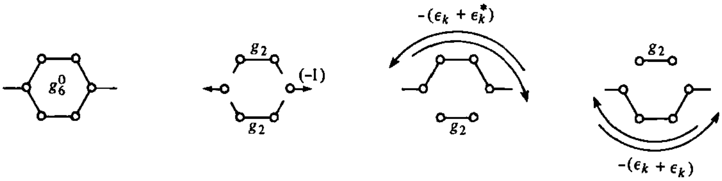


The corresponding characteristic equations are $g_2 - (\varepsilon_k + \varepsilon_k^*) - 1 \mp g_1 = 0$, and the results are

$$x = \tfrac{1}{2}(\pm 1 \pm \{9 + 8\cos[\pi k/(N+1)]\}^{1/2}) \qquad (k = 1, 2, \ldots, N).$$

For the residual ethylene, we obtain $g_2 = 0$, $x = \pm 1$. Coulson (1948) first obtained these results with the determinant method.

Example 4. Polyparaphenylene. Its structural unit graph and successive subgraphs are



The corresponding characteristic polynomials are $g_6^0 - g_2^2 - 4g_2 \cos\theta_k$ where $k = 1, 2, \ldots, N$. From the preceding Example 1 of Section V, it has been shown that $g_6^0 = g_2^3 - 3g_2^2$. Substituting it into the original characteristic polynomial, one has $g_2(g_2^2 - 4g_2 - 4\cos\theta_k) = 0$ where $k = 1, 2, \ldots, N$. Finally, we obtain

$$x = \pm 1, \quad \pm\{1 + 2[1 \pm (1 + \cos\theta_k)^{1/2}]\}^{1/2} \qquad (k = 1, 2, \ldots, N).$$

In the results of Example 4, θ_k only satisfies Eq. (29). But, when the numbers of the chain units $N = 10$, and is replaced by a mean value $\bar{\theta}_k$,

$$\bar{\theta}_k = \tfrac{1}{2}\left[\frac{\pi(k-1)}{N} + \frac{\pi k}{N}\right],$$

then we are ready to understand that the difference between $\cos\bar{\theta}_k$ and $\cos(\pi k/(N+1))$ is less than 1%, and the difference between two characteristic values is far less than this.

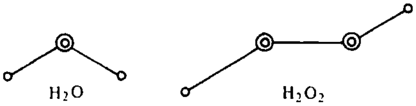
VIII. Extending to Stereomolecules and σ Bonds

From the preceding sections, it has been shown that for planar systems with various symmetries, there is a simple and general graph-theoretical method to calculate the characteristic values. For molecules with stereo configurations with the relations between atoms being the same, King (1977) has given a simple graph-theoretical method. Randić (1976, 1977), and Gutman and Hosoya (1978) have also studied this problem, and obtained some results, individually. Yan and Wang (1978c) started from the structural characteristics of the characteristic matrices, and obtained a simple and general graph-theoretical method for the LCAO–MO characteristic equations.

A. Graph of the Multiple Point

In the graph theory of Hückel molecular orbitals, the atoms or atomic orbitals correspond to the points (vertices) of the graph, and the bonds between the atoms or overlaps between the atomic orbitals correspond to linked lines (edges). Because only one atomic orbital is studied on each carbon atom, it is not important whether the point of the graph corresponds to an atom or an atomic orbital in the molecule. But if this method is extended to σ systems, then either point-to-atom or point-to-atomic orbital becomes inportant. At this time, there are many atomic orbitals on an atom that have to be studied. By its very nature, it is apparent that the points of the graph have corresponded to the atomic orbital. If an atom has more than one orbital being studied, then it is impossible to represent an orbital with a general point as in the preceding sections.

The multiple point which is drawn as an overlapped circle has been introduced to represent the atomic orbitals on an atom. For example, the molecular graphs of H_2O and H_2O_2 may be represented as follows

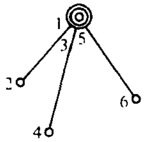


where the double points represent two 2p orbitals on the oxygen atoms.

B. Graphic Derivation

After the multiple point is introduced, it is easy to write out the characteristic matrices of the molecular graphs by numbering the atomic orbitals by way of symmetry. It is clear that these characteristic matrices show the structural characteristics corresponding to their own symmetry. The molecular graphs with inversion symmetry have matrices like Eqs. (9) and (10), and the molecular graphs with cycle symmetry have matrices like Eqs. (16) and (21). Thus, one can factorize the characteristic determinants with Eqs. (11), (12), (18), and (22). We cite some examples to illustrate the applications of the preceding principle.

Example 1. Ammonia NH_3. The graph of the multiple point for this molecule is



According to this graph, if the mutual actions between the nonbonding orbitals are not included, its characteristic matrix is

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_0 & \mathbf{H}_1 & \mathbf{H}_2 \\ \mathbf{H}_2 & \mathbf{H}_0 & \mathbf{H}_1 \\ \mathbf{H}_1 & \mathbf{H}_2 & \mathbf{H}_0 \end{pmatrix},$$

$$\mathbf{H}_0 = \begin{pmatrix} a_{pp} & b_{ps} \\ b_{ps} & a_{ss} \end{pmatrix}, \qquad \mathbf{H}_1 = \mathbf{H}_2 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix},$$

where

$$a_{pp} = \varepsilon - \alpha_{pp}, \qquad a_{ss} = \varepsilon - \alpha_{ss},$$

$$\alpha_{pp} = \int \phi^*_{N,p,}\hat{\mathbf{H}}\phi_{N,p}\,d\tau, \qquad \alpha_{ss} = \int \phi^*_{H,s}\hat{\mathbf{H}}\phi_{H,s}\,d\tau,$$

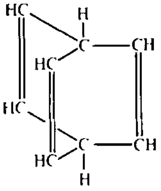
$$b_{ps} = \beta_{ps} = \int \phi^*_{N,p}\hat{\mathbf{H}}\phi_{H,s}\,d\tau,$$

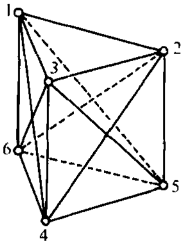
where $\phi_{N,p}$ is the 2p orbital of nitrogen and $\phi_{H,s}$ is the 1s orbital of hydrogen.

According to Eq. (18), we obtain

$$\varepsilon = \tfrac{1}{2}\{(\alpha_{ss} + \alpha_{pp}) \pm [(\alpha_{ss} - \alpha_{pp})^2 + 4\beta_{ps}]^{1/2}\} \qquad (k = 0, 1, 2).$$

Example 2. Bicyclooctatriene $CH(C_2H_2)_3CH$. The stereoconfiguration of this molecule and its molecular graph are





Here, the independent approximation with σ—π separation is used, but the mutual actions between 2p orbitals like 1–2 and 1–4 are included. The points on the graph are first numbered by means of the horizontal symmetry plane, and then by means of the threefold symmetry axis. If the points on the graph are first numbered by means of the threefold symmetry axis, and then by means of the horizontal symmetry plane, then the final results are just the same as the former case. According to the molecular graph, the characteristic matrix like Eq. (9) may be used, where

$$\mathbf{A} = \begin{pmatrix} a & b' & b' \\ b' & a & b' \\ b' & b' & a \end{pmatrix}, \qquad \mathbf{B} = \begin{pmatrix} b'' & b'' & b \\ b'' & b & b'' \\ b & b'' & b'' \end{pmatrix}.$$

In these matrices, $a = \alpha - \varepsilon$, $b = \beta$, $b' = \beta'$, and $b'' = \beta''$, where α is the Coulomb integral of the 2p orbital of the carbon atom, and β; β', and β'' are the exchange integrals between 1–6, 1–2, and 1–4 carbon-atomic 2p orbitals, respectively.

According to Eq. (11), we obtain

$$\mathbf{A} + \mathbf{B}[|] = \begin{pmatrix} a+b & b'+b'' & b'+b'' \\ b'+b'' & a+b & b'+b'' \\ b'+b'' & b'+b'' & a+b \end{pmatrix},$$

$$\mathbf{A}[\cdot] - \mathbf{B}[-] = \begin{pmatrix} a-b & b'-b'' & b'-b'' \\ b'-b'' & a-b & b'-b'' \\ b'-b'' & b'-b'' & a-b \end{pmatrix}.$$

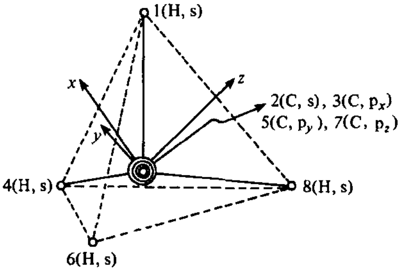
Both these matrices have the structure with threefold symmetry axis like Eq. (16). According to Eqs. (11) and (18), it is finally given that

$$\varepsilon = \alpha \pm \beta + 2(\beta' \pm \beta'') \qquad (k = 0),$$

$$\varepsilon = \alpha \pm \beta - 2(\beta' \pm \beta'') \qquad (k = 1, 2).$$

The results are the same as those obtained by Cotton (1971) in terms of the group method.

Example 3. Methane. The graph of multiple points for this molecule is



The points on the graph are already numbered by means of threefold symmetry axis. If the following symbols are used,

$$\begin{aligned}
a_{\mathrm{H}} &= \alpha_{\mathrm{H}} - \varepsilon, & \alpha_{\mathrm{H}} &= \int \phi_{\mathrm{H}}^{*} \hat{\mathbf{H}} \phi_{\mathrm{H}} \, d\tau, \\
a_{\mathrm{s}} &= \alpha_{\mathrm{s}} - \varepsilon, & \alpha_{\mathrm{s}} &= \int \phi_{\mathrm{C,s}}^{*} \hat{\mathbf{H}} \phi_{\mathrm{C,s}} \, d\tau, \\
a_{\mathrm{p}} &= \alpha_{\mathrm{p}} - \varepsilon, & \alpha_{\mathrm{p}} &= \int \phi_{\mathrm{C,p}}^{*} \hat{\mathbf{H}} \phi_{\mathrm{C,p}} \, d\tau,
\end{aligned}$$

$$\begin{aligned}
b_{\mathrm{s}} &= \beta_{\mathrm{s}} - S_{\mathrm{s}}\varepsilon, & \beta_{\mathrm{s}} &= \int \phi_{\mathrm{C,s}}^{*} \hat{\mathbf{H}} \phi_{\mathrm{H}} \, d\tau, & S_{\mathrm{s}} &= \int \phi_{\mathrm{C,s}}^{*} \phi_{\mathrm{H}} \, d\tau, \\
b_{\mathrm{p}} &= \beta_{\mathrm{p}} - S_{\mathrm{s}}\varepsilon, & \beta_{\mathrm{p}} &= \int \phi_{\mathrm{C,p}}^{*} \hat{\mathbf{H}} \phi_{\mathrm{H}} \, d\tau, & S_{\mathrm{p}} &= \int \phi_{\mathrm{C,p}}^{*} \phi_{\mathrm{H}} \, d\tau,
\end{aligned}$$

where α, β, and S are the Coulomb integral, exchange integral, and overlap integral, respectively. Then according to the preceding Eq. (21), we will obtain

$$\mathbf{B}_0 = \begin{pmatrix} a_{\mathrm{H}} & b_{\mathrm{s}} \\ b_{\mathrm{s}} & a_{\mathrm{s}} \end{pmatrix}, \qquad \mathbf{B} = \begin{pmatrix} b_{\mathrm{p}} & 0 \\ 0 & b_{\mathrm{s}} \end{pmatrix},$$

$$\mathbf{H}_0 = \begin{pmatrix} a_{\mathrm{p}} & b_{\mathrm{p}} \\ b_{\mathrm{p}} & a_{\mathrm{H}} \end{pmatrix}, \qquad \mathbf{H}_1 = \mathbf{H}_2 = \begin{pmatrix} 0 & -b_{\mathrm{p}} \\ -b_{\mathrm{p}} & 0 \end{pmatrix}.$$

Thus, it may be obtained from Eq. (22) that

$$\begin{aligned}
(a_{\mathrm{s}}a_{\mathrm{H}} - 4b_{\mathrm{s}}^2)(a_{\mathrm{p}}a_{\mathrm{H}} - 4b_{\mathrm{p}}^2) &= 0 \qquad (k = 0) \\
a_{\mathrm{p}}a_{\mathrm{H}} - b_{\mathrm{p}}^2\{1 - 2\cos[\tfrac{1}{3}(2\pi k)]\}^2 &= 0 \qquad (k = 1, 2).
\end{aligned}$$

Solving these equations, the energy levels of the molecular orbitals of methane are given as

$$\varepsilon = \frac{\alpha_{\mathrm{s}} + \alpha_{\mathrm{H}} - 8\beta_{\mathrm{s}}S_{\mathrm{s}} \pm [(\alpha_{\mathrm{s}} - \alpha_{\mathrm{H}})^2 + 16(\alpha_{\mathrm{s}}S_{\mathrm{s}} - \beta_{\mathrm{s}})(\alpha_{\mathrm{H}}S_{\mathrm{s}} - \beta_{\mathrm{s}})]^{1/2}}{2(1 - 4S_{\mathrm{s}}^2)} \qquad (k = 0)$$

$$\varepsilon = \frac{\alpha_{\mathrm{p}} + \alpha_{\mathrm{H}} - 8\beta_{\mathrm{p}}S_{\mathrm{p}} \pm [(\alpha_{\mathrm{p}} - \alpha_{\mathrm{H}})^2 + 16(\alpha_{\mathrm{p}}S_{\mathrm{p}} - \beta_{\mathrm{p}})(\alpha_{\mathrm{H}}S_{\mathrm{p}} - \beta_{\mathrm{p}})]^{1/2}}{2(1 - 4S_{\mathrm{p}}^2)} \qquad (k = 0, 1, 2).$$

If all the overlap integrals are neglected, then the above results will be simplified as

$$\begin{aligned}
\varepsilon &= \tfrac{1}{2}\{(\alpha_{\mathrm{s}} + \alpha_{\mathrm{H}}) \pm [(\alpha_{\mathrm{s}} - \alpha_{\mathrm{H}})^2 + 16\beta_{\mathrm{s}}^2]^{1/2}\} \qquad (k = 0) \\
\varepsilon &= \tfrac{1}{2}\{(\alpha_{\mathrm{p}} + \alpha_{\mathrm{H}}) \pm [(\alpha_{\mathrm{p}} - \alpha_{\mathrm{H}})^2 + 16\beta_{\mathrm{p}}^2]^{1/2}\} \qquad (k = 0, 1, 2).
\end{aligned}$$

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Index